Fritz Scholz *Editor*

Electrochemistry in a Divided World

Innovations in Eastern Europe in the 20th Century

Springer

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With contributions by

A.A. Andriiko, Kh. Z. Brainina, A.K. Demin, S. Fletcher, Z. Galus, U. Guth, M. Heyrovský, G. Inzelt, J. Jindra, H. Kaden, N.A. Kolpakova, J. Lipkowski, V.G. Mairanovsky, A.A. Milchev, O.A. Petrii, R. Ramanauskas, J.D. Sister, F. Scholz, P. Shuk, E.A. Zakharova

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"It was the best of times, it was the worst of times. . ."
From A Tale of Two Cities *by Charles Dickens (1859)*

Romanization of Cyrillic Letters

In this book, the Romanization of Cyrillic letters generally follows the rules of the U.S. Board on Geographic Names. Exceptions have been made in cases where authors have used different ways of Romanization of their own names in publications.

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Chapter 1
Introduction

Fritz Scholz

Progress in science has been always achieved by a diverse community of researchers, working in different countries, under different social, economic, and political conditions, with different traditions, and usually speaking different languages. Despite these profound differences, a common framework of theories and experimental methods has gradually been built up, in which the individual contributions are often partly or totally hidden. Science is an international achievement, and textbooks and monographs are often written without reference to true origins of scientific ideas and without reference to the conditions under which the science was developed. As a result, the reader gets only half the picture. In fact, science has been strongly shaped by the individual researchers. Terminology, symbols, paradigms, and prototypes, i.e., the language of science, are deeply rooted in the thinking of the individual scientists having lived under specific historical conditions. The experimental methods and techniques mirror the individual abilities of the scientists as well as their living and working conditions. Developed by other scientists under different conditions, they would have been different. Between the most ancient inventor and the most recent user exists an evolutionary chain of developments with unpredictable twists and turns, sometimes also revolutionary steps. Similarly, theories are coined by the thoughts and ideas of the people who have developed them; they got the stamp of the time and place of their origin. When I started writing this introduction, the idea that the social environment of a scientist can affect the way in which science is growing, was so plain to me that I did not give it a second thought. I have concluded this from reading original papers written at different times and places and by observing ongoing scientific developments. Later I have seen that sociologists had severe fights about this question, and only in the past decades it became accepted that there are different "Styles of Thought," as Jonathan

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Harwood entitles his analysis of the history of genetics in the USA and Germany. Harwood writes: "Since the 1970s, however, a substantial literature on the sociology of scientific knowledge has made the search for styles of science altogether plausible. What this literature demonstrates is that the cognitive processes whereby scientific knowledge is constructed—for example, observation, classification, theory formation, and theory testing—are routinely shaped by the social circumstances of the scientist concerned." [1].

Science and arts differ in many respects. It is often been said, if Shakespeare had not written *Romeo and Juliet*, nor Goethe *Faust*, then nobody else would ever have written these plays in precisely the same way [2]. On the other hand, if Einstein had not developed the theory of relativity, nor Planck the concept of the quantum, then someone else certainly would. Although this is surely true, it is equally true that these concepts would have been presented to us from a different angle, using different notation, and illustrated by different paradigms. Of course, the building of science possesses an objective core structure, proven to be *true* in the framework of *what we know*. Science is an intellectual reflection of the outer world, arts and religions being others. Science appears to be completely impersonal, but if searched for, the individual polish comes up everywhere. The question whether we have to care for the individual features is not uniformly answered by contemporary scientists; however, the authors of this book and the editor are united by the idea that for a full understanding of science one needs information about its subjective growing mechanisms. Iwan N. Stranski [2] felicitously described the situation in science as follows: "*Here again let me hark back to intuition and understanding. All scientists try to discern (albeit dimly) connections within their field of endeavour which promise the most progress. This happens by intuition. And if they perceive the connections properly, even without the benefit of a rigorous formulation, then that is already a kind of insight. The exact formulation gives the theory. Nevertheless, it should be emphasized that any creative individual working in the exact sciences, including mathematics, also works as an artist, because he has the freedom to introduce inaccuracies, and, indeed, must use that freedom in order to achieve a result. Otherwise, almost every problem would turn out to be hopelessly complicated.*"[1] (Jointly translated by Steve Fletcher and Fritz Scholz) It is especially the choice of these "inaccuracies" (or approximations) which best reflects the individuality (in rare cases the genius) of the scientists.

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[1] "Hier möchte ich nochmals auf die Intuition und Erkenntnis zurückkommen. Jeder Wissenschaftler ahnt mehr oder weniger innerhalb des von ihm bearbeiteten Gebietes Zusammenhänge, die einen Fortschritt versprechen. Das war die Intuition. Und wenn er die Zusammenhänge richtig erfaßt, ohne sie unbedingt formuliert zu haben, so ist es bereits eine Erkenntnis. Die exakte Formulierung ergibt die Theorie. Es sei hier nochmals betont, das jeder Schaffende auch in den exakten Wissenschaften einschließlich der Mathematik eigentlich als Künstler wirkt. Denn er hat die Freizügigkeit, Ungenauigkeiten einzuführen, und er muß von dieser Gebrauch machen, um überhaupt erst zu einem Ergebnis zu kommen. Sonst würde sich fast jedes Problem als hoffnungslos kompliziert ergeben."

The political history of the twentieth century is marked by momentous developments. In Europe, four empires disintegrated as a result of the First World War I (WW I): the German, the Austro-Hungarian, the Russian, and the Ottoman. This led to the formation of a number of independent countries, like Czechoslovakia, Poland, Hungary, and Yugoslavia, and to the formation of the first communist country, the Soviet Union. In 1939, Germany ignited the Second World War (WW II), with the repercussion that in the second half of the century, the wider world was divided into two parts: one led by the USSR and the other by the USA.

The USA made astonishing progress in science and technology during the twentieth century. At the end of the nineteenth century, a US scientist typically had to get a PhD from Germany if he wanted to become a recognized professor at home. The book "Ostwald's American Students" [3] gives ample examples of this, including such luminaries as Morris Loeb, Arthur Amos Noyes, Theodore William Richards, Frederick Gardner Cottrell, and many others. By the end of the twentieth century, the situation had reversed, and a PhD from a US university (or post-doctoral experience in the USA) had become a normal career pathway for Western European scientists. If one tries to structure the twentieth century, one may distinguish the following periods: (1) 1900–1914: the time prior to WW I; (2) 1914/18–1933: the time between WW I and the Nazi regime; (3) 1933–1945: the Nazi regime in Germany; (4) 1945–1989: the existence of two global political blocs; and (5) 1989–2000: the breakdown of the bipolar world. The time before the outbreak of WW I was essentially a continuation of the nineteenth century and was dominated scientifically by Germany, the UK, France, and the Austro-Hungarian Empire. Scientific visits between European scientists were normal, and scientists from further afield, such as the USA and Japan, felt compelled to visit Europe to keep up with developments. Russian scientists normally studied for their higher degrees in Western Europe. World War I eventually destroyed these cordial and ad hoc arrangements, and many scientists became increasingly employed for military and political ends. Eventually, the creation of the Soviet Union meant a complete turning around of social and political norms on its territory, and this had most far-reaching consequences for all the scientists living there. Likewise, the Nazi epoch in Germany from 1933 to 1945 was not only a human catastrophe but also a catastrophe for German science, with the death or departure of so many great German-Jewish intellectuals. The mass emigration of Jews from central Europe, mainly to the USA but also to the UK and Palestine/Israel, weakened the scientific base of central European countries to such an extent that its very existence was put at stake. The migration of Jews to the USA was clearly an important factor in its postwar scientific dominance.

The situation following WW II is often called the "Cold War," during which two strongly armed political blocs came into existence and direct communication between the scientists in the two blocs virtually ceased. US scientists who attempted to communicate with East European colleagues were viewed in their own country with deep suspicion, while scientists in Eastern European countries were routinely prevented from travelling, even within their own bloc. There were restrictions on writing letters, on receiving letters, on telephoning, and even on research topics. Severe restrictions applied also to East German scientists because of the special situation of the divided Germany. Only in the late eighties did these restrictions ease somewhat. When the Berlin Wall finally came down in 1989, this signalled the breakup of the Eastern bloc, and also the disintegration of the Soviet Union. It reopened channels of communication that had been closed for about 70 years. That is a long time in human history, and it is a period in which several generations of scientists were educated. The aftermath is not yet over, and at the time of finalizing this introduction, the thread of another Cold War period is felt throughout Europe.

Electrochemistry is only a small part of science. Modern electrochemistry is rooted in eighteenth and nineteenth century Europe and connected with the names of giants such as Galvani, Volta, Davy, Ritter, Faraday, Schönbein, Grove, Lippmann, Ostwald, Arrhenius, and Nernst. (Some of them, like Ostwald, Arrhenius, and Nernst, survived into the twentieth century.) More recently, in the middle of the twentieth century, a blossoming of electrochemistry occurred in Eastern Europe. The main figures were Jaroslav Heyrovský and Alexander Naumovich Frumkin. Very interestingly, both were *not* students of any of the abovementioned giants, although Heyrovský has worked with F. G. Donnan in London, and Frumkin was in Strasbourg and Bern. Instead, they are convincing examples of self-made scientists, touched by divine inspiration, as it were.[2] The careers of Heyrovský and Frumkin also reveal how accidental circumstances shape future developments. They both stand at the cradle of modern electrochemistry, and their scientific descendants are now spread over the entire world. To a large extent, the strength of electrochemistry in Eastern Europe can be traced back to them. Other features which contributed to the rapid development of the field were the strength of mathematical education in the Soviet bloc and the comparatively low cost of electrochemical instrumentation, which made electrochemistry attractive in poorly funded states.

The authors of this book also discuss a number of other flourishing research groups which cannot be directly derived from or related to Heyrovský and Frumkin. The existence of these groups proves how important it is to have a high scientific culture and scientific standards set by excellent leading groups. In other words, the groups of Heyrovský and Frumkin had a very far-reaching influence on the whole of electrochemistry in Eastern Europe, and also worldwide.

The division of the world in the twentieth century resulted in a serious mutual deficit of knowledge about the people on the other side. Whereas scientific information permeated through the iron curtain (albeit sluggish and incomplete)—the dissemination of knowledge about the scientists was very restricted. The freedom for Eastern European scientists to travel, be it to conferences or for research stays, varied strongly among the different countries, and it also varied in time. Thus, it was not always the professional abilities of scientists that determined their chances

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[2] Fritz Haber's was a similar case: "He worked his way into the fields of electrochemistry and thermodynamics, which were critically important for his research, in a most astounding and quite unusual fashion—without having an intellectual mentor in any of the scientific schools." (Stoltzenberg D (2004) Fritz Haber. Chemist, Nobel Laureate, German, Jew. Chemical Heritage Foundation, Philadelphia, p xxi.)

to travel but more often their political position (proximity to the ruling parties) and ranking in the University (or Academy) hierarchy. This fuelled some mistrust of Western colleagues towards those Eastern Europeans who were allowed to travel, also a part of the aftermath of the divided world.

It is the aim of this book to make the wider world better acquainted with the golden age of East European electrochemistry and to keep alive the memory of those scientists who devotedly served science under very trying conditions. Many of them were never properly recognized in their lifetimes because of their isolation.

It was not our intention to be prescriptive about the contents of this book. Obviously, it is impossible to completely cover such a vast field. Therefore, the guiding principle was this: to trace back, where possible, the genesis of the most important ideas and to place them in the context of the lives of the individual scientists concerned. The authors and the editor are also aware of the distinct disparities between the included people; some of them have influenced the whole of electrochemistry, while others have left their imprint on only a very small subfield, but nevertheless we feel obliged to include them. Further, we have to apologize for neglecting a large number of electrochemists, and even some countries; this was not done on purpose but because we could not find authors willing to cover the missing topics. It would also be nice if this book could be complemented by similar books presenting the development of electrochemistry in other parts of the world, e.g., the USA, Western Europe, Japan, and China.

The book is written for people who are already acquainted with the culture and terminology of electrochemistry. However, it can also be read by historians, since it provides a unique source of new information about an important epoch in science history.

The idea to prepare this book is itself a product of the divided world of the twentieth century: I grew up in East Germany, at the periphery of Berlin. At school, I have learned Russian and English. Knowledge of Russian tremendously helped me in communicating with Russian colleagues and also helped me to make extended Internet searches in that language. I was 34 when the Berlin Wall came down, i.e., politically I have experienced the East and the West, and so I acquired an understanding of the people on both sides. I am deeply convinced that command of languages is an important attribute in science, not only because it allows us to read the original papers, and facilitates personal contacts. It always opens the hearts of people when you can approach them in their mother tongue. The sever problem of languages for communication science has recently be treated very thoroughly by Michael Gordin in the book “Scientific Babel: The language of science from the fall of Latin to the rise of English” [4]. Several personal recollections of authors of “Electrochemistry in a divided world” could serve as illustrations of what Gordin discusses in relation to Russian language, and the disadvantages Russian scientists had from voluntarily and nonvoluntarily publishing their findings in their own language.

I understand the legacy of the scientists included in this book as a plea for a peaceful world in which scientists cooperate and compete, without political restrictions, and directed towards the benefits of mankind.

Finally I like to acknowledge the cooperation of all authors, who have written down their memories in order to preserve precious historical details. This was a very demanding task.

Greifswald, April 2015.

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Chapter 2
Electrochemistry in a Divided World: The Political Background

Stephen Fletcher

The “Cold War” was a state of extreme military tension that arose after 1945 between the Western Powers (principally the United States and its NATO allies) and the Eastern Bloc (principally the USSR and its Warsaw Pact allies). The tension emerged at the end of the Second World War, as the United States began to reform the global economic system, while the USSR began to consolidate its political and military control over Eastern Europe. The Cold War split the fragile wartime alliance against Nazi Germany, leaving the United States and the USSR as two opposing “superpowers” with divergent political and ideological interests: the former being a multiparty capitalist state and the latter being a single-party Marxist–Leninist state. Among the prewar powers, Germany itself was demilitarized and partitioned, while France and the British Empire were financially ruined.

The origins of the Cold War can be traced to the closing years of the First World War. As a result of the 1917 Bolshevik Revolution, Soviet Russia found itself isolated from international diplomacy. Its first Head of Government, Vladimir Il’ich Ul’yanov (Lenin), worked hard to overcome this isolation, and by late 1924, the USSR had secured the political recognition of all the world’s major governments except the United States. Nevertheless, Lenin remained philosophically opposed to the world capitalist system and called on workers around the world to organize themselves into communist parties to overthrow capitalism. This call was widely answered in the colonial world, even though communism was far from secure inside Russia itself. After Lenin’s death in 1924, his successor Iosif Vissarionovich Dzhugashvili (Stalin) brutally eliminated all internal opposition in Russia. Although it cannot be denied that Stalin successfully increased industrial output, his forced collectivization of agriculture cost millions of lives. During the

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Great Terror of the 1930s, his purges of supposed "enemies of the state" resulted in the torture and execution of innumerable innocent people and the transfer of millions into the gulag system of forced labor. The historical triumph of Stalinism cast a dark shadow across Europe, which, with its improving communications, should have been moving towards a second enlightenment.

The Second World War from 1939 to 1945 drew in all of the great powers and led to the creation of two unstable military alliances: the Allies and the Axis. The Allies included the Soviet Union, the United States, and the United Kingdom, whereas the Axis included Germany, Japan, and Italy. It was the most destructive war in history, with the participants focusing their entire economic, industrial, and scientific capabilities behind the war effort, erasing the distinction between civilian and military research. The war in Europe ended with the surrender of Nazi Germany on May 8, 1945, but, incredibly, the Japanese continued to fight on.

In early August 1945, the United States dropped two atomic bombs on Japan, destroying the cities of Hiroshima and Nagasaki. In Hiroshima, it was estimated that 45,000 people died on the first day and a further 19,000 during the subsequent 4 months. In Nagasaki, 22,000 people died on the first day and another 17,000 within 4 months. These remain the only use of nuclear weapons for warfare in history. The Japanese government finally surrendered on 15 August 1945.

The realization that the United States had nuclear weapons, and was willing to use them against civilian populations, profoundly shocked the Soviet Union. They immediately embarked on an urgent program to develop their own nuclear weapons. The Cold War had begun. Between 1946 and 1962, the Soviet Union conducted 221 atmospheric tests in Semipalatinsk (Kazakhstan) and Novaya Zemlya (Russian Federation). Meanwhile, the United States conducted 216 atmospheric tests, 106 of which were only 63 miles from Las Vegas! The fallout from these tests contained radioactive materials which were widely dispersed by the wind. As a result, millions of people across the northern hemisphere were exposed to radiation.

With the victory of the Communist side in the Chinese Civil War and the outbreak of the Korean War (1950–1953), political tensions between the USSR and the United States became acute. Competition was particularly fierce in Latin America, in Southeast Asia, in the Middle East, and in the rapidly decolonizing states of Africa. Meanwhile, the Hungarian counter-revolution of 1956 was halted by the intervention of Soviet tanks. The Cold War also sparked a series of dramatic political crises, such as the Suez Crisis (1956), the Berlin Crisis (1961), and the Cuban Missile Crisis (1962). Following this last crisis, a new phase began, with Russia and China moving apart inside the communist bloc and France and the United States moving apart inside the capitalist bloc. Meanwhile, the USSR crushed the 1968 "Prague Spring" liberalization program in Czechoslovakia, and the Vietnam War (1955–1975) ended with the defeat of the US-backed Republic of South Vietnam, prompting a reconsideration of U.S. foreign policy.

The Cold War had a huge effect on the development of science and technology in both the United States and the Soviet Union. Initially, atomic bombs were designed to be dropped by airplanes. However, their ease of interception soon led to the development of Intercontinental Ballistic Missiles (ICBMs), which could travel through space at high speed before reentering the atmosphere above their targets. Because these missiles could not be recalled if launched by accident, their existence created great anxiety. As the number of nuclear weapons spiraled out of control during the 1950s, both sides found themselves wanting to maintain nuclear parity with the other, yet simultaneously alarmed at the pace of the arms race and the growing possibility of a nuclear holocaust.

At the human level, the scientific and industrial rivalry between the two superpowers compelled both sides to restrict the employment and travel of their leading scientists. Stalin was willing to imprison scientists who were ideologically suspect or non-performing; meanwhile, the United States was gripped by a series of "red scares," in which it was thought that communist subversives were poisoning the minds of America's youth. On both sides, dissent from Cold War orthodoxy led to rapid dismissal (in the Soviet Union, much worse). Adding to the overall sense of paranoia, data interception and espionage became commonplace tools of the intelligence services.

For 20 years, vast sums of money were spent on uranium processing, atom bomb tests, nuclear submarine programs, satellite development, and ICBMs, with little or no regard for the cost to civil society or the damage to the environment. Despite all this military hardware, the resolution of the Cold War was, ironically, brought about by a change in the western economy, from old-style acquisitive capitalism, with its focus on property and class, to modern Keynesian capitalism, with its focus on infrastructure development and rapid circulation of capital. This led to an unprecedented rise in the standard of living of most Western countries, which the Soviet Union was unable to match.

By the 1970s, both sides were militarily fatigued and sought to reach a political accommodation. A period of détente followed, in which Strategic Arms Limitation Talks took place, and the US opened diplomatic relations with the People's Republic of China. Unfortunately, détente collapsed at the end of the decade following the Soviet invasion of Afghanistan.

The early 1980s saw a return to high tension, with the Soviet downing of Korean Air Lines Flight 007 (1983) and the provocative "Able Archer" NATO military exercises (1983). The United States boosted its military spending at a time when Soviet industry was suffering from profound structural problems. In an attempt to stave off economic collapse, the new Soviet leader Mikhail Gorbachev introduced the liberalizing reforms of glasnost ("transparency," 1985) and perestroika ("reorganization," 1987) and also ended Soviet involvement in Afghanistan. However, around this time, pressures from national independence movements were also emerging in Eastern Europe, causing further instability. In a remarkable change of long-term policy, Gorbachev refused to intervene. The result in 1989 was a wave of counter-revolutions that peacefully (with the exception of the Romanian Revolution) overthrew all of the Communist regimes of Central and Eastern Europe. On 9 November 1989, the East German government permitted its citizens to travel freely to the west. Throngs of East Germans immediately clambered over the "Berlin Wall." These symbolic actions paved the way for German reunification, which was formally announced on 3 October 1990. Soon afterwards, the Communist Party of the Soviet Union itself fell from power and was banned following an abortive coup attempt in August 1991. This in turn led to the formal dissolution of the USSR in December 1991 and the collapse of Communist regimes in other countries such as Mongolia, Cambodia, and South Yemen. The "Cold War" had ended.

Ironically, despite 45 years of confrontation, the West had few plans for dealing with the Soviet Union's collapse, and there were no adequate political or military structures in place to accommodate the re-emerging countries of the Eastern Bloc. As a result, many of them have simply been absorbed into the existing structures of NATO and the EU, thus alienating Russia. At the time of writing (2015), a long-term settlement remains elusive.

Time line
1914 August: Outbreak of World War I.
1917 March: The Tsar's government falls, replaced with a Provisional Government.
1917 April: Lenin returns to Russia from exile in Switzerland.
1917 November: Bolsheviks overthrow Provisional Government, seize power.
1917–1922: Civil war in Russia. Trotsky organizes Red Army.
1922 December: Official founding of Union of Soviet Socialist Republics.
1922 April: Stalin appointed General Secretary of the Communist Party.
1924 January: Death of Lenin.
1924 December: Stalin publicly articulates his theory of "Socialism in One Country."
1927 December: Stalin consolidates his power at the Fifteenth Party Congress.
1928 Beginning of the first Five-Year Plan.
1929 December: Collectivization begins.
1932–1933: Terrible famine across the Soviet Union; millions die.
1934 December: Beginning of "Great Terror," which continues until 1938.
1937 June: Purge of the army; top generals tried and executed.
1939 August: Nazi–Soviet Pact is signed in Moscow.
1939 September: Outbreak of World War II.
1940 August: Trotsky assassinated, by Stalin's agents, in Mexico City.
1941 June: Hitler invades the Soviet Union.
1942 August–February 1943: Battle of Stalingrad. Nazis are defeated, marking the turning point in the war.
1945 February: Stalin meets Roosevelt and Churchill at Yalta.
1945 April: Red Army controls most of Eastern Europe.
1945 August: The United States uses atomic bombs against Japan, ending the war in the Pacific.
1945–1991: The "Cold War."
1946 March: Churchill makes "Iron Curtain" speech.
1948 February: Communists take power in Czechoslovakia, completing Soviet control of Eastern Europe.
1948 June (to May 1949): Soviet Union blockades West Berlin.
1949 April: Ten West European nations join the U.S. and Canada to form NATO.
1949 August: Soviet Union explodes its first atomic bomb.

1949 October: Mao Tse-tung founds the People's Republic of China (PRC).
1950 February: Sino-Soviet Treaty.
1950–1953: Korean War.
1953 March: Death of Stalin.
1953 June: Uprising in East Germany.
1955 May: Warsaw Pact formed.
1956 June: The Poznań protests in Poland.
1956 November: Red Army crushes the Hungarian Counter-revolution.
1957 October: Soviet Union launches Sputnik 1 (first man-made satellite).
1959 February: Fidel Castro becomes Premier of Cuba.
1959 September: First "Summit Meeting" (President Dwight Eisenhower and Premier Nikita Khrushchev).
1961 August: East Germany builds the Berlin Wall.
1962 October: Cuban Missile Crisis.
1964 October: China explodes its first atomic bomb.
1965 March: First U.S. combat troops land in South Vietnam.
1968 August: Red Army crushes Czech Uprising.
1972 February: U.S. President Richard Nixon visits China.
1975 April: Saigon falls to Communist forces.
1979 January: U.S. and China establish diplomatic relations.
1979 December: Soviet Union invades Afghanistan.
1980 August: Polish shipyard workers strike; first "Solidarity" Union formed.
1985 March: Mikhail Gorbachev becomes leader of the Soviet Union.
1989 September: "Solidarity" forms the first post-war non-communist government in Poland.
1989 December: End of Communist government in Czechoslovakia.
1990 May: Free parliamentary election in Hungary.
1989 November: East Germany allows unrestricted travel to West Germany.
1990 October: Reunification of Germany.
1991 June: The last Soviet troops leave Hungary.
1991 August: Communists stage unsuccessful coup against Mikhail Gorbachev.
1991 December: The Soviet Union is dissolved. Boris Yeltsin becomes President of the Russian Federation.
1994 September: The last Russian troops leave Germany.

Chapter 3
The Czech (Czechoslovak) Electrochemistry 1900–1990

Jiří Jindra and Michael Heyrovský

3.1 General Electrochemistry

Jiří Jindra

In our time review, we shall proceed according to institutions where electrochemistry was dealt with. In the educational sphere, they were Czech, later Czechoslovak, universities in Prague, Brno, Olomouc, Bratislava, and Košice and technical universities in Prague, Pardubice, Příbram, Brno, Ostrava, Bratislava, and Košice. In the academic sphere, they were institutes of the Czechoslovak Academy of Sciences in Prague and Brno and institutes of the Slovak Academy of Sciences in Bratislava. Third group consists of industrial research institutes in Prague, Slaný, Ústí nad Labem, Hradec Králové, and Mladá Boleslav.

3.1.1 *End of Nineteenth Century*

Electrochemistry as a part of physical chemistry could be found in Bohemia at the Charles-Ferdinand University and at Czech Technical University in Prague; exceptionally it was used in industry. The Czech scientific electrochemistry began in the

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Fig. 3.1.1 Otakar Šulc (1869–1901)

nineties of nineteenth century when some physicists and chemists were so far nonsystematically dealing with electrochemical problems. Among them were university assistants—physicist Vladimír Novák (1869–1944) and chemist Otakar Šulc (1869–1901) (Fig. 3.1.1), who applied voltameter in connection with galvanic polarization of platinum electrodes and with electrolytic formation of silver superoxide [1, 2]. At the end of the nineties, Šulc lectured at the technical university on electrochemistry; he has published papers about hydration produced by metals and about the catalytic effect of metals in hydrolytic reactions [3]. He also studied conductivities of sodium-substituted nitro-paraffins. Together with B. Mašek (1868–1955), he published a paper about electrochemical constants of some salts.

The mentioned and few other communications were published by the authors in foreign periodicals; in general, technical papers appeared mainly in Czech journals.

3.1.2 The Years Between 1900 and 1920

After the first steps in the area of electrochemistry towards the end of nineteenth century, the beginning of twentieth century brought increased activity of Czech chemists. The mysterious electrolytic silver superoxide still attracted attention of V. Novák, O. Šulc, J. Baborovský (1875–1946) (Fig. 3.1.2), and B. Kužma (1873–1943) [4, 5]. Experiments to determine the voltage of anodic decomposition of sodium hydroxide were carried out by F. Plzák (1877–1944). The papers on the abovementioned topics were published in Czech or in German.

From 1905, the electrochemical problems were taken over by the university assistant J. Baborovský. He started by a preliminary communication about magnesium suboxide [6], followed by a study of phenomena at magnesium anodes [7], and by description of experiments to determine the electrochemical potential of metallic magnesium in ethanolic solutions of magnesium chloride, as well as by the study on transfer numbers of magnesium chloride in ethanolic solutions. The paper by

Fig. 3.1.2 Jiří Baborovský (1875–1946)

J. Heyrovský (1890–1967) from the university chemical institute about amphoterity and electroaffinity [8] appeared in 1920.

Electrochemistry was the research topic also of the Prague Technical University chemists E. Votoček (1872–1950) (Fig. 3.1.3), E. Ženíšek, J. Šebor (1875–1944), and F. Jirsa (1890–1952). For example, Šebor studied ionic theory of solution conductivity [9], and Jirsa published results about disintegration of oxidation products of silver electrodes in alkaline medium [10], and he studied the conditions on copper electrodes in alkaline hydroxides.

In 1912, Baborovský moved to the Technical University in Brno. There he contributed to the determination of liquid cells between various solvents. In 1917, he published in Czech a short but fundamental work about a new method for determination of ionic hydration. This and related topics were Baborovský's field of research for the next almost 30 years.

Apart from the quoted works, it was mainly at the Prague Technical University where electrochemical problems were studied. The beginnings of Czech electrochemistry are connected with the names O. Šulc, J. Baborovský, and J. Šebor. Their papers were published mostly in Czech periodicals—this is why their results were not well known abroad.

3.1.3 The Years Between 1921 and 1939

In Czechoslovakia in 1919, a new Czech University was founded in Brno. Its faculty of science has opened the possibility to study among other subjects also electrochemistry. From 1922 physical chemist V. Čupr (1897–1985), specialized in electrochemistry, was employed there. He studied hydrolysis of salts [11], diffusion currents, and mainly corrosion [12]. At the Technical University in Brno, J. Baborovský founded his "electrolytic school," not intended to compete with

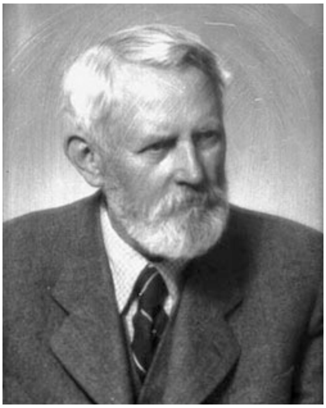


Fig. 3.1.3 EmilVotoček (1872–1950)

Heyrovský's polarographic school. His leading problem was hydration of ions and electrolytic transfer of water; in his laboratories research of electro-osmosis was carried out. Within the years 1920–1939, Baborovský himself and with his coworkers published about 80 papers [13, 14].

At the Prague Institute of Chemical Technology, F. Jirsa studied anodic oxidation of gold [15]; later he published an important paper about silver electrode for a silver–iron battery [16]. Jaroslav Chloupek (1899–1975), partly with V. Daneš (1907–1980) and B. Danešová, studied the electrode potential in solutions of mixed manganese salts [17], the solubility and activity coefficient of Ag_2SO_4 in some solutions [18], the ions and deviations from the approximation of Debye–Hückel theory [19], the liquid potentials [20], and the anomalous valency effect of strong electrolytes in aqueous solution [21].

At Charles University in Prague, Jaroslav Heyrovský (Fig. 3.1.4), first docent and from 1926 an ordinary professor of physical chemistry, was dealing with a number of electrochemical problems. He was interested in the concept of electrode potential [22–25], in the theory of overpotential [26], in the electrokinetic potentials of galvanic elements [27], and in the electrolytic potential of iron amalgam [28]. After the discovery of electrolysis with dropping mercury electrode, he founded polarographic school and devoted himself to polarography (cf. Sect. 3.2).

In the Sugar Research Institute in Prague, K. Šandera (1903–1959) constructed an original conductometer for determination of ash in products of sugar factories. Šandera himself or with his coworkers published by the end of 1950s a number of papers (in Czech) about the use of conductometry, mainly in sugar production.

Electrochemistry was also practiced at the Mining Academy in Příbram. Professor A. I. Glazunov (1888–1951), Russian emigré, investigated there by himself and with coworkers the nature of crystallization center, the linear speed of crystallization in electrolysis of metals [29], the effect of agar and of gelatine on cathodic silver deposits, the protection of aluminum by anodic oxidation, the problems occurring in electrolyses of salts, and the distribution of streamlines in electrolytes

Fig. 3.1.4 Jaroslav Heyrovský (1890–1967)

during electrolysis [30]. He introduced the electrographic method based on colored reactions of anodically dissolved metals [31].

3.1.4 The Years Between 1940 and 1969

That period is characterized in society, and hence also in science, by totalitarian regimes (with exception of the period from May 1945 till February 1948): first it was German occupation of Czechoslovakia and, after February 1948, communist totalitarianism. Closing the Czech universities in November 1939 strongly affected the promising development of Czechoslovak science which concerned also electrochemistry. The Czech physical chemists specialized in electrochemistry, who were employed in various institutions still functioning in the "Protectorate of Bohemia and Moravia," could work in the field of electrochemistry and publish in the allowed Czech journals; almost no Czech chemist published in the accessible German journals. Publishing of the "Collection of Czechoslovak Chemical Communications" in the years 1940–1946 was stopped, and access to American, English, and French journals was impossible. For that reasons not many Czech electrochemical papers appeared in the years 1940–1945. Those published concerned mainly polarographic topics (Heyrovský, Brdička—see polarography in Sect. 3.2).

After the end of the Second World War, the electrochemists returned to the university institutes. Their new generation was full of enthusiasm and zest for scientific work. The practiced research was either continuation of the prewar topics or a start in a completely new direction. It was essential to get acquainted with all novelties which occurred in science in course of the past 6 years.

The strict political conditions eased to some extent in the next decade which allowed some electrochemists to experience affiliations with scientific institutions in West European countries or in the USA. Before that it was possible to affiliate or to participate in conferences only in the "people's democratic" countries. For Czechoslovak scientists, it became more accessible to publish in foreign scientific journals. Such situation had its positive effect on the improving level of Czechoslovak electrochemistry which was accepting modernizing ideas. Unfortunately, the occupation of Czechoslovakia by the "Warsaw pact countries" (with exception of Romania) in 1968 had its negative effect on scientific activity.

An important event in development of science in Czechoslovakia was the establishment, according to the Soviet example, of the Czechoslovak Academy of Sciences in 1952 and of the Slovak Academy of Sciences in 1953. The physicochemical problems including electrochemistry were studied in the Polarographic Institute of the Academy, in the Institute of Physical Chemistry of the Academy, and in the Institute of Analytical Chemistry of the Academy, and in Slovakia, it was in the Chemical Institute of the Academy.

Research in Schools—Universities

In Charles University until 1950 prevailed research in polarography, inspired among others by M. Kalousek (1915–1995) (Fig. 3.1.5). After part of the electrochemists from the university went over to the Academy institutes at the beginning of the 1950s, the subject of research turned to biological molecules like proteins, studied mainly by V. Kalous and his coworkers. Their results were published usually in Chemické Listy and in Collection of Czechoslovak Chemical Communications. The method most often applied remained polarography [32], partly in connection with conductometry [33] and electrophoresis [34–38].

In the University of Brno, V. Čupr continued in the research of corrosion [39]; he constructed a mechanical potentiostat. In the laboratories of theoretical and physical chemistry, kinetics of electrode processes was studied by means of constant current electrolysis [40–43]; later there were followed phenomena at the electrode/solution interface which led to determination of rate constants of electron transfer between electrode and the reacting particle [44, 45].

At the Palacký University in Olomouc, professor F. Šantavý (1915–1983) (Fig. 3.1.6) was a creative personality in botanical and medical applications of polarography [46]. Junior electrochemists measured redox potentials of various dye indicators [47]; the methods thereby used were amperometry, polarography, and voltammetry [48, 49].

Technical Universities

At the Prague School of Chemical Technology, the problems of technical electrochemistry, concentrated on the possibilities of electrolytic preparation of some inorganic compounds, e.g., solubility diagrams of complex cyanides for electrochemical production of potassium ferrocyanide and of persulfates used in production of hydrogen peroxide, were studied [50–52]. Among the topics of

Fig. 3.1.5 Mirko Kalousek (1915–1995)

Fig. 3.1.6 Šantavý, František (1915–1983)

electrochemical engineering were being solved the problems concerning intensification of various types of electrolysers [53] and appropriate current densities, and final voltages on electrolysers were calculated [54–56]. The topic of corrosion was the field of research in the department of chemical technology of metals—the corrosion of titanium was studied there [57]. R. Lukeš (1897–1960) (Fig. 3.1.7) continued in the prewar studies of electrolysis of some organic compounds [58], especially of ketoacids [59]. Many organic substances were prepared electrochemically [60]. The first systematic work on electrophoresis of proteins was published by B. Keil and coworkers in 1950 [61].

In the School of Chemical Technology in Pardubice founded in 1950, at the department of physical chemistry, the study of reaction kinetics of redox reactions of second and third order, of two competing consecutive reactions, and the determination of rate constants of homogeneous reactions from potential–time curves

Fig. 3.1.7 Rudolf Lukeš (1897–1960)

studied from the time dependence of electrode potential, which was used for a number of bimolecular reactions, was continued [62–64].

In the Brno School of Chemical Technology, after professor Baborovský passed away in 1946, the research continued in the traditional topic of ionic hydration and electro-osmosis. In 1951, the technical university was abolished, and instead of it was founded a Military Technical Academy, in which neither physical chemistry nor electrochemistry was studied—hence in the years 1952–1969, no electrochemical activity took place there.

Academy Institutes

Polarographic Institute of the Czechoslovak Academy of Sciences

The main subject of research was polarography (see Sect. 3.2) and from the 1960s, it was additionally the research concerning electrochemical power sources. For those the non-platinum catalysts were studied, appropriate for the then fashionable fuel cells. The research led to a number of publications about catalysts for oxidation of fuels (hydrogen, hydrazine) on basis of nickel [65] and for reduction of oxidizing agents (oxygen, hydrogen peroxide) [66] on basis of silver [67, 68] and of carbon [69, 70] working in alkaline medium. From active carbon could be prepared oxygen or air electrodes functioning irrespective of the fuel dissolved in the electrolyte [71–74].

In the 1960s, the department of electrocatalysis was led by J. Koryta (1922–1994) (Fig. 3.1.8) who was many-sidedly active in electrochemistry: he was expert in polarography of complexes [75–78], with coworkers he studied electrode kinetics [79–86], followed catalytic processes [87, 88], and theoretically solved electrochemical reactions [89–92] and the effect of adsorption in electrode kinetics [93–97] including the use of solid electrodes [98–100]. The role of electrode double layer in electrode processes was also studied [101–109]. In the Polarographic Institute were also developed long-time electrochemical analyzers [110–113], and

Fig. 3.1.8 Jiří Koryta (1922–1994)

due attention was concentrated on electrochemical instrumentation—e.g., on apparatus for measuring electrode impedance [114]. Reactions on solid electrodes were also being often solved [115].

From the initiative of the director of Polarographic Institute, professor A. A. Vlček (1927–1999) (Fig. 3.1.9), a regular international electrochemical forum called Heyrovský Discussion was founded in 1967, to which foreign scientists both from East and West were being invited. Every year a different topic was selected: the first discussion in 1967 was about adsorption on electrodes and its effect on electrode processes, the next one in 1968 was about adsorption and processes on catalytic electrodes, and in 1969 it was about the mechanism of redox reaction proper (cf. Sect. 3.2).

Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences

The electrochemical topics studied in this institute were similar to those studied at the Prague School of Chemical Technology, as professor A. Regner (1905–1970) (Fig. 3.1.10) was the head of the department of inorganic technology and at the same time the director of Institute of Inorganic Chemistry. The topics studied were the solubility diagrams of complex ferro/ferri cyanides and the kinetics of electrochemical oxidation of complex ferrocyanide [50, 116]. Other subjects of research were the solubilities of persulfates [52, 117–119], the determination of specific heat, density, and viscosity of sodium and potassium amalgams [120, 121], and the effect of brine impurities on amalgam electrolysis of alkaline chlorides.

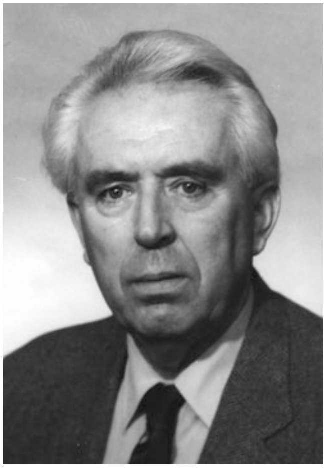


Fig. 3.1.9 Antonín A. Vlček (1927–1999)

Fig. 3.1.10 Albert Regner (1905–1970)

Research Institutes

State Research Institute of Material Protection (First of Its Kind in the World)

M. Pražák constructed an original electronic potentiostat which became the basic instrument for study of corrosion. It was used, for example, for following corrosion of corrosion-proof steels and alloys [122–124]. The effects of temperature on potentials of metals, on kinetics of their dissolution, and on activation energy of iron passivation in sulfuric acid were tested in the institute [125–130].

3.1.5 The Years Between 1970 and 1990

The "Prague Spring" in 1968 was the beginning of democratization of Czechoslovak society, interrupted by forceful occupation of the country by the "socialist armies" in August 1968. Under Soviet supervision, the life in Czechoslovakia was "normalized," i.e., it was returned to conditions before "Prague Spring." In November 1969, the state borders were tightly closed again. By November, but already after August 1968, thousands of Czechoslovak citizens emigrated, among them scientists including electrochemists. Czechoslovak electrochemistry lost a number of prominent middle-aged scientists (e.g., P. Zuman, P. Valenta), but also young ones (L. Němec). Some electrochemists first emigrated but then soon returned back (J. Koryta). Emigration to the West continued even later—the country was left, e.g., by J. Balej, A. Hofmanová, and J. Honz, in the 1980s by members of younger generation, as P. Vanýsek or D. Homolka. However, the majority of Czechoslovak electrochemists stayed at home and worked hard, although with less facilities than had the emigrés. The informal rule that a scientific worker is allowed to travel to the West once in 5 years was held in the Czechoslovak Academy—that, of course, did not concern communist officials. In spite of all the restraints, the Czechoslovak electrochemists managed to keep up with the world of electrochemistry, as can be seen from the following survey.

Research in Schools

Universities

At the department of physical chemistry of Charles University, the research continued along the projects started in the 1960s. Electrochemical methods were applied in the doctoral theses of the main department members: about orosomucoid [131] and about the system hemoglobin-heptaglobin [132]. Even further studies concerned heptaglobin [133–135]. At the department of analytical chemistry, the important subject was hydrodynamic electrochemistry, studied both theoretically and experimentally. Results of the mentioned studies have been condensed in a monograph [136].

In the Brno J. E. Purkyně University (former Masaryk University), at the department of physical chemistry, the research was first continued from the 1960s, i.e., study of kinetics of chemical reactions connected with electrochemical processes [137]. New trend of electrochemical research was experiments with nonaqueous and mixed electrolytes [138, 139]. In order to determine ionic association in aqueous medium, exact measurements of conductivity of electrolytes and electrode processes on rotating disk electrodes were studied. From the second half of the 1970s, some electrode processes were interpreted quantum chemically [140]. The department started a successful cooperation with the Brno Institute of Biophysics of Czechoslovak Academy of Sciences in the field of bioelectrochemistry (guanine and its derivatives). The measurements of conductivity of polyelectrolytes containing mono- and bivalent counterions were also carried out. The effect of medium on electrochemical behavior and reactivity of solution components and the electrochemistry with mixed and nonaqueous solvents were studied [141–145].

In Olomouc at the department of analytical chemistry of the Palacký University, the electrochemical problem of penetration of chemicals into ecosystem in the case of reduction mechanism and determination of nitrogen-containing biologically active compounds was studied [146].

Technical Universities

At the Prague School of Chemical Technology in the department of inorganic chemistry the main research concerned electrolytic problems. Activation energies for development of oxygen and chlorine on oxide electrodes were determined experimentally [147]. The team led by I. Roušar (1931–1996) followed the transfer of matter and heat in electrolysis [148–154] and the decomposition of amalgams [155–161]. From the 1980s in the department the research of electrochemical machining, polishing, and drilling was taking place [162–164].

At the Department of physical chemistry of the School of Chemical Technology in Pardubice continued the study of reaction kinetics of second and third order redox reactions [165], of two competing consecutive reactions [166], and the determination of rate constants of homogeneous reactions including description of the determination of rate constants from potential–time curves [167, 168]. It was recommended to use currentless potential–time curves for determining rate constants of other than redox reactions [169].

In the Electrotechnical Faculty of the Technical University in Brno, in the mid-1960s, a new department of electrotechnology was formed in which, among others, the electrodes for electropower sources were studied. There developed the idea to form electrodes in which the conducting (active) material is supported by plastic (e.g., polyethylene, teflon). These electrodes were named plastic-bonded ones. In Brno for the first time the plastic-bonded silver oxygen electrodes for fuel cells in alkaline electrolyte were tested; however, these electrodes were not comparable with metallic silver electrodes. At the same time, plastic-bonded lead electrodes were being developed. Even various modifications of active materials (Cd, Fe, and Ni-oxide) were performed [170–173].

At the Ostrava Mining University, the problems of determining basicity of the in situ oxide melts and of oxidizing properties of oxide melts were studied in the chemistry department by means of high-temperature potentiometry. A probe for measuring oxygen activity in oxide melts was thereby developed [174].

At the Technical University in Košice, compounds in aqueous and nonaqueous solutions, electrolytic deposition of aluminum and its alloys from nonaqueous electrolytes [175–177], and electrochemical separation of rare earth elements were studied [178].

Academy Institutes

Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences

Phase diagrams of three- and four-component systems and their application for solving electrolytic processes were studied [179–182]. Special interest was concentrated on peroxo disulfates [183–186]. A new method was the decomposition of amalgams on small TiC-Ni tablets. Electrochemical properties of TiC (impedance, kinetics of redox reactions occurring on it) were followed [187–189]. Other subjects of research were reduction of nitrogen oxides on Pt electrodes [190], utilization of electrochemical methods in study of hydrogenation reactions, and characterization of Pt and Pd catalysts [191, 192]. The effect of mercury on hydrogen overvoltage at solid electrodes was also studied [193–195]. In the topics of electrochemical power sources, the catalysts based on tungsten bronzes and the insertion of lithium into manganese dioxide and into monoxides of transition metals were investigated [196]. Adsorption of hydrogen on transition metal oxides was another subject of research [197–201]. In the 1970s, the surface oxides on Pt electrodes in sulfuric acid were studied [202, 203]. Part of the research program was also the study of porous carbon electrodes used for formation of hydrogen peroxide by cathodic oxygen reduction [204–206].

The Jaroslav Heyrovský Institute of Physical Chemistry and Electrochemistry of the Czechoslovak Academy of Sciences

This institute was formed in 1972 by merger of the J. Heyrovský Polarographic Institute with the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences. From the 1970s, studies of charge transfer across the interface [207–211], of the boundary between two immiscible electrolytes [212–220], and of electrolysis with the dropping electrolyte electrode were undertaken there [221–223]. This topic was included in a further number of communications from the Heyrovský institute [218, 224–233]. Electrochemical reactions of oxygen and hydrogen peroxide on various electrodes were studied there already from the 1960s [73, 234–239]. Minor works in electrochemical instrumentation as well as sophisticated apparatuses for electrochemical research were being developed in the institute [240]. Among the problems studied were the electrochemistry of sulfur adsorbed on carbon [241], the carbon prepared by electrolytic reduction of polytetrafluoroethylene [242–245], and the TiO_2 electrodes modified by Nafion [246, 247]. Pt and other solid electrodes were used in the institute [248, 249], for example, for study of adsorption [250–258].

The electrochemical instrumentation was digitalized, and by 1980, the experiments were controlled on-line by a small computer of institute's construction. This instrumentation allowed measurements of broadband impedance spectra on basis of a pseudo-random signal and of Fast Fournier Transform. Later the Fast Walsh-

Hadamard and the Fast Haar Transforms were employed and implemented [259]. The nucleation and growth of compact monolayers were investigated in a large series of systems. This was achieved by means of time-resolved capacitance measurements. The fractal character of certain monolayers was discovered, and the growth was simulated by Monte Carlo simulation [260]. Lipid monolayers undergo phase transitions at a critical temperature called Kraft point. Impedance techniques allowed a new method for determination of the Kraft point [261]. The electrocatalytic reduction of nitrogen to ammonia called nitrogen fixation was carried out by an organic molybdenum catalyst [262].

The Arrhenius theory of electrolytic solutions was quantitatively restored by explaining the properties of strong electrolytes without activity coefficients on basis of ionic solvation and incomplete dissociation [263–266].

The effect of light on electrode processes [267–269] and the surface interaction of organic compounds in electrode reactions should be mentioned from other subjects [270, 271].

The catalysts tungsten carbide (WC) [272–274] and carbon [275–279] for electrodes working in acidic electrolyte were studied in the topics of fuel cells.

In the 1970s, part of the workers dealing with electrochemical power sources changed their topics from fuel cells to plastic-supported (bonded) electrodes for storage batteries, especially for their suitable production. Soon were obtained hopeful results, e.g., [280, 281], successfully presented abroad (England [282, 283], India [284], Bulgaria, Romania, Hungary, and East Germany). It concerned plastic-bonded cadmium and nickel oxide electrodes. In the attempt to utilize the plastic-bonded electrodes in hermetic batteries, it was necessary to study the recombination of oxygen produced during charging the battery cells [285–288]. The problems of porous electrodes for batteries were being solved also theoretically [289–292]. From the second half of 1970s, in the Heyrovský institute lithium electrodes were studied with the intention to develop Li–CuO system [293]. Other topics were the conducting polymers [294, 295] and the composite electrodes [296–302] for chargeable cells. The Heyrovský institute workers engaged in studies of electrochemical sources of current were cooperating with Czechoslovak battery companies Bateria Slaný, Prague battery factory Mladá Boleslav, with other technical institutions (ČKD Semiconductors, Research Institute of Electrotechnical Ceramics), and with the department of electrotechnology of the Technical University Brno, so that the workers of these establishments were often coauthors of publications and patents. This cooperation exceeded even state borders, i.e., to East Germany, Bulgaria, Hungary, and Sweden.

The first successful Heyrovský Discussions were followed by further discussions in the 1970s and 1980s. Their topics were: Products and intermediates of electrode reactions (1970), Products and intermediates of redox reactions (1971), New principles in electroanalytical chemistry (1972), Deposition and oxidation of metals (1973), Electrochemistry in nonaqueous solvents (1974), Electrochemical phenomena in biological systems (1975), Redox reactions of coordination compounds (1976), New horizons of polarography (1977), Electrochemical energy conversion: expectations, achievements and critical assessment of perspectives (1978), Electrochemistry in environmental protection (1979), Electrochemical phenomena on membranes and biomembranes (1980), Fundamentals of preparative organic electrolysis (1981), New principles in electroanalysis (1982), Photochemical stimulation of redox reactions (1983), Electrochemical processes in two-phase liquid, microemulsion and micellar systems (1984), Recent aspects of electrocatalysis (1985), New aspects of electrochemical materials fundamentals (1986), Ecoelectrochemistry (1987), Electrochemistry of separation and synthetic processes at liquid/liquid interfaces (1988), Catalytic homogeneous processes combined with electrochemical charge or group transfer (1989), and Electrochemistry on organized molecular and polymolecular structures (1990). In the enumerated discussions, the introductory lectures were presented from the side of the hosts by J. Volke (1926–2012), E. Paleček, J. Koryta, and others, and from the foreign participants there spoke professors Bockris, Fleischmann, Pardone, Albery, Conway, de Levie, and others, i.e., prominent electrochemists.

Institute of Biophysics, Academy of Sciences of the Czech Republic, Brno

The Institute of Biophysics developed into an internationally recognized center of bioelectrochemical research headed by professor E. Paleček. Electrochemical behavior of nucleic acids and proteins was studied systematically, and sensitive methods were developed for their determination. It was proved that DNA structure depends on the sequence of nucleotides [303, 304], or that the double helix of DNA is polymorphous [305]. Activities of the Brno group of bioelectrochemists were several times reviewed, e.g., [306]. Institute of Biophysics cooperated with Institute of Physical Chemistry of the Brno University [307–309] (bioelectrochemistry of adenine, guanine, and guanidine).

Research Institutes

State Research Institute of Material Protection, Prague

The research on corrosion, started in this institute in the 1950s, continued successfully further. The intergranular corrosion of steels was measured by an electrochemical potentiodynamic reactivation method [310–312]. Since the 1960s, the passivity of brass was further studied, the rates of corrosion were measured by polarization resistance, the effect of deformation on anodic dissolution of steels was followed, and the surface roughness of metals was measured; other subjects of research were, e.g., the behavior of passive films on steel, the effect of composition and motion of electrolyte on corrosion of passivated aluminum, the cathodic protection of passive metals against corrosion, the anodes for cathodic protection of steels, etc.[313–316]. Measurements of polarization resistance in the system iron—concentrated sulfuric acid or boiling nitric acid, of corrosion and matter transfer of asthenic and ferritic steels in liquid sodium, etc., were important [317–324]. Even corrosion of copper and brass was followed [325–330].

Research Institute of Inorganic Chemistry in Ústí nad Labem

The subject of study in the electrochemical section of the above institute was mainly industrial electrolysis. The problems being solved were activation of titanium anodes and causes of their losing activity [257, 331], the state of anodes when electrolysis is turned off, the use of titanium anodes in amalgam electrolysis, the utilization of active layer on anodes, and the replacement of graphite plates by activated Ti anodes in electrolysis of NaCl. Electrolysis of aqueous solutions of alkaline chlorides using catex membranes was tried and evolution of hydrogen and oxygen was measured in electrolysis of alkaline brines. The electrochemical engineering problems concerning the measurement of mercury filling, of current density, and of optimization of electrolyzer dimensions were being solved.

Research Institute of Electrotechnical Ceramics, Hradec Králové

In this institute, the problems of primary high-temperature electrochemical sources of current with solid electrolytes, of primary zinc-silver cells for watches and calculators, and mainly the problem of silver electrodes were studied [332].

Prague Battery Factory, National Enterprise, Mladá Boleslav

From the 1970s, it studied plastic-supported electrodes. As the factory had a close cooperation with the J. Heyrovský Institute, factory workers (J. Malík (1921–1988), V. Koudelka (1931–1995) and others often participated in the research publications from the institute [280–282]). In the factory it was decided that the production of electrodes for Ni-Cd batteries was disadvantageous for both technological and economical reasons.

Bateria Slaný

Since 1981 in the laboratories of the monopolistic producer of primary cells and of closed Ni-Cd batteries, the research of Czechoslovak lithium batteries was taking place. The systems lithium-polycarbonfluoride [333] and lithium-cupricoxide were studied. In the 1980s it was tried to replace the classical electrodes in small closed Ni-Cd batteries by the plastic-supported electrodes. However, for various reasons, such adjusted batteried did not come to production, although the plastic-supported Cd electrodes were applicable in closed Ni-Cd cells of capacity up to 4 Ah [334].

ČKD Semiconductors Prague

The electrochemical and technological laboratory which studied and developed oxygen-hydrogen fuel cells was in this production plant. Raney nickel and silver were used as catalysts.

The workers prepared metallic hydrophilic porous electrodes of areas up to 45 cm^2 and plastic-supported semihydrophobic electrodes. They put together a five-membered hydrogen-air module with alkaline electrolyte of the output first to 500 W, later up to 1000 W [277, 335–342]. Fuel cells with liquid fuel, hydrazine [343] and formiate, were also tested.

3.2 The Development of Polarography as a Component of Czechoslovak Electrochemistry

Michael Heyrovský

3.2.1 The Years Between 1921 and 1939

The primary element of polarography, the dropping mercury electrode, was introduced in science by the Czech physicist Bohumil Kučera (1874–1921) (Fig. 3.2.1) [344] in order to improve the Lippmann's method of surface tension measurement of polarized mercury [345].

The Kučera's method enabled surface tension measurement with high precision; however, in addition, it produced some unexplained phenomena. Later, when Kučera became professor of physics at the Czech Charles University in Prague, he suggested to Ph.D. student Jaroslav Heyrovský (1890–1967) to study the method more thoroughly. Heyrovský, with his experience in electrochemistry from the laboratory of professor F. G. Donnan (1870–1956) at the London University College, tried in Prague at the University department of chemistry to use the dropping mercury electrode in 1 M aqueous solution of NaCl for surface tension measurement in parallel with measurement of electrolytic current/voltage curve. The result of repeated complex measurements was perfectly reproducible—thus it happened on Friday 10th February 1922 in the afternoon that polarography was initiated, creating stimulus for further research. Heyrovský published this novelty in Czech [346] and in English [347] and spoke about it at a General Discussion of the Faraday Society in 1923 [348]; an announcement of it appeared also in French [349]. The English communication drew attention of a young Japanese scientist, Masuzo Shikata (1895–1964) (Fig. 3.2.2), who was at that time on a study stay in Europe. Shikata joined Heyrovský in Prague where they designed an instrument for automatic photorecording of current/voltage curves by means of a Kohlrausch drum

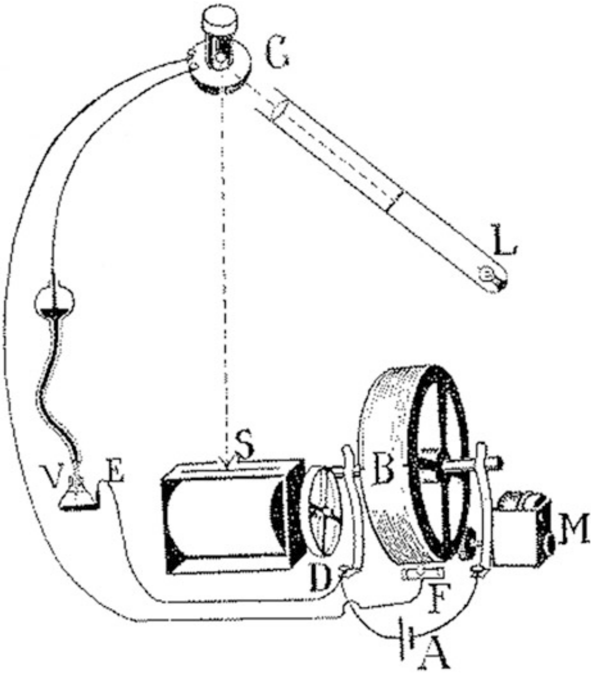
Fig. 3.2.1 Bohumil Kučera (1874–1921)

Fig. 3.2.2 Masuzo Shikata (1895–1964) and Jaroslav Heyrovský

potentiometer and a mirror galvanometer, with which they then systematically studied polarization of the reproducible dropping mercury electrode in various solutions; as in that way they recorded the electrode **polar**ization photo**graph**ically, they called the new instrument **polarograph** [350] (Fig. 3.2.3) and from there the method got the name **polarography**. The first few laboratory models of the polarograph were set up by two university department workshop workers. Technical production and development of polarographs were then started by Heyrovský's student Vladimír Nejedlý in Prague.

The first public presentation of the results of polarographic measurements was carried out by an international group of students and coworkers of the then docent Heyrovský at the Physico-chemical Institute of Charles University in Prague, when their results were published in May 1925 as "Researches with the dropping mercury cathode, parts I.-XI." in a special issue No. 5, vol. 44, of the Dutch journal Recueil des Travaux Chimiques des Pays-Bas, published in honor of 70th birthday of the Czech chemistry professor Bohuslav Brauner. In 1925 Shikata presented a paper before the Faraday Society about electrolysis of nitrobenzene with the mercury

Fig. 3.2.3 Polarograph



dropping cathode [351], and then he returned to Japan taking one of the models of polarograph with him. At the Kyoto University, he initiated active polarographic research in Japan.

In 1926 Heyrovský became an ordinary professor of physical chemistry, and the Physico-chemical Institute under his heading became and remained for many years the center for systematic study of polarography. Of Heyrovský's foreign students who then continued actively working in polarography in their home countries were Italian Giovanni Semerano (1907–2003) [352], Pole Wiktor Kemula (1902–1985) [353] (see Chap. 11), Russian Yevgenia N. Varasova (1905–1938) [354] (see Sect. 5.1), German-American Otto-H. Müller [355], Frenchman Edgar-Théophile Verdier (1913–1999) [356], and others. The journal Collection of Czechoslovak Chemical Communications founded in 1929 by Jaroslav Heyrovský and his friend Emil Votoček (1872–1950), professor at the Prague Institute of Chemical Technology, helped in spreading the knowledge of polarography in the world of science. Every year from 1938 till 1958 (with the intermission from 1940 till 1945), Heyrovský, with O. H. Müller as occasional coauthor, published the "Bibliography of publications dealing with the polarographic method" in Collection, and from 1959 till 1964, it was then separately printed by the Publishing house of the Czechoslovak Academy of Sciences. The Polarographic Society of Japan has been publishing since 1954 the Journal Review of Polarography.

One of the advantages of mercury as electrode material is its high hydrogen overvoltage, which allows in aqueous solutions more negative potentials to be

Fig. 3.2.4 Rudolf Brdička (1906–1970)

reached than with other electrodes. In polarography, it was soon found that some compounds cause catalytic evolution of hydrogen which could be utilized in analysis [357–360]. Heyrovský's student Rudolf Brdička (1906–1970) (Fig. 3.2.4) has discovered that in ammoniacal solutions of cobalt salts, a sensitive polarographic catalytic current is produced by proteins, an effect known since then as "Brdička reaction" [361], which was being successfully used in cancer diagnosis [362].

To make polarography known in his own country, Heyrovský wrote a short booklet in Czech [363] which was translated into Russian. The knowledge of polarography in USA was spread by J. Heyrovský in 1933 when he lectured for several months as Carnegie Visiting Professor at universities in California and in middle and eastern states. The German-speaking scientists were becoming acquainted with polarography since 1936 from the Heyrovský's chapter in the second volume of W. Böttger's textbook "Physikalische Methoden der analytischen Chemie."

From the amount of experimentally gathered material, it was gradually possible to derive the basic quantitative relations in polarography. The current flowing in the polarographic circuit, when the solution of the supporting electrolyte does not contain any electroreducible or electrooxidizable substance, is a pure "charging" or "capacity" current. Its quantitative formula was derived by Heyrovský's assistant Dionýs Ilkovič (1907–1980) (Fig. 3.2.5) [364]. The equation of the common electrolytic polarographic current controlled by linear diffusion of the electroactive species to the electrode was presented also by Ilkovič [365], who then together with J. Heyrovský derived an equation for a diffusion-controlled reversible polarographic step-shaped current–voltage curve or "wave" [366], by means of which the term "half-wave potential ($E_{1/2}$)" was introduced, indicating the quality of the studied substance. Since then in analytical handbooks, various tables of half-wave potentials of inorganic and/or organic compounds have been appearing. In analytical practice, it became common to determine concentration of polarographically active species by measuring the height of its polarographic wave at a constant

Fig. 3.2.5 Dionýs Ilkovič (1907–1980)

potential by the method of “polarometric titration” [367]. The Ilkovič equation of diffusion-controlled polarographic current was later solved by about 3 % more accurately by Jaroslav Koutecký (1922–2005) (Fig. 3.2.6) [368] who correctly considered spherical rather than linear diffusion of the electroactive substance to the mercury drop.

3.2.2 *The Years Between 1940 and 1969*

During the war (1939–1945), when under German occupation the Czech universities were closed up, professor Heyrovský could continue using his laboratory, thanks to his friend, the latent anti-Nazi German Johann Böhm (1895–1952), professor of physical chemistry, whom the German authorities made in charge of the Czech university chemical institute. In that way polarography continued developing when Heyrovský kept in contact with his students and colleagues under aggravated conditions. At that time he wrote in German the textbook “Polarographie,” published in 1941 by Springer-Verlag in Vienna [369].

If an electroactive substance has the tendency to adsorb at the electrode surface, it affects the shape of the polarographic curve, as Rudolf Brdička has derived and demonstrated by the case of electroreduction of methylene blue [370, 371]. Much attention was then also concentrated upon polarographic effects of adsorption of electroinactive compounds [372].

Karel Wiesner (1919–1986) (Fig. 3.2.7) has found that some polarographic currents are controlled by the rate of chemical reaction producing the electroactive substance near the electrode [373]; a quantitative formulation of an equation for such polarographic “kinetic” currents was then presented by Brdička and Wiesner [374, 375].

Fig. 3.2.6 Jaroslav Koutecký (1922–2005)

Fig. 3.2.7 Karel Wiesner (1919–1986)

On the course of polarographic curves often appear current maxima exceeding the limiting current—those of sharp shape, falling discontinuously down to limiting current of the curve near the point of zero charge, described for the first time by M. Shikata in the paper read before the Faraday Society [351], have been called "maxima of the first kind"; another type of maxima, of rounded shape, occurring in concentrated electrolyte solutions and increasing the original wave up to five times over the diffusion-controlled current or creating a new wave, distant from the point of zero charge, has been known as "maxima of the second kind" [376]. Both types of maxima depend on the way how the dissolved substance affects the surface tension of mercury. The cause of polarographic maxima of the first kind was discussed by mainly Russian [377] and German [378] authors, the maxima of the second kind were satisfactorily explained by T. A. Kryukova (1906–1987) (see Chap. 4) [379].

After the attempt by Matheson and Nichols [380] to utilize the progress in electronics by using cathode-ray oscilloscope instead of galvanometer for displaying polarographic curves, an essentially new method called "alternating current oscillographic polarography" for studying electrolysis with dropping mercury electrode by alternating current was introduced by Heyrovský and Forejt [381]. In this method, instead of the polarographic current–potential curves, the potential–time curves and their derivatives were displayed on the screen of the oscilloscope. That approach has opened for experimental electrochemistry new possibilities to follow fast chemical, electrochemical, and adsorption processes; for that purpose, in addition to the dropping mercury electrode, the "mercury jet" or "streaming mercury" electrode was adopted [382]. An important contribution of the "a.c. oscillographic polarography" to biophysical chemistry was the discovery by Emil Paleček of a sensitive electrode reaction of deoxyribonucleic acid (DNA) [383].

Thanks to the activities of the Czechoslovak and Japanese polarographic groups and their foreign colleagues, polarography was becoming internationally known, and polarographic instruments were already produced in several countries before the outbreak of the Second World War. During the war, the advantages of polarography in various military industrial analyses were especially appreciated—e.g., in the "Manhattan project," it was used for determining transuranium elements [384]. In 1946 polarography belonged to the five most frequently utilized analytical methods. The total number of evidenced polarographic publications at the end of 1938 was 608, by the end of 1945 it went up to 1631.

In Italy the "Centro di Studio per la Polarografia" in Bressanone organized annual meetings on polarography and published periodically "Contributi teorici e sperimentali di polarografia" and "Bibliografia polarografica." In various cities of USSR, a regular "All-union Conference on Polarography" was taking place. In London "The Polarographic Society" was publishing "Journal of the Polarographic Society" and was announcing occasional polarographic lectures or symposia; similarly active was also "The Australian Polarographic Society." Some of the companies producing polarographs, like Leybold (Germany) or Radiometer (Denmark), were also publishing polarographic periodicals.

The term "polarography" was originally introduced and used for electrochemical measurements of current–voltage curves with the dropping mercury electrode (DME) and later also with the mercury jet electrode [385]. The fundamental polarography, as it developed in the first half of twentieth century, has been referred to as "classical polarography." That stage of polarography was systematically treated in several textbooks [356, 369, 386, 387]. The American professor I. M. Kolthoff (1894–1993) from the University of Minneapolis, Minnesota, who visited Heyrovský's laboratory several times, wrote with his junior colleague J. J. Lingane (1909–1994) a textbook on polarography [388] which appeared in two editions and was translated into several languages.

In the textbook equations, the electrode reactions were then considered fast and reversible. Theoretical equation for the common irreversible polarographic curves was suggested by Smutek [389], a more exact formulation was provided by

Koutecký [390]. An experimental method how to study polarographic reversibility was started when Kalousek (1915–1996) [391] introduced into the polarographic circuit an electric switch interrupting discontinuously the polarizing voltage. That method was used by many authors in research of electrode reactions (e.g., [392–395]). With the aim to enrich the originally simple polarographic method, several other instrumental modifications were gradually developed. Breyer (1900–1967), Gutmann, and Hacobian [396, 397] started "polarography with alternating current" when on top of the d.c. polarizing voltage, an a.c. voltage of small amplitude was superimposed and the resulting small alternating current was measured—on the polarographic curves then instead of "waves" appeared a.c. current maxima or "peaks"; with solutions of surface active substances, the "a.c." modification of polarography became "tensammetry" [398]. When instead of simple a.c. voltage a right-angle a.c. voltage of small amplitude was introduced and the electrolytic current was measured before the end of the drop time, the sensitivity of current measurement was considerably increased—that method got the name "square wave polarography" [399] which underwent various modifications [400]. As in classical polarography, with growth of the mercury drop, the charging current component decreases and the electrolytic current component increases, it was suggested to measure total current just before the drop falls off—that increased the sensitivity of the method called "tastpolarography" [401]. Similarly, in "pulse polarography" [402] a gradually increasing single constant voltage pulse was applied to each mercury drop and the resulting current was measured shortly before the drop fell off; if the current was measured before and after the pulse the method was called "differential pulse polarography" (gen. rev. [403]).

In 1950 the Czechoslovak communist government introduced a new system of organizing scientific and technical research—in this connection the "Central Polarographic Institute" was established in Prague beyond the university, with J. Heyrovský as its director, who invited some of his coworkers from the university to join him there. Components of the new institute were dispersed in Prague in several places. Docent Rudolf Brdička followed Heyrovský in professorship of physical chemistry at the university.

In February 1951 the **First International Polarographic Congress** was organized in Prague. As at that time Czechoslovakia was isolated from the free world by the "iron curtain," apart from official guests from the "East-European socialist countries," about 400 active congress participants were Czechoslovak citizens; however, 41 written contributions were sent to the organizers from various foreign countries and were included in the three volumes of the printed proceedings. The congress program consisted of 8 main lectures and 57 brief communications from the field of theoretical as well as of applied polarography. In 1952 the Polarographic Institute became one of the institutes of the then established Czechoslovak Academy of Sciences, and Heyrovský was appointed academician.

The attitude of the Czechoslovak political regime towards professor Heyrovský was ambiguous—on one hand, he was officially praised, on the other hand, his contacts with foreign countries were strictly controlled, and some of his frequent invitations from abroad were not allowed to be realized.

In August 1955, the Hungarian polarographers organized the Hungarian–Czechoslovak polarographic conference in Veszprém, in June 1958 the reciprocal Czechoslovak–Hungarian conference was held in Prague. In February 1956, a Polish polarographic congress was organized in Warsaw in which also several Czech polarographers participated. In June 1957, a polarographic colloquium took place in Dresden (then East Germany), and in October 1958, an international polarographic colloquium was organized in Bonn (then West Germany).

In August 1959, the **Second International Congress on Polarography** took place in Cambridge, at that time 20 active participants from Czechoslovakia were officially allowed by the regime to attend. The congress proceedings were published by Pergamon Press in three volumes under the title "Advances in Polarography."

On 10th December 1959, Jaroslav Heyrovský received in Stockholm the Nobel Prize in chemistry from the hands of the Swedish king Gustaf VI Adolf—for the discovery and development of polarography [404] (since 1934, the Nobel committee had been receiving from different countries altogether more than 30 proposals for the prize to Heyrovský).

In September 1962, in Jena (then East Germany) was organized an international symposium "Polarography in chemotherapy, biochemistry and biology" (in German) with the proceedings published by Akademie-Verlag, Berlin. The **Third International Congress on Polarography** took place in July 1964 in Southampton, UK, with only five active Czech participants allowed to attend; the proceedings were published in two volumes at Macmillan under the title "Polarography 1964."

In 1964 professor Heyrovský resigned from directorship of the Polarographic Institute because of his declining health; to that post was appointed professor Brdička. To commemorate its founder, the institute got from 1.01.1964 the official name "Jaroslav Heyrovský Polarographic Institute."

In July 1966, the Czechoslovak Chemical Society celebrated its 100th anniversary by organizing in Prague the **Fourth International Congress on Polarography**, the scientific contributions appeared in a special December 1965 issue of Collection of Czechoslovak Chemical Communications published in honor of Jaroslav Heyrovský's 75th birthday. In September 1966, the Japanese polarographers organized the **Fifth International Congress of Polarography** in Kyoto; the proceedings were published in a special issue of the Japanese journal "Review of Polarography."

On March 27th 1967, Jaroslav Heyrovský passed away. The journal Revue de Chimie Minérale published a special issue (vol. 5, number 2, 1968) dedicated to Jaroslav Heyrovský. In Heyrovský's memory, the Prague Polarographic Institute, then headed by professor Antonín A. Vlček (1926–1999), introduced in Czechoslovakia an annual **international Heyrovský Discussion**, which since 1967 has been concentrating every year on different electrochemical problems—in 1990 the 24th Heyrovský Discussion took place (cf. Sect. 3.1).

3.2.3 The Years Between 1970 and 1990

In 1972 the Institute of physical chemistry was joined with the Polarographic institute under the name "The J. Heyrovský Institute of Physical Chemistry and Electrochemistry of the Czechoslovak Academy of Sciences." The electrochemical part of the combined institute consisted of three departments: department of redox processes, of electrocatalysis, and of electroanalysis.

In Riga (Latvia) in 1977 was organized the all-union conference "Polarography: Problems and Perspectives." In August 1980, the **J. Heyrovský Memorial Congress on Polarography** took place in Prague, attended by participants from all around the world. In 1986 in Fermo (Italy) was organized an international symposium "New trends in polarography and related techniques." After the fall of the "iron curtain" of major international scale was then the 41st Meeting of International Society of Electrochemistry organized jointly with the **J. Heyrovský Centennial Congress on Polarography** in August 1990 in Prague. Compared with the First International Congress in 1951, it had 668 participants from all around the world and the scientific program consisted of 11 plenary lectures, 15 microsymposia, and presentation of 803 posters. So in the second half of twentieth century, polarography was intensively developing on international scale spurred by many special conferences which presented new theoretically based variations and new practical applications of the method.

For the general case when not only DME but any electrode is used for studying current–voltage curves, Kolthoff and Lingane [405] suggested already in 1939 the term "**voltammetry**" (**volt**s applied, **am**peres **me**asured). According to this suggestion, later officially accepted by IUPAC, the original polarography has become voltammetry with DME. Equations of voltammetric curves recorded with hanging mercury drop electrodes (HMDEs) by "cathode-ray polarograph" were published independently by Randles (1912–1998) [406] and Ševčík (1926–2006) [407]. Utilization of HMDE for studying electrode reactions by means of traditional polarographic apparatus was first described by Čermák (1920–1980) [408] and by Kemula and Kublik (1922–2005) [409]. Theoretical equations for voltammetric curves of electrode reactions recorded with HMDEs appeared also under the title "stationary-electrode polarography" [410, 411]. Voltammetry with HMDE provides the chance to accumulate the product of electrode reaction on the electrode surface under a constant potential and then to record stripping of the product from the electrode by opposite potential scan—this leads to a considerable increase of analytical sensitivity [412]. Cyclic voltammetry by providing mutually corresponding cathodic and anodic reactions by peaks on one closed curve with two branches is an ideal method for studying electrode processes [413, 414].

In the 1950s, the alternative to voltammetry started appearing among electrochemical methods: the controlled current was applied and the ensuing electrode potential was measured—it was called "chromato-polarography" [415] or "potentiometric polarography-controlled current scanning" [416]. In these methods, the

HMDE has been mostly used [417]. For sensitive electroanalytical measurements, derivative chronopotentiometry was introduced [418, 419].

Electrochemical activity of biopolymers inspired the development of adsorption transfer voltammetric stripping [420] and of derivative constant current chronopotentiometric stripping analysis [421, 422]; the latter method turned out to be particularly sensitive for determining catalytic evolution of hydrogen at mercury electrode by the "peak H" [423, 424].

Polarography, started as "electrolysis with the dropping mercury cathode" [346, 347], was developing successfully due to its simplicity, sensitivity, wide applicability, and low cost. Its basic theoretical principles were worked out initially by the Prague group, and its various modifications were gradually being introduced by specialists in different countries. First it became electrolysis with dropping mercury electrode (not only cathode), then also with mercury jet electrode, and with hanging mercury drop electrode. According to officially accepted terminology, it became voltammetry with mercury electrodes, and with applied current and measured potential, it turned into chronopotentiometry. After all these possible changes and modifications, the electrolysis with mercury electrodes has maintained in current chemical language the simple general term "polarography," with casual nearer specification. A computer-controlled instrument with appropriate software has enabled to realize electrochemical measurements in the many modifications of the original polarography.

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Chapter 4
The Frumkin Era in Electrochemistry

O.A. Petrii, in collaboration with S. Fletcher

4.1 Introduction

Alexander Naumovich Frumkin was one of the leading scientists of the twentieth century. He was born in Kishenëv (now Chişinău, the capital of the Republic of Moldova) on October 24, 1895, and died on May 27, 1976, while attending a scientific conference in Tula (now the Russian Federation). Thus, a large part of his adult life coincided with the period we know as the "Cold War." In his final years, he managed to retain his penetrating intellect, amazing memory, and capacity to do work, to the astonishment of all who knew him. Roger Parsons famously noted that his indefatigability was a source of some frustration to his younger colleagues, who perhaps hoped to succeed him—if only they knew how! John O'M Bockris believed that Frumkin's scientific longevity was simply the result of his intellectual superiority.

Whatever the source of Frumkin's inner abilities, his outward achievements are plain enough to see. Despite innumerable petty restrictions caused by the "Cold War", his prestige as a thinker, and his encyclopedic erudition, made him the most sought-after electrochemist of his age. He played a leading role in a number of crucial scientific conferences around the mid-century, and his influence is still being felt 40 years after his death.

Looking back, it seems remarkable that Frumkin was able to combine the creativity of an abstract thinker with the business acumen of an industrialist, while dominating global electrochemistry. As Ya. P. Stradyn, member of the

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Academy of Sciences of Latvian SSR, astutely noted, the history of Soviet and world science cannot be reconstructed without considering Frumkin's contributions.

Frumkin was a man of high culture and very wide interests and had well thought-out positions on many arcane subjects. His singular personality has been well captured in a series of reminiscences written by people who knew him [1]. However, anyone hoping to summarize his scientific achievements in a few words will soon find themselves defeated by his immense output of published papers, scientific reports, letters, and personal correspondence.

Fortunately, Frumkin's scientific career falls into a series of different periods, each corresponding to a major development in world history. Indeed, it will soon become apparent that many aspects of Frumkin's life and work can be viewed as responses to the profound political developments occurring around him. Nevertheless, one should also keep in mind the unique personality of Frumkin himself.

4.2 The Odessa Years

Alexander Naumovich Frumkin came from a Jewish background. He was the youngest child of Naum Yefimovich Frumkin (1855–1934), an insurance salesman, and Margarita L'vovna Frumkina (1863–1949), his wife. Soon after the birth of Alexander, the family moved to Odessa, a cosmopolitan seaport on the Black Sea. It was there that Alexander passed his childhood and youth. A formative influence on his scientific development was his enrolment in St. Paul's Secondary School (*Realschule*) in Odessa. This was a culturally German school, which served the diverse population of this thriving community.

Frumkin's abilities manifested early. He fell in love with chemistry and developed a deep knowledge of its history. His parents were naturally proud of their son. On one occasion, during a holiday abroad, the family happened to meet an elderly chemist, who asked "Shura" (his pet name) if he knew anything about iodonium compounds. Despite the obscurity of the topic, Shura was able to describe them in some detail.

". . .and do you know who discovered them?"

"Why, of course, Willgerodt," replied Shura.

"Well, I'm Willgerodt!" came the startling reply (Conrad Willgerodt, 1841–1930, German chemist).

Frumkin graduated from St. Paul's School in 1912, and, after passing a further examination in Latin, he entered the Universität Straßburg (then part of Germany, now Strasbourg, France). At University, Frumkin's ability to solve complex problems allowed him to advance rapidly. He recalled that one of the problems he solved was how to prepare pure silicon. In those days, 99 % silicon was considered "pure," but to achieve that target, a large-scale electrolysis was needed with a controlled resistance in the circuit. The cell was designed by Frumkin as follows: a cast iron cylinder was immersed in a tank filled with alkaline solution and could be

Photo 4.1 Young Frumkin (1913–1914)

moved up and down. The deeper it was immersed, the smaller was the resistance. By this elegant means, the composition of the silicon could be very closely controlled (Photo 4.1).

In Strasbourg, Frumkin was reunited with an old friend of his family, the famous physicist, Leonid Isaakovich Mandelshtam (Mandelstam) (1879–1944). Mandelshtam was a key figure in the history of Soviet physics. He and A. F. Ioffe (1880–1960) were responsible for the creation of two of the largest scientific schools in the USSR, which contributed to the eminence of Soviet physics. Mandelshtam came from a similar background to Frumkin, having attended the same school in Odessa and having completed his scientific education in Strasbourg. After graduating with a doctorate in 1902, Mandelshtam had remained at the University to work with the Professor of Physics, Karl Ferdinand Braun (1850–1918). Those must have been exciting years for Mandelshtam: Braun received the Nobel Prize in 1909.

Mandelshtam had a strong influence on Frumkin's future career. Although Frumkin was never a pupil of Mandelshtam, and was never a "pure physicist," he always considered Mandelstam as his mentor. In 1913, on advice by Mandelshtam, Frumkin moved to the University of Bern (Switzerland), where he worked briefly with Volkmar Kohlschütter (1874–1938), an inorganic chemist who had moved to Bern from Straßburg (now Strasbourg) in 1909. It was in Bern that Frumkin published his first scientific paper, on the physicochemical properties of phosphorus.

In 1914, however, an international catastrophe occurred. Austria–Hungary declared war on Serbia on 28 July 1914, and 4 days later, Germany declared war on Russia. The United Kingdom then declared war on Germany on 4 August 1914. In these momentous circumstances, Frumkin returned to Odessa without receiving his Diploma. However, he obtained special permission from the Ministry of Education to sit in the final examinations of the Physical and Mathematical Faculty at the Imperial Novorossiya University without attending classes. He passed 24 exams with excellent marks in only 6 weeks, even though this usually took 4 years!

Despite his formal success (and despite an appeal by several University professors to appoint him to the faculty), Frumkin was compelled to take a job at a nearby metallurgical plant. However, during his free time, he frequently visited the University to carry out fundamental research. It was during this period that he became seriously interested in electrochemistry and published his first study on the theory of electrocapillarity (1917) in which he considered the movements of a mercury drop under the effect of an electric current [2].

After the February Revolution of 1917, the abdication of Tsar Nicholas II, and the formation of a Provisional Government, Frumkin was finally admitted to the University, in the Laboratory of Inorganic and Physical Chemistry, headed by Aleksandr Sakhanov (1886–1976). It was therefore in Odessa that Frumkin prepared his dissertation *Electrocapillary Phenomena and Electrode Potentials*, which was finally completed in 1919 [3]. During the period 1920–1923, short extracts were published in scientific journals in English, German, and Russian [4–6]. Frumkin once remarked that the examiner of his dissertation had pointed out that it contradicted many of the established concepts of electrochemistry at the time. He also remarked that a paper explaining the contradictions was rejected by the Editorial Board of *Zeitschrift fur Physikalische Chemie*.

In these early studies, Frumkin not only demonstrated his remarkable experimental skills but also revealed his deep understanding of natural phenomena, which was rare for someone so young. For example, he provided a complete and rigorous analysis of electrocapillarity theory and also derived the general relationship between the surface tension (reversible work of surface formation) and the surface electric charge, valid for solutions of all compositions. The Lippmann equation was included as a special case. He also experimentally confirmed the validity of the results by carrying out measurements on a mercury electrode. The concepts developed by Frumkin changed the established view of electrode potentials, accepted since the time of Nernst.

Outside his window, however, political events were developing rapidly. In early 1919, the newly formed Bolshevik government suddenly withdrew most of the Red Army from Ukraine, leaving Odessa defenseless. In August, the city fell to the White Army. They retained military control until 1920, when the Red Army once more displaced them. The Red Army's victory in the south eventually led to the foundation of the Union of Soviet Socialist Republics (USSR) in 1922. The situation in Odessa was well described by Aleksey Nikolayevich Tolstoy; "The city was crowded with Russian refugees of every type and class... Princes and Generals swept streets, waited on cafes and, if they were lucky, drove taxis. The Tolstoys were no exception amid the general misery..."

Once Frumkin told an amusing anecdote from those times. It was the story of how his key results came to be published in the *Philosophical Magazine*, one of the oldest and most prestigious scientific journals in the world. As the Red Army gradually approached the city, ships full of refugees were leaving the Port of Odessa. Artillery fire could be heard. At that moment, an anxious young man appeared on the quayside, pleading with the passengers to take an envelope overseas, which contained his *magnum opus*. Of course, the youth was Frumkin, and the scientific work was "*On the Theory of Electrocapillarity, Parts I and II.*" Amazingly, one of the strangers consented, and ultimately the parcel found its way to the Editorial Board of the Journal in London.

During this dramatic period, Frumkin's dissertation was published by the publishing house (and printing company) of Moshe F. Shpentser (1860–1927), the father of the poet Vera Mikhailovna Inber (1890–1972). [Inber was the name of her first husband.] Frumkin married Vera in 1920. However, their marriage was short-lived. Very soon, Vera left Odessa for Moscow. Later, she became a famous writer. Having spent 3 years in Leningrad during the Siege (1941–1944), she movingly described life in the city in verse and prose. Leon Trotsky (1879–1940), one of the founders of the Red Army, was a cousin of her father, and had actually lived in Odessa with the Shpentser family for a while during his childhood.

During the period 1920–1921 in Odessa, Frumkin also became a member of the artistic council of a small but very popular theater group headed by V. Tipot, Vera Inber, and Rina Zelenaya and even took part in some of their performances.

4.3 The Karpov Institute

In 1922, Frumkin also departed for Moscow, where he hoped to perform some experiments that he could not perform in Odessa, due to the lack of equipment. In Moscow, he encountered Aleksey Nikolayevich Bakh (1857–1946) the famous biochemist and political radical, who, 5 years earlier, had returned from exile overseas. This meeting was crucial for the future life of Frumkin.

In 1918, together with Lev Yakovlevich Karpov (1879–1921), Bakh had founded the Central Chemical Laboratory of the Supreme Council of the National Economy in Moscow. He became the first Director of this laboratory and, after Karpov's untimely death in 1921, it was renamed the L. Ya. Karpov Physicochemical Institute. For many years, this was the largest (and only) center for physical chemistry in the USSR. Despite the chaotic circumstances of its birth, it soon developed into one of the world's leading scientific centers, making important contributions to various fields of physical chemistry (electrochemistry and corrosion, theory of catalysis, chemistry of polymers, etc.). Famous scientists who worked in the Institute included A. N. Frumkin, Ya. K. Syrkin, N. M. Zhavoronkov, V. A. Kargin, I. V. Petryanov-Sokolov, S. S. Medvedev, K. A. Kocheshkov, Ya. M. Kolotyrkin, Kh. S. Bagdasar'yan, G. K. Boreskov, and M. I. Tëmkin.

It was to this intellectual powerhouse that Bakh invited Frumkin. Step by step, the best young chemists in the Soviet Union were being assembled there. It was in the Division of Surface Chemistry that the electrochemistry group originated (Revekka Khaimovna Burshteyn (1904–1992), B. P. Bruns). Later, several of Frumkin's former pupils from the Department of Electrochemistry of the Faculty of Chemistry of Moscow State University also joined the group, most notably Boris

Photo 4.2 A. N. Bakh and A. N. Frumkin (the fourth from *left*) in the Presidium of the Joint Meeting of scientists of the Karpov Institute, the Institute of Nitrogen, and the Institute of Chemical Physics dedicated to the 80th birthday of A. N. Bakh on February 11, 1937

Nikolayevich Kabanov (1903–1988), M. A. Proskurnin, and N. A. Balashova (Photo 4.2).

Frumkin remained at the Karpov Institute for 25 years, first as a researcher and later as Head of the Division of Surface Chemistry (1924–1946). In 1929, he became the Vice-Director of Scientific Issues in the Institute and remained in that post until 1944 (Photo 4.3).

The meticulous study of the effects of adsorption of organic compounds on the electrocapillary curves of mercury, which was accomplished by Frumkin at the Karpov Institute, led to the discovery of the famous isotherm that now bears his name (the "Frumkin isotherm" [7]). Whereas the Langmuir isotherm was based on the somewhat naive assumption that adsorbed species did not interact, Frumkin showed that such interactions were often very strong indeed. In addition, Frumkin combined his results with an electrical model of two capacitors in parallel, which later became the prototype for many multistate models.

In 1926, Frumkin and his coworkers embarked on a classical series of studies of the adsorption of ions on very large surface area substrates, such as activated carbon and platinum black. Later, this topic was taken up by the Department of Electrochemistry of the Moscow State University (MSU). In the same year, Frumkin and Amaliya Davydovna Obrucheva (1894–1968) [8] began to investigate the formation of the double layer. They were the first to identify the phenomenon known as "potential-determining adsorption" or, for electrodes interacting with acids and alkalis, "hydrolytic adsorption" (Photo 4.4).

In 1928, the classic paper by Frumkin and A. V. Gorodetskaya [9] appeared, in which they introduced the concept of the *zero charge potential*. This allowed the

Photo 4.3 A. N. Frumkin in a group of scientists of the Karpov Institute in the 1930s (R. Kh. Burshteyn is third from *right* in the *top row*)

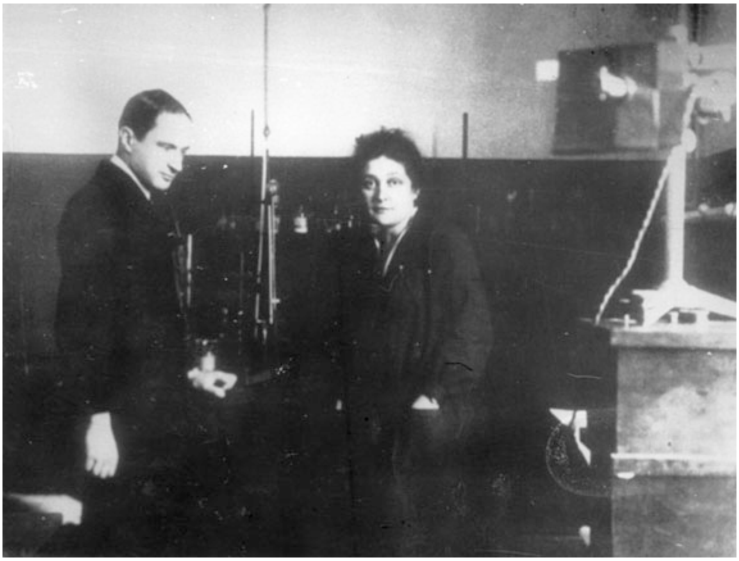

Photo 4.4 Frumkin and Obrucheva at the Karpov Institute

classical Volta problem to be solved, namely, the problem of the relationship between electromotive force and contact potential difference. Further development of this theory soon revealed the crucial role of zero charge potentials in electrocapillary and electrokinetic phenomena, the structure of interfaces, the mechanics of solids, the photoemission of electrons into solution, and the kinetics of electrode processes. Also in 1928, Frumkin published a comprehensive review about the electrocapillary curve in the series “Ergebnisse der exakten Naturwissenschaften” [10].

In 1935, Frumkin and M. A. Proskurnin [11] used ac measurements to measure the electric double layer capacitance. This permitted empirical values of the double layer capacitance to be compared rigorously with theory for the first time. The authors were successful because they carried out their experiments under conditions of exceptional cleanliness, such as glassware that had been acid-cleaned and water that had been multiply distilled. This work had an enormous impact internationally, because it demonstrated how reproducible measurements of the electrical double layer could be obtained. Indeed, Frumkin’s experimental methods soon became legendary among western scientists. From that time forward, the ac method became the standard method of measuring interfacial capacitance.

In 1939, while carrying out ac measurements in dilute electrolyte solutions, Frumkin and M. A. Vorsina [12] discovered an unexpected minimum in the differential capacitance curves of mercury. They correctly associated this minimum with the behavior of the diffuse part of the double layer in the vicinity of the zero charge potential.

Besides his fundamental studies of the electrical double layer, Frumkin also developed an interest in electrode kinetics. This work began in 1932, after Frumkin’s attention had been drawn to the work of Tibor Erdey-Grúz and Max Volmer on the theory of electron transfer. These authors had proposed a theory of the Tafel equation based on an analysis of the rate of electron transfer across the double layer. In 1932, in a very brief paper (only two pages long) [13], Frumkin showed that the basic equation describing the rate of charge transfer could be derived from the well-known Brønsted relationship according to which the change in the activation energy amounts to a certain fraction α ($0 < \alpha < 1$) of the change in driving force.

It should be noted that, in 1931, the physicist Ronald Wilfrid Gurney (1898–1953) had already published an astonishingly prescient theory of the elementary act of charge transfer across an interface, based on quantum mechanics. However, this work was not fully appreciated by electrochemists until three decades later.

In his own paper, Frumkin also analyzed the effect of the sodium amalgam concentration on the rate of electrolysis of water, and arrived at the conclusion that even for physically and chemically uniform surfaces, the processes of anodic metal dissolution and cathodic hydrogen evolution could occur simultaneously at the same potential. This same idea was later used by K. Wagner and W. Traud (1938) in their formulation of the theory of the “mixed potential,” the cornerstone of modern corrosion theory.

In 1933, Frumkin [14] became the first person to relate the rate of an electrode process to the structure of the double layer, by taking into account an effect which he called the psi-prime (ψ_1) effect (now universally referred to as “the Frumkin correction”). Thus, a close relationship was established between the two great divisions of electrochemistry, namely the *double layer* and *electrode kinetics*, which had been developed separately until that time. Soon after this, Frumkin further demonstrated [15] that the double layer structure could affect the kinetics of the hydrogen evolution reaction, if the electrolyte was dilute enough. This effect was not considered by the Erdey-Grúz-Volmer model. From Frumkin's analysis, it became clear that very large effects might be expected in the cathodic reduction of anions because the electrons would have to be transferred from a negatively charged electrode to a negatively charged ion, which might be electrostatically repelled in certain ranges of potential. This prediction was experimentally confirmed 13 years later.

In 1940, in a study P.I. Dolin, Boris Vul'fovich Ershler (1908–1978), and A.N. Frumkin [16, 17], the rate of discharge of hydrogen ions to form hydrogen atoms was determined experimentally for the first time. This work triumphantly confirmed the Frumkin approach (known in Russia as "the slow discharge theory"). The electrode processes were modeled by an equivalent circuit, which latter became better known as the Ershler–Randles circuit. The authors were also the first to introduce the term "exchange current" into electrochemical kinetics. Much later, in 1950, V. A. Pleskov developed the method of radioactive tracers for measuring the exchange current of electrochemical reactions.

Frumkin was elected to full membership of the Academy of Sciences of the USSR in 1932. This acknowledged the outstanding contribution that he had made to the development of science in the USSR. His new status consolidated his political position and provided him with a privileged position in Soviet society. At the same time, many new duties were also imposed upon him. Thus, in the period 1935–1939, he was also a member of the Presidium, the highest organ of the USSR Academy of Sciences. In subsequent years, he continued to take an active part in the work of the Academy of Sciences and its Division of Chemistry. In 1936, Pyotr Leonidovich Kapitsa (1894–1984), a Fellow of the Royal Society (and future Nobel Prize winner), who had recently been denied the right of return to the UK by Stalin, wrote a personal letter to Sir Ernest Rutherford, in which he described the members of the Presidium of the USSR. He wrote that Frumkin was the only person of scientific weight in the Presidium and, "even if he is somewhat inconspicuous, he is smart and honest and devoted to science, being a person outwardly melancholic, absolutely calm, and with some cynical mentality." He clearly appreciated Frumkin as a person.

The "Karpov period" was a very fruitful one for Frumkin and allowed him to complete a truly remarkable series of studies which are now firmly established in the foundations of electrochemical science. At the same time, Frumkin also made a number of organizational contributions to the development of the Karpov Institute and contributed to its emergence as one of the leading centers of physical chemistry in the world (Photo 4.5).

Photo 4.5 A. N. Frumkin with a group of chemists at the Karpov Institute in the late 1930s. From *left* to *right*, sitting: M. M. Feinberg, Ya. K. Syrkin, A. N. Fumkin, V. A. Kargin; standing: Ya. M. Kolotyrkin, P. I. Zubov

4.4 The University of Wisconsin–Madison (1928–1929)

In 1924, Frumkin made a lecture tour of Austria and Germany. One of his lectures, in Göttingen (Germany), was attended by Max Born, James Frank, and Robert Wichard Pohl. He also visited the University of Leiden (The Netherlands) where Paul Ehrenfest was Head of the Department of Physics. In Ehrenfest's house, there was a special room for guests who were encouraged to leave their signatures on one of the walls. Among the many great physicists, there is also the signature of Alexander Naumovich Frumkin (Photo 4.6).

Toward the end of the 1920s, the Soviet school of physical chemistry began to gain international recognition. Its seminars and scientific conferences were attended by foreign scientists, and its publications were widely read overseas. As an example of its growing influence, an invitation was received in 1928 for one of its scientists to work at the University of Wisconsin (U.S.A.) for a year. At that time, such invitations were very rare. A. N. Bakh decided that Frumkin would be the best choice. So it was that Frumkin, together with Amaliya Davydovna Obrucheva (1894–1968), whom he had recently married, traveled to Madison. There, Frumkin became a visiting Professor in Colloid Chemistry, a post vacated a few years earlier by the Nobel Prize winner Theodor Svedberg (30 August 1884–25 February 1971). It seems that the University considered offering Frumkin a permanent appointment, but he preferred to return to the USSR. As regards science, Frumkin regarded this American interlude as extremely inefficient (it clearly failed to match his hopes); however, a few scientific results were obtained on the electrocapillary properties of

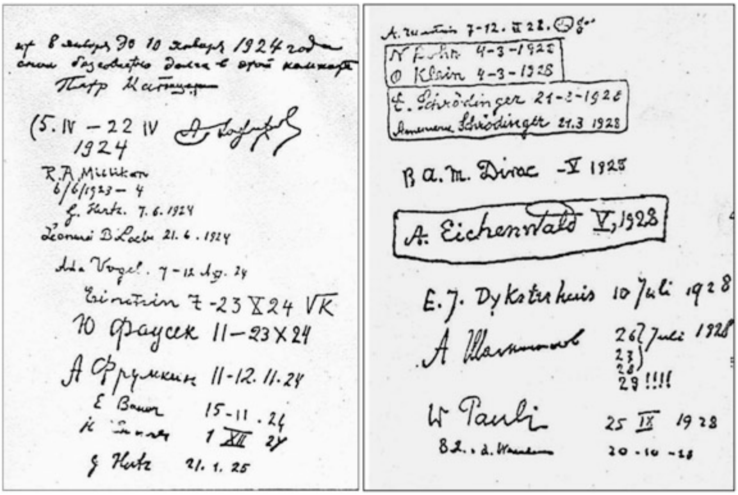

Photo 4.6 Part of the wall in Ehrenfest's house, showing the signatures of great scientists

amalgams, and these were duly published in the Journal of Physical Chemistry in 1930 (jointly with a student, F. J. Cirves).

During his time in the United States, Frumkin not only gave lectures to the staff and students of the University of Wisconsin but also toured many other universities. In this way he met many important American scientists and actively discussed their work with them. For example, at the University of Chicago, he visited the Laboratory of William Draper Harkins (December 28, 1873–March 7, 1951) and also met with Arthur Holly Compton (September 10, 1892–March 15, 1962). In Princeton, he discussed the polymerization of unsaturated compounds with Hugh Stott Taylor (6 February 1890–17 April 1974) and at Johns Hopkins University in Baltimore, he discussed the field of electrocapillary phenomena with Karl Ferdinand Herzfeld (February 24, 1892–June 3, 1978). In Philadelphia, he was delighted to meet George Borisovich Kistyakovsky (1900–1982), a chemist with Ukrainian-Jewish roots.

Frumkin established contacts with many other scientists, including Izaak Maurits Kolthoff (February 11, 1894–March 4, 1993) who in one of his later publications thanked Frumkin for his help in explaining an error that arises when a platinum electrode is used in pH measurements in media close to neutral.

Finally, Frumkin very much enjoyed a visit to the General Electric Laboratories in Schenectady, New York, where he was hosted by Irving Langmuir (31 January 1881–16 August 1957). Frumkin also delivered a lecture at Stanford University, California, at the invitation of the Canadian chemist James William McBain (22 March, 1882–12 March, 1953).

On his way back to Russia from the USA, Frumkin visited Berlin. That was in the summer of 1929. At the Kaiser Wilhelm Institute of Physical Chemistry and Electrochemistry, then headed by Fritz Haber (9 December 1868–29 January 1934), he met Herbert Max Finlay Freundlich (28 January 1880–30 March 1941) who invited Frumkin to work in Germany, but Frumkin was intent on returning to Moscow [18].

4.5 The Department of Electrochemistry at Moscow State University

Frumkin joined the Chemistry Faculty at MSU in late 1929 (Photo 4.7), and in May 1933, the Department of Electrochemistry was reorganized under his Chairmanship. He remained in that post for 44 years until his death. Even before 1930, MSU could boast a long history of innovation in electrochemistry. For example, in 1809, the German-born scientist Ferdinand Friedrich von Reuss (Reuß) (26 January 1778–21 March 1852) had reported the discovery of electrophoresis while passing electric currents through porous media. Later, in 1887, Aleksey Petrovich Sokolov (1854–1928) had used alternating currents to measure electrode capacitance. Finally, in the opening years of the twentieth century, there had been a remarkable series of innovations (including electropolishing) by Yevgeniy Ivanovich Shpital'skiy (16 September 1879–23 November 1931) [19].

Photo 4.7 A group of electrical engineers of the Moscow Research Institute of Chemistry. In the *bottom row*: Z.A. Iofa is the second and A.N. Frumkin is the third from the *left*

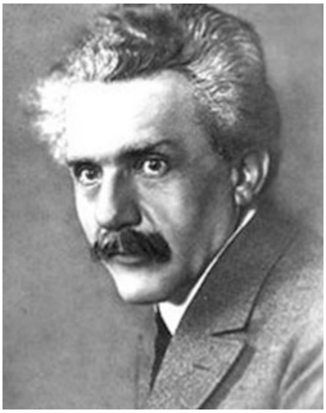

Photo 4.8 Yevgeniy Ivanovich Shpital'skii

Shpital'skiy graduated from Moscow University in 1904 and was subsequently employed there. His best-known work dealt with catalysis and electrochemistry. After graduation, he initially briefly moved to Heidelberg for postgraduate study. However, he soon returned to Moscow, where he developed the theory of intermediates in homogeneous catalysis. In 1911, he famously filed a patent for the electropolishing of metals, possibly the first time this term was used. Unfortunately, the First World War, followed by the Russian Civil War, disrupted his priorities, and Shpital'skiy's energies were diverted toward munitions (Photo 4.8).

By the mid-1920s, however, Shpital'skiy's laboratory had returned to normal, and he began to employ many notable young scientists, including N. N. Petin, Z. A. Iofa, Nikolay Ivanovich Kobozev (1903–1974), N. I. Nekrasov, V. V. Monblanova, and several others. All of them subsequently became well known in their fields. Meanwhile, Shpital'skiy's own papers were achieving European recognition, particularly in Germany. He was elected a member of the Bunsen Gesellschaft and became friendly with some of its members (particularly Walter Nernst).

However, tragedy struck in 1929. Shpital'skiy was arrested as a supposed member of the *Prompartiya* ("Industry Party"). In the ensuing show trial, he and a number of codefendants were accused of sabotaging Soviet industry and plotting a coup against the Soviet state. The case against Shpital'skiy was flimsy, but damagingly included the existence of several German patents for his inventions. Despite the absurdity of the prosecution claims, he was sentenced to death. Several prominent scientists, including Vladimir Nikolayevich Ipat'yev (Ipatieff) (1867–1952), pleaded for leniency. Perhaps due to these appeals, the death sentence was commuted to 10 years imprisonment, but this just led to further problems. Shpital'skiy was not sent to a normal prison. Instead, he was assigned to one of the first Soviet "sharashkas" (secret laboratories in the Gulag labor camp system, later described by Aleksandr Isayevich Solzhenitsyn (11 December 1918–3 August 2008). Initially, he somehow managed to complete the registration of several patents. However, in the harsh conditions, his health began to deteriorate. Within months, a foot was amputated due to blood poisoning, and he died of a heart attack in November 1931.

The arrest of Shpital'skiy led to a reorganization of research at MSU. With the appointment of Frumkin, the focus shifted to theoretical and practical studies in the field of electrode processes. During this turbulent period, Z. A. Iofa and A. I. Shlygin became close colleagues of Frumkin. Frumkin and Shlygin began work on the adsorption of oxygen and hydrogen [20], and later perfected the method of charging curves. Parallel studies were carried out by Ershler (Karpov Institute). Shlygin maximized the surface area of the electrodes (e.g., by using platinized platinum), whereas Ershler minimized the volume of solution, thus creating the first thin-layer cell. The development of these novel methods made it possible to study adsorption under conditions close to equilibrium, in contrast to the perturbation methods favored by overseas scientists such as Bowden, Rideal, and Butler, who had used high currents. Most importantly, Frumkin and Shlygin discovered that the equilibrium charging curve of platinum was linear in the region of hydrogen adsorption. Based on this surprising result, Mikhail (Menasiy) Isaakovich Tëmkin (1908–1991) developed his well-known *logarithmic isotherm*, in which the heat of adsorption decreased with increasing coverage. This was a considerable advance over the Langmuir adsorption isotherm.

Besides his fundamental studies of adsorption, Frumkin also carried out some important research on corrosion [21]. This work was performed in collaboration with Ya. M. Kolotyrkin, Z. A. Iofa, and V. A. Kuznetsov and was crucial for the further development of the field. At the same time, Frumkin initiated studies on the structure of the solution/air interface (with M. A. Gerovich) which were also widely acclaimed (Photo 4.9).

Photo 4.9 Department of Electrochemistry of MSU in the 1940s. From *left* to *right*, sitting: M.A. Gerovich, A.N. Frumkin, Z.A. Iofa, A.D. Obrucheva; standing: V.A. Kuznetsov, B.S. Gurenkov, V.S. Bagotzky, N.B. Moisseeva, Kuznetsova (?), A.I. Fedorova, S.Ya. Mirlina

In the 1945/1946 academic year, Frumkin delivered a famous series of lectures on electrochemical kinetics. These proved to be immensely popular with his students, who also urged him to compile them in a textbook. The eventual publication of such a book in 1952 under the title of *Kinetics of Electrode Processes* (in co-authorship with V. S. Bagotskiy, Z. A. Iofa, and B. N. Kabanov) [22] was a milestone in the history of electrochemistry, coming, as it did, almost 10 years before the famous monograph by Klaus Jürgen Vetter (1916–1974) ("Elektrochemische Kinetik," Springer, Berlin 1961; translated into Russian in 1967). However, because Frumkin's text was published in the Cold-War period, it was officially translated only into Chinese (1957) and remained largely unknown in the West. Nevertheless, the text was translated into English in India [23]. According to [24], an English translation was also made in the USA in 1967 ("Kinetics of Electrode Processes," Foreign Technol. Div. No. FTD-HT-67-153, Wright-Patterson Air Force Base, Ohio), although this is now a bibliographic rarity.

Despite the language barrier, the remarkable contributions of the Frumkin Group to the development of world electrochemistry were acknowledged by J. O'M. Bockris and A. Reddy in their well-known textbook "Modern Electrochemistry" (1970): Frumkin's group… "*was at the cutting edge of physical electrochemistry and stimulated much of the post-WWII work in this field in Europe, and eventually in the United States.*"

4.6 Institute of Colloid Electrochemistry: The Institute of Physical Chemistry

Besides his work at MSU, Frumkin was also involved in the development of the Institute of Colloid Electrochemistry, which was renamed the Institute of Physical Chemistry in 1946.

The Institute of Colloid Electrochemistry had originally been founded by V. A. Kistyakovskiy [25] in Leningrad (now St. Petersburg) in 1929. Kistyakovskiy was a graduate of St. Petersburg Imperial University and had worked in Leipzig under Wilhelm Ostwald. In 1934, when the Institute was officially moved to Moscow, various students of Kistyakovskiy (including K. M. Gorbunova, D. I. Mirlis, I. V. Krotov, and A. T. Vagramyan) became the Heads of the new laboratories. The Institute was also renamed the "Institute of Colloid Electrochemistry of the Academy of Sciences of the USSR" (Photo 4.10).

By 1939, however, Kistyakovskiy was 74 years old, and Frumkin was appointed to succeed him. In 1940, Frumkin founded the laboratory of electrode processes. Initially only B. N. Kabanov and A. V. Gorodetskaya worked there, having transferred from the Department of Surface Phenomena at the Karpov Institute. However, during the period 1941–1947, various other scientists joined them,

Photo 4.10 Vladimir Aleksandrovich Kistyakovskiy (1865–1952)

Photo 4.11 A.N. Frumkin—the Director of the Institute of Physical Chemistry of the USSR (1939)

including N.A. Bakh, R.Kh. Burshteyn, N.A. Balashova, S. D. Levina, and N. A. Shumilova. Frumkin's loyal secretary for 50 years, A. S. Gurylëva, also moved there. Most notable of all, Veniamin (Benjamin) Grigor'yevich Levich (30 March 1917–19 January 1987) joined in 1940 (Photo 4.11).

4.7 The Second World War

The Second World War, or "The Great Patriotic War" as it is known in Russia, began for the USSR in June 1941 and had an immense influence on the development of scientific research in the USSR. Almost immediately, the leading scientists of the USSR, including Frumkin, were asked by the State Defense Committee to concentrate all their efforts on solving problems for the military. As the Nazi front line approached Moscow, the task of evacuating the Academy and the Institutes also became urgent. In response, the Institute of Colloid Electrochemistry, together with its Director, was evacuated to Kazan. They did not return until summer 1943. Despite this disruption, new types of heat- and frost-resistant galvanic cells were successfully developed, a new method of manufacturing activated carbon was invented, and novel electrochemical fuses were produced that were widely adopted on the home front.

Following the entry of the United States into the war on 11 December 1941, Frumkin made two visits to the USA [23]. There is no reliable information about these visits, but they were clearly related to the defense needs of the USSR.

A new collaborator of Frumkin during the wartime years was Vladimir Bagotsky (this is the way his name is given in English publications; the transliteration is Bagotskiy) (1920–2012) [24]. His father, Sergei Yustinovich Bagotskiy, was a well-known revolutionary and disciple of Lenin, who had organized Lenin's famous train trip through Germany to Russia in 1917. In 1937, Bagotskiy senior, who by then was acting as the USSR Representative at the United Red Cross and Red Crescent Society in Switzerland, was recalled to the safety of Russia with his family. In 1939, Bagotsky junior entered the Faculty of Chemistry of MSU. By the end of 1943, when the Faculty returned to Moscow, Bagotsky was able to begin his diploma studies under Frumkin. Finally, in 1947, he defended his "Candidate of Science" thesis (equivalent to a PhD) on the kinetics of electrochemical hydrogen evolution on mercury. This thesis was a triumphant confirmation of Frumkin's theory of slow discharge.

For the next 2 years, Bagotsky continued to work in the Department. However, in 1949, he found himself accused of so-called cosmopolitanism. This term was a catch-all phrase used in that era to describe intellectuals who were suspected of harboring pro-Western feelings, or who might be thought to lack sufficient patriotism. Bagotsky was fired from the Faculty of Chemistry (his accusers noted that he had studied *Esperanto* as a child, and occasionally dressed in shorts, which were evidently a *bourgeois* affectation!) He remained unemployed for half a year, but then, thanks to Frumkin, he was restored to a position at the Research Institute of Elemental Carbon (later, the All-Union Research Institute of Current Sources—VNIIT) where he worked successfully until 1965, first as a staff member but later as the Head of New Electrochemical Systems. Under his direction, studies were successfully completed on mercury/oxide cells, magnesium batteries, and mercury/zinc cells. This was followed by a series of studies on the development of silver–zinc secondary batteries for aviation, missiles, and rockets. These studies were carried out in collaboration with the Experimental Design Bureau headed by Sergey Pavlovich Korolëv (1907–1966), the leading Soviet rocket engineer and spacecraft designer. The first Earth satellite (Sputnik I) launched into Earth orbit on 4 October 1957 was equipped with silver–zinc batteries developed by the Institute.

4.8 The Soviet Atomic Bomb Project

One of the most significant technological problems that Frumkin helped to solve was the development of the Soviet Atomic Bomb. Information on this topic has only recently become available, although certain details (and even the scope of the project) still remain classified [23].

In 1939–1940, Yu. B. Khariton and Ya. B. Zeldovich were the first scientists in the world to publish calculations on the rates of nuclear fission reactions. They showed that with a slight enrichment of uranium-235, the conditions could be created for a self-sustaining chain reaction. In 1940, the Presidium of the Academy of Sciences established a Committee on Uranium, which was given the responsibility of exploring the possibility of generating nuclear energy. The Committee was chaired by V. G. Khlopin, and its members were V. I. Vernadskiy, A. F. Ioffe, S. I. Vavilov, A. E. Fersman, A. P. Vinogradov, I. V. Kurchatov, and Yu. B. Khariton. However, Soviet research in nuclear fission was badly disrupted by the war. Many nuclear scientists joined the army, while others diverted their efforts toward more conventional problems.

Everything changed when Soviet intelligence reported the first test of an American atomic device on 16 July 1945 at Alamogordo, New Mexico. One month later, the State Committee on Defense established a Special Committee approved by Stalin. This committee was chaired by Lavrentiy Pavlovich Beriya (Beria) (29 March 1899–23 December 1953) and was charged with "the management of all activities for the utilization of nuclear energy from uranium."

In order to accelerate the production of nuclear weapons, the committee considered it necessary to involve more than 20 institutions in the project. Among them was the Colloid Electrochemistry Institute Academician A. N. Frumkin. The problem allocated to Frumkin's Institute was to develop an industrial method to separate plutonium from nuclear fuel. (The first Soviet atomic bomb, the RDS-1, was detonated on 29 August 1949, and used a solid plutonium core.)

S. Z. Roginskiy was appointed as the Head of these studies. By December 1945, he and Frumkin had developed a work program which was presented to the Technological Council for approval. In March 1946, a special laboratory for the development of radiochemical technologies was opened in the Institute of Physical Chemistry. Four subdivisions were created: the division of G. V. Akimov (testing corrosion-resistant metals for the plutonium separation plant); the division of S. Z. Roginskiy (eliminating fission products from waste); the division of P. A. Rebinder (Rehbinder) (testing the strength of irradiated materials); and the division of Frumkin (testing the effects of radiation on chemical processes).

By September 1948, Frumkin was under immense personal pressure to fulfill Beria's objectives, so that prototype devices could be built. In response, he had to cut down certain researches at the Institute and hire new staff. Several of his colleagues were unhappy with these developments; however, Frumkin persisted.

Construction of an industrial plant to produce highly enriched uranium by gaseous diffusion had begun in December 1945 in the Urals town of Verkh-

Neyvinsk, about 50 km from Sverdlovsk (now Yekaterinburg). Isaak Konstantinovich Kikoin (28 March 1908–28 December 1984) was in charge of the works. However, many difficulties were encountered, and progress was slow. The most troublesome parts of the machinery were the gaseous diffusion filters. The technical parameters for the filters were very strict: they needed to be made of nickel and be intersected by pores of 25 nm diameter (about one-tenth the mean free path of a UF_6 molecule). Unfortunately, it was found that sintered nickel easily became blocked by tetravalent uranium compounds. Kikoin asked Frumkin to solve problem. A working group consisting of R. Kh. Burshteyn, P. I. Dolin, and S. D. Levina was organized under Frumkin's supervision. They tested various methods of passivating the surface of the filters to prevent the catalytic decomposition of the uranium hexafluoride gas, and finally solved the problem. The purified uranium-235 was eventually used in the third Soviet atomic bomb test, based on a plutonium/uranium composite core, which was detonated on 18 October 1951.

It should be noted that, during the atom bomb project, a number of German and Austrian scientists had been coerced (or volunteered) to assist in the development work. These included the Nobel Prize winner Gustav Ludwig Hertz (22 July 1887–30 October 1975), Baron Manfred von Ardenne (20 January 1907–26 May 1997), Peter Adolf Thiessen (6 April 1899–5 March 1990), Max Volmer (3 May 1885–3 June 1965), Nikolaus Riehl (24 May 1901–2 August 1990), and Rudolf Heinz Pose (10 April 1905–13 November 1975). They were not released until 1953. Most famous of all, Max Volmer returned to the German Democratic Republic (GDR) and eventually became the President of the Academy of Sciences of the GDR.

4.9 The Anti-cosmopolitan Campaign in the USSR. University Professors vs. Academicians

In 1946, Stalin made a speech in which he expressed his dismay at the direction of contemporary Soviet culture. This triggered a period of social history in the USSR known as the "battle against cosmopolitanism." Stalin thought that a dangerous tendency had evolved in the cultural sphere, such that literary and theatrical works were gradually falling under the control of foreign influences. In 1947, similar ideas were expressed about Soviet science, and even the famous physicist Pëtr (Pyotr) Leonidovich Kapitsa (8 July 1894–8 April 1984) fell under suspicion. He, along with numerous other scientists, was publicly denounced for his support for "bourgeois science." Initially, the anti-cosmopolitan campaign was directed at liberal intellectuals, but soon it degenerated into a form of anti-Semitism. By March 1949, more than 70 % of the people who were being vilified in the Soviet press were Jewish.

At the Institute of Physical Chemistry, a small group of staff decided to take advantage of this situation to remove Frumkin from his post as Director. In a letter to the Central Committee of the Communist Party, they argued that the popular article “Physical Chemistry,” written by Frumkin and Ya. K. Syrkin, and published in the Great Soviet Encyclopedia (first edition), contained “unpatriotic errors” such as downplaying the historical importance of Russian scientists (e.g., M. V. Lomonosov, A. M. Butlerov, etc.), and failing to realize the significance of the Periodic Law of Dmitri Ivanovich Mendeleev (8 February 1834–2 February 1907). Their ire was also directed at the Institute of Physical Chemistry, particularly in regard to its supposed failure to support the State economy. Later (May–October, 1950), when all the departments of the Academy of Sciences fell under scrutiny, a notorious note was passed to the Central Committee claiming the “Jewish infestation” of certain Institutes. The Institute of Chemical Physics, the Institute of Physical Problems, the Lebedev Physics Institute, and the Institute of Physical Chemistry, all found themselves on this list.

In his memoirs, Ya. P. Stradyn recalled Frumkin’s remarks that the campaign had begun with a letter directed against him and Nikolay Nikolayevich Semënov (Semenov) (15 April 1896–25 September 1986). Semënov, who would later receive the Nobel Prize, had dedicated his classic monograph “Chain Reactions” to J. van’t Hoff and S. Arrhenius, neither of whom was Russian. It seems the letter was written by people who believed they were being deliberately hindered in their career or who thought they were being unfairly overlooked. Frumkin was called “Cosmopolitan No. 1.”

The shameful letter was signed by 15 professors, mainly from the Institutes of Higher Education (including the Faculties of Physics and Chemistry of MSU). However, a few were from the Institute of Physical Chemistry. The authors claimed that Frumkin was monopolizing the subject of physical chemistry and controlling the journals that published it. Other scientists who were singled out as “cosmopolitans” were S. Z. Roginskiy, Yakov Borisovich Zel’dovich (8 March 1914–2 December 1987), Yakov Kivovich Syrkin (2 December 1894–8 January 1974), and Yuliy Borisovich Khariton (27 February 1904–19 December 1996). In a much later article [26], A. S. Sonin identified the situation as a conflict between scientists at the Academies on one side and those at the Institutes of Higher Education on the other (i.e., “academicians vs. professors”).

At the height of the crisis, Frumkin lived in fear of arrest. He recollected that for several months, he and Amaliya Davydovna stayed awake till 4 in the morning [27], because they wanted to be fully clothed when taken into custody. (It was rumored that arrests took place at 3 o’clock in the morning.) Night after night they looked out their window, waiting for a police car to arrive to take them away for interrogation. Fortunately, it never came. Possibly Frumkin’s scientific activity was too important for the State, and he was left in peace.

The repercussions of the “battle against cosmopolitanism” persisted for a long time, as may be judged from the written records of the third and fourth All-Union Conferences on Electrochemistry held in 1950 and 1956. According to Lev Isayevich Krishtalik (b. 23 November 1927) [1], the atmosphere was particularly hostile at the meeting of 1950 where a group of scientists had organized a noisy campaign aimed at discrediting Frumkin and his school. Despite being the target of a series of attacks, Frumkin displayed extraordinary calmness and composure. He only took part in discussions of truly scientific problems, and in his concluding remarks pointed out to his critics that no serious scientific arguments had been raised against the general concept of his “slow discharge” theory.

The claims that he underestimated the historical achievements of Russian scientists did hurt Frumkin, however, and briefly he turned his attention to the history of electrochemistry in Russia in order to reevaluate Russian contributions. He rated the studies of Moritz Hermann von Jacobi (21 September 1801–10 March 1874) most highly. (The Russian version of his name is *Boris Semyonovich Yakobi*[1].) Jacobi had discovered the maximum power theorem, and his name is also associated with the development of galvanic cells for testing electric motors. In addition, Frumkin noted the priority of Pyotr Romanovich Bagration (24 September 1818–17 January 1876),[2] who had created the first galvanic dry cell in 1843. Finally, Frumkin drew attention to the work of Kazan professor Robert Andreyevich Colley (Kolli) (25 June 1845–2 August 1891)[3] back in 1878. Colley was the first person to use the shift of the electrode potential in a certain period of time as a measure of the interfacial capacitance and found a value of 150 μF cm^{-2} for platinum.

Despite all these efforts, Frumkin was eventually compelled to leave his position as Director of the Institute of Physical Chemistry in spring 1949, following a resolution of the Secretariat of the Central Committee of the Communist Party. The same fate befell several other famous directors of academic institutes, such as Ioffe and Kapitsa. Nevertheless, Frumkin continued to work in the Institute and remained in charge of the Division of Electrochemistry. He also remained the Head of the Department of Electrochemistry at MSU, in defiance of all attempts to remove him from that position.

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[1] M. H. von Jacobi was the brother of the famous mathematician Carl Gustav Jacob Jacobi, born in a wealthy Jewish family in Germany. His father was the personal banker of Frederic Wilhelm III, King of Prussia. In 1837, M. H. von Jacobi came to St. Petersburg via Königsberg in Eastern Prussia (now Kaliningrad, Russia) and Dorpat (now Tartu, Estonia) where he held positions before. Jacobi stayed in Russia until the end of his life.

[2] Pyotr Romanovich Bagration originated from one of the oldest Russian-Georgian noble families (Knyaz is usually translated to English as Prince, in German it is Fürst). Educated at the Military Academy of St. Petersburg, and being a Governor of the Tver Governorate and the General-Governor(ate) of the Baltic Governorates, he undertook research work at the Physics Institute of the St. Petersburg Academy of Science under the guidance of Moritz Hermann von Jacobi.

[3] Robert Andreyevich Kolli (he spelled his name in foreign publications Colley, which was the original English way of writing it) was born in Petrovsko-Razumovskoe near Moscow in a merchant family originating from England. Being a professor of physics and physical geography at Kazan University, his research concerned mainly electromagnetism, electrochemical phenomena, electrolytes, electrode polarization, etc. Kolli published 13 papers in *Annalen der Physik* (vol. 219 (1871) 125; 231 (1875) 467; 233 (1876) 370; 233 (1876) 624; 243 (1879) 206; 252 (1882) 39; 253 (1882) 55; 251 (1882) 94; 262 (1885) 432; 264 (1886) 1; 280 (1891) 102; 280 (1891) 109), some of them were the German translations of papers previously published in Russian.

4.10 Foundation of the Institute of Electrochemistry

Nearly a decade later, in 1958, the Presidium of the Academy of Sciences founded the Institute of Electrochemistry and installed A. N. Frumkin as its first Director. The purpose of the Institute was to develop fundamental electrochemistry and to solve practical problems. In particular, the stated research directions were: developing new chemical power sources for the economy and defense; developing the fields of electrochemical kinetics and electroplating of metals; solving the problems of electrochemistry of semiconductors and physicochemical problems associated with electron emission; working out new methods of electrosynthesis; and studying the problems that arise at the boundary between electrochemistry and radiation chemistry.

The laboratories established inside the Institute were organized as follows: *electrochemical kinetics* (Frumkin), *electrode processes in current sources, and the electrochemistry of metals* (B. N. Kabanov); *contact potentials and gas cells* (R. Kh. Burshteyn); *theoretical electrochemistry* (V. G. Levich); *radiation chemistry* (N. A. Bakh); and *special issues* (P. I. Dolin). A little later, a *Laboratory of New Electrochemical Systems* was organized under the leadership of P. D. Lukovtsev. By 1965, two further laboratories had been formed, concerned with *the kinetics of electrolytic processes* (L. I. Krishtalik) and *the behaviour of fuel cells* (V. S. Bagotskiy). In 1967, a *Laboratory of Electrochemical Instrumentation* (L. L. Knots) was also organized. In 1971, the laboratory headed by P.D. Lukovtsev was renamed the *Laboratory of Electrochemical Sensors*; after the death of Lukovtsev, this laboratory was transferred to B. M. Grafov. In 1973, the laboratories of Bagotsky and Burshteyn were united into the *Division of Power Sources and Aqueous Electrolysis* under the leadership of Bagotsky. The overall organization of the Institute of Electrochemistry made it possible to intensify research not only in the fields explored earlier but also in some new directions. From the outset, the Institute of Electrochemistry took part in coordinating research across the USSR.

After the death of A. N. Frumkin on 27 May 1976, his student Vladimir Yevgenyevich Kazarinov (5 December 1933–12 February 1999) was appointed as his successor. Some years later, momentous changes took place inside the USSR. After Mikhail Gorbachev was appointed General Secretary of the Communist Party of the Soviet Union in March 1985, he began a series of political reforms known as "perestroika," which were accompanied by great financial and political turmoil. After the death of Kazarinov in 1999, the Directorship briefly passed to Boris Mikhailovich Grafov. Despite difficult times, the Institute continued to maintain its place among the chemical institutes of the Russian Academy of Sciences. However, in 2004, a new stage in the history of the Institute began when it was merged with the Institute of Physical Chemistry, and a new Director was appointed, Academician Aslan Yusupovich Tsivadze (b. 1943). Finally, in 2008, the combined Institute was renamed the *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry*.

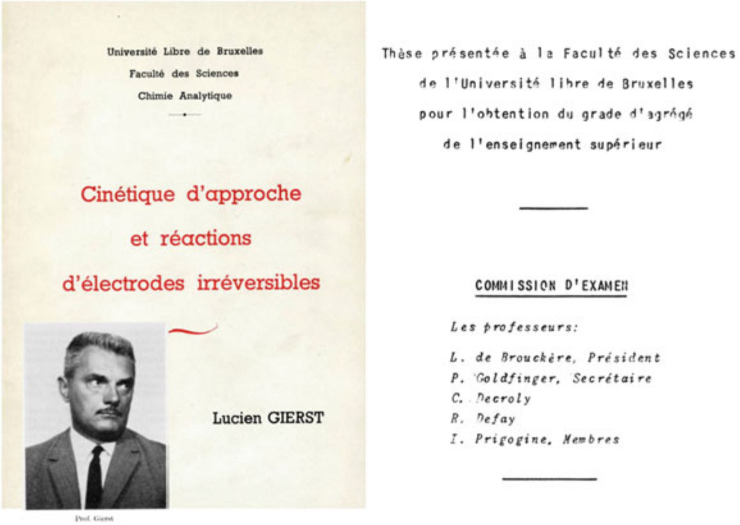
4.11 Department of Electrochemistry MSU in the 1950s–1970s

In the 1950s–1970s, the studies at the Department of Electrochemistry and the Institute of Electrochemistry proceeded in close collaboration, often supplementing one another. The students and postgraduates replenished the staff of both the Institute and the MSU department. Graduates from other institutes of higher education also came to work at the Institute of Electrochemistry.

Most attention was still focused on problems associated with interfacial structure and the kinetics of electrode processes. In 1949, Tat'yana Aleksandrovna Kryukova (1906–1987) had observed a polarogram of very unusual shape for persulfate anion reduction in dilute solutions: a descending current region at increasing overpotential and a deep current minimum which disappeared upon the introduction of supporting electrolyte. In 1952, Frumkin and G. M. Florianovich identified this minimum as the repulsion of anions from the negatively charged electrode surface, as predicted by the Frumkin theory of 1933. In further studies by Frumkin, O. A. Petrii, and N. V. Nikolayeva-Fedorovich [28], a method was developed for determination of the charge of the reacting species and the magnitude of the transfer coefficient by analyzing the dependences of the overall rate on the concentration of inert electrolyte and on the electrode potential. Nikolayeva-Fedorovich and coworkers later studied the electroreduction of several other anions and carried out measurement on various electrode materials (Photo 4.12).

During the 1950s, western electrochemists P. Delahay, L. Gierst, and others also developed an interest in “double layer effects” on electrode kinetics. Delahay was probably influenced by M. Breiter, who worked in the USA and was well acquainted with the Frumkin School. Interestingly, L. Gierst had shown that the repulsion of reacting species from electrodes could also be observed during the oxidation of Eu^{2+} cations at positively charged surfaces. His interesting studies conducted at the Free University of Brussels were summarized in his dissertation. It is notable that Frumkin brought this dissertation to the Department of Electrochemistry from one of his trips abroad, disregarding the fact that the committee which had approved it included the Nobel Prize winner Ilya Prigogine (1917–2003) whose

Photo 4.12 T. A. Kryukova, G. M. Florianovich, and N. V. Nikolaeva-Fedorovich



Université Libre de Bruxelles
Faculté des Sciences
Chimie Analytique

Cinétique d'approche
et réactions
d'électrodes irréversibles

Lucien GIERST

Prof. Gierst

Thèse présentée à la Faculté des Sciences
de l'Université libre de Bruxelles
pour l'obtention du grade d'agrégé
de l'enseignement supérieur

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Photo 4.13 L. Gierst and the title pages of his dissertation

name was banned in the USSR. (Prigogine was born in Moscow shortly before the October Revolution, and his parents had left Russia in 1921 because of opposition to the Soviet system.) (Photo 4.13).

The effect of the double layer on the kinetics of anion electroreduction was demonstrated by O. A. Petrii [29] when studying the current vs. time curves on the mercury electrode in the presence of tetraalkylammonium organic cations. Professor Jaroslav Koutecký (1922–2005), who worked in the Institute of Electrochemistry in this period, was much intrigued by these curves and even wanted to describe them theoretically. However, he had no time for this and the theory of *current* vs. *time* curves in the presence of organic cations was developed in the Institute of Electrochemistry by A. Ya. Gokhshtein, who also developed the theory of current oscillations during the reduction of anions which today is regarded as the model process involving negative differential resistance.

In the early 1950s, Frumkin's attention was drawn to the studies of US electrochemist David Caldwell Grahame (21 April 1912–11 December 1958) who had developed a technique for the precise measurement of the double layer capacitance of the dropping mercury electrode. Grahame had obtained high-quality data in various electrolyte solutions, thus making a fundamental contribution to the development of models of the electric double layer. Frumkin drew the attention of Boris Borisovich Damaskin (b. 16 May 1932) to these studies. This resulted not only in the adoption of Grahame's procedures but also in the formulation of a general phenomenological theory of reversible adsorption of organic and inorganic ions on electrodes. In the course of their discussions with Grahame, the presence of specific adsorption of inorganic cations on mercury was established (Photo 4.14).

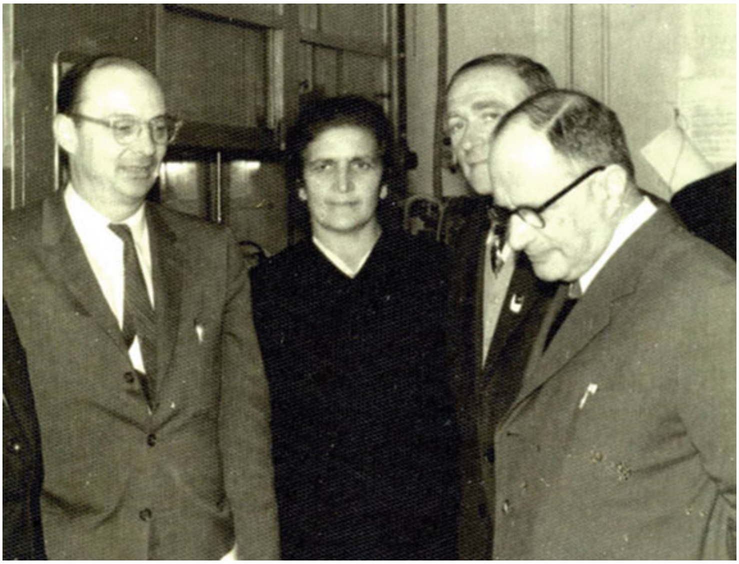

Photo 4.14 D.C. Grahame, R.Kh. Burshtein, M.I. Temkin, and A.N. Frumkin

At the Institute of Electrochemistry, Irina Alekseyevna Bagotskaya[4] (1921–2007) et al. extended the classical studies on mercury to include studies on liquid gallium and gallium-indium alloys. Measurements of the double layer capacitance of solid electrodes were also carried out, both at the Institute of Electrochemistry and at MSU (V. V. Batrakov). At the Institute, these studies were organized by D. I. Leikis in cooperation with Bulgarian scientists (E. Budevsky, T. Vitanov, A. Popov, and Z. Stoynov). Their measurements were carried out on single crystal faces of silver and formed the basis of further studies of the effect of crystallographic orientation on the properties of the electrode/solution interface.

In 1958, Frumkin put forward the idea of a new experimental method—the method of the rotating ring-disk electrode, which allowed the direct observation of intermediates of electrode processes. The apparatus was built by L. N. Nekrasov, and the theory was elaborated by V. G. Levich and Yu. B. Ivanov [30]. Since then, the method of the rotating ring-disk electrode has become one of the standard techniques of electrochemical science. For example, it has played an important role in the study of oxygen electroreduction, with applications in fuel cells (Photos 4.15 and 4.16).

Many experiments that took place at the Institute and MSU were devoted to the improvement of fuel cells. These studies were carried out by R. Kh. Burshteyn, V. S. Bagotsky, Yu. B. Vassiliev, A. M. Skundin, A. G. Pshenichnikov, M. R. Tarasevich, N. A. Shumilova, V. E. Kazarinov, and Yu. M. Volfkovich at the Institute of Electrochemistry; and by O. A. Petrii and B. I. Podlovchenko at

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[4] I. A. Bagotskaya was the first wife of Vladimir Sergeyevich Bagotsky.

Photo 4.15 Members of the Department of Electrochemistry MSU in 1963 on the stairs of the Faculty of Chemistry

MSU. The studies at MSU were supervised by Frumkin much more intently than those at the Institute. On the other hand, Frumkin always thoroughly read all the papers before submitting them for publication. These studies had made fundamental contributions to the theory and practice of electrocatalysis, especially with regard to the dissociative adsorption of organic compounds, the nature of adsorbates, and the rate-determining step of electrooxidation processes. Methods were also developed for optimizing the structure of porous electrodes. The method of "standard contact porosimetry" was widely used to quantify various materials. Finally, the book by W. Vielstich "*Brennstoffelemente*" was translated into Russian with a preface written by Frumkin.

On Frumkin's initiative, work was also begun on the behavior of lithium electrodes in aprotic solvents, supervised by Yu. M. Povarov. He put forward the idea of a surface film that controlled the rate of reaction between electro de and solvent.

In 1965, after Frumkin had been transferred to hospital after a heart attack, he started to think about some unsolved problems posed in his early studies back in the 1930s. As a result, he revisited the thermodynamic theory of the perfectly polarizable electrode, and its experimental checkup then appeared [31, 32]. These studies were carried out by O. A. Petrii and coworkers at the Department of Electrochemistry MSU. This not only resulted in the development of some new experimental techniques (e.g., potentiometric titrations under isoelectric conditions) but also led

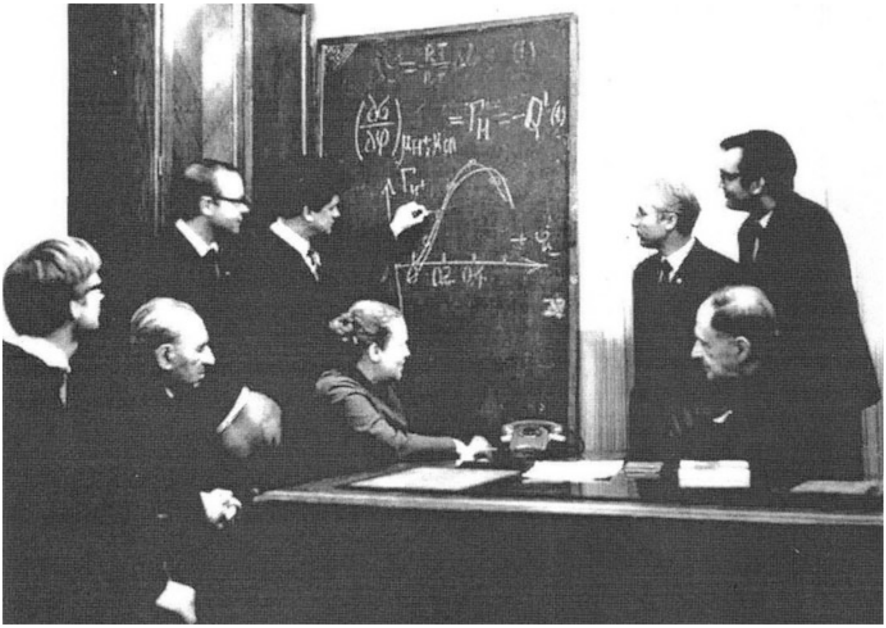

Photo 4.16 A. N. Frumkin and his pupils at the Department of Electrochemistry MSU in the early 1970s. From *left* to *right*: B.I. Podlovchenko, Z.A. Iofa, V.V. Batrakov, B.B. Damaskin, N.V. Fedorovich, L.N. Nekrasov, A.N. Frumkin, and O.A. Petrii

to the formulation of a new concept of electrode charge. In particular, the concepts of *total charge* and *free surface charge* have since become an intrinsic part of electrochemistry.

In 1966, V. E. Kazarinov developed a new radioactive-tracer method for studying the adsorption of ions and organic substances on platinum group metals. In his studies in cooperation with O. A. Petrii, this method provided a stunning confirmation of the thermodynamic theory of platinum electrodes. Subsequently, A. Ya. Gokhshtein developed a radical new method for studying surface phenomena on solid electrodes, the so-called *estance method*. This method has been used in the USSR but has not so far been taken up abroad.

By the late 1960s, Frumkin had launched himself into a series of investigations into the emission of photoelectrons at the metal/solution interface. Theoretical studies (A. M. Brodskiy, Yu. Ya. Gurevich) and experimental studies (Yu. V. Pleskov, Z. A. Rotenberg) led to the formulation of a new law of photoemission.

Theoretically, Frumkin strongly supported quantum theoretical studies of the elementary act of electron transfer. In the Theoretical Division, led by V. G. Levich, several epochal studies were carried out by R. R. Dogonadze, Yu. A. Chizmadzhev, and A. M. Kuznetsov. In 1967–1968, Dogonadze, Kuznetsov, and Levich put forward the first quantum-mechanical theory of proton transfer; later, A. M. Kuznetsov, J. Ulstrup, Ya. I. Kharkats, and M. A.Vorotyntsev systematically considered different aspects of the transfer of electrons and heavier particles in physics, chemistry, and biology. The conclusions of these studies were experimentally confirmed by L. I. Krishtalik. The latter also theoretically predicted and experimentally discovered a new class of electrode reactions—the barrierless processes. Yu. A. Chizmadzhev also inaugurated a new research direction at the Institute of Electrochemistry; namely, the bioelectrochemistry of membranes. Undoubtedly, the achievements of the Frumkin School laid the foundations for much of what was to follow in the field of surface electrochemistry in the late twentieth century. The onset of the new era was heralded by the Conference on "*Non-traditional Approaches to the Study of the Solid-Electrolyte Interface,*" at Snowmass, Colorado, in 1979.

In the 1960s–1970s in the USSR, some significant progress was also achieved in the field of instrument design for electrochemical measurements. These developments attracted the attention of Western scientists, and J. Tacusell visited Moscow to become acquainted with several instruments manufactured in the USSR.

4.12 Scientific Contacts and Certain Peculiarities Concerning Publication of Scientific Papers

Throughout his life, Frumkin made lasting friendships with colleagues from overseas. Initial encounters with foreign scientists occurred in 1912–1914. However, more substantial contacts were established in 1924, when Frumkin made a lecture tour of Austria and Germany. He also visited the University of Leiden (The Netherlands). Then, in 1928/1929, he spent a year on sabbatical at the University of Wisconsin in Madison. This not only allowed him to meet many well-known American scientists but also allowed him to visit Berlin on his way home.

In September 1934, Frumkin actively participated in The Faraday Discussion on Colloidal Electrolytes, held at University College, London. This meeting was chaired by Frederick George Donnan (6 September 1870–16 December 1956), and Eric Keightley Rideal (11 April 1890–25 September 1974), Herbert Max Finlay Freundlich (28 January 1880–30 March 1941), Hugo Rudolph Kruyt (3 June 1882–31 August 1959), and Karl Wilhelm Wolfgang Ostwald (known in the scientific literature as Wo. Ostwald), the son of Wilhelm Ostwald, were also present.

A major disappointment for Frumkin was his inability to attend the Faraday Discussion on Electrode Processes held at the University of Manchester in 1947. Present at that meeting, among many others, were Jaroslav Heyrovský (20 December 1890–27 March 1967), Nevill Francis Mott (30 September 1905–8 August 1996), Joseph Joshua Weiss (30 August 1905–9 April 1972), John Edward Brough Randles (26 August 1912–13 February 1998), and Bernhardt Patrick John O'Mara Bockris (5 January 1923–7 July 2013). Archie Hickling, the inventor of the potentiostat was also present. Although Frumkin, Levich, and Ershler all submitted preprints for the conference, which were published, they were unfortunately denied exit visas from the Soviet Union on the grounds of national security.

Throughout the period 1929–1945, Frumkin maintained an active correspondence with the Hungarian-born chemist, Michael Polanyi (11 March 1891–22 February 1976). Frumkin wrote him 23 letters which are now deposited in "The Michael Polanyi Papers" of the University of Chicago Library. During the early 1930s, Polanyi had visited the USSR where he met Frumkin and Semënov. The latter were, at that time, members of the Editorial Board of the Journal "Acta Physicochimica URSS," and it was in this journal that the famous paper of M. Polanyi and Juro Horiuti (1901–1979) was published, entitled "*Outlines of a theory of proton transfer*" (in German). This theory was based squarely on Frumkin's ideas, and the authors expressed their gratitude to him. Frumkin also visited Polanyi several times in Manchester, where he famously advised him to heat-treat platinum electrodes in dry hydrogen gas to reduce platinum oxide, prior to making any electrochemical measurements (Photo 4.17).

During the 1930s, Éva Amália Striker (later Zeisel), (13 November 1906–30 December 2011), the daughter of Michael Polanyi's sister Laura Polanyi, lived in Moscow. Eva was an industrial designer, very well known for her ceramics. She worked at the porcelain plant in Dulevo as artistic director. In 1936, she was arrested and falsely accused of participating in an assassination plot against Stalin. Among the evidence against her was the claim that some salt shakers which she had designed would form a swastika if assembled in fours. Alexander Naumovich Frumkin went together with her mother to the Lubyanka building to plead for her release. Later, he was summoned alone and politely warned: "We think well of you but advise you not to interfere in this affair. It is very complicated and tangled." After 16 months, mostly spent in solitary confinement, Eva was finally released and permitted to go abroad.

Although two of his pupils, Eugene Paul Wigner (in Hungarian Wigner Jenő Pál) (17 November 1902–1 January 1995) and Melvin Ellis Calvin (8 April 1911–

Photo 4.17 A. N. Frumkin and M. Polanyi (1935)

8 January 1997) went on to win Nobel Prizes, Polanyi eventually abandoned science in favor of economics and philosophy. Frumkin was very disappointed. In 1940, Polanyi published a collection of essays entitled "The Contempt of Freedom," which was a polemic against Marxism. Two years later, in Kazan, Frumkin unexpectedly received a letter from Polanyi in which the latter expressed his hopes that after the war, conditions might develop for a better understanding between Great Britain and the Soviet Union. Frumkin answered that "first of all we must win the war." This was the end of their correspondence.

In the 1930s, foreign scientists rarely visited the USSR. However, Frumkin was well aware that the exchange of ideas was vital for the development of science. For this reason, he enthusiastically attended scientific conferences in different fields of physical chemistry. He also urged the Soviet authorities to invite prestigious foreign scientists to visit his laboratories. For example, in 1934, the Nobel Prize winner Niels Henrik David Bohr (7 October 1885–18 November 1962) was invited by the Academy of Sciences of the USSR to visit Moscow. Frumkin had previously met Bohr in 1927. Bohr presented a lecture on the stochastic-statistical nature of quantum mechanics in the MSU building in Mokhovaya Street, while Frumkin translated the lecture from German into Russian.

In September 1936, a Mendeleev Congress was held in Moscow, organized by the Academy of Sciences to celebrate the 100th birthday of the discoverer of the Periodic Table of the Elements. By invitation of the Academy of Sciences, the then-recent winners of the Nobel Prize, Irène Joliot-Curie (12 September 1897–17 March 1956) and Frédéric Joliot-Curie (19 March 1900–14 August 1958) were the guests of honor. On September 29, 1936, Frédéric presented his lecture "*The Structure of Matter and Artificial Radioactivity*" at the Physical Faculty of MSU. The famous Soviet scientists S. I. Vavilov, N. D. Zelinskiy, L. I. Mandelshtam, A. Y. Fersman, and Frumkin were all present. The Joliot–Curie couple also visited the Karpov Institute, where Frumkin showed them around (Photo 4.18).

1945 saw the celebration of the 220th anniversary of the founding of the Academy of Sciences in Russia. Despite immense destruction wreaked by the Nazi forces, an international meeting of scientists was convened on the 15–28 June. This occurred just 4 weeks after the Red Army had entered Berlin, and only 7 weeks before the United States would detonate atomic bombs over Hiroshima and Nagasaki. Many famous scientists attended the meeting, including Irving Langmuir, Frederick George Donnan, Theodor Svedberg, and Robert Robinson. In a bright and extremely interesting article "Science and Incentives in Russia," Langmuir [33] described in detail all the twists and turns of his journey to Moscow under wartime conditions. He also reflects on some of the amazing features of life in the USSR at that time.

The US delegation included five chemists, among them Izaak Maurits Kolthoff and James William McBain (22 March 1882–12 March 1953), both of whom were good friends of Frumkin. On their arrival in Moscow, the American delegation was met by a large group of Soviet scientists which included Kapitza, Frumkin, and Frenkel. Having visited several research institutes in Moscow and Leningrad,

Photo 4.18 A. N. Frumkin, Frédéric and Irène Joliot-Curie, N. A. Bakh, and A. N. Bakh

Langmuir remarked that progress in science in Russia was much more impressive than he had expected.

Besides good personal contacts, Frumkin also thought that good scientific journals were needed for progress. Initially, the Journal "Zhurnal Russkogo Khimicheskogo Obshchestva" ("Journal of the Russian Chemical Society") was the only chemical journal in the USSR, but clearly it could not meet all the needs of modern scientific life. Frumkin therefore initiated several new scientific journals. One of the most important of these was the "Zhurnal Fizicheskoy Khimii" ("Journal of Physical Chemistry"). Its first issue was published in 1930, and Frumkin remained on its Editorial Board for 37 years.

Frumkin was also keen for Soviet research to be accessible abroad. Thus, in 1934, he helped to found the journal "Acta Physicochimica URSS" which had a provision for publication in foreign languages. This popular journal later played an important role in disseminating the achievements of Soviet scientists to the rest of the world.

4.12.1 The «Cold War» Severely Complicated All East-West Contacts

On June 9, 1947, the Presidium of the Supreme Soviet of the USSR published an edict on the *Responsibility for the Disclosure of State Secrets* which forbade public disclosure of many types of information. This edict covered the disclosure of discoveries, inventions, and improvements of a nonmilitary nature, for which the punishment was 8–12 years in a forced labor camp. Immediately, the Politburo of the Central Committee of the Communist Party banned the publication of journals of natural science in foreign languages in the USSR. Sadly, "Acta Physicochimica URSS" was among those closed down.

As the "Cold War" progressed, permission to publish scientific papers of any kind became increasingly hard to obtain. In order to publish a paper, one had to obtain a certificate of approval, which was not always a mere formality. Indeed, publication in foreign journals became almost impossible, since the contents were subject to strict censorship, and the legal sanctions for noncompliance were so severe. These harsh regulations remained in place for a very long time. However, those who worked with Frumkin did sometimes get lucky. Frumkin used the following trick. First, the whole paper (or its component parts) was published in the USSR, which provided proof that it contained nothing restricted. Then the material was redrafted for publication abroad. However, since the final publication often took years to achieve by this route, Russian scientists frequently appeared to lag behind their western counterparts, with the result that they were also deprived of the proper recognition of their scientific priority.

Frumkin was a member of the Editorial Boards of several journals. These were: "*Uspekhi Khimii*" ("Russian Chemical Reviews") (1932–1939), "*Izvestiya Akademii Nauk SSSR*" ("Russian Chemical Bulletin") (1936–1949), and "*Doklady Akademii Nauk SSSR*" ("Proceedings of the USSR Academy of Sciences") (1934–1964). On his initiative, the journal "*Elektrokhimiya*" ("Russian Journal of Electrochemistry") was founded in 1965, Frumkin remained its Editor-in-Chief until his death.

A partial restoration of contacts with foreign colleagues began in 1956 with the fourth All-Union Conference on Electrochemistry, which was organized by Frumkin in Moscow. On the invitation of the Presidium of Academy of Sciences, numerous foreign scientists were in attendance. These included Rostislav Atanasov Kaishev (Bulgraia), Tibor Erdey-Grúz (Hungary), Kurt Schwabe (German Democratic Rep.), Stefan Minz (Poland), M. Smialowski (Poland), Jiři Koryta (Czechoslovakia) and Jaroslav Koutecký (Czechoslovakia), Roger Parsons (UK), John O'M. Bockris (USA), David Grahame (USA), Brian Evans Conway (USA), Karl Friedrich Bonhoeffer (Federal Rep. of Germany), and René-André Audubert (France) (Photo 4.19).

At this conference the extraordinary breadth and depth of Soviet electrochemistry was once again demonstrated, and this helped considerably toward the establishment of an Institute of Electrochemistry in the Academy of Sciences of the USSR.

Frumkin ventured abroad again in 1957. First he visited Poland to present some lectures; then he visited Bulgaria to become familiar with their Research Institutes in Physical Chemistry. Later, his travels became more systematic. Mostly, he visited socialist countries. For example, in autumn 1958, Frumkin, A. D. Obrucheva, and B. N. Kabanov visited the People's Republic of China. Following

Photo 4.19 A. N. Frumkin and R. Parsons (1956)

this visit, several Chinese undergraduates, postgraduates, and trainees or invited researchers began to attend MSU and the Institute of Electrochemistry. For example, in the Department of Electrochemistry, Chuan-Sin Cha worked as an invited scientist. Later he became one of the leading scientists in China. In his memoirs, he wrote that when he worked in the Department, he felt himself being "adsorbed" by the electrode/solution interface. He also wrote that he treasured his original manuscripts with corrections made by Frumkin. It is noteworthy that, despite thoroughly correcting papers, Frumkin modestly refused to be their coauthor. Guo-Dong Li was also trained at MSU. Later he became the Director of the Institute of Current Sources in China. Similarly, Tszu-Zhang Yui defended his candidate dissertation at the Institute of Electrochemistry and later became a Professor of Fudan University in Shanghai.

In 1957, Frumkin was elected as the National Secretary of Soviet Electrochemists, so that he could take his place on the *Comité International de Thermodynamique et de Cinétique Électrochimiques* (CITCE). This was the international committee on electrochemical thermodynamics and kinetics which, after 1970, became the International Society of Electrochemistry. Two years later, in 1959, the international journal "*Electrochimica Acta*" was founded by CITCE and Frumkin became a foundation member of its Editorial Board.

Also in 1959, Frumkin was awarded the Palladium Metal of the American Electrochemical Society, "for outstanding achievements in elucidation of fundamentals of theoretical electrochemistry and corrosion processes." Initially, the award ceremony was supposed to be held at the closing session of the 116th Meeting in Columbus (Ohio). However, Frumkin was unable to attend that session, so the medal was given to him the next year in Chicago (Illinois). There, Frumkin was hosted by J. O'M. Bockris (Photos 4.20 and 4.21).

In 1961, at the 12th CITCE Meeting in Brussels, Frumkin was elected as the CITCE vice president. The CITCE also agreed to hold the 14th CITCE Meeting in Moscow, from August 19 to 24, 1963. Frumkin became the Chairman of the

Photo 4.20 Frumkin in Bockris laboratory at the University of Pennsylvania (1960)

Photo 4.21 Frumkin and Bockris at the University of Pennsylvania (1960)

Organizing Committee. This meeting turned out to be a spectacular success, attracting 500 scientists from 22 countries.

In 1965, at the 16th CITCE Meeting in Budapest, Hungary, Frumkin was elected as the CITCE President. According to J. Koryta, CITCE was transformed by Frumkin's leadership into a society of true enthusiasts. In 1971, Frumkin organized in Moscow the International Symposium on the Kinetics of Elementary Act of Chemical Reactions and the Double-Layer Structure.

In the 1960s and 1970s, Frumkin attended conferences and symposia in India, Italy, Sweden, Czechoslovakia, England, France, Hungary, Japan, German Dem. Rep., Romania, Poland, and Yugoslavia. He delivered many plenary lectures and was awarded many honors.

On these trips, old friendships were renewed and new friendships were established. The Polish electrochemist, Viktor Kemula (6 November 1902–17 October 1985), who had known Frumkin since 1940, noted that Frumkin's lectures always had a stimulating effect on research in his laboratory. Joanna Taraszewska, Zbigniew Galus (b. July 7, 1934), and Jerzy Sobkowski (b. 1929) all visited the Department of Electrochemistry and the Institute of Electrochemistry.

On Frumkin's initiative, several bilateral seminars were also organized. Some of these took place regularly (e.g., the Soviet–Japanese seminar), others were held only occasionally (e.g., the Soviet–French seminar). The Soviet–Japanese seminar was held alternately in the USSR and Japan. The first seminar took place in Tokyo in October, 1974. The Japanese organizing committee was headed by G. Sugino and A. Matsuda. The following seminar was organized in Moscow on May 22–26, 1976. This was the last seminar in which Frumkin took part and made his last report.

Improved East-West relations in the 1960s allowed foreign guest workers to study in Moscow. Thus, Stanley Bruckenstein worked at the Institute of Electrochemistry for a year. In 1960, Lothar Müller (DDR) was a postgraduate student at the Department of Electrochemistry MSU. Later, having become a professor at Humboldt University, Berlin (GDR), he organized several symposia to which he invited Soviet and foreign scientists including those from western countries (Photo 4.22).

Indian scientists have long had a special interest in Frumkin's school. For example, Hira Lal worked at the Department of Electrochemistry as an invited scientist and published work on fuel cells and on the electrooxidation of organic compounds on platinized platinum. Previously, Lal had worked with Bockris in Philadelphia. Similarly, in the late 1960s, the Japanese scientist, Reiko Notoya came from Hokkaido University (Sapporo) to the Department of Electrochemistry.

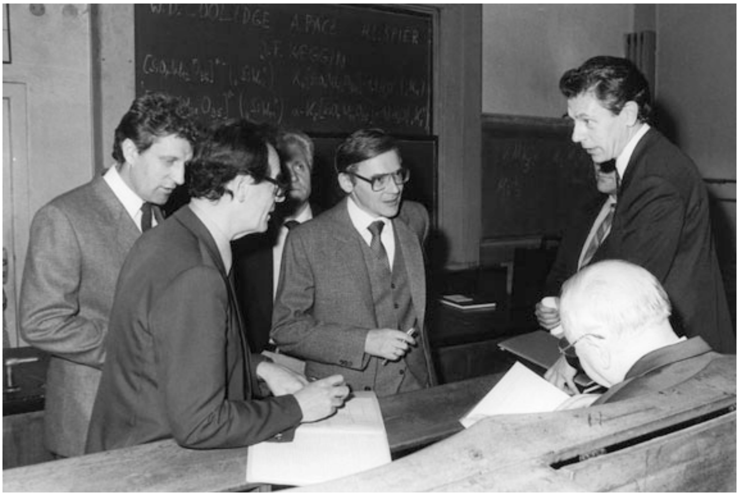

Photo 4.22 Lothar Müller (in the *center*) at the meeting of the Habilitation Council of Humboldt University of Berlin (Habilitation of Dr. Hans-Joachim Lunk on March 17, 1982). In the front, with his back to the viewer, academician V. I. Spitsin sits, who was the official opponent

Photo 4.23 O.A. Petrii, R. Notoya, V.V. Topolev, and M.I. Revushkin at the Department of Electrochemistry in 1971. M.I. Revushkin is the famous glassblower, the coauthor of numerous electrochemical cells used in the studies

She undertook research on the surface thermodynamics of reversible electrodes under supervision of Frumkin and Petrii. In addition, students and postgraduates from Bulgaria, Hungary, Vietnam, GDR, Algeria, Egypt, Iraq, Syria, India, Canada, Columbia, Mexico, USA, France, and Ecuador were also trained in the Department (Photo 4.23).

In the 1960s, a few Soviet scientists were allowed to visit Western countries. Vladimir Yevgenievich Kazarinov worked in the Bockris Laboratory in Philadelphia. He made radiotracer studies of the adsorption of organic substances on metals. Likewise, Lev Nikolayevich Nekrasov (22 February 1931–19 March 2010) trained for a year in Cleveland in the laboratory of Ernest B. Yeager (26 September 1924–8 March 2002). However, the majority of Soviet scientists were not permitted to work overseas.

4.13 Scientific Schools of Electrochemistry in the USSR

A characteristic feature of research in the USSR was that it took place inside Scientific Schools presided over by eminent scientists. It is of course impossible to summarize the history of all the Soviet Scientific Schools in one small chapter. However, one such School was founded by V. A. Kistyakovsky in the Colloid Electrochemistry Institute (CEIN).

An Institute of somewhat different character was the Department of Technology of Electrochemical Industrial Processes, at the Mendeleev Institute of Chemical Engineering in Moscow. This was headed by Nikolay Alekseyevich Izgaryshev

Photo 4.24 Nikolai Alekseevich Izgaryshev

(4 November 1884–21 March 1956). He was a corresponding member of the Academy of Sciences of the USSR (1939) and a member of the communist party from 1945 (Photo 4.24).

Izgaryshev entered Moscow University in 1903. In 1906, he joined the laboratory of Wilhelm Ostwald (1853–1932) in Leipzig, Germany, as a student. After graduating in 1909, he then worked with Fritz Haber (9 December 1868–29 January 1934) in Karlsruhe. After this, he returned to Moscow, becoming a professor in 1917. Later, he was invited by A. N. Bakh to work at the Karpov Institute as a specialist in the field of applied electrochemistry. In 1937, Izgaryshev became the Head of the Laboratory of Electrolysis and Electrocrystallization in CEIN. After 1943, he was the Head of the Department of Technology of Electrochemical Industrial Processes at the Mendeleev Institute of Chemical Engineering in Moscow.

Izgaryshev made many studies of the effects of colloids on metal electroplating. He also explored metal passivation phenomenon and was able to demonstrate that the interaction of oxygen with the surface of several metals in alcohol and pyridine resulted in the formation of peroxides. His studies on the electrochemical deposition of antimony, tin, niobium, lithium, and other nonferrous metals greatly assisted the development of electrochemical industry in the USSR. In cooperation with Nikolay Tikhonovich Kudryavtsev (1901–1979), Izgaryshev also made many contributions to the development of electrolytic methods for synthesizing metal powders and sponges. Between 1938 and 1951 he investigated the reaction of ferrous metals with vapors of salts of other metals. Today, these reactions are used in chromizing and other thermochemical methods of protecting metals and alloys from corrosion.

In 1932, a special session of the Academy of Sciences of the USSR took place, focussed on the problems of the Ural–Kuznetsk region (south-central Russia). This had important consequences for the development of the Ural Division of the

Photo 4.25 Sergey Vasil‘evich Karpachëv

Academy of Sciences of the USSR. A delegation, which included Frumkin, V. A. Kistyakovskiy, S. I. Vavilov, N. N. Semënov, and P. P. Lazarev, visited several towns in the region, which is rich in mineral resources, especially iron ore. As a result of this visit, a resolution was made to organize a complex of 11 research institutes, which formed the basis of the Ural Affiliation of the AS USSR. On Frumkin’s initiative, the Ural Physicochemical Institute was organized as an affiliate of the Karpov Institute. In this Institute, Sergey Vasil‘evich Karpachëv (1906–1987) became the Head of a Laboratory of Electrochemistry of Molten Salts (Photo 4.25).

Frumkin not only supported the establishment of this laboratory but also strongly influenced the selection of research problems. As a result, the zero charge potentials of various liquid metals were determined there. Periodically, members of Karpachëv’s team were invited by Frumkin to attend the Karpov Institute for further training. Most notably, Armin Genrikhovich Stromberg (1910–2004) visited in 1934. Later Stromberg became a famous scientist in his own right, the founder of the Tomsk school of electrochemistry.

In 1957, after prompting by Frumkin, the Presidium of the Academy of Sciences adopted a resolution to reorganize the Institute of High Temperature Electrochemistry of the AS USSR. Karpachëv became its Director from 1963 to 1977 and worked in close cooperation with Frumkin. Among eminent Ural electrochemists, the name of Oleg Alekseyevich Esin (7 September 1904–13 February 1979) should also be mentioned (Photo 4.26).

Esin graduated from the Ural Polytechnical Institute in 1925 and remained there as a postgraduate student within the Department of Electrochemistry. After finishing his postgraduate courses, he trained with Erich Müller (1870–1948) at the Institute of Physical Chemistry and Electrochemistry in Dresden, Germany. In 1930, he returned to Yekaterinburg and immersed himself in various problems of theoretical electrochemistry. During the period 1937–1939, he developed the

Photo 4.26 Oleg Alekseevich Esin

theory of mixed electrode kinetics. In 1940, in cooperation with B. F. Markov, he famously quantified the discreteness-of-charge effect on the electrocapillary curves of mercury in electrolyte solutions. Later, Grahame called this phenomenon the "Esin–Markov" effect. Between 1938 and 1944, Esin acted as the chairman of the Department of Theoretical Electrochemistry, which he organized. Among his important discoveries should be mentioned the concept of the charge reversal of the electric double layer at the electrode/molten electrolyte interface. In 1944, Esin left the Department of Electrochemistry and began new research on the theory of metallurgical processes. Many of the ensuing results have formed the basis of future work in the field.

Another famous school of electrochemistry was at the Karpov Institute and was concerned with the corrosion of metals. This was directed by Yakov Mikhailovich Kolotyrkin (14 November 1910–2 November 1995). Kolotyrkin graduated from the Department of Electrochemistry of Moscow State University in 1937. In 1941, he published two papers with Frumkin on the dissolution of nickel. Later he worked in the Karpov Institute where he organized (1956) the Laboratory of Electrochemistry of Metals which he headed until his death. After 1957, he was the Director of the Karpov Institute for 32 years. Under his supervision, many new electrochemical and radiotracer methods were developed for studying the kinetics of electrode processes and for determining the surface state of metals.

Frumkin also influenced the development of electrochemical research in the Estonian and Georgian republics of the USSR. At Tartu University (Estonia), V. E. Past and U. V. Palm were strongly influenced by the Frumkin School. They initiated the organization of conferences on the electrical double layer and adsorption on solid electrodes. Frumkin supported these initiatives and took an active part in several conferences (1968, 1970, 1972, 1975). The conferences in Tartu played an important role in the development of electrochemistry in the USSR.

In Georgia, Dzhondo Ivanovich Dzhaparidze (1933–2008), a student of Frumkin, became Director of the R. I. Agladze Institute of Inorganic Chemistry and Electrochemistry (Tbilisi). This Institute made important contributions to the industrial electrochemistry of manganese, chromium, and copper. Together with his Georgian students, Dzhaparidze also initiated work on the theory of charge transfer in condensed systems and the electrochemistry of nonaqueous solutions. After the death of Frumkin, Dzhaparidze also organized two symposia inspired by Frumkin's contributions on Electrochemistry.

4.14 Nobel Prize Nominations: Heyrovský and Frumkin

Frumkin was nominated for the Nobel Prize in Chemistry on several occasions (1946, 1966, 1974), by the Presidium of the Academy of Sciences USSR, and by various authoritative Soviet and foreign scientists. The details of these nominations came to light only decades after the events. As regards Soviet nominations, the relevant information has been collected and discussed by A. M. Blokh in a monograph [34]. It appears that contact with the Nobel Committees on Physics and Chemistry was initiated in 1945, when various Soviet scientists were invited to nominate candidates. Unfortunately, the Nobel Committee waited in vain for a formal reply. The mail system between the Soviet scientists and foreign colleagues was blocked.

Some private correspondence did, however, get through. For example, the Nobel Prize winner in chemistry, Theodor Svedberg (30 August 1884–25 February 1971), exchanged letters with Frumkin even before the end of World War II. Frumkin sent him 12 of his recent scientific publications. They had known each other since 1929. In 1934, Svedberg visited the USSR for the first time as the foreign guest in the VII Mendeleev Congress. His second visit to Moscow was in the summer of 1945 when he took part in the great Jubilee Session of the Academy of Sciences. As with the other foreign guests, Svedberg was deeply impressed by the high level of achievements of Soviet science. Among the scientists nominated for the Nobel Prize in physics and chemistry in 1946 were Frumkin, P.L. Kapitsa, N.N. Semënov, and V.A. Engelgardt. Frumkin's nomination was organized by Izaak Maurits Kolthoff, who was Professor and Head of the Division of Analytical Chemistry of the University of Minnesota (St Paul). However, his nomination received a chilly response from Stockholm. The Swedish biochemist Arne Tiselius (who later won the 1948 Nobel Prize for his studies of electrophoresis) reviewed Frumkin's work and noted his contributions to fundamental electrochemistry (interfacial potentials and double layers). But he concluded that Frumkin's studies lacked the originality and significance necessary for a Nobel Prize.

In mid-1960s, Frumkin was again proposed for a Nobel prize, this time by the Committee of the International Society of Electrochemistry (led by J. Koryta). Simultaneously, the Academy of Sciences of the USSR and Academician N.A. Semënov nominated Frumkin and Max Volmer for the Nobel Prize. To their regret, nothing came of these attempts. Nevertheless, J. Koryta believed that the achievements of Frumkin deserved acknowledgment. Professor J. O'M. Bockris was among those who strongly supported Frumkin's nomination. According to

Ya. P. Stradyn [1], the failure to win the Nobel Prize was most probably due to the underestimation of the role of electrochemistry in the broader system of chemical sciences, rather than a failure to recognize Frumkin's personal contribution. (Kolthoff himself was also overlooked, despite being one of the most highly cited chemists in the world.)

One electrochemist who did win the Nobel Prize (in 1959) was the Czech scientist, Jaroslav Heyrovský (20 December 1890–27 March 1967) "for his discovery and development of the polarographic methods of analysis." It is difficult to assess how much this event affected his relations with Frumkin. Their relationship was always rather fraught, involving scientific frictions and possibly other factors. Indeed, away from the formality of scientific conferences, and in his private correspondence, Frumkin always expressed reservations about the wider applicability of polarography, since it was mainly restricted to mercury. He also thought that the equations of polarography were rather complex, due to the nature of the drop-growth-separation process. Heyrovský harbored similar doubts about Frumkin's work. According to J. Koryta, it was unwise to mention the transfer coefficient α in the Heyrovský's presence! At the same time, Frumkin made substantial contributions to the theory of polarography, such as the explanation of polarographic maxima (together with V.G. Levich) [35–37], the discovery and interpretation of maxima of the second kind (together with T. A. Kryukova), and later maxima of the third kind (together with coworkers at the Department of Electrochemistry MSU) (Photo 4.27).

The different approaches of Heyrovský and Frumkin to the kinetics of electrode processes emerged in many places. For example, Heyrovský often focussed attention on events taking place in the bulk of solution (e.g., the formation of ion pairs)

Photo 4.27 Heyrovský and Frumkin in Prague (1964)

as the most significant as regards the kinetics of electrode reactions. On the other hand, Frumkin tended to consider interactions inside the double layer as more important. Thus, Frumkin placed great emphasis on the adsorption of reactants, products, and intermediates.

By a strange coincidence, on the day of Frumkin's death, the 10th Lectures in memory of J. Heyrovský were being held in Liblice (28 km northeast of Prague). R. R. Dogonadze, who was present at the event, transmitted the sad news to the audience. Everyone was upset to hear this.

4.15 The Final Years

The final years of Frumkin's life were marked by many tragic events. First, in 1968, his wife Amaliya Davydovna died. Fortunately, Emiliya Georgiyevna Perevalova, a Professor of Moscow State University, took care of him toward the end. After Frumkin's death, Emiliya also organized receptions in Frumkin's flat for the participants of the Frumkin Memorial Symposia. On her initiative, various visits to the Frumkin's tomb at the Novodevichy Cemetery were also organized (Photo 4.28).

Another misfortune that arose soon after his 75th birthday was a series of complications with regard to his reappointment as Director of the Institute of Electrochemistry. However, his greatest source of disillusionment seems to have been with one of his closest collaborators, Veniamin Grigor'yevich Levich (30 March 1917–19 January 1987). As a theoretical electrochemist, and a member of Frumkin's school, he was a close ally of Frumkin for 30 years. They published many studies together on the movements of mercury drops in electric fields [36,

Photo 4.28 Amaliya Davydovna Obrucheva and Emiliya Georgievna Perevalova. December 30, 1966

37]. Later, they carried out remarkable studies on the quantitative analysis of polarographic maxima. During his wartime evacuation to Kazan, Levich also developed the theory of diffusion to moving boundaries. In close cooperation with Landau and Frumkin, Levich even succeeded in creating a new scientific subdiscipline—*physicochemical hydrodynamics*. Later, Frumkin stimulated Levich's studies in the field of the rotating ring-disk electrode. In 1958, Levich began work in the newly founded Institute of Electrochemistry where he immediately became the Head of the Theoretical Division. The work of this Division gained them both world recognition. In fact, Levich even developed his own school. This allowed many leading scientists to collaborate (R. R. Dogonadze, Yu. A. Chizmadzhev, A. M. Kuznetsov, Yu. I. Kharkats, V. S. Krylov, M. A. Vorotyntsev, A. A. Kornyshev, A. M. Brodskiy, Yu. A. Gurevich, M. I. Urbakh, V. I. Filinovskiy, and many others). Finally, Levich postulated the idea of nonequilibrium double layers and described them theoretically.

In 1972, Levich surprised Frumkin by applying for permission to leave the USSR for Israel. Thus Levich became the first corresponding member of the Academy of Sciences of the USSR to express a wish to emigrate from the Soviet Union. This was a huge blow for Frumkin, who greatly admired the scientific achievements of Levich and saw him as his successor as Director of the Institute of Electrochemistry. He called Levich's decision a betrayal. Meanwhile, the Soviet government removed Levich from his position as Head of the Theoretical Department, and he was fired by MSU. Because Levich had access to secrets, he was even threatened with imprisonment.

After he appealed to leave, other USSR scientists were forbidden to cite his studies. For example, when B. B. Damaskin and O. A. Petrii were preparing their book "*Introduction to Electrochemical Kinetics*" for publication, the publishing house "Vysshaya Shkola" asked them to remove Levich's name wherever it was mentioned. Frumkin appealed on their behalf to the Department of the Central Committee of the Communist Party but could only get permission for three references. So, the book was published in 1975 with only three references to Levich.

After the death of Frumkin in May 1976, things got even worse. Thus, the monograph "*Rotating Ring-Disk Electrode*" by M. R. Tarasevich, E. I. Khrushcheva, and V. I. Filinovskii was published by Nauka without any mention of Levich, although it was published as late as 1987. This absurd situation was widely discussed by the International Society of Electrochemistry. Some scientists who knew nothing of the factual background even blamed Frumkin for the problem, which was absurd.

After a 6-year struggle, and with help from the international scientific community, as well as a visit to the Soviet Union by Senator Edward M. Kennedy, Levich and his wife were finally allowed to emigrate to Israel on 1 December 1978. In March 1979, he accepted an invitation to become the Albert Einstein Professor of Science at City College, New York, where he established the Institute of Applied Chemical Physics and became its first Director.

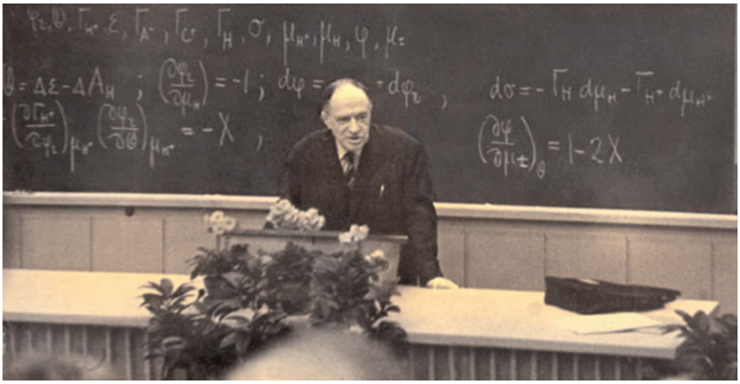

Photo 4.29 Frumkin delivers a lecture on the thermodynamics of the hydrogen electrode

In the midst of all these momentous events, and despite advancing years, Frumkin continued to carry out his own researches, successfully organizing scientific meetings and participating in various conferences. In 1974 alone, more than 20 scientific articles by Frumkin were published in Soviet and foreign journals (Photo 4.29).

Around the same time, Frumkin took part in scientific discussions with Sergio Trasatti on the problem of the zero charge potential and its relationship with the electron work function. With Klaus Jürgen Vetter (1916–1974), Wolfgang Lorenz, Joachim Walter Schultze (1937–2005), and Waldfried Plieth, he discussed the problem of partial charge transfer at electrodes [38].

In December 1975, Frumkin went to Paris as the leader of the Soviet delegation to the First Soviet–French Seminar on Electrochemistry. In the ancient buildings of the Sorbonne, he delivered a classic lecture on new methods of studying the electrode/solution interface. He spoke impeccable French, and his speech impressed everyone by its depth of insight.

Until the very end of his life, Frumkin continued to work on a monograph conditionally entitled "*Zero Charge Potentials*." During the writing process, new ideas kept coming to him, which led him to initiate new experiments at MSU and the Institute of Electrochemistry. Unfortunately, Frumkin could not finish the manuscript in time. It was finally completed by B. B. Damaskin and O. A. Petrii, and published in 1979 [39].

Frumkin was an active and enthusiastic advocate of electrochemical science, and superb speaker. A fine example of this was his lecture at the XI Mendeleev Meeting on General and Applied Chemistry held in Alma-Ata in September 1975. Thousands of listeners rose and applauded the senior Soviet scientist after he reminded people that Aphrodite was born from the foam of seawater, a structured electrolyte solution. In the surroundings of that general chemistry conference, with strong emphasis on oil and natural gas chemistry, everyone immediately understood that the beautiful Aphrodite was an allegory for electrochemistry.

Frumkin always focused attention on the future prospects of electrochemistry. In his last years, he used to cite the words of Michael Faraday: "*Wonderful as are the* *laws and phenomena of electricity when made evident to us in inorganic or dead matter, their interest can bear scarcely any comparison with that which attaches to the same force when connected with the nervous system and with life*."

4.16 Conclusion

The intense creativity of Frumkin lasted for more than half a century. The list of his scientific publications contains an astonishing 755 articles. On his 75th birthday, his friend, the famous Soviet scientist P. A. Rehbinder said that of all chemists, Michel Eugène Chevreul (1786–1889) lived the longest calendar life. Nevertheless, he knew of no one who had lived a longer *scientific* life than Frumkin.

A. N. Frumkin never joined the Communist Party, but he was a sincere and eager supporter of the Soviet state and always remained a patriot. Throughout his life, he displayed a deep interest in the home and foreign policy of the USSR and studied Party documents carefully.

In April 1974, the US senator Edward Kennedy visited the USSR (with his wife and children). His main goal was to seek complete prohibition of nuclear tests and to eliminate the obstacles that prevented the emigration of Soviet citizens abroad. The Kennedy family visited Frumkin in his dacha in the village of Lutsino near Moscow. The senator knew Frumkin as a foreign member of the US Academy of Sciences. During their talk, Frumkin was able to display his extensive knowledge and deep understanding of world politics (Photo 4.30).

Photo 4.30 A.N. Frumkin, E.G. Perevalova, and Edward Kennedy with his family in Lutsino (April 1974)

The Soviet State highly esteemed the research abilities and organizational skills of Frumkin and his enduring support for the Soviet state. He was awarded many orders and medals of the Soviet Union, including its highest award—Hero of Socialist Labor. At the same time, Amaliya Davydovna and Frumkin tried to give their moral and material support to persons unwarrantedly persecuted. In the book, "*Word-for-Word Translation. The life of Liliana Lungina told by Oleg Dorfman in his film*" (Astrel, 2009) both are mentioned several times. Amaliya Davydovna was the aunt of Liliana Lungina. The latter recalled that Amaliya Davydovna always eagerly donated money to help dissidents, but preferred to do so anonymously.

In this regard, the appearance of Frumkin's signature on a letter denouncing the political activities of Andrei Dmitrievich Sakharov (21 May 1921–14 December 1989) in 1975 appears very strange. Frumkin recalled that he was virtually forced to sign the letter. Apparently, he was summoned to the office of the vice president of the Academy of Sciences on his 80th birthday. He went there imagining that he was going to be congratulated. Instead, the vice president was away, and he was subjected to various threats. Being old and under pressure, he signed the letter.

Ten years earlier, in happier times, Frumkin was given two pictures by his coworkers in the Department of Electrochemistry, which imitated the works of Picasso and Gauguin. These were to celebrate his 70th birthday. They symbolized the brighter aspects of Frumkin's life—his love of science, his constant urge to travel, and his deep admiration for nature, art, and poetry (Photo 4.31).

Photo 4.31 Pictures imitating Picasso (the authors are O.A. Petrii and R.V. Marvet) and Gauguin (A.A. Lopatkin), which were presented to A.N. Frumkin on his 70th birthday

Almost 40 years have now passed since the death of Frumkin. The intervening years have only served to highlight his greatness as a scientist and as a person. In future, this period of electrochemistry will rightly be called the *Epoch of Frumkin*.

Acknowledgments I am grateful to Professor F. Scholz for valuable remarks and suggestions during the preparation of the manuscript; to E. I. Khrushcheva, the director of the Memorial Frumkin Museum at the Frumkin Institute of Physical Chemistry and Electrochemistry RAS for the opportunity to familiarize myself with the manuscript "*A. N.Frumkin. Students and Associates*"; and to use some photographs. I am also grateful to T.Ya. Safonova who translated the first draft of the present paper and made it possible to use various materials from the archive of Academician Ya. M. Kolotyrkin.

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Chapter 5
The Development of Voltammetric Electroanalysis in the Former USSR

Fritz Scholz, El'za Arminovna Zakharova, Nina A. Kolpakova, Julia D. Sister, and Victor G. Mairanovsky

5.1 Introduction

Fritz Scholz

Voltammetric electroanalysis has played a very prominent role in the USSR. The famous geochemist Vladimir Ivanovich Vernadskiy very early understood the significance of Jaroslav Heyrovský's development of polarography (see the Sect. 3.2), and thanks to Vernadskiy the method was successfully introduced to the USSR (see the Sect. 5.2). The development of electroanalysis in the USSR was also catalyzed by Alexander Naumovich Frumkin (see the Chap. 4). Other factors which favored the development of electroanalysis in the USSR were (1) students

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Fig. 5.1.1 Participants of the 2nd All-Union Conference on Polarography in Kazan in 1962. First row (from *left* to *right*): 3rd Sof'ya Il'inichna Sinyakova (Moscow, GEOKHI), 4th Armin Genrikhovich Stromberg (Tomsk, TPU), 5th Yevgeniya Nikolyayevna Vinogradova (Moscow, University), 6th Tatyana Alexandrovna Kryukova (Moscow, Institute of Physical Chemistry and Institute of Current Sources), 7th Ol'ga Al'fredovna Songina (Alma-Ata, University), 8th Vera Fyodorovna Toropova (Kazan, University), 10th Mikhail Tikhonovich Kozlovskiy (Alma-Ata, University). Second row (from *left* to *right*): 5th Borukh Yakovlevich Kaplan (Moscow, GIREDMET), 9th A. A. Gabovich (Kishinyëv, Agricultural Institute). Third row (from *left* to *right*): 11th Inga Putninya (Riga), 16th Mark Borisovich Bardin (Kishinyëv). Fourth row (from *left* to *right*): 3rd Viktor Aronovich Igolinskiy (Tomsk, TPU), 4th Stella Florianovna Gurskaya (Tomsk, TPU), 5th Lidiya Filipovna Zaichko (Tomsk, TPU), Matvey Safonovich Zakharov (Tomsk, TPU), 7th Vladimir Yevgen'yevich Gorodovykh (Tomsk, TPU), 7th Ivcher Tasya (?)

of chemistry got a very serious training in mathematics, physics, and physical chemistry, of course including electrochemistry. This provided the intellectual basis for very serious research work, and (2) that the instrumentation was rather inexpensive, and thus very attractive for application.

Here, at the beginning of the chapter about electroanalysis in the former USSR, it is the right place to show a rare photographic document: Fig. 5.1.1 shows the participants of the 2nd All-Union Conference on Polarography in Kazan in 1962. It is interesting under two aspects: (1) it shows almost all major players in USSR electroanalysis, and (2) there is no foreign participant! Although this was a national conference, it is still unusual, at least from our perspective now, that there were no foreign guests. Of course, this mirrors how deep the division of the world was, and how isolated the USSR scientists were.

5.2 Yevgeniya Nikolaevna Varasova: The Woman Who Has Transferred Polarography to Russia

Fritz Scholz and El’za Arminovna Zakharova

Yevgeniya Nikolayevna Varasova[1] was one of the first Russians to publish papers on polarography (the first was N.V. Emelianova), and she was the scientist who has transferred polarography to the USSR.

Ye. N. Varasova was born on May 17th, 1905, in Malaya Vishera, a small town on the railway line from Saint Petersburg to Moscow. The distance to Saint Petersburg is 162 km. The town has the same name as the river (Malaya Vishera, also Malaya Visherka, meaning “little Vishera”) it is situated at. Ye. N. Varsova’s parents were Natal’ya Petrovna Pushkova[2] and Nikolay Mikhaylovich Varasov (Fig. 5.2.1),[3] a merchant, city council head, and (hereditary) Honorary Citizen of Malaya Vishera.

Nikolay Mikhaylovich Varasov was a member of the foundation committee of the “Pushkin Library” (a public library) which has been opened in 1900 in Malaya Vishera. Nikolay M. Varasov served as its head from 1903 to 1907. His wife was a member of the steering committee of the women’s gymnasium.[4] Yevgeniya N. Varasova had two sisters, Natal’ya and Tat’yana, and one brother.

After finishing the school in Malaya Vishera (June 17th, 1921), Ye. N. Varasova entered Petrograd State University, but because her father, like all officials of tsarist Russia, was deprived of his election rights,[5] she was expelled, despite the protests of professors who told the University authorities that it would be a great loss for science to expel such a talented girl. Aleksandr Chistovskiy, a good friend of her who lived in Czechoslovakia, has sent her an invitation to come to Prague, pretending the wish to marry her. This was a common way to escape from the USSR, and so she could enter Charles University in Prague in 1924. Figure 5.2.2 shows a photo, which she has sent to her mother with the following words (in - Russian) on the backside: “To my dear mummy lest she will forget her daughter who is so far away from her. Feb. 13th 1925.” On February 6th, 1930, she had major rigorous examination in mathematics and inorganic and physical chemistry, and on April 25th, 1930, a minor rigorous examination in experimental physics (both with distinction). She successfully defended her excellent doctorate thesis published in

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[1] This chapter is based on a previous publication [1].

[2] In Russian: Наталья Петровна Пушкова.

[3] In Russian: Николай Михайлович Варасов.

[4] This information was partly provided by Natalya Pavlovna Sidorova (a relative of Ye. N. Varasova), Yelena Sirotkina (radio journalist), and the Pushkin Library, Malaya Vishera, partly it is accessible in the internet (see: http://aspbiblmv.sehost.ru/page9/1/1).

[5] Constitution of the RSFSR (Russian Soviet Federative Socialist Republic) of 1918, Part 30th, No. 65, depriving all people of the active and passive election rights who previously served the tsarist state, the church, or who have been assigned to be capitalists, landowners, etc.

Fig. 5.2.1 The parents of Yevgeniya Nikolayevna Varasova: her mother Natal'ya Petrovna Pushkova and her father Nikolay Mikhaylovich Varasov

Collection of Czechoslovak Chemical Communications [2] and got promoted at Charles University on May 2nd, 1930. The doctoral work has been already done in the laboratory of Jaroslav Heyrovský, where she continued after her PhD defense as one of Heyrovský's assistants at the Department of Physical Chemistry. During her studies in Prague, she met her future husband Yevgeniy Ivanovich Vasil'yev who was born in 1904 in Orel. Figure 5.2.3 shows the couple in Prague, and Fig. 5.2.4 shows her in the research group of J. Heyrovský.

It is still not completely clear how it happened that Ye. N. Varasova joined the laboratory of Jaroslav Heyrovský and worked with him from 1927 to 1930. In some sources it is said that V. I. Vernadskiy (1863–1945) has sent her [3, 4]; according to another source, A. P. Vinogradov (1895–1975), the successor of Vernadskiy, and Varasova were sent together by Vernadskiy [5, 6], but this is unlikely and in contradiction with the CV of Vinogradov. It is more likely that Vernadskiy met her during his visit to Prague and to Heyrovský's laboratory and he may have advised her to help in transferring polarography, a method which he highly rated, to

Милой моей Мамочке, чтобы
не забыла свою дочку, которая
теперь так далеко от нее.
13 февр. 1925 г

Fig. 5.2.2 Yevgeniya Nikolayevna Varasova in Prague, 1925

Fig. 5.2.3 Yevgeniya Nikolayevna Varasova and Yevgeniy Ivanovich Vasil’yev in Prague

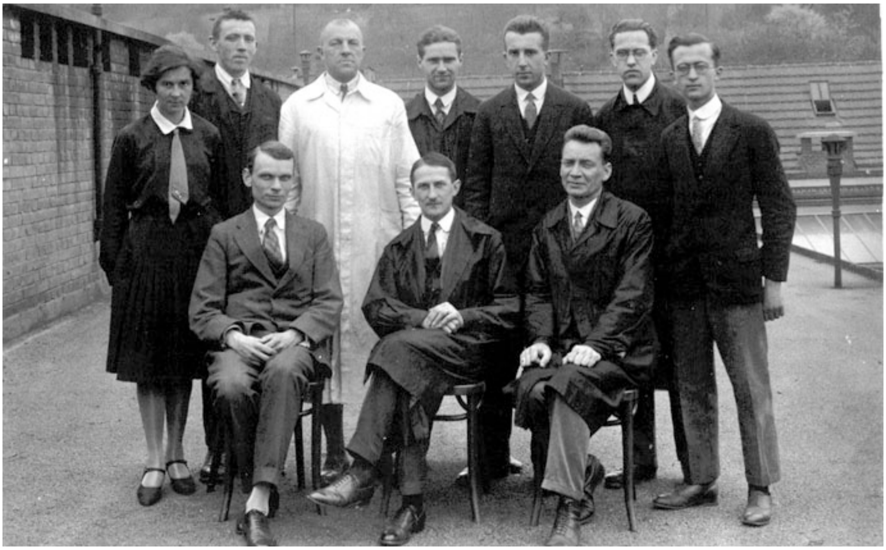

Fig. 5.2.4 Yevgeniya Nikolayevna Varasova (1905–November 3, 1938) standing on the *left side*. Jaroslav Heyrovský is sitting in the *middle*; standing row: fourth from *left* is Rudolf Brdička; first from the *right* is Dionýz Ilkovič. The photo was taken in 1930 on the roof of the Chemical Institute building at Albertov, Prague (Courtesy of M. Heyrovský, Prague)

Russia. Her later husband Yevgeniy Ivanovich Vasil'yev[6] was an electrical engineer, who worked in the Soviet Trade Mission[7] in Prague, Czechoslovakia. Varasova has translated Heyrovský's first book [7] on polarography to Russian [8] and she has published some early papers on polarography,[8] [9–12]. The papers [9–11] were definitely the first publications on polarography in USSR journals. J. Heyrovský wrote in his preface to the Russian translation of his book: "In the Russian translation a theoretical part was added and the experimental part was extended in accordance with new data of polarographic studies. Due to this the size of the book almost doubled. I am very indebted to my former pupil and coworker E. N. Varasowa (Leningrad) for the exact and careful translation from Czech." In his diary Vernadskiy wrote in 1937: "In 1937 a book was translated from Czech (language) by E. N. Varasova-Czech, who worked with me. *I do not know anything about her fate*."[9] The original Russian phrase "Е.Н. Варасовой – чешки" is here

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[6] In Russian: Евгений Иванович Васильев.

[7] In 1922 a treaty about the establishment of Trade Missions was signed between the Czechoslovakia (Československo) and the RSFSR (Russian Soviet Federative Socialist Republic), and only in 1934 full diplomatic relations have started.

[8] See Footnote 5.

[9] http://vernadsky.name/wp-content/uploads/2013/03/vernadsky.pdf: V. I. Volkov (edt) (2006) V. I. Vernadskiy. Dnevniki 1935–1941. Vol 1 (1935–1938), p 152: "В 1937 году вышла по моей инициативе (книга), переведенная с чешского работавшей у меня Е.Н. Варасовой - чешки. *Не знаю ее судьбы*."

translated as “Varasova-Czech,” but this does not reflect the real meaning in colloquial Russian language, where it indicates that Varasova was in Czech (oslovakia) and was able to speak Czech, but it does not mean that she was of Czech nationality. Also according to the memory of Michael Heyrovský,[10] the son of Jaroslav Heyrovský, his father always spoke about Varasova as a Russian lady. It is interesting that Vernadskiy highlighted in his diary the words “*I do not know anything about her fate*.” Probably he would not have done so if he would not have had some suspicions. Of course, it would have been much too dangerous for him to note any such thoughts.

In the laboratory of J. Heyrovský in Prague, Yevgeniya N. Varasova has studied the behavior of oxygen maxima of the first kind and especially the damping effects of various anions, establishing the well-known series from Cl^- (least effect) to CN^- (strongest damping).[11] She also undertook polarographic studies of soap solutions [9]. Her Russian review on polarography published in 1935 [9] was the first description of polarography to the Russian scientific community (Fig. 5.2.5). The other two papers which she has published concern mineral analysis [10] and a reply [11] to a paper in which a Russian scientist [13] has published his disbelief in the linear concentration dependence of limiting currents. Ye. N. Varasova has provided the correct proof based on the experimental data collected by V. F. Toropova during her stay in Ye. N. Varasova’s laboratory.

In 1930 Ye. N. Varasova and Ye. I. Vasil’yev returned to Leningrad and Ye. N. Varasova worked at the State Institute of Applied Chemistry. On June 16, 1931, her son Andrey Yevgen’yevich Vasil’yev (Fig. 5.2.6) was born.

Yevgeniya Nikolayevna Varasova was arrested on November 13, 1933, i.e., when her son was 2 years old. She was sentenced on March 29th, 1934, to 3 years CLC (so-called corrective labor camp) *on probation*. On June, 1st, 1938, she was arrested again, and on October 31, 1938, she was sentenced to death and shot on November 3, 1938.[12,13] The prosecution was based on Article 58 of the Criminal Code of the RSFSR (1926) concerning “counterrevolutionary activities,” and specifically 58–6, concerning espionage. Her husband, Yevgeniy Ivanovich Vasil’ev (born in 1904 in Orël), was sentenced to 10 years of CLC in 1934, and

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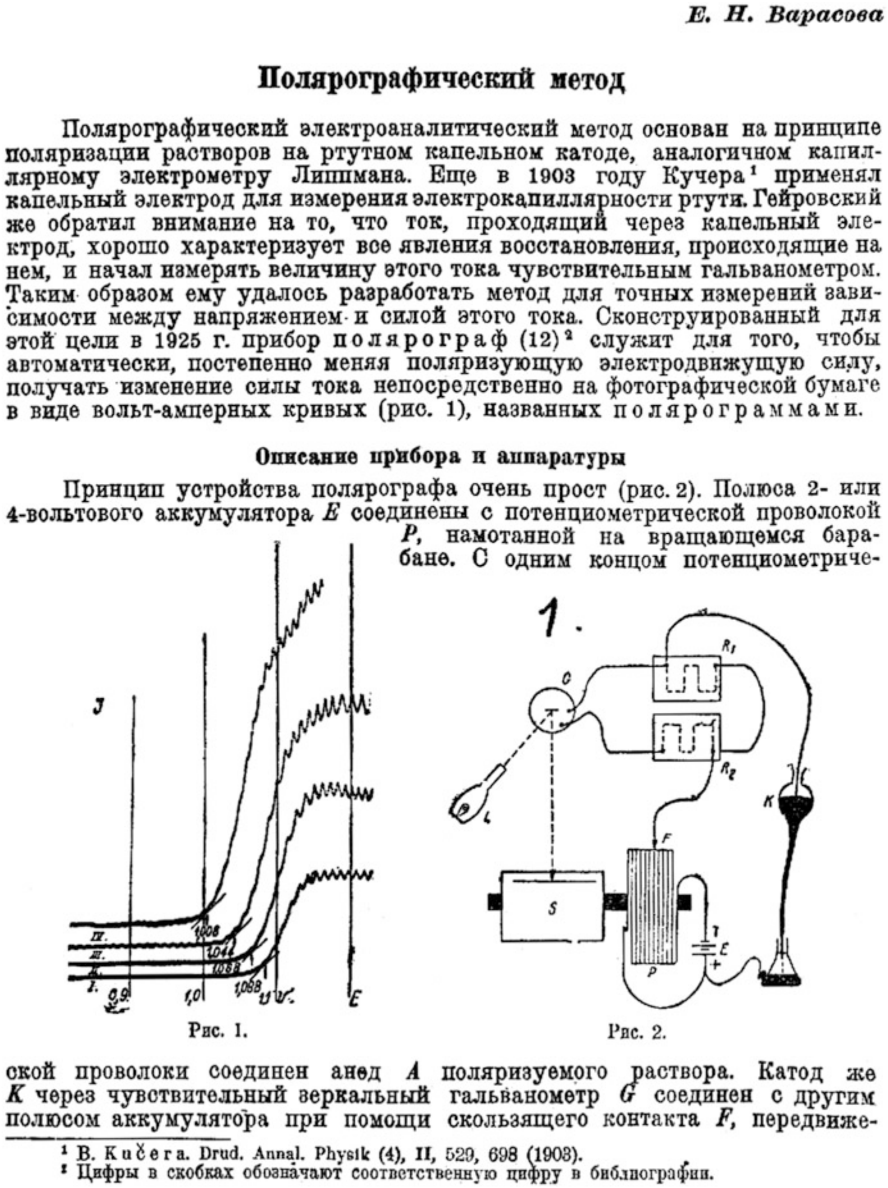
[10] Personal communication from Dr. Michael Heyrovský, March 2013.

[11] See Footnote 5.

[12] Prestuplenya Stalina i Stalinizma (The crimes of Stalin and Stalinism): “Варасова Евгения Николаевна, 1905 г. р., уроженка г. Малая Вишера, русская, беспартийная, в СССР прибыла из Чехословакии в 1930 г., ст. химик Института прикладной химии, проживала: г. Ленинград, Прядильный пер., д. 8, кв. 32. Арестована 13 ноября 1933 г. Коллегией ОГПУ 29 марта 1934 г. осуждена на 3 года ИТЛ условно. Вновь арестована 1 июня 1938 г. Особой тройкой УНКВД ЛО 31 октября 1938 г. приговорена по ст. 58-6 УК РСФСР к высшей мере наказания. Расстреляна в г. Ленинград 3 ноября 1938 г. (Ее муж и одноделец Евгений Иванович Васильев осужден в 1934 г. на 10 лет ИТЛ, отбывал срок в Инталаге, в 1944 г. осужден снова на 10 лет.).” http://antiput43.livelournal.com/469601.html

[13] Vozvrashchyënnyye imena (Returned names): same text as in foregoing reference. http://visz.nlr.ru/searchword.php?qs=%EF%F0%EE%E6%E8%E2%E0%EB%E0&rpp=20&p=108



Е. Н. Варасова

Полярографический метод

Полярографический электроаналитический метод основан на принципе поляризации растворов на ртутном капельном катоде, аналогичном капиллярному электрометру Липпмана. Еще в 1903 году Кучера[1] применял капельный электрод для измерения электрокапиллярности ртути. Гейровский же обратил внимание на то, что ток, проходящий через капельный электрод, хорошо характеризует все явления восстановления, происходящие на нем, и начал измерять величину этого тока чувствительным гальванометром. Таким образом ему удалось разработать метод для точных измерений зависимости между напряжением и силой этого тока. Сконструированный для этой цели в 1925 г. прибор полярограф (12)[2] служит для того, чтобы автоматически, постепенно меняя поляризующую электродвижущую силу, получать изменение силы тока непосредственно на фотографической бумаге в виде вольт-амперных кривых (рис. 1), названных полярограммами.

Описание прибора и аппаратуры

Принцип устройства полярографа очень прост (рис. 2). Полюса 2- или 4-вольтового аккумулятора *E* соединены с потенциометрической проволокой *P*, намотанной на вращающемся барабане. С одним концом потенциометрической проволоки соединен анод *A* поляризуемого раствора. Катод же *K* через чувствительный зеркальный гальванометр *G* соединен с другим полюсом аккумулятора при помощи скользящего контакта *F*, передвиже-

Рис. 1.

Рис. 2.

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[1] B. Kučera. Drud. Annal. Physik (4), II, 529, 698 (1903).

[2] Цифры в скобках обозначают соответственную цифру в библиографии.

Fig. 5.2.5 First page of the review on polarography published by Ye. N. Varasova in 1935 [8]

Fig. 5.2.6 Yevgeniya Nikolayevna Varasova with her son Andrey Yevgen'yevich Vasil'yev (before 1938)

in 1944 again to another 10 years. He was detained in the labor camp Intalag,[14,15] which was a system of camps in the Komi ASSR in the vicinity of Workuta and Inta, where the detained had to work in coal mining. Only in 1956, after his rehabilitation, he could see again his son Andrey. In 1934 Yevgeniya N. Varasova was accused of having known about the activities of the Socialist Revolutionary Party, a political party which was severely fought by the Bolshevists. Additionally she was accused of espionage for Germany in 1938. Yevgeniy I. Vasil'ev was accused in 1934 of having been a member of the Socialist Revolutionary Party (file No. 494-N-57 of April 29, 1957 of the Military Tribunal of the Leningrad Military Region in which both have been rehabilitated with respect to the court decision of 1934 for Vasil'ev, and the court decision of 1934 and 1938 for Varasova). It is well known that among the Russian students in Prague, agents of the NKVD (so-called Peoples Commissariat for Internal Affairs, i.e., the Soviet security service) were actively searching, and many of the returned students were arrested and even shot. Among the arrested and shot were also former NKVD agents.

Unfortunately, in some papers it is still wrongly stated that Yevgeniya N. Varasova perished in a camp [3]. This was a common lie spread by the NKVD when people were executed (see the husband of Songina in the respective chapter). For the readers who are not acquainted with the history of the USSR it should be stressed: these repressions were part of the great purges during the Stalin time and completely unjustified from any point of view of civil rights.

The son Andrey Yevgen'yevich Vasil'yev was brought up by his aunt Natal'ya N. Varasova because of the repression of his parents. The repression of his parents has prohibited him entering the prestigious University of Leningrad, and he had to join the "Forest Technical Academy" where he studied botany. He became a famed

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[14] See Footnote 12.

[15] "Васильев Евгений Иванович. Родился в 1904 г., г. Орел; русский; заключенный Интлага НКВД. Арестован 10 мая 1943 г. Приговорен: Особое совещание при НКВД СССР 5 января 1944 г., обв.: по ст.ст. 58-2 УК РСФСР, 58-10 ч.2, 58-11 УК РСФСР. Приговор: 10 лет лишения свободы." http://lists.memo.ru/d6/f268.htm

Fig. 5.2.7 Andrey Yevgen'yevich Vasil'yev, the son of Yevgeniya N. Varasova

professor at the Komarov Institute of Botany of the Academy of Science in Leningrad and professor at Leningrad University (see Fig. 5.2.7). On July 8th, 2011, he passed away without leaving children [14, 15].

Yevgeniya Nikolayevna Varasova was a very gifted and talented young scientist who just made the first steps in science. She has transferred polarography to the USSR. Her repression and execution has terminated a most promising carrier and the life of a devoted scientist. Her biography is an example of the immense intellectual losses the USSR has suffered during Stalin's reign.

5.3 The Development of Stripping Voltammetry in the Former USSR

5.3.1 Introduction

Nina A. Kolpakova

Modern voltammetric methods of analysis, including stripping voltammetry (SV), are well suited to solve problems in physical and analytical chemistry and also for studies of solid materials. They are frequently used to analyze environmental, medical, biological samples, products of food and ore processing industry, materials of semiconductor industry, etc. Stripping voltammetry lends itself for determining inorganic and organic compounds in the sub-micromolar range. It is an advantage that SV allows a selective determining of the species in their natural state (speciation analysis). SV methods have doubtless a number of advantages over other methods: high sensitivity, selectivity, speed of analysis, and tolerance of measurements to a possible salt content of samples. The instrumental developments of the last years, both with respect to software and hardware (e.g., coupling with dispensers, flow-through systems, etc.), have also contributed to a widening of applications of electroanalytical techniques. It is a general tendency that mercury electrodes are more and more substituted by mercury-free electrodes (Au, Bi, Nafion-covered electrodes, etc.) [16], also to increase the sensitivity. The instrumental developments lead to a decrease of manual labor and an increase of reproducibility. Now it is difficult to imagine the time without SV, although it is only 50–60 years ago when the methods have been introduced. In the USSR, besides the scientific school in Tomsk, there was the school of Kh'yena (Anna) Zalmanovna Brainina in Donetsk, and later in Sverdlovsk (now Yekaterinburg). In Tyumen was Professor Matvey Safonovich Zakharov, who recently passed away, who has established an SV school (Tyumen Industrial Institute and Tyumen State University). Very active groups are also working in Kazan, led by German Konstantinovich Budnikov (a former student of Vera Fëdorvna Toropova), and in Ufa a group led by Valeriy Nikolaevich Maystrenko. In Moscow SV was started in MSU by Yevgeniya Nikolayevna Vinogradova, Lyudmila Nikiforovna Vasil'yeva, and Anatoliy Ivanovich Kamenev and later extended to research institutes (e.g., by B. Ya. Kaplan, R. F. Salikhdzhanova, S. I. Sinyakova, Yu. I. Vainshteyn, N. A. Yezerska). Each of them had his own field of research in SV, and without all of them, one cannot depict a complete picture of the rise of SV. The group of electrochemists in Alma-Ata had a special profile and it released a number of first-ranking scientists. Without them the amalgam-based electrometallurgy would not have developed. To this group belonged O. A. Songina, M. T. Kozlovskiy, V. P. Gladyshev, and A. I. Zebreva.

This chapter is devoted to those scientists who, like all the others in the USSR, were simple and rather poor people. Many of them have survived a difficult childhood and even starvation periods, but never lost their love of life, education, and science. Even when some of them by virtue of circumstances have changed their working profile, they remained scientists in their mind, in the way of life, and their passion for life. In this chapter, we cannot write about all these enthusiasts, whom we remember and know that it was only thanks to them that SV has developed to what it is now.

5.3.2 *About the Terms "Inverse Voltammetry," "Amalgam Polarography with Preconcentration," "Thin-Film Polarography with Preconcentration," and "Stripping Voltammetry"*

Nina A. Kolpakova and Fritz Scholz

In 1952, G. C. Barker and I. L. Jenkins were the first who have shown that a reductive preconcentration of metals at a mercury electrode gives the possibility to decrease the detection limit of analytical determinations [17]. Although they have understood the potential of this approach, they did not realize its real value, as they did not see a need to determine such low concentrations at that time. Nevertheless, Barker and Jenkins have to be regarded as the true fathers of stripping voltammetry (inverse voltammetry) [18]. In the years 1956–1958, a number of papers popularizing inverse voltammetry have been published by W. Kemula and Z. Kublik from Warsaw (see the chapter “The Warsaw school of electroanalytical chemistry”). All this work was an offspring of the development of polarography by the Czech academician Jaroslav Heyrovský in the early 1920s of the last century, for which he received the Nobel Prize for Chemistry in 1959. Already in 1937, the first book of Heyrovský on polarography has been translated by Yevgeniya Nikolaevna Varasova to Russian (see the Sect. 5.2) [8]. In 1965 Heyrovský’s famous book “Fundamentals of Polarography” has also been translated to Russian [19]. Beginning 1946 in Russia, A. G. Stromberg studied amalgam polarography and has defended his doctoral thesis (equivalent to Habilitation in Germany, and Doctor of Science in the UK) entitled “Theory and practice of polarography, especially amalgam polarography” in Sverdlovsk in November 1951. This thesis had the focus on the theory of amalgam polarography and its experimental verification. In amalgam polarography, a metal amalgam is dropping out of a glass capillary and the voltammetric response of the amalgams is studied. This work was new, especially in the USSR, which was practically cut off from the scientific communities of other countries. In that time, the USSR has developed new technologies using electronic devices. A bottleneck were analytical measurements, necessary to determine impurities in semiconductor materials with high sensitivity. Those methods were missing. In 1962 A. G. Stromberg started in Tomsk a so-called a Special Research Laboratory (in Russian “problemnaya laboratorya”) with the basic research direction focused on voltammetry at stationary electrodes. As stationary electrode they used either a mercury droplet on a silver wire, or a silver wire covered by mercury. Since the electrodes were amalgam electrodes, the method was called “amalgam polarography with preconcentration” (“amal’gamnaya polarografiya s nakopleniem” in Russian). The first papers dealing with that method have been published in 1960 by A. G. Stromberg and Vladimir Yevgen’yevich Gorodovykh in the journal “Industrial Laboartory” (“Zavodskaya laboratoriya” in Russian) [20] and at the same time by Ye. N. Vinogradova and Ye. N. Prokhorova (MSU) [21] and by S. I. Sinyakova and Shen’ Yu-chi (GEOKhi, Moscow) [22]. The first review of SV in Russian literature has been published in 1961 by A. G. Stromberg and his daughter E. A. Stromberg [23]. Experiments with a hanging mercury drop electrode have been performed under the supervision of Vera Fëdorvna Toropova at Kazan State University. There the determination of amalgam forming metals has been studied with the help of oscillopolarography. The new method proliferated and the number of determined elements was increased. The largest number of papers on the new method has been published by the Tomsk group of Stromberg (about one-half to one-third of all papers on IV in the USSR). A number of elements could not be determined by SV on mercury because of too positive oxidation potentials. For this other electrodes, e.g., Pt and graphite, were used. Such methods employing solid electrodes have been mainly developed by the group of Kh’yena (Anna) Zalmanovna Brainina (Donetsk) and they were called "*thin-film polarography with preconcentration*" (plënnochnaya polarografiya s nakopleniem" in Russian) [24]. In a review, A. G. Stromberg [25] wrote: "Until now the two methods '*amalgam polarography with preconcentration*' and '*thin-film polarography with preconcentration*' have developed like two different voltammetric methods, with different theoretical basis and experimental technique. The factors separating the two varieties of polarography with preconcentration were primarily rooted in their history: (1) both methods developed in different research teams and even in different countries. (2) The two methods used different electrodes, mercury and graphite electrodes with different working ranges. (3) Theoretical aspects were different: in '*amalgam polarography with preconcentration*' the anodic peak of metal oxidation was primarily depending on the concentration of the metal in the amalgam, and in '*thin-film polarography with preconcentration*' it was depending on the activity of the metal in the thin film on the surface of the graphite electrode. Further, in the later method, the researchers focused on studying the heterogeneous reactions in the solid phase and on achieving a highly reproducible graphite surface.

However, between these two varieties of polarography with preconcentration, there are more common than separating features. From a theoretical point of view both varieties of polarography with preconcentration are united by the electrochemical laws concerning the basic limiting steps of the electrode process, i.e., the delivery of the compound to the electrode surface and the removal of the compound from the electrode surface, as well as the electrochemical reaction itself. Only that in '*thin-film polarography with preconcentration*' this process is more complicated by the nucleation and growth of a solid phase and its electro-dissolution. Thus, it is advisable to see the two varieties from one point of view. This is particularly clear in the case of mercury film electrodes on graphite, which in one case behave like mercury electrodes, in another like a graphite electrode [26, 27]. For a reversible electrode process at a thin-film electrode, the equation describing the current of electrooxidation of the metal has the same form, independent of the fact whether it is a thin solid metal film or an amalgam film.

From a practical point of view, any sample contains microconstituents, which can be determined with '*amalgam polarography with preconcentration*' (i.e., using a mercury electrode), and other microconstituents which can be determined with the help of '*thin-film polarography with preconcentration*' (i.e., with a graphite electrode). We remark here that the sensitivity of determination of any element is higher on mercury than on graphite because the surface of mercury is more reproducible with respect to surface area and surface properties. Therefore, it is not expedient to determine those elements on graphite, which can be also determined on mercury. Besides this, on solid electrodes, the interaction of metals in the deposit is very pronounced and often makes a determination difficult or even impossible if the elements are simultaneously deposited on the electrode. All these considerations lead to the conclusion that it is advantageous in the analysis of sample to use both methods '*amalgam polarography with preconcentration*' and '*thin-film polarography with preconcentration*'."

The development of techniques based on an electrochemical preconcentration of compounds on mercury and other electrodes and the subsequent electrooxidation of the deposit led to the new term "*inverse voltammetry*" or "*stripping voltammetry*" in foreign languages. This term comprises all varieties of such methods, independent on the electrode material and the electrode reactions (cathodic or anodic).

5.4 The Tomsk School of Electroanalytical Chemistry

5.4.1 Armin Genrikhovich Stromberg

Nina A. Kolpakova and Fritz Scholz

It is difficult to overestimate what Armin Genrikhovich Stromberg (Fig. 5.4.1.1) has achieved for the foundation and proliferation of stripping voltammetry. The foundation of the Special Research Laboratory ("problemnaya laboratorya") and then of a scientific school devoted to the theory and practice of stripping voltammetry—all that would have been impossible without the talent, dedication and unbelievable working capacity of A. G. Stromberg. Stromberg was born September 16, 1910, in Breslau, Germany (now Wrocław, Poland) during a business stay of his father Genrikh Genrikhovich who was "Private Docent" at the Military-Medical Academy in St. Petersburg. Stromberg's mother was a graduate of the Bestuzhev Courses in natural sciences (the Bestuzhev Courses were the largest and most prominent women's higher education institution in Russia). Stromberg wrote about his parents: "To some extent I am chemist by heredity. My grandfather had a private chemical laboratory in Yekaterinburg. My father died in WW I as chief of a military field hospital. My mother worked for 40 years at the chair of general and inorganic

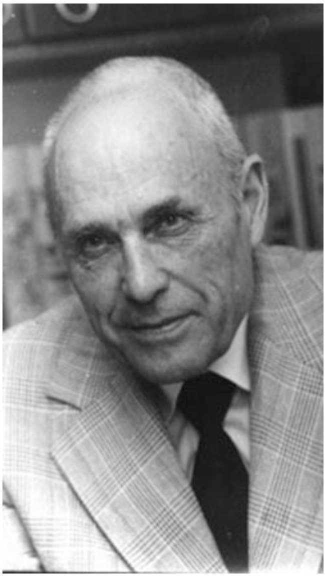

Fig. 5.4.1.1 Armin Genrikhovich Stromberg

chemistry of the Ural Polytechnic Institute." Also Stromberg's daughter went to chemistry working in stripping voltammetry.

The life of Stromberg and his family background has been described in detail in a book [28]. The main periods of his life are: From 1927 to 1930 he studied at the Ural Polytechnic Institute according to the curriculum of the electrochemical division of the chemical faculty, which he finished in chemistry with a specialization in electrochemistry as a technology engineer. Then he worked in the laboratory of molten salts of the Ural Physico-chemical Institute, which was a dependency of the Karpov Institute of Physico-Chemistry in Moscow. In 1939 Stromberg has defended his PhD thesis entitled "About the viscosity of molten salts" at the Ural Industrial Institute. In March 1942 he was formally enlisted in the army, but in fact illegally repressed and sent to a special NKVD camp for "Soviet-Germans" in Nizhniy Tagil, where he had to work in a brick factory. He was released in 1943 (and rehabilitated in 1992) and returned to his working place at Ural Physico-chemical Institute where he was the leader of the analytical chemistry laboratory. In August 1950, he moved to Ural University where he became a docent at the chair of physical and colloidal chemistry. In November 1951, he successfully defended this thesis entitled "Theory and practice of polarography, especially amalgam polarography" in Sverdlovsk before the scientific council of the Ural Polytechnic Institute. In July 1954 he started as professor at the Ural University. After the defense of his doctoral thesis, Stromberg lived with his family in Sverdlovsk (now again Yekaterinburg, like before the October revolution) in a small 2-room apartment, without any hope of possible improvements of living conditions. The supply of apartments was very restricted in the USSR after WW II. The country did a lot to repair the war damages and improve its economy. The living conditions only improved when Stromberg moved to Tomsk where he got a comfortable 5-room apartment in which until now his daughter lives. The Tomsk Polytechnic Institute to which he moved changed the fate of Stromberg.

5.4.2 *The History of the School of Stripping Voltammetry in Tomsk*

Nina A. Kolpakova and Fritz Scholz

Following his move to Tomsk, in 1962, Stromberg was full Professor (Chair) of physical and colloidal chemistry at Tomsk Polytechnic Institute (TPI). There he has continued his work on (a) the potential–current dependencies at amalgam electrodes and the effects of complex formation and formation of intermetallic compounds in mercury; (b) instrumental development started with the upcoming of microprocessors; (c) catalytic waves in polarography and their theoretical understanding; (d) polarographic coulometry; (e) the effect of the substituent on the half-wave potential of organic compounds; (f) the determination of complex stability constants which undergo a reversible reduction on mercury and other electrodes, etc. [29]. All these topics were studied despite the fact that discussions with scientists

Fig. 5.4.2.1 Armin Genrikhovich Stromberg with coworkers in the early years of the PLM ("problem laboratory for microconstituents") (first row: Kh. A. Lel'chuk, R. S. Tyutyun'kova, A. G. Stromberg, A. I. Kartushinskaya, M. S. Zakharov; second row: O. N. Tarasova, unknown person, V. M. Pichugina, K. R. Voronova, A. L. Pozdnyakova; third row: A. A. Kaplin, V. I. Kuleshov, unknown person, V. S. Smorodinov)

abroad were practically forbidden. The situation of Stromberg was even aggravated by the fact that he was regarded as a German (due to his birthplace and name). Luckily, Stromberg has thoroughly studied English, so that he could read the foreign literature. In 1962 Stromberg has established at TPI, a unique laboratory, the Special Research Laboratory, named "problem laboratory for microconstituents" (Fig. 5.4.2.1). This was, also in his own opinion, his main life achievement. The basic direction of this laboratory, which he headed for 23 years, was the development of "*amalgam polarography with preconcentration*" [30]. It was a continuation of his previous research in polarography and other electroanalytical methods. The Special Research Laboratory was founded on initiative of I. P. Alimarin.

Stromberg has elaborated a parametric theory of stripping voltammetry [31] which allowed understanding the effects of various experimental parameters on peak currents. It was the basis of tens of fundamental papers, and also found its way into foreign literature [32]. On the basis of this theory, the improvement of signal separation [33], sensitivity [34], and the effect of so-called ammonium amalgam [35] could be understood. Several papers dealt with effects of formation of intermetallic compounds [36, 37], the role of mixed potentials in polarography [38, 39] and the behavior of metal complexes in stripping voltammetry [40, 41]. Theoretical and experimental studies played an important role in decreasing the detection limits for trace determinations in the range of 10^{-9} to 10^{-6} % in metals and alloys of highest purity, produced for nuclear, semiconductor and laser technology, and microelectronics, in products of food industry, oil industry, drinking water production, and for the analysis of ores and minerals. The scientific output of Stromberg's laboratory is documented in more than 800 papers, 100 PhD theses, and 8 doctor of science theses. Stromberg is the author of a textbook on physical chemistry, which is very popular in Russia [42].

Stromberg has very carefully supervised his PhD students, discussing their research in detail. At that time students said, that going to the professor was like x-raying. Stromberg was a very calm and thoroughgoing person. The scientific group seminars were very important and all discoveries were discussed there. Sometimes Stromberg received his students at home where his large study was filled with books, reprints, and notes. The atmosphere at his home was always very friendly and pleasant. I remember that once his little granddaughter has painted on one of the precious notes, but Stromberg did not grumble but only smiled. Stromberg was a very erudite person with a good sense of humor. Even in his last years, he played each day 1 hour at his piano, preferably Chopin, he wrote his memoires, and continued his scientometric research (earlier papers are [43, 44]). It is well remembered that Stromberg also took care of cleaning the yard of his University flat, combining the necessary with the chance of physical activity, using that time effectively for contemplating about science. Stromberg has in detail planned the time of his working days, never wasting a minute, and he recorded the daily schedule in notebooks.

5.4.3 Students of Armin Genrikhovich Stromberg

Nina A. Kolpakova and Fritz Scholz

Out of the 100 PhD students of Stromberg, only a very few can be remembered here. A much more detailed appraisal of the achievements of his students Stromberg has published at the end of his life [45].

Victor Aronovich Igolinskiy (June 2nd 1936, Omsk–February 23, 1996, Kemerovo) (Fig. 5.4.3.1) was one of the first PhD students of Stromberg in Tomsk. His father was a military doctor and neurosurgeon and his mother a drafter. In his PhD thesis, Igolinskiy analyzed the voltammetric current–potential dependencies of the anodic peak current in stripping voltammetry, taking into account the limited diffusion regime in the mercury droplet, and also its curvature [46, 47]. He has shown that the sensitivity of SV depends on the geometry of the electrode, and that it can be significantly increased using mercury film electrodes. He has derived equations for reversible systems using constant potential and linear scan regimes. He has introduced a method in which the potential scan was terminated shortly after the anodic peak potential, but the current was continued to be recorded, so that the charge underneath the peak could be exactly measured. Igolskiy was also a gifted experimenter, developing micro-cells for SV. Together with Kuleshov, he has introduced amalgamated silver electrodes for SV, which are still popular among electroanalytical chemists in Tomsk. Stromberg highly appreciated Igolskiy and said that “the ideas poured out of him like from a cornucopia.”

Fig. 5.4.3.1 Victor Aronovich Igolinskiy

Fig. 5.4.3.2 Vladimir Ivanovich Kuleshov

Vladimir Ivanovich Kuleshov (April 18, 1931–July 8, 2006) (Fig. 5.4.3.2) was born in the small village Kochki (Novosibirsk Oblast') in a peasant family; his father was a smith. Kuleshov remembered that his father was, compared to other people in the village, much better off and even could buy a "Singer" sewing machine for the family. So it happened that in 1932, the authorities declared his family to be Kulaks and the five-member family was moved around in Siberia. Kuleshov studied in Leningrad at the Leningrad Chemical-pharmaceutical Institute, finishing it as an engineer of microbiology in 1955. He met Stromberg because he needed his consultation, and in 1961, he started his PhD work in Tomsk. Kuleshov was an excellent experimenter with golden hands. He developed cells with exchangeable beakers for SV, electrolyzers with circulating solutions [48], and introduced several different electrodes for SV. Kuleshov's and Stromberg's families became close friends.

Vladimir Yevgen'yevich Gorodovykh (December 20, 1934 Stalinsk (now Novokuznetsk)–April 10, 1988) (Fig. 5.4.3.3) has studied at Tomsk State

Fig. 5.4.3.3 Vladimir Yevgen'yevich Gorodovykh

Fig. 5.4.3.4 Anatoliy Aleksandrovich Kaplin

University. His main contributions concern the anodic peak current calculation for reversible processes taking into account the sphericity and limited volume of the mercury droplet [49, 50]. Gorodovykh was also interested in the effects of organic surface-active compounds on the kinetics of electrode reactions.

Anatoliy Aleksandrovich Kaplin (October 20, 1937–July 27, 1989) (Fig. 5.4.3.4) has developed SV for the determination of traces in semiconductor and other high-purity materials [51]. He was an excellent organizer, not only of research work (he has supervised 20 PhD theses) but also of conferences, e.g., of four All-Union Conferences on Stripping Voltammetry in Tomsk (1973, 1982, 1986, 1990) under the chairmanship of Stromberg. Parallel to Ye. Ya. Neyman who worked in Moscow, Kaplin started to study the formation of complex amalgams, intermetallic compounds in mercury, and solid solutions under the conditions of SV. Anodic currents of such systems were described by Kaplin on the basis of regular solution thermodynamics. Kaplin defended his doctoral thesis entitled "Inverse voltammetric analysis of micro-samples, crystal layers and films" before a commission in Moscow.

Yuriy Aleksandrovich Karbainov (September 3, 1940–November 9, 2007) (Fig. 5.4.3.5) was born in the village Karbainovka, Buryat ASSR, in the family of a

Fig. 5.4.3.5 Yuriy Aleksandrovich Karbainov

Fig. 5.4.3.6 Lyubov' Sergeyevna Anisimova

peasant. After the death of the parents, one of his sisters took care of him and his siblings. Karbainov studied in Tomsk at TPI. In 1966 he defended his PhD thesis on SV, devoted to studies of solutions of metal complexes. His doctoral thesis concerned chemical reactions preceding and following up the charge transfer reaction [52]. It was entitled "Inverse voltammetry of solutions of metal complexes and extracts." There he also described hybrid methods comprising extraction and SV in the extract. He has also proved that sensitivity and selectivity of SV of metal complexes is superior on mercury film electrodes compared to a mercury drop electrode [53].

Lyubov Sergeyevna Anisimova (May 31, 1949–June 27, 2009) (Fig. 5.4.3.6) was born in Bakchar, Tomsk Oblast'. Her father was an officer and fought in WW II. He died at the age of 35 and her mother also died early from tuberculosis. Anisimova was raised up together with a younger brother and sister in a Children Home (orphans home) in Tomsk. She studied at Tomsk State University (Chemical Faculty). From 1980 to 1984, she worked for her PhD in the group of Stromberg. The thesis was entitled "Inverse voltammetry of sulphur containing organic compounds and elaboration of analytical methods for their determination." Anisimova has developed cathodic stripping voltammetry of organic sulfur compounds [54].

Among the many other PhD students of Stromberg, the following need to be mentioned: Boris Fëdorovich Nazarov (*1967) a talented theoretician and Yuriy Alekseyevich Ivanov (*1971) who is actively developing automated instrumentation for SV analysis. Nina Aleksandrovna Kolpakova (*1942) who has devoted her scientific life to the SV of platinum-group metals and silver and gold became full Professor at TPI, Tomsk, where she is still guiding a research group. She has also an important share in the textbook on physical chemistry, published by Stromberg. Stromberg's daughter El'za Arminovna Zakharova (*1938) (Fig. 5.3) is still actively working in the laboratory and elaborating SV methods for modern instrumentation (together with Tomanalyt, a prolific company of electroanalytical instrumentation). She is also very actively cultivating the memory of the Tomsk electroanalytical school [28] and the memory of those people repressed during the Soviet time.

5.5 The Development of Solid-State Electroanalysis and Stripping Voltammetry at Solid Electrodes

5.5.1 *Solid-State Electro*analysis*: Pioneered in the USSR by Ol'ga Al'fredovna Songina*

Fritz Scholz

Biographical Sketch of Ol'ga Al'fredovna Songina

Ol'ga Al'fredovna Songina (Fig. 5.5.1.1),[16,17] was born on April 17, 1901, in Saint Petersburg as daughter of Alfred Borisovich Rode (Rohde) (Governorate of Livonia, Russian Empire, 1864–Leningrad 1922), an engineer coming from a German farmer family. Her mother was Vera Danilovna Rode (Rohde) (Blagodar', Ural, 1871–Alma–Ata 1950), a Russian. Alfred Borisovich Rode was the technical director of the factory "Krasnyy Vyborzhec" in Leningrad (now Sankt Peterburg).[18] In 1918 O. A. Songina finished the middle school. From 1919 to 1922, she worked in "Politprosvet" and lectured for preschool educators in the town Luga, which is situated about 100 km south of Sankt Peterburg. From 1922 to 1928 she was the secretary of the technical director of the company "Krasny Vyborzhec." From 1928

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[16] This chapter is based on previous publications [56, 57].

[17] In Russian: Ольга Альфредовна Сонгина; The sign used in the transcription of Russian words and names, e.g., in "Ol'ga Al'fredovna," indicates that the preceding consonant is palatalized (softened).

[18] "Krasnyy Vyborzhets" means "Red Vyborger"; Vyborg is the name of a town. The factory was founded in 1857 by the Baltic mechanic Fëdor Gosh, in 1863 became the property of Karl Rosenkrants, and it became a State company after the revolution. The factory still exists.

Fig. 5.5.1.1 Ol'ga Al'fredovna Songina in 1928 [55]

to 1931 she stayed at home, most probably because she gave birth to a daughter, and in 1931 she entered the "Leningrad Metal Factory"[19] as secretary of the teaching section of the technical school, later of the entire technical center, where she lectured on general chemistry. In autumn 1931 O. A. Songina began to attend lectures at the Metallurgical Faculty of the "Leningrad Industrial Institute for Distance Education" which has been founded in 1929. In October 1937 she moved to the central laboratory of the "Leningrad Metal Factory" working on her diploma thesis. In December 1937, on the order of the NKVD (so-called People's Commissariat for Internal Affairs, i.e., the secret police organization of the Soviet Union), she had to move from Leningrad to Frunze[20] (now Bishkek), then capital of the Soviet Republic of Kirgizia. The expulsion of O. A. Songina from Leningrad was part of the repression against her husband Iosif Vladislavovich Songin (Fig. 5.5.1.2).[21]

Iosif Vladislavovich Songin was born in 1894 in Rostov-on-Don, and was the son of Vladislav Osipovich Songin,[22] the director of the "Sankt Peterburg Metal Factory"

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[19] The "Leningrad Metal Factory" was founded in 1857 by Sergey Nefed'yevich Rasteryayev, and from 1867 to 1891, its director was the German engineer Otto Georg Krehl. The factory is still working.

[20] Named after the Bolshevik leader Mikhail Vasil'yevich Frunze (Михаил Васильевич Фрунзе), Bishkek 1885–Moscow 1925.

[21] In Russian: Иосиф Владиславович Сонгин.

[22] In Russian: Владислав Осипович Сонгин.

Fig. 5.5.1.2 Iosif Vladislavovich Songin (1894–November 27, 1937), the husband of Ol'ga Al'fredovna Songina (Courtesy of Alla Vital'yevna Shapran, Museum of the Leningrad Metal Factory)

(the later "Leningrad Metal Factory" [58]) from 1911 to 1917. Iosif V. Songin was of Polish origin which, most probably, was one of the reasons for the repression in 1937 as he was accused with two other Poles[23] of being a member of a "counterrevolutionary Polish nationalistic group." It is well documented that ethnic Poles suffered disproportionally to their share in the overall population of the USSR [59].[24] According to the KGB files,[25] Iosif Vladislavovich Songin had declared (most likely

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[23] Konstantin Stanislavovich Olevskiy (Константин Станиславович Олевский) (born 1901 in Tbilisi, arrested on November 23rd, 1937, sentenced to death on December 15th 1937, and executed on December 20th 1937) and Romual'd Romual'dovich Czerwiński (Ромуальд Ромуальдович Червинский) (born 1909 in Sankt Peterburg, arrested on September 2nd, 1937, sentenced to death on October 1st, 1937, and executed on October 6th, 1937).

[24] Nikolay Ivanovich Yezhov (Николай Иванович Ежов), from 1936 to 1938 head of the NKVD and the main inquisitor, issued the NKVD Order No. 00485 "On liquidation of Polish sabotage and espionage groups and units of POW (Polish Military Organization, Polska Organizacja Wojskowa)," approved August 9, 1937. This order was the basis of most severe repressions of national Poles in 1937/1938.

[25] From the files No. P-25620, as reported by the "Federalnaya Sluzhba Bezopasnosti Rossiyskoy federatsii" in a letter to El'za Zakharovna from October 9th, 2012, file No. 10/21-Z-1893/386. This document is kept by the author. In this document is written: „Постановлением Комиссии НКВД и Прокурора СССР от 22 ноября 1937г. Осужден к высшей мере наказания-расстрелу. Проговор проведен в исполнение 27 ноября 1937г. В Ленинграде.» See also the web page "Vozvrashchënnyye imena" (Returned names): http://visz.nlr.ru/searchword.php?razdel=1&qs=%F1%EE%ED%E3%E8%ED&ok=%CD%E0%E9%F2%E8„Сонгин Иосиф Владиславович, 1894 г. р., уроженец г. Ростов-на-Дону, поляк, беспартийный, инженер-конструктор завода им. Сталина, проживал: г. Ленинград, Полюстровская наб., д. 25/2, кв. 39. Арестован 4 октября 1937 г. Комиссией НКВД и Прокуратуры СССР 22 ноября 1937 г. приговорен по ст. ст. 58-7-9-11 УК РСФСР к высшей мере наказания. Расстрелян в г. Ленинград 27 ноября 1937 г."

when he was arrested in 1937) that his father Vladislav Osipovich Songin was a nobleman (in Russian “dvoryanin”) and member of a shareholder of the “Sankt Peterburg Metal Factory” [58] where he served in different functions, and from 1912 to 1916 as director (these dates differ from those on the official website of the factory[26] given above). Being a nobleman has certainly aggravated the case of his son Iosif Vladislavovich. According to the declaration of Iosif Vladislavovich Songin, he had a sister, Sof’ya Vladislavnova Songina, at that time 47 years old, and his wife (i.e., Ol’ga Al’fredovna Songina) had a brother, Boris Al’fredovich Rode (Rohde) (Sankt Peterburg 1893–Frunse 1944) at that time 44 years old. O. A. Songina did not receive any information about the fate of her husband until the year 1957 when she has received an official note that he died in a camp in 1942. However, in fact, he was arrested on October 4th, 1937, sentenced to death on November 22nd 1937, and executed on November 27th 1937 [60]! In August 1957, her husband and the two others [61] were officially rehabilitated (file No. 6202 of August 31, 1957, of the Military Tribunal of the Leningrad Military Region). The execution of I. V. Songin was part of the “Great Purge” in 1937/1938, i.e., the political repressions of the Stalin time in the Soviet Union. In a handwritten CV, dated April 12th, 1959, Songina mentions: “In 1957, I received the information that my husband died in January 1942 in a camp, and in August of the same year (1957) my husband was post-mortem rehabilitated (reference 31/VIII-57, No. 6202) of the Military Tribunal of the Leningrad Military District.” The author of this paper has a copy of the latter document. There is indeed only written “The decision of the Commission of the NKVD and the Procurator of the USSR of November 22nd 1937 in relation to I. V. Songin is cancelled and the case is dismissed for lack of produced evidence.” Indeed it must be assumed that O. A. Songina has never received the true information about the murder of her husband. In 1937 the only daughter of O. A. Songina died at the age of 8 from scarlet fever in Leningrad.[27] In February 1938 Songina started in Frunze in the “Kirgizian Pharmacy Control Board,” first as analytical chemist, then as head of the laboratory, and finally as head of the chemical department. In 1939 she could start her own research work, and in 1941 she went to Leningrad to defend her diploma thesis which was granted with distinction. Figure 5.5.1.3 shows a photo of O. A. Songina from 1942, and it is clear what hardship she has experienced in the years before.

In 1943 she was invited to join the Institute of Chemistry of the then created Kirgizian Branch of the USSR Academy of Sciences. There she worked in the area of analytical chemistry of rare metals. During the Second World War, Songina participated in establishing ore laboratories in the Tian Shan mountains; in particular she developed express methods for the determination of molybdenum and tungsten. During that time she also lectured on analytical and pharmaceutical chemistry at a medical school, and she gave a course on general chemistry at the

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[26] http://lmz-150.ru/content/view/19/43/

[27] Information from Nadiya Serikbayevna Sharipova (Надия Серикбаевна Шарипова), Alma-Ata.

Fig. 5.5.1.3 Ol'ga Al'fredovna Songina in 1942 [55]

Frunze-division of the "Leningrad Institute of Electro-technique and Transport of Communication Engineers." In April 1945, she defended her thesis of a "candidate of science" (equivalent to Ph.D.) in Alma–Ata (now Almaty; Alma–Ata was the capital of the Kazakh Soviet Republic) at the Chemical-Metallurgical Institute of the Kazakh Branch of the USSR Academy of Sciences. The title of her thesis was "The determination of tungsten in natural products." After the defense, Songina was invited to join the Institute of Mining and Metallurgy of the Kazakh Academy of Sciences and to read a lecture course on rare metals. In the autumn of 1945 she moved from Frunze to Alma–Ata. Being a metallurgical engineer she gave a course of lectures on the metallurgy of rare metals and supervised research on mineral resources and analysis of rare elements. The lecture course was the basis of the monograph "Rare Metals" [58] published in 1951 as the first book on that topic in the USSR. This book is still regarded as an encyclopedic source and the former students of Songina have translated it in 2005 to Kazakh language [62]. In 1957 O. A. Songina became "Doctor of Science" (equivalent to "habilitation" in Germany; qualifying her for a Professor position). From 1950 to the last days of her life, Songina worked at the Kazakh State University (S. M. Kirov University[28] during USSR times, now Al–Farabi University[29]), first as Professor of Analytical Chemistry (since 1959), later heading the Chair of Chemistry of Rare Elements. In 1970 O. A. Songina became a corresponding member of the Academy of Science of the

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[28] Sergey Mironovich Kirov (Сергей Миронович Киров) (1886–1934) was a Russian revolutionary and leader of the Communist Party of Leningrad when he was shot in his office in the Smol'nyy Palace in 1934.

[29] Abū Naṣr Muḥammad ibn Muḥammad ibn Tarkhān al-Fārābī (c. 872–c. 950) was a universal scholar who has contributed to astronomy, alchemy, physics, psychology, philosophy, etc. (see [63]).

Fig. 5.5.1.4 O. A. Songina in 1961 [55]

Soviet Republic of Kazakhstan, which was an exceptional high honor. She has received a number of other honors, e.g., in 1968 she became a honorary member of the "All-Union Mendeleev Chemical Society" (now "Mendeleev Russian Chemical Society"), and she has received the "Order of the Red Banner of Labor." She was a member of the editorial board of "Zhurnal analiticheskoy khimii" (Russian Journal of Analytical Chemistry) and of "Talanta," and an associate member of the IUPAC commission on electroanalytical methods of analysis. Figure 5.5.1.4 shows O. A. Songina in 1961.

Solid-State Electroanalysis

The scientific work of O. A. Songina covers a wide spectrum of topics, including polarographic solution analysis of dissolved inorganic and organic compounds, amperometric titrations, and direct electroanalysis of solid compounds. In Russia, Songina is still mainly remembered best for her work on amperometric titrations which she has described in three books [61, 64, 65]. Here, the focus will be on her contributions to the development of electroanalytical techniques to study solid materials without a preliminary dissolution, i.e., to study the electrochemistry of solid materials *directly*. It is not surprising that she has very early understood the need to develop such techniques in the course of her work devoted to the analysis of ores and minerals. The first approach to the electrochemistry of solid materials was to perform polarographic measurements in suspensions of solid particles, and later she started to work with graphite paste electrodes poised with solid particles, the analyte.

Studies of the Electrochemical Behavior of Suspensions of Solid Particles

In the middle of the last century, Herbert Laitinen [60] and Izaak M. Kolthoff [66] have shown that silver halides exhibit electrochemical activity when suspended in aqueous solutions [67–71]. Soon after, Karel Micka started at the *Jaroslav Heyrovský Institute* in Prague systematic studies of the polarography of suspensions [72–77], and Robert Kalvoda has reported on the oscillopolarographic behavior of particle suspensions [78]. The interest of Songina in the electrochemistry of suspensions was apparently fueled by her work on amperometric titrations where "anomalous" titration curves have been observed when precipitation titrations were followed by amperometry, as for example in case of the precipitation of mercury(II) ions by iodide ions [79]. In 1961 Songina published together with Vladimir Zakharov (see Fig. 5.5.1.5)[30] a paper on the electrochemical behavior of mercury(II) iodide on a rotating platinum wire electrode (length 4 mm, diameter 0.5 mm) [80]. This electrode was the same which she usually used in amperometric titrations. The literature survey in that paper covers the international literature until 1960, which is remarkable at a time without electronic transmission of papers, and given her rather remote working place, Alma–Ata in Kazakhstan. In this publication, Songina showed that HgI_2 can be reduced to Hg, and they supposed that the oxidation to I_2 (possibly even to iodate) proceeds with the intervening of platinum oxides. In 1965 Songina published together with Mariyam Dausheva (see Fig. 5.5.1.6)[31] another paper on the electrochemistry of sparingly soluble compounds of mercury (red and yellow HgO, Hg_2Cl_2, Hg_2Br_2, Hg_2I_2, and HgI_2), this time using a dropping mercury electrode [81]. There the authors describe the visual observation that the suspended particles stick to the surface of a stationary (hanging) mercury drop at and around the potential of zero charge (pzc), i.e., in that potential range where a broad current peak is observed (see Fig. 5.5.1.7).

Referring to Micka, the authors explain their findings as being due to adsorption of the particles at and around the pzc, similar to the adsorption of organic compounds. According to a personal communication from Dausheva,[32] Alexander Frumkin [84] became interested in these studies [82] as he has previously studied the attachment of gas bubbles to surfaces (see further down). Frumkin has invited Dausheva to the Institute of Electrochemistry in Moscow, and Dausheva has worked there for 2–3 months per year to study the attachment of positively and negatively charged carbon particles. She continued these studies in Alma–Ata. Dausheva and Songina published a most remarkable review on the electrochemistry of suspensions in 1973 in the Russian journal "Uspekhi khimii" [85] (the English

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[30] Vladimir Andreyevich Zakharov (Владимир Андреевич Захаров) was a student of O. A. Songina and he followed her in 1981 as Chair of Analytical Chemistry at the University of Alma-Ata, keeping that position until 1995.

[31] Mariyam Rakhimovna Dausheva (Мариям Рахимовна Даушева) made her PhD with O. A. Songina in 1969, and worked as postdoc in the Frumkin Institute of Electrochemistry in Moscow.

[32] Mariyam Rakhimovna Dausheva, December 2012.

Fig. 5.5.1.5 O. A. Songina with V. A. Zakharov in 1984 (reproduced with permission—[55])

Fig. 5.5.1.6 O. A. Songina in 1961 together with her students. First row from *left* to *right*: Gena Makarov, Sonya Sinickaya, Ol'ga Al'fredovna Songina, Anya Yermenko, Nadiya Sharipova. Second row from *left* to *right*: Vadim Grigor'yevich Barikov, Zoya Borisovna Rozhdestvenskaya, Olya Enyutina, Mariyam Rakhimovna Dausheva, Andrey Brandt (Courtesy of M. R. Dausheva)

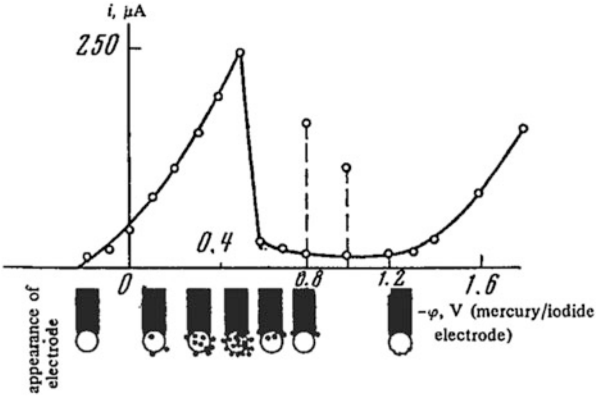

Fig. 5.5.1.7 Voltammogram recorded in a suspension of Hg_2I_2 (0.01 mol L^{-1}) in a KNO_3 solution (0.1 mol L^{-1}). Underneath the voltammogram sketches of the electrodes with the visually observed adhering particles are displayed. This figure was originally published in [82]; the figure shown here is reproduced from [83]

translation co-published in "Russian Chemical Reviews" [86]). This review is not only a very detailed analysis of the literature, but the authors present theoretical conclusions and explanations of the mechanisms governing the electrochemistry of suspensions. Obviously these interpretations have been influenced by Dausheva's work in Moscow and her discussions with Frumkin. Referring to papers published by Frumkin in 1938 [87, 88] on the stability of surface films, especially with reference to flotation, the authors argue that it is the stability of the solution film separating the electrode and the particle: The interfacial tension (γ) depends on the electrode potential (E) according to the Lippmann equation:

$$\gamma = \gamma_{\max} - C\left(E - E_{\text{pzc}}\right)^2/2$$

($\gamma_{\max}$: maximum surface tension, E_{pzc}: potential of zero charge, C: differential capacitance). Frumkin has shown in his two papers that gas bubbles most easily attach to an electrode surface at the potential of zero charge (pzc), and the increasing interaction of the charged electrode with the electrolyte solution at potentials deviating from the pzc leads to an increasing stability of the solution film and hence to a more difficult attachment of gas bubbles. One may understand the attachment of dispersed solid microparticles on an electrode as a competition of the electrowetting of the electrode surface by the electrolyte solution, and the interaction of the electrode surface with the surface of the particles. Clearly the latter kind of interaction will also comprise van-der-Waals interactions between the electrode and the particles, and, if the particles are charged, also Coulomb interactions.

The Development of Paste Electrodes to Study the Electrochemical Behavior of Solid Phases

Referring to the papers of Ralph Adams [89] in 1958 and 1960 in which he has introduced graphite paste electrodes [90, 91], and to the paper of Kuwana and French published in 1964 [82] where the preparation of a graphite paste electrode with an admixture of solid particles has been described, Songina started to study the electrochemistry of minerals by using graphite paste electrodes with an admixture of mineral powder. In 1966 Songina and V. G. Barikov(see Fig. 6) filed a USSR patent [92], cited in [93] for using modified graphite paste electrodes for analysis. It is surprising that modified graphite past electrodes have been used rather late for analytical purposes, because Morehouse and Glicksman started already in 1956 to publish a series of papers on using composite carbon paste electrodes for evaluating the properties of solid inorganic and organic compounds for use in batteries [83, 94–96]. The time lag of 8 years between these papers and that of Kuwana and French may indicate that there was already a lack of communication between electrochemists working in the battery business and in analysis. Songina has published a number of papers on the electrochemical behavior of solid compounds in graphite paste electrodes: sulfides of Zn, Pb, and Cu [97, 98], tungsten oxides and tungstates [99], vanadium oxides,[33] and copper oxides [101, 102]. Songina has studied the vanadium oxides V_2O_3, V_2O_4, and V_2O_5. V_2O_3 is oxidatively dissolved to vanadium(IV) in acid electrolyte solutions, whereas in neutral or alkaline solutions, it is oxidized to vanadium(V). V_2O_4 is oxidatively dissolved only in neutral and slightly acidic solutions. V_2O_5 can be reductively dissolved in sulfuric acid. Conditions could be defined to selectively quantify V_2O_3 in the presence of V_2O_4 and V_2O_5. One paper of Songina was devoted to the reproducibility of measurements with composite carbon paste electrodes, as this is for analytical purposes a most important feature: she has reported that standard deviations between 2 and 3 % can be achieved, although 2–11 % are frequently observed [103, 104]. In another publication Songina considered the different possible mechanisms of electrode reactions of solid compounds dispersed in carbon paste electrodes: she clearly identified three possibilities [105]: (1) The solid compound does not chemically react with the electrolyte solution and is converted electrochemically in a solid-state reaction; (2) The products of the direct electrochemical conversion of a solid compound react with the electrolyte to form a sparingly soluble product which is not electroactive; and (3) The solid compound undergoes a chemical reaction (dissolution) with the electrolyte solution, in which case the dissolved species may be (a) less electroactive or (b) more electroactive than the solid. To distinguish these different cases, she has formulated clear criteria which refer to the dependence of peak currents on the electrolyte concentration and on the time of contact of the paste electrode with the electrolyte solution. In this paper, one can see Songina's clear-cut thinking and elegant arguing. Especially V. G. Barikov and Z. B.

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[33] [100], and papers cited there.

Fig. 5.5.1.8 O. A. Songina with Zoya Borisovna Rozhdestvenskaya in the laboratory

Rozhdestvenskaya (see Fig. 5.5.1.8) have collaborated with Songina in the paste electrode project. Figure 5.5.1.8 shows O. A. Songina together with Z. B. Rozhdestvenskaya in the laboratory.

Paste electrodes are still a topic of research and development, as three recent reviews testify [106–108]. Unfortunately, there the contributions of Russian scientists have been widely ignored.

The Legacy of Ol'ga Al'fredovna Songina

Ol'ga Al'fredovna Songina's life was paved with hardships which are unimaginable for contemporary Western scientists. The torments connected with the loss of the dearest persons, her husband and her daughter, could not prevent that she became a most respected scientist who has greatly contributed to the development of electrochemical solid-state analysis. Growing up and receiving her basic education before the revolution of 1917 in the capital Sankt Peterburg, she had to experience the total turnaround of all social conditions, the debasement of what was then regarded as bourgeois values, like the knowledge of foreign languages, etc. Her life is a typical example for what intellectuals experienced during the Soviet time; and yet they usually did not speak to anybody, even not to nearest friends about their problems. A deep love of their country and of science kept them working and striving for truth and educating the youth in the spirit of scientific ethics and human values. This is also what her students remember. In Songina's research group was nothing of the then popular and ideologically based campaigning "against foreign influence," etc. People who do know her from conferences still remember her elegant and erudite style, her mastery of language, her logics of arguing, and her highly cultivated manners as signs of a civil education long gone by.[34] We should

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[34] Personal communication from El'za Arminovna Zakharova (Tomsk).

never forget Ol’ga Al’fredovna Songina for her exceptional human qualities and intellectual contributions to science. All people who had the great fortune to work with O. A. Songina vividly remember her human qualities (see, e.g., the memories of M. R. Dausheva and E. A. Mambetkaziev in Footnote 25). Although her personal fate was so hard, she was most kindly attached to people, especially to her students and coworkers, always being most attentive to their problems. The level of erudition, not only with respect to science, but also to culture and languages, was exceptional and highly admired by her environment.

Songina’s contributions to electrochemistry were especially far-reaching, as her publications on modified carbon paste electrodes paved the way for a rapid and very intensive development of the electroanalysis of solid materials in the USSR, especially by Brainina [109–111], Zakharchuk[35] and others. Reading her papers one can easily see that she was much ahead of her time, and many of the problems, especially the mechanism of direct electrochemical conversion of one solid phase to another, are still intriguing problems which now can be studied, e.g., with AFM [112–117] allowing much deeper insight. Songina’s work will always be remembered as fundamental for the establishment of solid-state electroanalysis as a scientific field of its own [118].

5.5.2 *The Electrochemical School of Kh’yena (Anna) Zalmanovna Brainina*

Fritz Scholz

Kh’yena (Anna) Zalmanovna Brainina (Fig. 5.5.2.1) was born on May 26, 1930, in Stalingrad (now Wolgograd). She was a diploma student of A. G. Stromberg [119, 120], when he was at the Ural State University in Sverdlovsk (now Yekaterinburg). After finishing University, she wanted to start her PhD, but was not allowed so because of her Jewish descent. At that time, such discrimination was a common practice in the USSR. So, she had to move to Ufa. At the same time, Stromberg left Sverdlovsk for Tomsk. Two years later, she returned to Sverdlovsk and worked as an engineer on the chemical factory, but her love for polarography was still alive. She worked for her PhD from 1956 to 1959 in Sverdlovsk. From 1959 to 1968 she was a senior researcher at the All-Union Scientific and Research Institute of Chemical Reagents (VNII khimicheskikh reaktivov) in Donetsk (now Ukraine). There she had to solve the task to determine traces of silver in lead. Of course, silver could be electrodeposited on mercury, but the selective anodic dissolution was not possible. She remembered the talks of Stromberg, Yudif’ Isaakovna Vajnshteyn, and Yevgenya Nikolayevna Vinogradova about stripping voltammetry at the Kishinyev conference on polarography (1959), and she had the idea to use solid

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[35] See the special issue (2012) J Solid State Electrochem 16, No 7.

electrodes instead of mercury electrodes. At that time people approached the new idea with great skepticism, but Aleksandr Naumovich Frumkin said (freely translated from [121]) “Why should it be impossible? One should get it.” This statement of Frumkin strongly encouraged Brainina to be on the right track and was most important and dear to her. Of course, it was just another example of Frumkin’s open-minded thinking and imaginative abilities (see also the Chap. 4). In 1967 Brainina defended her doctoral thesis about SV at solid electrodes entitled “Film voltammetry. Theory and practice of the method” at Moscow University. In this thesis, she described the behavior of solid electrodes, which are only partially covered by electrodeposited solid compounds. This was the basis of the first book about SV with solid electrodes, published in Moscow (1972) [122] and 2 years later its translation was published by Wiley&Sons (1974 [123]). Together with Ye. M. Royzenblat she has discovered that the poor reproducibility of SV on solid electrodes is due to the formation of solid solutions and intermetallic compounds. They solved the problem by adding mercury ions to the solution as to plate simultaneously mercury and the trace metals [124]. The paper was submitted in 1966 to Elektrokhimiya but only printed in 1969; the known paper of Florence (who did not know the Russian paper) [125] was published a year later. (See also the Chap. 16). Brainina has published the results in a number of mentioned and other books, which also have been translated to English [109, 126, 127]. There she has summarized the investigations made in Donetsk and in the first years in Sverdlovsk (now Yekaterinburg), where to Kh.Z. Brainina has been invited.

In 1968 Kh.Z. Brainina was invited as a Professor and Chief of physical and analytical chemistry Department in the new Sverdlovsk Institute of National Economy (now Ural State University of Economics). There she has started investigations in development and application of electroanalytical methods in environmental and health monitoring. There, in Yekaterinburg, phenomena connected with transitions in the raw macro-micro-nanoelectrodes attracted the attention of Brainina’s team, in particular of N. Stozhko. The approaches and results have been published in coauthorship with N. Stozhko in JSSE [128, 129]. Later, a series of papers devoted to the electrochemistry of nanoparticles and its application in chemical and biochemical sensors have been published in the same and other journals [130, 131]. The approach is based on taking into account thermodynamics of nanoparticles (including Gibbs Free Energies). The theory was verified with several examples, e.g., of bismuth nanoparticles [132], of gold nanoparticles [133], and of silver nanoparticles [134]; polydispersity and size effects [135] and substrate effects [136] were examined. It has been shown that transition from macro to micro and nanostructured electrodes is accompanied by changing of their electrochemical properties, which improves the sensory properties. Fundamental research in this field served as the basis for the development of solid sensors for analytical and bioanalytical applications [128, 129, 137–140]. These results also showed that electrochemical methods can be used to provide information on the thermodynamic and kinetic properties of nanoparticles itself.

The other new and important branch of Brainina’s team is the development of assays for the oxidant/antioxidant activity (detection of radical scavengers) in the

Fig. 5.5.2.1 Kh'yena (Anna) Zalmanovna Brainina

chain food-nutrients-pharmaceuticals-biological fluids. The realization of this chain, in particular in medical diagnostics, provides the possibility to evaluate oxidative stress in human body. The proposed method is potentiometry with the use of a mediator system. It is developed in two variants: (1) solutions analysis (food, etc. [141], blood and its fractions [142], invasive variant, and other biological liquids) and (2) skin antioxidants/oxidants level evaluation-nonivasive variant [143]. Semiautomatic potentiometric analyzers «Antioxidant» for liquids and «PA-S» for skin have been developed.

In 2013 a special issue of J. Solid State of Electrochemistry has been dedicated to Anna Brainina [144].

5.5.3 Yefim Mikhailovich Royzenblat, Eleonora Yakovlevna Sapozhnikova and the Development of Electrochemical Solid-State Phase Analysis in Donetsk

Nina A. Kolpakova and Fritz Scholz

Yefim Mikhailovich Royzenblat (Fig. 5.5.3.1) was born January 8, 1937, in Kiev in the family of a worker. During the war the family has been evacuated to Tyumen, returning in 1945 to Kiev. His father was killed in WW II at the front already in 1941. Royzenblat joined the Faculty of Chemical Technology of the Kiev Polytechnic Institute in 1954. After finishing the Institute, he was accepted at the All-Union Scientific and Research Institute of Chemical Reagents (VNII khimicheskikh reaktivov) in Donetsk (Ukraine) and joined the group of Kh. Z. Brainina. He has defended his PhD thesis entitled "The determination of microquantities of anions with the method film polarography with preconcentration" in 1964. The work was jointly supervised by Brainina (Donetsk) and Stromberg (Tomsk). The following about 25 years he has devoted to electroanalytical chemistry. Eleonora Yakovlevna Sapozhnikova (Fig. 5.5.3.1) defended her PhD thesis entitled "Application of organic reagents in film polarography" in 1967. The work was supervised by Brainina. Together with his wife Sapozhnikova and other coworkers, Royzenblat has cultivated the use of paste electrodes for the study of solid compounds dispersed in carbon paste electrodes. This direction of research was started by Kuwana and French in the USA [82] and cultivated by Songina and her group in Alma-Ata (see the Sect. 5.5.1) [92, 145]. Electrochemical studies of solid phases, be they dispersed in a graphite paste electrode or dispersed as deposits on the surface of solid electrodes, did nowhere in the world find more attention in research than in the former USSR where this work is inseparable connected with the names O. A. Songina (Alma-Ata), Kh. Z. Brainina (Donetsk, Sverdlovsk/Yekaterinburg), Ye. M. Royzenblat/E. Ya. Sapozhnikova (Donetsk), and N. F. Zakharchuk (Akademgorodok/Novosibirsk). This research is a kind of solid-state phase analysis with the ultimate goal to establish the relations between structure and composition of solid phases and their electrochemical behavior. Knowing these relations is essential (1) for qualitative phase analysis, i.e., answering the question, what phases are present; (2) for quantitative phase analysis, i.e., determining the ratio of phases; (3) for acquiring information about the corrosion behavior of solid phases; (4) for understanding the pathways of solid-state electrochemical transformations; (5) for developing theories of solid-state electrochemical transformations and dissolutions of solids (see Sect. 5.5.2); and not at least (6) for understanding stripping voltammetry when solid phases are involved. Thus, this topic is of very wide significance. The papers of Royzenblat and Sapozhnikova are clearly demonstrating this. Relations between the electrochemical behavior of solids and their inner as well as their surface structure have been elucidated (see, e.g., [146–152]). They have addressed also the mechanism of electrochemical reactions of electronically nonconducting phases, where the electrochemical conversion is preceded by a chemical reaction forming electrochemical active species at the three-phase boundary. According to the proposed model, the electrode process starts with the formation of a protonated surface complex localized at the three-phase junction graphite-oxide-solution. The mass transport is confined to a surface layer of the oxide. The overall current was statistically modeled as the sum of the currents of the single microelectrodes. The theoretical model was supported by experimental data for the reduction of γ-Fe_2O_3, PbO_2, and MnO_2. Royzenblat also studied the dissolution of metals from mercury film electrodes [153–155].

Royzenblat (together with Kh. N. Brainina) was the first who published what is now known as the *thin-film mercury electrode* (on graphite) [124] (see the Chap. 16). He has also developed impregnated graphite electrodes [156] which have been used very successfully around the USSR.

Yefim Mikhailovich Royzenblat and Eleonora Yakovlevna Sapozhnikova have been a married couple and they have been inseparable in their research.

Fig. 5.5.3.1 Yefim Mikhailovich Royzenblat and Eleonora Yakovlevna Sapozhnikova (January 1, 1938–May 25, 1986)

5.5.4 Electrochemistry in Akademgorodok/Novosibirsk

Fritz Scholz and Nina A. Kolpakova

Many innovative contributions to *electroanalysis* came from Nina Fyodorovna Zakharchuk (Fig. 5.5.4.1), working at the Institute of Inorganic Chemistry of the Academy of Science (Siberian Division), Akademgorodok (the Academy city near Novosibirsk). She was born in Omsk Oblast (south-western Siberia), the daughter of a farmer in the former Soviet Union. She studied chemistry at the University of Alma-Ata (now Almaty) in Kazakhstan where she worked for her *candidate of science* degree (PhD). There, her scientific work supervised by Mikhayl Tikhonovich Kozlovskiy, a leading specialist in electrochemical analysis, and also by Ol'ga Alfredovna Songina (see the Sect. 5.5.1). In 1966 Iosif Gershevich Yudelyevich (1920–1993) invited N. F. Zakharchuk to build up an electroanalytical group at the Institute of Inorganic Chemistry in Novosibirsk and N. F. Zakharchuk moved to this place in the same year and continued her work there as a senior researcher. In 1968 she submitted her scientific work as a PhD thesis (in USSR/Russia: candidate of science degree) at the State University of Kazakhstan in Alma-Ata, although she never had the official status of a PhD student there. Over her lifetime, Zakharchuk has contributed significantly to a wide spectrum of topics in electrochemistry and electroanalysis, especially stripping voltammetry. One of her most important achievements has been the development of electrochemical methods of phase analysis. In particular, she has developed techniques, which allow obtaining specific signals for various phases when the latter are present on electrode surfaces. This technique has found wide application in the phase analysis of oxide films on semiconductor surfaces [157–161] and was reviewed recently in [162]. In addition, she has cooperated widely with solid-state chemists inside her Institute, and has succeeded in studying the electrochemistry of various metal

Fig. 5.5.4.1 Nina Fyodorovna Zakharchuk

cluster compounds and high-temperature superconducting phases [163]. Besides solid phase analysis, Zakharchuk has also had a long-standing interest in graphite paste electrodes for electrochemical phase analysis, and several of her papers concern the preparation and properties of mercury film electrodes for stripping voltammetry of soluble species [164–166]. Indeed, stripping voltammetry has always been of central concern to her, and in this field, she has contributed a large number of important papers. Recently, she has even extended her research to the field of biochemical analysis, such as the determination of thiols and disulfides in blood [167, 168]. Together with M. S. Zakharov (see the Sect. 5.8), she has published a monograph on electrochemical methods for natural and waste-water analysis [169].

Robert Yul'yevich Bek (Fig. 5.5.4.2) was an eminent electrochemist working at the Chemical-Metallurgy Institute of the Siberian Division of the Academy of Science in Akademgorodok. Born in Baku on May 22, 1933, he has studied in Moscow at the Mendeleev Institute of Chemical Technology which he finished in 1956. He then worked for 2 years at a factory in Podolsk, but because this work did not satisfy him, he returned in 1958 to the Mendeleev Institute working for his PhD until 1961. In 1962 he moved to Akademgorodok. His main research interest concerned the kinetics of metal deposition. He has discovered the effect of acceleration of mass transport during cathodic metal deposition from solutions containing complex cations of multicharged metal ions with negatively charged ligands [170]. He has also developed porous flow-through electrodes for metal extraction [171], which were applied in industry for gold production. He is also the inventor of a device for mechanical removing an upper layer of the electrode surface directly in the electrolyte solution so that the electrochemistry can be studied on a freshly prepared electrode surface [172]. Most important contributions to technique of in situ cutting a layer from the electrode surface were made by Yuriy Borisovich Klyetenik (Fig. 5.5.4.3), a coworker of Bek. This technique allowed studies of the role of adsorbed ions on metal deposition, e.g., the effect of adsorbed lead hydroxo complexes on silver electrodeposition [173]. The invented method of surface renewal was also suggested for electroanalysis [174, 175]. Bek also

Fig. 5.5.4.2 Robert Yul'yevich Bek (May 22, 1933–June 6, 2012)

Fig. 5.5.4.3 Yuriy Borisovich Klyetenik (1937–1997)

addressed the effect of high voltage for electrodeposition, even for electroanalysis [176].

5.6 Stripping Voltammetry in Moscow

Nina A. Kolpakova and Fritz Scholz

In the beginning of the 1950s, the USSR government has decided to establish a number of so-called problem laboratories (here the less literal but better translation "Special Research Laboratory" will be used) to improve the scientific research. On suggestion of academician I. P. Alimarin, three centers for the development of voltammetric and chronopotentiometric methods were founded: at Moscow State University (MSU), at the Vernadsky Institute of Geochemistry and Analytical Chemistry, and in Tomsk at Polytechnic Institute. In Moscow this research was

Fig. 5.6.1 Yevgeniya Nikolyayevna Vinogradova

started by Yevgeniya Nikolyayevna Vinogradova (1901–1987) (Fig. 5.6.1). She was born on December 11, 1901, and graduated at the Chemical Faculty of MSU at the chair of Physical Chemistry. Before her studies she worked at "Okna ROSTA" (meaning window of ROSTA, i.e., the Russian Telegraph Agency), which was an enterprise producing political propaganda posters, and she worked also in a kindergarten in Khot'kov. She stayed at the chair of Analytical Chemistry at MSU from 1949 to 1973. Under her supervision, one of the first polarography laboratories in the USSR was established and stripping voltammetry was the main topic.

As mentioned before, the first publications on the use of a stationary mercury drop electrode in stripping voltammetry have been published by Stromberg and Gorodovykh (Tomsk) and Vinogradova and Prokhorova (Moscow), and Sinyakova, Shen' Yu-chi (Moscow) [20, 177, 178]. At MSU the first scientists using stationary electrodes for stripping voltammetry were Galina Vasil'yevna Prokhorova, Lyudmila Nikiforovna Vasil'yeva, and Anatoliy Ivanovich Kamenyev. Important contributions to the development of stripping voltammetry came from Lyudmila Nikiforovna Vasil'yeva (Fig. 5.6.2). She was born April 19, 1934, and she finished her studies at MSU in 1956, where she then started her PhD project. At the beginning, she studied the distribution of the deposited metal in the mercury droplet [179], the effect of electrode surface area, electrolysis time, and stirring rate of solution. At that time there was some controversy in the literature about the distribution of the deposited metal in the mercury droplet and about the effect of drop radius, time of deposition, and stirring rate of solution on the results. To approach these questions by theory, the heat transfer through a sphere was studied. Results showed that for drop of radius 0.4 mm and average diffusion coefficients, after 30 s of electrolysis there is at any point in the droplet a metal concentration linearly depending on preconcentration time, which was the basis of understanding theoretically the experimentally found dependencies of anodic peak current on electrolysis time and metal concentration in solution [179, 180]. Analogous results have been obtained by the coworkers of Stromberg in Tomsk [181, 182]. In [180] the exhaustion of the solution was addressed. These studies were continued by Vasil'yeva using graphite and mercury film on graphite electrodes. They are reported in a book published in 1973 [183]. The task to determine gold prompted

Fig. 5.6.2 Lyudmila Nikiforovna Vasil'yeva

studies of electrodeposition on graphite electrodes. Vasil'yeva was the first to realize that two energetically different forms of deposits have to be distinguished, namely a monolayer, and a bulk deposit [184, 185]. Vasil'yeva could determine the surface area of the metal deposit based on rather simple models [186, 187]. In the following years, these studies have been continued by the coworkers of Stromberg in Tomsk [188, 189]. Vasil'yeva's papers were frequently cited and she defended her "doctor of science" thesis and became a leading scientist in GINCVETMET ("Gosudarstvennyy Nuchno-issledovatelskiy Institut Cvetnykh Metallov" in Russian, i.e., State Research Institute of Non-Ferrous Metals).

Electroanalysis has developed in Moscow also thanks to the lasting achievements of Sof'ya Il'inichna Sinyakova (Fig. 5.6.3) (March 8, 1901–November 1, 1970). From 1920 to 1927, she studied at Moscow University [56] at the Faculty of Physics and Mathematics (which later became the Chemical Faculty). From 1927 to 1936 she worked at the All-Union Institute of Work Safety. In 1938 she became "candidate of science" (PhD) in Biology. In 1936, she joined the Vernadskiy Institute of Geochemistry and Analytical Chemistry (GEOKHI), where she worked under the guidance of V. I. Vernadskiy, developing methods for the determination of small metal concentrations by colorimetry and polarography. Vernadskiy became acquainted with polarography in Prague when he visited the laboratory of Heyrovský (see the Sect. 3.2 and also the Sect. 5.2). She has developed many stripping voltammetric and polarographic analyses methods, including those using catalytic polarographic currents, e.g., for the determination of Mo, Nb, and Fe. Together with T. A. Kryukova and Tat'yana Vasil'yevna Aref'yeva, she has published a book on polarography, which was very popular in the second half of the twentieth century [190].

AT MSU, analysis with stripping voltammetry was continued by Anatoliy Ivanovich Kamenyev (Fig. 5.6.4), born on November 7, 1933. He finished chemistry studies at MSU in 1956 and then started his PhD project under the supervision of Ye. N. Vinogradova. In 1974 at the chair of Analytical Chemistry there was founded a united laboratory for electrochemical methods under the guidance of

Fig. 5.6.3 Sof'ya Il'inichna Sinyakova

Fig. 5.6.4 Anatoliy Ivanovich Kamenyev and Elza Arminovna Zakharova, Tomsk 2010

Prof. Perch Karlovich Agasyan (Fig. 5.6.5). This laboratory dealt for many years with fundamental questions of electroanalysis, including stripping voltammetry [191]. The researchers of the laboratory studied the electrochemical behavior of Tl, Bi, Sb, Pb, Cd, Cu, In, and Co at a mercury drop hanging on a gold, silver, or platinum wire, or at a Kemula-type mercury drop electrode [192–194]. They showed that a Hg drop hanging on silver has to be preferred. Mathematical design of experiments allowed finding the optimal conditions for highest sensitivities. Later Anatoliy Ivanovich Kamenyev was the leader of this laboratory, and both stripping voltammetry and stripping chronopotentiometry have been further advanced, methodologically and by instrumental developments [195–197].

To the Moscow electroanalysts belonged also Yevgeniy Yanovich Neyman (Fig. 5.6.6), who much too early passed away. Part of his legacy are two remarkable books published written and published by Kh'yena Zalmanovna Brainina together with him [198, 199]. In 1968 Neyman has defended his PhD thesis dedicated to the determination of mercury on a graphite electrode. He worked in a special laboratory of a central institute of the Ministry of Natural Resources ("Minprirody" in Russian). In 1978 he has defended his doctor of science thesis entitled "Inverse

Fig. 5.6.5 Perch Karlovich Agasyan

voltammetry of microcomponent systems and its application to materials of non-ferrous metallurgy." He has studied the interaction of components in the deposits on electrodes [197, 200], and developed determinations based on adsorptive stripping voltammetry [201].

In the Kurnakov Institute of Inorganic Chemistry of the Academy of Science worked a research group on the determination of platinum-group metals using catalytic voltammetric hydrogen waves, as at that time stripping voltammetric methods for these elements have not yet been available. The main specialist for platinum-group metals was Natal'ya Anatol'yevna Yezerskaya (Fig. 5.6.7), who was born in Moscow August 23, 1924. Finishing her chemistry studies at MSU in 1947 she worked for her PhD there until 1951 and then until 1956 as scientific coworker at the Central Scientific Research Institute of Non-Ferrous and Nobel Metals ("Central'nyy Nauchni-issledovatel'skiy Geologorazwedochnyy Institut Cvetnykh I Blagorodnykh Metallov" in Russian). A result of this work was the book "Instruction for chemical analysis of platinum-group metals and gold" [202]. In 1955 Yezerskaya defended her PhD thesis entitled "Application of polarographic and amperometric methods for the analysis of gold-containing products." After the defense, she returned to the laboratory of analytical chemistry of platinum-group metals at the Kurnakov Institute, where she worked until her retirement in 2007. The second book on analytical chemistry of platinum-group metals and gold was published in 1965. Yezerskaya was a highly esteemed specialist in coordination chemistry, electrochemistry, and analytical chemistry of these metals. In 1972 she has published together with coauthors the book "Analytical chemistry of platinum-group metals" in the series "Analytical chemistry of the

Fig. 5.6.6 Yevgeniy Yanovich Neyman

Fig. 5.6.7 Natal'ya Anatol'yevna Yezerskaya

elements" [203]. There the physical and physicochemical properties of these elements were covered as well as their analytical determination, including electrochemical methods like those based on catalytic hydrogen waves and coulometry. When Yezerskaya later visited the USA, she discovered a translation of her book in a bookstore. At that time translations have been published without mutual permission, and she decided to buy her own book. In 2003 the next book on analytical chemistry of Pt-group metals and gold has been published and Yezerskaya actively participated [204]. During all her years at the Kurnakov Institute, she has elaborated voltammetric (e.g., [205]) and coulometric [206] methods for the determination of Pt-group metals, Ag, and Au in inorganic and biological samples.

5.7 Development of Electrochemistry and Electroanalytical Chemistry in Moldavia[36]

Julia D. Sister

5.7.1 *Electrochemistry*

The story about the development of electrochemistry in Moldavia has to start with one of the greatest electrochemists of the twentieth century, with Aleksandr Naumovich Frumkin (Fig. 5.7.1) who was born in Kishinëv in 1895.

From 1812 to 1918, Bessarabia (this is a territory now situated partly in the Ukraine and partly in the Republic of Moldova) was part of the Russian Empire, and for 22 years (1918–1940) it was part of the Kingdom of Romania. After that, with the exception of the war years (1941–1944), it was as the so-called *Moldavian Soviet Socialist Republic* (MSSR) part of the USSR. Now it has the official name *Republica Moldova*. Shortly after Frumkin's birth, his family moved to Odessa, where he received his education and made the first steps in science. The role of Frumkin in science is dignified in detail in Chap. 4. Although Frumkin did not take part in the organization of electrochemistry in Moldavia, the beginnings are neatly connected with his school: the organizer and first Professor and Head of the Physical Chemistry Section of the Kishinëv State University (KSU) was a student of Frumkin, Professor Aleksandr Ivanovich Shlygin (Fig. 5.7.2).

Shlygin was an outstanding electrochemist and a remarkable person. He took part in WW II, and as scientist he worked in Kishinëv (now Chişinău) from 1950 to 1953. Among the first students at the Physical Chemistry Section were Valentina

Fig. 5.7.1 Aleksandr Naumovich Frumkin (1895–1976)

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[36] Translated from Russian by Fritz Scholz.

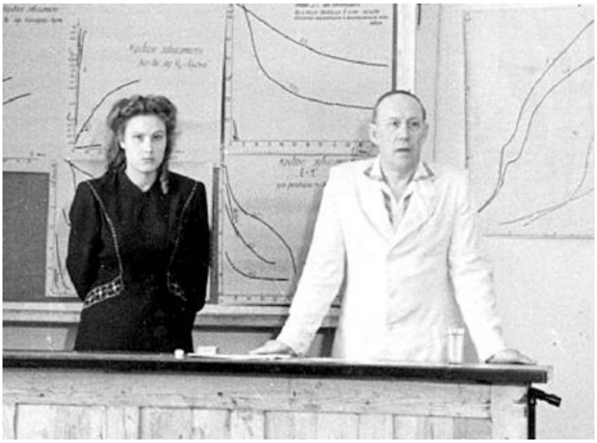

Fig. 5.7.2 Aleksandr Ivanovich Shlygin (1905–1979) (*right*) with his assistant Valentina Ochkina

Ochkina, Emma Grinberg, and Iosif Vayntraub, who have decided to study at that Section because of the personality of Shlygin. They all became scientists, and Ochkina together with Galina Serova, who soon joined her, used electrochemical methods in their research. In the Institute of Electrochemistry of the Academy of Science of USSR (AS USSR) people worked from the Analytical Chemistry Section of KSU and of the Laboratory of Analytical Chemistry of the Institute of Chemistry of the Academy of Science of the Moldavian SSR (MSSR) (A. Solonar', Yu. Sister, R. Tyurin, I. Fishtik, and others). Figure 5.7.3 shows Yakov Iosifovich Tur'yan, one of the best electrochemists of the USSR, together with his students, who stayed as teaching staff at KSU. Tur'yan was in the 50th a docent at the Physical Chemistry Section of KSU (see Sect. 5.10.1).

It needs to be mentioned that the young researchers were trained in the spirit of traditions of Physical Chemistry, i.e., to keep to clean reagents, ensure exactness of electrochemical measurements, knowing the world literature, being able to analyze experimental data. These values were passed on from generation to generation, and so proceeded the nucleation of the electrochemical school of Moldavia.

One of the specialists who used electrochemical methods on a wide basis was Professor Mark Khaimovich Kishinëvskiy (Fig. 5.7.4). His research was focused on the fundamental laws of mass transfer under turbulent flow conditions at interfaces, especially at the solid–liquid interface. Electrochemical methods have been used to model these processes based on measuring limiting currents.

Outside KSU, at the same time started also research on applied aspects of electrochemistry at other institutions of higher education of the Moldavian SSR.

On the first place, the polarographic school of Professor, and later Academician (AS MSSR), Yuriy Sergeyevich Lyalikov (at KSU and at Institute of Chemistry of MSSR) (Fig. 5.7.5) needs to be mentioned.

The Lyalikov school of polarography was not only in the USSR well known, but also outside. Kishinëv became a Mekka of polarographists, where not only All-Union meetings on polarography took place, but also polarographic meetings

Fig. 5.7.3 Yakov Iosifovich Tur'yan (standing) with Galina Serova, Emma Grinberg, and Valentina Ochkina (from *left* to *right*)

Fig. 5.7.4 Mark Khaimovich Kishinëvskiy (1917–1993)

for people from industrial laboratories. Research on electroanalytical chemistry was located at the Institute of Chemistry of the MSSR, at the Analytical Chemistry Section of KSU (M. B. Bardin-Shteyn, I. A. Gershkovich), at the Physical Chemistry Section of KSU (M. Ye. Manzheley, Yu. S. Gorodetskiy), and at the Kishinëv Agricultural Institute (A. A. Gabovich and others).

Mark Borisovich Bardin-Shteyn (1919, Odessa–1987, Kinshinëv) (Fig. 5.7.6) was doctor of chemical science and fought in WW II. In 1947 he started to teach at KSU and rose from assistant to professor. From 1964 to 1975, he was dean of the chemical faculty. He was a specialist in polarography of platinum metals. His studies on the determination of Pt and Pd on solid electrodes and on the application of a rotating Pt microdisc electrode for polarography are well known.

At the same time, at the Agricultural Institute was started research on electrochemical machining, especially of parts of agricultural machines, as well as on galvanic coating of machine parts, under the supervision of Academician (of MSSR) Yuriy Nikolyaevich Petrov (Fig. 5.7.7).

Petrov was not an electrochemist, but a mechanical engineer who has applied electrochemical techniques for solving problems in material science. At the beginning of his activities, he was the only person possessing the degree of Doctor of

Fig. 5.7.5 Yuriy Sergeyevich Lyalikov (2.04.1909, Ekaterinoslav (Dnepropetrovsk)–12.10.1976, Kishinëv)

Fig. 5.7.6 Mark Borisovich Bardin-Shteyn (1919–1987)

Technical Science in the MSSR. He has established a successful school of research engineers of high qualification, and he has supervised more than 100 Doctor of Science and Candidate of Science theses. The Petrov-school was the most important generator of cadres of technical sciences in Moldavia in 1960s–1980s; and this was a result of R&D in electrochemical machining. After establishing the Institute of Applied Physics (IPF) of the AS of the MSSR, led by Boris Romanovich Lazarenko (Fig. 5.7.8), this research direction dominated the activities of the institute. Together with his wife Natal'ya, B. R. Lazarenko was the inventor of Electrical Discharge Machining, and this research direction became one of the main topics of the IPF. Lazarenko has invited Petrov to join the IPF. Petrov headed at the beginning the laboratory of electrochemical machining of metals, and later established on the basis of that laboratory the department for problems of strength and extended durability of machine parts.

Fig. 5.7.7 Yuriy Nikolyaevich Petrov (1921–1990)

Fig. 5.7.8 Boris Romanovich Lazarenko (1910–1979)

At the IPF several directions of applied electrochemistry have been developed: electrochemical machining of metals (Yu. N. Petrov, A. I. Dikusar, G. N. Zaydman, B. P. Saushkin, G. R. Engel'gardt, and others). Another direction was the machining of metals and alloys by electrochemical heating (of electrolyte) (B. R. Lazarenko, P. N. Belkin, V. N. Duradzhi, E. A. Pasinkowskiy). Both these directions concerned "extreme" electrochemistry, i.e., electrochemistry far away from thermodynamic equilibrium, at high current densities and large potentials. There, thermal effects play a crucial role, and are even process determining in case of machining by electrochemical heating. Fundamental science and the technology of machining are most neatly connected and especially important in case of machining of blades for turbines and also for surface modification with the aim of achieving special functional properties and strength.

In the period when Moldavia was part of the USSR, and its industry was part of USSR industry, the electrochemical technology was crucial for electronic companies and those of general and agricultural machine production, etc. The

Fig. 5.6.9 Aleksandr Ivanovich Dikusar

technologies for machining developed by the group of Petrov were utilized in many enterprises of the USSR and the MSSR. This was also true for the machining by electrochemical heating, especially for devices used in the textile industry.

In 1959, after finishing school, Aleksandr Ivanovich Dikusar (Fig. 5.7.9) and his family moved to Moldavia (Dikusar's father occupied the Chair of Agrochemistry at Moscow University). A. I. Dikusar joined the Chemical Faculty of KSU and graduated in 1964. His candidate of science work concerned electrochemical studies of the turbulent flow at interfaces. It was supervised by M. Kh. Kishinëvskiy. Since 1970 his professional life is connected with the IPF of AS of the MSSR.

There, first under the leadership of Petrov, later independently, Dikusar and his coworkers were running studies of electrode processes proceeding far away from thermodynamic equilibrium conditions, especially in case of electrochemical machining. The results formed the basis of a theory of thermo-kinetic effects in high-rate electrode processes. After defending his doctor of science thesis in 1988, his research at the Institute of Applied Physics was focused on what could be called "electrochemical machining—from macro to micro and nano-machining."

A list of publications of the Institute of Applied Physics is given in A. I. Dikusar's article "Development of Electrochemistry and Electroanalytical Chemistry in Moldova," published in "Electronic processing of materials" (Surface Engineering and Applied Electrochemistry), 2012, 18 (6), 1–12. I like to express my gratitude to the author for kindly providing this information to me.

5.7.2 The School of Polarography of Yu. S. Lyalikov

Without any doubt, the development of polarography in Kishinëv is inseparable from the name of Yuriy Sergeyevich Lyalikov. He belonged to those scientists who can very clearly define the most actual and perspective scientific problems and find the optimal solutions for them. Scientific intuition, creative initiative, the desire to be at the forefront of science led to a wide diversity of his scientific research interests. Despite the fact that his research concerned various physical and chemical methods of analysis, he has devoted a considerable part of his forces and talent to polarography. Polarography was founded by Jaroslav Heyrovský (see Chap. 4). Very early, Academician Vernadskiy realized the great potential of the method and supported the Russian translation of the first book on polarography by Ye. N. Varasova (see Sect. 5.2). A. P. Vinogradov, a student of Vernadskiy, also played an active role in popularizing polarography. This marked the start of polarography in the USSR. Lyalikov started to use polarography already in the 1930s. In 1952 Lyalikov won the competition for the professorship and position of Head of the Analytical Chemistry Section at KSU. After 1 year he defended his doctoral thesis "Polarography of molten salts" at GEOKhI in Moscow. Soon after, he became Professor. However, he did not stop working and soon turned to questions of economic importance for Moldavia.

We equipped ourselves with alternating-current polarography, entered organic chemistry and introduced new ideas.

A new period of Lyalikov's activities started when he has moved to the Moldavian Branch of the Academy of Science of USSR in 1958, where he headed the laboratory of analytical chemistry. In that laboratory worked also the author of these lines since 1959. In 1960 began the work in a new field of polarography, in alternating-current polarography (ACP). In that year Lyalikov visited the Polarographic Institute in Prague where he met Jaroslav Heyrovský and other Czech electrochemists. He returned not only with interesting stories but also with new ideas. One of these was the application of ACP to the study and analysis of organic compounds. At that time practically nobody used that method in the USSR because there were no instruments for ACP. I was very eager to start this topic, when it was suggested to me. We decided to build such instrument, as the circuitry was known. I learned how to solder, how to work with an AC bridge etc., and started to wind a wire into small coils that give the desired resistance. A battery served as a DC source, and an AC generator served as a AC source. In our first device, we used a mirror galvanometer. In the workshop a metal box was made to house all parts, and to have the control knobs outside. All the labels I made by hand drawing, then photographed them, and taped them at the respective knobs. It was a device for visual recording of results (Fig. 5.7.10). Lyalikov and I loved to work with this instrument, like children rejoicing first successes. We have always been proud of having been one of the first in the USSR, and the first in Moldavia who have "armed" themselves with that promising method of investigation and analysis. Later, an automatic system was built with the help of Vil' Vasil'yevich Senkyewich (*1926), a physicist who has previously entered our laboratory. When the first AC polarographs have been produced in the USSR by the company GINTsVETMET, we got one of the firsts. With ACP we studied aldehydes of the aromatic and furan series with the dropping mercury electrode (DME). That allowed another investigation of the reduction of aldehydes and an increase of sensitivity down to 10^{-8} mol L^{-1}. The idea came up to use the adsorption–desorption peaks of organic

Fig. 5.7.10 Yu. D. Sister working with the first AC polarograph constructed in Moldavia

compounds in ACP for analysis, and by this the equivalence point of acid–base titration could be easily detected. From the dependence of peak height and peak potential of a series of organic compounds (Methyl orange, Thymol blue, etc.) on pH of the solution, one could detect the equivalence point of titrations. This method has been used for titrations of colored and opaque solutions, and using an Eriochrome black derivative one could indirectly determine calcium and magnesium. The study of the adsorption–desorption processes at the DME opened new possibilities for the application of polarography. The first results in this field have been presented at the 2nd All-Union Meeting on Polarography in Kazan in 1962. Yu. D. Sister, V. I. Bodyu, and I. V. Kozlova and others took part in this research.

Lyalikov did understand very well that environmental protection was a serious task for the country. Therefore, he introduced the analysis of pesticides as a new task of the laboratory. The task was very topical, interesting, and complicated. New matrices had to be analyzed, e.g., water, soil, air, and biological materials, and new questions had to be answered, e.g., do the poisonous chemical accumulate in living organisms? If so, in what organs? What happens to the chemicals in the environment? These and other questions had to be answered. The analytical chemistry of pesticides was at that time still in a virgin state. Lyalikov was convinced that one needs to bring together all analytical chemists working in this area. He was a member of the State Chemical Commission of Experts at the Ministry of Agriculture of the USSR, and in 1968, on his initiative the first All-Union Conference on Methods of Analysis of Pesticides in th e Environment was organized in Kishinëv. Lyalikov has given his diploma and PhD students topics concerning the analysis of pesticides by electroanalytical methods. When I already defended my PhD thesis I had to supervise many PhD and diploma students in this ecologically important field of research, using several modern polarographic techniques, not only for pesticides but also for other biologically active compounds. In agriculture chlororganic compounds, like hexachlorobutadiene, octachlorocyclopentene, and hexachlorocyclopetadiene, found wide application. Hexachlorobutadiene was an effective means in the fight against Phylloxeridae (family of insects). Several options for its polarographic determination have been elaborated and the electrode reaction on mercury has been studied. Using ACP, in wastewater the detection limit was 0.2 mg L^{-1} and in soils 0.4 mg kg^{-1}. In the studies of hexachlorocyclopentene and hexachlorocyclopetadiene, the pH dependence of the reduction of halogenated hydrocarbons which did not contain any other functionalities was observed. The varying dependence of limiting currents on pH was the basis for their simultaneous determination. The use of pesticides in agriculture has confronted the analytical chemists with another problem: to find the active ingredient in the technical preparations, as well as the quality control of products during the manufacturing process and at the stage of application and storage. At the 2nd All-Union Conference on the Analysis of Pesticides in Tallinn (1971), Lyalikov outlined the main areas of research: the development of new and the improvement of the existing methods for the determination of new pesticides in food, air, and soil. Of particular importance are methods for the determination of trace amounts of pesticides and their metabolites in biological materials in order to identify possible poisoning action. He also mentioned the importance of developing the theory of analytical methods and suggested the creation of a set of glassware apparatus for analysis and a unification of methods, as well as the introduction of special courses on pesticides at the Universities. At our laboratory the analysis of detergents with the help of polarography was another new topic. The results were encouraging, and companies producing detergents were interested in implementing our methods in their laboratories. Still today the research of the institute is directed on actual environmental problems.

The emerging new trends in polarography allowed solve new problems in electrochemistry and analysis. In the 60s first studies of thin-layer voltammetry have been published. In this method, the solution is placed between two parallel plate electrodes with different diameters; the volume of the test solution is not more than 10^{-2} to 10^{-3} mL. From an analytical point of view, this method was promising for the analysis of thin films, coatings, trace amounts of substances, expensive materials, etc. This gave also a possibility for combining chromatography and voltammetry (Yu. D. Sister) (Fig. 5.7.11) [207].

This approach was used in paper chromatography: the chromatographic spot was wetted with electrolyte solution and sandwiched between Pt electrodes or amalgamated electrodes and a voltammogram was recorded. It was also possible to use thin-layer chromatography, when a copper plate with an alumina layer supported by

Fig. 5.7.11 Yu. D. Sister, S. G. Mayranovskiy and L. G. Madan at a polarography conference in Riga

gypsum served as a counter electrode, and an amalgamated gold electrode as a working electrode. This allowed the determination of compounds with very similar R_f values by recording voltammograms along the line of elution.

At that time chemists became more and more interested in process where the electron transfer at the electrode surface is associated with some sparingly soluble compounds: The application of polarography (voltammetry) to the study of suspensions was such case (see also the Sect. 5.5.1). In case of a dropping mercury electrode, two processes happen: (1) The attachment of solid particles to the mercury surface due to capillary forces, and (2) the cathodic reduction of these particles. In case of solid particles of ethylen-bis-dithiocarbamate of zinc, a peak is observed at −0.7 V, both in DCP and in ACP. However, in polarography of suspensions, one faces problems: the stabilization of particles in the suspension plays an important role, and the signal of the solid particles overlaps with the wave of dissolved compound, and the constant flux of particles to the surface has to be maintained. Unlike the flux of ions, which is controlled by diffusion, the flux of particles is controlled by the stirring of the solution, which has to be very well controlled to achieve reproducible results (Lyalikov, Sister) [208].

The abilities of alternating current polarography, including second harmonic polarography, etc., have been widely utilized in our laboratory to achieve very low detection limits (10^{-7} and 10^{-8} mol L^{-1}) based on their adsorption/desorption behavior.

Studies and Analysis of Semiconductors

First attempts to use semiconductors were made at the beginning of the twentieth century. However, only much later they found a wide application. One may call the twentieth century the century of high-purity materials. The fight for such materials was very fruitful. The interesting properties of silicon and germanium was driving the progress in semiconductor industries. The rise of semiconductors also faced analytical chemists with new tasks. In our laboratory Larisa Stepanovna Kopanskaya (Fig. 5.7.12) (born in 1930, in Tiraspol) started to work in this field, studying the kinetics of electrode processes of metal ions and the ways to determine metals and semiconductors. The analysis of semiconductors was developed in close collaboration with physicists. Dr. N. A. Goryunova was head of the laboratory of semiconductors of the A. F. Ioffe Physico-Technical Institute. She correctly identified the situation (at that time) of semiconductor chemistry, and the resulting analytical tasks for the development of new semiconducting materials. The former student of Goryunova, the later Academician (AS MSSR) and head of the Laboratory of Semiconductors of the Institute of Applied Physics of the MSSR, S. I. Radautsan, started the development of research and synthesis of semiconductors in Moldavia. Academician Lyalikov headed the research on analysis of these materials in the two abovementioned institutions. The first studies performed in the 60s, concerned solid solutions of the ternary system In-Sb-Te, synthesized as ingots and epitaxial layers in the Institute of Applied Physics of the MSSR and at the State-

Fig. 5.7.12 *Left* to *right*: L. S. Kopanskaya, L. G. Madan, Yu. D. Sister, P. M. Novik

University at Kishinëv. The analysis of eptaxial layers induced the phase analysis of heterogeneous alloys, a task which is very important to study the homogenization in various technologies, like zone melting. Phase analysis was performed using XRD and methods to determine the micro-hardness. The composition of isolated phases of the system In-Sb-Te was determined by polarography. The synthesis of $ZnGeP_2$ and the analysis of products revealed heterogeneities. The complex analysis of the ingots allowed to adjust the technology of this compound. This is another example where the phase analysis of mechanically isolated phases has led to semiconductors belonging to the class $A^{II}B^{IV}C^{V}_{2}$. For the chemical analysis, we have used ACP and used instruments which have been later also introduced in the whole country. Since the method of mechanical phase isolation is limited by the size of grains of phases, later the method of "spark erosion" developed by Academician B. R. Lazarenko has been used. This cooperation with physicists resulted also in the development of a new device to measure the micro-hardness with an electrochemically sharpened tip. When working with such electrochemically sharpened tip in spark erosion, very small amounts of sample could be dissolved (0.1–0.7 μg) and analyzed by ACP. Together with XRD and micro-structure analyses, this allowed obtaining a detailed picture of the studied phases. It was also important to study the kinetics of dissolution of semiconductor materials in various solutions, because the dissolution had to be performed prior to any analysis. After 5 years of intensive studies of analysis of semiconductor materials, Lyalikov decided to organize the 1st All-Union Meeting on Analytical Chemistry of Semiconductors, which took place in Kishinëv in 1965. Parallel to the development of polarographic methods of analysis, the kinetics and reaction mechanisms of the respective ions have been studied, as these reactions were the basis of the electroanalytical methods. For this an arsenal of techniques was employed: classical DCP, oscillopolarography, ACP, and radio-frequency polarography. Of special interest were the electrode reactions of Se, Te, and Ge.

The analytical chemists also had to study the deviations from stoichiometry, especially in case of the $A^{II}B^{IV}C_2^{V}$ compounds. Another important issue were trace impurities, especially in case of the latter mentioned semiconductors. Deviations from stoichiometry and impurities strongly affect the physical properties of semiconductors. The analytical determination of impurities is difficult, especially because of the complex composition of the semiconductors. The fastest and simplest analytical determinations of the impurities needed their preliminary extraction from solutions, and the polarographic analysis of extracts. The extraction of large aqueous volumes with small volumes of the organic phase allows already a preconcentration. If then stripping voltammetry is used, a further enrichment is achieved for the sake of reaching low detection limits. The analytical chemistry of semiconductors was one of the main topics of the laboratory, and many PhD theses were defended in this field, as well as monographs have been written, and special courses have been run at University and the Polytechnic Institute.

Polarography and Complex Formation

Nowadays it is difficult to imagine analytical chemistry without a deep knowledge of complex formation. In electroanalysis, complex formation of metals is vital to achieve a high sensitivity and also selectivity, due to the well-known effect of complex formation of the characteristic potentials (half-wave or peak potentials). This was also the starting point of research in our laboratory. In 1960, Lyalikov published a paper entitled “on the question of calculating stability constants,” in which he proposed a new method based on least-square analysis of polarographic data for the determination of the consecutive stability constants of metal–ligand complexes. This method was positively distinguished by allowing to use a lager interval of ligand concentrations. With this method, the complexes of Cu, Fe, Mn, Co with trioxy-glutaric acid have been studied, as well as the complexes of Sb, Sn, Bi, and a range of transition metal ions with 8-hydroxyquinoline and 1-hydroxyethylidene-1,1-diphosphonic acid, which have been synthesized in the Institute of Chemical Reactives in Moscow. Systematic studies of the electrochemical behavior of metal complexes have accompanied their application in electroanalysis. These investigations have been made by Elena Grigor’evna Chikryzova (Fig. 5.7.13), Lyudmila Georgievna Kiriyak, and Ivan Ivanovich Vataman (Fig. 5.7.14).

Ivan Ivanovich Vataman (1937, Khotinsk county, Bessarabia–1993 Kishinëv) was Doctor of Science, author of 150 papers, and since 1973 until his passing away the head of the laboratory which Lyalikov headed before. He was also a member of

Fig. 5.7.13 Elena Grigor'evna Chikryzova (February 26, 1921–May 1, 2008). She is the daughter of the well-known geologist Grigoriy Stepanovich Chikryzov (1894–1957). She has entered the Institute of Chemical Technology in Leningrad in 1940, and because of WW II moved to Tashkent where she graduated, and then taught analytical chemistry and worked in research. In 1951 she defended her candidate of science thesis (PhD) and moved to Kishinëv

the Union of Writers of the MSSR and a distinguished artist in the field of literature. In 1967/1968 he realized the urgent need to produce manganin (Cu, Mn, Ni alloy) micro-wires as resistors for instruments. At the beginning it was necessary to analyze the alloy manganin and the glass coating. The diameter of the wires was only some hundredth of a mm. The results of studies of complex formation of Cu and Mn with 8-hydroxyquinoline in mixed aqueous-organic solvents were the basis for the analytical determinations. The task was also complicated by the small amounts of sample (1–2 mg). Iyuliya Vladimirovna Aronina has dedicated her PhD thesis (1970) the analytical studies of the casting process of manganin using ACP. The reversible reduction of the complexes of Bi, Sb, Sn, and Pb with oxine derivatives has then been applied for the analyses of several alloys containing these metals.

All these studies gave the impetus for thorough and systematic studies of catalytic and adsorption effects in polarography of metal complexes.

Electrodes for Polarography

For a long time the dropping mercury electrode was the basic electrode used in polarography. However, with time, new problems needed for their solution new electrode materials, as mercury cannot be used in the anodic range. This was the case for the direct polarographic determination of some anions, for some organic compounds, and for noble metal and rare-earth metal ions. The mercury electrode

Fig. 5.7.14 Ivan Ivanovich Vataman

was also not useful for molten salts. Therefore, more and more often electrodes of Pt, Au, Ag and graphite had to be used. Systematic studies of such solid electrodes were started by H. Lingane and I. M. Kolthoff in the 40s. In the USSR, E. M. Skobets defended his Doctor of Science thesis "Polarography at solid electrodes" in 1950. In this field, Lyalikov also has his merits (first papers he has published in 1946). The most important issue in using solid electrodes is the maintenance of the electrodes surface to get reproducible results. Lyalikov has suggested to solve the problem by directing a gas stream toward the stationary solid electrode, so that by stirring rather reproducible conditions could be established. Later, an electrode was developed which was given the name "dipping electrode" (in Russian makayushchiysya elektrod): a metal wire melted in a glass tube was housed in a second glass tube so that its end was slightly outside the orifice of that outer tube. A gas stream was fed in the outer tube, so that, when the electrode was in a vertical position in the solution, gas bubbles very regularly evolved from the orifice of the outer tube and periodically allowed the solution to contact the end of the metal wire in the moment the bubble was dispatched. This electrode, which allowed recording of wave-shaped voltammograms, was called the Lyalikov electrode.

The first papers on polarography of salt melts were published in 1948, and in 1953 Lyalikov defended his Doctor of Science thesis entitled "Polarography of molten salts." Between 1947 and 1952, a series of papers on the determination of Ag, Cd, Pb, Zn, Bi, Fe, and other elements in salt melts of nitrates, chlorides, and silicates of low melting point (200–1000 °C) have been published.

The introduction of solid electrodes has considerably widened the application of voltammetric techniques, and the many systematic studies by Lyalikov and his coworkers were indispensable steps on that route.

We Are Earning Money

There came a moment when we had to earn 25 % of our salaries by contract work. Our laboratory signed contracts with a number of companies which were in need for our analytical methods. We quickly made ourselves acquainted with the needs of industry and all our analytical methods were introduced in Standards and implemented in practice. We organized conferences for people from industrial laboratories. We developed a method for the polarographic determination of iron and zinc in limestone, a feed additive for poultry and livestock. This was an important issue and the method became a so-called GOST, i.e., a State Standard and it was used in practice. And how satisfied were the users, with whom we established very friendly relations! The respective analytical method, developed by me, Chikryzova, and Mashinskaya, has been published in a scientific journal [209]. For this work, we have received a medal on the VDNCh (Vystavka Dostizheniy Narodnogo Khozyaystva, i.e., Exhibition of the Achievements of National Economy. This was a permanent fair in Moscow). State Standards also became our methods for the determination of pesticides and other chemicals.

In these works, all coworkers of the laboratory participated, and we did so with great enthusiasm because we were convinced that our methods are needed in industry and agriculture, and we did an important job, which not only yielded money,but also great satisfaction.

Scientific Contacts and Cooperation Within the Soviet Union

Once, it was in 1970, I remember that Lyalikov entered the institute in very good mood, obviously hiding important news: then he told us that Frumkin will visit the institute! It was the only visit Frumkin ever made to the town of his birth (Fig. 5.7.15). And we listened to his brilliant lecture. On Sunday, a group of university staff and of our lab went to a picturesque place on the bank of the Dniester, to Vadul lui Vodă (in Russian Vadul-Luy-Vode). On the way, we made jokes, laughed, had serious discussions on polarography, the development of chemistry in Moldavia, about the big building places in the country, and then again jokes, which Lyalikov was a great master of. The virility of Frumkin surprised us because he was already 75. He was interested in everything. We barely had time to respond to his many questions. After the trip, I asked the famous guest, whether he liked his hometown—Yes, I like it, he said. So two men met, one who was born in Kishinëv, and became a world-renowned scientist, and another, who has arrived to Kishinëv, and thanks to him, the city became one of the largest centers of polarography.

The polarographists of the different schools in the USSR did know each other very well, and often private contacts have been established and a very fruitful cooperation, frequently resulting in joint publications. Such cooperation we had with Yu. I. Usatenko and A. M. Arishkevich (Dnepropretrovsk), G. S. Supin (Moscow), F. P. Vayntraub and G. F. Vylegzhanina (VNII for Biological Methods of Plant Protection, Kishinëv), and M. S. Kakhana and N. A. Muzlayeva (Kishinëv University). We also had very good contacts with the polarographic school in Riga, with the Institute of Electrochemistry of the Academy of Sciences of the USSR (S. I. Zhdanov, L. G. Feoktistov). Practically all polarographic schools of the USSR

Fig. 5.7.15 Frumkin in Kishinëv in 1970. *Left* to *right*: I. G. Gershkovich, O. Nikitina (Kuybishev, now Samara), A. Dikusar, M. B. Bardin-Shteyn, A. Frumkin, A. D. Obrucheva (second wife of Frumkin), Yu Sister, V. Ochkina. The photo was taken by Lyalikov

had intensive relations with each other, something which was also mentioned by Frumkin.

Editorial Activities

Our laboratory was not only well known for the organization of conferences on polarography, analysis of pesticides, semiconductors, especially also for people from industrial laboratories, etc., but also for its editorial activities: all polarographists did know the "Bibliographies of Polarography" [210] starting with the first paper on polarography. 25 (may be even more) of such collections have been published. The Editor-in-Chief and initiator was Lyalikov, and as scientific editors have worked at different times: E. G. Chikryzova, R. M. Novik, L. S. Kopanskaya, Yu. D. Sister, L. G. Madan, L. G. Kiriyak, I. I. Vataman, L. Odobesku, V. Meryan, V. M. Ropot, A. Russu, S. M. Bardina, I. V. Aronina, B. Orgiyan, and others. Lyalikov has published monographs and textbooks together with his coworkers, with colleagues from other places, and sometimes also as the single author. Some examples are listed in the references.[37] By these publications the publishing house Shtiintsa in Kishinëv became especially famous for literature on polarography.

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[37] The following references are examples of publications of the Lyalikov school: [211–234].

5.8 Electroanalysis in Kazan, and Tyumen

N.A. Kolpakova and F. Scholz

5.8.1 Vera Fyodorovna Toropova

Kazan is the capital of Tartastan, a Republic within the Russian Federation. Since 1804 Kazan has a University, at which a number of famous chemists have worked: K. E. Klaus (1796–1864), N. N. Zinin (1812–1880), A. M. Zaytsev (1841–1910), S. N. Reformatskiy (1869–1934), and V. V. Markovnikov (1837–1904). Since the middle of twentieth century Kazan was also a center of electrochemical analysis. It started with Vera Fyodorovna Toropova (Fig. 5.8.1.1), who was born November 20, 1915, in Mologa, a very old Russian town (first mentioned in 1149), which disappeared in the waters of the Rybinsk Reservoir in 1940, when the Volga river and its tributaries were dammed for the Rybinsk Hydroelectric Station. Toropova's father was Fyodor Aleksandrovich Toropov (Theodor Toropoff) (1884–1953). His life well illustrates Russian twentieth century history: after taking part in revolutionary activities in 1902–1907, he had to immigrate to Switzerland (Bern), where he received a PhD for a work with the same Volkmar Kohlschütter, with whom A. N. Frumkin has worked (see the Chap. 4). Interestingly, his PhD concerned an electrochemical problem, the electrolytically deposited "black silver." Later he moved to Kiel (Germany) where he worked with Albrecht Bethe about electrochemical processes in physiology. After his return to Russia, he has worked in some institutes and chemical factories. In 1929 FA Toropov was convicted by the Military Collegium of the OGPU for 10 years under Article 58-8-10 of the Criminal Code of the USSR. He was delivered by special escort to a Radium factory from Arkhangelsk on October 7, 1930. From 1932 until his death he was the head of the central plant laboratory and at the same time the chief technologist of that factory. He was released on parole in 1932, and in 1936 the conviction was finally canceled.

Fig. 5.8.1.1 Vera Fyodorovna Toropova

He has been decorated by the Lenin medal and received the Stalin award for his merits in building up a radium industry, which had great significance during WW II.

Vera Fyodorovna Toropova studied from 1933 to 1935 at the Kazan State Institute of Technology and then continued until 1938 at Kazan State University (KSU). During her studies she worked, probably in 1937, in the laboratory of Ye. N. Varasova in Leningrad (see the Sect. 5.2). Her work has been acknowledged in one of the few papers of Varasova [12]. From 1938 to 1941, she worked for her PhD entitled "Polarographic studies of the stability of some complexes of iron and copper with carboxylic acids" [235] which she has defended a day before the start of WW II. During the war she worked until 1943 in military factory. After her return to the analytical division of KSU, she continued polarographic studies of metal complexes. In 1959 she defended her Doctor of Science thesis, also devoted to the polarography of metal complexes. From 1958 to 1986, she was chair of analytical chemistry at KSU. The topics of her research expanded to electroanalytical chemistry of nonaqueous and mixed solvents, voltammetry of chelates, combination of extraction with voltammetry (e.g., [236]), use of catalytic currents [237, 238], and electrochemical and chemical [239] preconcentration for the enhancement of sensitivity, etc. V. F. Toropova died on December 31, 2008, leaving a large group of scientists educated under her guidance: V. M. Gorokhovskiy (*1943), who was the first student of Toropova and later actively worked in oscillopolarography. His work and that of V. I. Gorokhovskaya (*1924) in oscillopolarography was made possible only by the instrumental developments under the guidance of Rashid Shakirovich Nigmatullin, chair of Radio Technique and Radio Electronic (1923–1991). Voltammetric analysis was also fostered by German Konstantinovich Budnikov (*1936), who worked in 1961 for 6 months with Robert Kalvoda, in the laboratory of Heyrovský in Prague. Kalvoda was the first to show that adsorption can be used to increase the sensitivity of voltammetry. Budnikov research concerned the voltammetry of metal chelates in aqueous and nonaqueous solution [240] as well as the electrochemistry and electroanalysis of organic compounds.

5.8.2 Matvey Safonovich Zakharov

Tyumen' is one of the oldest Russian settlements in Siberia. It started as a fort of Cossacks in 1586. Now it has the Tyumen' State University of Oil and Gas, which developed out of the Tyumen Industrial Institute. In 1969, Matvey Safonovich Zakharov (Fig. 5.8.2.1) arrived there from Tomsk, where he has studied, defended his PhD, and afterward became assistant of A. G. Stromberg. Zakharov was born on August 14, 1929, in Novomariinka, a small village in Siberia (Krasnoyarskiy Krai). He was disabled since birth (hunchback), which affected his entire life. People in the village were rather poor and illiterate. Zakharov's father, however, could read, write, and count, as his son remembered. Zakharov joined the school only at the age of 9, together with his brother, because to reach school he had to cross a forest, and the parents were afraid of bears. Zakharov's grandmother taught him reading with the Psalters even before school. In 1948 his father sent him to Tomsk for studies, and to reach the railroad to that town, they had to use a raft on a river, as there were

Fig. 5.8.2.1 Matvey Safonovich Zakharov

no roads. After his joining of the Stromberg group and foundation of the special laboratory ("problem laboratory for microconstituents"), he headed one section. In 1968 he has defended his doctoral thesis entitled "Studies on the theory and applications anodic amalgam voltammetry for the analysis of high-purity materials." In the same year, Zakharov moved together with Vladimir Vasil'yevich Pnev (PhD 1968, DSc 1983) and Vyacheslav Ivanovich Bakanov (PhD 1968, DSc 1987) to Tyumen where he has build up an active research group studying the possibilities of chronopotentiometry (especially of stripping chronopotentiometry [241]) for analysis and the stripping voltammetry of anions. Together with Pnev and Bakanov, he has published a monograph on chronopotentiometry [242], and together with N. F. Zakharchuk (see Sect. 5.5.4) a monograph on electrochemical methods for natural and wastewater analysis [169].

5.9 Semёn Borisovich Tsfasman and Ivan Yemelyanovich Bryksin: Pioneers of Soviet Polarographic Instrumentation[38]

Victor G. Mairanovsky

Among the centers where polarographic equipment has been developed in the USSR, the group of Semёn Borisovich Tsfasman and Ivan Yemelyanovich Bryksin played a special role in TSLA VNII Chermet.[39] The developed commercial serial instruments

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[38] Translated from Russian by Fritz Scholz.

[39] Tsentral'naya Laboratoriya Avtomatiki Vsesoyusnogo Nauchno-Issledovatel'skogo Instituta Chёrnoy Metallurgii (VNIIChermet), Central Automatics Lab of the All-Union Scientific Research Institute of Ferrous Metallurgy.

provided the basis for wide development and application of polarography in the Soviet Union. It needs to be said that the organization of commercial production of scientific equipment in the USSR was not only difficult but also a thankless task! However, both Tsfasman and Bryksin have had a harsh life, and so they were prepared to overcome everything. I was familiar with the two men. With Tsfasman, I met a few times, but these were short business contacts (the acquisition of polarographs); vivid memories I have of many meetings with Bryksin.

5.9.1 Semёn Borisovich Tsfasman[40]: From the Atomic Project to the Vector-Polarography

Tsfasman was born in Poltava (Ukraine), in 1917. In 1920, during the civil war, his parents and a baby were shot in their home in the pogroms against the Jews in Poltava [243]. Together with three other siblings he grew up in an orphanage. They all finished school and received higher education. After finishing the Moscow Energy Institute (Moskovskiy Energeticheskiy Institut, MEI) Tsfasman went to the front in autumn 1941, where he served until 1945 as signal corps officer (Fig. 5.9.1.1). After the war he worked in the super-secret Moscow Scientific-Research Institute of the Nuclear industry (NII-9), on the pilot plant for separation of plutonium, and then at the radiochemical production. He participated in the atomic project (the atomic bomb) at the plant "Mayak," Ozёrsk city, near Chelyabinsk as the main expert on measuring instruments. He was well acquainted with Kurchatov, Semёnov, and Khariton. Despite the fact that Tsfasman proved to be an excellent engineer and organizer (he was awarded the Order of Lenin), he lost his job [244] as a result of the infamous anti-Jewish mass campaign of the early 1950s in the USSR. It was difficult for him to find employment in VNIIChermet, where he became the head of the team developing electrochemical instrumentation. And this was truly a new beginning. It has to be said that in the so-called socialist camp[41] there was a production of polarographs at that time, e.g., in Czechoslovakia the LP60 and LP7, in Hungary the OH-102 and OH-104, and in GDR (East-Germany) the GWP series. However, access to these instruments was in the USSR very limited and restricted. The development of a polarograph by Benevolskiy and Tsfasman [245], which later became the serially produced instrument PE-312, changed this situation. The PE-312 was a wonderful polarograph; its originality and stability were very convincing; one could easily see the origin from military developments—from the resistors to the shielding of cables connecting the polarographic cell. Like other instruments of that time, the PE-312 did not yet have a

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[40] I am very indebt to Dr. Grigoriy Matveyevich Tsfasman, son of the elder brother of S. B. Tsfasman for providing biographic details and a photo.

[41] "Socialist camp" was used to designate the Socialist States, which have been established following World War II.

Fig. 5.9.1.1 Semën Borisovich Tsfasman (Courtesy of Dr. Grigoriy Tsfasman, Moscow Russia)

potentiostat, but it had an original circuit for *iR* compensation. Of particular importance was the fast responding recorder, allowing response rates up to 0.25 m s^{-1}. This feature was very different to the standard tendency of strong damping of oscillations on polarographic curves by using slowly responding recorders, like in case of the Czechoslovak EZ-2. The recorder of the PE-312 was not a special development for polarography, but a modification of the fast responding recorder TsLA; Benevolsky and Tsfasman found a original solution for suppression of the oscillations [245]. Thus the PE-312 was very useful to record polarograms with the hammer's controlled DME, also at the beginning and at the end of a drop life and for recording *i*–*t*-curves (cf. ref [13]). The inventive talent and vast experience of Tsfasman, gained in the development and operation of devices for the atomic program, paid back later in the development of the so-called vector polarograph [246]. Based on Barker's original ideas, Tsfasman found a solution for phase-selective ac measurements to realize the full advantages of ac polarography. Professor Oleg Petrii (Moscow) correctly remarked in a personal communication to the editor of this book that the electrochemical devices developed by TSLA can be regarded as a by-product of the Soviet atomic project. This is true, not only because of the personal and material basis but also because polarographic analysis was vital for the atomic project. A sad consequence of Tsfasman's participation in the atomic project was his destroyed health. The work at the Mayak plant, where frequently accidents happened (which are only now getting to be declassified [247]) had its aftermath. Tsfasman died on 31st of December 1964 at the age of 47 years. His ideas were lasting. For example, the idea of vector-polarography was further developed by Bryksin, Petrii, and coworkers [248]. In 1960, Tsfasman has published the book "Electronic Polarographs" [249]. The list of references proves that he knew all the important Western publications, in both journals and books; and he noted in the preface, this was the first book devoted only to polarographs, i.e., to polarographic instruments.

5.9.2 Ivan Yemelyanovich Bryksin. Memories of an Outstanding Personality

The beginning of my contact with Ivan Yemelyanovich Bryksin (Fig. 5.9.2.1) was rather unusual; it started in May, 1962, in Moscow, Novokuznetskaya Street 7/11. There was a new laboratory on the uppermost floor of the building of the "Experimental Plant for Vitamin Production" (Moskovskiy Eksperimentalnyy Vitaminyy Zavod = MEVZ) in a large empty room of the former pumping station, with high ceilings. It was designated for the development of analytical procedures for the production control of Vitamin A with the help of gas chromatography (GC) and polarography. The GC was the task of Mikhail Yanotovskiy, the former chief engineer of the MEVZ, and I had to take care of the polarography. The pilot plant for Vitamin A production was nearby (see Fig. 9.12). I was particularly attracted by oscillographic polarography, with the Soviet made polarograph PO-5122 (TSLA company), because Misha Yanotovskiy and I have used a combination of these two methods [250–252] (GC-EC, Chap. 9). It was necessary to introduce some changes in the circuitry of the PO-5122. I had to expand the range of scan rates to smaller values, down to 50 mV s^{-1}, for recording "classical" polarogramms [253] because they were better suitable for GC-EC, but this I have believed only at the beginning...

Then, in the middle of May a trainee of a chemical college (a first educational institution, after grade 7) came to us; a nice modest boy, to learn about our work and to see our devices. After a couple of hours of work, Misha and I decided to have a break and to go to a cafeteria nearby because there was no in the MEVZ. The trainee also left the lab and went to the vitamin A pilot plant, but he did not come back after the break, and we started our work. But I could not switch on my PO-5122. I took it out of its housing, and was stunned as except the oscillographic tube, there was almost nothing in! I got the boy's home address, where I met his mother. I told her what happened. She sobbed and said that will pay all repair costs, "but please do not go to court." Then she returned a cardboard box with the parts of the polarograph. But what to do with them? I remembered that Sasha Ershler, my friend from the Institute of Electrochemistry IELAN, talked about his collaboration with Ivan Yemelyanovich Bryksin from TSLA, the developer of the PO-5122. I called TSLA, and a few days later Bryksin came, a tall, thin man, broad-shouldered, with high cheekbones, and a little stuttering. He asked for a screwdriver, looked inside the polarograph and began to laugh loudly: "Well done!" The device was taken to TSLA, and soon Ivan Yemelyanovich returned it, all fixed. When we were talking about the cost of repair, he asked for a very tiny amount of money, only counting the costs of the new parts, and the incident was over. Bryksin noticed traces of my alterations (even in the destroyed device!) and began to ask in detail, what I wanted to have changed, and promised that he will do everything for free. He only asked me not to touch the device again with a soldering iron. "Mind your own business!" Then he repeatedly came to us. Among my wishes was to modify the electronic device in such a way as to record the *i*–*t* curves on the first drop (I had

Fig. 5.9.2.1 Ivan Yemelyanovich Bryksin (Courtesy of Prof. Yuri Orlov, Cornell University, USA)

used a simple circuit with an electromagnetic relay [254]). He managed this task. Several of our "improvements" (scan rates down to 10 mV s^{-1}, *i–t* recording on first drop, triangular potential sweep) were introduced in the following models of PO 5122 (PO-02, -02A, and -03) [255]. In the P-03 model, the minimal scan rate was even as small as 2.5 mV s^{-1}. Recalling my experience with "express polarography" [253], I thought that this was not necessary, but Bryksin loved to go to the margins, like a real inventor. At one of our first meetings, he said that they make "fool-resistant devices." Noticing my reaction to this statement, he said that it does not relate to me personally, but equipment must stay mishandling. Indeed, it was amazing and admirable: the instruments developed in TSLA, with the involvement of Bryksin, never broke down during decades (!) of operation in our laboratory. In addition to the PO 5122 we are talking about two polarographs PE-312 and two potentiostats P-5827. This powerful tube potentiostat-galvanostat, which was serially produced at the instrumentation plant in Gomel (Belarus), provided an output voltage up to 200 V, which was essential for electrosynthesis in nonaqueous solutions. For comparison, I would say that one of the world's best potentiostats of the mid-1970s, the PAR-178 (Princeton Applied Research, the all-transistor model) gave an output voltage up to 100 V. But there were no such powerful output transistors in the USSR then. Of course, the P-5827 was a large, heavy instrument (it was kept on the floor under the lab bench), but it "honestly did his job"...

At Bryskin's visits, Misha Yanotovskiy and I always arranged for a tea and put something tasty on the table. However, I.Ye. touched this only, and then took his own sandwiches from his own box. We had a good conversation and he remarked "How great you live here! Complete freedom! Only some few people in this huge room! One could put in a second floor!" Indeed, the working conditions at TSLA were different. I frequently visited Bryksin there; sometimes Misha went to TSLA to pass over something on my request. Many people were in TSLA, and not enough space. Of course, we were careful with respect to political issues, but we could trust each other. I remember a conversation. Knowing that I was a radio amateur, he asked what I was working with. As a school boy I made a superhet receiver with 16 m and 19 m bands, and since my student days I had the brilliant "Riga 10."[42] "And what do you listen to?" asked Bryksin, and I said "of course, Voice of America, especially Willis Conover's "Time of Jazz"; then Anatoliy Maksimovich Gol'dberg on BBC"; then Radio Liberty... Bryksin: "Is it interesting?" I: "Yes, of course." Bryksin: "And you know a lot about our Russia?" I: "I think, sufficiently much." Bryksin: "I doubt this. Do you know, for example, that in 1913 Russia became the world's leading economic country, in agriculture, and in technology? And if not for the Bolsheviks ...—And do you like the Tsar?—Of course, he was weak and incompetent ...". I also remember how I told him that I always wanted to do something with technique, and that I after grade 10 went to the selection committee of the Fiztech (PhysicoTechnical Institute, a prestigious college near Moscow), where a young committee assistant told me quietly: My advice is, you take your documents; no chance, you will be rejected for sure; try to enroll in another college. Clearly he knew that a Jew had no chance to be accepted at this institute. Bryksin replied to this: "It is very good that you did not go to Fiztech, your electrochemistry is a very interesting science; and much safer." I told him that then, in 1954 they also sorted me out at the Petroleum Institute: In the entrance exam, I made a mistake in the formula cryolite, which is added to reduce the temperature of the melt in the electrolytic production of aluminum (it was electrochemistry, but beyond the school chemistry); I started to study only in 1955, after rejecting an oil institute...

Oleg Petrii recalls that Bryksin was a genius of analog technology. His oscillographic polarograph PO-5122 was a remarkable instrument. It had a large screen used in military radars. Attached was a very handy device with a camera to record the curves on the screen (cf. Fig. 9.17). When the first computers appeared, Bryksin said that he could improve the measurement technique, if they would be in his possession. Unfortunately, his work at TSLA was not cloudless. The company constantly tried to give him other tasks than to develop electrochemical instrumentation. Once, Oleg Petrii organized a visit of Frumkin to TSLA in order to rescue the electrochemical devices.

Bryksin did not speak much about himself. From Sasha Ershler I knew that he was kept for some time in a secret research and development laboratory, which was part of the Soviet Gulag labor camp system (the informal Russian name of such institutes was Sharashka), but Sasha did not tell me anything else. Later I have learned from Sasha that Bryksin died: According to Sasha, Bryksin once returned home late, and at a bus stop some guys began to molest a girl. He tried to defend her, but one guy hit him. He fell and was injured, laying there for a long time, until he was taken to the hospital, where he died. A slightly different version can be found in

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[42] I bought this radio secondhand for a low price at a commission shop, and it turned out that it had a defective power supply. I rebuilt it for the shortwave bands (13, 16 and 19 m). All Soviet radios started only at the "legitimate" 25 m band, and all Western radio stations could not be received because of active interference stations (so-called glushilka's).

Solzhenitsyn's book Arkhipelag GULAG: Bryksin was beaten down by two hooligans in a Moscow suburb, and he died in a nearby hospital after 9 days lying without any medical care… This all happened in the summer of 1978, when I was not in Moscow, so I could not say farewell to Ivan Yemelianovich. He will forever remain in my memory, and only a short line of gratitude remained in a journal article [254].

Over the years, some more facts become available. The inventive talent of Bryksin has shown up also in the time when he worked in the Marfino's Sharashka, where he was together with Solzhenitsyn and Lev Kopelev [256]. In 1951, Bryksin (in the group of seven engineers) was released early from Sharashka for his contribution to the development of an original communication system, a top-secret phone, but he continued to work there as a civilian worker [256]. In the short time between his final departure from Marfino and his tragic death, he has achieved so much! During that time he worked in a group of highly talented enthusiastic people at the TSLA, headed by Semёn Tsfasman. The references [245, 246, 248, 249, 255, 257–266] give some impression of the achievements of Tsfasman and Bryksin as inventors and designers of electrochemical instrumentation. The patent relating to the measurement of the capacitance of the electrical double layer [266], appeared, when Ivan Yemelyanovich was no longer. This relates to Tsfasman's paper [261] in which the complete scheme of the vector polarograph has been given.

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5.10 Catalytic Polarographic Currents

Fritz Scholz

Chemical reactions associated with electrode reactions in polarography have attracted much attention in various research groups of the former USSR. Among the chemical reactions, catalytic systems were of special importance for analysis because they allow achieving very low detection limits, and they have also been extensively studied to provide thermodynamic and kinetic data of chemical reactions. In the former USSR, catalytic polarographic currents have been studied by S. I. Sinyakova (Moscow) (see Sect. 5.6), S. G. Mayranovskiy (Moscow) (see Sect. 5.6), V. F. Toropova (Kazan) (see Sect. 5.8), Ye. G. Chikryzova (Kishinyёv) (see Sect. 5.7), Ye. N. Vinogradova (Moscow) (see Sect. 5.6), Yu. S. Milyafskiy (Moscow, Krasnodar), G. V. Prokhorova (Moscow), S. M. Bardina (Kishinyёv), O. Ye. Ruvinskiy (Krasnodar), P. M. Zaytsev (Moscow), and very extensively by Yu. I. Tur'yan (see Sect. 5.10.1). Milyafskiy and Sinyakova [267, 268] have suggested the two terms "current catalysis" and "potential catalysis" to distinguish two major types of catalytic currents. Although these terms are somehow imprecise (Milyafskiy and Sinyakova were aware of this), they well describe some characteristic features: "Current catalysis" denotes systems where a homogeneous chemical reaction of the product of an electron transfer reaction recycles the educt of electrode reduction. A standard example is the reduction of chlorate ions by electrochemically produced Ti(III) (from Ti(IV) reduction). At the potential of the Ti(IV)/Ti(III) system, an exaltation of current is observed. As "potential catalysis," they denote systems where a ligand (this may be also an adsorbed ligand) catalyzes the electrode reaction of a dissolved compound on the electrode surface. The irreversible response of that compound is shifted by the ligand toward the reversible response. Catalytic hydrogen waves of protonated organic compounds belong to this class, as well as many electrode reactions catalyzed by surface-bond catalysts. In reality, the mechanisms of catalytic currents are much more complex than the two simplified categories "current catalysis" and "potential catalysis" can distinguish, and it were S. G. Mayranovskiy [269] and Ya. I. Tur'yan [270–272] who have given the most detailed description of catalytic systems, and generally of chemical reactions, in polarography.

Pëtr Mikhaylovich Zaytsev (*February 2, 1932)

Owsey Yewelevich Ruvinskiy (*October 23, 1936)

5.10.1 Yakov Iosifovich Tur'yan

F. Scholz

Chemical reactions associated with electrode reactions in polarography have attracted much attention in various research groups of the former USSR. Tur'yan and his coworkers have studied the chemical reactions preceding the electron transfer stage using in addition to polarography, indirect pH-potentiometry [273], and redox-potentiometry [274]. The chemical reactions in polarography could proceed in the solution volume as well as at the electrode surface. The principles of the surface reactions with participation of adsorbed species in polarography have been developed by S. G. Mayranovskiy [269] (see Chap. 9). These principles have been applied by Mayranovskiy to the analysis of protonation reactions of organic compounds [269] and have been also used by Tur'yan to study the polarographic catalytic currents of the electroreduction of metal ions.

Tur'yan and his coworkers [270–272] have developed the theory of polarographic kinetic and catalytic currents with accompanying chemical reactions. They have described reaction mechanisms according to the order of chemical and electrochemical steps, according to the ratio of concentrations of the involved compounds, and according to the chemical properties of the involved species. Tur'yan has used the term "polarographic catalymetry" [271, 275] for the description of techniques using polarographic currents for the purpose of analysis. The term "catalymetry" was very popular in Russian literature, but rarely used in English, where this kind of analysis is referred to as kinetic (or more specifically,

Fig. 5.10.1 Yakov Iosifovich Tur'yan

catalytic) methods of analysis. Catalymetry received much attention in the former USSR, with K. B. Yatsimirskiy [276] being its best-known exponent. The scientific environment for the development of theories and experiments in the wide field of catalysis in electrochemical analysis was very fruitful and did not possess the exotic flavor it had in Western countries.

Yakov Iosifovich Tur'yan (Fig. 5.10.1) was born on July 25, 1922, in Il'intsy, Vinnitskaya Oblast', Ukraine. His father, an engineer, graduated from the Polytechnical Institute in Belgium. His mother, a doctor, passed away when Yakov has been 21-years-old. In 1944 he graduated from the Middle-Asian Industrial Institute in Tashkent, Uzbekistan, as technical engineer for electrochemical industry. Because of an eye failure, he did not serve in the army. From 1944 to 1951, he was a PhD student and assistant at the same Tashkent Institute at the division of physical chemistry. The topic of his PhD thesis was "The oxygen overpotential at nickel electrodes." It was supervised by V. N. Fiseyskiy, a highly erudite specialist in chemical technology and patenting. The thesis led to his fist patent [307]; overall Tur'yan has 41 patents. Other scientists who have strongly influenced Tur'yan were A. N. Frumkin, A. G. Stromberg, J. Heyrovský, and S. G. Mayranovskiy. From 1952 to 1958, Tur'yan was a docent at the division of physical chemistry of the University of Kishinyëv, Moldova. From 1958 to 1961 he led the analytical laboratory of the Institute of Nitrogen Industry in Severodonetsk, Ukraine. Tur'yan remembered that in 1952 when he entered the University of Kishinyëv, he had to witness anti-Semitism in the USSR: he was not allowed to work in Leningrad, despite previous agreements, and a series of other refusals. This happened at the time of the so-called Doctor's plot, when medical doctors of Jewish origin were blamed of attempting the assassination of Soviet leaders. The most important results, which are still valid, from the period 1944 to 1961 concerned the mechanism of polarization of a Ni-anode during the oxygen evolution reaction involving the participation of Ni(III) and Ni(IV) oxides [277–280]. Parallel to these studies, in 1946 Tur'yan started to use more and more polarography to study chemical reactions. One of the most important papers of that time was about the polarographic prewave of Ni^{2+} in pyridine containing solutions [270], which marks the beginning of a new direction in polarography, the study of catalytic waves of metal ions. From 1961 to 1969, Tur'yan led the analytical laboratory of the Institute of Monomers in Yaroslavl', Russia, where during Stalin's reign existed the so-called chemical prison. There, behind barbed wire, excellent chemists who were completely innocent had to work. This was also the place where the first factory for the production of synthetic rubber in the world has been established! From 1969 to 1991, he was the Chair (Professor) of the Division of Analytical Chemistry of the Krasnodarsk Polytechnic Institute, Krasnodar, Russia, [281], and from 1991 to 2004, he worked at the National Physical Laboratory in Jerusalem, Israel. In 2004 Tur'yan moved to the USA on the basis of a program for extraordinary scientists. Tur'yan and coworkers have considerably deepened and widened the theory and analytical applications of prewaves of many metal ions which possess high overpotentials of reduction of their aqua complexes [Ni^{2+}, Co^{2+}, Fe^{2+}, In^{3+}, Ga^{3+}, Ti(IV), Sn(iv), and Ge(IV)] [271, 282]. This was possible mainly due to the developing of the theory of parallel heterogeneous catalytic reactions of formation of electroactive complexes [283–287]. For the first time, the rate constants of formation of the complexes with adsorbed ligands were determined and the principal differences were reported in the electrochemical behavior of these complexes with those of the same composition, but formed in solution and then adsorbed on the electrode surface [288]. In 1966 Tur'yan defended his doctor of science thesis, devoted to chemical reactions associated with electrode processes in polarography, before the scientific council in Moscow, headed by A. N. Frumkin. In 1967, Tur'yan was granted the title of Professor of Physical Chemistry. Tur'yan has elaborated the theory of kinetic polarographic currents for (1) electrode reactions with stepwise protonations of organic acids with one slow reaction step [272, 289], (2) two slow consecutive dehydration reactions (de-cyclization) and protonation of the organic acid [290–295], and reactions in the reverse direction, protonization and dehydration of carbonyl compounds in alkaline solutions [296, 297]. It should be mentioned that for a number of dehydration products (de-cyclizations) or protonations of carbonyl compounds, reaction products have been detected in the solution volume [295], and (3) parallel protonization of the products produced from the interaction of formaldehyde with amines and amino acids [270, 298, 299]. The analytical utilization of these reactions, especially of the carbonyl-amine interactions, has been the topic of the papers [272, 300].

Turyan et al. have developed an indirect redox-potentiometric method for the determination of the peroxide number of oils and fats without titration [274, 301] and suggested this method also for the determination the antioxidant number [302]. They have also developed the theory and analytical application of an indirect pH-potentiometric method for the determination of the acidity number of oils and fats without titration [273, 303], and a modified Brdička method as cancer assay [304, 305]. Tur'yan is the author of more than 500 papers, among which are 4 monographs [270, 271, 300, 301]. He has supervised 40 PhD theses, and 4 doctor of science theses [306].

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Chapter 6
The Development of Electrochemistry in Lithuania

Rimantas Ramanauskas

6.1 Introduction

Lithuania may be reasonably proud that origin of electrochemistry science is associated with this country as well. Theodor Grotthuss, the world-famous founder of the theory of electrolysis, grew up and spend the main part of his life on his mother's estate in Gedučiai (Geddutz), which on today's map is located in the northern part of Lithuania. A theory of water conductivity was proposed in his 1806 publication "Theory of decomposition of liquids by electrical currents" [1], and some think it could have been worthy of a Nobel Prize, if such had existed at that time.

However, 100 years had to pass till next serious electrochemical investigations in Lithuania began. The development of science in the period of nineteenth to twentieth centuries in Lithuania was inevitably related to the historical turning points, the dates of which should be mentioned here. In the nineteenth century, the Lithuanian territories, which belonged to the Grand Duchy of Lithuania, were annexed by Russia and until 1917 Lithuania was a part of the Russian Empire. Although Vilnius University, founded in 1579, is one of the oldest and most famous academic institutions in Central and Eastern Europe, it was closed in 1832 by the order of Tsar Nicholas I, because professors and students of the university took active part in the rebellion of 1831. The university remained closed till 1919. Lithuania regained its independence in 1918 and maintained the status until 1940, when it was occupied by Soviet Union. One part of the Lithuanian territory with the capital Vilnius was occupied by Poland in the period between 1922 and 1939. The independence of Lithuania was reestablished at the end of twentieth century, on March 11, 1990. There is no doubt that these historical facts have greatly influenced

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the activities of universities and the development of science in the country on the whole.

Scientific research in the area of electrochemistry and the lectures on its fundamentals in the university in Lithuania started in the beginning of the twentieth century and are related to the name of Professor V. Čepinskis [2]. In 1922, on the initiative of a group of prominent professors with V. Čepinskis among them, the Lithuanian University, which later was named Vytautas Magnus University, was founded in Kaunas. It was in this university where the foundations for the development of chemical science in Lithuania in the twentieth century were laid. The merits of V. Čepinskis include the tradition of chemistry teaching, publishing handbooks, the foundation of laboratories with equipment suitable for electrochemical investigations and studies, and the initiation of scientific research. J. Matulis and J. Janickis were the most talented and creative disciples of V. Čepinskis. They both had worked for 1 or 2 years in foreign scientific centers and had obtained academic degrees before 1940 [3, 4].

World War II had brought great losses for Lithuanian science. Some part of the qualified staff moved to the West, the others have suffered from being exiled to other Soviet Republics, while the country remained under Soviet occupation. Despite unfavorable external factors, the electrochemical science in Lithuania began gaining momentum and was developed in universities. In the Department of Physical Chemistry of Vilnius University, headed by J. Matulis, the spirit of V. Čepinskis was alive with strong focus on electrochemical research, whereas in the Department of Physical Chemistry of Kaunas University, the mood and ideas of the Dresden (Germany) electrochemical school prevailed, because J. Janickis had worked there [5]. In the postwar period, Lithuania began training its own qualified electrochemistry specialists having skills of scientific research. J. Matulis, who headed the Department of Physical Chemistry in Vilnius University in the period of 1945–1950, initiated research related with electrolytic deposition of metal coatings. Under his guidance, the first thesis entitled “Relation between cathodic polarization and adsorption” [6] was defended already in 1948. In Kaunas University, from which the University of Technology had later branched out, the most important works of J. Janickis and co-workers, which had greatly influenced the research of other scientists, were those related to investigations of electrochemical reactions of manganese and selenium [7]. Therefore, J. Janickis can be considered as being among the founders of manganese and selenium electrochemistry.

Scientific research in the Soviet system was carried out in research institutes, which belonged to the Academy of Science. After the foundation of the Lithuanian Academy of Science (AS) in 1941, the Institute of Chemistry and Chemical Technology (IChChT) was established in 1945 in Vilnius mainly, on the initiative of J. Matulis [8]. At the beginning, organic and mineral raw materials (peat, clay, etc.) as well as underground waters were studied in this institute. Electrochemical research began in 1949 and was supervised by J. Matulis. The first doctoral thesis in the area of electrodeposition of metals was defended by A. Bodnevas in 1950 and was entitled “Influence of organic materials on cathodic polarization of Cu and Ni” [9]. In the period between 1953 and 1954, O. Galdikienė and R. Višomirskis defended their doctoral dissertations in the same field [10, 11]. Systematic investigations of regularities of overvoltage variations during discharge of Cu, Ni, Sn, Cr, Co, Fe, and Zn ions from various electrolytes began (V. Skominas, R. Sližys, A. Steponavičius). The reasons for the formation of bright coatings were investigated, whereas later the attention was focused on precious metals (S. Chotianovič) [12]. In 1956, J. Matulis became the director of the institute and he held office for 20 years. In the period from 1946 until 1984, he also was the president of Lithuanian AS [13].

The question may arise: why the main field of investigations and main achievements of Lithuanian electrochemists in Soviet years, i.e., until the beginning of the tenth decade of the twentieth century, was related to electrodeposition of metal coatings? The formation of the scientific schools of J. Matulis and R. Višomirskis in the area of metal electrochemistry and their worldwide recognition show that the choice of direction of investigations was correct. The insightfulness of J. Matulis and the logical evaluation of the external circumstances, most likely, were the main reasons of such choice.

One of the reasons for choosing this scientific direction is related to the inequality in the level of practical galvanotechnics in Western Europe, USA, and the Soviet Union. After World War II, a real revolution in the industry of metal processing took place. The automotive industry as well as the producers of tools and house ware rose new requirements for mechanical as well as corrosion resistance of the coatings and also for their decorative appearance. In 1950–1955 in Western countries, the traditional galvanic processes were replaced by new technologies of bright coating deposition, and the galvanic workshops of the factories were transformed into the most clean production departments. In the meantime, this area of production in the Soviet Union was utterly lagging behind. Soviet electrochemists engaged in investigations of the mechanisms of elementary electrochemical acts and having leading positions in this area in the world, showed little interest for electroplating and the processes of metals electrocrystallization, as well as applied research in this field [14].

Another argument for choosing this research direction was the fact that many qualified electrochemists were trained in the Department of Physical Chemistry of Vilnius University headed by J. Matulis in postwar years. Many of them came to work in IChChT. Half of the doctoral dissertations (16 of 32) defended in the institute in the period between 1948 and 1965 were in the area of electrochemistry and their number increased gradually [8].

A new additional impulse toward galvanotechnics in the middle of seventh decade was related to the decisions of the central Soviet government [15]. The Soviet Academy of Sciences decided that the institutes of the Lithuanian AS should contribute to solving problems of the Soviet Union. The reason behind that decision was the realization that the research institutions of the Soviet Union were not competitive with those in Western European and the USA. In these countries, the number of scientific laboratories increased rapidly, their equipment improved, and the scientific production also increased (e.g., the number of scientific journals doubled during 5–8 years). The funds allocated for the development of science in the Soviet Union were significantly lower, whereas the funds given for institutes of the Lithuanian AS were even 4–5 times smaller than those for the central institutes [8]! Therefore, the institutes of the Lithuanian AS were unable to function properly and to solve numerous problems at the same time. There were proposals for the IChChT to perform research in photochemistry and electrochemistry of organic materials; however, because of the lack of suitable equipment and specialists, J. Matulis considered these directions as not promising and the best possible choice was the electrodeposition of metals [15]. J. Matulis believed that at that time they could achieve better results in this area. Thus in 1965, in accordance with a resolution of the Soviet Council of Ministers, the IChChT was obliged to fully focus its investigations on electrodeposition of metals and their alloys and the applied research [15]. By the same resolution, the IChChT was given the status of a leading institute in the whole Soviet Union. According to J. Matulis, the institute since then should have been titled “Institute of Electrochemistry and Galvanotechnics.” The development of scientific research in the area of formation of protective and decorative coatings, having only one main direction, made it possible to allocate the available resources to the creation of progressive galvanic, chemical, and conversion coating technologies, based on the unity of fundamental and applied research.

Since the seventh decade of the twentieth century, the IChChT is the largest and main electrochemical research center in Lithuania; therefore, the major part of this review will be devoted to the description of developments of this institution, achievements of its workers, and the problems, which were encountered.

In 1965 the first technology of bright nickel plating was developed in the IChChT, and its introduction into production in Lithuania and outside began. The number of nickel plating technologies increased and they were introduced all over the Soviet Union. Since 1969 automotive factories began placing orders and making contracts for the development and introduction of nickel, zinc, chrome plating, and conversion coating technologies. A major achievement was the creation of alkaline zinc plating technology, which replaced the cyanide zinc plating processes. The first contract with foreign country was with the VEB Galvanotechnik Company of the German Democratic Republic in 1979, while later on, the contracts with institutions in Bulgaria, Poland, Czechoslovakia, and other countries belonging to the Council for Mutual Economic Assistance were constituted [8].

Aside from applied research, fundamental investigations were also performed in the institute. In the middle of the seventh decade, new research directions emerged: in 1968, A. Survila started investigations of electrode processes in the systems of labile complexes of metals, later he engaged in photoelectrochemistry, and the group headed by R. Sližys searched for new electrochemical research methods and performed the first works in probing of the diffusion layer with microelectrodes. The scope of research expanded. A. Vaškelis initiates studies of chemical metallization processes including applied research. L. Simanavičius, who came from Vilnius University, started the investigations of electrodeposition of metals from nonaqueous electrolytes. Other works included electroforming, aluminum anodizing and electrolytic painting, and formation of conversion coatings. In 1976, R. Višomirskis became the director of the institute and held this position until 1992.

The studies performed by the members of the scientific school of J. Matulis and R. Višomirskis advantageously combined scientific investigations with application of the obtained results in practice; therefore, several dozens of metals and dielectric surface treatment technologies were designed which were applied widely in industry. At that time, the institute coordinated scientific studies in the field of metal electrodeposition in the Eastern European countries [8].

After Lithuania had regained its independence, the status of the institute changed. The reform of the studies in the institute was started with the idea to enable the institute to take part in handling the problems of Lithuanian national economy as well as to integrate it into the international science system. During the first years after regaining the independence, the signs of crisis became vivid: although the number of scientists in the institute increased during the ninth decade and dissertations were defended, the scientific production of the institute was not increasing, and since 1989 it even began to decrease [15]. This was caused by intensive commercial activities of selling the technological processes. These activities were profitable for the institute; however, less attention was paid to scientific research and the creation of new technological processes. This was understandable, because after decades of investigating the same systems, it became more and more difficult to obtain new valuable results. The crisis revealed that some of the applied research was not future-oriented, and it became clear that a reform was necessary. In 1991 the name of the IChChT was changed to "Institute of Chemistry" (ICh) and A. Vaškelis became the director in 1992. New research directions were identified with a focus on an integration into global chemistry science in the areas, where the institute had scientific potential, and another priority was the development of research areas relevant to Lithuanian national economy and its needs. The following main research directions were formulated: studies of electrochemical, catalytic, and sorption processes in solutions and their practical application; materials science and metal corrosion, environmental chemistry, spectroelectrochemistry, and synthesis; and studies of organic compounds [16].

The last decade of the twentieth century, the decade of Lithuanian independence, offered a lot of new opportunities in science and also new challenges, which the scientists at the Institute of Chemistry and other electrochemists had to face. It will be interesting to compare the development of electrochemistry and achievements in Lithuania during 50 years of isolation under Soviet occupation with those of the last decade of an independent country open to the whole world. We will try to do this after getting acquainted with the achievements of the most prominent Lithuanian electrochemists of twentieth century.

6.2 The Initial Stages of the Scientific School Formation (V. Čepinskis)

Vincas Čepinskis (1871–1940): He was a Lithuanian chemist, physicist, diplomat, member of the Constituent Assembly of Lithuania, and the First Lithuanian Seimas (Seimas = Parliament). He graduated from Saint Petersburg University, Faculty of Physics and Chemistry in 1894, and worked for 2 years in Russia's Depository of Weights and Measures as an assistant of D. I. Mendeleev. *In 1896–1899, he specialized in physical chemistry in Zurich Polytechnic Institute and got acquainted with physicochemical and electrochemical investigations in the universities of Göttingen (Prof. W.* Nernst*) and Leipzig (Prof. W.* Ostwald*). In 1920–1922, he actively participated in the establishment of Lithuanian University in Kaunas. He has been a professor since 1922 and prorector and rector of this university from 1922 to 1933* (Fig. 6.1).

Professor and statesman V. Čepinskis is considered to be the founding father of physical chemistry and physics in Lithuania [2]. His scientific steps coincided with the rapid development of classical chemical thermodynamics and the rise of chemical industry. He became a master of many precise measurement techniques and could operate precise equipment, and all his life was fascinated by experimental research. The choice of Switzerland for his postgraduate studies was not accidental: Zurich at that time was among the main centers of physicochemical research. There was, however, another personal reason: his doctors have recommended that the mountain climate would be beneficial for V. Čepinskis' health. In Zurich Polytechnic Institute, he acquired strong knowledge of electrotechnics and attended lectures of technological sciences. In the same period, he got acquainted with physicochemical and electrochemical investigations in the universities of Göttingen (Prof. W. Nernst) and Leipzig (Prof. W. Ostwald) [2]. However, most of his time was spent in the laboratory of Prof. H. A. Lorentz, one of the few European laboratories specialized in electrochemistry. In this laboratory, famous for research in molten

Fig. 6.1 Professor of Vytautas Magnus University, V. Čepinskis. Kaunas, 1932

salts, V. Čepinskis verified that the Gibbs–Helmholtz equation is also valid at high temperatures when the galvanic cell contains molten salts of heavy metals. His work entitled “On free energy changes of some heavy metal halogenides” was published in *Zeitschrift fur anorganische Chemie* [17], one of the most reputable chemical journals at that time. Later in the same laboratory, he performed a series of experiments investigating the electromotive force of hydrogen–oxygen cells. The second scientific paper of V. Čepinskis was entitled “Measurements of some gas circuits” [18], and there he reported on the possibility to transform the energy of fuels into electricity, which was a new topic at that time. The paper was published in the same journal in 1902.

Since 1918, V. Čepinskis worked in Lithuania. He was among the founders of the Lithuanian University, which was later named Vytautas Magnus University. In 1925 he established the Department of Physical Chemistry and Electrochemistry and took care of the construction of the Institute of Physics and Chemistry [2]. V. Čepinskis had no practical possibilities to perform scientific research during his first 10 years at the university. For seven years, he worked as rector or prorector; established two departments and equipped the laboratories; wrote handbooks, monographs, and science popularization papers; and publicized. Together with his students, V. Čepinskis analyzed the phenomena of photochemistry, metal passivity, and catalysis and investigated the relations between the solubility of salts and their activity and galvanic polarization; he also performed electrolytic synthesis of materials. At the same time, he attempted to return to research which he had began in Switzerland. He continued the investigations of entropy changes performed in Zurich, replacing melts of the salts with their solutions. In 1934 the Journal of Vytautas Magnus University published the paper of V. Čepinskis entitled “The simplicity of entropic variety of ionic reactions” [19]. V. Čepinskis described a regularity, which had never been reported before, i.e., that the temperature coefficient of electromotive force is constant in any galvanic circuit, irrespective of whether the reaction proceeds in high-temperature melts or in room temperature solutions, and the ratio of these coefficients in monovalent, bivalent, and trivalent salt systems is 1:2:3. This paper is the most valuable of his scientific works and it had not received the appropriate response abroad. V. Čepinskis failed to establish his priority because the journal was not known in Europe, and the paper was written in Lithuanian, so that foreign physicochemists could hardly read it. Similarly, his intuitive hypothesis about the participation of monovalent ions of Al, Mg, Zn, and other metals of otherwise higher valence in the electrode processes taking place in aqueous solution of the salts is now unfortunately also not associated with his name.

The contribution of V. Čepinskis to the further development of electrochemistry in Lithuania is related to his creative pedagogical work, education of talented students, and caring for their internships in foreign universities. His great merit is the establishment of modern and technically equipped physicochemical laboratories in Vytautas Magnus University. The most talented of his students—J. Matulis and J. Janickis—continued the research started by their teacher in the area of electrochemistry.

6.3 The Soviet Period and the General Trend Toward Metal Electrodeposition

6.3.1 Theoretical and Practical Studies in Metal Deposition (J. Matulis)

Juozas Matulis (1899–1993): He was the most distinguished chemist of Lithuania in the twentieth century. He graduated from the Lithuanian University, Faculty of Mathematics and Natural Sciences in Kaunas in 1929. He was a student of V. Čepinskis and had his postgraduate studies in Leipzig University in 1931–1933. He was a doctor of science in 1934 and habilitated doctor of science in 1936 from Vytautas Magnus University, *professor since 1940, dean of the Faculty of Natural Sciences and Mathematics at Vilnius University from 1940 to 1941, and head of the department of Physical Chemistry at the same university from 1941 to 1943 and 1945 to 1950. He was the president of the Lithuanian Academy of Sciences from 1946 to 1984 and director of the Institute of Chemistry and Chemical Technology in Vilnius from 1956 to 1976. J. Matulis was awarded two Prizes in Science of Lithuania in 1975 and 1982 and a Prize of the Soviet Union Ministry Council in 1984.*

The research fields of J. Matulis were photochemistry, chemical kinetics, and electrochemistry. The electrochemical studies were the most important and were carried out most intensively. They were initiated in the late 1940 at Vilnius University and latter expanded at the IChChT. The majority of almost 500 scientific papers published by J. Matulis are devoted to electrochemistry, and the largest part of them was dedicated to metal electrodeposition [13]. He studied the electrochemical and chemical processes in copper, nickel, chromium, cobalt, zinc, silver, iron, and other salt solutions as well as characteristics of deposited metal and alloy coatings. His works covered a wide range of problems, from fundamental questions of metal crystallization to the developing of new technological processes in electroplating and other fields of surface finishing [20]. A typical feature of J. Matulis research was that he gave attention to real complicated systems and the study of not only the main processes, e.g., charge transfer or diffusion, but also to the accompanying secondary reactions at the metal surface. Among his most important and extensive investigations are the behaviors of various additives [21], especially for achieving brightness [22] in the electroplating processes and the mechanism of chromic acid reduction and chromium electrodeposition [23] (Figs. 6.2 and 6.3).

J. Matulis founded a large scientific school and he supervised 85 PhD theses. His postgraduate students (R. Višomirskis, V. Kaikaris, R. Sližys, A. Steponavičius, R. Ramanauskas, and others) together with their students (K. Juodkazis, E. Juzeliūnas, G. Niaura) further developed investigations initiated by J. Matulis and expanded them. At present, the total number of scientists of his school amounts to over 200 [21]. The studies performed by the electrochemists of the scientific school of J. Matulis advantageously combined scientific investigations with application of the results obtained in practice; therefore, several dozens of metals and

Fig. 6.2 J. Matulis with the students in the laboratory of electrochemistry of Vilnius University, 1950

Fig. 6.3 From *right*: J. Matulis, O. Galdikienė, A. Antropov, and A. N. Frumkin during the conference on metal deposition in Vilnius, 1956

Fig. 6.4 From *right*: J. Matulis and Dr. A. Vegys in the Laboratory Ni deposition of the Institute of Chemistry and Chemical Technology, Vilnius, 1969

dielectric surface treatment technologies were designed which are applied widely in industry. J. Matulis initiated a widely applied research work at the IChChT, and it became the leading institute in the former Soviet Union in the field of electroplating. Many technological processes developed at the institute were introduced in to the industry at many enterprises throughout the former USSR.

The largest part of J. Matulis scientific papers were published in Russian in the journal *Lietuvos TSR MA Darbai* (Proceedings of the Lithuanian Academy of Sciences), which has been founded by him. Only ca. 9 % of his papers were published in Moscow and ca. 5 % in Western journals. Therefore, not all of J. Matulis works are well known in the scientific world. Nevertheless, in the twentieth century, J. Matulis was one of the most widely cited Lithuanian chemists. His paper "On the characteristics of cathodic processes of nickel electrodeposition" by J. Matulis and R. Sližys published in *Electrochimica Acta* in 1964 [24] up to 1990 was the most frequently cited paper of the IChChT. J. Matulis was an excellent lecturer, and he published several textbooks on physical and colloid chemistry [25, 26].

J. Matulis was not only an outstanding scientist and research manager but also a man of high moral and ethical standards. Being a high-ranking official, he protected scientists from communist functionaries as much as possible. Many victims of the Soviet regime, who have been found unwelcome in other scientific institutions, were employed in the Academy of Science of Lithuania (Fig. 6.4).

6.3.2 Kinetics and the Peculiarities of Metal Deposition from Complexing Electrolytes (R. Višomirskis)

Romanas Višomirskis (1927–1995): He was the first habilitated doctor of science in the field of electrochemistry in Lithuania. He graduated from Vilnius University, *Faculty of Chemistry, in 1951, and a postgraduate student under the supervision of professor J. Matulisat the Institute of Chemistry and Chemical Technology. He defended his doctoral thesis on the subject of overvoltage of hydrogen evolution at chromium in 1954 and his habilitation doctoral thesis in 1966. He was a deputy director and director of the Institute of Chemistry and Chemical Technology from 1958 to 1976 and from 1976 to 1992, respectively, a professor since 1968, and an academician of the Lithuanian Academy of Science since 1976. R. Višomirskis was awarded a Prize in Science of Lithuania in 1971 and a Prize of the Soviet Union Ministry Council in 1984.*

R. Višomirskis was one of the most outstanding electrochemists in Lithuania. He was famous for his deep knowledge of the theoretical, experimental, and applied aspects of electrochemistry, high standards of experimental work, active teaching, and successful scientific administrative activity. He started his scientific career at the IChChT and remained faithful to the institute until the last days of his life. Two important aspects that were to become significant throughout his scientific research activity were apparent from the very beginning. The first one, taking into account the demands of the time, was the area of kinetics and the mechanisms of electrode reactions occurring at the discharge and ionization of metals in solutions of complex salts and the electrochemical behavior of numerous inorganic and organic substances commonly used in electroplating, as well as the interaction of these substances with metal ions and metal substrates [27]. Secondly, R. Višomirskis, like J. Matulis, saw real possibilities to use the results of fundamental in industry and applied investigations not only in Lithuania or the former Soviet Union but also in other countries. The second important aspect was that R. Višomirskis actively worked on many problems of electroplating and made a substantial contribution toward this area, including studies of applied type and original technologies for electrodeposition of Cu, Cd, Zn, Au, Ag, and Pd and some of their alloys. At that time, due to the results obtained by the groups under the supervision of J. Matulis and R. Višomirskis, the IChChT quickly gained a top position in the field of metal plating in the former Soviet Union and in the countries of the former Council of Mutual Economic Assistance. At that time, the leading position ensured a significant additional financial support.

Experimental data obtained by the professor himself and in cooperation with his associates were summarized in his doctoral (now habilitation) thesis entitled “Studies on the kinetics of electrolytic deposition of metals from complex electrolytes” [28], his monograph “Kinetics of electrolytic deposition of metals from complex electrolytes” [29], and in the fifth chapter of the multi-author book “Bright electrodeposits” (ed. J. Matulis) [22]. His publications (there were more than 250 of them) well illustrate the impressive results of research works performed by his group. Many of these publications are certainly a guiding reference for future generations of electrochemists (Figs. 6.5 and 6.6).

R. Višomirskis was known for being a successful teacher. He personally supervised 12 and together with his colleagues 24 doctoral (PhD) theses.

Fig. 6.5 Professor R. Višomirskis (the first from the *left*) one of the organizers of the 37th ISE Meeting in Vilnius, 1986

Fig. 6.6 From *left*: R. Višomirskis, A. Steponavičius, and J. Matulis during the celebration of the 90th birthday anniversary of J. Matulis, Vilnius, 1989

R. Višomirskis had some likings and hobbies. While being a student, he was captivated by chess and was the winner of many prestigious competitions. Later, he became an excellent and successful bridge player.

6.3.3 The Phenomenological Studies of Autocatalytic Metal Reduction and Electrocatalysis (P. A. Vaškelis)

Povilas Algirdas Vaškelis (1937–2009): He was a worldwide recognized expert in the investigations of the autocatalytic metal ion reduction reactions and graduated from Vilnius University, Faculty of Chemistry, in 1959. He had scientific degrees of doctor of science in 1963 and habilitated doctor of science in 1982 at the Institute of Chemistry and Chemical Technology. He was a professor since 1985, academician of the Lithuanian Academy of Science since 1998, and director of the Institute of Chemistry from 1992 to 2001. P. A. Vaškelis was awarded two Prizes in Science of Lithuania in 1989 and 2000. He had internship in J. Heyrovsky Institute of Physical Chemistry in Czechoslovakia in the field of polarography.

The major part of the scientific work of P. A. Vaškelis was devoted to systematic studies of the kinetics and mechanism of electroless deposition of metals and their alloys, as well as to the related processes in solutions (equilibria of metal ion complexes, stability of electroless plating solutions, formation and properties of colloidal metal nanoparticles) and to surface heterogeneous catalysis and electrocatalysis, activation of surfaces, determination of the real surface area, etc. Shortly after the defends of his doctoral thesis using the advantages of polarography, he investigated the formation equilibria of transition metal ion complexes in alkaline and strongly alkaline aqueous solutions, where other methods appeared to be considerably less informative. During the period between 1962 and 2000, he published more than 40 scientific papers related to polarography [30–32].

A significant part of P. A. Vaškelis' scientific work has been devoted to systematic studies of the kinetics and mechanism of electroless deposition of metals and their alloys, as well as to the related processes in solutions (the already mentioned equilibria, stability of electroless plating solutions, formation and properties of colloidal metal nanoparticles) and on the surface (heterogeneous catalysis and electrocatalysis, activation of surfaces, determination of the real surface area, etc.). With these major scientific contributions, P. A. Vaškelis became a worldwide recognized expert in the field [33]. This was achieved by successfully combining fundamental and practical—complementing each other—aspects of scientific research. In 1967, independently of M. Saito (1965, Japan) and M. Paunovic (1968, USA), P. A. Vaškelis proposed a pioneering interpretation of electroless metal ion reduction mechanism on the basis of mixed-potential theory which had been earlier used to describe corrosion processes [34]. This made it possible to figure out that the so-called electroless (or "chemical") metal deposition is just a coupling of two (sometimes even more) partial processes simultaneously occurring

Fig. 6.7 P. A. Vaškelis (on the *right side*) in discussion with J. O'M. Bockris and A. Steponavičius during the 37th ISE Meeting in Vilnius, 1986

on the surface with equal rates, transferring electrons via the depositing metal. This interpretation stimulated the use of electrochemical methods for studying these processes in the whole world, supporting its validity and correctness. However, in due course, it became evident that electrochemical methods of measurement alone are not sufficient for investigating such complex processes inasmuch as the current, measured by varying the electrode potential, represents the overall contribution of several electrochemical reactions, whereas individual contributions remain unknown. All this stimulated the development and utilization of novel combined investigation methods, making it possible to determine the contribution of individual reactions to the overall process. It should be mentioned that a new online electrochemical mass spectrometry method intended for direct analysis of gaseous reaction products was applied for the first time for studying the mechanism and kinetics of chemical metallization using labeled isotopes. Along with this method, for in situ studies of partial reactions of chemical metallization, P. A. Vaškelis et al. were among the first to apply the quartz crystal microbalance technique which enables to determine the variations in electrode mass (with a sensitivity of 10^{-9} g) during metal deposition (Fig. 6.7).

Along with the obvious scientific novelty, these electroless plating processes are distinguished also for their technological novelty (the possibility to electrochemically regenerate the consumed reducing agent by reducing trivalent cobalt ions back to divalent), allowing formation of metal coatings with high technological characteristics on dielectric surfaces, permitting to avoid the use of toxic chemicals (formaldehyde). Therefore, the new electroless metallization processes proposed by P. A. Vaškelis and co-workers attracted the attention of international companies dealing with electroless plating of metals and their alloys. P. A. Vaškelis has written two books [35, 36] and published more than 200 scientific papers whose citation number approaches 1000.

Fifteen doctoral theses were prepared and defended under his guidance and supervision, and two of the 15 doctors later became habilitated doctors. Thus, P. A. Vaškelis has established his own scientific school.

6.3.4 The Relationship and Collaboration with the Frumkin School in Moscow (A. Survila)

Arvydas Survila (1942): He was a disciple of the A. N.Frumkin electrochemistry school in Moscow. He is currently a chief research associate in the Department of Electrochemical Materials Science in the Institute of Chemistry of the Center for Physical Sciences and Technology in Vilnius. He graduated from Moscow State University in 1964 and had his postgraduate studies under the supervision of Prof. A. N. Frumkin and B. B. Damaskin and the scientific degree of doctor of science in 1967 and habilitated doctor of science in 1985 at Moscow State University. He has been a professor since 1992 and head of the Department of Kinetics at the Institute of Chemistry from 1993 to 2007. A. Survila was awarded a Prize in Science of Lithuania in 1993. He had internships in the electrochemistry in the universities in the USA, Germany, and Poland.

As a successful student of Vilnius University, where A. Survila specialized in chemical engineering, he was elected to continue his studies at Moscow State University. After graduation he was invited to continue education in postgraduate studies. Adsorption of some organic compounds on mercury was the subject of his doctoral studies during which A. Survila succeeded to obtain experimental material for seven publications, among which was the article by A. N. Frumkin, B. B. Damaskin, A. A. Survila "The congruence of the adsorption isotherm with respect to the electrode potential or charge and the choice of an independent electric variable" [37], which became one of the key studies and has not lost its value up to date (Fig. 6.8).

After returning to Vilnius A. Survila has been employed in the IChChT. At that time, the institute's work has been directed toward the development of various electroplating processes with a view to their implementation in industry. Studies conducted here were mainly of applied character. There was a certain control on publications of results of the research, which could be the subject of practical application. Publications in international journals were not promoted, and materials

Fig. 6.8 From the *left*: A. Survila, O. Petrii, and B. Damaskin in Moscow State University, 1964

prepared for such rare submissions were subject to special procedures. Therefore, the main journals were the local *Proceedings of Lithuanian Academy of Sciences* and, in some cases, the Russian journal *Elektrokhimiya*.

A. Survila had to change his research interests and switch to the study of electrodeposition of metals from solutions containing complex compounds. In addition to these scientific interests, photoelectrochemistry also played a certain role. During the period of 1968–1990, he has published more than 40 scientific articles, among which there are 13 theoretical publications, written by one author. During this time, he prepared and successfully defended (1986) his habilitation thesis, the materials of which have been published as monograph: "*Electrode processes in systems of labile complexes of metals*" [38]. He was appointed as the head of the Department of Electrochemical Kinetics at the Institute of Chemistry. At the same time, A. Survila engaged intensively in pedagogical activities, teaching at Vilnius Pedagogical University, Vilnius University, and the newly restored Vytautas Magnus University (Kaunas). In total he has read more than ten different courses, including physical chemistry, electrochemical kinetics, photoelectrochemistry, electrochemistry of complex compounds, etc. He was a supervisor of 12 PhD researches. A. Survila has received numerous scientific awards including the Prize in Science of Lithuania and J. Matulis Award from Lithuanian Academy of Sciences.

6.3.5 Bioelectrochemistry and Biosensors (J. Kulys, V. Razumas)

Juozas Kulys *(1944): He is a Lithuanian biochemist, currently the head of the Department of Chemistry and Bioengineering at Vilnius Gedimino Technical University, and a principal research associate in the Institute of Biochemistry of Vilnius University. He graduated from Moscow State University in 1967 and had his scientific degree of doctor of science in 1970 at Moscow State University and habilitated doctor of science in 1982 at the Moscow Institute of Chemical Physics. He has been a professor since 1984 and academician of the Lithuanian Academy of Sciences since 1996. J. Kulys was awarded a Prize in Science of Lithuania in 1987.*

Valdemaras Razumas *(1955): He is a Lithuanian biochemist, currently the president of the Lithuanian Academy of Sciences, and a principal research associate in the Institute of Biochemistry of Vilnius University. He graduated from Vilnius University, Faculty of Chemistry, in 1978 and had his scientific degrees of doctor of science in 1981 and habilitated doctor of science in 1990 at Moscow State University. He has been a professor since 1993 and became the director of the Institute of Biochemistry in Vilnius, from 1992 to 2004. V. Razumas was awarded with a Prize in Science of Lithuania in 1987.*

Bioelectrochemistry belongs perhaps to one of the most efficient fields of Lithuanian electrochemistry. It integrates many branches of physical sciences, like electrochemistry, biochemistry, enzymology, polymer synthesis, etc. The field arose in the mid of 1970s at the Institute of Biochemistry. It was initiated by J. Kulys and performed by his numerous students and successors, the most prominent of which were A. Malinauskas and V. Razumas. At that time, with a few exceptions, it seemed unlikely to combine the redox or electron transfer processes occurring in living systems, with electrochemical processes taking place at electrode–electrolyte interface. Therefore, at its very beginning, this field was met with a lot of skepticism, both from the traditional electrochemists and from traditional biologists and biochemists. However, just the first attempts to combine enzyme-catalyzed and electrochemical electron transfers were highly successful, and the research developed in various directions. First, bioelectrochemical systems with the participation of oxygen-dependent oxidases were studied. Among them, highly important enzymes like glucose oxidase or lactate oxidase were incorporated into electrochemical systems, and important so-called first-generation biosensors for the detection of glucose and other metabolites were created, based on electrochemical detection of the reaction product hydrogen peroxide. In collaboration with some Lithuanian enterprises, these glucose sensors have been successfully commercialized to the market of medical diagnostics, known as Eksan-G. Numerous studies have been performed on bioelectrochemical systems with the use of electron transfer mediators—low molecular mass compounds able to shuttle the electrons between the enzymes and electrode. Systems comprising a variety of redox enzymes including oxidases or dehydrogenases have been studied, and numerous prototypes of "second-generation" biosensors were developed. Also, more complex biological components like coenzyme-dependent biocatalysts and intact or processed bacterial or yeast cells were studied in bioelectrocatalytic systems. Interestingly, some non-redox enzymes were also successfully included into bioelectrocatalytic systems. Later, bioelectrochemical systems with direct electron exchange between the biocomponent and electrode material were created, based on a numerous PQQ-dependent enzyme class. J. Kulys and V. Razumas have written several books [39–41], while J. Kulys published more than 400 scientific papers whose citation number approaches 4000. Both J. Kulys and V. Razumas are among the most cited scientists in Lithuania.

6.4 The Period of Restored Independence (The Last Decade of the Century)

6.4.1 Conductive Polymers and Spectroelectrochemistry (A. Malinauskas, G. Niaura)

Albertas Malinauskas (1952): He is the most cited electrochemist in Lithuania and is currently the head of the Department of Organic Chemistry in the Institute of Chemistry of the Center for Physical Sciences and Technology in Vilnius and Professor of Chemistry faculty at Vilnius University (part-time). He graduated *from Vilnius State University, Faculty of Chemistry, in 1975 and had his scientific degree of doctor of science in 1979 at Moscow State University and habilitated doctor of science in 1994 at the Institute of Chemistry and his internships in the electrochemistry of conductive polymers at universities in Germany and Sweden.*

Gediminas Niaura (1956): He is a recognized expert in spectroelectrochemistry and Raman spectroscopy. He is currently a chief research associate in the Department of Organic Chemistry in the Institute of Chemistry of the Center for Physical Sciences and Technology. He graduated from Vilnius State University, the Faculty of Physics in 1979, and got his scientific degrees of doctor and habilitated doctor of sciences from the Institute of Chemistry (Vilnius) in 1992 and 2002, respectively. G. Niaura spent 3.5 years as a quest researcher at the National Institute of Standards and Technology in the USA. In 1997, he returned to the Institute of Chemistry in Vilnius.

In the early 1990s, some new research directions appeared at the ICh, thus going out of the narrow frame of metal electrochemistry, practiced during the last few decades. As one of these new directions, electrochemistry of modified electrodes along with the synthesis and study of new materials for this modification has been developed. Thematically, this direction resembled the tendencies of modern science of that time; therefore, it appeared reasonable to start this study, while the pioneer in ICh in this area was A. Malinauskas. The second reason for this choice was in that some of its simplest aspects do not require any sophisticated equipment. The 1990s was perhaps the most difficult period for research in Eastern Europe since World War II, especially in terms of financing. Despite of this, it appeared realistic to start this direction with the use of actually available equipment, leaving the more sophisticated studies for a hopefully better future.

The first works relate to polyaniline—one of the simplest and most extensively studied materials at that time, presenting the newly discovered class of conducting polymers. Thin layers of polyaniline were deposited onto inert electrodes following either chemical or electrochemical polymerization, and studies on their properties have been performed, including the dependence of redox properties of the resulting material on reaction variables used in its preparation, the specific effects of these layers like the slow electrochemical relaxation, etc. [42, 43]. Also, copolymers of aniline with related materials have been prepared, and their specific properties were studied [44, 45]. Next to this, electrocatalytic reactions of solution species at electrodes covered with conducting polymers were studied [46, 47]. Attention has been paid to the use of these modified electrodes as amperometric sensors for the determination of some analytes like ascorbic acid. Next to conducting polymers are electrodes modified with inorganic complexes, and electrocatalytic reactions at these electrodes were studied. Based on this, amperometric sensors for hydrogen peroxide were developed. With the use of additional layers containing enzymes and some polymers, biosensors for glucose, lactate, and other biologically important substances were developed [48].

Raman spectroscopic studies of electrochemical interface at the IChChT have been started in 1986 under the supervision of the prominent spectroscopist, the chief of the department of Organic Chemistry Z. Alaunė. The Raman spectrometer has been adapted for in situ surface-enhanced Raman spectroscopic (SERS) study of the structure of adsorbed species at electrode surfaces under electrochemical potential control by A. Malinauskas and the PhD student G. Niaura. In the period from 1986 to 1993, the work has been focused on the spectroelectrochemical analysis of the redox transformations of adsorbed phenazine dye [49] and on the structure of inorganic ions (Cl^-, ClO_4^-, and SO_4^{2-}) at copper electrode surface [50, 51]. ^{63}Cu and ^{65}Cu isotopes have been introduced for the analysis of Cu−Cl vibrational mode [50]. In 1991 the first SERS spectrum of specifically adsorbed SO_4^{2-} ions was published [51]. Considerable broadening and frequency shift to lower wavenumbers as comparing with solution species was detected. A detailed potential-dependent SERS study on the adsorption of ClO_4^- and SO_4^{2-} ions at copper electrodes was published in 1998 [52]. In this work, spectroscopic markers useful for the discrimination of chemisorption vs. physisorption of oxyanions were provided. Based on these markers, the following adsorbtivity order of anions at Cu electrode was found: $Cl^- > SO_4^{2-} > ClO_4^- \geq HSO_4^-$. An important consequence of chemisorption of anions at interface is the possibility of formation of ion pairs with organic cations [53]. It was demonstrated that the acridinium cation can be detected by SERS technique in the form of an ion pair with Cl^- anion on Cu electrode at solution concentrations down to 6.7×10^{-9} M [54]. Starting from 1995, the potential-dependent SERS studies were extended to the analysis of structure and orientation of adsorbed biomolecules at Cu electrode surface. In close collaboration with scientists from the Institute of Biochemistry in Vilnius, V. Razumas, and Z. Talaikytė, different adsorption states of histidine, depending on solution pH, electrode potential, and the presence of SO_4^{2-} or Cl^- anions were spectroscopically detected [55]. In 1999−2000, the spectroelectrochemical research was focused on the potential-dependent interaction of OH^- anions with Cu surface and formation of surface oxide [56]. Two different states of adsorbed OH^- ions at Cu electrode surface have been discovered. A. Malinauskas and G. Niaura were awarded Lithuanian Science Prize in 2003.

6.4.2 *Electrochemical Materials Sciences (E. Juzeliūnas, R. Ramanauskas)*

Eimutis Juzeliūnas (1958): He is the initiator of the electrochemical materials science research in Lithuania. He is currently the rector of the Klaipėda University and (part-time) a chief research associate in the Department of Electrochemical Materials Science in the Institute of Chemistry of the Center for Physical Sciences and Technology at Vilnius. He graduated from the Faculty of Chemistry of Vilnius State University in 1981 and got his scientific degree of doctor and habilitated doctor of sciences from the Institute of Chemistry (Vilnius) in 1986 and 1994, respectively. He became professor since 1998, a fellow of Alexander von Humbolt foundation 1993–1988, and director of the Institute of Chemistry in Vilnius, since 2001 till 2010.

Rimantas Ramanauskas (1952): He is currently the deputy director of Center for Physical Sciences and Technology and the head of Institute of Chemistry in Vilnius *and (part-time) professor of Chemistry faculty at Vilnius University. He graduated from the Faculty of Chemistry of Vilnius State University in 1975 and got his scientific degrees of the doctor of science in 1980 from Institute of Chemistry and Chemical Technology, Vilnius, and habilitated doctor of science in 1999 from Institute of Chemistry. He was a member of the International Metal Corrosion Testing laboratory, Havana, Cuba, in 1987–1989, and a research associate at the Research and Advanced Study Center in Merida, Mexico, in 1994–1998.*

The last decade of twentieth century saw rapid development in the area of research which can be identified as electrochemical materials science. This multidisciplinary field of science included not just investigations of electrodeposition of functional coatings with exceptional anticorrosive, magnetic, or other properties but also the application of electrochemical methods for the processes related to environmental protection, corrosion of metals in the atmosphere, model systems and geothermal water, as well as the development of noninvasive methods for the evaluation of corrosion damage. Significant results in this area were achieved by the scientific groups supervised by E. Juzeliūnas and R. Ramanauskas.

In the area of environmental electrochemistry, E. Juzeliūnas studied the electrochemical behavior of metal complexes with EDTA and corrosion of metals in geothermal water. Comprehensive analysis of electrochemical reduction of Me-EDTA complexes was performed using methods of voltammetry and quartz crystal microgravimetry [57]. The results of these investigations are important, primarily, for the development of environmental technologies for binding heavy metals into complexes in soil and using subsequent recovery of metals on the electrodes in situ. When investigating the possibilities to remove nitrogen monoxide (NO) by means of electrochemical methods, Fe(II)-EDTA compound was applied as complexing agent [58, 59]. Under the guidance of E. Juzeliūnas, wide-ranging work was done studying the corrosion of metals in geothermal water (Devonian and Cambrian) of western Lithuanian region [60]. The studies were funded by European Commission (program Joule 2).

Using the most sensitive modern magnetic sensors, E. Juzeliūnas demonstrated that it is possible to remotely detect corrosion activity even through dielectric ambience as well as under hydrodynamic conditions. The results obtained promoted the development of noninvasive detectors of corrosion activity. The work was performed in cooperation with experts of SQUID magnetometry and device producers from Germany (FIT Messtechnik GmbH) and USA (Vanderbilt university) [61–63]. In the period 1990–2000, E. Juzeliūnas had won prestigious research fellowships, grants, and awards from the Alexander von Humboldt foundation (Germany) and the American Chemical Society (USA). Beside traditional investigations in the field of metals electrodeposition, he pioneered the research in the area of magnetronic sputtering of alloys, which gained momentum in the following decade [64].

During the period between 1987 and 1989, R. Ramanauskas initiated investigations on the atmospheric corrosion of Zn electrodeposits in the tropical climate of Cuba, and he continued similar studies later on (1994–1998) in Mexico. In spite of the aggressive conditions of the tropical climate, atmospheric corrosion studies last for several years. Therefore, one of the most important results of these investigations was the elaboration of the model of Zn coating corrosion, which was designed on the basis of statistical analysis of the data obtained under the natural and accelerated test conditions. The latter model enables to make predictions of the metal corrosion losses under different conditions, if the data on the pollutant concentration and the time of wetness are available [65].

The fundamental research on the relationship between metal structure and corrosion behavior of Zn and Zn alloy coatings was carried out by R. Ramanauskas with a view to enhance the corrosion resistance of Zn coatings. The aim of these studies was to elucidate the reasons of higher corrosion resistance of some of the alloys. The results obtained indicated that inhibition effect is related to the structural and electronic properties of the oxide films formed on the metal surface [66]. However, the most complete understanding of the nature of corrosion behavior of Zn and Zn alloy coatings was achieved when the relationship between the corrosion rate and the metal structural parameters such as its texture, morphology, grain size, and number of lattice imperfections was established [67, 68]. Apparently the structure of Zn coatings enhances the stability of passive films on their surface.

Clarification of the influence of metal structure on its corrosion behavior extends the limits of perception of this electrochemical phenomenon and enables to seek for new strategic solutions in the field of metal corrosion protection.

The research activities in the field of electrochemical materials science included electrochemical studies of metals and alloys, which were conducted, employing such methods as cyclic voltammetry, electrochemical impedance spectroscopy, quartz crystal nanogravimetry, etc. These investigations in all cases were supported by the characterization of crystalline structure and chemical and phase composition of deposited layers, by means of transmission electron microscopy (TEM), electron diffraction, scanning electron microscopy with microprobe (EDX) analysis, X-ray and Auger electron spectroscopies (XPS), and X-ray diffraction (XRD) techniques. The latter studies were conducted in collaboration with the colleagues from the ICh department of materials structure characterization (R. Juškėnas, A. Selskis, and V. Jasulaitienė).

For their research activities in the field of electrochemical materials science, which began in the last decade of the twentieth century, E. Juzeliūnas and R. Ramanauskas were awarded Lithuanian Science Prize in 2007.

6.4.3 Electrocatalysis (E. Norkus, Z. Jusys)

Eugenijus Norkus *(1955): He was a student and successor of Prof. P. A. Vaškelis. He is currently the head of the Department of Catalysis in the Institute of Chemistry of the Center for Physical Sciences and Technology in Vilnius. He graduated from Vilnius State University, the Faculty of Chemistry, in 1978. He got his scientific degrees of doctor of science in 1988 from the Institute of Chemistry and Chemical*

Technology, Vilnius, and habilitated doctor of science in 1999 from the Institute of Chemistry, has been a professor of Chemistry at Vilnius University (part-time) since 1996, and has internships in the field of electroless metal plating at the universities in Germany and the USA.

Zenonas Jusys *(1959): He was a student and successor of Prof. P. A. Vaškelis. He is currently a leader of the electrocatalysis group at the Institute of Surface Chemistry and Catalysis, Ulm University, Germany. He graduated from Vilnius State University, the Faculty of Chemistry, in 1982. He got his scientific degrees of the doctor of science in 1990 from the Institute of Chemistry and Chemical Technology, Vilnius, and habilitated doctor of science in 1998 from the Institute of Chemistry. In 1993–2000, he was a division leader at the Institute of Chemistry and in 1998–2004 associate professor at Vilnius Pedagogical University (part-time). He had postdoctoral experience in Germany (1991, 1993, 1995, and 1997) and the USA (1998–1999).*

During the last decade of the twentieth century, E. Norkus and Z. Jusys together with their tutor P. A. Vaškelis and individually, joining international research teams, proceeded with research of the kinetics and mechanism of electroless metal deposition processes [69, 70]. Individual partial reactions were systematically studied using online mass spectrometry (oxidation of reducing agent), deuterium labeling, the kinetic H/D isotope effect, and in situ quartz crystal microbalance (reduction of metal ions) [71–73]. Fundamental aspects of the novel class of electroless plating processes, involving metal ion complexes as the reducing agent, were studied intensively [74, 75]. The potential dependence of partial reactions, their mutual interaction, their individual rates under open-circuit conditions, and the rate-determining step were independently examined and specified. This series of works was awarded J. Matulis award of the Lithuanian Academy of Science in 1997 and the Lithuanian state Science award in 2000 (P. A. Vaškelis, E. Norkus, Z. Jusys).

Z. Jusys initiated electrochemical remediation studies of wastewater from toxic pollutants, namely, chlorinated phenols, by their oxidation on polycrystalline Pt electrode in alkaline solution, for the product detection applying electrochemical, microgravimetric, gas chromatographic, and mass spectrometric techniques [76]. Electrochemical degradation efficiency of these hazardous contaminants was found to depend on the degree of chlorination and the substituent position in the aromatic ring.

6.5 Electrochemistry in Kaunas Technical University

Jonas Janickis (1906–1998): He was the founder of manganese and selenium electrochemistry school at Kaunas University. He graduated from Technische Hochschule Dresden (now Technical University) in 1930, had his scientific degrees of a doctor of science in 1931 from Technische Hochschule Dresden and habilitated doctor of science in 1949 from Moscow State University. He was a professor of

Vytautas Magnus University (since 1949), head of the department of Physical Chemistry at Kaunas Technical University from 1951 to 1977, and academician of the Lithuanian Academy of Sciences since 1956.

Acquaintance at Dresden Higher Technical School with professor of inorganic chemistry Fritz Förster caused J. Janickis to get interested in the chemistry of sulfur and selenium compounds. He worked under the guidance of the famous electrochemist Professor E. Müller at the Department of Electrochemical and Physical Chemistry in Dresden. Here he became interested in electrochemistry and began his first serious research in this field. The rather exotic phenomenon, current and potential oscillations of iron and nickel electrodes, was investigated, and the results were published in "Zeitschrift für physikalische Chemie" in 1932 [77]. His studies in Dresden helped him to acquire sound basic skills of research in inorganic as well as electrochemistry.

Soon after the end of the World War II, J. Janickis became interested in a new and promising research field—manganese electrochemistry. The discovery (1954) that selenious acid in manganese electrolyte highly enhances current efficiency, stabilizes the whole process, as well as enables to deposit manganese from unrefined solutions was a strong stimulus for further research [78]. It was widely applied in electrochemistry at one of the largest centers of manganese electrochemistry in Tbilisi, Georgia (Acad. R. J. Agladze, N. T. Gofman et al., Georgian Academy of Sciences). During later years, J. Janickis was in touch with the Georgian school of electrochemistry (Fig. 6.9).

For a long time, no satisfactory explanation of the effect of selenium compound additive on electrodeposition of manganese could be offered. The problem has been recently cleared after having investigated the process of metallic manganese dissolution in electrolytes containing selenium compounds. These investigations resulted in the formulation of the principles of behavior of selenium containing additives and, consequently, the peculiarities of their effect on manganese electrodeposition.

During the late 1950s, J. Janickis turned his attention to electrochemistry of selenium compounds. The first experiments were related to electrolytic oxidation of selenothionates. Then the experiments acquired a more practical bias and developed into a more practical contemporary scientific school. A systematic research of sodium selenite oxidation process resulted in a new method of obtaining crystalline sodium selenate by means of electrolysis. He published over 200 articles in scientific journals. Forty-eight theses for doctor degree were maintained under his direct supervision, seven of them for a habilitated doctor degree by presently well-known scientists, V. Zelionkaitė, A. Kazragis, E. Pacauskas, A. Prokopčikas, A. Sadūnas, K. Sasnauskas, and B. Stulpinas.

J. Janickis published two manuals. The first one, *Introduction into Physical and Colloid Chemistry*, was published in 1947 [79], while the first edition of the *Physical Chemistry* appeared in 1963 [80], the second reviewed edition being published in 1987.

Fig. 6.9 From *left*: J. Janickis and R.I. Agladze during the 37th ISE Meeting in Vilnius, 1986

6.6 Electrochemistry in Vilnius University

It was the initiative of Prof. J. Matulis to begin the electrochemical research in the Department of Physical Chemistry of Vilnius University, which was established in 1941 and headed by J. Matulis himself. As a matter of fact, very soon, in 1950, J. Matulis resigned as head of Department and worked part-time, but his postgraduate students set the tone and direction for the whole scientific research in the department for long years [6]. By the end of sixth decade, Lithuanian electrochemists decided that it would be appropriate to differentiate the research areas and scientists of Vilnius University engaged in studies of silver electroplating. The works of head of the department Prof. V. Kaikaris and his co-workers received recognition not only in Lithuania but abroad as well. V. Kaikaris generalized the investigations of his postgraduate students (I. Pivoriūnaitė, T. Jankauskas, V. Skučas, etc.), and in 1969 he defended doctoral dissertation in chemistry entitled “Study of silver electrodeposition processes” [81]. V. Kaikaris proposed bi-factor theory of bright coatings formation and new morphological classification of electrodeposited coatings and brighteners. Later, investigations of electrodeposition of silver alloys with other metals were successfully performed by P. Juzikis, V. Daujotis, G. Baltrūnas, H. Cesiulis, who defended dissertations in the Department of Physical Chemistry. Over 250 papers published by the workers of the Department are devoted to problems silver electrodeposition.

J. Matulis was also the initiator of studies of electrochemical processes in nonaqueous solutions, which were performed by L. Simanavičius and A. Levinskas in the Department of Physical Chemistry of Vilnius University. These scientists set up the Laboratory of Electrochemistry of nonaqueous solutions in 1963 and began investigations of aluminum electrodeposition. Workers of the department (A. Sinius, B. Ingaunytė, S. Armalis, G. Zagidulinas, etc.) performed thorough studies of two- and three-component aluminum halogenide ether systems for aluminum plating. The research was generalized in A. Levinskas dissertation "Investigation of aluminum electrodeposition from ether electrolytes," which was defended in 1976 [82]. About 120 papers were published by the workers of Laboratory of Electrochemistry of nonaqueous solutions.

After J. Matulis and V. Kaikaris, the Department of Physical Chemistry in the second half of twentieth century was headed by Professors A. Levinskas, A. Survila, G. Baltrūnas, and T. Jankauskas.

6.7 Final Remarks

Twentieth century was extremely favorable and productive for electrochemical sciences worldwide and in Lithuania as well. Achievements in this field of science made during the periods of independence (1900–1939 and 1990–2000) as well as in the meantime, which brought about specific restrictions, are undeniable. To be fair, it should be acknowledged that before the World War II, only the foundations for development of electrochemical science were laid, while the most important accomplishments belong to the later period. Fundamental and applied research initiated by J. Matulis spread out into such areas as autocatalytic metal reduction, bioelectrochemistry, spectroelectrochemistry, and electrochemical materials science. The development of electrochemical science in Lithuania was greatly influenced by insightful decision of J. Matulis, made in the period of the profiling of the institutes of Lithuanian Academy of Sciences, to choose the area of metal electrodeposition, which was promising in all respects. Another factor of no less importance was the Department of Physical Chemistry, founded by the same J. Matulis in the Faculty of Chemistry of Vilnius University, which kept high scientific and educational standards and became a productive training center of qualified electrochemists [6]. One more impetus for the development of electrochemical science in Lithuania is related with the activities of the group of talented disciples of J. Matulis, headed by R. Višomirskis. Theoretic seminars, organized by R. Višomirskis, during the period of two decades (1970–1990), educated the new generation of Lithuanian electrochemists and laid foundations for their future achievements. The majority of chemists, who graduated from Vilnius University, came to IChChT (Institute of Chemistry and Chemical Technology) and started their PhD studies under the guidance of Professors J. Matulis, R. Višomirskis, A. Prokopčikas, and A. Vaškelis. Almost all PhD students had to pass the mandatory examination in electrochemical kinetics, with R. Višomirkis as examiner, and the course was based on the famous handbook by K. Vetter *Electrochemical Kinetics* [83], which was translated into Russian. It should be noted here that access to scientific literature was sufficiently well organized, at least in IChChT. Owing to world-famous A. Frumkin school in Moscow, Soviet Union subscribed high-ranking international electrochemical journals and book series (monographs), which reached the library of IChChT. At present, this library is proud to have the following collections of journal series, *Journal of Electrochemical Society*, since 1952; *Transactions of the Institute of Metal Finishing*, since 1955; *Electrochimica Acta*, since 1959; *Corrosion Science*, since 1961; *Journal of Electroanalytical chemistry*, since 1962; soviet journals *Electrokhimiya and Metal Protection*, since 1965; etc., and the following books as *Modern Aspects of Electrochemistry* [84], *Advances in Electrochemistry and Electrochemical Engineering* [85], *Electroanalytical Chemistry: A Series of Advances* [86], *Encyclopedia of Electrochemistry of the Elements* [87], and *Comprehensive Treaties of Electrochemistry* [88]. In the second half of the twentieth century, many translated books by K. Vetter [83], E. Yeager and A. J. Salkind [89], J. S. Newman [90], and J. A. Plambeck [91] were issued in the Soviet Union along with those of Frumkin school authors, such as A. N. Frumkin [92, 93], B. B. Damaskin, O. A. Petrii [94], etc. These books were available in the specialized bookshops as well as in the libraries of universities and institutes. Thus, Lithuanian scientists were quite well informed about the international achievements in electrochemistry, though this information was a little late, because part of the journals obtained by the library of IChChT (e.g., *Electrochimica Acta*) were not originals, but the copies were made in the Soviet Union. In the second half of the twentieth century, the scientists of IChChT were quite well provided with Soviet-made electrochemical equipment, the possibilities of which were, however, quite limited. Therefore, in order not to lag behind the foreign colleagues, they constructed the equipment of measurements themselves. For instance, K. Juodkazis and B. Šebeka made an installation for nonsteady-state polarization measurements [95], P. Miečinskas with colleagues constructed computer automated measurement and control workstation for the study of electrochemical kinetics by impulse methods for the determination of electrode capacitance and solution resistance by short current pulses, and in the period between 1987 and 1990, computerized data collection and control program for electrochemical quartz crystal microbalance (EQCM) method was implemented. Materials science-related research requires the equipment for structural characterization. In the IChChT, transmission electron microscope JEM-5W started to work in 1965, and scanning electron microscope-microanalyzer JXA-50A started operating in 1976, whereas X-ray photoelectrons and Auger electron spectrometer ESCALAB-MK-II were launched in 1986.

Could there be more accomplishments in electrochemistry in Lithuania in the period after the World War II and could they be more significant? Comparison of the achievements of Lithuanian electrochemists during the last decade of twentieth century with those of postwar period can help to find the answer to this question. The major drawback of the soviet system was the isolation of the Soviet Union from the outside world. Extremely limited and only formal contacts with colleagues abroad were possible. Training, cooperation, and use infrastructure of foreign scientific centers were practically impossible. In small Soviet republics, like Lithuania, this isolation was even more severe. A kind of discrimination, often pointed out by the president of Lithuanian Academy of Sciences J. Matulis, consisted in the fact that funding for subdivisions of Soviet Academy of Sciences was less compared to Moscow institutions. Restrictions were also imposed by the central government regarding the changing or expansion of the research areas.

The last decade of twentieth century was sufficiently difficult for Lithuanian science, as it was the period of cardinal reforms, reorganizations, and severe lack of funding for science, education, as well as other spheres of life. Because of changes in political and economic relations with Russia, almost all contracts with Russian companies were broken, the financial situation of IChChT grew worse, and therefore, the number of employees reduced almost twice. The scientific research had to be focused on serving the purposes of Lithuania. At the same time, relations with western scientists were intensified. Representatives of such companies as "MacDermid," Schering, and Blasberg, Shipley visited Institute of Chemistry and discussed the joint research programs. In 1990 the US company, "MacDermid" acquired the license for alkaline Zn-Co alloy plating. In 1993 "Atotech" company acquired the license for technology of conductive sulfide films formation on dielectric surface. The reform of organizing conferences and scientific journals was beneficial for dissemination of research results and joining the international research community. Since 1955, the journal *Works of Lithuanian Academy of Sciences: Natural and Applied Sciences* was published in Russian. Since 1990 this journal was reorganized into journal *Chemija*, the papers in which are published in English. The proceedings of conferences of Lithuanian chemists are also published in English since 1993, whereas the conference itself has become international. The last decade of twentieth century saw the boom in the number of electrochemistry-related conferences both in Lithuania and neighbor countries. In 1996, First Baltic Conference on Interfacial Electrochemistry took place in Tartu, Estonia. Second Baltic Conference on Electrochemistry was held in 1998 in Lithuanian resort of Palanga. Both conferences were supported by International Society of Electrochemistry (ISE). Attention of ISE toward these regional conferences meant the international acknowledgment of the works of Lithuanian electrochemists and increasing prestige of Lithuanian science. The number of ISE members in Lithuania as well as participation of Lithuanian scientists in ISE conferences gradually increased. A. Vaškelis became the first regional representative of Lithuania in ISE. In 1997 and 1999, the Institute of Chemistry organized joint trips of scientists to the Joint International Meeting of the Electrochemical Society and International Society of Electrochemistry in Paris and to the 50th Annual ISE Meeting in Pavia, Italy. Oral and poster presentations were made by a number of scientists of the Institute of Chemistry. When various scientific research support funds, like Soros fund, began their activities in Lithuania, not just leading scientists but also the younger ones could go to conferences and even to remote countries. In 1998, A. Vaškelis, A. Survila, R. Ramanauskas, and PhD

Fig. 6.10 From *left*: R. Ramanauskas, A. Survila, D. Jelinskienė, and A. Vaškelis during 49th Annual ISE Meeting in Kitakyushu, Japan, 1998

Fig. 6.11 From *left*: E. Gileadi and R. Ramanauskas during second Baltic Conference on Electrochemistry in Palanga, Lithuania, 1999

student D. Jelinskienė made presentations in the 49th Annual ISE Meeting in Kitakyushu, Japan (Figs. 6.10 and 6.11).

After reestablishing independence, individual initiatives of Lithuanian electrochemists in search for international cooperation were also successful. In 1991 V. Reipa began working in National Institute of Standards and Technology in the USA, and G. Niaura worked in the same institute in the period of 1994–1995. In 1993 P. Juzikis received European Union grant for work in Germany; in the period between 1995 and 1998 E. Juzeliūnas won prestigious research fellowship from the Alexander von Humboldt-Stiftung foundation (Germany); Z. Jusys has won Volkswagen fellowship; R. Ramanauskas worked in the Research and Advanced Study Center in Merida, Mexico, since 1994 till 1998; and A. Malinauskas during the period between 1994 and 1996 worked in Chemnitz University of Technology (Germany) and later, in 1998, in Lund University (Sweden). In 1994 group of scientists headed by A. Vaškelis has won the grant of International Foundation for Science for studies of catalytic reactions. All these facts demonstrate that efforts of Lithuanian electrochemists to integrate into international research area and to search for new scientific contacts and possibilities of cooperation in the last decade of twentieth century were productive. A qualitative change occurred in the field of scientific production as well. In the period between 1950 and 1990, 227 doctoral and 13 habilitation theses were defended in the Institute of Chemistry and Chemical Technology, and the majority of them were in the field of electrochemistry and physical chemistry. During 1991–2000, 46 doctoral and eight habilitation theses were defended. It should be pointed out that before 1990 scientists of Institute of Chemistry published 160 papers in the ISI Web of Science journals, whereas during 1991–2000, 119 such papers were published. Not merely the increase in number is important here, but the international acknowledgement as well. While the majority of papers belonging to soviet period were practically inaccessible to global scientific community due to language barrier and insularity of the journals and, consequently, scarcely cited, the papers written during the last decade of twentieth century by Lithuanian electrochemists, A. Malinauskas [44–48], G. Niaura [56, 96], J. Kulys [97, 98], R. Razumas [99–101], Z. Jusys [71], and R. Ramanauskas [68], are cited at least 70 times or more. A. Malinauskas is the leader of the list: his papers published in the period of interest were cited more than 1300 times. It should be noted that the most cited publication of the soviet period is the abovementioned paper by J. Matulis and R. Sližys written in 1964 [24], which is cited 46 times. These figures plainly illustrate the fact that working in the open international scientific community is much more productive and more favorable for creation of research output of higher quality. Hopefully, the Lithuanian electrochemical science, which develops now under such conditions, will contribute to global progress in this particular area of research.

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Chapter 7

Before the Iron Curtain Came Down: Electrochemistry and Electrochemists in Kiev in the Last Quarter of the Twentieth Century

Aleksandr A. Andriiko

Looking back over the history of the electrochemistry in the twentieth century, it is important to understand that the pre-war generation of scientists of the former Soviet Union did not yet feel that they were living in a Divided World. The scientific world remained united for them. They knew Western European languages, they had published papers in Western European journals (mostly Germans), and they kept connections with Western scientists by mail. “Why should I be afraid of Germans? I know Tamman, I know Nernst—very nice people they are”. These were the words of Prof. Plotnikov according to Prof. Yuriy Fialkov’s memory. Plotnikov decided to stay in Kiev during the Nazi occupation in 1941. It was a tragic decision which ruined his scientific carrier and life—because he did not understand that, by then, the world was in fact already divided.

The world became ultimately and severely divided in times of the Cold War. The Iron Curtain fell down at the end of the 1940s, and we were totally isolated from the West. Publishing papers in the international journals became only a dream. Any direct communication with Western colleagues was impossible for Soviet scientists because of severe censorship.

Thus, we were cut off from the scientific mainstream. Evidently, that is why we cannot find such prominent figures as Faraday or Nernst among the Ukrainian electrochemists. However, we have nothing to be ashamed of. There are some significant scientific results of worldwide importance, which were obtained in the Ukraine.

It is hardly ever possible to overview all scientific achievements of Ukrainian electrochemists in the twentieth century. That is why I restricted my memory to only a few most prominent scientists who were working in Kiev over the last

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30 years of the twentieth century and whom I knew personally. They were working in the Institute of General and Inorganic Chemistry (IGICh) of the Ukraine or tightly collaborated with this institute.

7.1 The Institute of General and Inorganic Chemistry and Its Directors at the End of the Century

The institute was founded in 1918, when academician V. I. Vernadsky, the first president of the Academy of Sciences, set up a chemical laboratory within its Physical and Mathematical Department. It was transformed into the Institute of Chemistry in 1929–1930.[1]

Academician Yuriy Konstantinovich Delimarskiy (1904–1990) was the director of IGICh since 1960. In 1973, he retired from the directorship and concentrated on his duties as the head of the Department of Molten Salt Electrochemistry.

He was already an old man when I joined his department in 1974. Everybody in the institute named him unofficially as "grandpa". Nevertheless, he was a highly organised person with a fantastic scientific productivity. I remember his "organiser" in those precomputer times. It was manifold narrow (about 5 cm wide) strips of paper (we called it *garmoshka*), each fold of it containing a note about a certain task for a certain hour of a day. Two handwritten pages were his daily assignment.[2] The results of this hard work were more than 800 papers, 83 inventions and 17 monographs covering all aspect of the chemistry and electrochemistry of molten salts.[3]

Biographical Reference

Yuriy Konstantinovich Delimarskiy was born on April 23, 1904, in the village of Krasnopolska, Vinnytsia district, Ukraine. He graduated from the Kiev Institute of People's Education in 1928 and worked at the Kiev Polytechnic Institute from 1932 to 1934. Since 1934 till the end of his life, he was working in the IGICh.[4] He was a member of the Ukrainian Academy of Sciences since 1957 and professor of Kiev State University from 1974. He was a recipient of the following awards: the

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[1] For the history of IGICh, see www.ionc.kar.net.

[2] There was his own typist whose formal position was a technician. She typed his manuscripts, then it was corrected and improved, and after that the manuscript was retyped again. Sometimes he himself typed his manuscripts at home. I remember his portable foreign-made typewriter in the apartment on Vladimirskaya Str., which was the subject of my envy (no common citizen could buy such thing in the USSR).

[3] Surely, the larger part of his works was written by his co-authors; however, he read and corrected each paper of the co-workers.

[4] Then this institute was known as Institute of Chemistry of the Ukrainian Academy of Sciences. During the war, in 1941–1944, he was working in the Chemical Institute of the Uzbekistan Academy of Sciences, where the institute was evacuated from Kiev.

Fig. 7.1 Yuriy Konstantinovich Delimarskiy (1904–1990) (Photo: Mykola Zakharchenko, 1986)

Mendeleev gold medal of the USSR Academy of Science, Order of the Red Banner of Labour and Symbol of Honour (Fig. 7.1).

Apart from his outstanding personal scientific results, his great achievement was the Department of Molten Salt Electrochemistry, which he founded and headed since 1946. This was the largest department of IGICh till the end of the 1970s (Fig. 7.2).

One can see almost all members[5] of this department on the photo above. It had been taken in April 1974, when the 70th anniversary of Yu. K. Delimarskiy was celebrated. Several generations of high-temperature electrochemists were trained at the department. Some of Delimarskiy's apprentices had soon become independent and headed their own scientific labs or departments. Among them are Oleg G. Zarubitskiy (Department of Molten Salt Electrolysis), Nelly H. Tumanova (Lab of Low-Temperature Melts, end of the 1980s, now Department of Ionic Liquids) and Viktor I. Shapoval, absent in the photo (Department of High-Temperature Electrochemical synthesis, 1976). Presently, the department is named for Delimarskiy and headed by his apprentice Prof. Eduard V. Panov.

Yuriy Konstantinovich Delimarskiy died on June 4, 1990, in Kiev. The Iron Curtain was then transformed into the rusty mesh and fell apart very soon. The director of IGICh over the last years of the Soviet Union was Aleksandr Vladimirovich Gorodyskiy (1930–1992).

Academician A. V. Gorodyskiy was a well-known expert in the field of electrochemical kinetics. His scientific style was a rare and lucky combination of experimental skills and deep theoretic approach. For example, he introduced many new experimental techniques into the research practice. He had more than 50 inventions, mainly in the field of electrochemical energy storage. On the other hand, he deeply understood and developed further the modern quantum theory

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[5] Upon my memory, five more members are absent in this photo.

Fig. 7.2 Department of Molten Salt Electrochemistry, April 1974. From *left* to *right*: *1st row*, sitting, L. I. Zarubitskaya, V. F. Gryshchenko, A. A. Kolotiy, A. V. Chetverikov, Yu. K. Delimarskiy, N. H. Tumanova and O. G. Zarubitskiy; *2nd row*, standing, Zh. A. Khramkova, B. V. Yakovlev, K. G. Ivanova, V. M. Beldiy, L. V. Bogdanovych, N. A. Pavlenko, V. F. Makogon, G. V. Reznik, A. F. Perchyk and N. I. Parkhomenko; *3rd row*, standing, A. D. Tsokolenko, V. T. Meliokhin, B. F. Dmytruk, B. S. Belen'kiy, V. L. Kyslenko, S. O. Kirillov, M. U. Prykhod'ko, M. M. Sarmavskiy, E. V. Panov, L. I. Sirenko, V. A. Bagriy, V. I. Taranenko, M. F. Zakharchenko, A. P. Nizov, V. G. Lutsenko, V. G. Budnik and O. P. Perepelytsia (Photo: courtesy of Mykola Zakharchenko)

(Markus-Dogonadze-Levich) of electron transfer. In particular, he performed quantum mechanics calculations for electron transfer in condensed media.

For the last period of his career, he was deeply obsessed with the concept of so-called limiting overvoltage. This became his idée fixe.

The concept of "limiting overvoltage" is as follows [1]. Supposed we have an electrochemical system with pure kinetic limitation, that is, with no concentration overvoltage, and the Ohmic drop being eliminated. Then, at first, the system obeys the Tafel law. Further on, as the current increases, the activation energy of the electrochemical reaction decreases and finally attained zero value at certain value of the overpotential. After this event, the overpotential cannot increase anymore, and the current would increase limitlessly up to infinitely large values at constant "limiting overpotential". According to calculations of A. V. Gorodyskiy, this limiting overpotential is quite attainable. For example, its value for the discharge of hydrogen ions in acid electrolytes is about -2.1 V. According to Gorodyskiy, that is the reason why alkali metals cannot be liberated from aqueous solutions: their discharge potentials are more negative than the "limiting overpotential" and, thus, cannot be practically achieved at any current values.

No doubt, the regime of electrolysis at the condition of "limiting overpotential" is very attractive from the practical point of view. That is why numerous attempts

Fig. 7.3 Aleksandr Vladimirovich Gorodyskiy (1930–1992)

to confirm the concept were made by co-workers and postgraduate students[6] of academician Gorodyskiy. Alas, the results were (and still are) ambiguous. Thus, the problem is still open for future generations of electrochemists.

Biographical Reference

Aleksandr Vladimirovich Gorodyskiy was born in Kiev May 1, 1930. His father, Vladimir Ivanovich, also was an electrochemist, holding a PhD (kandidat nauk).[7] A. V Gorodyskiy graduated from KPI in 1951. Since then, he was working in the IGICh and was the head of the department since 1970, deputy director from 1971 to 1973 and since 1973 director of the institute. He was a member of the Ukrainian Academy of Sciences (1978) and awarded with the Pisarzhevskiy Prize of the Ukrainian Academy of Sciences in 1972. A. V. Gorodyskiy died early from a melanoma on August 8, 1992. Upon his death, the long and controversial era of Soviet electrochemistry was over. A new history began, with a young generation of electrochemists. As for myself, I have to remember a few more outstanding Kiev electrochemists of the end of Soviet times. The first of them is Prof. L. I. Antropov. He was not working in IGICh but, being the head of the electrochemical chair of KPI, trained very many future scientists who were working in this institute (e.g. A. V. Gorodyskiy and many others) and elsewhere in Ukraine and abroad as well (Fig. 7.3).

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[6] One of my friends, being a postgraduate student of A. V. Gorodyskiy, was trying to achieve "limiting overpotential" regime for the process of aluminium electrolysis in chloride melts. After about 2 years of experimental work, his results were negative. Thus, he was blamed as incompetent and fired. Later on, he prepared and defended his thesis on the electrochemical behaviour of aluminium complexes in chloride melts under the supervision of Yu. K. Delimarskiy.

[7] He stayed in Kiev during the Nazi occupation and worked together with academician Plotnikov as scientific secretary of the Chemical Institute. Upon my knowledge, no repressions were applied from the Soviet authorities either for him or for his son.

7.2 Electrode Potential: Lev Ivanovich Antropov

Now we know that electrode potential is a thermodynamic value. Thus, as any thermodynamic characteristics (except for entropy), it can be determined with an accuracy up to some arbitrary constant. However, in the early years of electrochemical science, there were many attempts to define an "absolute" scale of the electrode potentials.

One of such attempts was made by Ostwald. He believed that the potential of zero charge on mercury (Lippman, 1875), about −0.20 V on the hydrogen scale, corresponds to the absolute zero potential. Of course, the Ostwald scale was not absolute. To comprehend that, a deeper understanding of the nature of zero charge potential was necessary.

Several electrochemists worked in this field (Gouy, Frumkin, Butler, Graham, Parsons and others) over a few decades. One of them was the Ukrainian electrochemist Lev Ivanovich Antropov (1913–1994).[8]

The main contribution of Antropov can be summarised as follows.

First of all, he clearly distinguished the difference between the terms "zero charge potential" and "potential of uncharged surface". The first is a constant for each metal; the second may vary in the presence of some surface-active substances. That is, these two terms relate similarly to the terms "standard potential" and "equilibrium potential"—the first is constant and the second depends on the activities of ions in the electrolyte.

Antropov also proposed the so-called normalised or φ-scale of electrode potential:

$$\varphi = \varepsilon - \varepsilon_N$$

where ε is an actual electrode potential and ε_N is the zero charge potential. Thus, the potential in this "φ-scale" is calculated as the difference between the electrode potential at certain conditions and its zero charge point. This scale is now known in literature as "Antropov's scale".

Of course, Antropov's scale cannot be used for thermodynamic calculations (directions of redox reactions, emf of a galvanic cell, etc.). However, it proved to be very useful for studies of the electric double layer, specific adsorption and the nature of adsorbed particles and, eventually, for corrosion studies and development of corrosion inhibitors—L. I. Antropov was a well-known expert in this field. It is worthwhile to note that two distinguished Western electrochemists, J. O'M. Bockris and B. E. Conway, mentioned L. I. Antropov among the 12 scientists who created the fundamentals of modern electrochemistry.[9]

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[8] To be exact, he became a Ukrainian scientist since 1960, when he headed the chair of electrochemical technology at Kiev Polytechnic Institute, now National Technical University of Ukraine "Kyiv Polytechnic Institute" (NTUU "KPI"). Before that, he received higher education and worked first in Russia and then in India (see Biographical Reference).

[9] Record of Chemical Progress (1964), 23, #1, 33

Biographical Reference

L. I. Antropov was born September 30, 1913, in Berlin, Germany. After graduating from a secondary school of Irkutsk, Russia, in 1929, he worked for 2 years at some temporary jobs.[10] In 1931, Antropov became a student of the chemical faculty at the Eastern Siberia University of Irkutsk. From 1934, he continued his education at the chemical faculty of the Ural Polytechnic Institute (UPI) in Sverdlovsk (now Yekaterinburg). He had started his scientific research activity under the supervision of Prof. O. A. Esin in 1935, being a 4th grade student of UPI. His first studies were devoted to the kinetics of copper electrodeposition and dissolution. These results were published in three papers in major Soviet scientific journals. Over the years 1937—1940, Antropov conducted research and pedagogical work at the chair of theoretical electrochemistry of UPI. His main research interests in this time were in the field of electrochemical analysis of drugs and other substances. In 1939, he defended his PhD thesis (kandidat nauk) and received the degree from the Scientific Board at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences (IGICh USSR). In 1940, he received the diplomas of associated professor (docent) and senior scientific researcher. In 1940, he moved to Yerevan (Armenia) where he had the chair of electrochemistry, physical and colloid chemistry (1940–1948). From 1948 till 1960, he was working in Novocherkassk where he had the chair of electrochemical technology. In 1945, he defended his doctor of science thesis at the Colloid-Electrochemical Institute (now Institute of Electrochemistry) of the USSR Academy of Sciences (Fig. 7.4).

The main achievements of L. I. Antropov in this period were related to applied electrochemical kinetics (corrosion inhibitors, metal coatings, electrochemical synthesis of organic compounds). He substantiated the ideas about the significant effect of double layer charge and adsorption phenomena in the electrolysis processes. Another fundamental series of Antropov's works in this period concerned the hydrogen overvoltage on different metals and its influence on the processes of electrochemical reduction of organic substances. He divided the metals in two large groups where the mechanism of hydrogen evolution was different (either slow recombination or slow discharge). Using this approach, he was able to predict the reducing agents (adsorbed hydrogen atoms, activated hydrogen ions or electrons) and thus to predict the direction of the electroreduction of many organic substances.

From 1957 till 1960, Antropov has been in India as the expert of UNESCO. He founded the chair of electrochemistry at Bombay Technological Institute,

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[10] There is a wide gap in the biography from the Berlin to Irkutstk, which I am not able to completely fill. His father, Ivan Aleksandrovich Antropov (1888–1938), was a professor of law who has studied in 1912/1914 in Berlin, Germany (which explains the birthplace of L. I. Antropov). In 1918, Ivan A. Antropov was a legal consultant of the Temporary All-Russian Government of Admiral A. V. Kolchak. In the 1930s, he was the head of the legal department of a power company in Sverdlovsk. In 1938, during the great purges, he was arrested and sentenced to death [Shishkin V. I. (2002) K istorii gosudarstvennogo perevorota v Omske (18–19 noyabrya 1918). Vestnik NGU. Seriya: istoriya, filologiya. Vol 1, No 3, Novosibirsk, pp 88–97]. For anybody knowing Soviet history, it is clear that the life of L. I. Antropov must have been severely affected in this or that way by his father's vitae.

Fig. 7.4 Lev Ivanovich Antropov (1913–1994)

conducted researches together with Indian co-workers and published 6 papers in English in Indian journals. In these papers, Antropov further developed his ideas about the effect of adsorption on the mechanism of the action of the corrosion inhibitors.

Starting in 1960, Antropov lived and worked in Kiev, Ukraine. There he had the chair of electrochemical technology at Kiev Polytechnic Institute from 1960 to 1986. Since 1986 and till the end of his life, he was working as a consultant professor of this chair and was the head of the Laboratory of Corrosion Inhibitors, which was founded by him in 1962.

The Kiev period was very fruitful for Antropov. He further elaborated his ideas on corrosion inhibitors. For example, he proposed a new quantitative theory, which could explain and permit to calculate the intermoleculary and intramoleculary synergetic effects of the inhibitors action and gave rise to the purposeful choice or synthesis of the inhibitors. This was called by him as the “formal theory”. It is widely used now by most scientists, which are working in the field of inhibiting metal protection.

The chair of electrochemical technology at KPI became a powerful scientific and technological centre under the guidance of Antropov. New research directions were opened and developed together with his co-workers, such as the direct deposition of metal coating in acid media in the presence of surfactants (together with I. S. Pogrebova), galvanic composite coatings (together with M. I. Bykova), development of corrosion rate-measuring devices (together with Yu. S. Gerasimenko), intensification of the electrochemical processes in chlorine and alkali production (together with V. P. Chviruk) and others.

Antropov is known also as a brilliant lecturer and talented trainer of young electrochemists. He has supervised the work of hundreds of electrochemical engineers, 8 doctors of science and more than 50 PhD students (kandidat nauk).

The course “Theoretical Electrochemistry”, which is obligatory in the training of electrochemical engineers in all FSU countries, is based on the excellent textbook of Antropov. This book was first published in 1965 [2]. There were three other Russian language editions and Ukrainian, English (two), Hungarian and French translations. For this book, Antropov received the Ukrainian State Award in 1975.

Lev Ivanovich Antropov died July 8, 1994.

7.3 Electrochemical Thermodynamics: Boris Fedorovich Markov

“The potential of uncharged surface, measured vs a reference electrode with constant potential, varies linearly with the logarithm of concentration (activity) of the electrolyte” [3]. This phenomenon, which is the criterion for the specific adsorption to take place, is known in literature as *Esin-Markov effect*. It was discovered by the well-known Russian electrochemist from Sverdlovsk Prof. Oleg Anatolievich Esin[11] and his young student Boris Fedorovich Markov.

The larger part of the life and scientific activity of Markov (since 1946 till the end of his life) was related to the Institute of General and Inorganic Chemistry (IGICh) in Kiev, Ukraine. For a long time, he was the head of the Department of Physical Chemistry and Thermodynamics of Molten Salts at this institute.

His main research activities in Kiev were focused on the thermodynamic and other properties of molten salts by electrochemical means.[12] First of all, he studied the emf of a large variety of galvanic cells where potential-determining reactions corresponded to the formation of individual metal chlorides, so-called formation circuits (Me| molten $MeCl_n|Cl_2$ (gas)|graphite). It permitted him to calculate the standard metal electrode potentials vs. chlorine gas reference electrode in chloride melts. This significant contribution to the electrochemistry of molten salts became an essential part of the well-known monograph [4]. Markov was also the first who has studied thermogalvanic cells with molten salts as electrolytes. By measuring the emf of such cells, he was able to determine the Seebeck effect (thermopotential) and, thus, the transported entropies of ions in molten salt electrolytes. Even now, such data are of importance for understanding the properties of molten electrolytes. Besides, Markov substantiated the validity of the Thomson relation between the emf of a thermogalvanic cell and the Peltier heat for metal—molten electrolyte interface: $\Pi = \varepsilon T$. Before him, this relation was well known only for the junction of

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[11] Being an outstanding scientist by himself, Prof. Esin became the “godfather” for two distinguished Ukrainian electrochemists—L. I. Antropov (see above) and B. F. Markov.

[12] Thus, the research directions of B. F. Markov in Kiev had nothing in common with his early studies in Sverdlovsk. As far as I remember, he never even mentioned the “Esin-Markov effect” or other works related to the electrochemistry of aqueous solutions in his biography. I do not know why. My guess is that he did not considered this early student work to be significant in comparison with his profound studies of ionic melts.

two different metals. As far as I remember, he was really happy when his prediction was experimentally proved [5].

Thermodynamic studies were abruptly terminated in IGICh in the end of the 1970s. The director of the institute, academician A. V. Gorodysskiy, who was mainly interested in electrochemical kinetics, eliminated Markov's Department of Physical Chemistry and Thermodynamics of Molten Salts in 1979.[13] After that, Markov became a consultant professor at the IGICh till he completely retired in 1986. Together with his pupils, he summarised the vast collection of thermodynamic data in a monograph [6], which became a handbook for researchers working in the field of molten salt chemistry.

Biographical Reference

Boris Fedorovich Markov was born March 20, 1912, in Liepaya (this was the Russian name; the German name was Libau), Courland province of the Russian Empire (now Liepāja, Latvia), in the family of a state employee. After the beginning of the First World War in 1914, Markov's family lived in Vyatka (later Kirov) district, Russia. Here, Boris graduated from 8-year secondary school and entered forestry engineering technical school in 1928. After graduating from this school in 1930, he worked for 3 years as a forester in the Kirov district. From 1933 till 1937, he was a student of Sverdlovsk State University where he began his first electrochemical scientific works under the supervision of Prof. Esin, which resulted in the discovery of the Esin-Markov effect mentioned above. After graduating from the university in 1937, he began his first researches in molten salt electrochemistry working as a junior scientific researcher in the Ural Scientific Research Institute. He studied there the electrochemical processes of magnesium production under the supervision of Prof. L. M. Shcherbakov. Markov was mobilised to the Soviet Army in 1939. He served there in an automotive repairing military unit till 1946, when he was demobilised in the rank of lieutenant. For his military service, he was awarded with the medal "For the Victory over Japan". Soon after the demobilisation, in August 1946, Markov became a postgraduate student in IGICh, Kiev. His PhD (kandidat nauk) study, which was devoted to the electrolytic production of magnesium, was performed under the supervision of famous academician V. A. Plotnikov, the founder of electrochemistry of nonaqueous solutions and molten salts in the Ukraine.[14] He defended this thesis in 1948, already after the death of his supervisor in 1947. Evidently, Markov was the last postgraduate student of V. A. Plotnikov.

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[13] According to my memory, his words were as follows: "It is useless to develop the thermodynamics in our Institute. If you need any thermodynamic data, you should find them in literature".

[14] I know this fact from the memory of my older colleagues at IGICh and KPI. However, working recently in the archive of IGICh, I found no information on the candidate thesis of Markov in his personal dossier dated in 1956. Neither abstract nor supervisor nor even title—nothing at all! Evidently, the name of V. A. Plotnikov was committed to oblivion by official Soviet science till that time. I imagine that the Markov's decision to become a student of the disfavoured old academician required a great deal of courage from him.

Fig. 7.5 Boris Fedorovich Markov (1912–1992)

In 1949, Markov took the position of senior scientific researcher at IGICh. Since that time, he conducted a series of researches on the emf of galvanic cells with molten electrolytes, which permitted him to calculate the thermodynamic properties of numerous molten salt systems.[15] He summarised the results of these studies in his doctor of science thesis, which he defended in 1956. After defending his doctor of science dissertation, Markov worked as a part-time professor in KPI, teaching the course "Theoretical Electrochemistry" over 3 years since 1957. Markov became the head of a lab at IGICh in 1957. First, it was the Laboratory of Titanium Chemistry and Technology, since 1959—the Laboratory of Chemistry and Thermodynamics of Molten Salts. In 1962, the laboratory was transformed into the Department of Physical Chemistry and Thermodynamics of Molten Salts. Professor (since 1960) Markov headed this department till 1979. The final dates of Prof. B. F. Markov's biography are as follows: 1979–1986, consulting professor at IGICh; June 30, 1986, exempted from IGICh[16]; and January 16, 1992, died in Kiev (Fig. 7.5).

Short Afterword

I remember Boris Fedorovich Markov as a very honest and serious scientist with rather rigid principles. He had, unlike most of the IGICh professors, never been a member of the Communist Party. He rarely took part in official events that did not belong to the province of science (like the official celebrations of communist holidays). I could say that science was all of his life—but it would not be quite true. Boris Fedorovich had two hobbies—fishing and hunting. He had always at

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[15] B. F. Markov was an outstanding experimenter. I remember the laboratory furnaces of his design with platinum thermoresistor, which could keep the working temperature with the precision less than 0.1 °C. The regulating electric circuitry for this furnace was invented by B. F. Markov together with old IGICh's technician Moisei Abramovich Mednik.

[16] The official formulation was "dismissed due to the shortening of staff".

hand a number of wonderful and funny stories about this part of his life.[17] He was a prominent scientist with a bright personality—this is my impression about Professor Boris Fedorovich Markov.

I acknowledge the valuable help of Prof. Anatoliy Omelchuk and Mykola Zakharchenko from IGICh in preparation of this essay.

7.4 Polyfunctional Conductors: Avenir Akimovich Velikanov

For the first time, I learned about Velikanov's ideas on the electrochemical behaviour of liquid conductors with mixed ionic and electronic conductivity when I was attending his lecture at a summer school for young researches in 1975 (Bakuriani, Georgia). Below is an excerpt from my old conspectus of his lecture (Fig. 7.6):

This is Velikanov's idealised polytherm for conductivity of a *polyfunctional conductor* (the term was invented and introduced by A. A. Velikanov himself; it became widely accepted at least in the USSR).[18]

Velikanov modelled the properties of PFC with three constant resistors connected in parallel—first for ionic, second for semiconductive and third for metallic types of currents—with each of them possessing its own temperature dependency according to the proposed polytherm.

Now we know that such model is very simplified, because these resistors are non-linear and the partial conductivities depend on the applied current [7]. However, even this simplified model turned to be very useful—first of all, for the development of electrolytic processes for production of metals from chalcogenide (mainly polysulphide) ores. Evidently, for the successful electrowinning of such metals as Sb, Tl, In, Cu, Ag and others from its sulphide, selenide or telluride compounds, the electronic (both semiconductor and metallic) conductivity must be suppressed. For that purpose, Prof. Velikanov proposed and realised, together with his numerous scholars, the additions of compounds with pure ionic conductivity, such as sulphides of sodium and potassium. By studying the conductivities in many binary molten systems, he was able to choose the optimal compositions with high

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[17] I remember one of them as follows. It was in 1982 or so, and we were waiting together for the audience with the director of IGICh academician Gorodyskiy (everybody for his own purposes, of course). To kill the time, Boris Fedorovich begins to tell his fishing tale: "Just imagine, Sasha! Yesterday I caught a pike like this (shows by his arms the size of more than 1 meter). I put it in the grass on the shore, it stiffened. When coming back home, I used it as a walk stick. So, I am walking, and everybody watches me, and everybody envies!"

[18] Prof. Konstantin Kazdobin remembers the specific way of the first presentation of the model in 1968. The scientific seminar was carried out in tourist tents on the bank of the Desna River. The idea was supported by outstanding physicist Anatoliy R. Regel, director of the Ioffe Institute for Semiconductor from Leningrad, and chemist Yu. K. Delimarskiy.

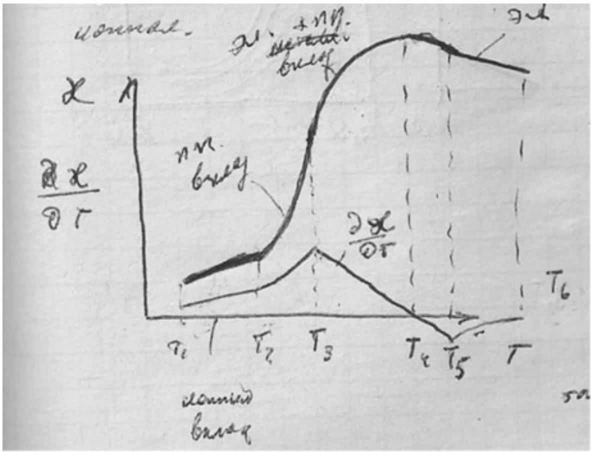

Fig. 7.6 Velikanov's polytherm of conductivity of a polyfunctional conductor.
Dependence of specific conductivity of polyfunctional conductor (PFC) on temperature according to A. A. Velikanov:
T_1–T_2, linear growth, mostly ionic conductivity;
T_2–T_3, exponential growth, semiconductive component prevails over the ionic one;
T_3–T_5, metallic conductivity onsets after T_3 and became prevailing over semiconductive component after T_4;
T_5–T_6, linear decrease, almost pure metallic conductivity

ionic conductivities and performed successfully the electrolysis processes for production of metals from chalcogenide ores.

Further development of Velikanov's concept of the PFC proved its usefulness not only for electrolysis of chalcogenide melts. For example, representation of the oxide film on a metal surface as PFS easily explains the Tamman's parabolic law for growth of such film in the air corrosion process of metals. Formation of a film of intermediate compounds on the surface of electrode explains many regularities of long-term electrolysis of the melts containing compounds of polyvalent metals (see [7] for more details).

Thus, Avenir Akimovich Velikanov was the first who brought a wide variety of objects with mixed electronic-ionic conductivity into electrochemistry. This contribution to the modern electrochemical science cannot be overestimated.

Biographical Reference

Avenir Akimovich Velikanov was born March 6, 1931 in Saratov, Russia. His father, Akim Aleksandrovich (1902–1960), was a railroad bridge building engineer, and the mother Ligiya Georgievna (1911–1992) was also working in the bridge building industry. Velikanov's family lived in Kherson, Ukraine, when the war begun in 1941. His father was recruited to a train-based military engineering unit, and the family was evacuated to Saratov. After the liberation of the Ukrainian capital in 1944, the family moved to Kiev. Since then A. A. Velikanov lived and worked permanently in this city. In 1949, he entered the chemical faculty of Kiev

Fig. 7.7 Avenir Akimovich Velikanov (1931–1983)

State University. He graduated from Kiev State University in 1954 and then worked at the chemical faculty of this university till 1975: first, as an assistant, then senior teacher, then assistant professor (docent) and, finally, full professor since 1973 (Fig. 7.7).

In 1964–1965, Velikanov was a participant of student exchange programme while attending the University of Illinois, USA, for 10 months. His main interest there was the electrochemistry of molten salts, as it follows from the citation below: "Velikanov received permission to go to Los Angeles but not to stay there long enough for a conference on molten salts which he had asked to attend. He attended anyway and was expelled on May 30, a week ahead of his normal departure date" (Spokane Daily Chronicle, June 19, 1965).[19]

He received his doctor of science degree from the Scientific Board of IGICh in 1971. In 1975, he became the head of the general chemistry chair at the Kiev Automobile Road Institute (now Ukrainian Transport University). He had this position till his death in October 2, 1983.

There were three main research directions of Prof. Velikanov:

1. The above-mentioned ideas about modelling of electrochemical properties of PFC were developed as the result of studies of more than 200 chalcogenide and oxide systems. As practical results of these studies, several technological processes were developed which permitted obtaining from the chalcogenide ores not only the metals but also sulphur (it is worthwhile to note that sulphur is the main pollutant in the existing pyrometallurgical technologies).
2. Development of the cathode materials based on sulphides of iron and titanium. He and his co-workers developed several cathode material compositions that

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[19] http://news.google.com/newspapers?nid=1338&dat=19650619&id=d1dYAAAAIBAJ&sjid=n_cDAAAAIBAJ&pg=7373,4943389. This information is a courtesy of Arkadiy A. Furman from Chicago.

Fig. 7.8 Avenir Akimovich Velikanov is discussing the plans of scientific works with his young co-workers, Kiev State University, 1972. From *left* to *right*: postgraduate student Grigoriy Zagorovskiy, engineer Nadezhda Rozha, Dr Oleg Mustiatsa, senior engineer Ivette Ostrovskaya

turned to be very efficient for application in lithium and sodium-sulphur batteries.

3. Velikanov and his team developed several interesting materials for optic and microelectronics based on A(II)–B(IV) chalcogenide systems, such as cadmium sulphides, selenides and other similar compounds. He showed that the thin films of such compounds are very promising materials for modern electronics. Really, such materials are now widely studied and used in modern electronic devices.

All these studies were conducted together with his numerous scholars—graduate and postgraduate students mainly. Velikanov enjoyed very much to work with young generation of electrochemists. In the photo below, one can see him among his younger colleagues in Kiev State University (Fig. 7.8).

Velikanov was the supervisor of 12 PhD (kandidat nauk) theses and very many graduate students who learned electrochemistry under his supervision. Many of his students became well-known scientists—Profs. O. Mustiatsa, V. Zinchenko and A. Omelchuk and Drs. V. Lisin and O. Boiko and many others are among them. All of them remember their maitre with great warmth and gratitude.[20]

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[20] In turn, I am grateful for the help of many of the Velikanov's students. Especially I acknowledge the valuable help of Prof. Oleg Mustiatsa and Dr. Vladimir Lisin—they provided me with photos and basic biographical information.

7.5 Electrochemical Film Systems: Aleksandr Tikhonovich Vas'ko

Being now a blossoming research field, solid state electrochemistry made its first steps in the last decades of the twentieth century. The development of solid phase reduction mechanism for the electrodeposition of polyvalent metals was possibly the most significant achievement of this newly emerging branch of electrochemistry. The Kiev Professor Asleksandr Tikhonovich Vas'ko was among the pioneers.

The main research interests of Vas'ko were related to the electrochemistry of refractory metals where he was a well-known expert. He developed the process of galvanic coating of W-Ni and Mo-Ni alloys from aqueous electrolytes. Trying to explain the mechanism of this process, he assumed two stages of the formation of such alloys: first, the deposition of solid film consisting of low-valency compounds and, second, electrochemical reduction of the film at the inner surface by solid mechanism. Thus, the solid non-metal film on the electrode surface for the first time became an active participant of the electrochemical process rather than simple passivative layer. This was a breakthrough. Further on, this electrochemical film system (EFS) concept was usefully applied not only in the aqueous electrochemistry but in the electrochemistry of molten salts and ionic liquids as well (see [7] for more details).

Biographical Reference

A. T. Vas'ko was born on May 19, 1931, in Khmel'nytskiy, Ukraine. The family moved to Kiev in 1932. He entered the secondary school in 1939. During the German occupation, he stayed in Kiev. For 3 years, from 1941 till 1943, his studies were terminated. After the liberation of Kiev in 1943, he entered again the secondary school and graduated in 1949. He was a student of Kiev Polytechnic Institute in 1949–1954. After graduating from KPI, he was working as a master on some military-oriented industrial plant for about 1 year. Since 1955, he was working in IGICh, first as an engineer and then junior researcher (1961–1965) and senior researcher (1965–1977). In 1977, the Laboratory of Non-metal Systems Electrochemistry was established, which became the department since 1979. He got his PhD (kandidat nauk) in 1963 and his doctor of science degree in 1974 based on his thesis "Investigation on the electrochemistry of tungsten". In 1984, he became a professor. He retired from IGICh in 1999. After that, he lived in Kiev, visiting sometimes his son Vladislav in the USA. Vas'ko died on Sept. 4, 2013 (Fig. 7.9).

Though I was not working directly with Vas'ko, I am obliged to him very much for his constant and strong support of my scientific activity. He was an opponent at the defence of my doctor of science thesis. I never forget our scientific discussions, which were extremely useful and, I dare say, refreshing. God bless the soul of this extraordinary man.

Such is my memory about the 6 distinguished Kiev electrochemists of the last quarter of twentieth century. Ideologically, they were different. B. F. Markov, I suspect, was a latent anticommunist, while A. A. Velikanov was an eager supporter

Fig. 7.9 Aleksandr Tikhonovich Vas'ko (1931–2013)

of communist idea. A. T. Vas'ko seemed to be totally indifferent to any ideology, while Yu. K. Delimarskiy and A. V. Gorodyskiy simply used their membership in the Communist Party as a means for career promotion.[21] Who cares for that now, when the Iron Curtain is gone? All of them remain the knights of electrochemical science in our memory forever.

Acknowledgements Many people helped me in the preparation of this chapter sharing their memory, documents and photos: Profs. K. Kazdobin, A. Omelchuk and M. Zakharchenko and Dr V. Zaychenko from IGICh, Prof. O. Mustiatsa from Kiev Transport University and Profs. I. Astrelin and M. Donchenko from KPI. I am grateful for their help. Special thanks to Prof. F. Scholz for his finding about the fate of Antropov's father and many other valuable suggestions.

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[21] Nobody could possess a position higher than head of department if he was not a member of the Communist Party in the Soviet Union.

Chapter 8
The Ural School of Solid State Electrochemistry in the USSR

Anatoliy K. Demin and Pavel Shuk

8.1 Introduction

If anyone wants to find what research in the field of solid oxide electrolytes was carried out in the Soviet Union during the second half of the twentieth century and will appeal to any database, for example, Scopus, he will find that the first work of Soviet scientists in this area appeared in 1965 and was published in out of reach of the Western readers Soviet journal *Ogneupory* (*Refractories*). According to Scopus, the next paper appeared in the same journal in 1974, and in 1975 several papers were published in the Soviet journal *Elektrokhimiya* (now, *Russian Journal of Electrochemistry*) having an English translation, making these Russian publications better accessible to the Western scientists. But given the small number of printed copies of the magazine, access was very limited.

Of course, Scopus does not present the complete truth: Pioneering works in the field of solid state electrochemistry started many years earlier at the Electrochemistry Laboratory of the Chemistry Institute of the Ural Subsidiary of the Academy of Sciences of the USSR in Sverdlovsk. The first solid state ionics papers were published in *Trudy Instituta Khimii Ural'skogo Filiala Akademii Nauk SSSR* (Reports of the Chemistry Institute of Ural Subsidiary of the Academy of Sciences of the USSR) in 1958 (see, e.g., [1]). Somehow, academic institutions were considered to have a higher reputation when they published a periodical journal;

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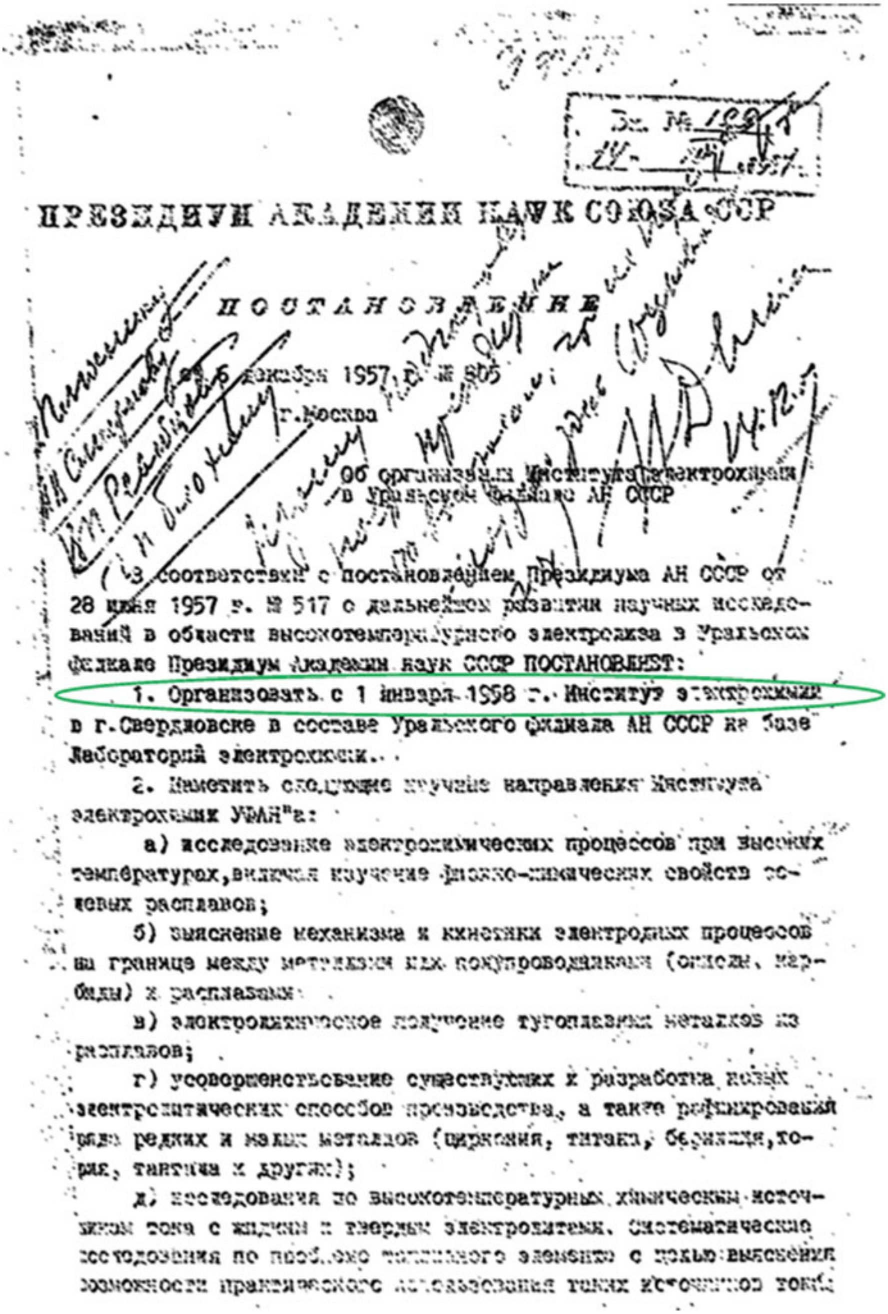
F. Scholz (ed.), *Electrochemistry in a Divided World*,
DOI 10.1007/978-3-319-21221-0_8

however, these journals were not well distributed and not translated to English, giving them a very little chance to be seen and recognized by the foreign scientists.

In 1958 according to the Decree of the Presidium of the Academy of Sciences of the USSR (Fig. 8.1), the Electrochemistry Laboratory of the Ural Subsidiary of the Academy of Sciences of the USSR was reorganized and had formed the new "Institute of Electrochemistry of the Ural Subsidiary of the Academy of Sciences of the USSR" (IE US AS USSR). The Decree has defined the scientific directions of the new institute that can be generalized as physical chemistry and electrochemistry of melts and solids. Among them were research of electrochemical processes at high temperatures, research of high-temperature power sources with liquid and solid electrolytes, and systematic research on the problem of fuel cells with the aim to clarify the possibility of their practical application. Thus, from the first day, research on solid electrolytes was established at this institute, and during many decades it was recognized as the leading institution in the USSR and in the Eastern European countries for the research and development of oxygen ion-conducting solid electrolytes (SEs) and electrode processes in SE cells. During its history, the institute had several other names: since 1971 till 1988 the "Institute of Electrochemistry of the Ural Scientific Center of the Academy of Sciences of the USSR," till 1991 the "Institute of Electrochemistry of the Ural Division of the Academy of Sciences of the USSR (IE UD AS)," and in 1991 the institute obtained its present name the "Institute of High-Temperature Electrochemistry of the Ural Division of the Russian Academy of Sciences" (IHTE UD RAS).

From the beginning, the R&D of the new institute was focused on different aspects of solid electrolytes, from basic research to various applications. This can be seen from the list of the publications of the scientists of IE US AS/IE UD AS. This list reflects the breadth of the research and includes mainly publications that are not covered by Scopus. Many papers have been published in the leading scientific journals of the USSR, e.g., in *Zhurnal neorganicheskoy khimii* (*Journal of Inorganic Chemistry*) [2, 3], *Doklady Akademii Nauk SSSR* (*The Proceedings of the USSR Academy of Sciences*) [3–12], *Zhurnal fizicheskoy khimii* (*Journal of Physical Chemistry*), [13], *Fizika tvërdogo tela* (*Solid State Physics* [14], *Kinetika i kataliz* (*Kinetics and Catalysis*) [15, 16], and *Neorganicheskie materialy* (*Inorganic Materials*) [17, 18], which were practically unknown to the Western scientists. The most important papers were published in the *Doklady Akademii Nauk SSSR*. The publication process in this journal was very difficult and the publication was considered as a great honor for the authors. But unfortunately the English version of *Doklady Akademii Nauk SSSR* was published in very limited copies, and foreign researchers practically had no access to most of the publications of some very interesting results of the Soviet scientists. The specialized journal *Elektrokhimiya* (*Electrochemistry*) was founded in 1965 by A. N. Frumkin in Moscow, and very significant contributions from the Ural electrochemists have been published there in the 1960s, 1970s, and 1980s [19–38]. Although from the beginning, this journal was translated to English and the English version was published by Plenum Press (now the Russian publisher MAIK Nauka/Interperiodica publishes the journal and the



ПРЕЗИДИУМ АКАДЕМИИ НАУК СОЮЗА ССР

ПОСТАНОВЛЕНИЕ

[illegible]6 декабря 1957 г. № 805
г. Москва

Об организации Института электрохимии
в Уральском филиале АН СССР

В соответствии с постановлением Президиума АН СССР от 28 июня 1957 г. № 517 о дальнейшем развитии научных исследований в области высокотемпературного электролиза в Уральском филиале Президиум Академии наук СССР ПОСТАНОВЛЯЕТ:

1. Организовать с 1 января 1958 г. Институт электрохимии в г. Свердловске в составе Уральского филиала АН СССР на базе Лаборатории электрохимии.

2. Наметить следующие научные направления Института электрохимии УФАН"а:

а) исследование электрохимических процессов при высоких температурах, включая изучение физико-химических свойств солевых расплавов;

б) выяснение механизма и кинетики электродных процессов на границе между металлами или полупроводниками (окислы, карбиды) и расплавами;

в) электролитическое получение тугоплавких металлов из расплавов;

г) усовершенствование существующих и разработка новых электролитических способов производства, а также рафинирования ряда редких и малых металлов (циркония, титана, бериллия, тория, тантала и других);

д) исследования по высокотемпературным химическим источникам тока с жидким и твердым электролитами. Систематические исследования по проблеме топливного элемента с целью выяснения возможности практического использования таких источников тока;

Fig. 8.1 Decree on the organization of the Institute of Electrochemistry. “1. Organize since January 1, 1958 the Institute of Electrochemistry. . .”

English version of Russ. J. Electrochem. is distributed by Springer), information about the publications on solid state ionics was not covered by Scopus until 1974.

However, most of the scientific papers were published in "Trudy Instituta Elektrokhimii Ural'skogo Filiala (since 1971—Ural'skogo Nauchnogo Tsentra) Academii Nauk SSSR" (Reports of the Institute of Electrochemistry of Ural Subsidiary (since 1971—Ural Scientific Center) of the Academy of Sciences of the USSR, Reports of IE US (USC) AS USSR) founded in 1960 (see, e.g., [39]). Prior to 1980, 30 volumes of "Trudy Instituta Elektrokhimii Ural'skogo Filiala (Ural'skogo Nauchnogo Tsentra) Academii Nauk SSSR" were released and a considerable part of them was related to research in solid state ionics. Every year a special issue on the various aspects of solid state electrochemistry was released. Unfortunately, this journal was only available to researchers in the USSR and partially to the Eastern European scientists and was practically unknown to people in the West. Only some Western scientists did know about it, thanks to personal contacts. There were also many publications in journals with very limited access even for the USSR scientists (see, e.g., [40–42]). It must be noted that some areas of research were secret, especially what was related to solid electrolytes, electrodes, and technology of electrochemical cells and electrochemical devices. It was a common practice that nobody was revealing the secrets and the know-how and considered himself as the leader of the race, but at the end, everyone was losing due to this lack of information exchange! The first paper of the Ural scientists on solid oxide electrolytes was published, according to Scopus, in the *International Journal of Electrochemical Society* in 1975 [43]. That was the first article cited in the publications of foreign scientists actually only 15 years after its publication. More or less systematical publications of Russian scientists in international journals have started only in 1984 in *Electrochimica Acta* [44], *Solid State Ionics* [45–47], *Physica State Solidi* [48], *Ceramic International* [49], and *Sensors and Actuators* [50].

The Institute of Electrochemistry of the Ural Subsidiary/Ural Division of the Academy of Sciences of the USSR regularly organized various scientific events, which have widely presented the research on SEs and other solid oxide conductors (SOCs) as well as on electrodes and electrode kinetics. Since 1960, every 3–4 years, All-Union Conferences on "Physical Chemistry and Electrochemistry of Melts and Solid Electrolytes" were held, where about 50 % of the presentations were on solid electrolytes. Further, various specialized seminars on SOC, in particular, the All-Union Seminar on "Solid Electrolytes and Their Analytical Application," took place. Training courses and regularly organized seminars for young scientists very much supported the popularity of solid state ionics in the former USSR.

However, at that time, the exchange of scientific information was actually very unidirectional: Soviet scientists had access to the leading international scientific journals, and Western scientists knew almost nothing about the research carried out in the USSR. Only leading scientists of the Soviet Union had the rare opportunity to travel abroad. Very rare were the trips to international conferences, mainly in the East European countries, and only since the early 1990s, Soviet scientists were able to travel abroad to the conferences and visit Western universities and some industrial corporations for joint research.

8.1.1 Who Was at the Forefront?

Sergey Fëdorovich Pal’guyev (Palguev) contributed greatly to the new ideas on solid oxide electrolytes (SOEs) and electrode process in solids since the late 1950s. In 1963, Sergey Vasil’yevich Karpachëv (Karpachev) was appointed as the institute director, and he had a decisive influence on the recognition of the electrochemistry of solid electrolytes as a separate field of electrochemistry. The ideas behind the kinetics of electrode processes in solids and the processes of charge transition on the boundary of the SOE are intimately connected with the name of Professor Mikhail Vasil’yevich Perfil’yev (Perfiliev, Perfil’ev), the recognized leader of the Russian electrochemists investigating oxygen ion-conducting solid electrolytes in the 1960s–1990s. The theoretical understanding of all phenomena taking place in SOEs and on its interfaces with gas and electrodes was developed by Professor Vasiliy Nikolayevich Chebotin, who unfortunately very early deceased. Professor Chebotin published four monographs, including the book *Electrochemistry of Solid Electrolytes* (1978), coauthored by Professor Perfil’yev. This was the first well-known monograph on the solid electrolytes in the USSR. The advanced research on solid electrolyte electrochemical devices, especially on solid oxide fuel cells and electrochemical sensors, is associated with the name of Dr. Anatoliy Dmitriyevich Neuymin (Neujmin). Other significant contributions to the foundation of the solid electrolyte electrochemistry were coming from Dr. Zoya Semënovna Volchenkova, Dr. Anatoliy Trofimovich Filyaev, Dr. Lilya Moiseyevna Solov’yëva (Soloviova), Dr. Victor Nikolayevich Srekalovsky, and many others. Without a doubt, solid electrolyte research at the Institute of Electrochemistry/High-Temperature Electrochemistry was and is unique with respect to its variety and the depth of the basic science, as well as practical application.

The list of publications [1–50] covers the period from 1958 to 1990, i.e., up to the very last years of the united Soviet Union. It includes only a small part of the publications and still reflects the wide variety of research on solid electrolytes at the IE US AS/IE UD AS and the journals publishing these results. There were many theoretical and experimental studies on electrochemical cells with solid electrolytes [1, 4, 5, 21, 39] and an extensive research on the phase composition of oxide ionic conductors [2] and their electric properties [3, 6, 8, 10, 13, 14, 17, 18, 20, 30, 34, 48]. Many papers were related to practical applications like solid electrolyte degradation [33, 47] or application limits related to the electronic conductivity of the solid electrolytes [5, 30, 40, 43]. There were many publications on the implementation of different electrodes and on the kinetics of electrode processes [23, 27, 31, 35, 36, 45], on investigations of the electrode overvoltage [7, 12, 25, 28], on impedance spectroscopy of solid electrolytes [19, 27], and on isotope exchange research [15, 16]. The double layer and electrocapillarity of solid electrolytes were studied in detail [9, 11, 19, 32, 44]. Systematic studies were performed on the thermo-EMF of different solid electrolytes [22, 24, 29], the EMF of electrochemical cells with solid electrolytes [26, 39], and the thermodynamics of oxygen in molten copper [41]. Applied research was focused on electrochemical oxygen pumps

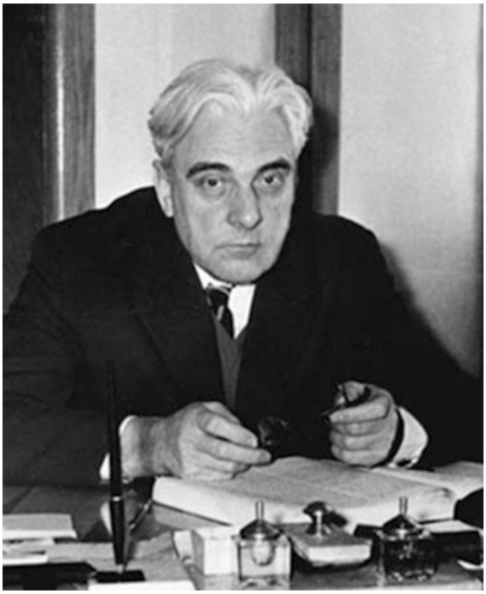


Fig. 8.2 Professor Sergey Fëdorovich Pal'guyev

[37, 42], water vapor electrolyzers with solid electrolytes [38], and new materials for interconnects and electrodes [46, 49, 50]. Probably, it is difficult to find any other research organization, not only in the former Soviet Union but throughout the world, where solid electrolytes have been investigated in such a systematic way.

8.1.2 Sergey Fëdorovich Pal'guyev (Fig. 8.2)

Sergey Fëdorovich Pal'guyev (1919–2001) is a celebrated Russian scientist, one of the founders of the school of high-temperature electrochemistry of solid oxide electrolytes. He graduated in 1941 from the Chemistry Department at the Ural State University in Sverdlovsk (Yekaterinburg). The scientific career after the graduation was postponed for 5 long years (World War II) and he was working as an inspector foreman at URALMASH, the biggest engineering plant in the Soviet Union. Pal'guyev completed his PhD program and the thesis in 1949 and received his second scientific degree, Doctor of Science (DSc), in 1966.

The Laboratory of Physical and Chemical Properties of the Solid Electrolytes (shortly known as the Laboratory of Electrolytes) was one of the first laboratories established at the Electrochemistry Institute in 1958. Pal'guyev was the first head of the laboratory and was in charge of the solid electrolyte research until 1987. In fact the first research in the field of solid oxide ionic conductors was started in his laboratory. This laboratory was directly or indirectly the base of all laboratories and groups related to high-temperature solid state electrochemistry, i.e., Laboratory of the Kinetics in Solids, Theoretical Group, Laboratory of the Electrochemical Devices, Analytical Laboratory, Laboratory of Gas Electrolysis, and Laboratory of Solid Oxide Fuel Cells. Many members of this laboratory were later leaders and heads of other laboratories of the Electrochemistry Institute. Sergey Vasilievich Karpachëv founded in 1965 and headed the new Kinetics Laboratory, followed by Professor Mikhail Vasil'yevich Perfil'yev and then by Dr. Boris Leonidovich Kuzin as the head of the laboratory. In 1983 Anatoliy Dmitriyevich Neuymin organized and headed the Laboratory of Electrochemical Devices. Vasiliy Nikolayevich Chebotin organized and was in charge of the theoretical group since 1973. V. N. Strekalovskiy headed the Analytical Laboratory from 1972 till 2003. Dr. Anatoliy Konstantinovich Dëmin (Demin) organized in 1990 the Laboratory of Gas Electrolysis and headed it until 2011. Later he headed the Laboratory of Solid Oxide Fuel Cells. Dr. Valeriy Pavlovich Gorelov headed the Laboratory of Solid Oxide Fuel Cells (reorganized from the Electrochemical Devices Laboratory) from 2002 till 2011.

The young generation of the institute remembers Pal'guyev as a tall, slightly round-shouldered, and white-haired man. He was kind, although he was rarely seen smiling. He was not afraid of new concepts. He quickly became familiar with a computer when he was already 78 years old, writing and reviewing new publications.

He has achieved success due to his hard work and ability to prioritize. He implemented the great commandment of successful people: "Be ahead of the others, at least by one step."

His achievements at the end of his career included more than 500 publications, four monographs, and 45 patents. Twenty-six of his students defended PhD theses and two of his scholars defended a Doctor of Science thesis.

The laboratory staff worked very amicably and fruitfully. Much attention was paid to the development of original techniques, e.g., in 1958 a method for measuring the electromotive force, or EMF, of electrochemical cells was developed, which is now very widely used. There has been a very extensive research on the conductivity of single and mixed oxides (binary, ternary, and multicomponent) in a wide temperature range (400–1500 °C) in various gaseous environments. In all cases, ionic and electronic conductivities were characterized depending on the composition, temperature, and oxygen partial pressure in the gas phase. X-ray diffraction (including high temperature up to 1580 °C), chemical phase, microscopic analysis, and other methods were used to study crystal and defect structure of many oxide systems.

In 1965, the worldwide first 50 W solid oxide fuel cell based on yttrium-stabilized zirconia solid electrolyte was developed and tested in the Laboratory of Electrolytes. Unfortunately, all publications in this field were strictly secret and nobody in the world knew about this priority of the Soviet scientists.

In 1968 under the leadership of Pal'guyev, a new chemical synthesis technique of solid electrolytes based on ZrO_2 coprecipitation from hydroxides was developed. Hydroxide coprecipitation was a fundamentally new method reported by French researchers from the Lefèvre group. Highly homogeneous and very dense ceramic samples were obtained. Using this synthetic method numerous systems based on ZrO_2–Y_2O_3, ZrO_2–Sc_2O_3, and ZrO_2–Yb_2O_3 were prepared, investigated, and optimized.

The first solid electrolyte electrochemical oxygen sensors of the USSR were developed in the institute. Also, for the first time in the USSR, the oxygen permeability of the solid electrolytes with dominant ionic conductivity and negligible electronic conductivity as well as of electronic conductors with small ionic conductivity was investigated (see, for instance, [8, 19]). The method for measuring the oxygen permeability was later patented under the name "Arzhannikov's method for determination of partial conductivities of solid electrolytes" (SU patent 1208501, 30.01.86).

Further, the first electrochemical devices based on oxide ion-conducting solid electrolytes, i.e., solid oxide fuel cells, water vapor electrolyzers, and oxygen concentrators, were also developed in the Institute of High-Temperature Electrochemistry. In 1978 the Laboratory of Physical and Chemical Properties of Solid Electrolytes has been renamed to the Solid Electrolytes Laboratory. Different cation-conductive solid electrolytes were investigated in the laboratory. Oxide semiconductor materials with fast ion and electron transport have been studied for different electrode applications in high-temperature electrochemical devices and MHD generators.

The Laboratory of Solid Electrolytes carried out an extensive advanced research on the implementation of solid electrolyte oxygen sensors at power plants and in laboratories for oxygen measurements. The economic effect of this implementation was many millions of US dollars.

8.1.3 Sergey Vasil'yevich Karpachëv (Fig. 8.3)

Sergey Vasil'yevich Karpachëv (1906–1987) is a famous Russian scientist, one of the founders of the school of high-temperature electrochemistry. He was born in the city of Kostroma. Karpachëv started working in 1925 as a laboratory assistant at the Ural Polytechnic Institute in Sverdlovsk (Yekaterinburg). In 1930, he graduated from the Polytechnic Institute, and from 1932 to 1948 he was the head of the Electrochemistry Laboratory of Molten Salts of the Ural Physical-Technical Institute, later becoming part of the Ural Subsidiary of the USSR Academy of Sciences. In 1940, Sergey Karpachëv defended his Doctor of Science thesis. In 1941, he became a professor and was in charge of the Physical Chemistry Department of the Ural State University for the next 6 years and vice-president of the university in 1946–1947. From 1949 to 1956, Karpachëv was involved in important government tasks of development of defense equipment and was the president of the Ural State University in 1957–1963. In 1963–1977, Karpachëv served as a director of the Institute of Electrochemistry of the Ural Subsidiary/Ural Scientific Center of the Academy of Sciences of the USSR. From 1965 to 1984, he headed also the Solid

Fig. 8.3 Professor Sergey Vasil'yevich Karpachëv

Fig. 8.4 Professor Sergey Vasil'yevich Karpachëv in his office

Electrolytes Electrochemical Kinetics Laboratory. In 1970, S. Karpachëv was elected as a corresponding member (Fellow) of the USSR Academy of Sciences.

Karpachëv's (Fig. 8.4) research was mainly focused on the electrochemistry of the molten salts and solid electrolytes. His early studies were directed toward the processes of magnesium and aluminum production, where his activities helped to solve a number of theoretical and practical problems of the electrochemical technology. Under the guidance of Karpachëv, research on electrode polarization in melts and contact potential difference of metals and other works have still not lost their importance and have made a significant contribution to the world of electrochemical science. He is considered as one of the founders of the Ural's School of Electrochemistry (Fig. 8.5). Karpachëv was the author of many fundamental papers in the field of electrochemical kinetics in the solid electrolytes. In the 1960s under the direction of Karpachëv, the research on the kinetics of electrode processes in solid oxygen ion electrolytes has produced some groundbreaking results (esp. by A.D. Neuymin, A.T. Filyaev, and later M.V. Perfil'yev). Initial studies showed that the value of the polarization depended strongly on the electrode material and the availability of partial electronic conductivity of the solid electrolyte (in which case it significantly decreased). He first obtained data on the capacity of the electrical double layer in solid electrolytes and regularities of the kinetics of exchange reactions of oxygen between the electrolyte and the gas phase. All these studies have furthered its development in the studies of kinetics of solid electrolytes.

For many years, Karpachëv headed the Section of Solid Electrolytes at the Scientific Council of Academy of Sciences of USSR focusing on the physical chemistry of ionic melts and solid electrolytes. Often the section meetings took place in Moscow at the Institute of Electrochemistry of the Academy of Sciences of the USSR where people from the whole Soviet Union gathered. Most of the laboratory staff of kinetics attended these so-called annual Frumkin readings, which gave them the opportunity to expand their scientific horizon.

Fig. 8.5 Professor Sergey Vasil'yevich Karpachëv among his colleagues from the laboratory of kinetics. (1) Sergey Somov, (2) Valentin Sal'nikov, (3) Mikhail Inozemtsev, (4) Dimity Bronin, (5) Gennadiy Fadeyev, (6) Mikhail Glumov, (7) Mikhail Perfil'yev, (8) Anatoliy Dëmin, (9) Boris Kuzin, (10) Ilia Remez, (11) Ludmila Yushina, (12) Anatoliy Filyayev, (14) Sergey Vasil'yevich Karpachëv, (15) Alexander Lipilin

Karpachëv paid extensive attention to the young scientists in the laboratory and at the institute as a whole. Therefore, he repeatedly gave a series of lectures on various topics, especially on thermodynamics and on the calculation of the EMF of electrochemical cells. He was a spectacular lecturer. He had a clear understanding of the complexity of the material and was trying to mix his lectures occasionally with funny scientific stories or other random matter. Many of his listeners remember the words at the end of one of his lectures: "Even the singing birds get bored if they sing too long!" This does not mean that he liked to stray too far away from the topic. In one of the workshops where a heated discussion was underway, he abruptly interrupted the discussion with the words, "Enough! The house cannot be built from words, let us to do the building work!"

Karpachëv was the supervisor of 28 PhD theses. Eight of his scholars defended Doctor of Science theses and headed scientific laboratories. For a long time, Professor Sergey Karpachëv was the head of the "Solid Electrolytes and Physical Chemistry of the Ionic Melts" Section of the Scientific Council of the USSR and was a member of the International Electrochemical Society. For his significant merits in the development of the advanced science and defensive techniques, Karpachëv was two times awarded the honorary title of Laureate of State Prize, the Order of Lenin, four Orders of the Labor Red Banner, the Order "Sign of Honor," and numerous medals.

8.1.4 Mikhail Vasil'yevich Perfil'yev (Fig. 8.6)

Mikhail Vasil'yevich Perfil'yev (1935–1997) was a famous Russian scientist and one of the founders of the school of the high-temperature electrochemistry of the solid oxide electrolytes. He was born in Chelyabinsk region (South Ural). In 1959 he graduated from the Physical-Technical Department of the Ural Polytechnic Institute, and in 1961 he became a PhD student of the Ural Division of the USSR Academy of Sciences. His PhD thesis "Kinetics of Electrode Processes in Solid Electrolytes" was defended in 1965. In this work, a model of charge transport at gas electrodes was proposed and developed for the first time in high-temperature electrochemistry. The basic principles of this model are still used today. In the late 1960s, Perfil'yev devoted extensive time to the impedance measurements of electrochemical systems with solid oxide electrolytes. He developed the bulk and grain conductivity separation method for polycrystalline solid electrolytes in 1971 publishing some important results in this field. This method opened many opportunities to study the effects of grain boundaries in polycrystalline solid electrolyte on its transport properties. In his subsequent works, he focused on the regularities of the conductivity of polycrystalline oxide electrolytes, depending on the grain size, as well as the availability of the grain boundaries for the segregation of various impurities.

Fig. 8.6 Professor Mikhail Vasil'yevich Perfil'yev

In the early 1970s, Perfil'yev established a very strong research group investigating different aspects of the grain boundaries effect, e.g., on the transport properties. Another and the most important subject area included the high-temperature electrolysis of gases. Systematic research on the kinetics of electrochemical decomposition of CO_2 and H_2O was studied. Kinetic regularities of CO electrochemical reduction up to carbon in solid oxide electrolytes were obtained for the first time. In those works, for the first time, an electrochemical cell with a gas diffusion barrier was used, which gave a powerful impetus for further analytical research for use of solid electrolytes. A number of highly active electrodes for high-temperature electrolysis cells were developed. The model of charge transport at electrodes comprising a porous metal matrix filled and mixed with an electronic-ionic conductor was created. Additional research established various cell designs and stacks of these cells were developed. The main issues related to the operation mode of electrolyzers for steam decomposition were solved. Extensive experimental results for electrolyzer tests, electrode cycling tests, single cells, and stacks were documented. A series of studies on the aging of solid electrolytes based on ZrO_2 was performed.

Together with Karpachëv, Perfil'yev initiated studies on the kinetics of isotopic exchange of oxygen-containing molecules of the gas phase with oxygen of the solid oxide electrolyte. Perfil'yev's group obtained fundamental information on the kinetics of oxygen exchange of various electrolytes and mixed conductors with an oxygen-containing gas phase, showed the peculiarities of the oxygen transport in the surface region of some oxides, and for the first time determined the exchange rate of a number of electrode system by a direct method. This made it possible to verify experimentally a variety of routes of electrode reactions (with the predominant involvement of the electrode surface or of the electrolyte or on parallel routes), depending on the chemical nature of electrolyte, electrode, and gas phase.

The first monograph *Electrochemistry of Solid Electrolytes*, written by Perfil'yev and coauthored by Chebotin, was published in 1978. This fundamental work summarized the experimental data and theoretical concepts of the electrochemistry in solid electrolytes. In 1984, this monograph has been published in the USA. His second monograph *High-Temperature Electrolysis of Gases* was published in 1988 in coauthorship with members of his laboratory.

A brilliant researcher, Perfil'yev constantly paid attention to the development of the research methodology in the solid electrolytes. The results of such activities have already been reported on the impedance method of the polycrystalline solid electrolyte conductivity investigation and development of the electrochemical cell with diffusion channel for the analytical chemistry and instrumentation. To define the lower temperature limit for the electrode equilibrium of the electrochemical cells, he has proposed a very original method based on the measuring the thermo-EMF of the electrochemical cells.

In 1984, Perfil'yev successfully defended his Doctor of Science thesis, and in 1985, after Prof. Sergey Karpachëv retired, he was appointed as a head of the Kinetics Laboratory. In this period he devoted much attention to the development of the solid oxide fuel cells (SOFCs). Largely thanks to his support, the 1 kW SOFC prototype was designed, manufactured, and tested in 1989.

He provided his younger colleagues (Fig. 8.7) with creative freedom and never set them under pressure. His kindness and sense of humor made him an exceptional advisor. He was essentially a wholehearted, passionate, and caring person. Outwardly calm, at heart he was emotional but only occasionally let that side of him to be seen. He always listened attentively without interrupting. In response, he did not say clear phrases; it was interesting not to listen to him but to watch. Every detail in his response was important to notice, such as his facial expressions, gestures, subtle moves, or shouting. In result, you received full, yet exhaustive, information. But that was why he could not speak in public; he behaved as if he was an actor at a cameral theater.

Perfil'yev supervised five PhD students, two of his students defended their Doctor of Science thesis, and four of them headed laboratories in the IHTE. He was serving as president of the Russian branch of the Solid State Ionics (SSI) International Society. He participated in some international conferences that were held in socialist countries, in particular in Czechoslovakia, GDR (Fig. 8.8).

Fig. 8.7 Professor Mikhail Vasil'yevich Perfil'yev with the young scientists at the Solid Electrolytes School in Donbai (USSR), 1984. *Left* is Dr. Pavel Shuk

Fig. 8.8 Prof. Mikhail Vasil'yevich Perfil'yev at "Festkörperchemie komplexer oxidischer Systeme, VIII. Tagung AG Festkörperchemie" (Binz, GDR, 1989) with Professor Michael Kleitz, Professor Alim Vecher, and Dr. Pavel Shuk

Fig. 8.9 Professor Vasiliy Nikolayevich Chebotin

8.1.5 Vasiliy Nikolayevich Chebotin (Fig. 8.9)

Vasiliy Nikolayevich Chebotin (1938–1985) was a well-known theoretician who made major contributions to many sections of the physical chemistry and electrochemistry of the solid electrolytes.

He was born in the Kurgan region (Western Siberia). In 1955, he graduated with honors from high school and began his studies at the Physical-Mathematical Department of the Ural State University graduating in 1960 with an "honors" degree in theoretical physics. Immediately he started working at the Institute of Electrochemistry of the Ural Subsidiary of the Academy of Sciences of the USSR, where he worked for almost 25 years.

In 1965, Chebotin defended his PhD thesis on "Electronic conductivity of ionic crystals in equilibrium with a gas phase." In 1971, at the age of 33, he presented his Doctor of Science thesis on "Research on the theory of solid electrolytes" and became the youngest Doctor of Science in the Ural Scientific Center of the Academy of Sciences of USSR. It is interesting to note that all the calculations he has performed were done using a slide rule.

He was a tall, dark-haired fellow that was always present in a suit with a tie, wearing his glasses. He was a noble man with natural dignity, but at the same time simple and open. He did not even exude a trace of arrogance and conceitedness. He understood and respected the experiments and was well versed in the details. He often repeated the words, "If the experiment contradicts the theory, so much the worse for the theory." And he knew his way around the laboratories. One anecdote involves a crucible furnace, which Chebotin used to heat his room in the winter time: it burned! Usually technicians spent no less than 2 days on the repairs because it was necessary to disconnect the housing, remove the external insulation, and fully disassemble ceramic elements, in which a spiral was hidden. Then in reverse, it was necessary to put a new spiral in the middle of the ceramics, stuff the asbestos, and mount the housing. One of the technicians was surprised to find the job done and noted that, "Vasiliy Nikolayevich replaced the heater in an hour without disassembling the furnace! It's impossible to understand!"

One characteristic feature of Chebotin, which was rare among the people, was that he did not like to talk about anybody and never spoke bad behind one's back. During public scientific discussions, however, he was ruthless if somebody presented inadequately prepared work.

In 1973, Chebotin founded a theoretical group at the Institute of Electrochemistry and headed this group till 1983. Besides his research activities, Vasiliy Nikolayevich paid serious attention to pedagogical activity. Fifteen of his students defended PhD theses and two defended Doctor of Science theses. He was a brilliant lecturer, who was able to explain the issue and make it understandable for the students with the different backgrounds. For many years he gave lectures at the Ural State University and taught a special course on the theory of disorder and transfer phenomena in solids. Moreover, he constantly educated young specialists from different universities and research centers in the chemistry and electrochemistry of solids (Fig. 8.10).

The scientific work of Chebotin was distinguished by many accolades and accomplishments already during his lifetime. Already in the first few years after graduation, he published a series of works on the theory of electron conductivity of ionic crystals in equilibrium with a gas phase. He continued this progress until the last years of life. From 1984 to 1985, he published 11 articles in leading scientific journals, and six articles were published in 1986, the year after his death. During his 25 years of active research, he published 170 papers. Those works included the textbook *Transport Phenomena in Ionic Crystals* (1968), the monograph *Electrochemistry of Solid Electrolytes* (1978) coauthored by Professor Perfil'yev, the monograph *Physics and Chemistry of Solid State* (1982), and the monograph *Chemical Diffusion in Solids* (1989) finished after his death by his scholars Dr. Igor Vasil'yevich Murygin (Fig. 8.11) and V. G. Gorodetsky.

Chebotin's scientific interests were characterized by a variety of topics and covered nearly all aspects of solid electrolytes electrochemistry. He made a significant contribution to the theory of electron conductivity of ionic crystals in equilibrium with a gas phase and solved a number of important problems related to the statistical-thermodynamic description of defect formation in solid electrolytes and mixed ionic-electronic conductors. Vital results were obtained in the theory of ion transport in solid electrolytes (chemical diffusion and interdiffusion, correlation effects, thermo-EMF of ionic crystals, and others). Chebotin paid great attention to the solution of actual electrochemical problem—first of all to the theory of the double layer and issues related to the nature of the polarization at the interface of the solid electrolyte and gas electrode.

Fig. 8.10 Professor Vasiliy Nikolayevich Chebotin gives a lecture for the young scientists (1978)

Fig. 8.11 Dr. Igor Vasil'yevich Murygin (fourth from the *left*) from Prof. Chebotin's theoretical group together with Dr. Andrejs Lūsis, Prof. Alim Vecher, and Dr. Pavel Shuk meeting Professor Takehiko Takahashi (Japan) at the Institute of Solid State Physics (Riga, USSR, 1984)

In his research, Chebotin always focused on the research subject. He was rarely interested in the theoretical tasks and believed it was much more important to find a simple and productive model that could explain the observed experimental facts. In many cases the experiment was parallel with the theory development, and Chebotin took a direct role in the planning and staging of the new experiments.

The scientific biography of Chebotin is short but monumental. His scientific ideas still influence the work on the solid electrolytes such that his articles are cited, and monographs are used by the senior scientists, lecturers, and tutors for the preparation of the young scientific staff.

Fig. 8.12 Dr. Anatoliy Dmitriyevich Neuymin

8.1.6 Anatoliy Dmitriyevich Neuymin (Fig. 8.12)

Anatoliy Dmitriyevich Neuymin (1932–2014) graduated from the Physical-Technical Department at the Ural Polytechnic Institute in 1956 and entered the Laboratory of Physical and Chemical Properties of Solid Electrolytes of the Institute of Electrochemistry in 1958. In 1964 he obtained his PhD thesis.

Neuymin's research interests were extremely wide. At the early stage he synthesized new solid oxide electrolytes and measured their conductivity and transfer numbers and studied electrode kinetics in the solids. But his main interest was the development of various electrochemical devices based on solid oxide electrolytes, e.g., solid oxide fuel cells (SOFCs), electrolyzers, oxygen pumps, and sensors. From the morning till late in the evening, he was at the institute, and actually he led the laboratory.

Mainly thanks to Neuymin's activity, the first in the world 50 W solid oxide fuel cell based on yttrium-stabilized zirconia electrolyte was built in 1965 and tested for 1000 h in the Laboratory of the Electrolytes. All kinds of oxygen sensors were developed by him or under his supervision. On the base of these scientific achievements, the Soviet industry began the production of the first sensors and laboratory oxygen analyzers, e.g., "Agate," "ANG," and "SIVE." Sensors for detecting oxygen in the copper and iron melts were also developed by Neuymin and his co-workers.

In 1981 he founded and headed the Laboratory of the Electrochemical Devices.

A lot of prototypes were created in this laboratory, e.g., modern oxygen sensors, widely used in the industry, pumps for extra-pure oxygen and so-called mountain air (air depleted with oxygen) production, and, most importantly, his latest brainchild, various solid oxide fuel cell battery prototypes from 100 to 700 W.

Neuymin was a cheerful, energetic man and his optimism, sincerity, and openness attracted many people to his personality. He was a very, very bright and knowledgeable person who never knew irresolute problems; it seemed that he

Fig. 8.13 Dr. Zoya Semënovna Volchenkova

knew everything and was ready to advise on many different subjects. Researchers and engineers from all parts of the Soviet Union came to him to discuss with him the problems of implementing electrochemical devices developed in the Institute of High-Temperature Electrochemistry.

Neuymin was awarded the Order of Red Banner of Labor for his extraordinary contribution to solid electrolyte applied research.

8.1.7 Zoya Semënovna Volchenkova (Fig. 8.13)

Zoya Semënovna Volchenkova (1923–2006) was one of the pioneers in the solid oxide electrolyte research. She graduated from the Chemical Department at the Ural Polytechnic Institute in 1945 and defended her PhD theses in 1952. Since the foundation of the Institute of Electrochemistry, she worked in the laboratory headed by Prof. Sergey Fëdorovich Pal'guyev.

Her group has systematically studied many binary systems CeO_2–MO (M = Be, Mg, Ca, Sr, Ba), ZrO_2–MO (M = Be, Ca, Mg, Sr, Ba), ZrO_2–M_2O_3 (M = Y, Yb, Sc), HfO_2–MO (M = Be, Mg, Ca, Sr, Ba), HfO_2–M_2O_3 (M = Sc, Y, La, Nd), and ThO_2–MO (M = B, Mg, Sr, Ba). The phase diagrams, electrical conductivities, and ionic transport numbers were investigated in details. All these results were a good addition to XRD confirming the formation of the new chemical phase. She studied also other oxides by "small increments." For example, the work on Y_2O_3 and Sc_2O_3 defect structure was very classical. Later she studied the thermal EMF in the oxides. Volchenkova was one of the best experts in the field of electric transport and defect structure of oxides.

Fig. 8.14 Dr. Anatoliy Trofimovich Filyayev

8.1.8 Anatoliy Trofimovich Filyayev (Fig. 8.14)

Anatoliy Trofimovich Filyayev (1931–2006) graduated from the Physical-Technical Department at the Ural Polytechnic Institute in 1956. Filyayev began his scientific work in 1956 at a branch of the All-Union Institute of Aluminum and Magnesium in Berezniki (West Ural). In 1959, he entered the Institute of Electrochemistry where he obtained a PhD degree in 1965. In 1963, he and his co-workers for the first time in the world showed that in solid oxide electrolytes the dependence of the electrode capacitance on the electric potential of the electrode is as close to the parabolic form. They made the assumption that the potential minimum of this dependence corresponds to the potential zero charge. The group headed by Filyayev studied the properties of the electric double layer in solid electrolytes and used such complex experimental methods in the measurement of the contact angle, the definition of the maximum interfacial energy dependence on the electrode potential, and the measurement of the differential capacitance and resistance. A model of the structure of the electric double layer was created, which explained the behavior of the differential capacitance as a function of the electrode potential and temperature for all types of solid electrolyte.

Filyayev was a very responsible and respectable person, whose opinion was always taken into account (not only on scientific matters but also in the social life of the institute). He generously and unselfishly shared his knowledge and experience with colleagues and helped the young colleagues. People went to see him for help and knew that they would get it.

8.2 Development of Solid State Electrochemistry in Ural After 1990

In the late 1980s the situation of the Soviet science became worse and worse because of the decreasing funding in all sectors of the Soviet economy. In 1991, the Academy of Sciences of the USSR was divided into national academies of science. The biggest national academy became the Russian Academy of Sciences. That time the institute obtained its present name: Institute of High-Temperature Electrochemistry of Ural Division of the Russian Academy of Sciences (IHTE UD RAS).

Unfortunately, because of galloping inflation in the early 1990s, the Russian fundamental science could hardly survive. That time the institute paid major attention to establishing collaboration with Russian and Western scientific and industrial organizations. In the field of solid oxide electrolytes, the Institute of High-Temperature Electrochemistry signed a number of agreements: with the Special Design Electrochemical Bureau (Moscow) in the field of solid oxide electrolyzers; with the Russian Federal Nuclear Center (Snezhinsk, Chelyabinsk region), the Special Boiler Design Bureau, and the Institute for Accumulation and Transformation of Energy of CNR (CNR-TAE, Messina, Italy) in the field of SOFC; and with the Air Products and Chemicals, Inc. (Allentown, PA, USA) in the field of oxide conductors with mixed ionic-electron conductivity (MIEC). The IHTE workers visited several times the CNR-TAE which bought the 150 W SOFC prototype made in the IHTE for mutual investigation. Several papers were published in this collaboration (see, for instance, [51]). Due to the various reasons, mainly the insufficient funding, the works with these institutions did not provide the expected result and the works were stopped. The institute in fact stopped the SOFC development and limited the activities to the fundamental research and theoretical modeling.

However, since the beginning of the 1990s, the Russian scientists were given the new opportunity to invite foreign colleagues, i.e., the gurus in the solid state ionics field Prof. Brian Steel, Prof. Takehiko Takahashi (Fig. 8.15), and Prof. Per Kofstad visited the Institute of High-Temperature Electrochemistry. The Russian scientists were also participating in several international conferences and symposiums, thanks to the Russian and international grants (Figs. 8.16, 8.17, 8.18).

Some recovery of the works took place at the beginning of 2000. The institute participated in the INTAS project (2000–2002) and INCO-COPERNICUS project (2001–2003). However, the basic salaries in the academic institutes that time remained very low: 70–80 USD for the researchers and about 100 USD for the head laboratory. The Russian Academy of Sciences and the biggest Russian company Norilsk Nickel (nickel and palladium mining and smelting) signed an agreement on the collaboration in the field of hydrogen energy and fuel cells in the beginning of 2004. The Norilsk Nickel was willing to spend $30 million per year for the research and development projects in the frame of this agreement and intended to support the research activities for 10 years. More than 40 institutes of the Russian Academy of Sciences were involved in the projects under this agreement. The

Fig. 8.15 Prof. Mikhail Vasil'yevich Perfil'yev with his scholars Dr. Alexander Lipilin (second from the *left*) and Dr. Anatoliy Dëmin meeting in Yekaterinburg the famous Prof. Takehiko Takahashi (1991)

Fig. 8.16 Prof. Mikhail Vasil'yevich Perfil'yev with his scholar Dr. Anatoliy Dëmin at the Ninth World Hydrogen Energy Conference in Paris, France (1992)

institute actively participated in several R&D projects. However, the Norilsk Nickel lost interest in the mutual project very soon and the funding ended in 2006.

Fortunately the Russian Academy of Sciences initiated in 2006 the so-called Pilot Project, the main aim of which was to increase the salary of scientific workers. It was planned that during several years salaries had to be raised to

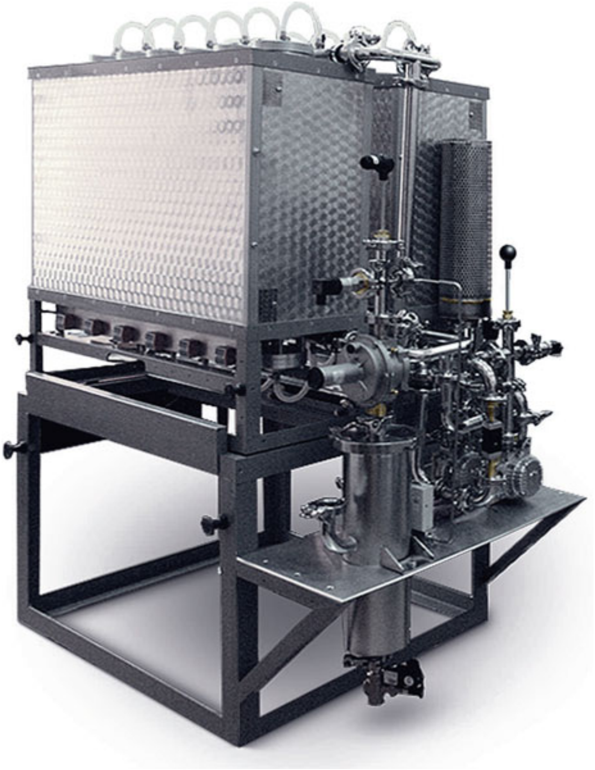
Fig. 8.17 Dr. Anatoliy Dëmin meeting Prof. H. H. Mobius at the Second European SOFC Forum in Oslo, Norway (1996)

Fig. 8.18 Dr. Sergey Bredikhin, Dr. Anatoliy Dëmin, and Dr. Pavel Shuk with Professor Ulrich Guth (Germany) at the Ninth Euroconference on Science and Technology of Ionics in Rhodes, Greece (2002)

ca. 400–600 USD for the researchers and to ca. 700 USD for the heads of the laboratories. However till now the salaries do not reach the planned values.

The activities in the solid state electrochemistry field was given new life after Professor Yuriy Zaykov was appointed as a new IHTE director in 2006. Recognizing the very promising future of the solid oxide fuel cell development, Professor

Fig. 8.19 1.5 kW solid oxide fuel cell prototype



Zaykov initiated the solid oxide fuel cell prototyping and testing. He established the relations with Russian industrial partners who agreed to finalize the SOFC development. The 100 W SOFC prototype was built in 2008 and tested in the real condition of the Ural winter climate for ~4000 h without losing significantly in performance. Then the IHTE designed and constructed the 200 W SOFC prototype for demonstration and the 300 W prototype for the Tomsk Polytechnic University. In 2013, the IHTE built the 1.5 kW SOFC prototype (a peak power 2.0 kW) in cooperation with the electrochemical converter plant (Novouralsk, Sverdlovsk region) and public corporation Uralintech (Yekaterinburg) for Gazprom (Fig. 8.19). This SOFC prototype was tested at the factory and an outdoor test on the pipeline is now in progress.

In the last years, the institute participated in international programs in particular in the project "SOFC-Life" in the frame of FP7. In 2014 the institute won a grant of the Ministry of Education and Science, in the frame of which Professor Panagiotis Tsiakaras from the University of Thessaly (Volos, Greece) as the leading scientist headed the Laboratory of Electrochemical Devices based on solid oxide proton electrolytes. This laboratory was specially created in the IHTE in the frame of the Russian government program aimed "to attract the world's Leading Scientists to Russian institutions of higher learning, research organizations of the governmental academies of sciences, and governmental research centers of the Russian Federation."

On the whole it can be stated that the Ural School of Solid State Electrochemistry could survive and now is getting the second life.

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Chapter 9
Organic Electrochemistry in the USSR

Victor G. Mairanovsky

The English scientific literature commonly refers to this field as “electroorganic chemistry,” often emphasizing the synthesis and its connection to organic chemistry. The first electrosynthesis of an organic compound—the anodic conversion of acetate to ethane—was conducted 180 years ago by Faraday [1]. Kolbe made a preparative procedure of this [2], which, as “Kolbe electrolysis,” is now considered to be the birth of “electroorganic chemistry” [3, 4]. In the Russian scientific literature, the term “electrochemistry of organic compounds” (“**e**lektro**kh**imiya **o**rganitscheskikch **s**oedineniy” = “EKhOS”) is used for the English “organic electrochemistry.” Both these terms describe the whole field of electrochemistry, which, in addition to electroorganic chemistry, includes determination of mechanism of electrode processes along with kinetic parameters of its stages, studies of electrode and pre-electrode effects (adsorption, electric field, etc.), combined spectral and electrochemical methods, analytical applications, etc. Thus, given the vast range of methods and objects falling under the domain of organic chemistry—from simple molecules to complex natural compounds and macromolecular polymer structures—organic electrochemistry opens very wide fields for research. The work of Fritz Haber [5] may be considered as the beginning of EKhOS. He was the first to recognize the importance of the electrode potential in formation of various products and to conduct electrolysis of an organic substance (nitrobenzene) at controlled electrode potential, establishing the sequence of transformations.

So what is left over from organic electrochemistry in the USSR? More than 20 years after the disintegration of the USSR, those works are now history, as is the era in which we lived and worked. In this article, I will describe the research and also the circumstance under which it was done, and I will share some of my personal experience (Sect. 9.2). The systematic bibliography at the end may be

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useful for a reader interested in the history of science. As a rule, the references are given to the original Russian sources.

In contrast to applied electrochemistry and fundamental (theoretical) electrochemistry (Frumkin and his disciples), organic electrochemistry was not considered as a priority in the USSR until 60-ies. For example, in the textbook on kinetics of electrode processes [6], published by Frumkin et al. in 1952, only a few pages relate to electrochemical transformations of organic compounds. There were also no state-run programs to develop specialists in the field.

The advances made in polarography in the USSR became a decisive factor for a considerable acceleration of organic electrochemistry. In the early 1950s, first studies were published on organic polarography outside of analytic applications (Moisei Neiman, Stal' Mairanovskii, Emmanuil Levin) (e.g., [7, 8]). This direction was also promoted by the Czech polarographic school on the theory of kinetic and catalytic currents (Koryta, Koutecky, Hanuš) and by Peter Zuman's studies on the relations between the half-wave potential $E_{1/2}$ and the structure of compounds. The school of Frumkin and its achievements in detailed studies of the processes on the dropping mercury electrode (DME), including adsorption phenomena, polarographic maxima of the first and second kind, features of the electroreduction of anions, etc., has played an important role (Krjukova, Nikolayeva-Fedorovich, Damaskin, Petrii, et al.).

The beginning of the USSR production of instruments for electrochemical measurements played a major role in further developments. Those instruments were developed primarily by S.B. Tsfasman and I.Ye. Bryksin in the TSLA (Tsentralnaya Laboratoriya Avtomatiki, Moscow) [9]. Advanced equipment from TSLA became available: the polarograph PE-312 with fast recording; the oscillographic polarograph PO-5122 with a recording oscilloscope; the powerful potentiostat P-5827 with an output voltage up to 200 V; the a.c. "vector polarograph" (see Chap. 5, Sect. 5.9). A strong group developing electrochemical equipment has been established at the Kazan's Aviation Institute (R. Sh. Nigmatullin, M. R. Vyaselev, A. I. Miroshnikov et al., oscillographic polarographs with differential mode and with fractional differentiation, etc), Zaretskiy's and Bruk's group in Ordzhonikidze, North Ossetia (automatic polarografic analyzers), etc. [10–12].

A series of regular scientific conferences of electrochemists started in the late 1950s; in the spirit of the time, they were called "soveshchanie" (meetings) instead of "konferentsiya" (the Russian word borrowed from foreign languages). The first polarographic conference took place in Kishinev (Moldova) in 1958 (hereinafter "conference" will be used instead of "soveshchanie"). The first conference on EKhOS was held in Moscow the same year in the Institute of Electrochemistry, Academy of Sciences, IELAN. Proceedings of the conferences became available from the fifth EKhOS conference (Moscow 1965) onwards as a series of books *Progress of Electrochemistry of Organic Compounds*. There were seven such books published prior to 1990; they formed the "EKhOS encyclopedia" [13–20]. Frumkin initiated the EKhOS conferences which he believed of great importance for the future developments in that field. It so happened that he passed away in

Tula on the first day of the EKhOS-76 conference which was planned to start with his opening. I remember him on a sunny morning of May 27, 1976, standing by a column in the lobby of a Dom kultury ("house of culture") of a chemical plant. He felt ill; there were few people around him. In the meantime, it was getting late and the conference participants were ushered into the meeting room. Alexander Naumovich Frumkin was taken to the hospital; a few hours later he passed a way.

By the first half of the 1970s, the Soviet Union had several centers specializing in various areas of organic electrochemistry. At that time, an intensive growth of that field began in many cities of the USSR—in Moscow, Kazan, Riga, Kharkov, Novocherkassk, Tula, Alma-Ata, Karaganda, Kishinev, Tbilisi, and other cities. Here is a brief description of few of these centers, direction of their work, and staff. The information is arranged by "geographical principle."

9.1 Organic Electrochemistry in the USSR: The Main Centres and Fields of Work

9.1.1 Moscow and the Moscow Region (up to 200 km)

First of all, there were two centers founded and led by Frumkin: the Department of Electrochemistry of Lomonosov Moscow State University (MGU) and the Institute of Electrochemistry of the USSR Academy of Sciences (IELAN). Their role was invaluable in the formation of modern theoretical concepts and also in the developments of applied electrochemistry. Organization of all aspects of EKhOS conferences, from selection of the principal theme to publication of the next volume of *Progress of EKhOS*, was held under the auspices of IELAN. The Electrochemistry Department of the MGU published a textbook [21] focused on adsorption of organic substances on electrodes—an issue previously not addressed in any textbooks. Important contributions to the study of the adsorption of organic compounds on the electrode were made by G.A. Tedoradze, A.B. Ershler, L.G. Feoktistov, and M.M. Gol'din, all at IELAN (see G.A. Tedoradze [13], p. 23).

Considerable efforts were made to develop new methods applicable to EKhOS: photo-electrochemical methods, photoemission techniques (Yu.V. Pleskov, Z.A. Rotenberg, etc.), chronopotentiometry (A.B. Ershler [17], p. 199), etc. The pioneering work on ring-disk electrode was published by Frumkin and Nekrasov [22]; this technique has proven particularly useful for the study of electroorganic reactions. The two "Frumkin centers" (MGU and IELAN) were also invaluable for specialists from other centers. For instance, I remember with gratitude the regular EKhOS seminars by Leonid Feoktistov. In IELAN, I met and became friends with Alexander Ershler (Fig. 9.1) and Zakhar Rotenberg; later on we had several joint projects. This book includes a separate article on the contribution of Frumkin's school by Oleg Petrii who was one of the leading scholars of that school (Chap. 4).

Fig. 9.1 Dr. Alexander Borisovich Ershler (1935–1989) with his group. From right Dr. chem. A.B. Ershler, Ph.D. phys. Eduard M. Podgaetskii, Engr. Tatyana S. Orekhova, Ph.D. chem. Ida M. Levinson; another member of the group, postgraduate student Vladimir Kurmaz, was drafted at this time into the Soviet army. Areas of research: adsorption theory of neutral organic compounds and its influence on kinetics of electrode reactions, electrode reactions of organomercury compounds, development of new electrochemical methods (high-speed pulse chronopotentiometry, electroreflection, and optical transitions at the metal–electrolyte interface, etc.). IELAN, 1975

The Department of Organic Chemistry of MGU cultivated another direction—electrochemistry of organometallic compounds. In the late 1960s, Kim P. Butin investigated systematically mercury-organic compounds by polarography, as part of joint research with Ershler. One of the outcomes was a method for estimation of pK_a of weak CH acids based on the relationship between pK_a and $E_{1/2}$ of the "organic calomels" R_2Hg. That method was used to determine the CH acidity of about 50 hydrocarbons starting with methane [23–25]. Later, Butin's laboratory studied intramolecular charge transfer complexes, electrocatalytic methods, and electrochemical modeling of enzymatic catalysis [26].

There were three research institutes of the USSR Academy of Sciences (USSR AS) in Moscow with groups working in organic electrochemistry. The largest center was at the Institute of Organic Chemistry (IOKH). It all started with Stal' Grigorievich Mairanovskii who joined the Institute in 1956 as a 30-year-old, already a Ph.D.. Stal' Mairanovskii (Stal' Mayranovskiy in Russian transcription) is rightfully regarded as belonging to Frumkin's school, although he specialized in technology of organic chemistry at the Moscow Lomonosov Institute of Fine Chemical Technologies (MITKhT) during 1943–1948.[1] Numerous papers and

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[1] He performed the thesis "Study of polarizability of complex molecules" under the supervision of Yakov Kivovich Syrkin, a member of the USSR Academy of Sciences, one of the leading Soviet theoretical chemists. In 1951, Syrkin was accused of "cosmopolitanism and propaganda of

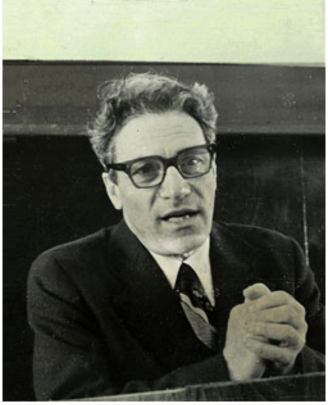

Fig. 9.2 Prof. Dr. Stal' Grigorievich Mairanovskii (1926–1991). Graduated from M.V. Lomonosov MITKhT (1943–1948), Ph.D. (1953), Dr. chem. (1962), professor (1986). The work at the chemical plant "Akrikhin" (1948–1956), from 1956 to 1991 leader of the electrochemical group in the IOKH USSR AS

books published by him and in cooperation with Soviet and foreign scientists (Frumkin, Levich, Kharkaz, Khaykin, Tedoradze, Ershler, Stradin, V.D. Bezuglyy, Koutecky, Hanuš, et al.) show the breadth of his scientific interests (Fig. 9.2).

Stal' Mairanovskii started out in organic polarography in 1950 at the chemical pharmaceutical plant "Akrikhin" near Moscow. After an unsuccessful interview attempt for a postgraduate course at Moisei B. Neiman's laboratory at the Institute of Chemical Physics of the USSR AS (as an "A" student, he "failed" in the philosophy exam—a common trick in the USSR to block "persons of Jewish nationality" from universities, postgraduate studies, etc.), he continued to work at that plant. He was at Akrikhin from 1948 to 1956 working his way up from being an engineer to head of production facility. During that time, he carried on his research and completed several projects with M.B. Neiman, which Frumkin submitted for publication in the journal *Doklady AN SSSR* [7, 27, 28]. Almost 20 of Stal' Mairanovskii's articles were recommended by Frumkin for publication in the prestigious *Doklady AN SSSR* in the 1950s–1960s, and Frumkin was highly selective!

Mairanovskii defended his Ph.D. thesis in 1953. The new theory of catalytic hydrogen evolution (B and DH are the catalyst and proton donor) was a part of that thesis:

$$\begin{aligned} &\mathrm{B} + \mathrm{DH} \leftrightarrows \mathrm{BH}^+ + \mathrm{D}^- \\ &\mathrm{BH}^+ + \mathrm{e} \leftrightarrows \mathrm{BH}^\cdot \\ &2\mathrm{BH}^\cdot \rightarrow 2\mathrm{B} + \mathrm{H}_2 \end{aligned} \tag{9.1}$$

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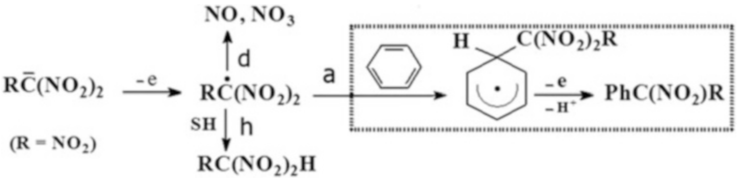
ideologically misguided resonance theory" and, together with Frumkin, of underestimation of the "decisive contribution of Russian scientists to physical chemistry" (due to their joint article in the *Great Soviet Encyclopedia*). This was followed by dismissal of Syrkin from the Karpov Institute of Physical Chemistry and by dismissal of Frumkin as director of the Institute of Physical Chemistry of the USSR Academy of Sciences.

Stal' Mairanovskii was one of the first to apply the results of Koutecky and Hanuš for investigating electrode processes with chemical stages, and in so doing, he introduced the concepts of "volume" and "surface" chemical stages [29] and demonstrated the role of "surface" reactions. Several studies on the verification of schema (9.1) were carried out in cooperation with Czech scientists [30–32]. This material demonstrating a new approach to the analysis of polarographic waves to find the kinetic parameters taking into consideration adsorption and electrical double layer effects was summarized in [33, 34]. That monograph became one of the first books of Soviet electrochemists translated and published in the West. A number of pioneering ideas were presented in the monograph. Among them were the concept of "inheritance effect" (according to which the product of the electrochemical stage may retain structural elements and the adsorption orientation of the initial reagent), prediction and a proof of significant pH change in pre-electrode layer due to a strong electric field, and application of polarography at hydrostatic pressures up to 3000 kg/cm^2, in particular for the study of surface chemical reactions [35–37]. Stal' Mairanovskii himself and in cooperation with other scientists published several other monographs [38–40], which helped to advance EKhOS in the Soviet Union. The first results directly related to electroorganic chemistry included the discovery of a difference in the electroreduction of *cis*- and *trans*-1,2-dibromethenes [41], establishment of an activating effect of the nitro group during cathode rupture of the C–halogen bond [42], and determination of electroreductive transformations of polynitroalkanes (PNAs) with regard to α-CH acidity [43–45]. The works of Stal' Mairanovskii and his associates and postgraduates laid the foundation for the studies of EKhOS at the Institute in years to come. For instance, V.A. Petrosyan and M.E. Niyazymbetov's study of electrooxidative transformations of PNA led to the discovery of interesting synthetic pathways [46–48]. They found that the intermediate PNA radicals form corresponding nitroalkylaryl arene derivates in the presence of arenes, instead of expected deactivation radicals by a cleavage of C–N bond or by the attaching of H atom from the medium:



(9.2)

Based on that mechanism, the effective anode syntheses of polynitroalkyl arenes [50] and ylides (if heteroarene is taken instead of arene) were developed. The process involved an intermediate arenium cation following path –**ea**–**e**–**p** and –

Fig. 9.3 Prof. Dr. Vladimir Anashuvanovich Petrosyan. Graduated from D.I. Mendeleev MKHTI (1963), Ph.D. (1970), Dr. chem. (1982), professor (1986), IOKH USSR AS from 1963, head of the Laboratory of Organic Electrosynthesis since 1986

ea–ed, respectively.[2] Vladimir A. Petrosyan's group (since 1986, it is the Laboratory of Organic Electrosynthesis) studied other reactions of anodic substitution, S_N^H reaction, and generation of carbenes [51] (Fig. 9.3). The works on the cathodic de-protonation of weak acids [49, 50], which started in the late 1980s (electrochemical versions of Michaelis–Becker, Wittig–Horner, and Perkin reactions), found interesting preparative applications. A series of original electrosyntheses was performed also by Dr. Michael N. Elinson's group, in particular, synthesis using electrochemically induced chain reactions [52]. In 2011, 55 years after the beginning of EKhOS by Stal' Mairanovskii, the works of these two groups from IOKH were honored with the N.D. Zelinsky Award.

The Institute of Organoelement Compounds of the USSR AS (INEOS) was founded by A.N. Nesmeyanov (1899–1980, the president of the USSR Academy of Sciences from 1951 to 1961 and director of the INEOS AN from 1954 to 1980). The work on EKhOS was conducted in several directions. The polarographic behavior of the tropylium cation [53] was first investigated here in 1957. Active studies of non-benzoid aromatic compounds were started in the laboratory of D.N. Kursanov, corresponding member of the USSR Academy of Sciences, after Mark Efimovich Vol'pin has joined the laboratory.[3] In connection with research on the catalysis by metal complexes (Vol'pin's pioneering work on fixation of nitrogen

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[2] Here and below we use the system of abbreviated notation of electrode reactions (see Appendix). Thus, a complete schema of reactions (9.2) is written as "**–e(d)(h)a–e–p**," where "**–e,**" "**h**," and "**–p**" are transfers of electron, hydrogen, and proton, "**d**" and "**a**" are C–N bond **d**issociation and C–C bond **a**ssociation, and in the brackets (d)(h) are parallel stages.

[3] M.E. Vol'pin (1923–1996) was a Dr. chem. sci. (1959), an academician (1987), and the director of INEOS (1988–1996). Vol'pin got a contract at INEOS only as a result of persistent efforts of Kursanov in 1958, 3 years after he began work unofficially for free in Kursanov's laboratory, because of restrictions for persons of Jewish nationality (see [54]). I met them both during my unsuccessful application to INEOS in 1961 (see Sect. 9.2).

[55]), electrochemical studies on pi-complexes of transition metals and metallocenes were carried out in this laboratory [56–58].

Electrosynthesis works performed in the laboratory headed by academician Ivan Ludvigovich Knunyants deserve special mention. First of all, it is the reaction of acrylonitrile hydrodimerization (the term “hydrodimerization” was suggested by Knunyants and N.T. Gambaryan [59]). Using an electrochemically generated sodium amalgam, Knunyants and N.S. Vyazankin were first to get adipodinitrile, an intermediate in the caprolactam production, with reasonable yield [60, 61]. Direct electrosynthesis later proposed by Baizer [62] was implemented by Monsanto and became the world’s largest industrial organic electrosynthesis [63]. The $\mathbf{ea_2p}$ schema with dimerization of an intermediate anion radical was adopted for this process (DH is a proton donator)[4]:

$$CH_2 = CHCN + e^- + DH \overset{ea_2\,p}{\rightarrow} \frac{1}{2} NC(CH_2)_4CN \tag{9.3}$$

Another pioneering electrosynthesis was the “soft” fluorination developed by I.N. Rozhkov, I.L. Knunyants, etc. [64, 65]. Unlike the known “hard” fluorination in liquid HF [66], which leads to perfluorinated compounds, often accompanied by side reactions, the “soft” fluorination is a selective electrosynthesis. The process is performed on a Pt anode in MeCN at the oxidation potential of the substrate RH. The $\mathbf{-ea_N\!-\!e\!-\!p}$ mechanism is suggested for this reaction [67–69] (Figs. 9.4 and 9.5):

$$RH \overset{-e^-}{\rightarrow} RH^{\cdot+} \overset{F^-}{\rightarrow} RHF^{\cdot} \overset{-e^-}{\rightarrow} RHF^+ \overset{-p}{\rightarrow} RF \tag{9.4}$$

The direction of F^- anion attack is consistent with the distribution of the density of positive charge [64, 65]. The “soft” electrochemical fluorination very soon attracted attention in the West and is extensively used and developed [70]. Ionic liquids [71], alkali metal fluorides in poly(ethylene glycol) [72], etc., were proposed to be used instead of organic solvents. Just as the “hard” electrochemical fluorination was called the “*Simons process*,” the “soft” fluorination should be referred rightfully to as the “*Rozhkov–Knunyants reaction*.”[5]

As it happened, Knunyants became the opponent of my doctoral thesis. When Igor’ Rozhkov found out that I had prepared a doctoral thesis, he advised me to ask Knunyants to be the opponent. Rozhkov said that one of the research fields of Knunyants is the chemistry of natural compounds, and he is interested in electrosynthesis. Igor’ warned me, however, that he might decline—“Knunyants is known to be fastidious and now rarely examines dissertations.” Ivan Ludvigovich

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[4] Other mechanisms suggested [3, 63] are ↑**epe**↓**ap** and ↑**e**↓**apep** with the participation of the initial substrate RH in a bimolecular step “**a**” (for the notation, see Appendix).

[5] The “Knunyants’s lactone” for acetobutyrolactone and “Knunyants’s regrouping” are established terms in the literature.

Fig. 9.4 Academician Ivan Ljudvigovich Knunyants (1906–1990). Dr. chem., professor, general of engineer corps, laureate of the state (three times), and Lenin Prizes of USSR. He had developed physiologically active compounds and medicine drugs and organofluorine monomers and fibers; the founder of the Russian school of organofluorine chemistry and head of the organofluorine laboratory in INEOS RAS (1954–1986). Lecturer of the Military Academy of Chemical Protection (head of the department since 1938). The founder and chief editor of the Zh. Vses. Khim. Obstsh. im. Mendeleeva (1956, Mendeleev communications since 1990), editor-in-chief of the chemical encyclopedia (Moscow 1988–1990)

Fig. 9.5 Ivan Ludvigovich Knunyants with several members of his lab, INEOS AN SSSR. Third from the right Igor' Nikolaevich Rozhkov (1934–1993). Rozhkov graduated from M.V. Lomonosov MITKhT (1953–1959), Ph.D. (1964), Dr. chem. (1978), head of the Laboratory of Electrochemistry of Organoelement Compounds (1989–1993)

met me quite coldly and silently looked through the thesis. When he reached the section on the electrosynthesis of the oxytocin hormone, he perked up; he was previously involved in the chemical synthesis of this compound. Two weeks later, he agreed to be my opponent. Knunyants came to the Academic Council of Moscow State University wearing his general's uniform and began his speech with an apology that he was due to have a meeting at the military academy later. He praised my thesis in his statement.

Ivan Ludvigovich was an outstanding scientist and an extraordinary person. In addition, to the well-known brilliant scientific achievements, in the narrow circles, he was also known for his so-called Knunyants absences (as per S.M.). Unlike many other prominent academicians, Knunyants did not sign condemning political letters in the Soviet newspaper *Pravda*. Every time he learned of a letter being prepared, he took a business trip and only few trusted people were privy to his whereabouts. On the contrary, Knunyants signed what became known as the "*Letter of 13*" against Stalin's rehabilitation (1966). Along with academicians A.D. Sakharov and P.l. Kapitsa, in 1970, he also signed the "petition in support of Zhores Medvedev"—a scholar and a writer persecuted for his revelatory book on T.D. Lysenko.

The Institute of Chemical Physics of the USSR AS in Chernogolovka. Dr. Vladimir Vasiljevitch Strelets (see Fig. 9.20) must be mentioned here as a renowned scholar in the field of electrochemistry of organometallic compounds and electrocatalysis by metal complexes. Dr. Strelets and coauthors performed pioneering studies on electroreduction of carbon oxide to methane with vanadocene as catalyst (electrochemical equivalent of Fischer–Tropsch process) as well as investigated the mechanism of transformation [73, 74]. Of great interest are also his other works on the electrochemistry of metallocenes including those carried out in post-Soviet period, e.g., studies on complexation of ferrocenes by cyclodextrins [75], generation of cobaltocene cations and anions over an extremely wide 6-volt potential range ±3 V SCE [76], etc. I first met Vladimir in 1963 in Alexander Ershler's laboratory (IELAN) and we kept in touch for many years until Vladimir Strelets, an original scholar and excellent experimentalist, passed away in Chernogolovka on October 7, 2014.

In the 1970s, a scientific group devoted to photoemission methods was established in the same institute under the direction of V. A. Benderskiy. An original laser photoemission technique (LPE) was developed and pioneering studies of short-lived intermediates of organic electrode reactions were undertaken (V.A. Benderskiy, A.G. Krivenko, V.A. Kurmaz, A.S. Kotkin, etc.); and the LPE was supplemented by classical electrochemical methods [77]. Using the LPE-measurements the pK_a values of weak acids (alkanes, benzene and their halogen derivatives) have been determined [77]. Both the direct generation of intermediates by solvated electrons (**εc** schema, the analogy to the usual **ec** reaction) and indirect generation by interaction of reagents with $OH^{\cdot}$, $H^{\cdot}$ and other radicals (**εcc** schema) were developed. The photoemission measurements were supplemented by classical electrochemical methods. The results of more recent studies show the prospect of that approach for thermodynamic and kinetic characterization of short-lived intermediates [78, 79].

Among Moscow-based organizations, which successfully worked on EKhOS, were Moscow D. I. Mendeleev Institute of Chemical Technology (MKHTI) and a

Fig. 9.6 Prof. Dr. Mikhail Yakovlevich Fioshin (1927–1985). Graduated from D.I. Mendeleev MKHTI (1944–1949), Ph. D. (1953), Dr. chem. (1964), professor (1964), head of the Laboratory of Organic Electrosynthesis since 1986, head of the department

number of branch institutes. These organizations concentrated mainly on electrosynthesis for industrial applications.

The MKHTI's Faculty of Technology of Electrochemical Productions was established in 1933, but research focused on electroorganic chemistry started in the 1950s–1960s by Mikhail Yakovlevich Fioshin and colleagues; Fioshin has also headed the new "EKhOS Laboratory" of MKHTI. Fioshin's team was first to use Brown–Walker synthesis and "additive dimerization" for sebacic acid and highly unsaturated dicarboxylic acid production [80–82]. The manufacturing of sebacic acid, an effective plasticizer for polymer materials, was established on a large scale by G.N. Freydlin (see Sect. 9.1.2) subsequently. Leonid Aleksandrovich Mirkind, M.Ya. Fioshin, and coworkers developed a technology for the production of drying oils implemented on a large industrial plant [83, 84]. In the course of these works, adsorption of neutral molecules at high positive potentials was unexpectedly revealed. This phenomenon was studied in detail by a number of electrochemical methods including radioactive indicator measurements [83, 84] and was registered as a discovery by the USSR State Committee on Inventions and Discoveries (no. 149, L.A. Mirkind, M.Ya. Fioshin, 1963) (Fig. 9.6).

Fioshin and coworkers also proposed the electrochemical synthesis of calcium gluconate [85] and diacetone-2-keto-L-gulonic acid (intermediate product in vitamin C synthesis [86, 87], see Sect. 9.2.7, "Electrosynthesis of Diacetone-2-Keto-L-Gulonic Acid in the Vitamin C Production"). In collaboration with electrochemists in Khar'kov (the group of Dr. Vasiliy Danilovich Bezuglyy, Sect. 9.1.6), they developed the technology for the production of salicylaldehyde [88]. M.Ya. Fioshin lectured applied electrochemistry to students, and a large number of specialists trained in his department continued to work in EKhOS.

A significant contribution to the development of technology of organic electrosynthesis was made by Dr. Andrey Petrovich Tomilov and his group at the State Scientific Research Institute of Organic Chemistry and Technology

Fig. 9.7 Prof. Dr. Andrey Petrovich Tomilov. Graduated from D.I. Mendeleev MKHTI (1947–1952), Ph.D. (1955), Dr. chem. (1966), head of laboratory (1960), Lenin Prize of USSR (1971). Works on electrosynthesis (see text). Photo: Krasnoyarsk conference, 1987

(GOSNIIOKHT).[6] A.P. Tomilov (Fig. 9.7), similarly to M.Ya. Fioshin, graduated from MKHTI, and the topic of his diploma thesis was the determination of the conditions for production of pinacol by cathodic hydrodimerization of acetone (1952). This electrosynthesis continuously improved by Tomilov and coworkers was developed on an industrial scale of 3000 ton/year in Stalingrad (1970). This work was distinguished by the highest award, the Lenin Prize (1971); however, the production was soon stopped after signing the Chemical Weapons Convention [89]. Another process also on the order from the military department was the synthesis of 4,4′-dimethyl dipyridyl (broad spectrum herbicide "Edil") by cathodic dimerization of methylpyridinium chloride [90]. This process followed the classical $\mathbf{ea_2}$ schema and was implemented on a pilot plant [89]. A pilot-plant testing of electrosynthesis of adiponitrile was also performed by Tomilov and coworkers [91]. This process was more profitable than the initial version of the Baizer [62] synthesis because of significantly lower energy requirement. In 1964, the Belgian pharmaceutical company UCB became interested and a joint patent was lodged. However, due to unfavorable political circumstances, this method was not implemented despite promising pilot-plant tests. The development of these three processes took almost 40 years (!) of efforts by a large team of scientists and factory workers [89].

Tomilov and collaborators were the first to obtain trialkylphosphates by electrolysis of suspensions of phosphorus in alcohol + HCl [92]. This "direct" electrosynthesis of organophosphorus compounds using elementary phosphorus was further developed by the electrochemists in Kazan (joint publication [93]). It is worth mentioning that although Tomilov worked in a "closed" institute, he participated in many joint activities with electrochemists from "open" institutions

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[6] This "closed" organization was also called NII-42: a number is assigned to each "closed" organization and in everyday use they were called "numbered enterprises," "mailboxes," or simply "boxes."

in Karaganda, Ufa, Novocherkassk, Kazan, Charkov, and other cities. These contacts continued to post-Soviet times. I would like to mention, as an example, an elegant one-substrate paired electrosynthesis of γ-truxillic acid from the cinnamic acid (a joint work with the group by E.Sh. Kagan, Novocherkassk Polytechnic Institute [94]). The derivatives of the truxillic acid act as a ligand-activated transcription factor of genes involved in glucose metabolism. The electrosynthesis realized in a diaphragm-less cell involves both anodic and cathodic C–C coupling reactions by the schema ***A***–ea$_2$ *C*eea. Process ***A*** on the anode is the dimerization of the electrogenerated cation radicals, and process ***C*** on the cathode is the C–C cyclization reaction after two-electron transfer; the alternative (more probable) schema is ***A*↑–e↓a *C*ea**, with the coupling-reaction between cation-radical and started molecul [94].

Tomilov took an active part in organizing and holding EKhOS conferences; he wrote several monographs on organic electrosynthesis in collaboration with Fioshin, S. Mairanovskii, and Smirnov. Some of the episodes from the scientific and organizational activities and memories of meetings with scientists are presented in his book [89].

All-Union Scientific-Research Institute of Vitamins (VNIVI). Electrochemical group headed by Victor G. Mairanovsky (in Russian transcription Viktor Grigorievich Mairanovskii). Main directions: mechanism of electroorganic reactions, homogeneous electrocatalysis, electrosynthesis in the chemistry of natural biologically active compounds incl. industrial processes (see Sect. 9.2).

9.1.2 Moscow Region, Tula

All-Union Research and Project Institute of Monomers (VNIPIM). Here, the initiator and supervisor of EKhOS was Dr. Gilya Naumovich Freydlin (1919–2009). He also enrolled in MKHTI in 1936.[7] In 1937, his father, a political worker of the Communist Party, was arrested as an "enemy of the people" and sentenced to 10 years of "bez prava perepiski" ("incommunicado"); this formulation was given in cases when the prisoner was shot. Gilya refused to formally condemn and abandon his father. The only reason he was not expelled from MKHTI was because of the support from two faculties (one of them was faculty of physical education because Gilya was among the top athletes of MKHTI). After graduating from MKHTI in May 1941, he was sent to work at the plant "Karbolit"—the largest Soviet plant for the production of plastics. The war began a month later and Freydlin was evacuated to Kemerovo, Western Siberia, together with the plant. At this plant, Freydlin was promoted from technologist to the head of the technology department of 700 (!) workers manufacturing a huge assortment of products. Starting from 1952, Freydlin worked in Yerevan at a "polyvinylacetate" plant

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[7] Biographical material is taken from [95].

(Armenia) and, from 1959, at the Severodonetsk branch of GIAP (Gosudarstvennyy Institut Azotnoy Promyshlennosti, "Azot" Association, Ukraine). In 1967, Freydlin came into VNIPIM and began with a team of coworkers to develop the world's first industrial-scale electrosynthesis of sebacic acid [96, 97]. The process includes condensation of methyl adipate according to Brown–Walker synthesis (−**eda₂** schema), with subsequent hydrolysis:

$$\mathrm{MeOOC(CH_2)_4COO^-} \overset{-\mathrm{ed}}{\rightarrow} \mathrm{MeOOC(CH_2)_4\cdot} \overset{\mathrm{a_2}}{\rightarrow} \overset{\mathrm{H_2O}}{\rightarrow} \mathrm{HOOC(CH_2)_8COOH} \tag{9.5}$$

Based on the experience by Fioshin et al. [80–82] (Sect. 9.1.1.), Freydlin and his team solved a number of complex technological problems ranging from increase in the yield and current efficiency to the minimization of Pt-anode wear. Studies with ^{197}Pt isotope were carried out in this connection (Freydlin et al. [18], pp. 28, 49, 74). Freydlin's talent and his huge engineering experience were fully revealed here. Freydlin's team included E.P. Kovsman, S.S. Glusman, B.G. Soldatov, A.A. Adamov, etc. It became the most powerful engineering-technological group of organic electrosynthesis in the Soviet Union. A pilot plant of sebacic acid with capacity of 1000 tons/year was put into operation in 1974 and worked for about 8 years. The 10,000 ton/year industrial production of sebacic acid was established at the Severodonetsk Industrial Association in 1989 and became the largest organic electrosynthesis process in the history of the USSR. They also proposed an elegant solution for technology of electrosynthesis of the p,p′-azobenzoldicarbon acid $\mathrm{HOOCC_6H_4N{=}NC_6H_4COOH}$, a valuable monomer for polyamide fiber production. The initial p-nitrobenzoic acid $\mathrm{HOOCC_6H_5NO_2}$ was reduced according to the Haber schema [5]. The continuous process on the pilot plant was performed in two consecutive diaphragm-less electrolytic cells with oppositely directed flows of electrolyte 1[anode → cathode] → 2[cathode → anode]; here 1 and 2 refer to the cell's numbers. Very high conversion (99.8 %) and product yields (97 %) were achieved (E.I. Kovsman et al. [18], p. 145). Unfortunately, the process has not been realized on an industrial scale.

Freydlin presented the works on the electrosynthesis of sebacic acid at Tula's EKhOS-76 conference ([18], p. 28). Frumkin knew about these works and he came to Tula's EKhOS-76. But as I have already said, Frumkin was not able to hear Freydlin's report…Following EKhOS-76, Freydlin and I kept meeting at other conferences and grew close over the years. Dr. Gilya Naumovich Freydlin retired in the late 1980s but for many years continued as a consultant at VNIPI. We last met in autumn 1992. I was visiting the Bolokhovskiy chemical plant, 40 km from Tula. My wife, Dr. Bella Lurik, the senior scientist at the All-Union Science Research Institute of Disinfection and Sterilization, had a working trip to the Tula Sanitary Disinfection Center, and our school-age daughter was also with her. Before returning to Moscow, we all met at Freydlin's dacha (Fig. 9.8). Tula's VNIPIM no longer exists, and there is no longer a production of sebacic acid in Severodonetsk. And now, as I write these lines, the area of Severodonetsk, Luhansk, and other Ukrainian areas are torn by the fratricidal war.

Fig. 9.8 Prof. Dr. Gilya Naumovich Freydlin (1919–2009). Graduated from D.I. Mendeleev MKHTI (1936–1941), Ph.D. (1957), Dr. chem. (1971). Works on industrial electrosynthesis (see text). At the Freydlin's dacha: in the *center* G.N. Freydlin, *left* Dr. B. Lurik, *right* me (Photo taken by my daughter Elena, Tula, autumn 1992)

9.1.3 Kazan

This is the city of the founders of the famous Russian school of organic chemists, starting with N. Zinin and A. Butlerov. This tradition continued also during the Soviet era. Several EKhOS centers grew here: the Kazan State University (KGU) with the A.M. Butlerov Scientific Research Chemical Institute (NIKHI); the Chemical Institute of Kazan Filial of the Academy of Sciences (KHIKFAN) and the Kazan Institute of Organic Chemistry of the Academy of Sciences (KIOKH), from 1965 as the A.E. Arbuzov Institute of Physical and Organic Chemistry (IOFKH); and the Kazan Institute of Chemical Technology (KKHTI). Organic electroanalysis and electroorganic chemistry branches of EKhOS were mainly developed in Kazan. In 1937, the fourth year student of the KGU Vera Fedorovna Toropova (1915–2008) started in the field of polarography on her practical attachment at GIPKh in Leningrad (State Institute of Applied Chemistry) at the laboratory of Evgenia Nikolaevna Varasova, a disciple of J. Heyrovsky (see Chap. 5, Sect. 5.1).[8] Polarography of metallo-complexes with the emphasis on its analytical applications was the main scientific area of Toropova (Ph.D., KGU, 1941; Dr. chem. dissertation 1959) and many of her postgraduate students. As the head of Analytical Chemistry department (1957–1986), she made a great contribution to the training of highly qualified specialists [98].

Polarography gave also the beginning to electroorganic chemistry, and the first investigations were performed in this field by Yuriy Petrovich Kitaev in the late

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[8] Biographical data for this section were mainly taken from the book [98].

Fig. 9.9 Prof. Dr. Yuriy Petrovich Kitajev. Front of the second war (since 1941). Graduated from KGU (1950), PhD (1955), Dr. chem. (1968), professor (1969), head of the Laboratory of Nitrogen Compounds, IOFKH (A.E. Arbuzov Institute of Physical and Organic Chemistry) (1965–1991)

1950s (Fig. 9.9). In 1941, Yu.P. Kitaev, a student of KGU, went to the front. After the war, he graduated from KGU and tried to attend a postgraduate course, but was blocked as a "member of the family of an enemy of the people." In 1954, academician Alexander Ermingeldovich Arbuzov took him as a postgraduate student in his Laboratory of Organic Chemistry in KKHTI. This prominent scientist, the founder of the Kazan school of organophosphorus chemistry, set a task to trace tautomeric transformations in a series of aryl hydrazones by polarographic methods. The study of these compounds was a research topic for Kitaev and his disciples in KIOKH for many years [99–104]. His group also carried out studies on electrogenerated particles by the electron spin resonance or ESR. The combined in situ electrochemical (EC)-ESR was performed jointly with V.A. Ilyasov. Anion radicals of *para*- and *ortho*-chloronitrobenzene [105] and subsequently anion radicals of nitrophenylhydrazones [106] were taken as objects. These studies were among the first EC-ESR researches in the Soviet Union.[9] Studies performed by the group of Kitaev strengthened the authority of Kazan electrochemists. In 1960, A.E. Arbuzov sent Yu.P. Kitaev on a scientific business trip to the Jaroslav Heyrovský Polarographic Institute, Prague, and this was the beginning of a strong cooperation. Within a few years, G.K. Budnikov (1961 and again in 1972), Yu.M. Kargin (1966), and T.V. Troepolskaya (1972) went on internships to Prague. The insight into the experience of Czechoslovak electrochemists proved very useful for the development of EKhOS in Kazan [98].

The main centers and areas of work were identified from the mid-1960s. Gennadiy Konstantinovich Budnikov (Ph.D. 1962, "Polarographic investigation of semi- and thiosemicarbazones" under Kitaev; later his works were also on organic polarography [101–103]) went from KIOKH to the Department of Analytical Chemistry, KGU, and focused on electroanalysis. On the other hand, Yuriy

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[9] Recall that the phenomenon itself and the method of ESR were discovered by Ye.K. Zavoysky in Kazan, KGU, in 1944.

Fig. 9.10 Prof. Dr. Yuriy Mikhailovich Kargin (1931). Graduated from KGU (1949–1954), Ph.D. 1959, Dr. chem. (1972), IOFKH (1961–1972), KGU, head of the department of physical chemistry (1972–1993). Organizer and leader of the Kazan's school of EKhOS

Mikhailovich Kargin (Ph.D. 1960, "Determination of low concentrations of some metals by differential oscillopolarography," under the head Toropova) moved from KGU to the Laboratory of Organic Chemistry of KIOKH and in 1961 began in organic polarography. Yevgeniy Alexandrovich Berdnikov (the Department of Organic Chemistry of KGU) was also involved in organic electrochemistry (α,-β-unsaturated sulfones and sulfoxides, Ph.D. 1968, Dr. chem. 1989).

Gradually, Kargin's group became the center of EKhOS in Kazan. As a result of the Prague internships, the Kalousek switch became widely used in addition to the classical polarography. Later, more sophisticated electronic equipment had been utilized, e.g., the TSLA's alternating current vector polarograph, the oscillographic polarograph with fractional differentiation developed by the R. Sh. Nigmatullin's group in the Kazan Aviation Institute, etc. In the studies started in Kitaev's group [105], the EC-ESR technique became widely applied. Kargin et al. also studied more complex objects producing less stable anion radicals, in particular, the derivatives of aromatic carboxyl acids (joint work with A.V. Il'yasov and Ya.A. Levin [107–109]). After defending his Dr. chem. thesis, Kargin became the head of the Department of Physical Chemistry at KGU and lectured on physical chemistry and organic electrochemistry. The faradaic impedance technique was added to the already established electrochemical methods (L.Z. Manapova, the study of heterogeneous electron transfer in a series of carbonyl and nitro compounds). In 1971, the next EKhOS conference was held in Kazan with the active participation of Kargin [16][10] (Fig. 9.10).

Along with the systematic study of the mechanisms of electroorganic reactions and electrochemical and chemical reactivity (aromatic nitro, carbonyl, carboxyl acid, S, Se derivatives, etc., Dr. Venera Zaripovna Latypova's group), also synthetic works were started. According to Kazan traditions in organophosphorus chemistry, the applicability of electrosynthesis here was first evaluated. Original

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[10] According to the memoirs of A.P. Tomilov, Yu.M. Kargin proposed to use an acronym EKhOS in the title of national conferences [89].

synthetic methods were developed in a series of works on electrooxidation of phosphines, esters of phosphorus acids, white phosphorus, etc. (Yu.M. Kargin, E. V. Nikitin [19], p. 115; [93]). Some of these transformations were difficult to implement with classical chemical methods. In addition to direct electrosynthesis, processes with mediators were also deployed (Yu.G. Budnikova, Dr. chem. thesis 1999, see review [110]). Since the 1980s, electrooxidative nitration was developed primarily for military products (nitrocellulose and nitroaromatic derivatives). Here, too, success was achieved, first in studying the oxidation mechanism of oxygen compounds of nitrogen and then in electrosynthesis of nitration agents (A.A. Chichirov, Dr. chem. thesis 1991). This work, which was conducted in NIIKHP (Science Research Institute of Chemical Products, Kazan), was awarded the Prize of the Council of Ministers of the USSR (1988). But because of the changes of the early 1990s and the lack of funding, this work was not completed and implemented.

Kargin created a large and prolific team of experts in organic electrochemistry; 6 doctor's degree and over 40 PhD dissertations were defended here. And on one of my visits to Kazan, I was invited to the house of the lovely "Kazan EKhOS" couple Yurij Mikhailovich and Nonna Mikhailovna Kargin and their daughter Olga who was then graduating from the university. Since 1995, Dr. Olga Kargin lives and successfully works in Canada. Since 2001, Yurij Mikhailovich Kargin has also lived and worked there and continues his collaboration with his former coworkers in Kazan. An impressive list of joint publications is presented in the book [98]; a series of papers on electrochemical amination are among them (Yu.A. Lisitsyn, review [111]). Several groups headed by the former Yu.M. Kargin's postgraduate students, first of all, by Drs. Yu.G. Budnikova and V.V. Yanilkin's, are actively working now. Thus the Kazan school of organic electrochemistry created by Kargin continues its life.

9.1.4 Riga (Republic of Latvia)

The Organic Synthesis Institute of the Academy of Sciences of the Latvian SSR ("OSI") was founded there in 1957. The initiator and the first director was academician Solomon Aronovich Giller (1915–1975). In 1957, a young graduate of the Riga's University Janis Paul Stradins[11] started to work at "OSI." An article by Ya.P. Stradyn and S.A. Giller, "Mechanism of Polarographic Reduction of the 2-Nitrofuran" [112], was published in 1958. And this was the beginning of EKhOS in this institution. Heteroaromatic and aromatic nitro derivatives were the subject of study. Among them were the original antibacterials solafur, furagin, and furadonin, and others developed at OSI. 2-Nitroselenophene [113] was first investigated allowing to expand the understanding of electronic effect of the ring heteroatoms (N, O, Se, S). Polarographic studies of reduction of nitro compounds and the analysis of

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[11] Yan Pavlovich Stradyn in Russian transcription.

Fig. 9.11 Academician Latvian AS Dr. Janis Paul Stradins (1933). Graduated from the University of Latvia (1951–1956), Ph.D. (1960), Dr. chem. (1968). Professor of phys. chem., University of Latvia (1972–1976); head, Laboratory of Physical Organic Chemistry, Latvian Institute of Organic Synthesis (1961–2006), professor, Institute of History of Latvia, University of Latvia, since 1990; vice-president, Latvian Academy of Sciences (1992–1998); president, Latvian Academy of Sciences (1998–2004)

structural effects became the subject of Stradyn's Ph.D. thesis and of his first book [114]. Ja.P. Stradins and his coworkers used the Hammet and modified Yukawa–Tsuno, Taft, and Palm equations for the separation of inductive, mesomeric, and polar effects to supplement and extend the results of the Czech school (Peter Zuman). Relations between the $E_{1/2}$ with energies of frontier molecular orbitals were also established (Fig. 9.11).

In addition to the nitro compounds, other groups of biologically active compounds such as heteroaromatic carbonyl compounds, diketones, quinoid systems, and phenols were investigated. The evaluation of "heterogeneous" electrode effects (adsorption on the DME, "surface" protonation stages, etc.) was taken as one the goals of these studies. Continuing the studies by Zuman and Lund et al., the activating effect of α-carbonyl group in reactions of cathodic bond dissociation in the series of phenacyl alkylthioethers [115] (process **edep**, dissociation of the C–S bond) and alkylamino indandiones (process $\mathbf{p_s}$**ede** with the previous surface protonation, dissociation of the C–N$^+$ bond) was found [116]. Thus, for C–S bond:

$$\mathrm{ArC(O)SAlk} + \mathrm{edep} \rightarrow \mathrm{ArCHO} + \mathrm{AlkS}^- \tag{9.6}$$

This activating effect was first observed in breaking the C–C bond—by the example of bis-2-arylindandiones-1,3 [117]. A series of original papers was related to the electroreduction of 1,4-naphthoquinones and their derivatives [118, 119] as well as to the oxidation of dihydropyridines, dihydropyrimidines [120–122], and phenol derivatives on a carbon electrode [123, 124]. Ya.P. Stradyn and R.A. Gavar were apparently the first in the Soviet Union to use in situ combined EC-ESR for studying organic electrochemical reactions.[12] It was a very new and intriguing direction to compare electrochemical data with the biological activity of compounds. Ya.P. Stradyn and S.A. Giller made a big joint presentation on this at Riga's EKhOS-73 ([17] p. 282).

Investigations of the electrochemical school in Riga were known in the West, and this group had the opportunity for contacts with foreign colleagues already in the Soviet era. Ya.P. Stradyn and his coworkers participated in many international meetings: in Prague, Liblice, Brno, Bucuresti, Warszawa, Wroclaw, Jena, Leipzig, Rostock, Berlin, Münster, Southampton, Sandbjerg, Uppsala, Lund, Rome, Venice, Tokyo, and Montreal. Ja.P. Stradins became also a highly respected and well-known scientist because of a series of scientific-biographical books and articles on Th. Grotthuss, P. Walden, and W. Ostwald and on the contribution of Baltic scientists and the role of the Baltics as "a mediator between the East and West" [129]. Biographical material on academician Ja.P. Stradins and his intensive and multifaceted scientific, literary, and social activities are presented in the recent book [130].

I shall briefly touch upon some other centers on organic electrochemistry, their staff, and main avenues of work.

9.1.5 Novocherkassk

Novocherkassk Polytechnic Institute (South Russian State Technical University)

1. Groups of Drs. V.A. Smirnov and M.G. Smirnova. Main areas: amalgam-based synthesis ([13], p. 219) and electrode materials for electrosynthesis ([17], p. 7 and [19], p. 318). Dr. V.A. Smirnov is a coauthor of several books on organic electrochemistry [39, 131].
2. Group of Dr. E.Sh. Kagan. A number of original electrosyntheses in a series of triacetone amine, piperidines, etc. [94, 132–135] (see also synthesis of γ-truxillic acid in collaboration with Tomilov, Sect. 9.1.1). This group continues now to actively work in the field of organic electrosynthesis.

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[12] Ya.P. Stradyn and R.A. Gavar presented this material on the CITCE's 14th meeting, Moscow, 19–25 August 1963 (as per Dr. V. Glezer). Their work [125, 126] on in situ EC-ESR of nitrofurans has been published about a year before that of the Kazan scientists [105]. Geske and Maki [127] are commonly considered the pioneers of the in situ EC-ESR. However, Alexander Galkin and coworkers in the Kharkov FT I (Kharkov Physics-Technical Institute) in 1957 [128] were the first to carry out in situ electrochemical generation in the ampule of an ESR spectrometer.

9.1.6 Kharkov (Republic of Ukraine)

All-Union Research Institute for Single Crystals. Dr. V. D. Bezuglyy. A large number of studies on organic polarography (cf. monograph [40]), electrosynthesis and production technology of salicylaldehyde [88] (see Sect. 9.1), electrochemical polymerization [18] p. 161, [19] p. 265, [136, 137], etc.

9.1.7 Kiev (Republic of Ukraine)

Institute of Macromolecular Chemistry, Academy of Sciences of Ukraine. Dr. G.-S. Shapoval. Electrochemical polymerization, electrochemical transformation of polymers, and electroreduction of perfluorocarbons ([19], p. 286; [138–140]).

9.1.8 Alma-Ata (Republic of Kazakhstan)

D.V. Sokolskiy Institute of Organic Catalysis and Electrochemistry. The group of academician D.V. Sokolskiy. Electrocatalytic hydrogenation [141, 142].

9.1.9 Karaganda (Republic of Kazakhstan)

Institute of Organic Chemistry and Carbon Chemistry. Dr. I.V. Kirilyus. Cathodic electrocatalytic hydrogenation processes, electrosynthesis of aliphatic alcohols, etc. [143].

9.1.10 Sverdlovsk

Institute of Chemistry and Metallurgy Ural Branch USSR AS and *Tomsk* Polytechnic Institute. Dr. A.G. Stromberg. The early works on organic polarography in the USSR [144–146] and polarographic and voltammetric methods for determining the trace of organic substances [147].

9.1.11 Other regions

Several EKhOS-related topics were also studied in Tbilisi (academician of the Georgian AS, Dr. D.I. Dzhaparidze, Dr. V.Sh. Tsveniashvili), Gor'kiy (Dr. Yu.V. Vodzinskiy), Leningrad (Dr. V.V. Berenblit), Krasnoyarsk (Dr. V.L. Kornienko), Tambov (Dr. A. B. Kilimnik), Donetsk (Dr. Kh. Z. Brainina, Dr. Ye.M. Royzenblat, Dr. E.Ya. Sapozhnikova), Kishinev (Yu.S. Lyalikov, Yu.D. Sister, V.V. Senkevich), L'vov (Dr. M.A. Kovbuz), etc. Research on issues close to EKhOS is also performed in some of these centers nowadays.

9.2 My Experience: From the End of the "Ottepel'" to the End of "Perestroika"

In this part of the article, I will talk of my experience at the All-Union Scientific Research Institute of Vitamins (Vsesoyuzniy NII Vitamin Institute, VNIVI) from 1961 up to 1993 (Fig. 9.12), i.e., from the end of the "ottepel'" ("thaw") up to the collapse of the USSR. VNIVI was a midsized institute of the midsized Ministry of Medical Industry. But the "climate" and working conditions which we had there were rather unusual for Soviet research institutes and for big research centers.

My entire electrochemical career was linked to this institute starting with the experiments on a homemade polarograph. I first was introduced to polarography by

Fig. 9.12 Victor G. Mairanovsky (1936) (in Russian transcription Viktor Grigorievich Mayranovskiy), graduated from M.V. Lomonosov MITKHT (1961), Ph.D. (1966), Dr. chem. (1980), professor (1985), engineer (1961), junior researcher (1963), head of the Lab of control methods of manufacturing (1969), head Phys.-Chem. Lab. (1972) at the Vsesoyuzniy NII Vitamin Institute (VNIVI). Since 1993 in Germany, co-organizer (1996) and board member of the Scientific Soc. WiGB at the Jewish commun. Berlins

my older brother, Stal' Mairanovskii. He gave me the book of Kolthoff and Lingane [148] which explained the basics. After that, Stal' took me to the analytical lab at IOKH, where he already worked then, demonstrated various instruments, and showed how to handle mercury and a dropping mercury electrode (DME). In 1958, as a fourth year student of MITKhT (Lomonosov Moscow Institute of Fine Chemical Technologies) with Stal's recommendation, I came to interview Gleb Ivanovich Samokhvalov in the Laboratory of Chemistry of Polyenic Compounds of VNIVI. I was allowed to conduct my experiments in his lab, allocated a place, issued a pass to VNIVI, and provided with a set of electrodes and some tips on the assembly of a polarograph by Stal'. And so began my evening polarographic experiments, after daily studies at MITKhT. This is how my brother destined me for a future in EKhOS.

At that time, VNIVI consisted of several laboratories on the second floor of the building of the Moscow experimental vitamin plant (MEVZ) in the center of Moscow, on Novokuznetskaya Street, only a 15-min walk from the Kremlin. In the late 1950s, the Soviet Union began building large highly productive factories for manufacturing synthetic vitamins; according to the federal plan, the products made on those factories had to satisfy all the needs of the USSR healthcare system. The Belgorod vitamin plant was built in the city of Belgorod and the Bolochovskiy chemical plant in the Tula region. A procedure for the industrial synthesis of vitamin A was developed in a short time in Samokhvalov's laboratory and debugged on a pilot plant at MEVZ (Fig. 9.13). Most of the control methods of production stages were based on traditional analytical procedures. Samokhvalov initiated the use of instrumental methods of analysis. The chief engineer of MEVZ, M. Ts. Yanotovsky (in Russian transcription Mikhail Tsalevich Yanotovskiy) was transferred to Samokhvalov's lab in 1960. He mastered gas chromatography (GC) and developed a set of GC-based analytical procedures, which were included in the regulations of the vitamin A production. My thesis "Polarographic study of the reaction of ketones with amines" was also linked with vitamin A synthesis. The work was conducted under guidance of Dr. Rimma Porfirievna Evstigneeva at the MITKHT's Department of Chemistry and Technology of Fine Organic Compounds. A professor and member of the USSR Academy of Medical Sciences, Nikolai Alekseevich Preobrazhenskii (1896–1968), a student of the famous Russian chemist Aleksey Ye. Chichibabin, was in charge of that chair.[13]

After my graduation from MITKhT (defending my graduation thesis Fig. 9.14), I was assigned to work at the Samokhvalov's laboratory and started in polarography in the newly equipped lab room, it was on the territory of the MEVZ; Misha

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[13] In a small room, in front of the cathedral library, we had worked together with Andrey Mirzabekov (1937–2003)—the future academician and director of V.A. Engel'gardt Institute of Molecular Biology USSR AS and future director of Biochip Technology Center at Argonne National Laboratory, USA. I worked on polarograph and Andrej on preparative chromatograph. The room was not equipped with ventilation and Nikolai Alekseevich asked us daily if there was any toxic contamination by mercury or solvent. Understanding our responsibility, Andrey and I worked neatly and carefully.

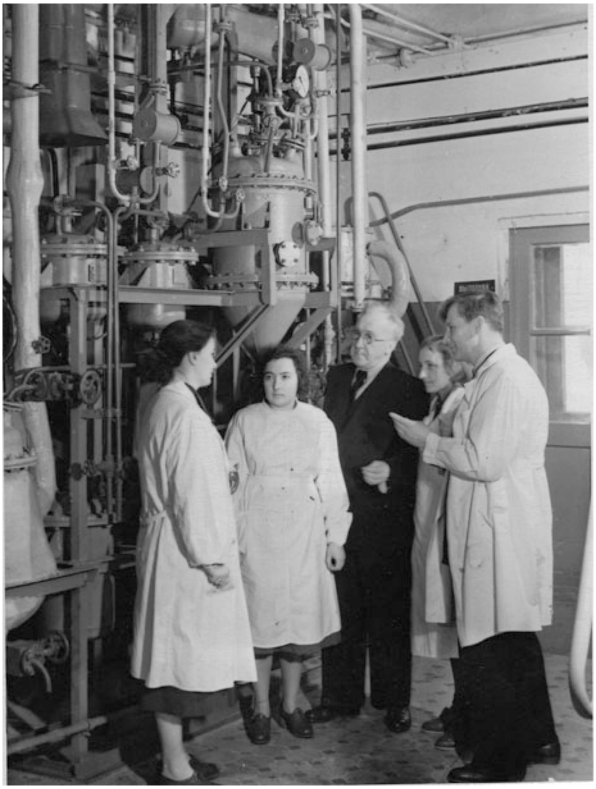

Fig. 9.13 Dr. Gleb Ivanovich Samokhvalov (first from the *right*), his colleagues, and Prof. Nikolaj Alekseevich Preobrazhenskii next to the pilot plant of vitamin A (the unit mounted under the guidance by Chief Engr. M.Ts. Yanotovsky). MEVZ, 1954. G.I. Samokhvalov (1914–1992) graduated from MITKhT in 1937 and started his postgraduate studies in 1939 under N.A. Preobrazhenskii. In 1941, he volunteered for the front, was taken prisoner, and worked in Germany at a chemical plant. After the war, he was saved by N.A. Preobrazhenskii from being sent to Stalin's GULAG camp. From 1948, he worked in VNIVI; Ph.D. (1956), Dr. chem. (1960), head of the lab (1958–1992). With a small group of associates, he developed and implemented the first in USSR industrial manufacturing of vitamin A. In the 1970s, he started research in bioorganic chemistry. Together with the G.I. Samokhvalov, we have performed over two dozen works on electrochemistry of natural compounds

Yanotovsky (PhD, 1965) became my friend for life. In 1962, together we developed the combined GC-polarography method or GC-EC [149–151]: the components separated with a carrier gas (He, Ar, etc.) passed through a heated capillary into a special cell coupled with the oscillographic polarograph PO-5122 TSLA. The GC-EC technique was used for the analysis of carbonyl compounds; both polarographic and GC data ($E_{1/2}$ and retention time) were used to identify the components [152]. The system was designed for micro-collection of the separated components [153].

Fig. 9.14 Prof. G.I. Samokhvalov, here the chairman of the State Examination Commission, congratulates me on being awarded the title of chemical engineer. On the *right* in the background Prof. N.A. Preobrazhenskii, on the *left* Dr. R.P. Evstigneeva. MITKhT, 18.02.1961

In the beginning of my career at VNIVI, I worked on analytical projects related to the production of vitamins A and D. For the first time, we then managed to produce a well-defined polarogram of polyenes at very negative potentials down to −3 V SCE. In 1964, we published our first articles on polarography of vitamins A and D [154] and the control of vitamin A manufacturing [155]. Two of our analytical methods were implemented at the Bolokhovskiy plant, applying the Hungarian polarograph OH-102 Radelkis. This series of successes was due to several factors: First of all, I had an excellent equipment, the Soviet-made polarograph PE312 TSLA. Well-chosen experimental conditions played also a very important role: in 1962, I started using DME with the dropping control by a hammer and tetraalkylammonium salts in dimethylformamide (DMF) as electrolyte solution. That type of solution was just introduced into polarography by Wawzonek [156, 157] and reagents were Soviet made and readily available. However, the most important was that in Samokhvalov's laboratory, we felt indispensable and independent at the same time. One of the memorable episodes happened in 1965: I had a newborn son and decided to do a polarographic analysis of vitamin D purchased in the pharmacy for babies. The polarogram had an additional stretched wave typical for peroxides. The drug was produced at the Kiev vitamin plant; the same product of the Leningrad plant was practically free of that wave. My assumption of peroxide presence in vitamin D was confirmed (it forms during vitamin D production by UV irradiation of ergosterin). I informed Samokhvalov about the findings—the situation was complicated because I encroached on someone else's territory: responsibility for the quality, and standards of vitamin production was the remit of the analytical laboratory under Dr. V.A. Devyatnin. But Samokhvalov was very supportive, and he said: “You present the issue on the Scientific Council, and I will support you if needed.” My report caused quite a commotion considering the toxicity of peroxides; to prove my findings, I demonstrated polarograms. As it turns out, the Kiev plant used UV irradiators with suboptimal spectral parameters. Shortly after, the technology in Kiev was modified, and the changes were also introduced into USSR's pharmacopeia standard for vitamin D. Following this, we discovered other drug impurities using polarography. These results were presented at the Mendeleev Congress [158]. The polarographic method was refined to become a standard control procedure in the production of vitamin D [159]. Thus, I was rather independent choosing my research topics in VNIVI. It was of course much helped by the fact that most of my associates were synthetic organic chemists, who shared my interest in mechanism of electrochemical transformations of organic compounds. But I had considerable "freedom of choice" virtually throughout all my time at this institute. How was that possible?

In 1964, VNIVI moved into a new beautiful building in the new southwest area of Moscow; even the new address was inspiring—"Scientific Passage, 14-a." By then, I have accomplished a lot of research, which formed the basis for my Ph.D. In 1966, I defended the thesis "Polarographic study of compounds with conjugated carbon bonds" at the Institute of Electrochemistry (IELAN) under the supervision of Professor Samokhvalov without a postgraduate course. Samokhvalov warned me then that I did not have any opportunity for a career in his lab, and I carried on as a junior researcher. In May 1969, through Alexander Ershler (IELAN), I was unexpectedly invited to the director of the Institute of Bioorganic Chemistry. Academician M.M. Shemyakin (1908–1970), famous scientist, head of the Soviet school of bioorganic chemistry told me of his plans to venture into bio-electrochemistry and offered me a job. It sounded like a dream come true—to work in an exciting novel field and that at an Institute of the Academy of Sciences![14] I notified Samokhvalov about the job offer, and shortly after, I was called to see the new director of VNIVI, Professor Viktor Andreyevich Yakovlev, a famous scientist in the field of enzyme kinetics (Fig. 9.15). Since his arrival in 1967, the institute received a powerful impetus to development. Yakovlev said he knew of Shemyakin's offer but asked me to wait with the final decision: he wanted to apply to the Ministry for approval of a new laboratory of control methods of manufacturing (abbreviated "Met-Co") with me as a director. I agreed, although I was skeptical that it would be approved, me being a Jew, too young, and not a member of the Communist Party. However, in July 1969, I was appointed as an acting head and soon after confirmed as a head of

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[14] I had a bad experience with another academic institution, INEOS. In 1961, prior to the work assignment to VNIVI, on the recommendation from my brother, Stal' Mairanovskii, I was invited for an interview by Dr. Zinaida Naumovna Parnes; she studied hydride transfer reactions. She gave me reprints of her articles and asked me to think about the application of electrochemistry. A few days later, in INEOS, I met Dr. Parnes and Dr. Mark Yefimovitch Vol'pin again to continue our discussion. They were satisfied with my interview and suggested I apply for employment to the Director, acad. A.N. Nesmeyanov and introduced me to D.N. Kursanov, corr. member of USSR AS, the head of their department. Kursanov signed my letter and wished me a bright future in INEOS. Just a week later, I had a call from Dr. Z. Parnes, and she asked me to come: INEOS's "pervyy otdel" blocked my admission (about the pervyy otdel, or first department, see Sect. 9.2.8).

Fig. 9.15 Prof. Dr. chem. Victor Andreyevich Yakovlev (1915–1977). Graduated from the Academy of Chemical Protection (1940) and worked in laboratories of chemical plant protection. Fields of research: kinetics of enzymatic reactions, electronic mechanism of enzymatic nitrogen fixation, etc. (monographs [160, 161]). Organizer and head of the Laboratory of Kinetics of Enzymatic Catalysis, Institute of Chemical Physics, USSR AS (1962–1967), director of VNIVI, and head of the biochemical laboratory (1967–1977). He ensured the organization of scientific and technological research, including electrosynthesis, in VNIVI and established creative climate. Photo: in his office in VNIVI, January 1970

the new lab. Initially, I have employed several young associates. Naftoliy T. Ioffe was one of the first ones; he was from a postgraduate school at INEOS (he had no offer to stay there) and soon defended his Ph.D. thesis and became my deputy, assistant, and friend. The lab acquired basic equipment (UV and IR spectrometers, gas chromatograph), and by the end of 1970, we completed several useful projects for vitamin plants. The laboratory was gaining momentum, and gradually, we became again engaged in EKhOS along with the analytical chemistry projects.

In 1972, VNIVI was shaken by dramatic events. The head of the physicochemical laboratory, Iosif Moiseyevich Kustanovich, Ph.D., member of the Communist Party, has resigned. It became known that he already had a permit to immigrate to Israel. V.A. Yakovlev, as a head of institute, was severely reprimanded for the “loss of vigilance” by the Communist Party and was temporarily suspended as a director. Yakovlev found himself in the same situation as Frumkin at the IELAN after B. Levich applied for immigration to Israel in the same in 1972; Frumkin’s situation was even worse because Levich did not resign in advance. After few months of uncertainty, Yakovlev was reinstated. But sadly this incident has taken its toll; Yakovlev prematurely died in spring of 1977, full of plans and ideas. His career was in continuous ascent and he was supposed to rerun for the title of corresponding member of the USSR Academy of Sciences in the near future; his plan was also to make the VNIVI as the institution of dual subordination (under the Ministry and the USSR Academy of Sciences).

But then, in December of 1972, Yakovlev offered me to become the head of the physicochemical laboratory. It is etched in my memory. Yakovlev's secretary called me asking to come up to the director's office. Yakovlev looked tired. I started to congratulate him that the "Kustanovich affair" was finally over, but he, with his characteristic humor, said that it was not over yet: the physicochemical lab was now left without a head. And he offered me the job. At first, I did not understand what was going on. I did not want to tell him directly that I feared it was politically precarious to make me the head of the lab following the "Kustanovich affair." And I said: "I am a chemist, so, Viktor Andreyevich, you maybe better find a *Physicist*?" I put a double meaning in that and I knew that he understood; Yakovlev answered very emotionally, with gestures: "We do not need any PHYSICISTS !!!" He asked me to consider the offer and give an answer a day or two later. When I was at the door, Viktor Andreevich, slightly embarrassed, asked, "one more thing, you are not planning to leave anytime soon?" At that time I was able to say "NO" quite confidently. The next day I agreed to move to the new lab but asked to take few employees with me. Misha Yanotovsky took over as the head of "Met-Co" lab.

Kustanovich left a well-equipped and smoothly running laboratory with groups for UV and IR spectroscopy and NMR and mass spectrometry. The main tasks of the laboratory were structural studies to help organic synthetic chemists. The team in Kustanovich's laboratory was initially wary of our new addition, but after a few years on, we found a common wavelength and formed a united young laboratory. There I worked until I left Russia; but it was not until 1993. Already in early 1973, we received a great chromatography mass spectrometer JMS-01-SG2 (JEOL). That spectrometer was used not only for the needs of VNIVI but also to provide service to other Moscow institutions of the Ministry. Later we got the latest 90-MHz Bruker NMR spectrometer. At that time, I met Uwe and Barbara Eichhoff. This German couple represented the company Bruker, working selflessly in the Soviet Union under extremely difficult conditions for foreigners. Subsequently, the "Bruker report" published our brief communication on the first in situ EC-NMR cell (Sect. 9.2.5, "In Situ Electrochemical NMR"). Nowadays, we enjoy Dr. phys. Uwe and Barbara Eichhoff's company when they visit Berlin.

Our work on EKhOS at VNIVI was closely connected to the other projects of the institute, and the main objects of research were natural biologically active compounds. At that time, those compounds were barely studied by electrochemists. That field was new and fascinating. At the same time, we had quite a bit of freedom to deviate from the main course of research and therefore our projects were very diverse. The following overview provides a somewhat arbitrarily grouped list of works. It seems strange now that I never had a joint article with my first teacher—Stal' Mairanovskii. My beginnings at VNIVI were defined by analytical projects, and my brother helped advise me but did not consider his contribution sufficient to be included as an author. Then I got interested in organic electrochemistry and electrosynthesis. Gradually, my research approached the field where Stal' was very active, and we were getting very close to working on something interesting together. Some of Stal's ideas ("inheritance effect," impact of the strong electric field near the electrode, the activating effect of substituents on cleavage of bond, etc.) were already reflected in my research. But the time allotted to us was too short.

9.2.1 Development of Experimental Techniques and Procedures

DME with the Dropping Control

The reduction of the surface tension in passing through the zero charge potential is accompanied by a significant decrease in drop time *t* of the DME (~20 times at the $E = -3$ V SCE, DMF), and the polarograms are distorted due to irregular dropping. The distortions are partially suppressed with the electrode with a trowel for forced drop separation proposed by Skobets and Kavetskiy [162]. The all-glass modification of this electrode proposed by S. Mairanovskii in the early 1960s became widely applied in most polarographic labs of the USSR, and a design with a sliding trowel to change *t*-values was developed [163]. D.P. Zosimovitsch et al. [164] in 1948 and somewhat later P.N. Teretschenko and V. Čermak and V. Hanuš [165, 166] employed a DME with a hammer for drop time control. This principle was very attractive, and I made an electronic control unit with a range of $t = 0.07$–7.0 s using my radio-amateur experience in electronics. Distinct polarograms were obtained by this technique even in the farthest cathodic range [154, 155]. It became possible to overcome challenges of analyzing mixtures of vitamins A and D using short drop times in order to reduce the interfering “kinetic” wave of vitamin A [167]. However, the drop time control with a hammer could lead to deviations from the theory. The results published in [168] did not solve the problem as these measurements were rather limited and conducted in the presence of a surfactant. My multiparameter testing showed that, even at the shortest drop time ($t = 0.07$ s), deviations from the theory of any of the parameters do not exceed ~3 % [169, 170].

It was of interest to further reduce the drop time. At first, it was a simple vibrating electrode with a dropping frequency of 50 Hz [171]. Unexpectedly, I found that, due to accelerated mass transfer, the “classic” polarogram could be produced with as little as 5–10 drops per 1 V, instead of 50–200 drops/V. The recording time of a polarogram was reduced to tenths of a second, and the method was called “express polarography” (Fig. 9.16) [171]. At the same time, the mercury consumption also reduced proportionally at carrying out the polarographic analysis. This technique proved effective in particular in combined gas chromatography-EC because it provided very fast measurements in a stirred liquid [152].

The dropping mercury electrode with adjustable vibrating frequency of 5 Hz up to a record-high value of 1 kHz was then made and studied in detail ([172, 173], p. 76) (cf. Fig. 9.17). This was achieved using wider glass capillaries which were drawn out at the end. With conventional flow rates of mercury ($m \approx 0.002$ g/s), this electrode made it possible to lower the time of contact t_c of the mercury with the solution to so low values like in case of the *Heyrovský's* streaming mercury

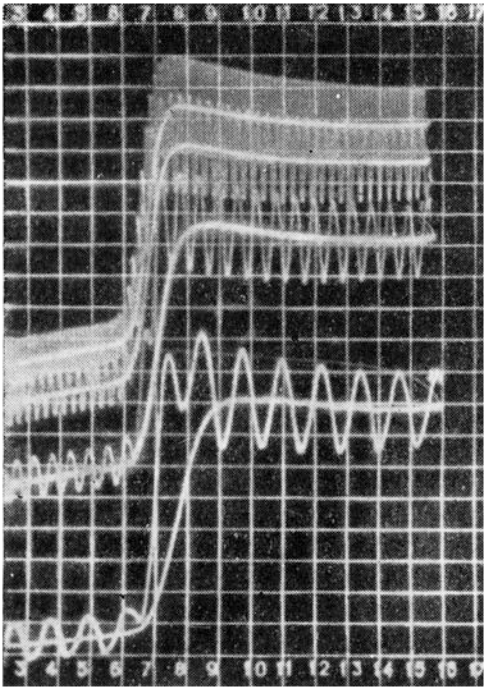


Fig. 9.16 Express polarography. Polarograms 10^{-3} M $CdCl_2$ in 0.1 M KCl, vibrating DME, $t^{-1} = 50$ Hz. Potential scan rates $v = 0.5$, 1.0, 2.0, and 4.0 V/s (from *top* to *bottom*). Polarograms without oscillations for respective "*v*" received with the 50-Hz filter enabled; scale division on the ordinate 0.71 μA. Polarograph-modified Soviet-made PO-5122 TSLA

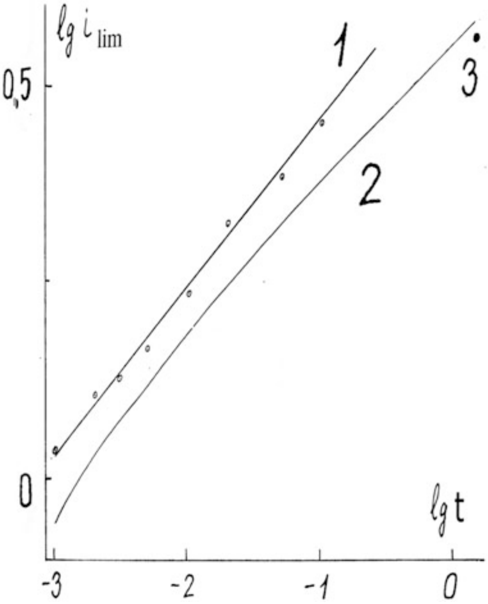


Fig. 9.17 Vibrating DME, frequencies 1 kHz – 5 Hz (dropping times $t = 0.001–0.2$ s). The impact of the drop time *t* on limiting current (μA). (1) Experimental dependence log $i_{\text{lim}} = f(\log t)$. (2) Theoretical dependence lg $i_{\text{lim}} = f(\log t)$ obtained by Ilkovič equation with the use of experimental values of mercury mass flow rate *m*. (3) Experimental point corresponds to natural dripping (with a switch-off vibrator), $t = 2.2$ s

electrode (t_c from 0.001 to 0.01 s at the m ≈ 0.2 g/s). The convective component of the limiting current depending on the vibrations frequency and amplitude was estimated (diploma thesis by Igor' Dmitriyev, 1970) [172]. This technique enabled studies of processes involving adsorption and fast chemical stages in a series of carotenes, porphyrins, etc. [174].

Accurate Measurement of Half-Wave Potentials on the SCE Scale in Nonaqueous Media

We accomplished this using semiautomatic recording of polarograms with reference potentiometer and a special reference electrode [175]. The $E_{1/2}$ values were related to the SCE scale by comparing with $E_{1/2}$ of K^+ ion according to Pleskov-Vlček [176]; the total standard error was less than 1 mV. The difference $\Delta E_0 = -3$ mV in the values of E_0 of 15,15′ *trans*- and *cis*-isomers of β-carotene was successfully assessed in particular [177] (Sect. 9.2.2, "Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins"). We regularly used this reference electrode in experiments, and the handy thermostating unit [175] was additionally employed for the most precise measurements (the potential of the electrode had a high temperature coefficient).

Voltammetry with the Symmetric Trapezoidal Voltage Pulses (VATZ)

Voltammetry with the symmetric trapezoidal voltage pulses (VATZ) [178] was created advancing the technique of W. Schwarz and I. Shain ([cf. 179]). The VATZ technique was more advantageous because the measurements were carried out at a constant rate of potential change and, hence, at the same contribution to the capacitive current, but with different delay times, T (the width of the trapezoid). Thus, it is possible to work at very high potential scan rates in both directions (more than 100 V/s) and with T values up to a few seconds. The VATZ method can be considered intermediate between a reverse-scan chrono-voltammetry and pulse polarography, and the theory of classical voltammetry with a triangular pulse voltage (VATR) was still applicable here. Two methods VATZ and VATR were compared in the study of the fast protonation kinetics of the dianion β-carotene [178] (Sect. 9.2.2, "Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins").

Electrolysis at a Constant "pH" ("pX") with Recording Equipment

Maintaining proper acidity of the medium is an important condition for electrosynthesis with special difficulties in nonaqueous media. The main problem is the strong, by a few hundred mV, influence of the electric field in the electrolyzer to the indications of a pH meter.[15] We solved this problem by using a special pH sensor where the end of the electrolyte bridge of the reference electrode was approached directly to the glass-electrode membrane; deviations of the pH meter in the electrolysis with such an electrode did not exceed a few mV [182, 183]. Combining this device with a commercial automatic titrator (Radelkis, Hungary, burette with solenoid valve) gave us a pH stat which reliably maintained the predetermined “pH” value during electrolysis. Some examples of “pH-static” electrosynthesis are given in Sects. 9.2.2, “Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins” and Sect. 9.2.6, “Electrosynthesis in the Chemistry of Biologically Active Compounds: Electro-deprotection Method”.

A recording apparatus with an integrated homemade titrigraph was also assembled [182, 183]. The amount of titrant was recorded amperometrically by means of “polarographic indication” in a special cell synchronously with the supply of titrant (two Radelkis burettes) [184, 185]. As a result, we were able to trace the progress of electrolysis at a given pH and to find the stoichiometry—the number of electrons n and protons m of the electrode reaction [182, 183]. Thus, values of $n = 2.04$ and $m = 0.94$ obtained upon reduction of tricresyl phosphate (Hg cathode, 0.04 M Et4NJ/DMF, titrant HCl in MeCN) indicate that the reaction goes along the path (9.7a) with the cleavage of C–O rather than the path (9.7b) with the cleavage of the P–O bond:

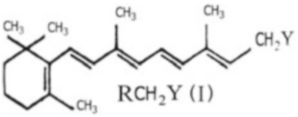
$$(\mathrm{ArO})_3\mathrm{P} = \mathrm{O} \xrightarrow{\sum 2\mathrm{ed}\,\mathrm{p}} (\mathrm{ArO})_2\mathrm{P}(=\mathrm{O})\mathrm{O}^- + \mathrm{ArH} \tag{9.7a}$$

$$(\mathrm{ArO})_3\mathrm{P} = \mathrm{O} \xrightarrow{\sum 2\mathrm{ed}2\,\mathrm{p}} (\mathrm{ArO})_2\mathrm{P}(=\mathrm{O})\mathrm{H} + \mathrm{ArOH} \tag{9.7b}$$

Note that another sensor, for example, an ion-selective electrode, can be used instead of the glass electrode, and in general, any combination of an electrolyzer and a “concentration-stat” could be used [182, 183].

9.2.2 Mechanisms of Electroorganic Reactions

Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins[16]



RCH$_2$Y (I)

Vitamine A: Y= -OH

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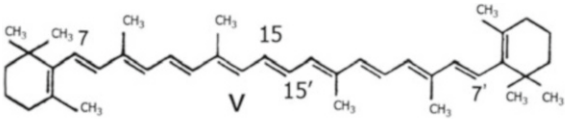
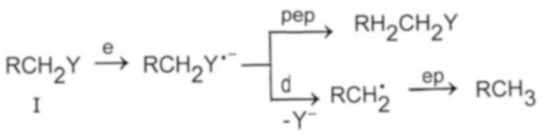
[15] This forces to interrupt electrolysis during pH measurements [180] or completely abandon pH monitoring. Thus, electrolysis was conducted in a diaphragm-less cell with a platinated Pt anode under hydrogen bubbling to prevent the alkalinization of the catholyte [181].

[16] The electrochemistry of carotenes and porphyrins was the topic of the Ph.D. theses of Askold Anatoliyevich Engovatov (carotenes) (1975) and Ichtior Muradovich Muratov (porphyrins) (1986).



β-Carotene

The conclusion of Japanese authors that the reaction proceeds along the “classical” path, i.e., with reduction of conjugated pentaenic vitamin A, derived from electronic spectra of the electrolysis products [186, 187] contradicted our observations, in particular, the abnormally strong effect of substitute Y = -OH, -OAc, and -OMe on $E_{1/2}$ [188]. We found that, just as with cinnamic alcohol [189], the process does not run with the reduction of the conjugated system but occurs with the rupture of C–O bond and formation of axerophthene (Y = H). The total schema includes competing **p** and **d** reactions of the radical anion according to the **e(pep)dep** process [190]:

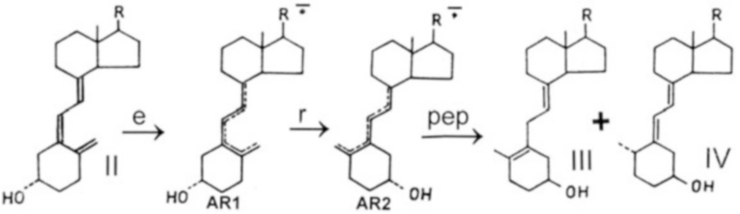


$$\underset{\mathrm{I}}{RCH_2Y} \xrightarrow{e} RCH_2Y^{\bullet -} \begin{cases} \xrightarrow{pep} RH_2CH_2Y & (9.8a) \\ \xrightarrow[-Y^-]{d} RCH_2^{\bullet} \xrightarrow{ep} RCH_3 & (9.8b) \end{cases}$$

These ideas were utilized for a number of new electrosyntheses. Deuterated axerophthene RCH_2D was obtained using a pH stat system and DCl/D_2O titrant [191]; the different derivatives of ubiquinone (coenzyme Q) [192] and vitamin K in two alternative ways (9.8a) and (9.8b) were obtained by simply changing medium protogenic activity [193]. Studies on electroreduction of cinnamyl derivatives [194, 195] in cooperation with my close friend Sasha Weinberg (1937–2012) gave rise to a new direction—“electro-deprotection” (Sect. 9.2.6, “Electrosynthesis in the Chemistry of Biologically Active Compounds: Electro-deprotection Method”).

A few incidents demonstrate here how little the Western chemists (not only electrochemists) were aware of the research performed in the USSR: just three examples. In 1976, J. Gourcy et al. “rediscovered” the electrosynthesis of axerophthene [196]. At around the same time, H. Lund and coworkers [197] proposed a schema completely reproducing (9.8a)–(9.8b). It seemed particularly odd, and we wrote a letter to the editor of *Electrochimica Acta* hoping for clarification from the authors. To our surprise, the journal reprinted the full text of our letter [198]; apparently, the editor in chief also considered this case unusual. And finally, the famous scientists E. Corey (Nobel Prize in 1990) and M. Tius proposed cinnamyl as a “new” protecting group [199] pointing out its advantages over known groups—10 years (!) after our works [194, 195]. But unlike us, they used a two-step chemical method for removing cinnamyl first by $Hg(OAc)_2$ and then by KSCN. Sasha Weinberg and I decided not to send any more letters to the editors, and the "cinnamyl authorship" was never clarified: the articles referring to Corey and Tius (cf. [200]). Although, our papers have been published in Russian, it is still surprising that the Western colleagues did not see them in the English abstracting services.

The mechanism of reduction of the triene structure of vitamin D (D_2 and D_3) also proved to be not a common **epep** process as we first assumed [201]. The wave had properties of "irreversible" type. At the same time, the subsequent protonation of the anion radical (AR) was not a "special" reaction: its rate constant $k_p = 6 \times 10^4\ s^{-1}$ obtained with high-speed pulse chronopotentiometry (HSCP), the new technique elaborated by A.B. Ershler et al., was in the range where other conjugated trienes gave "reversible" waves [202]. The slow **e** stage was accounted for by spatial rearrangement of the molecule. Developing this hypothesis further, we proposed a schema **erpep** with a fast *cis*- and *trans*-isomerization of anion radicals AR1 → AR2 [203]. Thus, the rate constant k_p found in [202] should have been assigned to the protonation of the secondary, i.e., *trans*-anion radical AR2:



(9.9)

Indeed, specially synthesized *trans*-vitamin D that immediately forms AR2 gave a reversible wave [203]. It was the first example where the *cis*- and *trans*-isomerization caused a slowing down of the preceding **e** stage. This stage "**r**" should be very fast in accordance with the formula "ultrafast chemical reaction is the cause of slow electron transfer" [204] (Sect. 9.2.2, "Cathodic and Gas-Phase Reactions of the Bond Cleavage"). Thus, it could not be tracked by the high-speed cyclic voltammetry (CVA, $v \leq 1000\ V\ sec^{-1}$) and by the HSCP [202]. The major reaction product is dihydrovitamin D (III), but dihydrotachysterol (IV) is also formed, which is effective in hypercalcemia (Sect. 9.2.7, "Dihydrotachysterol").

For a system of β-carotene (V) (11 conjugated bonds, drawing), we found four cathodic waves with two reversible one-electron steps $Car + e^- \leftrightarrows Car^{\cdot -} + e^- \leftrightarrows Car^{2-}$ [177, 205], in contrast to the data presented in [186, 187] and [206, 207]. The EC-ESR experiments curried out proved the formation of Car anion radicals [208]. The process runs along the way Car + epep → $CarH_2$ in the presence of proton donors [205, 209]. 7,7′-Dihydro-β-carotene was obtained with good yield as $CarH_2$ by electrolysis with weak proton donator [191]. Carotenes are easily oxidized; the two-electron anodic wave has reversible behavior according to β-carotene $- 2e^- \leftrightarrows$ β-carotene^{2+} [205] (the cyclovoltammetric experiments with $v = 1000$ V/s and $T = 273 \div 213$ °K [209]). The alternative schema of the process is $\downarrow$**-ee$_v$**$\uparrow$ with very fast cation radical disproportionation $2Car^{\cdot +} \leftrightarrows Car + Car^{2+}$ ([173], p. 153). High electron-donating activity of carotenes was confirmed by reactions with organic and inorganic electron acceptors [210]. For instance, the [β-carotene ·I]$^+$ cation formed according to the reaction of β-carotene + $I_2 \leftrightarrows$ [β-carotene · I]$^+I_3^-$ was detected by means of differential-pulse polarography [211]. Interestingly, the electroreduction of the complex [β-carotene · I]$^+I_3^-$ led to the neo-A-retrodehydro-β-carotene with 12 conjugated bonds, i.e., an unusual *cathodic dehydrogenation* occurs here. The family of carotenoids, β-carotene, α-carotene, lycopene, etc., was studied with the measurement of kinetic parameters [177, 178, 191, 205, 209]. The relatively high basicity of anion radicals of carotenes observed was used to perform catalytic endoergic electron transfer to β-carotene from anion radicals of chlorophyll and porphyrins [212] (Sect. 9.2.4).

Our first study of the electrochemistry of porphyrins coincided with the beginning of intensive study of these macrocycles [213–216]. In contrast to the conclusion made in [217], the third wave following the reversible $P + e^- \leftrightarrows P^{\cdot -} + e^- \leftrightarrows P^{2-}$ waves was found to be accounted for by the transfer of four electrons with formation of porphyrinogen PH_6 via fluorine as an intermediate product PH_2 [174, 218, 219]. The protonation kinetics of anionic particles was studied depending on proton donor strength and concentration; up to eight polarographic waves were observed and identified in these measurements. An additionally discovered prewave was associated with the adsorption of dimers $(P\text{-}P)^{\cdot -}$ of porphyrin and its anion radical on the electrode surface, schema $\uparrow e \downarrow a_s$ the dimer's particel size was estimated from polarographic data [174, 218]. Electrosynthesis of the mesomethyl porphyrin and its metallo-complexes [220] and cobalt alkylporphyrins (under EC-ESR control [221]) as well as introduction of Co porphyrins as electrocatalysts in dehydrogenation and radical polymerization processes [222] were among the preparative applications. The results of the electrochemical study of porphyrins are reviewed in the book [223].

Cathodic and Gas-Phase Reactions of the Bond Cleavage

The **ede** mechanism is here considered as a "classical" behavior [224]:

$$RX \xrightarrow{e} RX^{\cdot -} \xrightarrow{d} R^{\cdot} + X^- \xrightarrow{e} R^- + X^- \rightarrow \ \ldots \tag{9.10}$$

For CH_3Cl, it is transformed to the **{ed}e** with the "ultrafast" cleavage **d** stage (time of single oscillation, "synchronous" or "concert mechanisms").[17] The kinetic rather than thermodynamic factors (such as the energy of the lowest unoccupied molecular orbital of the substrate, etc.) became now deciding. We drew attention to the analogy of {**ed**} reactions with gas-phase dissociative electron capture process and

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[17] We consider it advisable to divide reactions into three groups: (1) with slow and moderately fast cleavage $0 < k_d^* < 10^3\ s^{-1}$ (SMFR) and (2) fast $10^3 < k_d^* < 10^{10}\ s^{-1}$ (FR) and (3) ultrafast cleavage (UFR) $k_d^* \geq 10^{10}\ s^{-1}$ [225].

used the results of gas chromatographic measurements with an electron capture detector. The expression for the gas-phase activation energy [225]

$$E_a^* = A + \alpha(D_{RX} - A_X) \tag{9.11}$$

obtained by using the Brönsted relation was confirmed by experimental data [226–228]. In Eq. (9.11), A and α are constants ($0 < \alpha < 1$), D_{RX} is R–X bond strength, and A_X is the electron affinity of the halogen X. Applying the Wentworth model [226, 227] based on the Morse function for anharmonic vibrations and accepting the Hammond postulate, the gas-phase activation energies $E_{a,e}^*$ and $E_{a,d}^*$ of e and **d** stages were calculated for a series of aryl and alkyl halides [204]. Antibate $E_{a,e}^*$ and $E_{a,d}^*$ changes with an extended straight portion turned out to be observed for a wide range of rate constants of **d** stages (Fig. 9.18). The dependence

$$\log k_e^* = -11 + 0.0155 E_{a,d}^* \qquad \left(\text{here,} \quad E_{a,d}^* \text{ in kJ/mol}\right) \tag{9.12}$$

therewith is satisfied predicting a slow electron transfer for the "ultrafast" **d** stage. Within the framework of these approximations, the formula for the inner reorganization energy was derived [204]:

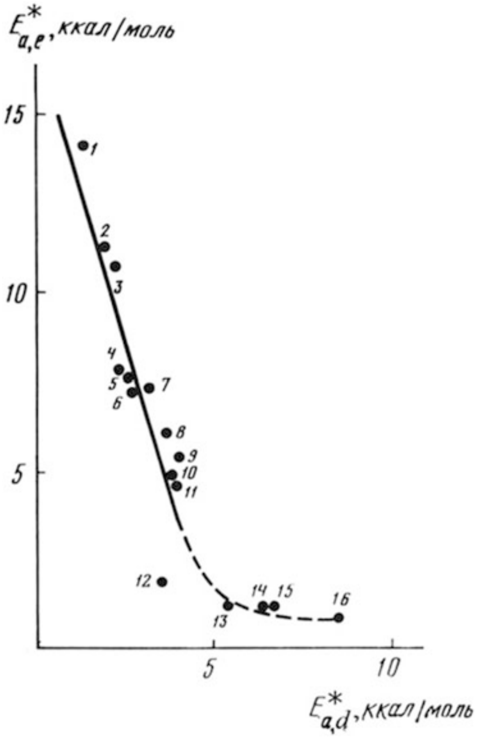

Fig. 9.18 The relationship between the activation energies $E_{a,e}^*$ and $E_{a,d}^*$ (in kcal/mol) for alkyl halides: 1-CH_3Cl; 2-$Cl(CH_2)_2Cl$; 3-$(CH_3)_3CCl$; 4-CF_3Cl; 5-CH_2Cl_2; 6-$CHFCl_2$; 7-$Br(CH_2)_3Br$; 8-$Br(CH_2)_2Br$; 9-$CHCl_3$; 10-CH_3Br; 11-CF_2CL_2; 12-CH_3I; 13-CH_2Br_2; 14-$CFCl_3$; 15-CCl_4; 16-$CHBr_3$

$$\lambda_i = D_0(1 - k_\mathrm{R}) \tag{9.13}$$

where $0 < k_\mathrm{R} < 1$ is the Morse function parameter, $D_0 = D_\mathrm{RX} + 0.5h\nu_0$, and ν_0 is the fundamental vibration frequency. It was also found the antibate relationship between λ_i and $E^*_\mathrm{a,d}$ [229] is confirmed by quantum-chemical AM1 calculations [230]. These results were applied then also under conditions of polar media (see Sect. 9.2.3, "Cathodic Reactions with Bond Cleavage"). An overview report on this issue was made in 1986 at the 37th ISE Meeting [231].[18]

9.2.3 *Chemical, and Electrochemical Reactivity*

Linear Conjugated Polyenic Hydrocarbons

We tested the Maccoll–Hoijtink relationship between $E_{1/2}$ and energies of the lowest unoccupied molecular orbitals (as m_LUMO coefficients) for linear conjugated polyenic hydrocarbons (LCPs) [236]. Using the perturbation theory for the substituent effect, the following simple formula was obtained:

$$m_\mathrm{LUMO} = 2\cos\varphi + \frac{2}{n+1}\sum h \sin^2(r\varphi) \tag{9.14}$$

where $\varphi = \pi\frac{(n+2)}{2(n+1)}$, r is the ordering number of the substituted atom, h is the induction parameter for the substituent, and n is the general number of π-electrons in LCP. The linear dependence

$$E_{1/2} = 2.19m_\mathrm{LUMO} - 1.24 \quad \text{(SCE)} \tag{9.15}$$

is valid for a wide range of LCPs starting from butadiene and up to β-carotene (the number of double bonds is between 2 and 11). Equations (9.14) and (9.15) were proved to be useful for determination of structure to property relationships in the series of LCPs; thus, the electron affinity (EA) and ionization potential (IP) of carotenoids were calculated [205].

Monofunctional Derivatives of Polyenes and Porphyrins

A universal procedure for prediction of $E^\mathrm{RX}_{1/2}$ for different classes of compounds (covering aromatic series, phenyl polyenes, LCP, etc.) was developed based

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[18] Equation (9.13) (without reference to [204, 231]) was later used by J.M. Savéant [232–235].

on the $E_{1/2}^{\mathrm{RH}}$ for the corresponding hydrocarbons RH and using the donor–acceptor constants of substituents ([173], p. 101, [237]). The linear correlations $E_{1/2}^{\mathrm{RX}} = f(S_{\mathrm{X}})$ intersecting at the "isopotential point" corresponding to the $E_{1/2}$ of the radical $\mathrm{RCH_2}$ lay at the core of this procedure. The slopes of the lines are determined by the electron affinity EA^{RH} of hydrocarbon RH, linearly decreasing with increase in EA^{RH}. Such correlations are also valid for porphyrins and metalloporphyrins MPO. For $\mathrm{M} = \mathrm{Ca}^{2+}$, Mg^{2+}+, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pd^{2+}, and Cu^{2+}, the effect of the metal M is taken into account by the constant S_{M} related to the Pauling's electronegativity [238]. For $\mathrm{M} = \mathrm{Co}^{2+}$, Mn^{3+}, and Fe^{3+}, the accepted electron is localized at the metal atom, and the slopes for $E_{1/2}^{\mathrm{RX}} = f(S_{\mathrm{X}})$ dependencies are much smaller (a weaker effect of substituent X). This fact can be used to elucidate the mechanism of the process. The values of S_{X} for a large number of substituents are given in ([173], p. 117, [237]). The validity of the classical Maccoll–Hoijtink equation for porphyrins was established in [219].

Cathodic Reactions with Bond Cleavage

A phenomenological approach, Sect. 9.2.2 was implemented for ultrafast reactions (UFR) $\mathrm{RX} + \mathrm{e} \rightarrow \mathrm{R}\cdot + \mathrm{X}-$ also in polar media, i.e for the estimation of the cathodic $\mathrm{E}_{1/2}$ ([173], pp 122–136; [225]). Gas-phase activation energy E_{a}^{*} being also considered as the decisive factor in this case. Assuming that the activation energies $E_{\mathrm{a}} = \alpha_{\mathrm{m}} E^{*}$ for the UFR processes in one and same polar media (solvent + electrolyte, coefficient $0 < \alpha_{\mathrm{m}} < 1$) and taking into account Eq. (9.11), we came to the expression:

$$E_{1/2} = A' - \alpha'(D_{\mathrm{RX}} - A_{\mathrm{X}}) \tag{9.16}$$

Thus, for UFR, for instance, alkyl halides (RX = AlkX), the values of $E_{1/2}$ may be easily predicted based on the available quantities of D_{RX} and A_{X} ([173], [225]). It should be noted that the coefficient $\alpha' = 0.018$ V·mol/kJ in Eq. (9.16) is almost the same as the values of slops in a set of particular experimental dependencies $E_{1/2} = C - \beta D_{\mathrm{RX}}$ found earlier by Evans and Hush for AlkX with different halogens X = Cl, Br, and I: B = 1048 0.013, 0.0173 and 0.018 V·mol/kJ, accordingly [239]. For a more detailed evaluation of this phenomenological approach, the values of $E_{1/2}$ (or of E_{p}) were measured in a wide temperature interval, and corresponding measurements in butyronitrile at temperatures down to −100 °C were scheduled. An excellent theoretical basis for this work was at the Faculty of Technology of Semiconductors of MITKhT led by Prof. Viktor Il'ich Fistul (cf. student work [240]). But these plans could not come true.

The reversible **e** stage takes place in **ed** process for the SMFR and FR cases, so the influence of the rate constant k_{d} of the **d** stage on $E_{1/2}^{\mathrm{RX}}$ is described here in terms of the conventional theory of the **ec** reactions as a "kinetic correction" $\Delta E_{1/2}$ [225]. The rigorous approach to the assessment of solvent effects is based on finding the reorganization energy λ_0. In developing the approach [225] based on the Wentworth' model and formula 9.13 for λ_i, Saveant calculated also the values of λ_0 according to Marcus–Hush [232–235]. However, as was shown by Grimshaw et al. on the example of alkyl halides, the Marcus–Hush calculations led to considerable deviations from experimental data in this case [241, 242]. A more rigorous analysis with quantum-chemical PM3 calculation of the λ_0 for alkyl halides was carried out by A.M. Kuznetsov and coworkers [243, 244].

ec Processes: Cross-Correlation Between Parameters of the e and c Stages

As follows from the consideration of slopes of linear dependence of $E_{1/2}^{\mathrm{RX}} = f(S_{\mathrm{X}})$ (Sect. 9.2.3, "Monofunctional Derivatives of Polyenes and Porphyrins"), the easier the system is reduced, the less is the influence of the substituent X on $E_{1/2}^{\mathrm{RX}}$ [237]. This pattern and the decrease of the rate constant k_{c} of chemical stage upon facilitation of reduction of the system are proved theoretically [245]. For **ed** processes, this directly stems from the antibate nature of the changes in activation energies $E_{\mathrm{a,e}}^{*}$ and $E_{\mathrm{a,d}}^{*}$ (Fig. 9.18). For **ep** processes with subsequent protonation stage, this follows from the results of a quantum-chemical consideration, for example, using Eq. (9.14). This conclusion can also be applied to other processes where the electron transfer is determined by the position of the substrate's frontier orbitals. In two limiting cases, we have infinitely long, graphite-like system with the delocalized electron (high electron affinity of the substrate M and low reactivity of the product $\mathrm{M}^{\cdot -}$) and solvated electron (low electron affinity of the substrate S, i.e., solvent, and extremely high reactivity of the product, i.e. e_{solv}) [245]. The "antibate rule" written as

$$\Delta \log k_{\mathrm{c}} = \pm 0.059 \alpha_{\mathrm{c}} \Delta E_0 \qquad (9.17)$$

we called as the "Brönsted cross relation," or BCR [246, 247]; here $T = 298$ K, the minus sign is for cathodic processes, and ΔE_0 is the difference in the standard potentials of the compounds compared. The BCR rule is fairly general; the conditions for its implementation are given in [245–247]. The experimental values of "cross transfer coefficient" α_{c} for different **ep**, **ed**, and **ea** (i.e., anionic polymerization) processes lie in the range from 0.1 to 0.5.

9.2.4 Homogeneous Electrocatalysis

The case in point is the reaction **[↓e]e$_{\mathbf{v}}$↑c** with endergonic **e$_{\mathbf{v}}$** stage with participation of a homogeneous catalyst regenerated at the electrode and followed the exergonic c stage. These systems became the subject of investigations in the early 1970s independently by three groups of researchers [248–252]. The first publication was the article by Lund and coworkers [248]; our work, fragments of which I reported in Riga's EKhOS-73 [250], was submitted by Frumkin for publication in *Doklady AN SSSR*[19] [251]. The "**d**" [248–252] and "**p**" and "**r**" [250, 251] reaction acted as the follow-up exergonic chemical stages.

The capabilities of the homogeneous electrocatalysis (HOMEC) processes for electrosynthesis and investigations of kinetics of **c** stages became immediately apparent (the first review [253]). The Koutecky approach for the simple catalytic schema was originally used for kinetic calculations: under certain conditions, the rate constant k_{ev} can be taken to be the half of the effective constant k_{eff} [248, 249, 251]. In general, however, this approximation cannot be used. As a general solution, we suggested a hybrid numerical–analytical method that made it possible to obtain a number of approximate formulas as applied to polarography and to voltammetry with rotating disk electrode, including "complicated" HOMEC cases, for example, with deactivation of catalyst or with other transformations [254, 255]. The new capabilities of HOMEC in studying the heterogeneous stages "**e**" of electrode kinetics were also shown [256]. This work incorporated later in my report on EKhOS-76 in Tula [253] was also submitted by Frumkin for publication in *Doklady AN SSSR*. This was in April 1976, 1 month before the death of Frumkin…One example. The increase in the electrolyte concentration and reduction in the size of the cation of the electrolyte in the series of Bu_4N^+–Et_4N^+–Me_4N^+ leads to a strong, up to +150 mV, shift in the $E_{1/2}$ of both chlorobenzene and vitamin D, but it has practically no effect on the rate constants of homogeneous electron transfer k_{ev}. Thus, the heterogeneous factors, in particular, the "compression" of the EDL with decreasing the size of the cation, have a crucial role here. The change in the ratio of heterogeneous/homogeneous reaction products was theoretically estimated for micro-electrolysis on DME [253]. The electron transfer reaction from the porphyrins and chlorophyll anion radicals to β-carotene was performed and studied by HOMEC (Sect. 9.2.2, "Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins"); other examples of HOMEC application are given in Sects. 9.2.6 "Electrosynthesis as an Investigation Tool: Pre-electrode Tomography", and "Electrosynthesis in the Chemistry of Biologically Active Compounds: Electrodeprotection Method". Synthetic and kinetic investigations of HOMEC were extensively carried out then by H. Lund, J.M. Savéant, and coworkers (see reviews [257, 258]).[20]

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[19] Publications in *Doklady AN SSSR* had to be submitted by a member of the Academy of Sciences (academician).

[20] The term "redox catalysis" [258] that is often used instead of HOMEC in the literature is inadequate, because it does not reflect the involvement of the electrode itself in the electrochemical reaction (stage "**e**") and the homogeneous character of the ET on the substrate (stage "$\mathbf{e}_{\mathbf{v}}$"). In additions, this term is widely applied to other phenomena. The involvement of the electrode is also not expressed by the term "homo-mediator system" [259]. Starting from Kobozev and Monblanova [260], the term "electrocatalysis" became accepted for heterogeneous electrode reactions, and the "homogeneous electrocatalysis," HOMEC, involves both **e** and $\mathbf{e}_{\mathbf{v}}$ stages.

9.2.5 Combination of Electrochemical and Other Analytical Techniques

By analogy to the chromatopolarography developed by Kemula and Górski [261, 262] in the early 1960s, we developed combined method of GC-EC with a polarographic detector [149–153]. The electrochemical technique being used here is an additional analytical method. On the contrary, in the study of the mechanism of electrochemical reactions, electrolysis is a “primary” process, and it is combined with the methods of studying electrogenerated particles (EGPs). We have used several of these combinations.

In Situ Electrochemical ESR

The EC-ESR technique became the “classical” combined method in the USSR from the beginning of the 1960s owing to the electrochemists of Riga and Kazan (see Sects. 9.1.3 and 9.1.4). The method allows, for example, to measure the rate constant k_{ex} of the symmetric electronic exchange of $\mathrm{M} + \mathrm{e}_{\mathrm{v}}^{-} \leftrightarrows \mathrm{M}^{\cdot -}$ in the substrate–anion radical pair. In order to study the influence of the structure of the substrate on the value of the rate constant, we measured the rate constants k_{ex} for a series of substituted nitrobenzenes X-$C_6H_4NO_2$ using an original microcell [263, 264] (symmetrical design, large surface of working electrode, and small currents in the signal acquisition mode). Also EC-NMR measurements were in parallel performed. Earlier proposed theoretical models, including the ellipsoidal model, were proved invalid for aromatic systems containing two or more polar substituents. Good results were obtained with the new “model of the determining specifying group” [263, 264]. The validity of this model was confirmed by quantum-chemical calculations of the solvent reorganization energies λ_0 [265]. The combined EC-ESR technique was often used in our studies of electrochemical reactions (carotenes, porphyrins, electro-deprotection reactions, etc.).

In Situ Electrochemical NMR[21]

Taking into account the large potentials of NMR, we have developed an in situ electrochemical NMR cell [266, 267]. The three-electrode EC-NMR cell with divided cathode–anode compartments and with a Hg-working electrode was placed in a standard 5-mm spinning NMR probe practically without distortion of the spectral resolution. Several EC-NMR regimes were tested, including continuous potentiostatic electrolysis and current pulse and continuous galvanostatic electrolysis with steady-state concentrations of the EGPs. The capabilities of the EC-NMR

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[21] These studies are included in the Ph.D. thesis of Leonid Yu. Yusefovich (1978).

method were demonstrated in solving numerous problems [268]. For reasons beyond our control, we could not publish the detailed design of the cell at that time. “The first practicable” EC-NMR cell (cited from [269]), with spinning 10-mm sample tube and a gold film rf-transparent working electrode, was published in the West only in 2000 [269]. Recently, we presented the EC-NMR cell [270], a radically advanced version of the cell developed 40 years ago.

Combined Electrochemical Stop-Flow Method

This method of direct study of reaction kinetics of the electrogenerated particles (EGPs) was implemented [271] on the basis of commercial stop-flow spectrophotometer with the EC cell mounted directly inside of the hydraulic system between the working syringe and the mixing camera. One- and two-channel modes were tested. Measurements were carried out for the protonation reaction of the EGPs as well for HOMEC processes. The EC-stop-flow technique is a powerful direct tool for studying the reactions of EGPs, including fast reactions with rate constants as high as 10^6–10^8 l/mol·s.

9.2.6 Organic Electrosynthesis

Electrosynthesis as an Investigation Tool: Pre-electrode Tomography

Results of electrosynthesis are often different from result of a “similar” chemical reaction. These differences are associated with the heterogeneous electrode factors, and they can be used as a tool for studying the phenomena occurring at or near the electrode. In this respect, HOMEC provides excellent capabilities for selection of a “similar” chemical reaction making it possible to run the process under the same conditions transferring it, however, from the electrode surface to the bulk solution (see Sect. 9.2.4).

We used such an approach in the study of dissociative **edep** reduction of the β, γ-unsaturated alcohols. Specially synthesized deuterated 2,4-pentadienol and its derivatives $CH_2{=}CHCH{=}CHCD_2Y$, where Y = -OH, -OAc, and -OMe, was taken as a substrate RY [272, 273]; the deuterium label is necessary to distinguish the 1,5-positions. In contrast to the cases studied earlier (cinnamic alcohol, vitamin A, etc., Sect. 9.2.2, “Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins”), the reaction proceeds here via the symmetric pentadienyl anion $[CH_2\text{-}CH\text{-}CH\text{-}CH\text{-}CD_2]^-$. Therefore, two piperylene isomers $CH_3\text{-}CH{=}CH\text{-}CH{=}CD_2$ (*a*) and $CH_2{=}CH\text{-}CH{=}CH_2\text{-}CD_2H$ (*b*) in the strictly equal amounts could be anticipated as products. However, the preferential formation of one isomer, with the $r_{\text{exp}} = [a]/[b] > 2$, was found experimentally. This anomaly was explained by nonequilibrium asymmetric arrangement of anion near the electrode due to the “orientation inheritance” of the original asymmetric molecule RY. This should lead to the intra-anion charge distribution and to the unequal rates of protonation in 1,5-positions. The situation is similar to the Stal' Mairanovskii's effect of "orientation inheritance" on the electrode surface [33, 34] (Sect. 9.1.1). But we were dealing here with the "volume inheritance," as the absence of adsorption on the electrode substrate was established. Hence, we determined the "effective" pre-electrode orientation of the pentadienyl anion, which was different for different substituents Y = -OH, -OAc, and -OMe in the starting molecule. Therefore, we hypothesized the existence of a "superviscous" pre-electrode layer with the ~10^4 to 10^5 times higher viscosity than in bulk [272, 273].[22] The drastic increase in the proportion of thermodynamically less favorable *cis*-configurations for both isomers *a* and *b* has to be mentioned among other revealed features.

The situation has radically changed when we used the HOMEC. The gradual increase in the HOMEC contribution in the electrolysis was accompanied by a regular decrease in the $r_{\text{exp}} \rightarrow 1$ [272, 273], and the percentage of *trans*-configurations species increased too [276, 277]. These changes in the structure of the products under layer-by-layer shifting of the process from the electrode surface to the bulk reflects "layered" changes of conditions, including the change of the electric field strength, in the pre-electrode region. The concentration profiles of the products in the pre-electrode layer as a function of HOMEC contribution are to be known for quantitative analysis of the results obtained. An important factor for the application of the method, which we called the "EDL tomography" [276, 277] (more general "pre-electrode tomography" or PELTO), is the choice of model substrate. At the same time, PELTO provides the way to investigate the changes in organic reactivity under the heterogeneous effects: adsorption and chemisorption, high electric field, etc.

Electrosynthesis in the Chemistry of Biologically Active Compounds: Electro-deprotection Method[23]

I have already provided examples of syntheses in a series of vitamins A and K, porphyrins, carotenes, etc. A special direction of investigation was the development of methods for electrochemical removal of protecting groups which we called as "electro-deprotection". Temporarily protecting the definite centers of a molecule is a tactic widely adopted in organic syntheses, especially in peptide and carbohydrate chemistry. Removal of the protecting groups is usually carried out by more or less severe chemical treatments. Mild conditions and the possibility of smooth variation in the strength of "reagent," i.e., the electrode potential, make electrolysis a very attractive for such conversions. In 1965, Horner and Neumann discovered the

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[22] This hypothesis is supported by the first results of viscosity measurements in the pre-electrode layer at a distance of $\delta < 6$ nm [274] using an idea of combined EC-AFM method [275]. After the symposium [275], Prof. Dieter Kolb introduced me to a group of scientists from Mainz, they invited me to hold a seminar and we had a joint project. Prof. Kolb followed it with great interest. I fondly and with gratitude remember this outstanding electrochemist (1942–2011).

[23] This work became the basis of Ph.D. dissertation by Nina Fyodorovna Loginova (1977).

removal of Tos (i.e., p-toluenesulfonyl) group at Hg cathode in Me_4NCl/methanol solution. The experiment carried out without potential control was explained by the reaction with electrogenerated amalgam: $Me_4N \cdot n$Hg [278].

We published almost simultaneously the direct electrochemical deprotection of Cin (cinnamyl, a new group), trityl (triphenylmethyl group), and Z (benzyloxycarbonyl group) groups by electroreduction in Alk_4NX–DMF solution [194, 195]. Later, we propagate this technique to a great number of other groups [279, 280]. In most cases, the process was carried out under pH control (Sect. 9.2.1, "Electrolysis at a Constant "pH" ("pX") with Recording Equipment"). The HOMEC is also efficient for labile substrates and for difficult reducible (oxydable) groups [279–281]. For example, the HOMEC's electron transfer beyond the supporting electrolyte discharge region was used to obtain glycine from its Z derivate with quantitative yield. Based on regularities governing the easiness of bond electro-cleavage and taking into account the decrease in the rate of the bond cleavage according to BCR rule (Sects. 9.2.3, "Cathodic Reactions with Bond Cleavage"), and "ec Processes: Cross-Correlation Between Parameters of the e and c Stages"), a method of activation of protecting groups by electron-acceptor substituents was developed. The activation method can be illustrated on benzyloxycarbonyl group (Z). Nonactivated Z cleavages at $E \approx -2.9$ V SCE, the activated (p-NO_2)Z at $E = -1.3$ V, i.e., activation shift is as high as +1.6 V (!). The p-(NO_2) phenylsulfonyl derivative is reduced at the lower cathodic potential $E = -1.0$ V, but *without* removal of the protecting group (a slow cleavage of C–N bond, in accordance with the BCR rule; it was demonstrated with the combined EC-ESR) [282, 283]. The theoretically predictable variation of the electrochemical activity, (Sect. 9.2.3), i.e., ease of cleavage of the protecting group is an important merit of the method.

We successfully used electro-deprotection reactions in the synthesis of various classes of natural compounds, such as amino acids, oligopeptides, glycoproteins, phospholipids, saccharides, polysaccharides, etc. [279–283]. Application of the method instead of chemical synthesis of oxytocin and desamino-oxytocins led, for example, to a twofold increase in the yield of these hormones with high degree of hormonal activity (joint work with the Riga's chemists [284]).

9.2.7 *Industrial Electrosynthesis*[24]

Dihydrotachysterol

This substance is an active agent for treating hypocalcemia and hypoparathyroidism (drugs A.T. 10, Perlen, etc., daily dose of 0.6–1.1 μg). The known chemical process for its preparation by Birch reduction of vitamin D provides a yield of about 20 %.

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[24] The materials given in this section were the object of a large number of "closed" USSR author's certificates; they entered in the closed (not openly accessible) Ph.D. dissertations by Inna Alekseyevna Titova (1979) and Isaac Grigorjevich Gitlin (1985).

As was noted above (Sect. 9.2.2, “Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins”, Eq. 9.9), dihydrotachysterol (IV) is also formed by electroreduction, but the thermodynamically less favorable dihydrovitamin D (III) is the main product in this case too. We found the ratio (IV)/(III) to be independent of the **e** stage but to decrease sharply with increasing of the protonation rate of the radical anion (AR_2): with increasing temperature ($-20 \rightarrow +50$ °C), with a decrease in donor numbers of the solvent (HMFT > DMSO > DMF > THF), with increasing water content in the solvent, and with increasing the acidity of the cation of the electrolyte ($Bu_4N^+ > Et_4N^+ > Me_4N^+$, HOMEC experiment). Acceptable conditions (dry DMSO, electrolyte Bu_4NJ, 20 °C, the yield of dihydrotachysterol ~40 %) were selected as a result of these studies [285–287].

The isomerization (III) → (IV) under the action of the strong base dimsyl (dimethylsulfoxide anion) was the second stage of the process, and the total yield of dihydrotachysterol increased to ~70 %. Here, the electrolysis of alkali salt in the dimethylsulfoxide on the graphite or carbon cathode was used to obtain dimsyl instead of the known Corey–Chaykovsky synthesis with sodium hydride [288]. This was our new “intersection” with E. Corey (cf. Sect. 9.2.2 “Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins”); in addition to safety, the advantage of electrolysis compared with the chemical method is also the possibility to easily produce dimsyl salts of various metals, including of the most active Cs^+-salt. These three original stages were the basis of manufacturing dihydrotachysterol (VNIVI, since 1977).

Electrosynthesis of Diacetone-2-Keto-L-Gulonic Acid in the Vitamin C Production

Vitamin C, ascorbic acid, was the first synthetically made vitamin (Reichstein’s synthesis, ETH Zürich Hoffmann-La Roche 1938). Vitamin C in world production of vitamin products takes the largest share – tens of thousands of tons per year. Diacetone-2-keto-L-gulonic acid (DAG), which is the product of the fourth stage of the Reichstein’s synthesis, is obtained by oxidation of diacetone-L-sorbose (DAS) via the $RCH_2OH + Ox \rightarrow RCOOH$ reaction. The hypochlorite NaOCl is the oxidant Ox, but for environmental reasons, the more expensive $KMnO_4$ is used at plants located in urban areas. The direct electrooxidation of the DAS is an attractive alternative here. The first industrial electrosynthesis of DAG was carried out in the “Pharmakon” plant in Leningrad (graphite anodes, current efficiency $\beta \sim 40$ % and capacity of 250 ton/year) in 1970 [289]. This technology was later used in the Yerevan vitamin plant (Armenia) and in the Stanke Dimitrov (from 1990 Dupnitsa city) plant (Bulgaria). Around the same time, Fleischmann et al. suggested the mechanisms of electro-oxidation of alcohols on the Ni anodes in alkaline solutions [290] creating the basis for further work.

The main problem here is the low current efficiency due to the side reaction of oxygen evolution. A team of the ETH Zürich and of Hoffmann-La Roche solved the problem of decreasing current by developing the so-called Swiss-roll cell with a very large area surface of the Ni foil anode. A mini-pilot plant with an annual

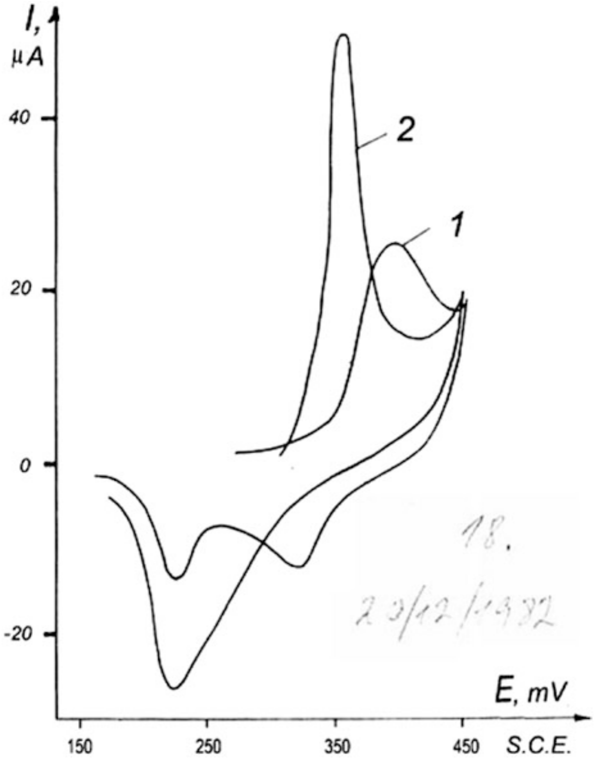

Fig. 9.19 DAG electrosynthesis, from the first voltammetric experiments, 1982. (1) Ni electrode, 0.05 M NaOH, 0.002 M $NiSO_4$; (2) the same with 0.02 M NH_3. A significant increase in the anodic peak, its shift to lower potentials, increase of the cathodic peak of the β-NiOOH, and disappearance of the cathodic peak of the γ-NiOO can be seen

capacity of 750 ton was established on this basis [291, 292]. Simultaneously with the ETH Zürich and Hoffmann-La Roche team, we also attempted to solve the problem but using another approach, namely, by increasing the catalytic activity of the Ni anode. This was really achieved by using amino compounds as Ni ion-complexing agents (cf. Fig. 9.19). The team of young employees, first Isaac Gitlin alone and then with together with Anna Kukushkina and Vladimir Gurevich, established the optimal conditions for electrosynthesis, which were confirmed on a small laboratory installation. Trilon B was used as an amino compound. Based on the experience of I.A. Avrutskaya, M.Ya. Fioshin, etc. [86, 87] (Sect. 9.1.1), the electrolysis was carried out with the addition of Ni^{2+} salt; the process was monitored by an original express spectropolarimetric procedure.

Two years later, the process came into operation in the Yoshkar-Ola vitamin plant [293–296]. The main contribution to the industrial implementation of the process was made by chief engineer Sergej Alexandrovich Rosanov. He found a number of original technical solutions, and the electrosynthesis was brought into use without stopping the running production. The production line of 1500 ton/year with current efficiency of $\beta = 70\ \%$ consisted of 10 similar units including the homemade electrolyzer (a simple and reliable bipolar undivided cell with stainless steel electrodes). The DAG electrosynthesis became the one of the largest in the USSR/Russia.

And the capacity, 1500 ton/year, determined by the power of the Yoshkar-Ola plant, could be increased by many times. The designing of new plants was started in lates 80 with a capacity of 5,000 and 10,000 ton/year of vitamin C (these projects were not implemented). We informed about our developments only in 1990 [295, 296], and a detailed description has been given in a recent paper [297].

I must say here that our director Viktor Andreyevich Yakovlev persuaded me to carry out research in DAG electrosynthesis back in 1975–1976. He saw the promise of this work, pointing out the true disadvantages of the "graphit anodes"-technology in Leningrad's "Pharmakon" plant. But I never got around to it then. In 1982, 5 years after the death of Viktor Andreevich, this work was prompted by special circumstances. The sharp deterioration of relations between the USSR and China led to termination of $KMnO_4$ deliveries from China and threatened vitamin C production in the Yoshkar-Ola vitamin plant. Under these circumstances, an effective electrochemical method was a task of utmost importance.

Completion of the History of the Vitamin Institute "ECHO"

The DAG electrosynthesis lasted for 10 years until 1994, when vitamin C production in Yoshkar-Ola has stopped. A few years later, the Institute of Vitamins, VNIVI, ceased to exist. In 1994, the former members of our electrochemical group, I.G. Gitlin and N.T. Ioffe, organized the research and production company "ECHO" (nauchno proizvodstvennaya kompaniya or NPK "ECHO"). This company now produces more than a dozen of drugs, including dihydrotachysterol, β-carotene, etc. And that is all that remains of VNIVI. The name of the company, "ECHO," composed in memory of the DAG electrosynthesis of "**e**lectro**ch**emical **o**xidation," sounds today like the echo of the once existing Institute of Vitamins that contributed so much to the vitamin and pharmaceutical industry of the USSR.

9.2.8 Conclusion: Scientists in a Divided World From My Experience

In conclusion, I will say a few words on foreign scientific contacts in the period 1960–1990, i.e., from the end of "ottepel'" until the end of "perestroika." I will start with the "literary" contacts. All of correspondence, letters, articles, etc., passed through the pervyy otdel (the first department) of the institute.[25] The authors signed a form confirming that the article "does not contain new data representing a

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[25] The pervyy otdel (first department) in the Soviet organizations oversaw the hiring of staff, travel abroad, access to information, foreign correspondence and publications, and use of typewriters and copiers (countering the "samizdat," i.e., reprint of banned literature). The information about employees, their political views, etc., was also filed there.

scientific or technical interest" (one wonders who needs such an article?). The manuscript was examined by the pervyy otdel and then presented by the director of the institute to the Ministry's UVS (Upravlenie Vneshnikh Snoshenij, Office of External Relations) for approval. Only articles approved by UVS could be sent for publication abroad. For instance, when one of my reviews [279] was blocked by UVS, V.A. Yakovlev had to petition in person and substantiate the plea emphasizing importance of that publication in the foreign journal *Angewandte Chemie*.

These obstacles meant that only a small fraction of Soviet scientific articles sipped through into the Western journals, and this led to rather rare citations of the papers of Soviet scientists abroad. I have already mentioned a few episodes from my practice (Sects. 9.2.2, "Natural Polyenes: Vitamins A and D, Carotenes, and Porphyrins" and "Cathodic and Gas-Phase Reactions of the Bond Cleavage"). The comprehensive bibliography of Soviet electroorganic chemistry including the USSR's author certificates compiled by Fritz Beck (Germany) is one the rare cases of fair recognition [3]. On the other hand, we had access to the Western journals in those years, naturally only for "technical" disciplines. Although, even in Moscow, the journals became available in libraries with a considerable time lag, and sometimes with missing pages (traces of censors work). But the infamous campaign against "cosmopolitan bowing to the West" had slowed down by the early 1960s, and even at a brief glance, one can see that the Soviet electrochemists extensively cited the works of foreign authors. Thus, the citation of articles in these years resembles a unidirectional West-to-East permeable membrane.

Significantly greater obstacles stood in the way of direct contacts. During my whole work in VNIVI, I had never been allowed to travel abroad, even not to a "socialist country," up to 1987. The only exceptions were the trip to GDR (German Democratic Republic) in 1968 at the invitation of friends with whom we, Bella and I, had studied at MITKhT, and to Bulgaria, together with the chief of the Yoshkar-Ola vitamin plant, engineer Sergej Rosanov, to the Stanke Dimitrov's plant, in connection with the electrosynthesis of DAG. "As UNESCO asked me to organize collaboration between organic electrochemists from East and West," the famous scientist Henning Lund (Aarhus, Denmark) wrote, "Sandbjerg meetings had participants from both sides and from all continents" [298]. But, unfortunately, not "from all continents." In the late 1970s, I did get indeed a letter from Henning Lund, in which he informed me that I was included in the list of participants of the regular Sandbjerg meetings on organic electrochemistry. But the ministry's UVS did not allow me to visit any one of them (there were three or four meetings and, therefore, letters from Lund). Over the time, I accumulated a sadly large pile of invitations from different countries to symposia, conferences, and congresses, none of which I could attend. In my case, the visits were restricted because, first of all, I was Jewish and, secondly, not a member of the Communist Party. I should say that although it was almost mandatory for laboratory heads to be members of the Communist Party, I had, in our institute, the freedom of choice also in this matter, without rigid ultimatums. Of course, in day-to-day life at the Institute the Director had regularly predicaments with the "pervyj otdel". Once, when I asked Prof. Yakovlev to take a physicist with an "inappropriate" (i.e., Jewish) name in the

NMR group, Viktor Andreevich agreed, but after some deliberation he suggested to postpone the issue until the time of his holiday. Ultimately, the application for a job was approved by the acting director, Vladimir Ivanovich Gunar, instead. However, the visits abroad were governed by “external forces,” and Yakovlev was powerless here.

Yet, one foreign contact took place, however, on “our territory.” In 1976, one of the leading scientists in organic electrochemistry, Dr. James Grimshaw from the University of Belfast, came to IELAN, Moscow. I got a call from my friend, Alexander Ershler from IELAN, who said that Dr. Grimshaw would like to visit our laboratory. V.A. Yakovlev gave permission. When Dr. Grimshaw and I first met, we felt mutual respect and sympathy and a 3-day “VNIVI program” was put together. We showed him our experimental techniques (he was, particularly, interested in “pH-static” electrosynthesis) and told him about our works and discussed them. A seminar was organized, and Dr. Grimshaw made a brilliant report on organic electrochemistry and his works to a large audience (translated by Ella Boltyanskaya from our lab). An evening concert in the Great Hall of the Moscow Conservatory was the starting point of our cultural program. There were three of us, along with my 11-year old son, who attended a specialist English language school and was very excited to meet a “real British gentleman.” And on Sunday, on request of Dr. Grimshaw, we took a trip to Zagorsk, to the famous Troitse-Sergiyeva Lavra (Holy Trinity Church-St. Sergius Lavra). It was a risky trip, because Dr. Grimshaw had no permission to leave Moscow. It was dangerous to go by train (70 km from Moscow) as we could be seen by controllers or “vigilant” passenger scammers. V.A. Yakovlev provided the institute minibus for Sunday with a “reliable” driver and gave instructions on how to behave in an event of extraordinary situation. Fortunately, all without incident, we took a tour guide and managed to see a lot of interesting places; among them is the Duchovskaya (Holy Spirit) Church, exactly 500 years after its construction (1496).

I was allowed to attend foreign meeting for first time in 1987, the Symposium in Sopron, Hungary [203]. But fundamentally, the situation with the invitations to the conferences changed only with the beginning of “perestroika.” At once, a vast geography opened: Praha-Liblice (Heyrovský discussions), May 1989 (Fig. 9.20); Stockholm (32nd IUPAC Congress), August 1989; Montreal (177th Meeting of Electrochem. Soc), May 1990; etc. Then, with great joy, I finally met Henning Lund, Norman Weinberg (Electrosynthesis Co., USA), and other electrochemists long known to me by their works. During my second visit to London (summer, 1991), as guest professor at the Queen Mary College (the laboratory of Prof. J.H.P. Utley), I was invited by Dr. James Grimshaw. In the few days I spent in the hospitable home in Belfast, I met James’s wife, Dr. Jadwiga Grimshaw, also an electrochemist and, as it turned out, a talented artist. I visited their laboratory at Belfast University. As a surprise, James, with a smile, found an article with Boltyanskaya [272, 273] published in *Doklady Chemistry*, an English edition of *Doklady AN SSSR*: his university subscribed to this magazine in English! Several copies of the article were made right there, and no permission of the “pervyy otdel” was required.

Fig. 9.20 Group of participants of Heyrovský discussion: Vladimir V. Strelets (first from *left*), Stal’ G. Mairanovskii (*center*), and me. Czechoslovakia, Liblice, May, 1989

In 1993, Professor Fritz Beck invited me to the 44th ISE meeting in Berlin [247]. Our documents for emigration to Germany had long been ready. Two weeks after my return to Moscow, on September 23, we all together, with my brother Felix and his family, flew to Germany (Felix, professor of hydraulics, worked as the head of the Hydrology Laboratory of NII VODGEO). In Russia, it was the time of another rampant anti-Semitic wave, this time headed by the “national–patriotic” society “*Pamyat*” (“Memory”). We were kept at the airport the whole day and finally allowed to board the last leaving airplane. We know firsthand what anti-Semitism is and did not want this for our kids. But that is another story.

Summing up, I can say that isolation from Western scholars has made substantial damage. It is hard to imagine how broad our horizons would have been if we had been able to interact with foreign members of the like-minded scientific community without interference. “We sat outside the fence, having fun in the kitchen, singing in the woods ...” is how satirist Mikhail Zhvanetskiy referred to the pre-“perestroika” time in the Soviet Union. Our work in VNIVI was akin to singing in a “small forest.” VNIVI had its own microclimate, which gave a sense of local “freedom” and an excellent opportunity to work. It is a merit of Prof. Viktor Andreevich Yakovlev. Of course, Moscow was exceptional because we had experts of the highest level working in various fields of chemistry and could discuss any topic among ourselves. On the other hand, EKhOS, being an extremely comprehensive field in itself, was the “big woods” covering the vast ranges of the USSR. Regular and lengthy meetings of specialists in organic electrochemistry from many cities and of different schools of thought, as well as the publication of conference proceedings and books on EKhOS, created a special bond and creative and stimulating climate. This is a merit of academician Alexander Naumovich Frumkin and his team of assistants, L.G. Feoktistov, A.P. Tomilov, M.Ya. Fioshin, S.G.

Mairanovskii, Ya.P. Stradyn, Yu.M. Kargin, V.D. Bezuglyy, Yu.S. Lyalikov, Yu. M. Tedoradze, L.I. Krishtalik, A.B. Ershler, D.I. Dzhaparidze, and others. The songs from this “big woods,” the EKhOS, were loud and echoed far although they were not always heard by our colleagues outside the fence.

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Appendix: Symbolization of Electrode Reactions (Based on [299])

Symbols “**e**,” “$\mathbf{e_v}$,” and “**ε**” refer, correspondingly, to the heterogeneous, “volume” (without of any electrode interface effects) and solvated ***e***lectron transfer; “**c**” and “$\mathbf{c_s}$” refer to the volume and “surface” chemical stages. Designation of chemical stages “**c**”: according to particle, “**p**” (***p***roton) and “**h**” (***h***ydrogen), “minus” for detachment of a particle, and for attachment of a particle the “+” sign is omitted; and according to the type of reaction, “**a**” (***a***ssociation, bond formation), “**d**” (***d***issociation, bond cleavage), and “**r**” (***r***earrangement, isomerization). The subscripts N, E, R, and M (**n**ucleophil, **e**lectrophil, **r**adical reagents, **m**aterial of the electrode) are used to indicate the nature of the substances; the subscript “2” is used for the dimerization reaction. The parallel reactions, the reactions of the second substance, and the “concert reactions” are written in the brackets ( ), [ ], and { }, correspondingly. The origin and the carry points of reagents may be indicated by the arrows “↑” and “↓,” correspondingly. Capital *A* and C letters may precede the reaction schema in order to distinguish between anodic and cathodic processes. The overall number of stages and the transported particles are given with the “∑” sign, for example, ∑**2edp** [cf. Reaction (9.7a)]. When written compactly, the symbols are entered directly in the reaction equation [cf. Reaction (9.6)].

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Chapter 10
Professor Kemula School of Electrochemistry and Electroanalytical Chemistry at the University of Warsaw in Time of a Divided World

Zbigniew Galus

It is not an easy task to write about work of Professor Wiktor Kemula, because his field of interest covered several aspects of chemistry. Therefore, in this short presentation, I will limit myself chiefly to his work in electrochemistry and electroanalytical chemistry, indicating only briefly his achievements in other branches of chemistry.

Before presentation of his achievements at the University of Warsaw, I will write briefly about his early work. Wiktor Kemula was born far from the borders of the present Poland in Ismail in Besarabia (at that time belonging to the Russian Empire, now Izmail, Ukraine), where his exiled father worked. At that time, at the beginning of twentieth century, Poland did not exist as an independent state, since the former State—the Union of Poland and Great Duchy of Lithuania was invaded at the end of eighteenth century by three neighboring states—Russia, Prussia, and Austria, and occupied until the First World War.

Wiktor Kemula's father was forced to leave his native country (Kazimierza Wielka, district of Kielce) after participation in anti-state movements. Kemula's father's occupation was connected to some extent with chemistry, since he worked in wool-dying industry. He died of tuberculosis, when Wiktor was a young boy. At the age of 15, young Wiktor Kemula lost his mother. Since that time he was under care of his grandmother.

In Ismail Wiktor Kemula attended the primary and secondary school, receiving very good grades. At home he learned German, French, and also to play piano. In addition to these mentioned languages, he knew Russian well since this language was used at schools in the Russian Empire. After 1918, when Ismail with Besarabia was incorporated into Romania, the language in the school was changed from Russian to Romanian. This gave young Wiktor Kemula a chance to learn

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Romanian, which he could use, as I remember, several decades later during meetings with his Romanian guests.

His excellent results in school, especially in the last 4 years before maturity, were the basis for granting him a foreign scholarship. As a Pole, he decided to go to Lvov (now in Ukraine) where well-known schools were located: Jan Kazimierz University founded in 1656 and the Polytechnic School founded in 1844. He applied to the University, but to be accepted he had to pass Polish language, history, and geography examinations, in order to nostrificate his maturity certificate which did not include grades from the three abovementioned subjects.

10.1 Early Work of Professor W. Kemula

After passing these examinations, he began to study chemistry at the University of Jan Kazimierz. However, soon his economic situation in Lvov got worse, because it was time of the great inflation. Money which he brought lost practically the value. In such situation, Wiktor Kemula used his music education and he played the piano when the silent-movies where shown in Lvov cinema. Due to this temporary job, his economic situation improved considerably, since this income was on the level of that of a university professor.

As a second year student, he got a job as an assistant of Prof. Stanisław Tołłoczko (1868–1935), head of the Chair of Inorganic Chemistry. At the age of 25, he received Ph.D. degree for the work on photochemistry of hydrocarbons. At that time, he studied hydrocarbons in the gas phase, their spectra, and their reactions in the excited states. After graduation, he received a scholarship from the Fund of the National Culture. Initially he intended to spend the fellowship working in Leipzig. However, shortly before his final decision, Prof. Tołłoczko visited Prague and listen to a seminar by then unknown young scientist Jaroslav Heyrovský (see Sect. 10.3). He was very much impressed by Heyrovský and the new technique that he invented and advised Kemula to split his stay abroad between Prague (laboratory of Jaroslav Heyrovský) and Leipzig [laboratories of Fritz Weigert (1876–1947) and Peter Debye (1884–1966)].

In Prague Kemula became deeply fascinated by polarography and phenomena, which occurred during electrochemical reactions on mercury electrodes. As a result, his thesis presented in 1932 to receive the Doctor of Science degree (Habilitation) was connected with polarography. Three years later, in 1935, Professor Kemula became the Head of the Department of the Physical Chemistry at the University in Lwów.

The totally different subjects of his Ph.D. and Doctor of Science degree theses point to his deep involvement with inorganic and physical chemistry as well as with electrochemistry and electroanalysis.

In the middle of 1939, before the beginning of the World War II, he was appointed as the Head of the Chair of Inorganic Chemistry of the University of

Warsaw. However, since universities and other academic schools in Poland were closed by the German occupants during the war, he could take this position only several years later, after the end of the war in the spring of 1945.

10.2 Beginning of the Work at the University of Warsaw

The conditions of his early work in the University of Warsaw were difficult, because the building of the Department of Chemistry in the Pasteur Street, newly constructed in 1939, was partly damaged during the war, when it was used by the German occupants as a military hospital. Therefore, at the beginning Kemula had to take care of the repair of the departmental buildings in addition to—of course—teaching. Therefore, until 1950 Professor Kemula published only three papers, based partly on his earlier results, not published before the war. In the meantime, in May 1946, Kemula, responding to the invitation of his foreign colleagues, has organized an academic trip for laboratory work in academic schools of Copenhagen for 250 students from Warsaw and other Polish universities, mostly studying chemistry but also biology and medicine. This event was a result of a very friendly offer of the Danish Society and Copenhagen University teachers to sponsor and arrange this chemical training for Polish students and to organize their laboratory work during summer months. This was very important because Polish laboratories were destroyed during the war. It shows that, during several years after the Second World War, there were no conditions in Poland to carry out scientific research. The organization of such Chemical Summer School and the stay of so large a group of Polish students with several Polish Professors was possible due to the generosity of Danish people, but also because in 1946, the Iron Curtain which separated Eastern and Western Europe was not as tight as in 1948 and in the forthcoming years. I am sure that such academic trip of many students would not have been possible, for political reasons, 2 years later, when Middle and Eastern Europe, including Poland, were already strictly separated from the West.

Several years after the war, when the communist rule became stronger, the people and various organizations started to be strictly controlled. Some persons were falsely accused and even put in jail. Such inhumane policy was extended also to academic schools. Professor Kemula, who in the years 1947–1950 was the Dean of the Department of Natural Sciences of the University of Warsaw, and later the Head of the cluster of chemical chairs (precursor of the Department of Chemistry), had some problems as well. In 1949, he travelled to Great Britain in order to buy basic equipment, instruments, and reagents, of course in limited quantities—as necessary for the Department—to supply the student laboratories and also to create the conditions necessary to start the laboratory research work. However, after this trip, he was harassed by the communist security forces, being accused of spying activity. Such accusations were dangerous; another Professor in the Chemistry Department [Antoni Łaszkiewicz (1904–1980)] accused of spying was imprisoned from 1949 to 1955, and another Professor of chemistry harassed by security forces committed suicide.

Though Professor Kemula was not imprisoned, the authorities were hostile to him for many years. When in 1951 the Polish Academy of Sciences was founded, he did not become a member of this body, though he evidently fulfilled the criteria of admission.

In Poland, the time when Europe was divided by the Iron Curtain, may be broken down into two or even three periods. The first lasted from the end of the WW II till 1956. In that year, under the pressure of people, significant changes in the government and in the state's internal policy took place. These changes were promoted by the death of Stalin and the information delivered by Khrushchëv regarding Stalin's crimes. Quite opposite to Hungary, where the changes were ended by the intervention of Soviet Union, changes in Poland were relatively quiet, without any military intervention, either by internal forces (Polish army dominated by Stalinists) or—as in Hungary—by external troops.

The second period, which begins in 1956 after nonviolent political changes in Poland, lasted till 1981. In that year, after the formation of the Solidarity movement, martial law was introduced. The third period lasted from 1982 to 1989 when the Iron Curtain was abolished. At that time several new countries separated from the Soviet Union and several Central European countries, including Poland, became truly independent. The barrier which divided Europe then disappeared.

Returning to the first period (years 1945–1956), it is worth mentioning that during the years immediately following the war—1945, 1946, and partly 1947—institutions and organizations which existed in Poland before the Second World War were restored and, for a short time, remained active. A limited exchange of people and ideas with Western Europe ended in the second half of 1947 and 1948, and then the system became very oppressive for several years.

In Poland, in that period, there were, as far as I know, no official regulations which would have restricted sending of research papers for publication abroad; however, in practice exchange of letters with people and institutions from the West was evidently controlled, what significantly limited our contacts with the Western countries.

In the University of Warsaw, in years 1945–1950, Prof. Kemula published only one paper in the *Reports of the Warsaw Scientific Society* (1948) on the catalytic electroreduction of oxygen. However, already in 1950, several papers prepared by Professor Kemula and his young coworkers appeared. All these papers, with one exception, were devoted to various aspects of polarography. These papers (6) were published either in Polish in *Reports of the Warsaw Scientific Society* (3) or in English, in Czechoslovak chemical journal—*Collection of Czechoslovak Chemical Communications*. In the latter journal, important papers on polarography were published earlier by researchers from different countries all over the world.

10.3 Further Development of Research

Six papers from 1950 were followed by eight others in 1951 and nine papers in 1952. Almost all of these 17 papers (years 1950–1952), namely 16, were also related to different aspects of polarography. The year 1952 was important for the development of polarography or more widely of electroanalytical chemistry in Warsaw. That was mostly due to the method introduced by Prof. Kemula and named by him "chromato-polarography." The first two papers based on the idea to combine the chromatographic separation with polarographic detection were published in *Roczniki Chemii* (Annals of Chemistry) by Prof. Kemula himself, while the third one was published in cooperation with Prof. Andrzej Górski.

Chromatopolarography appeared to be an important method, because on a well-chosen chromatographic column, substances which had almost identical voltammetric characteristics (half-wave potentials) could be separated, if their affinities to the column-filling material (stationary phase) were sufficiently different. After separation, they could be polarographically detected and their content determined. This method may be considered a precursor of many combined voltammetric techniques developed in forthcoming years and specifically electrochemical detectors in high performance liquid chromatography (HPLC) and microfluidics.

A few years later, in 1957, Wiktor Kemula and Zenon Kublik (1922–2005) introduced the hanging mercury drop electrode, which, in comparison with the classical polarographic dropping mercury electrode, decreased the limit of detection of metallic traces by 5–6 orders of magnitude, due to the initial electrolytic accumulation of metals in the hanging mercury drop. This electrode and method of determination became soon very popular in international electroanalytical practice. The use of the hanging mercury electrode exerted significant influence on the development of the mercury film electrodes and also cyclic voltammetry.

In the first several years after the war, the number of coauthors of the papers published by Kemula's group was quite limited (Fig. 10.1). Considering the papers which appeared after the war up to the end of 1952, papers were published either by Prof. Kemula himself (6) or with Jerzy Chodkowski (1926–2002), Zbigniew Ryszard Grabowski, Sławomir Siekierski, and Barbara Behr (1926–1984). Almost all these papers published to the end of 1952 (total 25) were connected with polarography, and only two were related to photochemistry. This situation and so strong engagement in polarography were changed in the forthcoming years. In the period 1953–1955, Professor Kemula and his team published 23 new papers. However, now only 16 papers were connected strictly with polarography. Though polarographic papers were in majority, their domination was now not so evident. Next year, 1956, was unique in that domination because Prof. Kemula and his team organized the Polarographic Conference—Warsaw 1956, attended also by Prof. J. Heyrovský. Papers presented at this Conference were published in 1957 in a special volume (see Bibliography). As a result, papers published by Prof. Kemula and his coworkers in the next 2 years, 1956 and 1957, in the total number of 36 (including Polarographic Conference papers), were mostly devoted to

Fig. 10.1 Professor Kemula and his wife with his group of young coworkers in 1957. Sitting from *left to right*: Anna Grabowska, Anna Siekierska, Wiktor Kemula, Maria Kemulowa (his wife), Barbara Behr, Danuta Sybilska; Standing: Jerzy Witwicki, Jerzy Chodkowski, Petr Zuman (from Prague), Emilian Weroński, Henryk Buchowski, Stanislaw Rubel, Jacek Kornacki, Sławomir Siekierski, Zbigniew R. Grabowski

polarography and chromatopolarography (33 out of 36). It is worth to observe the intense development of chromatopolarography, since 10 papers out of these 33 in this 2-year period were related to this new analytical technique. One should say that these papers were published by formally two groups, both headed by Professor Kemula, since in 1955 the Institute of Physical Chemistry of the Polish Academy of Sciences was founded. Professor Kemula became the chief of the Department of the Physico-Chemical Methods of Analysis of that Institute. Initially, the newly founded Institute did not have its own laboratory space and both groups of workers, employed by that Institute and by the University of Warsaw, headed by Prof. Kemula, worked in the same building of the Chemistry Department of the University.

In the 1950s and the early 1960s of the last century, many papers prepared by Polish researchers were published in Polish. This was rather not due to the communistic state restrictions. The tendency to publish papers in Polish resulted partly from the limited knowledge of English language in Poland and also because of the easier way to print such papers in Polish journals. In these times there were also researchers in Poland, who claimed that, for patriotic reasons, the papers, also chemical, should be published in Polish. One may add that the journal *Chemia Analityczna* (Analytical Chemistry), founded in Poland in 1955, started to publish papers only in Polish (one of the founders of that journal was Prof. Kemula who became its first editor-in-chief). Though in Poland between 1945 and 1956, there was no formal restriction with respect to publishing research papers in Western journals, the people were then oppressed, and in general any contact with the institutions and people residing on the other side of the Iron Curtain was treated with suspicion by the authorities. Even exchange of letters was not welcomed. People restricted their contacts with the Western World. The fact that the first papers from Professor Kemula's Laboratory were sent to Western journals in 1957, when the system became significantly less oppressive, may be tentatively explained by the change in the political situation.

Of course, chemical papers published in Polish were shortly reported in *Chemical Abstracts* and due to that the international chemical community was informed briefly about the work carried out in our laboratories and in other chemical laboratories in Poland.

The Polish Academy of Sciences, soon after its foundation, in 1953 started to edit a series of journals with the general French name *Bulletin de l'Academie de Sciences Polonaise*, mostly to publish papers of its members, organized in several departments. The chemical issue of that journal, devoted to publish chemical papers (and papers of other natural sciences), had the subtitle *Classe troisième* (*Cl.III*). The Academy journals were published only in foreign languages: English, French and German, with Russian summaries.

Many Polish chemical papers were printed in this *Bulletin* not only because they could be published in more widely known languages but also due to fast publishing process. Papers, after their presentation by the chemists, members of the Academy, and after editorial elaboration, could be quickly sent to printers. These papers were usually presented and printed in a short form; therefore frequently in the 1950s and the early 1960s, more extended papers, on the same subject, were published in Polish, for instance in *Roczniki Chemii* (Annals of Chemistry).

Though in theory chemical papers could be published in the Bulletin of the Academy of Sciences in three European languages, in practice they were published only in English and in French. Considering, for instance, the first volume (Cl.III) issued in 1953, out of 72 chemical, physical, and mathematical papers, 62 papers were published in English and 10 in French.

The formation of such *Bulletin* in 1953 by the Academy of Sciences, which published papers in Western languages, also shows that Polish science, including electrochemistry, in the time when the world was divided, tried to keep the links with the science on both sides of the Iron Curtain.

Though in the 1950s and the early 1960s, Prof. Kemula's group also published papers in that *Bulletin*; from the middle of 1960s of the last century, the papers from his laboratory were published in English mostly in Western journals.

After 1960, the research in the combined large laboratory led by Professor W. Kemula was carried out in four general fields:

1. Electrochemistry and electrochemical methods of analysis,
2. Chromatopolarography,
3. Photochemistry and chemistry of excited states,
4. Non-electrochemical methods of analysis.

At that time the research in three fields (1), (2), and (4) was directly led by Prof. Kemula, while the photochemistry group in the laboratory was headed by Professor Zbigniew R. Grabowski—even though his early papers were in electrochemistry. His research in the laboratory was carried out independently, with the friendly advice of Prof. Kemula.

Though Prof. Kemula was involved in three other directions of studies, electrochemical methods of analysis and chromatopolarography were his main fields of interest.

I separated chromatopolarography from other electrochemical methods of analysis because this method combines two methods—first chromatographic separation and later polarographic (electrochemical) analysis of the eluent.

10.4 Difficulties Experienced in the Research Work

The research in the Professor Kemula's Laboratory as in other laboratories in Poland at that time was carried out under difficult conditions. There was the limited access to modern literature. Because of the lack of the Western currency, only selected electrochemical journals were present in libraries in the main academic centers in Poland. In that situation, researchers who worked in electrochemistry and in electroanalytical chemistry in Warsaw were in advantageous situation because in this city, there were three relatively good libraries in the University, at Warsaw Technical University, and in the Institute of Physical Chemistry of the Polish Academy of Sciences. They were relatively well equipped with different journals.

More difficult was the situation with respect to the availability of new books and monographs published in the West. The academic libraries had very limited funds for their purchase. Also the purchase of books and monographs, published in the West, by the individual researchers was in practice not possible. In principle, one could apply for the purchase of such books officially; however, if the application was accepted, usually the time of waiting was longer than half a year. Finally, when the book arrived to Poland, the price in Polish currency for individual researchers was extremely high, because the exchange rate of dollars for zlotys was very high, about 72–80 zlotys for one USD, while the monthly salary of the young researcher was on the level of 2500 zlotys. Therefore, even a book sold in the West for 10 dollars only, in Poland amounted to one third of a monthly salary of a young worker of the University or a research institute.

This difficult situation in purchase of Western books was made easier, at that time, by the publishing policy of the Soviet Union. At that time Soviet Union did not sign the agreement on the translation of the books. Under such situation a lot of modern Western books were translated and published in Moscow. The translation process and further editing and publishing of the selected books were relatively fast and frequently a book published for instance in the United States was published in Soviet Union 3 years later. For instance, the important book for electrochemists and electroanalytical people by Paul Delahay entitled "New Instrumental Methods in

Electrochemistry," published in the United States in 1954, was available in Russian translation in 1957. Such translated books were available in special bookstores, in the academic cities in Poland, for a price usually 15–25 złotys (about 20–30 cents according to the trade rate) and could be easily purchased even by poorly paid university workers.

The availability of modern Western books in Russian translation and also cheap original Russian books was very important for Polish chemists and helpful in the development of electrochemistry and electroanalytical chemistry in Poland.

At the time of divided world, chemists and in particular electrochemists experienced serious problems with the availability of modern equipment and materials. These problems resulted, as in the case of books, from the shortage of the Western currencies. Again, as with books, we had to apply for such a purchase 1 year in advance. Such procedure was operative independently of the price of the ordered item. In the case of relatively expensive equipment, the researchers had to wait, usually several years, in order to get the promise that the order will be accepted by the authorities. This acceptance was dependent on the amount of dollars given by the Ministry of Higher Education to the specific university or institute. However, even for not very expensive material of the western origin, one had to wait many months to get it. For instance, in electrochemistry, it was difficult to get Western materials for construction of the electrodes, such as glassy carbon at the early stage of its use or very thin Pt wires for construction of ultramicroelectrodes. The same applied to the purchase of some more rare chemicals. As a result of these restrictions, many instruments used in electrochemical experiments were homemade. On the other side, frequently materials not expensive but necessary in the experimental work were brought from abroad by researchers, when they visited western laboratories or worked there for short or longer time. These materials were either purchased by them or were obtained as a gift from the western colleagues.

In 1964, the separation of two research groups of Prof. Kemula, who worked together in the building of the Chemistry Department of the University, occurred. At that time the people employed by the Institute of Physical Chemistry (IPC) of the Academy of Sciences in the Department of Physicochemical Methods of Analysis headed by Professor Kemula moved to the newly constructed building of the IPC. In the Department of Chemistry remained only the personnel employed by the University of Warsaw. The scientists employed by IPC have worked mostly in three research fields. One of these groups, led by Professor Barbara Behr, worked in electrochemistry and electroanalysis.

10.5 Electrochemistry in the University of Warsaw After Changes in 1968

The year 1968 saw political changes in Poland, which hurt many aspects of life—including academic. Some Professors and students were repressed, and the organization of the universities and their departments was changed.

As a result of these changes and repressions, Prof. Kemula was dismissed from the University and employed only by the Institute of Physical Chemistry, where he headed, as before, the Department of Physicochemical Methods of Analysis. However, his frequent contacts with the former coworkers from the University continued till his death in 1985. We could always discuss different problems with him, including also those not connected with our research work, looking for help and advice.

In 1981, when the political tension for short time was diminished, University of Warsaw distinguished Professor Wiktor Kemula by the Honorary Doctorate (Fig. 10.2). It was the initiative of his former coworkers and students.

The situation in the Department of Chemistry and reorganizational changes after 1968 call for a wider comment. Until 1968, there were 7 different chairs at the Chemistry Department of the University of Warsaw; one of them was the Chair of Inorganic Chemistry. The reorganization which occurred in 1968 was very extensive. Six chairs were transformed into one Institute of the Fundamental Problems of Chemistry and only one chair—Chair of Chemical Technology—remained as a

Fig. 10.2 Professor Kemula after Honorary Doctorate ceremony in February 1982 between his former students and coworkers Zbigniew Galus (*left*, promoter of the Doctorate) and Adam Hulanicki (*right*, Dean of the Department of Chemistry, University of Warsaw)

separate unit. Similar reorganizations, based mainly on political criteria at that time, were experienced practically by all departments of the universities and other academic schools in Poland.

From the teaching point of view, this Institute was divided into the Teaching Departments. One of such Departments embraced the former Chair of Inorganic Chemistry. More important changes occurred in organization of the research groups. From the former Chair of Inorganic Chemistry, headed by Prof. Kemula, four research groups headed by former coworkers and students of Prof. Kemula were formed.

The changes which occurred in the organization of departments of academic schools in Poland after 1968, forced by authorities for political reasons, principally did not hurt the research carried out by scientists from Prof. Kemula's school. Though serious limitations were imposed by not quite modern instrumentation, limited access to the newly produced chemicals and materials, steady progress in the research was observed. This progress was also due to the mutual friendly cooperation of these groups, because the problems developed in these research groups were mostly electrochemical or electroanalytical in nature and colleagues from one group could discuss their problems and cooperate with the colleagues from other groups.

The four research groups covered different problems, and the studies performed led to interesting results and concepts published in the well-known journals with the international circulation. The main problems and achievements are listed below.

- Double layer structure in different media with a special attention paid to (1) concentrated aqueous solutions of electrolytes, (2) nonaqueous solvents, and (3) mixed solvents. Influence of the double layer field on the reactivity of adsorbed weak acids and bases.
- New concepts in understanding of the inhibition processes of the electrode reactions. The development of new method to study inhibition of electrode processes. Determination of steric effects in inhibited electrode reactions.
- Study of the influence of water activity on the mechanism and kinetics of electrode reactions and their formal potentials in concentrated electrolytes.
- Investigations of the kinetics and mechanism of various electrode reactions in nonaqueous and mixed solvents, using solvents of different Lewis basicity.
- Investigation of free radicals generated in the electrode reactions in nonaqueous solvents and their interactions with cations of different background electrolytes. Stability of the ion pairs formed in these solvents, their change in the presence of water, and their other interactions.
- Development of the voltammetric trace analysis. Construction of the stationary micro electrodes useful for such analysis, especially mercury film electrodes. Special attention was paid to the determination of conditions useful for the precise determination of very minute quantities of analyzed substances. Theory of mercury film electrodes was also ameliorated.
- Fundamental studies related to ultramicroelectrodes and to peculiarities connected with the process controlled both by migration and diffusion.

- Deposition of monomolecular Langmuir–Blodgett and self-assembled films at electrodes, their properties, reactivities and influence on electrode reactions. Electrodeposition of thin layers of amorphous alloys and their properties.
- Basic concepts, construction, and analytical application of chemical sensors. Development of theoretical problems connected with the process of diffusion in ion-selective electrodes what enabled to decrease the limit of analytical detection for several orders of magnitude. Development of enzymatic biosensors for continuous control of the process of hemodialysis.
- Potentiometric detectors and formation of new types of sensors including detectors without internal solution (all-solid-state). The composition of ion-selective layers was considerably and aptly modified. New solutions and additives in the membrane electrodes were used and tested looking for analogy with biological membranes. Special applications of such electrodes in medicine were studied.
- Development of methods of the flow analysis, which was introduced to analytical chemistry in the last quarter of the twentieth century. A number of original results in the methodology of that method were obtained at the University of Warsaw, especially in the use in detection of electrochemical techniques.
- Number of interesting and new results were obtained in electrophoretic methods.

10.6 Personal Contacts with Foreign Electrochemists

In the development of electrochemistry at the University of Warsaw at the time of a divided world, an important role was played by the exchange of researchers with foreign academic schools and also the invitations of our researchers to work in foreign laboratories. Universities and research institutes in the so-called "socialistic camp" had usually an agreement for a limited exchange of workers for each year. Also our Department had such agreement with several universities, such as Lomonosov University of Moscow, Charles University of Prague, Humboldt University of Berlin, University of Budapest, and schools of other countries. We had such cooperation also with the Polarographic Institute in Prague (headed after its formation in 1950 by Professor J. Heyrovský) and Institute of Electrochemistry in Moscow (headed by Professor A. N. Frumkin). This was a very helpful situation, in view of very high level of electrochemical research in these schools, especially in Moscow and Prague. Contacts with Professor Frumkin and people of his Electrochemical Moscow School and also with Czech electrochemists were very important to us. On the other side, there were also invitations to the Western research centers. Such trips were initiated after political changes in Poland in 1956. From the laboratory of Professor Kemula, shorter trips to Western European countries started in 1956 and longer (1–2 years) to the USA in 1957. These trips could be realized either due to scholarships received from different Western Foundations, or as a result of the employment of our colleagues, usually in the post-doctoral positions, by well-known Professors mostly from the USA. While in the 1950s and the early 1960s, the scholarships from foundations were quite important, in later years employments in postdoctoral positions were prevailing. These research stays abroad, very often lasting for 2 years, were important for the further development of the electrochemistry in our Department. In fact, every leader of the research group was on such a stay, even more, almost all workers of the Department after receiving Ph.D., worked in such positions in good or very good Western laboratories headed by well-known researchers. During such stays abroad, our colleagues could publish, in cooperation, high quality papers, but also they could learn new methods and organization of laboratory work with the use of modern instrumentation.

Such stays were useful in the formation of further cooperation between our groups and different western laboratories.

To establish contacts with foreign researchers, also conferences and meetings were very helpful. Since the participation in the scientific meetings organized in the West was limited, rather not for political reasons, but because of the shortage of convertible currency, we organized meetings in Poland, such as Symposia of the Electrochemical Section of the Polish Chemical Society.

Inviting electrochemists to Poland was possible, because in this case Western currency was not needed. In such conferences, organized in 1970s of the twentieth century, many well-known electrochemists, both from the West and East, were participated, among them such prominent electrochemists as Prof. A. N. Frumkin, Prof. R. Parsons, Prof. S. Trasatti, Prof. R. R. Dogonadze, Prof. L. Gierst, Prof. A. M. Kuznetsov, Prof. W. Lorenz, Prof. B. E. Conway, Prof. R. Guidelli, Prof. L. I. Krishtalik, Prof. W. R. Fawcett and others. These meetings were attended by a lot of people, including quite young researchers, from different academic centers in Poland. Of course, it was then a good occasion for Polish electrochemists not only to present their results, but also to meet these persons and discuss different research problems with them. Returning to stays of our colleagues in the West, it happened at times that some researchers who left country temporarily to work in the postdoc position, stayed there for several years and some of them remained in the Western universities or research institutions permanently. The decision to leave Poland definitely was difficult for them, but it was undertaken mostly after introduction of martial law in Poland in December 1981. The list of several of them who obtained very significant academic positions includes Jacek Lipkowski, Professor of the University of Guelph, Canada, who was elected Fellow of the Royal Society of Canada, Andrzej Barański, Professor of the University of Saskatchewan, Canada; Andrzej Lasia, Professor of the University of Sherbrooke, Canada; Andrzej Więckowski, Professor of the University of Illinois at Urbana Champaign, USA; Marcin Majda, Professor of the University of Berkeley, San Francisco, USA; Andrzej Lewenstam, Professor of the Abo Akademi, Turku, Finland; Anna Brajter-Toth, Professor of the University of Florida, Gainesville, USA; Waldemar Górski, Professor of University of Texas at San Antonio, San Antonio, USA.

10.7 The End of the Divided World

After political changes in 1989, when the Iron Curtain which divided Europe was abolished, there were six research groups (Laboratories) at the Chemistry Department at the Warsaw University which have roots in the former laboratory of Professor W. Kemula.

1. Laboratory of Applied Analytical Chemistry; head—Professor Stanisław Rubel (1922–2008)
2. Laboratory of Basic Aspects of Analytical Chemistry; head—Professor Adam Hulanicki
3. Laboratory of Electroanalytical Chemistry; head—Professor Zbigniew Galus
4. Laboratory of Flow Analysis and Chromatography; head—Professor Marek Trojanowicz
5. Laboratory of Organic Electrochemistry; head—Professor Marek Kalinowski
6. Laboratory of Polarography; head—Professor Zenon Kublik

In addition, Marek T. Krygowski, who was earlier in the Professor Kemula's Laboratory, and later worked for several years in the Laboratory of Electroanalytical Chemistry, dealing partly with electrochemical problems, in the 1980s became a successful chief of the Laboratory of Crystalochemistry.

These laboratories had the status of the official administrative units responsible for research and development in the Department of Chemistry. In these six laboratories, the electrochemical research problems dominated; however, in analytical laboratories (1, 2, and 4), the practical analytical topics were solved also by using non-electrochemical techniques.

The names of these laboratories point to the general research interest of their members. Though the problems developed in these laboratories continued partly earlier interest of these groups, new problems corresponding to actual international trends were also developed. I will mention some of them below.

Using several methods, problems of biomonitoring and monitoring of industrial processes, study of composting plants, analysis of municipal and industrial waters, and soil contamination by fertilizers were studied. Speciation of elements in different matrices was determined.

The research program included also both the theory and practical aspects of ion-selective electrodes. Important part of these studies was the research on the selectivity of such sensors and interferents and the change of selectivity under influence of various factors. Potentiometric enzymatic sensors and sensors based on pH-electrodes were developed and used in clinical chemistry. Kinetic model of the biosensors response with consideration of all proteolytic reactions of substrates and products of enzymatic reactions and transport processes in the membranes was elaborated. Conducting polymers and bilayer lipid membranes were used to design sensors and biosensors.

Also constant current coulometry was applied to the study of ionic equilibria—dissociation of acids and formation of complexes.

Influence of single and mixed solvents on the rate of electrode reactions, electrochemical properties of organic redox couples and the complex formation of metal ions by macrocyclic ligands were studied. In addition, variation of the stability constants of complexes with solvent composition and modeling of probable structures of coordination compounds by computer simulation were investigated.

Mechanisms of electrochemical reactions of different systems, including transition metal complexes, were examined with a special attention paid to double layer effects and problems of generation and decay of intermediates which arise in such reactions. Electrodes modified with thin films of transition metal hexacyanoferrates and conducting polymers were investigated, also solid state electrochemistry in the absence of external supporting electrolyte were developed. Charge propagation rate in such mixed-valent solid systems and their electrocatalytic properties were studied.

Electrocatalysis and especially electrocatalytic processes of substances used in fuel cells such as oxygen and simple fuels were also investigated.

In the flow analysis, electroanalytical methods (mostly biamperometry, potentiometry, and potentiometric stripping methods) were used in the process of detection. Flow-through detectors were developed for the enzymatic determination of common substrates in physiological fluids. Also the capillary electrophoresis methods were developed.

Interactions of certain metal ions with biological systems or their synthetic models and also electrochemical properties of macromolecules and their complexes with metals were examined. This work was also oriented on the use of these complexes in modeling of biological receptors. Research on electrochemistry of some drugs was carried out.

Attempts were made to describe theoretically the current flowing at microelectrodes under various conditions, including also migrational transport. Deposition of monomolecular Langmuir–Blodgett films at electrodes, their different properties, as well as electrodeposition of amorphous metallic alloys were studied.

The large number of research laboratories and their wide research fields show that the group formed by Professor Kemula in Warsaw University did not disappear but grew and expanded in time. Later, in the 1990s, new Professors in the field of electrochemistry and electroanalytical chemistry: Renata Bilewicz, Mikolaj Donten, and Stanisław Głąb (1945–2008), Jerzy Golimowski, Jan Jaworski, Robert Koncki, Paweł Kulesza, Magdalena Maj-Żurawska, Krzysztof Maksymiuk, Agata Michalska-Maksymiuk, Marek Orlik, Krystyna Pyrzyńska, Zbigniew Stojek, and Piotr K. Wrona (1948–2004) started to create their research groups. Also Ewa Bulska was partly involved in that work.

These laboratories cooperated quite strongly not only in the form of everyday discussions of their members, on different research problems, but also by organizing common seminars, meetings, and lectures.

One should add that in the Chemistry Department of the Warsaw University, there were also three other groups of electrochemists originating from the earlier

Chair of Physical Chemistry headed by Professor Stefan Minc (1914–2003). In 1991 these people were organized in the following laboratories:

1. Laboratory of Electrochemistry [head—Prof. Jadwiga Jastrzębska (1929–1998)]
2. Laboratory of Interfacial Electrochemistry (head—Prof. Zbigniew Koczorowski)
3. Laboratory of Radiochemistry (head—Prof. Jerzy Sobkowski)

They carried out interesting electrochemical studies oriented mostly on adsorption and double layer phenomena, and use of tracers in the adsorption and electrooxidation of simple organic compounds on electrodes.

In the late 1990s of the former century and first years of the twenty-first century, further changes, both in the organization of all electrochemical research groups of the Department and very significant changes in their research plans, in order to be at the front of the actual research trends, were observed.

At the beginning of the twenty-first century, the research conditions in Poland were changed. The biggest change occurred when Poland became a member of the European Union.

The intense exchange of researchers and graduate students created a new situation and enforced intense international cooperation.

The significant limitation in the development of research and high education nowadays in Poland comes from the limited funds programmed in the state budget for these fields. In consequence, the salaries of the people employed in universities and research institutes are quite low—which may push well-qualified people either to better paid jobs or to emigration to Western countries. On the other side, the money granted to Poland by the European Union in recent years could be used mostly for the construction of new buildings in different universities in the country and to purchase new modern instrumentation. These investments make a good basis for better and faster development of chemical research in Poland in the near future. There are also good perspectives for further development of electrochemistry and electroanalytical chemistry at the University of Warsaw. A number of relatively young, apt, and well-educated electrochemists who are employed by the Department have both the potential and spiritual motivation to develop this science further.

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Chapter 11
Fifty Years of Electrochemistry in Poland and Abroad: Personal Account

Jacek Lipkowski

My career as an electrochemist began when I joined the Chair of Inorganic and Analytical Chemistry directed by Professor Wiktor Kemula as an M.Sc. student, in October 1965 (in the Polish system, a Chair was an organizational unit equivalent to a Division, and a full professor was the Head of the Chair. In North America, Chair is a position at a university). I did not like electrochemistry during my undergraduate studies. I was attracted to electrochemistry by the charismatic and enthusiastic personality of Dr. Marek Kalinowski. He had just graduated with a Ph.D. degree and was in the process of building an independent research group. A second person who joined that group was my friend and schoolmate Andrzej Lasia who later became a world-renowned expert in impedance spectroscopy. Thus, Kalinowski's personality was the main reason behind my decision. I like to tell my students a story about a rabbit and a wolf to illustrate the importance of this decision (Fig. 11.1).

> A rabbit was sitting on a lawn and writing something. A wolf approached the rabbit and asked him: "What are you doing?"
>
> "I am writing a PhD thesis", replied the rabbit.
>
> "What is it about?" asked the wolf.
>
> "It is about superiority of rabbits over wolves" replied the rabbit.
>
> "What! I will punch you"—exclaimed the wolf.
>
> "If you wish to punch me lets go to the bush," replied the rabbit. They disappeared in the bush. Soon screams and sounds of fighting could be heard from the bush. After a while, a smiling rabbit emerged from the bush. He was followed by a black bear and the wolf with a blue eye and a broken arm. The happy rabbit murmured then to himself; "it is not the subject of the thesis but who is your supervisor that matters."

Years later Roger Parsons told me that he also was attracted to electrochemistry by the charismatic personality of John Bockris. The choice of the supervisor matters!

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Fig. 11.1 Dr. Marek Kalinowski (1936–2014)- Picture taken sometime in the 1960s

Fig. 11.2 Professor Wiktor Kemula (1902–1985), Chair in Analytical and Inorganic Chemistry, Warsaw University, Poland. His messages were: citation from Michael Faraday "Work, finish, publish" and "a good measurement will withstand the proof of time, its interpretation may change"

The Chair of Analytical and Inorganic Chemistry headed by Professor Kemula was quite a large division that consisted of several research groups spanning several areas of Analytical Chemistry with Electroanalytical Chemistry being the most prominent. The structure of university departments was pyramidal at that time. The Chemistry Department of Warsaw University consisted of several big Chairs; Analytical and Inorganic Chemistry, Organic Chemistry, and Physical Chemistry, each headed by powerful Full Professors. Each Chair employed several associate and assistant professors who reported to the Head of the Chair (Fig. 11.2).

Professor Kemula was Head of the Chair at Warsaw University and in addition a Head of the Laboratory of Electroanalytical Methods at the Institute of Physical Chemistry, at the Polish Academy of Sciences. We had joint weekly research seminars which gave me an opportunity to meet and interact with several important personalities from the Academy including Dr. Barbara Behr and Dr. Zofia Borkowska, who later became my close professional friends. I also recall a seminar given by Dr. Halina Angerstein-Kozlowska shortly before her departure to Canada to work with Brian Conway. Friendly working and personal interactions between scientists from the Department of Chemistry UW and the Polish Academy of Sciences directed by Professor Kemula created a unique scientific and social environment that played a very significant role in the development of Polish Electrochemistry.

In contrast to some other Soviet bloc countries, Polish scientists were allowed to travel abroad and most of the scientific staff working with Professor Kemula had postdoctoral experience working in the USA or in Western Europe. This translated into a good knowledge of foreign languages and the cultural environment of the West. Professor Kemula frequently traveled abroad, was internationally known, and had many friends in Europe and the USA. He was fluent in several languages including English, German, French, Russian, and even Romanian (he was born and raised in Romania). Consequently, many scientists from both the West and the East visited his laboratory. As a young graduate student, I had the opportunity to hear lectures by renowned electrochemists such as Prof. Brdička and Dr. Smolar (Heyrovsky Institute), Prof. Pungor (Budapest), Dr. Randles (Birmingham), Prof. Kuwana (the USA), and Prof. Frumkin (Moscow) just to give a few examples. Marek Kalinowski was my tutor, but Professor Kemula was my formal supervisor. On the wall of his office was a framed quotation from Michael Faraday “Work, Finish, Publish.” I learned much later that this was a gift from Jaroslav Heyrovsky given to Kemula during his postdoctoral study in Prague in the 1930s. Kemula was very supportive of people with a drive for science. My laboratory was in front of his office and he visited our lab to see the progress of our work quite often. On one occasion he told me: “What really matters in science is to do a good measurement. If the measurement is good, its result will pass the test of time. Its interpretation may change.” The next 50 years of my career have shown me how true these words are. I have frequently repeated them to my students (Fig. 11.3).

My M.Sc. thesis concerned the polarographic reduction of nitrobenzene. My first literature source was a paper by Dieter Kolb (1942–2011), who studied the reduction of nitrobenzene in his Ph.D. thesis. This was an omen, about 25 years later I spent a sabbatical year working with Dieter at the Fritz Haber Institute, the beginning of a long-lasting collaboration. The other sources of literature for my thesis were papers by Holleck and Kastening also written in German. My knowledge of German was very poor and I spent long hours with a dictionary translating the texts word by word. Russian was the second foreign language that I used extensively at that time because there was a lot of pertinent literature concerning the polarography of organic compounds coming from the school of Mairanovskiy in Moscow. The Soviet Union did not respect copyright, and many textbooks and monographs written in English were translated and published in Russian. To promote the Russian language, these books were sold in Poland at a huge discount. Consequently, I had my own Russian translations of text books such as Paul Delahay’s ý’s “New Instrumental Methods in Electrochemistry,” Heyrovský’s and Kůta’s “Principles of Polarography,” several volumes of “Modern Aspects of Electrochemistry,” etc. This gave me the opportunity to learn the Russian language to the extent that I can still communicate in Russian today.

Fig. 11.3 Picture taken in Prof. Kemula's office with his visitors; from *left* to *right*: N. Tanaka, Z. Galus, R. C. Kapoor, A. Bard, W. Kemula. Due to Kemula's international stature, many visitors from the West and the East visited our Division and hence we did not have a feeling of working in isolation

Working with nitrobenzene, I quickly discovered that its polarographic reduction depends on the amount of alcohol added to the solution and on the concentration of the supporting electrolyte. To understand these phenomena, I was reading papers on the effect of the electrical double layer on electrode kinetics by Frumkin and Petrii (Moscow) and papers by Lucien Gierst (Brussels). Gierst's papers were published in English and hence I began to learn the English language. Initially, I attended English classes, and later I worked with a private tutor. My wife, Iza, and I took private lessons with one of the most expensive teachers of the English language in Warsaw, and we spent a significant fraction of our meager income to pay for these lessons. This was perhaps the best investment we have made in our life. I graduated with an M.Sc. degree in 1967. Soon I was drafted into the Polish army to be trained as a reserve officer. In March 1968, a prodemocracy movement shook Warsaw University. The movement was suppressed and repressions of prodemocracy activists followed. Professor Kemula who supported the prodemocracy movement lost his employment at the University. I had been in the army during this period and was released when the movement has already been pacified.

To reduce the power of Full professors in charge of big research and teaching Chairs (many of them supported the prodemocracy movement), the University was restructured. The institutes were divided into small research units headed by associate and assistant professors of a younger generation. One of them was Zbigniew Galus who graduated from the Chemistry Department of the University of Lodz in 1955 with an M.Sc. degree and in 1957 moved to Warsaw to start an academic career in the Division of Analytical and Inorganic Chemistry of Warsaw University under the supervision of Prof. Kemula. Working with Zenon Kublik, and Kemula, Galus participated in pioneering research on the formation of intermetallic compounds using the newly invented hanging mercury electrode. This research was the foundations of stripping voltammetry. A technique that remains a staple in most university undergraduate teaching laboratories to this very day. Galus was awarded his Ph.D. degree in 1960.

After graduation, Galus took a 2-year long postdoctoral study at the University of Kansas, the USA, where he worked with Professor R. N. Adams and collaborated with Prof. P. S. Rowland (Noble Prize, 1997) to elucidate complex mechanisms of electrooxidation of organic compounds, employing for the first time a rotating ring-disk electrode, electron spin resonance, and radiochemical methods. After his return to the University of Warsaw, his research interests were focused on the electrochemistry of transition metal complexes and particularly the mechanisms of electrode processes involving nickel complexes. This research was the cornerstone of his habilitation thesis defended in 1966. Zbigniew Galus created and has been the Head of the Laboratory of Electroanalytical Chemistry for 35 years. His Laboratory became one of the most vibrant centers of research and education in electrochemistry in Central Europe. Under his supervision, 23 students graduated with a Ph.D. degree, 6 habilitated and took academic positions in Poland and abroad. He is an author of about 200 papers and several textbooks. His most famous book is “Fundamentals of Electrochemical Analysis,” translated into many languages including, English, Russian, and Chinese. His achievements were recognized by awarding him many medals and awards and the highest Award of the Polish State the Order of Polonia Restituta (The Order of Rebirth of Poland) (Fig. 11.4).

I did not know Zbigniew Galus during my undergraduate studies because on his return from the USA, Prof. Kemula made him his deputy and released him from undergraduate teaching. I met Galus while attending his graduate course in Electroanalytical Chemistry and soon I started to participate in his research group seminars. I was fascinated by his rigorous, calculus based, approach to electrochemistry, deep knowledge of science, and friendly and enthusiastic personality. I had many scientific discussions with Galus that were stimulating and intellectually challenging. I decided to do my Ph.D. degree under his supervision. This was one of the best decisions I have made in my life. The goal of my Ph.D. research was to study the effect of mixed solvents on the kinetics of selected electrode reactions. About 10 years earlier, Sybilska and Kemula applied polarographic detection to chromatographic separation of organic compounds, introducing a technique named chromatopolarography, a precursor of present-day electrochemical detection—high performance liquid chromatography (HPLC). To improve the separation efficiency, the polarity of the mixed (organic-water) solvent and hence the composition of the solvent mixture were varied during the elution (gradient elution chromatography). At that time, little was known how the mixed solvent composition affected the rate

Fig. 11.4 Picture of Zbigniew Galus taken in the 1960s. “It is the choice of the supervisor that matters.”

of electrode processes and hence the performance of the polarographic detector. Working with mixtures of aliphatic alcohols and water, I soon learned that the organic solvent was adsorbed at the mercury electrode surface and that the adsorbed layer affects the rate of electrode reactions. This was incentive to study papers concerning adsorption of organic compounds at metal electrodes by Damaskin and Frumkin. I also had a habit to read the most recent literature. The main electrochemistry journals such as the Journal of Electroanalytical Chemistry, Electrochimica Acta, Journal of the Electrochemical Society, and Electrokhimia (in Russian) were easily available in our library, and I read (or at least perused) the content of every new issue. This was an exciting period of tremendous progress in the field of electroanalytical chemistry stimulated by the availability of operational amplifiers and later digital electronics. In Poland, we did not have access to operational amplifiers and hence we watched this development chiefly as spectators. Due to my interest in adsorption phenomena, I was particularly interested in the papers by Anson and Osteryoung describing a new technique, chronocoulometry. I presented these papers at our group seminars, and I dreamed to introduce this technique into my research (Fig. 11.5).

At the beginning of 1971, Zbigniew Galus attended a committee meeting at which the Chair of the Department asked the participants if they had a student who could be sent to Brussels as a part of the cultural exchange programme between Poland and Belgium? Galus immediately recommended me knowing my interest in the works of Lucien Gierst. Thus I arrived in Brussels for a 9-month scientific stay in October of that year. It was my first visit not only to the West but also outside

Fig. 11.5 From *right* to *left*, Prof. R. Adams, Mrs. Kemula (Prof. Kemula's wife), and Prof. Galus (Picture taken in Warsaw near Frederic Chopin monument in the 1960s)

Poland. It was a tremendous experience on all accounts. In communist propaganda, Coca-Cola and chewing gum were pictured as symbols of American imperialism and they were treated as "forbidden fruits." The first thing I did in Brussels was to taste these symbols. I learned that they were not worth the attention of the communist propaganda apparatus. I also discovered the charm of a pluralistic society. In the toilet next to Gierst laboratory were two cabins. In the first somebody wrote on the wall "vive le communisme." I was not a supporter of communism and hence I was not comfortable in that place. However, in the second cabin somebody wrote "mort au coco" (death on communists). Although I was not a communist, I was not sure if coming from a communist country I was not condemned to death as well. Consequently, I tried to use a more distant toilet with less radical inscriptions on the wall. Poland was devastated during the war and was a poor country. In contrast, Belgium was enjoying prosperity. I was amazed by the wealth of the country and the well-being of Belgians (Fig. 11.6).

Gierst's laboratory was spacious and very well equipped. In his teens, short wave radio was Gierst's passion. He recovered one from a tank destroyed in World War II and was spending nights communicating with other short wave radio fans from all over the world. Today internet plays that role. When the time for him to start his graduate degree came, he decided to use his radio to do research and in that way he entered the field of electrochemistry. He had always been a thinker, and he loved to build his own instruments. Most of the instruments in his lab were homemade. It was the first time I was introduced to an operational amplifier and to digital electronics. Importantly for my own career development, there were a few homemade chronocoulometers in his lab. They were built by Guy Quarin, a Ph.D. student

Fig. 11.6 Gierst laboratory in 1972. Gierst (1923–2004) is in the *middle* of the *back row* playing a Romanian pan flute. I am to his *right* with a big trumpet. Guy Quarin is on the *left* end of the *back row*, and Roger Diaz is on the *left* end of the *first row*

who became a good friend of mine and Roger Diaz, a technician whose background was electronics. For the first time in my life, I had the opportunity to put my hands on the most advanced electrochemical instrumentation. In Warsaw, we had quite outdated polarographic instruments equipped with a strip chart recorders and pH meters.

Lucien Gierst was one of the most intelligent people I have ever known. His brain was razor sharp. He was a renaissance man with diverse interests and a profound knowledge of music, literature, and fine arts (particularly old Flemish masters' paintings and the symbolism hidden in these paintings). Discussions with him were a source of illumination and intellectual enjoyment. He had a friendly and humane personality, always willing to help people who were in need. He was helping both a victim of the fascist regime in Chile and those oppressed in the communist countries (for example, he was very much involved in helping get Venyamin Levich out of the Soviet Union). He traveled a lot and was interested in people, their language, and their culture. For years, the former Yugoslavia was his preferred holiday destination and he learned Serbo-Croatian. Maybe because he was interested in so many subjects, Gierst was quite absentminded. He was frequently forgetting where he parked his car and it was not uncommon that the whole lab had to help him search the university campus to find his car. Gierst had very good sense of humor. He told me a story that happened at a Fisher Symposium in Karlsruhe, organized by Wolfgang Lorenz. He went to Karlsruhe by car. At the end of the last day of the meeting, he realized that he could not remember where he had parked. With Lorenz, they searched the campus of Karlsruhe University for several hours in vain. At the end, Gierst decided to return by train to Brussels and to abandon his relatively old car. He walked back to his hotel, and to his surprise, he found his car parked next to the hotel. He had forgotten that in the morning he walked to the conference.

I wrote earlier that Gierst was a man of Renaissance to emphasize his broad interests. However, intellectually he was more like a man of Enlightenment, rational with a profound education and an understanding of reality. Interacting with Gierst, I was exposed to Western thinking, based on rigorous logic, cold analysis of facts, efforts to understand roots of the scientific problem of interest, and the need to restrain oneself from jumping too early to a conclusion. When my stay in Brussels came to an end, Gierst contacted the Belgian Ministry of Foreign Affairs and arranged a formal collaboration between my laboratory in Warsaw and his laboratory in Brussels as a part of the bilateral cultural agreement between the two countries. This gave me the opportunity to visit Brussels for a few weeks almost every year until I left Poland in 1981. Gierst and his coworkers Guy Quarin, Philippe Buess, and Claudine Hermann-Buess visited us in Poland. This friendship and collaboration continues until today. After moving to Canada, I have continued to collaborate with Claudine Herman-Buess (Gierst's successor after his retirement), and today Thomas Doneux (Claudine's former Ph.D. student) is collaborating with Dan Bizzotto (my former Ph.D. student) (Fig. 11.7).

I returned to Galus' laboratory in 1972 and worked there for the next decade. This was perhaps the golden period of Polish Electrochemistry. There were many research groups working in Warsaw in this field and thanks to Galus' authority and friendly personality, we enjoyed free exchange of information, open scientific discussions, and collaborations. I have particularly fond memories of my interactions with Barbara Behr from the Institute of Physical Chemistry, Polish Academy of Sciences. Barbara belonged to the first group of students that entered university just after the end of World War II. Polish universities were destroyed and the first group of Polish students was sent to study abroad. Barbara and several of her colleagues studied chemistry in Denmark for a certain period of time. Her father was an electrical engineer and owned a small electrical equipment shop. Barbara worked in this shop as a technician during the war. Consequently, she had an excellent knowledge of scientific instrumentation which was so valuable in electrochemical research. She spent her postdoctoral stay in Birmingham with John Randles and introduced electrochemical impedance to researchers in Warsaw. In my laboratory, Jan Malyszko and Jadwiga Dojlido were trained by Barbara. There were tedious measurements involving a Wheatstone Bridge and manual adjustment of a box of variable resistors and a box of capacitors to find the compensation point. Such measurements are beyond imagination of our present Ph.D. students familiar with modern frequency analyzers to do impedance spectroscopy (Fig. 11.8).

Barbara Behr conducted research on the kinetics of electrode processes in mixed solvents and hence our research interests overlapped. I have had many discussions with her and benefited a lot from her inquiring questions and deep understanding of

Fig. 11.7 Lucien Gierst in Żelazowa Wola, Chopin's birthplace, during one of his visits to Poland (Picture taken in ~1975)

the problems. On several occasions, I volunteered to give a seminar to her research group to test my new ideas or to discuss some new results. She was very busy because many people were coming to her for help in solving scientific or personal problems. Barbara was a person of a tremendous personal qualities and personal courage. The Journal of Electroanalytical Chemistry edited a special issue on the occasion of the 60th birthday of Venyamin Levich in 1977. This was a part of international pressure on the Soviet Authorities to allow Levich to emigrate to Israel. Barbara submitted a paper with a personal dedication to that issue. Her paper was the only submission from the Eastern Block published in that issue. This was an act of political courage (Fig. 11.9).

Our intellectual life was vibrant. Galus attracted quite a number of very gifted students such as Andrzej Barański, Cezary Gumiński, Marek Lipsztajn, Piotr Wrona, and later Paweł Kulesza. In addition, Dr. Marek T. Krygowski, a physical organic chemist also worked in Galus' laboratory. Andrzej Barański was an exceptionally creative and imaginative scientist with a unique ability to solve theoretical problems, to build scientific instruments, and to design original experiments. He has

Fig. 11.8 *Left* picture of Barbara Behr (1926–1984), *right* Barbara Behr with John Randles (*middle*) and Prof. Stal Mairanovskiy (*left*) (Picture taken near Warsaw in mid-1970s)

Fig. 11.9 My friends from Warsaw University. From *left* to *right*, Andrzej Lasia, Marek Lipsztajn (1949–2013), and Piotr Wrona (1948–2004)

never followed trendy subjects and has always followed his own scientific path. After graduation with his Ph.D., Andrzej went to Canada to do postdoctoral research with Ron Fawcett, he married a Canadian girl and took a faculty position at the University of Saskatchewan in Saskatoon where he is working till today. I very much liked to exchange ideas with Andrzej and to listen to his opinion. In addition to colleagues from my own laboratory, I had friends working in electrochemistry in other research groups in our Department. Stripping voltammetry using thin mercury films at silver wire electrodes was developed by Zbigniew Stojek (today a full professor leading an active group at Warsaw University) in Zenon Kublik's laboratory. Stojek had an apartment close to my home, and we frequently commuted together chatting and discussing. Later Kublik's laboratory was joined by Marcin Majda (presently professor at Berkeley University) and Renata Bilewicz (presently professor of chemistry, running a vibrant research group in the field of bioelectrochemistry). Andrzej Lasia, my schoolmate and Jan Jaworski, performed organic electrochemistry (molecular electrochemistry) research with Marek Kalinowski. Andrzej has always been fascinated by computers and programming. It was a painstaking activity at that time. Our computer center was in a distant part of Warsaw. Andrzej had to write his programs on a card that was later encoded by an operator at the center into a stream of holes punched in a tape that was read by the computer. Andrzej spent hours traveling back and forth between the chemistry department and the computing center. It consumed a lot of his time. These efforts paid back when later he could transfer his computational skills to perform calculations on modern computers (Fig. 11.10).

An important personality in the Department of Chemistry was Andrzej Wieckowski. I am a year older and graduated 1 year earlier than Andrzej. However, we knew each other as undergraduates particularly because Andrzej was the best student in his class and hence was well known in our community. Even in those

Fig. 11.10 Prof. Kublik (developed the hanging mercury electrode) in *front* at the *right* and his coworkers; Zbigniew Stojek is standing *behind* Prof. Kublik and Renata Bilewicz is standing in *front* on the *left*

early days, Andrzej had a very charismatic personality, passion for science, and visionary imagination. He was a student of Prof. Jerzy Sobkowski, the head of the radiochemistry laboratory. During his Ph.D. study, Andrzej introduced radiochemical methods to study adsorption at platinum group metals. He attracted Piotr Zelenay (presently at Los Alamos, internationally renowned for his work on fuel cells) and Marek Szklarczyk (presently prof at Warsaw University) to electrochemistry. Andrzej Wieckowski and I had different personalities. He was bursting with enthusiasm; I was more cautious and skeptical. I recall a seminar in the late 1970s where he presented the now famous paper by Fleischman et al. on Raman spectroscopy of pyridine at silver. He concluded his talk with an emphasis "This is a revolution in electrochemistry!" My skeptical reaction was: "What a revolution? They just roughened electrode and were able to get a weak signal." Andrzej was right, and I was wrong. Today I am using surface enhanced Raman spectroscopy (SERS) in my research. On another occasion, about 10 years later (at that time we both were living in North America), we organized a symposium on electrochemistry at single crystal electrodes at the ECS meeting in Atlanta. The symposium was very successful and attracted the best researchers working in this area. Electrochemistry at single crystal surfaces was the most important topic of physical electrochemistry at that time. At the end of the symposium, we had a beer in a bar and were exchanging impressions. At one point I asked Andrzej: "what next?" Andrzej replied: "I will do electrochemical NMR." "NMR will not have enough sensitivity" I exclaimed. Andrzej replied: "I will do it on powders," and he did it. In the late 1980s, he used the term "powders," today these materials are called "nanoparticles." Andrzej was ahead of the others by at least a decade (Figs. 11.11 and 11.12).

Several other friends contributed to the unique scientific climate at the University of Warsaw. Andrzej Lewenstam (presently a professor at Abo Akademi University, Findland) working in Adam Hulanicki's laboratory was developing ion-selective electrodes. They collaborated with Prof. Pungor in Hungary. Together we discussed issues related to the electrochemistry of ion-selective electrodes. Lewenstam had deep interests in philosophy and as a hobby attended seminars on the philosophy of science in the Department of Philosophy. He helped me to pass a philosophy exam which was a prerequisite of a Ph.D. degree by telling me the favorite questions asked by the examiner. My schoolmate Zbigniew Figaszewski (presently professor at the University of Białystok) was working with Koczorowski on the development of electrocapillary transducers. Prof. Koczorowski and his coworkers performed very precise measurements of surface potentials. He collaborated with Sergio Trasatti, and thanks to this collaboration, Trasatti was a frequent visitor to Warsaw. Andrzej Czerwiński (presently professor at Warsaw University) was another student of Prof. Jerzy Sobkowski performing radiochemical measurements of adsorption at solid electrodes. His knowledge of radiochemistry was invaluable to me. Working with mixed solvents, I had problems to disentangle the bulk effect of the solvent on the activation energy of an electrode reaction from surface effects due to specific adsorption of the organic component of the mixture

Fig. 11.11 From *right* to *left* Zbigniew Galus, Ralf Adams and Paweł Kulesza (Picture taken at a conference in the U.S. in ~1981). Paweł Kulesza received his M.Sc. under the supervision of Prof. Galus and his Ph.D. at the University of Southern Illinois in Carbondale under the supervision of Prof. Cox. After spending several years in the USA, he returned to the University of Warsaw at the end of the 1980s. He has built a strong research programme in materials electrochemistry. He succeeded Prof. Galus after his retirement

Fig. 11.12 Andrzej Wieckowski—*left*, Andrzej Lewenstam—*center*, Marcin Majda—*right* pictures taken in the period 1970–1980

onto the electrode surface. Together Czerwiński and I performed parallel measurements of the kinetics of electron transfer between vanadium (II) and vanadium (III) in a homogeneous reaction in solution and at the electrode surface. We used radiolabeled vanadium and the stop flow technique to measure the rate of the homogeneous reaction. The half-life time of the vanadium isotope was ~14 days. We had to work days and nights over a period of about 6 weeks to collect the data. The result was a very elegant work. During that period, I established very close personal relations with Andrzej. This short account illustrates how diversified were the personalities working at that time in Electrochemistry at Warsaw University and how complementary were our specializations. Thanks to Prof. Galus' tolerance, support, and friendly attitude, we had free exchange of information and ideas, and we learned extensively from each other. The relationships between Prof. Galus and the other group leaders were friendly, and there was no animosity and pointless competition between various groups.

I graduated with my Ph.D. in 1974 and soon I moved my research toward understanding of the effect of thin organic films on the kinetics of electrode reactions (the so-called effect of organic inhibitors). This was a natural extension of my studies of electrode kinetics in mixed-solvents to the case where the organic compound is the minority component in the mixture. I also built a chronocoulometer, a modified version of the instrument I worked with in Brussels. I published several papers on the influence of organic inhibitors on the rate of electrode reactions which constituted the basis of my habilitation thesis I defended in 1978. Several people from abroad came to our lab to do collaborative research in this area. Dr. Michail Naurizbaiev from Alma Ata (now Almaty, Kazakhstan) came to visit sometime around 1974. He later sent to our lab two of his students for a short, 1-month visit. Dr. Libuse Kisova from Brno (Czechoslovakia) came for a 3-month visit. She was a very pleasant and a very hard working person. Two papers were the result of that relatively short stay in Warsaw. Hendrik Emons came from Halle (DDR). We also published two papers and for years, have maintained good personal relations. Hendrik is now director of a European Commission Analytical Laboratory in Belgium. Katsumi Niki from Japan visited us on one of his many trips to Europe to discuss inhibition phenomena. I have very pleasant recollections of meeting Oleg Petrii, Sasha Kuznetsov, Prof. Stal Mairanovskiy all from Moscow, Yurii Loshkariov from Dniepropietrovsk, Gunther Salié from Leipzig (DDR), and Ron Fawcett from Guelph (Canada).

Barbara Behr and Zbigniew Galus were organizers of several international symposia that played a very important role in scientific exchange between us (Polish electrochemists) and the international community. The second of that meeting took place in Jabłonna (a conference center near Warsaw) and was attended by Frumkin, Krishtalik, and Mairanovskiy from Moscow, Trasatti from Milan, Parsons from Bristol, Gierst from Brussels, Wolgang Lorenz from Leipzig (DDR), and Ron Fawcett (Canada). An important discussion of the concept of the absolute electrode potential between Frumkin and Trasatti took place at this symposium. The content of this discussion was later published in the Journal of Electroanalytical Chemistry. It was the first time I met Wolfgang Lorenz from Leipzig. I had read his papers, and I admired his work. Unfortunately, his papers were published in German and hence they were not very broadly read. I consider his papers on the kinetics of adsorption of organic molecules as the top publications in electrochemistry. They were written with a beautiful clarity and the rigor of a very clear scientific mind.

The title of the book is "Electrochemistry in the Divided World;" however, as my narrative shows, in Poland, we did not live in a "Divided World." In Galus' laboratory essentially everybody who graduated with a Ph.D. did postdoctoral studies either in North America or Western Europe, and this was a rule that applied to other laboratories of the Department of Chemistry, Warsaw University. The main problem with international exchange was financial. Our currency was not convertible, the government was short of convertible currencies, and we were not able to obtain funds to travel to the West. The "black market" exchange rate was prohibitive. We traveled to the West if our host covered living expenses and in many cases the transportation costs of our visits. Monetary issues were not a problem when we traveled to other "East Block" countries, but the bureaucracy was prohibitive. In the late 1970s, I wanted to send Waldemar Górski my M.Sc. student for a short visit to Budevski's Institute in Sofia (Bulgaria). We had to write an application that after approval of the President of Warsaw University was submitted to the Ministry of Education. We did not hear from the Ministry for a long time. In the end, I decided to visit the Ministry to learn about the status of our application. When I entered the office of the Department responsible for exchange with Bulgaria, I noticed my high school colleague siting behind the desk. After a short conversation, he pulled out Górski's file from the bottom of a large pile of applications at his desk and 2 weeks later Górski was in Sophia. Without this coincidence of a personal relation with the officer at the Ministry, Górski could have waited years for the decision. The result was that I visited only the University of Brno and the Heyrovský Institute in Prague during the years I worked at the University of Warsaw. This visit gave me the opportunity to meet several Czech electrochemists working in Brno whose names I knew only from the literature. They included Dr. Otto Fischer and his wife and Dr. Komenda. On my way back from Brno, I stopped in Prague to visit the Heyrovský Institute. I was very much touched to see Jaroslav's Heyrovsky's office preserved as a museum. I spent a very pleasant evening with Jaroslav Kůta who I admired as a coauthor of a book "Principles of Polarography." Kůta had a very pleasant and friendly personality, and I have very nice recollections of that visit. At the Heyrovský Institute, I met a trio of friends consisting of Michal Heyrovský (son of Jaroslav), Dr. Smolar (Jaroslav Heyrovský's first student), and Dr. Novotny. They invited me to their company for a cup of tea. Dr. Nowotny showed me his design of a capillary for polarographic measurements known later in the literature as the "Novotny capillary." He was a very kind man taking care of Dr. Smolar who was quite old at that time. To make concluding statement to this section, in the "Divided World," we were in fact in a position of a bridge between the West and the East. We had a good knowledge of the Russian language and Russian culture and a good knowledge of the West and Western languages. We could communicate and understand people from both sides of the Iron Curtin.

A Ukrainian student told me an anecdote about an oral exam in a Medical Department of Kiev University during the Soviet times.

> The professor of anatomy is showing a student two glass cabinets with skeletons and asked the student; "who are these skeletons?" "I do not know," replied the student. The prof made efforts to help him; "Look the skeleton on the left has narrow hips and broad shoulders, and the skeleton on the right has broad hips and narrow shoulders; who are these skeletons?" "I do not know," replied the confused student. At that point, the professor got irritated and

exclaimed: "what have we taught you during your four years at the university?" That remark ignited a spark of understanding in the eyes of the student who exclaimed: "These are Marx and Engels."

Political indoctrination was a part of education in many East bloc countries. However, I have to say that during all my high school and university years, I did not have to take any political courses. Poland had a period of political repressions between 1947 and 1955. Many members of the educated class were sent to prison and some were executed. My stepfather and several of my uncles spent several years as political prisoners in the Polish equivalent of Gulags. However, the political climate had changed by 1956. The period between 1956 and 1968 that covered my high school and university years was a period of relative tolerance. In high school, I had religion taught by a catholic priest rather than Marxism, and each year in the spring, we had a 1-week break from classes to attend religious preparations for Easter holidays in a church. I had no compulsory political courses during my undergraduate studies. I did, however, have to pass an exam in Marxist Philosophy of Nature to get my Ph.D. degree. However, the examiner, who had earlier in his life been a devoted Marxist, had become a dissident after 1968. On the advice of Andrzej Lewenstam, I prepared for my exam solely by studying the publications of French philosophers of the Enlightenment period and was never asked about Marx or Engels.

In Poland, staying away from politics meant that one could avoid political repressions (the exception was the period between 1968 and 1970). We were inundated with communist propaganda but our milieu was impervious to that. My wife and I did not read official newspapers, we did not have a television at home (our personal choice, TV is a thief of time), and our short wave radio was always tuned to the BBC World Service, to learn English and to get objective information about events around the world. Once a visitor from an East bloc country told me "I do not like to have any political discussion since I do not like to have material for my report." In the Divided World, reports were also written in the West. A Belgian friend who spent several years as a postdoc in the USA told me that his professor wrote a report to CIA after his visit to Moscow, on his own initiative. I traveled many times to Belgium, and I have never been asked to write a report. The only report was a presentation of my research at our group meetings. I have never been harassed by a security apparatus, and I do not know of any of my friends who had such an unpleasant experience. We traveled on the University passport that was given to us by the University administration, and I have never had contact with security agents before or after my trip abroad. The same applies to my colleagues.

I have heard that in some East Block countries, scientists needed permission to publish in international journals. We never had such problems. I published almost all my papers in the Journal of Electroanalytical Chemistry, and I would like to express my gratitude to Roger Parsons, its editor. He has always been tolerant and supportive of us. Our command of English was not good, and I recall a review of one of my papers with the referee's comment "The English is awful and occasionally hard to understand." Roger's added a comment in his hand writing: "do not worry; I will take care of it." We were not so well treated by other journals. I submitted a good paper to the Journal of Physical Chemistry. I did not hear from the Editor for about a year. When I wrote inquiring about the status of my paper, the Editor wrote back that he has difficulties to find a referee of my work. The paper was on the solvent effect on electron transfer kinetics and many electrochemists worked in that field, I gave him suggestions of about six names in my cover letter. I decided to withdraw the paper and submit it to the Journal of Electroanalytical Chemistry. The mail was slow and before my withdrawal letter reached that editor, I received positive referee reports on my paper from him. However, I had already made the decision to publish this work in Parsons' journal. On another occasion, Andrzej Wieckowski told me that he submitted a paper to the Journal of the Electrochemical Society. The paper was accepted and published. However, the editor wrote back to Andrzej asking him not to send more papers to this journal because he is not able to pay the page fee charges. In the Divided World, we had to deal not only with an authoritarian regime in the East but occasionally with a negative attitude from the West as well.

Polish culture was booming in the 1960s and 1970s. Polish cinema, represented by directors such Wajda, Zanussi, Kieslowski, and earlier by Polanski, was of superb quality. In contrast to banal Hollywood productions, these movies addressed deep human problems, see, for example, "Decalogue" by Kieslowski. Polish composers such as Lutosławski, Panufnik, Penderecki, Górecki, and Preisner made an international impact. We had a superb theatre that presented plays by "Western" and "Eastern" playwrights. Forty years later, I can still remember productions of "The Price" by Arthur Miller, "The Physicists" by Friedrich Dürrenmatt, and "Emigrants" by a Polish writer Sławomir Mrożek. We did not watch TV but read a lot of literature, American writers such as Hemingway, Dos Passos, Saroyan, Steinbeck; but also Russian (Soviet) writers Babel, Erenburg, Sholokhov, and Bulgakov. The book "Master and Margarita" by Bulgakov fascinated us, and we were reading it loudly with a group of about ten friends. I recall discussing with Gierst "Doctor Zhivago" by Borys Pasternak and telling him that "The Silent Don" by Sholohov is a much better book describing the same period of Soviet Revolution. Gierst did not know this book but soon was convinced when Sholohov was awarded the Noble Prize in Literature for this novel. In Poland, we were economically poor but intellectually rich.

I defended my habilitation thesis in 1978. Until that time, I had only worked with a mercury electrode. That year I attended the annual congress of the International Society of Electrochemistry (ISE) in Budapest. It was a milestone for my career. I was able to meet or to see many famous electrochemists and to get a sense in which direction electrochemistry was expanding. It became apparent to me that research at mercury was in decline and that electrochemical science was moving in the direction of solid electrodes. As a Private Dozent, I started to build my independent research group. I decided that we will work with solid electrodes. As I had no experience working with solid materials, I applied to Roger Parsons for a fellowship to spend 1 year in his laboratory at CNRS in Bellevue, France. I also suggested to Dr. Golędzinowski, my younger coworker, to take a 1-year postdoctoral study in the laboratory of Joachim Schultze in Dusseldorf. In addition, Waldemar Górski, my M.Sc. student, was sent for a short visit to Budevski's laboratory in Sophia to learn how to grow defect-free silver single crystal electrodes.

In August 1980, I attended another ISE meeting in Prague, Czecholslovakia. In Prague, I met Rolando Guidelli (Florence, Italy), and this was a beginning of our long-lasting friendship. I also met Dr. N. V. Nikolayeva-Fedorovich from Moscow State University. Nikolaeva-Fedorovich had done top quality studies of the effect of the double layer on the rate and mechanism of polarographic reduction of oxyanions. This subject was of interest to Rolando as well, and at one point, the three of us had a scientific discussion. I acted as the interpreter, translating between Russian and English. Although I have learned several languages, my linguistic skills have never been great and at one point, I started to talk in Russian to Rolando and in English to Dr. Nikolayeva. I still remember a deep surprise in the eyes of Rolando and his whisper, "But I do not know Russian." The meeting in Prague took place during the historical strikes in Gdańsk. However, we were completely cut out off from information about events in Poland. From Prague, I took a plane to Brussels where I was welcomed by Gierst with news about Lech Wałęsa, Solidarity, and the signature of the treaty of Gdańsk. Gierst rented an apartment for me in a walking distance from the University. I put my luggage in this apartment, changed a jacket, and we went for dinner. We were talking politics all the time. The dinner lasted quite long, and Gierst dropped me of in front of my apartment building after midnight. When he departed, I realized that I had no idea what the number of my apartment was nor did I even know which floor it was located. I decided to spend the night in a hotel, but then I realized that I had changed my jacket earlier in the evening, and my wallet and passport were in the old jacket locked in my apartment. Gierst's name was not listed in the directory, and I did not have my phone book with me. It started to rain. I had no choice but to walk to the University campus, awake a concierge who was living there and with his help find Gierst's phone number. I called Gierst probably at about 2 am, and finally I was able to reach my apartment. All this time, I was thinking about a pile of journals with news about Poland waiting for me in the apartment. I returned to Warsaw in October 1980. The Solidarity union had already been established with Andrzej Wieckowski chosen as its leader in the Chemistry Department. With his charisma and personal skills, he managed to lead this organization through the next difficult year of a power struggle between Solidarity and communist authorities without a major conflict.

Living conditions in Poland deteriorated quickly. The decline started in the second half of the 1970s and accelerated rapidly after 1980. Solidarity times are reported today as heroic. For me, the period from October 1980 until September 1981 was a very difficult time. I had two small children, and I struggled to secure their basic needs. The political struggle, a fear of Soviet intervention like in Hungary in 1956 or Czechoslovakia in 1968, contributed to a permanent feeling of insecurity. I was therefore relieved to receive a letter from Roger Parsons with an offer of a 1-year fellowship to do research in his laboratory. I arrived to Bellevue on September 1st 1981, and this opened a new chapter in my professional and personal life. This was a golden age of the Laboratoire d'Électrochimie Interfaciale (LEI).

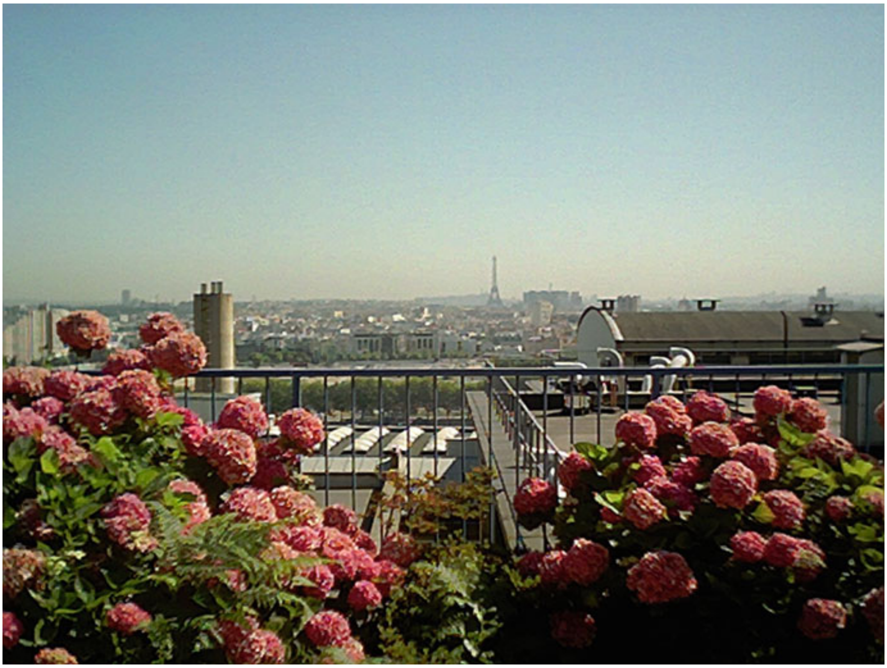

Fig. 11.13 View on Paris from the window of my laboratory at Bellevue

Jean Clavilier had just developed his famous flame annealing technique. Antoinette Hamelin had built a laboratory for gold and silver single crystal production and had developed experimental procedures to work with single crystal electrodes. Charlotte Hinnen carried out top class electroreflectance studies at single crystal surfaces, and Max Costa built an impressive ellipsometer. All this was new for me, and I enjoyed learning the new science, methods, and procedures. In Bellevue, I learned the significance of a carefully done experiment. For my French colleagues, the measurement was an art. They planned carefully and thoughtfully and later executed it with the impressive skills of gifted experimenters. A well-known example is the Clavillier's flame annealing technique. However, Antoinette Hamelin demonstrated comparable skills working with gold single crystal electrodes, and measurements of potential of zero charge of gold electrodes by Jean Lecoeur were also examples of the same qualities. "La manip" (experiment) was revered and its quality was appreciated (Fig. 11.13).

I worked primarily with Antoinette Hamelin, a person of great culture, intelligence, profound knowledge of single crystal electrochemistry, and a very strong personality. I also collaborated with Charlotte Hinnen on adsorption of organic molecules at gold electrodes. At Bellevue, cyclic voltammetry was used to characterize adsorption at gold electrodes. I was surprised to see that CVs recorded at the Au (111) surface displayed significant hysteresis. I have had seen nothing like that

Fig. 11.14 Antoinette Hamelin and Roger Parsons in the cafeteria of the Laboratoires de Bellevue

on a mercury electrode. I suggested that we apply chronocoulometry instead. In that way, we could measure the charge difference between adsorbed and desorbed states at equilibrium. The approach was successful, and later chronocoulometry became my major electrochemical tool when I built my own laboratory in Guelph, Canada (Fig. 11.14).

The personality of Roger Parsons had a significant impact on the activities of LEI. His friendly, quiet, and positive attitude cemented various research groups in this laboratory. He has always been helpful, deeply interested in the experiments performed in the lab, and made efforts to accommodate everybody's needs and ambitions. Bellevue was a leading center in surface electrochemistry at that time, and many scientists visited this lab. I was able to meet Ernst Yeager, Fred Anson, Adam Heller, and John Bockris just to mention a few famous names. Roger frequently invited me for lunch with his visitors to give me the opportunity of personal interaction with these influential people. Bellevue also attracted a younger generation of scientists. Wolfgang Schmickler spent several months there. We shared an office and soon became very close friends. In Bellevue, I met Ulrich Stimming. This was the beginning of our long-lasting friendship. I also had the pleasure to work with Shi-Gang Sun from Xiamen University. Shi-Gang arrived as an exchange student from China, and for 1 year, I was tutoring him. This was the beginning of over 30 years of friendship and collaboration. Antonio (Toni) Aldaz from Alicante was another visitor to Bellevue whose association with LEI made an impact on my future activities. Toni, and later Juan Feliu, the two prominent collaborators of Jean Clavilier, established the famous surface electrochemistry center in Alicante that continues the tradition of the Bellevue lab. Jean Clavilier is going twice a year to Alicante to perform research. I have an established collaboration with Juan Feliu and I visited Alicante quite often. These visits gave me the

Fig. 11.15 A get together in Alicante; Sitting from *right* to *left*, my wife Izabela, myself, Jean Clavilier; standing in the *second row*, Beatriz (Juan's wife), Juan Feliu, and Antonio Aldaz

pleasure to see Jean Clavilier and to enjoy the company of Jean and my Spanish friends. In a sense, these visits are a continuation of the Bellevue tradition (Fig. 11.15).

In December 1981, Roger Parsons organized a meeting sponsored by IBM on theoretical modeling of the electrical double layer. Revaz Dogonadze and Alexei Kornyshev came from Soviet Union. We had many discussions at this meeting and on the last day, I invited them home to talk about Solidarity and the political situation in Poland. In the end, Alexei was taken for a tour of Paris by French colleagues, and I spent a long night discussing politics with Revaz. I drove Revaz back to his apartment in the early morning hours. I returned home and shortly had to go for a walk with two small but bubbling with energy sons. At the corridor, I was met by a French neighbor who told me with excitement: "Sir something wrong happened in Poland, they talk about it all the time on TV." I returned back, turned on our TV set and learned that at the same time I had been discussing Solidarity's survival chances with Revaz, martial law was being introduced in Poland. Watching brutal repressions in Poland, I made a decision not to return to Warsaw and started to look for another academic appointment. The opportunity came a few months later at the ISE meeting in Lyon. I had lunch with Ron Fawcett and Claudine Hermann-Buess. During that lunch I asked Ron; what are the chances of me getting a position in Canada because I do not want to return to Poland? "My university is just looking for somebody like you," replied Ron. He helped me to structure curriculum vitae according to Canadian standards, he strongly recommended me to his Department, and I was invited to Guelph for an interview. I got the job and in August 1983, my family and I started the Canadian chapter of our lives.

This was an excellent choice. Guelph is a quiet University town, and it was so refreshing to be away from stresses of noisy politics. The Department provided me with laboratory space and good start up money. I was successful in securing funding for my research from the Natural Sciences and Engineering Research Council of Canada. I was able to attract students and postdocs and to develop a strong research programme in surface electrochemistry. During my 31 years at Guelph, about 25 students have graduated with their Ph.D. under my supervision. Six of them took academic appointments at Canadian university, others enjoy successful careers in Government laboratories or the private sector. I was not the only one who left Poland; Andrzej Wieckowski took an appointment at the University of Illinois Urbana-Champain; Marcin Majda at Berkeley, Andrzej Lasia at the University of Sherbrooke; Andrzej Barański at the University of Saskatchewan; Piotr Zelenay at Los Alamos; Waldemar Górski at San Antonio, Texas; Andrzej Lewenstam at Abo Akademi University, Finland; and Marek Lipsztajn and Maciek Golędzinowski took industrial positions in Canada. So many electrochemists left Warsaw. It took decades of Kemula's and Galus' efforts to build this strong research center, and it was so easy to destroy it by politics. We used to meet at the Electrochemical Society (ECS) meetings. I recall one occasion when a group of us (graduates of Warsaw University) were standing in a foyer during a break between sessions. An American friend passing by looked at us and remarked: "I see that to be a good electrochemist one has to come from Galus' lab."

The last stage of Electrochemistry in the Divided World happened during my stay at the Fritz Haber Institute in Berlin. I arrived in Berlin to take a 1-year sabbatical with Dieter Kolb in September 1989. On our way to Berlin, my family and I stopped for 2 weeks holidays in London. The day we landed at Heathrow, the first post Solidarity Government was formed in Warsaw. In Berlin, we watched the events in Eastern Europe with great attention. I vividly remember one evening in October. Working late in the lab I met Prof. Ertl (the director of the Institute, Noble Prize 2007) in the corridor. Ertl was apparently very excited and told me with emotion: "Do you know what happened? Honecker was deposed." The day with famous pictures taken near the Brandenburger Gate showing people on top of the Berlin Wall, Frank Henglein (Dieter's Ph.D. student) and I were doing measurements at BESSY (Berlin's Synchrotron). A friend came to us and said: "Stop doing measurements! History is being made!" We walked to Kurfürstendamm to mix with the happy crowd and to celebrate the event (Fig. 11.16).

The Fritz Haber Institute was a leading center for surface science and research on interfaces. I had the opportunity to work not only with Dieter Kolb but also with Bruno Pettinger. Ulrich Stimming was at the FHI on sabbatical leave from Columbia University, and Fred Wagner (General Motors Laboratory, Detroit) came for a few months visit. We used to meet for lunch at the Free University cafeteria to have many long discussions. I was interested in adsorption at solid electrodes, Ulrich in the double layer structure at interfaces at liquid nitrogen temperatures. Fred was interested in simulated double layers in vacuum. Ulrich and Fred were working with Jürgen Sass. At one point, we decided that we will give a series of tutorials to review the foundations of the double-layer theory. These were to be informal

Fig. 11.16 The end of Divided World, a picnic at remnants of the Berlin Wall in July 1990; from *right* to *left*, Marcela (Ulrich's wife), myself, Ulrich Stimming, and Jurgen Sass. My wife Izabela is standing *behind* Jurgen

seminars so that we can learn from each other. Jürgen sent out information about the tutorials to other research groups in West Berlin, and to my surprise, all the famous electrochemists from West Berlin showed up at these lectures. We ended up giving tutorials to Gerischer, Kolb, Plieth, Tribusch, Dobelhofer, Pettinger, etc. I was impressed by the willingness to participate in the tutorial activity of such well-known and established scientists. The tutorials gave me a deep understanding of all assumptions made in the derivation of the electrocapillary equation. Several years later, this knowledge allowed me to apply a thermodynamic method to determine co-adsorption of a underpotentially deposited metal ion and an anion ion at a gold electrode surface.

I took the opportunity of my stay in West Berlin to visit my colleagues in DDR: Utz Retter at the Akademie der Wissenschaften in Adlershof in East Berlin (Angela Merkel worked there at that time) and Hendrik Emons at the University of Leipzig. The last visit gave me the second opportunity to discuss with Wolfgang Lorenz. Utz visited later Guelph on two occasions, and we have published a paper together. I also went to Moscow on the invitation of Alexei Kornyshev in June 1990. It was my first visit to this important center for electrochemistry. I had the pleasure to meet Boris Damaskin who previously I knew only from the literature and to see many famous Soviet scientists such as Oleg Petrii, Sasha Kuznetzov, and Lev Krishtalik

Fig. 11.17 Pictures of Prof. Zbigniew Galus at our outdoor activities; hiking in Bruce Pennisula, Ontario, Canada,—*left* (~1998); mushrooms picking in Polish mountains (~2005)

just to mention a few names. Alexei and I shared the love of the book “Master and Margarita” by Bulgakov and Alexei took me to show places described in this book. I particularly remember our walk through the Arbat street at midnight. It was still twilight in Moscow in June.

11.1 Epilogue

I returned to Guelph in the summer of 1990. It was the end of the Divided World. I was able to resume my collaboration with Professor Galus and the University of Warsaw. Since 1990 I have visited Warsaw every year giving either research or tutorial lectures. Similar collaborations were established by Marcin Majda, Andrzej Wieckowski, and Andrzej Lasia. We were coming back to our Alma Mater. Professor Galus spent two several months long research visits in Guelph, and we published scientific papers together again. Professor Gaus and I enjoy outdoor activities, and we took occasion of these visits for hiking in Ontario and Polish Mountains or for mushroom picking in Poland (Fig. 11.17). I have also had the privilege to host quite a few Polish postdocs and exchange graduate students. Electrochemistry is thriving again at the University of Warsaw. Paweł Kulesza, who succeeded Prof. Galus after his retirement, Zbigniew Stojek, and Renata Bilewicz are leading world-class researchers in laboratories. Their research is well funded, and they have access to the most advanced scientific instrumentation.

Most importantly, my interactions with Polish postdocs and exchange students tell me that they have a bright, hard-working, and strongly motivated younger generation. This is an indication that Warsaw will be a leading center of electrochemical research for many years in the future.

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Chapter 12
Hungarian Comets in the Sky of Electrochemistry

George Inzelt

12.1 Introduction

The word “comets” in the title of this chapter needs explanation. I choose this word because many Hungarian electrochemists, whose contribution to the electrochemistry was a pivotal one, appeared in the sky of science as a new shining phenomenon but they disappeared rather quickly. It was due to either the historical events in Hungary or they did not continue their scientific research at high level because of the low financial support, or just enjoyed the professorship which gave a high reputation in the society. In many cases, both reasons prevailed. In order to understand at the first glance strange thing, it is necessary to give a short compilation of the history and tradition in Hungary. In the Middle Ages, Hungary was a strong and rich country due to its gold and silver mining and the agriculture. King Mathias (1443–1490) invited the most famous scientists from all parts of Europe. In the sixteenth century, Turks occupied the central part of the country, the Western part belonged to the Habsburg Empire, and only Transylvania remained more or less independent. First, protestant schools were established, which were followed by the foundation of a university in 1635 (presently Eötvös Loránd University, Budapest) initiated by catholic archbishop, Péter Pázmány in order to compensate the influence of the reformed churches. After the liberation of the country from the Turks in 1686, Hungary became a part of the Habsburg Empire practically as a colony but with special rights of the noble class. Several wars of independence have failed. Albeit there were scientific workshops and famous professors of Hungarian origin also in the territory of Hungary; however, we cannot talk of independent Hungarian scientific life. In the middle of the nineteenth century, a fight for reforms and the use of the Hungarian language have started. The latter is an important point

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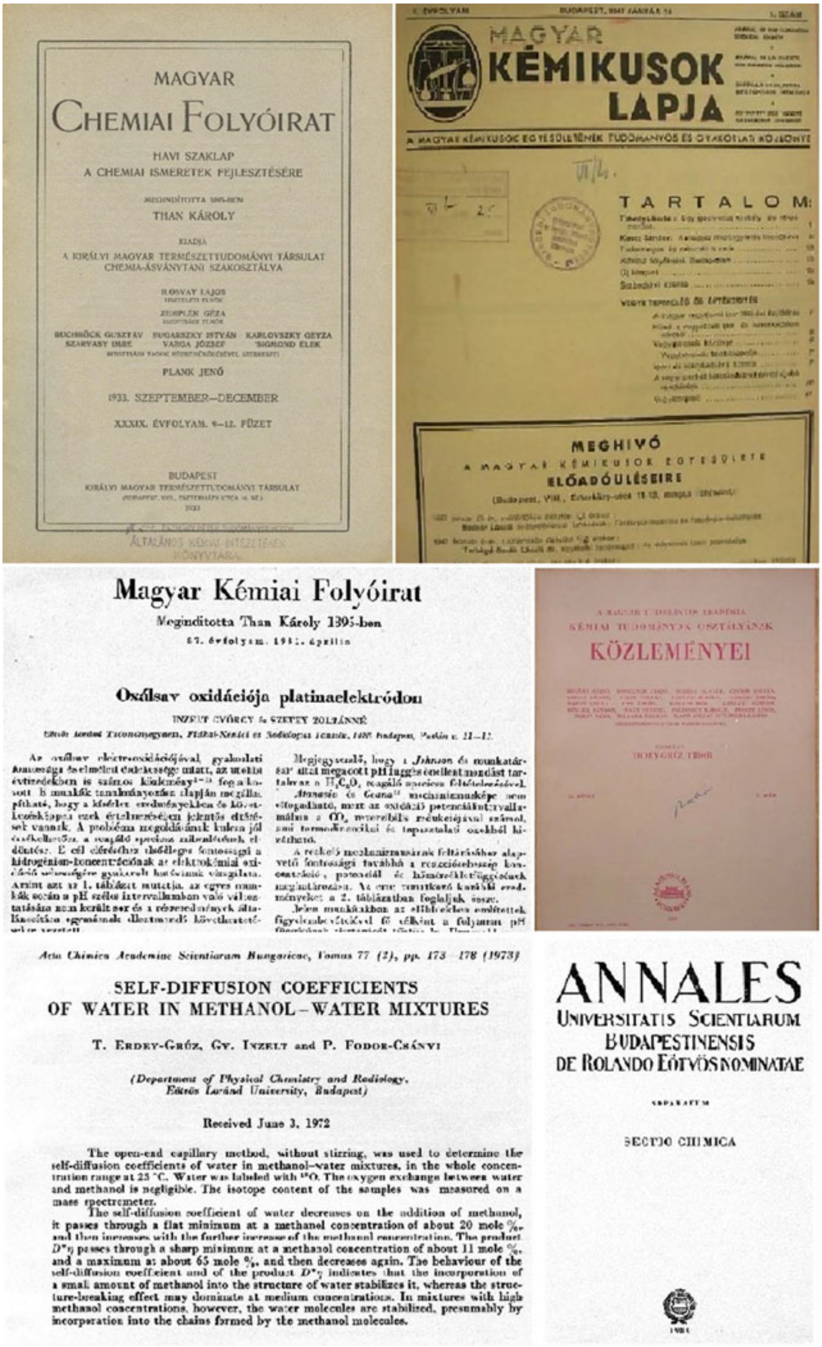
in respect of our story because otherwise it would be difficult to understand the motivation of many researchers who have published practically solely in Hungarian in the scientific journals founded in the second half of the nineteenth century. (Later it became the asylum of poor papers in the twentieth century both before and after 1945. Several professors who had been decorated with different titles and medals were just afraid to expose themselves to the peers' review internationally.) After the Settlement (Ausgleich) in 1867, a fantastic development of Hungary started within the Austro-Hungarian Empire. It involved the industry, the commerce, new railways, roads, buildings, and last but not least the civil rights. The industry, the agriculture, the health care, etc. needed more experts, therefore, the enrollment at the universities enormously increased. Practically all of the future scientists spent years at the famous German universities as graduate students or "postdocs" before starting their academic career in Hungary or in Austria. The only exception was the field of radioactivity which was studied in Vienna, Paris, Manchester, and Cambridge. A very sad turning point was the celebration of the millennium of the Hungarian conquest in 1896 which brought a wave of increasing nationalism and the counterattack from the feudal establishment. It led eventually to the emigration of the scientists mostly of Jewish origin after 1919 who felt that they were deprived of the opportunity of any scientific career or even their life was in danger. It was a great loss concerning the scientific life in Hungary. The development of the civil society stopped. Albeit under other ideology, the persecution of civil thought continued during the socialist period from 1948 to 1989. It also affected the scientific life whose prime element is the freedom, the exchange of ideas without any political influence. Furthermore, the "Iron curtain" prevented the traveling of researchers between East and West with very limited exceptions involving the ideologically fit persons. Until ca. 1960, the visit in any other socialist countries was rather limited, too. Later, the situation somewhat improved. First, conferences were organized for the researchers of socialist countries, and from the second half of 1970s, to go abroad from Hungary, where the ruling party allowed more to the people than in several other socialist countries, gradually became easier. Nevertheless, in many areas of science including electrochemistry, surprisingly good results were achieved even under these limited conditions. It was mostly due to the state's support of science and education as well as to outstanding personalities. The top scientists in the field of electrochemistry (Frumkin, Heyrovský, Kemula, Erdey-Grúz, and Schwabe) had contact with each other, and the younger researchers could visit the laboratories or institutes of these professors which was really a particular experience for them. Practically, journals in the official language of the country existed in all socialist countries, and in many cases, also multilingual journals. Multilingual meant that those journals accepted papers in German, in English, in French, and in Russian. Before the era of overwhelming domination of English, one could publish papers in these languages even in Electrochimica Acta, the journal of the International Society of Electrochemistry. These languages could also be used in conferences. By the way, the language problem also caused a communication problem. The old generation spoke German, some of them also French, English was the least spoken one. After 1945, Russian language was forced with no real success.

My professors used translators when they published in English or Russian. In Hungary I could publish in Hungarian in several chemistry journals such as *Magyar Kémiai Folyóirat, Magyar Kémikusok Lapja, and Kémiai Közlemények*, and in English *Acta Chimica Hungarica* and the journals of the universities, e.g., *Annales* of the Eötvös Loránd University (Fig. 12.1).

From the 1970s, it was allowed to publish also in international journals; however, a permission was needed from the head of the department and also from the state authorities including customs authority, and a declaration had to be made that there was no state secret in the paper or in the conference material. The relationship between East and West has slowly improved. In 1978, Hungary organized the *Annual Meeting of the International Society of Electrochemistry*. Many famous electrochemists have arrived in Budapest. I remember that it was the first time when I met such scientists as R. Parsons (U. K., but actually from France), A. Heller, R. P. Buck, S. Bruckenstein, S. Srinivasan, E. Yeager, Ch. W. Tobias, M. J. Weaver (U.S. A.), B. E. Conway, W. R. Fawcett (Canada), A. J. Arvia (Argentina), H. Lund (Denmark), Epelboin (France), F. G. K. Baucke, R. Fleischmann, R. Memming, W. Vielstich, G. Zundel (GFR), H. Gerischer (West Berlin), A. Fujishima, K. Honda (Japan), N. Ibl, D. Landolt, W. Simon, V. de Nora (Switzerland), E. Vianello (Italy), and E. Gileadi (Israel). The "Eastern team" was also strong: V. S. Bagotzky, R. R. Dogonadze, M. Ya. Fioshin, Ya. M. Kolotyrkin, L. I. Krishtalik, S. G. Mairanovskiy, Yu. V. Pleskov, Yu. B. Vasil'ev (Vasilyev) (Soviet Union), Z. Galus (Poland), K. Schwabe (GDR), J. Koryta, J. Kůta (Czechoslovakia), A. R. Despić, and D. M. Drazic (Yugoslavia). It was characteristic to the situation that it was the first trip abroad of many Soviet scientists due to their "secret" work. For instance, Vasil'ev told me that he and Bagotzky were not allowed to travel because they had been involved in the development of batteries for the Soviet spaceships.

During the socialist period, the salary was low, and a rather limited amount of money was available to buy more expensive instruments for foreign currency. (Unfortunately, both factors prevail after the change of the system.) In electrochemistry, there was a local production of electrodes, voltmeters, potentiostats, etc.; therefore we had access to a relatively good instrumentation. Our library purchased all the important journals and books even from the West, which is not the case anymore due to the financial problems. There were even strange things, for example, they bought more copies because several important or self-important professors insisted on their own copies. In the 1950s, research institutes were built which belonged to the Hungarian Academy of Sciences. Nevertheless, except a short period in 1950s, the Soviet instructions were not obeyed, and research activity remained also at the universities. The situation of the electrochemistry in Hungary separated by the Iron curtain from the West will be illustrated with the life and activity of three scientists: Tibor Erdey-Grúz, Ernő Pungor, and György Horányi whose achievements have been acknowledged all over the world, and of whose activities I have personal experiences from the end of 1960s. From the previous period I will deal with the fate and the works of five scientists. In this way, I can



MAGYAR
CHEMIAI FOLYÓIRAT
HAVI SZAKLAP
A CHEMIAI ISMERETEK FEJLESZTÉSÉRE
THAN KÁROLY
KIADJA
A KIRÁLYI MAGYAR TERMÉSZETTUDOMÁNYI TÁRSULAT
CHEMIA-ÁSVÁNYTANI SZAKOSZTÁLYA
PLANK JENŐ
1933. SZEPTEMBER—DECEMBER
XXXIX. ÉVFOLYAM. 9—12. FÜZET
BUDAPEST
KIRÁLYI MAGYAR TERMÉSZETTUDOMÁNYI TÁRSULAT

MAGYAR
KÉMIKUSOK
LAPJA

A MAGYAR KÉMIKUSOK EGYESÜLETÉNEK TUDOMÁNYOS ÉS GYAKORLATI KÖZLÖNYE

TARTALOM:

MEGHIVÓ
A MAGYAR KÉMIKUSOK EGYESÜLETE
ELŐADÓÜLÉSEIRE

Magyar Kémiai Folyóirat
Meginditotta Than Károly 1895-ben

Oxálsav oxidációja platinaelektródon

INZELT GYÖRGY és SZETEY ZOLTÁNNÉ

A MAGYAR TUDOMÁNYOS AKADÉMIA
KÉMIAI TUDOMÁNYOK OSZTÁLYÁNAK
KÖZLEMÉNYEI

Acta Chimica Academiae Scientiarum Hungaricae, Tomus 77 (2), pp. 173–178 (1973)

SELF-DIFFUSION COEFFICIENTS
OF WATER IN METHANOL–WATER MIXTURES

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Received June 3, 1972

The open-end capillary method, without stirring, was used to determine the self-diffusion coefficients of water in methanol–water mixtures, in the whole concentration range at 25 °C. Water was labeled with ^{18}O. The oxygen exchange between water and methanol is negligible. The isotope content of the samples was measured on a mass spectrometer.

The self-diffusion coefficient of water decreases on the addition of methanol, it passes through a flat minimum at a methanol concentration of about 20 mole %, and then increases with the further increase of the methanol concentration. The product $D^*\eta$ passes through a sharp minimum at a methanol concentration of about 11 mole %, and a maximum at about 65 mole %, and then decreases again. The behaviour of the self-diffusion coefficient and of the product $D^*\eta$ indicates that the incorporation of a small amount of methanol into the structure of water stabilizes it, whereas the structure-breaking effect may dominate at medium concentrations. In mixtures with high methanol concentrations, however, the water molecules are stabilized, presumably by incorporation into the chains formed by the methanol molecules.

ANNALES
UNIVERSITATIS SCIENTIARUM
BUDAPESTINENSIS
DE ROLANDO EÖTVÖS NOMINATAE

SEPARATUM

SECTIO CHIMICA

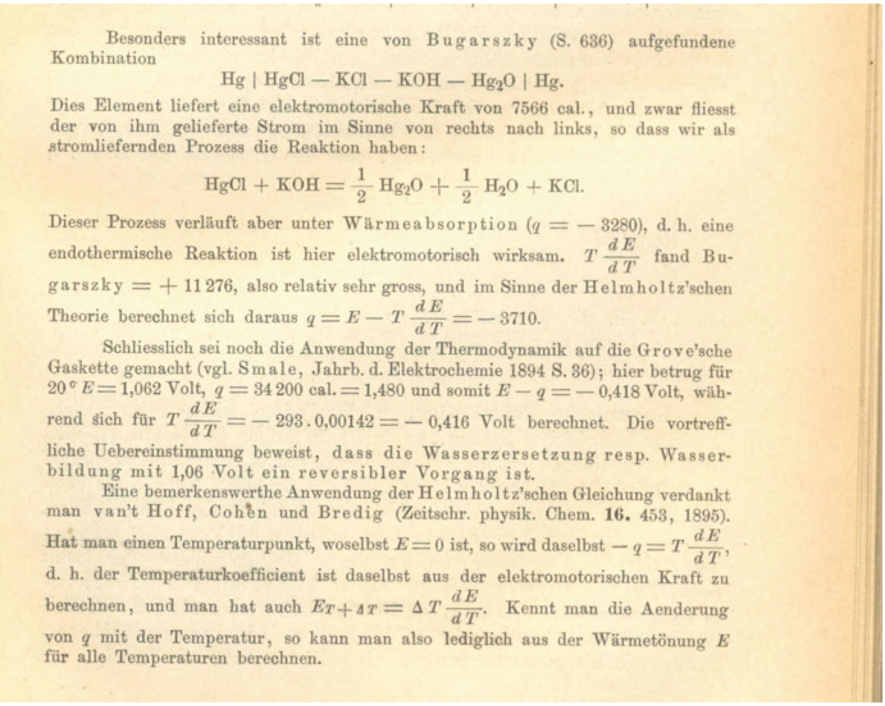
Fig. 12.1 Illustrative pages of the Hungarian chemistry journals present the essential features of the tradition of the electrochemistry in Hungary, which was continued by the three professors mentioned above.

12.2 The Heritage or the Most Important Contributions of Hungarians to the Electrochemistry Before 1945

12.2.1 István Bugarszky's Discovery: The Endothermic Galvanic Cell

Bugarszky (Fig. 12.2) was born on May 21, 1868 in Zenta (Austro-Hungarian Empire, now Senta, Serbia). He studied and received his doctoral diploma in chemistry at the Budapest University in 1891. He was appointed lecturer at the Veterinary College, Budapest and awarded the title of Professor of Chemistry in 1902. He worked at Nernst's laboratory in Göttingen in 1896. Bugarszky with Leo Liebermann (1852–1926), who was also a professor at the Veterinary College, dealt with the investigation of electrolyte solutions including biological fluids. They described the buffer effect of protein solutions [1] before Fernbach and Hubert introduced the term tampon or buffer in 1900 [2]. Nernst advised Bugarszky to search for the endothermic galvanic cell which might exist. This research led to his most famous achievement, the discovery of an endothermic galvanic cell $\mathrm{Hg} \mid \mathrm{Hg_2O} \mid \mathrm{KOH} \,\vdots\vdots\, \mathrm{KCl} \mid \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$; $\mathrm{Hg_2Cl_2} + 2\mathrm{KOH} = \mathrm{Hg_2O} + 2\mathrm{KCl} + \mathrm{H_2O}$ [3, 4]. It was the first evidence for that the endothermic reactions can proceed


Fig. 12.2 István Bugarszky



Besonders interessant ist eine von Bugarszky (S. 636) aufgefundene Kombination

$$Hg \mid HgCl - KCl - KOH - Hg_2O \mid Hg.$$

Dies Element liefert eine elektromotorische Kraft von 7566 cal., und zwar fliesst der von ihm gelieferte Strom im Sinne von rechts nach links, so dass wir als stromliefernden Prozess die Reaktion haben:

$$HgCl + KOH = \frac{1}{2} Hg_2O + \frac{1}{2} H_2O + KCl.$$

Dieser Prozess verläuft aber unter Wärmeabsorption ($q = -3280$), d. h. eine endothermische Reaktion ist hier elektromotorisch wirksam. $T \frac{dE}{dT}$ fand Bugarszky $= + 11\,276$, also relativ sehr gross, und im Sinne der Helmholtz'schen Theorie berechnet sich daraus $q = E - T \frac{dE}{dT} = - 3710$.

Schliesslich sei noch die Anwendung der Thermodynamik auf die Grove'sche Gaskette gemacht (vgl. Smale, Jahrb. d. Elektrochemie 1894 S. 36); hier betrug für 20° $E = 1{,}062$ Volt, $q = 34\,200$ cal. $= 1{,}480$ und somit $E - q = - 0{,}418$ Volt, während sich für $T \frac{dE}{dT} = - 293 . 0{,}00142 = - 0{,}416$ Volt berechnet. Die vortreffliche Uebereinstimmung beweist, dass die Wasserzersetzung resp. Wasserbildung mit 1,06 Volt ein reversibler Vorgang ist.

Eine bemerkenswerthe Anwendung der Helmholtz'schen Gleichung verdankt man van't Hoff, Cohen und Bredig (Zeitschr. physik. Chem. **16.** 453, 1895). Hat man einen Temperaturpunkt, woselbst $E = 0$ ist, so wird daselbst $- q = T \frac{dE}{dT}$, d. h. der Temperaturkoefficient ist daselbst aus der elektromotorischen Kraft zu berechnen, und man hat auch $E_{T + \Delta T} = \Delta T \frac{dE}{dT}$. Kennt man die Aenderung von q mit der Temperatur, so kann man also lediglich aus der Wärmetönung E für alle Temperaturen berechnen.

Fig. 12.3 Nernst W (1898) *Theoretische Chemie*. 2nd edn. Verlag von Ferdinand Enke, Stuttgart, p 651

spontaneously. Therefore, it supplied a verification of the concept of Gibbs and Helmholtz regarding the nature of affinity, i.e., the Gibbs free energy of reaction is of importance and not just the heat of reaction (enthalpy) as claimed by Marcellin Berthelot and Julius Thomsen. Nernst closely followed the work of Bugarszky since he discussed it in his book that appeared just the next year (Fig. 12.3).

Bugarszky became a professor at the Budapest University in 1913. After this appointment, Bugarszky practically finished his research activity, while he remained a professor until his retirement in 1935. Unfortunately, it was not a unique case in Hungary. Bugarszky became the corresponding member of the *Hungarian Academy of Sciences* (HAS) on May 5, 1899. On the same occasion, Nernst became an associate member of the HAS. Bugarszky died on March 3, 1941 in Budapest.

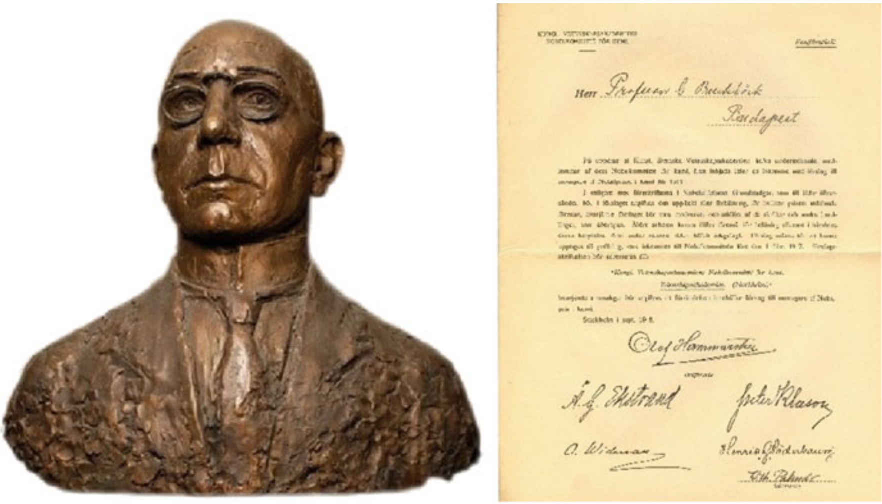


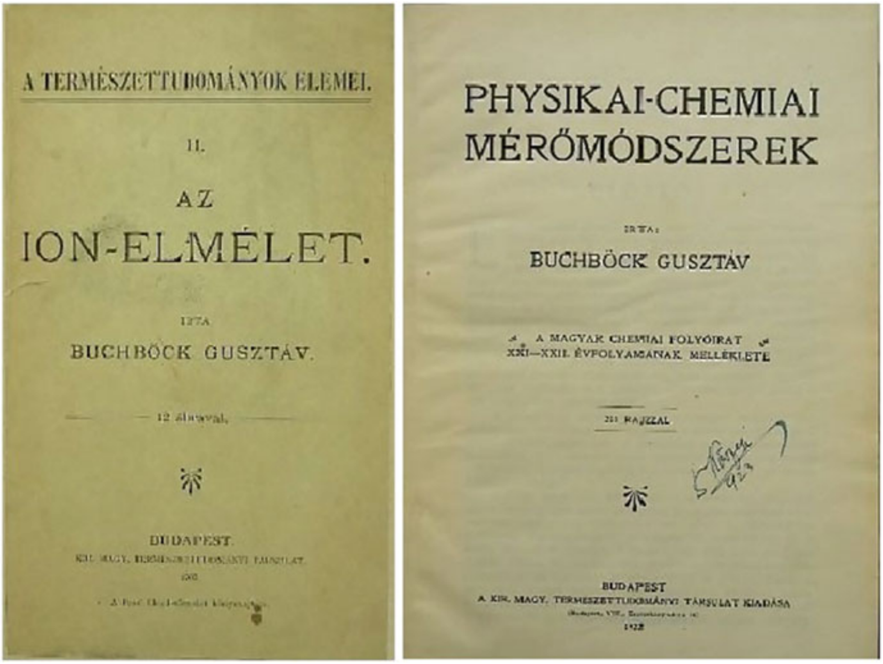
Fig. 12.4 The bust of Gusztáv Buchböck in the aula of the Faculty of Science of the Eötvös Loránd University, Budapest and the invitation from the Nobel Committee (1916)

12.2.2 Determination of the Hydration Number of Ions by Gusztáv Buchböck

Gusztáv Buchböck (Fig. 12.4) was born in Pozsony (Austro-Hungarian Empire, now Bratislava, Slovakia) on February 15, 1869. He graduated at the University of Budapest and started to work at the Chemistry Institute of Károly Than (1834–1908) of the same university. As it was usual at that time, he spent a longer study trip at the laboratories of Wilhelm Ostwald and Nernst in Leipzig and Göttingen, respectively. He became the professor of physical chemistry at the Budapest University in 1914, and he remained in this position until his death on October 1, 1935.

He was a well-known scientist (see e.g., the invitation from the Nobel Prize Committee for nomination). He elaborated a method for the determination of the hydration number of ions by measuring the transference numbers of the ions in the presence of indifferent (organic) compounds of different concentrations (Fig. 12.5). At that time, it was the most accurate measurement of the hydration number as pointed out by Nernst in his book [5].

He played an important role in the education of the next generation of physical chemists. He was the mentor of Hevesy and Erdey-Grúz (see later).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PHYSIKAI-CHEMIAI

MÉRŐMÓDSZEREK

ÍRTA:

BUCHBÖCK GUSZTÁV

A MAGYAR CHEMIAI FOLYÓIRAT

XXI—XXII. ÉVFOLYAMÁNAK MELLÉKLETE

BUDAPEST

A KIR. MAGY. TERMÉSZETTUDOMÁNYI TÁRSULAT KIADÁSA

Fig. 12.5 Books of Buchböck on theory of ions (1903) and on the physical chemical methods (1922)

Fig. 12.6 Pal von Szily

12.2.3 The Invention of Buffer Solutions by Pál von Szily

The career of Szily was a typical comet-like one. Perhaps the expression of shooting star would be even more appropriate. He was a physician as his father, Adolph

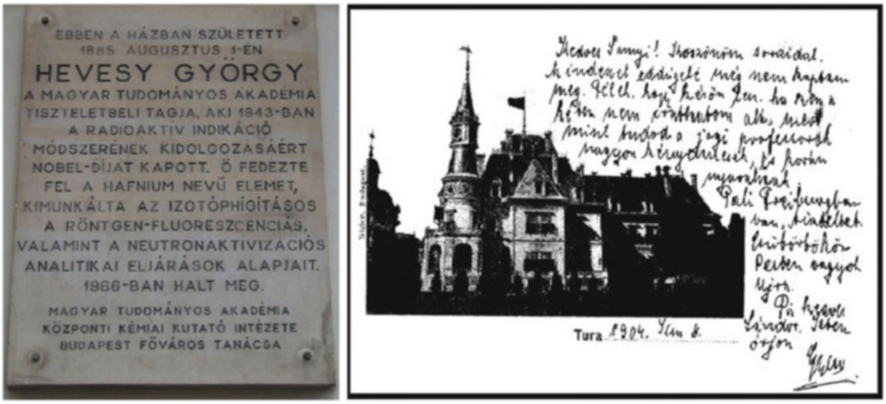
(1848–1920) and his younger brother, Aurel (1980–1945). The "von" in his name relates to the fact that the family, in fact his father, got nobility from Franz Joseph I, the Emperor of Austria and King of Hungary for his services as outstanding ophthalmologist.

Pál (Paul) Szily (Fig. 12.6) was born on May 16, 1878, Budapest, Hungary. He got his doctor of medicine degree at the Budapest University in 1901 and became an assistant at the Institute of Physiology there, where he initiated the colorimetric measurement of hydrogen ion concentration by using indicators [6, 7]. While working with H. Friedenthal in Berlin, he proposed the application of buffer solutions by mixing monobasic and dibasic phosphates [8–11]. The importance of this innovation cannot be overestimated. It should be mentioned that his diploma in medicine helped since physicians earlier recognized the importance of the pH than chemists.

He served in the army as a physician during the war between 1914 and 1918. Despite his zeal for research and his acknowledged results [6–11], he has not become a professor in Hungary due to the discrimination of scientists of Jewish origin especially from 1920s. He worked as a physician in different hospitals in Budapest, and from 1928 in Magyaróvár. He became an acknowledged physician whose work was cited in international journals. For instance, I found a review of his paper (Paul von Szily, *Wien Med. Woch.,* November 30th, 1912, p. 3226) even in *The Chinese Medical Journal* (1913) 27 (6): 60 entitled "Neosalvarsan in the prevention of syphilitic abortion." It was written that "… this has become the routine treatment in the Jewish women's hospital in Buda-Pesth with encouraging results as regards the children." Later he had no time and opportunity for research. He was taken to a concentration camp near Győr in 1944, with the help of his colleagues, he escaped the deportation but he had no medication for his diabetes and died on August 18, 1945, Magyaróvár, Hungary. A street was named of Pál Szily in Mosonmagyaróvár honoring his exemplary life.

12.2.4 The Radiotracer Technique Introduced by György Hevesy in the Study of Electrochemical Processes

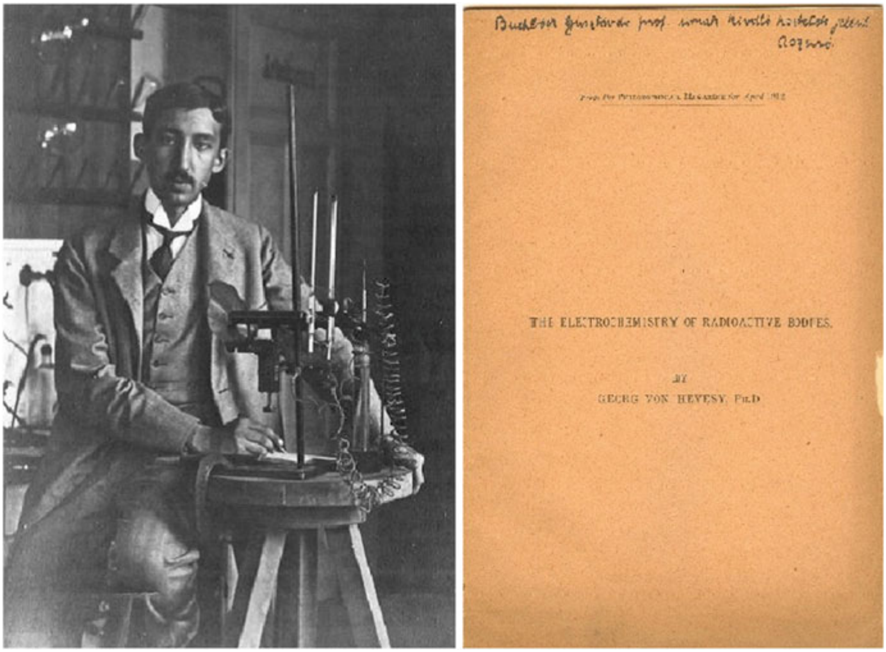
György Hevesy (also written as: Georg Karl von Hevesy, Georg Hevesy, George Charles de Hevesy, George de Hevesy, George Hevesy) was born on August 1, 1885, Budapest, in a wealthy Jewish industrialist-landowner family. His grandfather, David Bischitz got the nobility in 1895. His father, Lajos (Louis) Bischitz, used the name Hevesy related to the nobility together with his family name, that was replaced later by the name of Hevesy alone. His mother, Eugénia (Jenny) neé Baroness Schossberger de Tura came also from a rich family, her father was the first Jew who got nobility in 1863 (Fig. 12.7). George Hevesy had four older brothers, all of them became successful in different areas: Vilmos Hevesy was an electric engineer, he was the director of Blériot factory, and participated in the construction



EBBEN A HÁZBAN SZÜLETETT
1885 AUGUSZTUS 1-ÉN
HEVESY GYÖRGY
A MAGYAR TUDOMÁNYOS AKADÉMIA
TISZTELETBELI TAGJA, AKI 1943-BAN
A RADIOAKTÍV INDIKÁCIÓ
MÓDSZERÉNEK KIDOLGOZÁSÁÉRT
NOBEL-DÍJAT KAPOTT. Ő FEDEZTE
FEL A HAFNIUM NEVŰ ELEMET,
KIMUNKÁLTA AZ IZOTÓPHÍGÍTÁSOS
A RÖNTGEN-FLUORESZCENCIÁS,
VALAMINT A NEUTRONAKTIVIZÁCIÓS
ANALITIKAI ELJÁRÁSOK ALAPJAIT.
1966-BAN HALT MEG.
MAGYAR TUDOMÁNYOS AKADÉMIA
KÖZPONTI KÉMIAI KUTATÓ INTÉZETE
BUDAPEST FŐVÁROS TANÁCSA

Tura 1904.

Fig. 12.7 Memorial plaque on the wall of Hevesy's house of birth (Budapest, Akadémia utca 3.); and the manson of the family in Tura



From the Philosophical Magazine for April 1912

THE ELECTROCHEMISTRY OF RADIOACTIVE BODIES.

BY

GEORG VON HEVESY, Ph.D.

Fig. 12.8 The young Hevesy in his laboratory and one of his papers on the electrochemistry of radioactive substances [15] dedicated to Buchböck

of the airplane of Blériot. Andor (André de) Hevesy became a well-known writer in Paris. Ödön Hevesy continued the family business especially in the mining industry. Pál Hevesy was a high level career diplomat, who wrote an important book on the political consequences of the economic crisis in 1929.

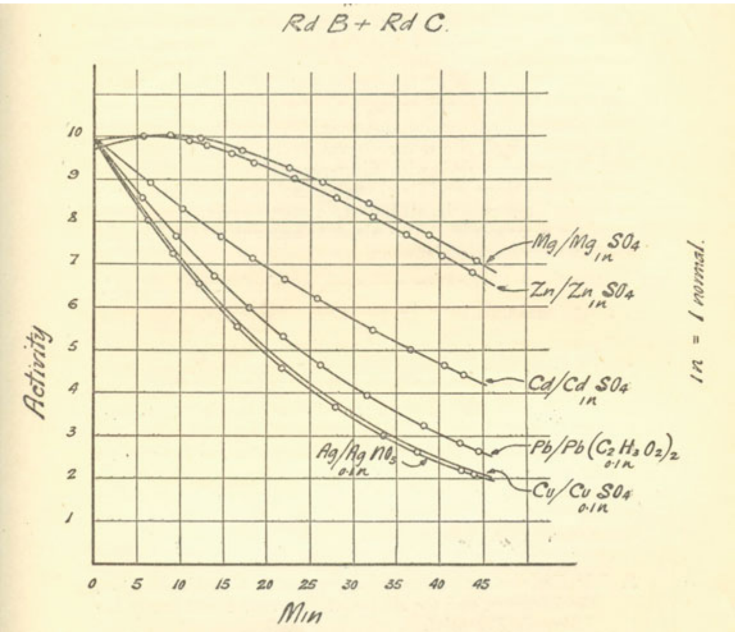


Fig. 12.9 The separation of products B and C and attainment of equilibrium in the radium series as a function of potential established by different metal–metal ion systems [15]

After matriculating at the Gymnasium of Piarist Order, Hevesy studied at Budapest University and Berlin Technical University. He gained his doctor's degree at the University of Freiburg in 1908. He worked in Zürich, in Berlin (with Fritz Haber), in Manchester (with Ernest Rutherford), as well as in Budapest (in the laboratory of Gusztáv Buchböck). He served in the Austrian–Hungarian Army during the war.

Hevesy started as an electrochemist, since the topic of his dissertation was the production of alkali metals by melt electrolysis [12]. He published several electrochemical papers on the electrolytic production of metals [13] but also on several other electrochemical topics, e.g., on the electrocapillarity [14]. Nevertheless, we do not consider him as an electrochemist since he became famous as a discoverer of a new element, hafnium, and especially as a leading person in the area of radioactivity. He studied the electrochemistry of radioactive elements (Figs. 12.8, 12.9, and 12.10) and used the electrochemical techniques successfully also in radiochemistry, ionic diffusion in electrolytes, and metals [15–19]. In 1913, he carried out the first radioactive tracer experiment with Friedrich Adolf Paneth in Vienna [20]. The use of tracer technique opened up new vistas also in electrochemistry. It provided a reliable method to investigate kinetics and equilibrium of electrode processes, e.g., adsorption dissolution, deposition, and underpotential deposition of metals.

By the help of radiotracer technique, he proved the existence of heterogeneous and homogeneous electron transfer reactions [21]. Hevesy with Zechmeister

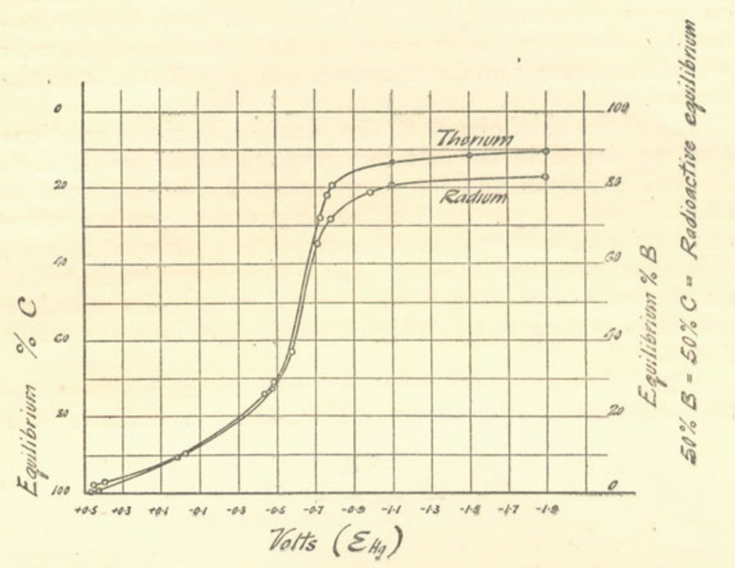


Fig. 12.10 Equilibrium concentrations of thorium and radium as a function of potential [15]

studied the isotope exchange reaction. They used ThB, i.e., ^{212}Pb for labeling. While investigating the Pb(II) acetate–Pb(IV) acetate systems, they concluded that "electrons of ions can directly transfer to isomer ions and also to the electrode and vice versa." [21]. It was a pivotal contribution to the understanding of the electron transfer processes in both homogeneous and heterogeneous systems since at that time only ionic charge transfer was considered as described in the theory of Nernst. It is interesting to note that László Zechmeister (1889, Győr, Hungary—1972, Pasadena, USA) became an internationally recognized scientist in the field of carotenoids and he was one of the founders of the modern chromatography [22]. Hevesy also introduced the concept of self-diffusion [23, 24].

Hevesy became professor of the University of Budapest in 1919. (In fact, he was proposed in 1918, only the appointment occurred in May, 1919.) After the fall of the Hungarian Soviet Republic in autumn that year the appointment was not recognized, and as a punishment, Hevesy's right to lecture as privatdozent was withdrawn. He decided that it was better for him to leave the country which suffered from the so-called white terror and anti-Semitism. We know his motivation from the letters that he wrote in October, 1919 to Niels Bohr: "Politics entered also the University, in my absence this summer two of my assistants absolutely honest and able have been deprived from their posts only because they are Jews and I understand that the same thing happened in nearly all Institutes, hardly anybody who is a Jew or a radical or is suspected to be a radical could retain his post," and to Rutherford: "… political feelings are running extremely high and University affairs have been mixed with politics in a way fully unknown to Western countries." [One of his coworker mentioned by Hevesy was Erzsébet Róna (Budapest, 1890–Oak

Fig. 12.11 The young Michael (Mihály) Polányi

Ridge, 1981) who worked with Fajans, Hahn, Stefan Meyer in Vienna, Iréne Curie, and later participated in the Manhattan Project in Oak Ridge in the United States.]

He went to Copenhagen at Bohr's Institute where he discovered the element hafnium (with D. Coster). In 1926 he became a professor at Freiburg University; however, he left Germany for Copenhagen in 1934. He elaborated the method of neutron activation analysis and prepared ^{32}P isotope which became a very useful indicator in physiological studies. He moved to Stockholm in 1943 and worked at the Stockholm University during the next 23 years. In 1943, he received the Nobel Prize in Chemistry "for his work on the use of isotopes as tracers in the study of chemical processes." After the Second World War, he returned to Germany and worked there until his death on July 5, 1966 in Freiburg im Breisgau.

12.2.5 By a Single Paper in the History of Electrochemistry: Mihály Polányi and the Transfer Coefficient

Mihály Polányi (Fig. 12.11)—similarly to György Hevesy—was not an electrochemist. Originally he was a physician who started to deal with physical chemistry. By the way, to decide who is an electrochemist is not an easy question! If one wants to monopolize, for instance, Faraday, Nernst, or even Volta, other chemists and physicists would be scandalized since the achievements of these great scientists were as important in other fields of science as in electrochemistry; however, we rightly consider them as the founding fathers of electrochemistry. It seems to be plausible that who publishes in electrochemical journals is/was an electrochemist. However, in this way, Einstein would be enrolled in our community since his two papers on the Brownian motion appeared in the *Zeitschrift für Elektrochemie* [25, 26]. Polányi's problem is even more complicated. He published several papers in the *Zeitschrift für Elektrochemie* between 1920 and 1929; however, those are mostly on the adsorption and reaction kinetics [27–37]. On the other hand, he also dealt with electrochemical topics such as conductance, ionic reactions [38, 39], electrolytic production of heavy hydrogen [40], ionization of hydrogen [41, 42], and overpotential [43] electrolytic dissociation [44]. However, he published a paper which played a pivotal role in electrochemistry [45], and it is the very achievement by which Polányi's name can be found in all books devoted to the history of electrochemistry, and it is also cited in books and textbooks in the chapter dealing with the kinetics of electrode processes [10, 46–56]. The title of the paper that appeared in *Acta Physicochimica URSS* (1935) 2: 505, was "*Grundlinien einer Theorie der Protonübertragung*" (Outlines of a theory of proton transfer).

Mihály Polányi was born in Budapest on May 11, 1891. His father, Mihály Pollacsek (the meaning of the name that the family came from Poland) inherited the ownership of a mill in Ungvár (now Uzhhorod, Ukraine) which was very profitable. He got his engineering diploma from the *Eidgenössische Technische Hochschule* in Zürich and worked in the then booming railways constructions. He married Cecilia Wohl, the daughter of the professor of the rabbi seminar in Vilnius (Vilna), in Vienna. She spoke Russian and had many Russian friends. Nevertheless, in the later connection of Mihály Polányi with Russian scientists—I think—this remarkable fact played no role. The family became very rich from railways constructions business; however, in 1899, due to the bankruptcy of both the mill and the railways company, they lost almost all of their wealth. Soon Mihály's father died, and his mother tried to take care of the two younger children, Mihály and Zsófia who still attended grammar school, with the help of the three older children. Polányi studied in the grammar school called Model Gymnasium (later Trefort Gymnasium) which belonged to the Budapest University and was founded by the Mór Kármán, the father of Tódor (Theodor) Kármán. This was one of the best schools; besides Kármán and Polányi, Edward Teller and Tibor Erdey-Grúz graduated in this high school.

Polányi became a Doctor of Medicine at Budapest University in 1913. He chose medicine following the advice of his mother; however, his interest turned to chemistry and physics. He got excellent marks both from Loránd Eötvös and Buchböck. He served as a medical officer during World War I. In the meantime, he worked on the application of quantum theory to the third law of thermodynamics and on the thermodynamics of adsorption. He got his Ph.D. degree from the Chemistry Faculty of Budapest University in 1917 for his work on adsorption. We may tell that he escaped from Hungary averting the possible persecution. Similarly to Hevesy—who invited him to work with him at the Budapest University—he did not participate actively in the events of Hungarian Soviet Republic in 1919, just continued teaching at the university. The fact that his brother was a socialist and of Jewish origin was enough to suffer the attack of the so-called counterrevolutionary forces, and he was dismissed from the University. In 1920 he moved to Berlin, and during the following 10 years, Polányi established himself as one of the leading physical chemists in Germany. In 1920 Polanyi received an appointment to the *Institute of Fiber Chemistry* in Berlin where he dealt with the X-ray diffraction of cellulose fibers. From 1923 he worked in the *Kaiser Wilhelm Institute of Physical Chemistry* in Berlin. Here he carried out fundamental studies in gas kinetics which led to the later work in chemical dynamics. Polanyi started to use contour maps for representing the potential energy of the species participating in chemical reactions. Polanyi with Henry Eyring (1901–1981)—who came from Wisconsin to study with him—worked on the calculation of activation energy using this entirely new approach in 1931 [57, 58]. Later he elaborated the transition state theory with his doctoral student, Eugen P. Wigner (1902–1995, Nobel Prize 1963), and then with M. G. Evans [59–61], the theory which was developed independently also by Eyring in 1935. It is interesting that one of the referees of Wigner's dissertation was Max Volmer (1885–1965) who will appear in our story later.

In 1933 he left Germany and became a professor of physical chemistry at the University of Manchester.

The work by way of which Polányi marched in the history of electrochemistry was, in fact, the application of the reaction rate theory in electrochemistry [45]. The paper that was written with Juro Horiuti (1901–1978) [45] was a milestone in the road that led the modern theory of electrochemical kinetics (Fig. 12.15). Five years earlier, T. Erdey-Grúz and M. Volmer published a paper [62] that provided an interpretation of the rate of electrochemical processes by using the theory of chemical kinetics. Erdey-Grúz and Volmer introduced heuristically a transfer coefficient (α) that was needed to reach an agreement with the experimental results.

The starting point of Horiuti-Polányi paper was the linear relationship between the heat (energy) of activation and the heat (energy) of reaction that had been established by Polányi and his coworkers at that time, which has become known as Polányi's rule [62]. It establishes that for a homologous reaction series, a simple linear relationship exists between the activation energy (Q) and the heat of reaction ($\Delta\chi$):

$$\Delta Q = -\alpha \Delta \chi, \tag{12.1}$$

where α is a proportionality factor (Fig. 12.12).

Today Polanyi's rule is used in the following form:

$$\Delta G^{\ddagger} = \alpha \Delta G \tag{12.2}$$

where $\Delta G^{\ddagger}$ is the Gibbs energy of activation (always positive), and ΔG is Gibbs energy change (which is negative for any spontaneous reaction), and $\alpha < 1$.

It has also been shown that similar reasoning can be used to interpret the relationship between the activation energy and the variation of electrode potential (ε) (Fig. 12.13) as well as between the activation energy and the energy of

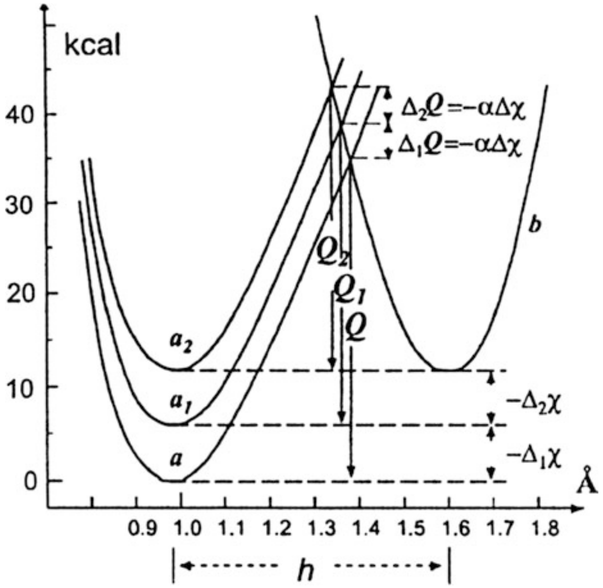


Fig. 12.12 Illustration of the relationship between Q and $\Delta\chi$ from [45]

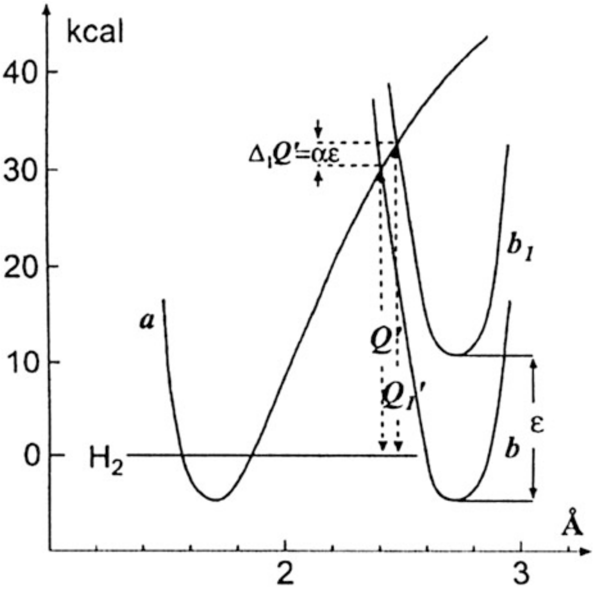


Fig. 12.13 Illustration of the relationship between the energy of activation of ionization/deionization processes (Q) and the electrode potential (ε). Figure 5 of [45]

adsorption (W) (Fig. 12.14). They neglected the dipole character of the Ni–H bond, any change of the electric field causes the increase or a decrease of the energy of hydrogen ions, consequently there will be a perpendicular shift of the parabola **b**, and the horizontal shift is minimal and can be neglected. Therefore it can be written

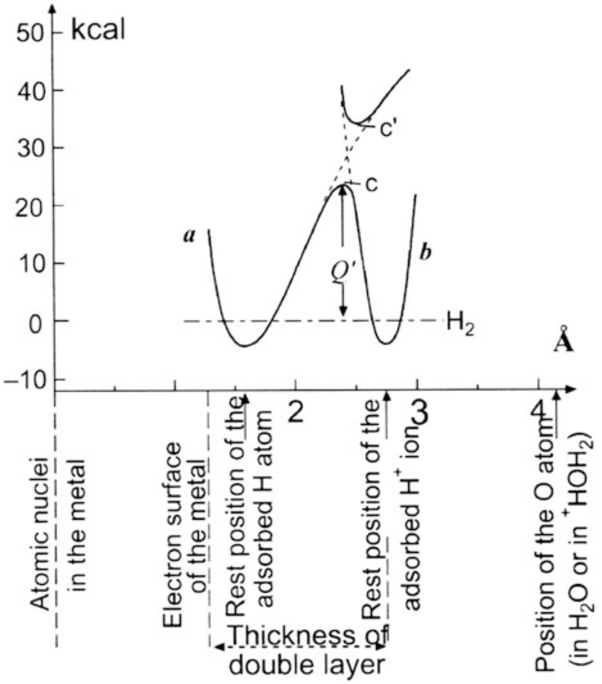


Fig. 12.14 Energy scheme of ionization (and deionization) of hydrogen at a metal surface. Figure 4 of [45]

$$\Delta_1 Q' = \alpha\varepsilon, \tag{12.3}$$

and

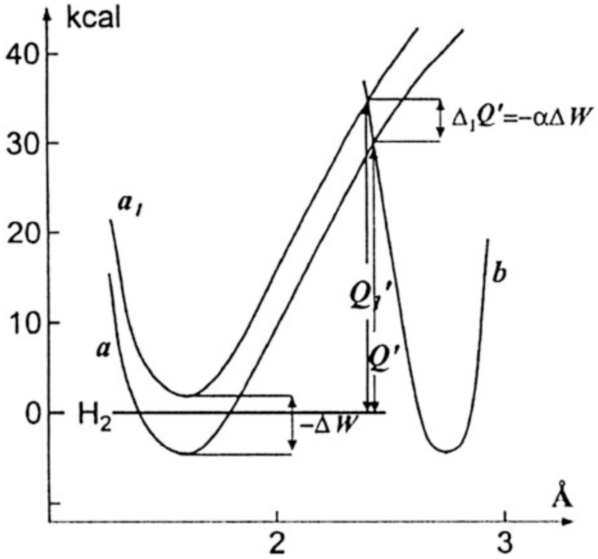
$$\Delta_2 Q = -(\varepsilon - \alpha\varepsilon) = -(1-\alpha)\varepsilon \tag{12.4}$$

It should be mentioned that the use of ε is somewhat disturbing in this paper. The authors defined ε as “full polarization voltage” or “electrode potential”; however, in Figs. 2–5 in the original paper—it is an energy, i.e., correctly $z_i F\ \varepsilon$ should have been written. Similar problems are there in the Eqs. (15)–(18) concerning the place of the F—which is supposedly the Faraday constant because its meaning was not given in the paper—in the kinetic Eqs. (17) and (18) [45]. The difference of the anodic and cathodic partial current was expressed as follows:

$$i = i_1 - i_2 = \text{const}\left(e^{-(\alpha\varepsilon)/FRT} - e^{-((1-\alpha)\varepsilon)/FRT}\right) \qquad (17\ \text{of}\ [40]) \tag{12.5}$$

and at high values of ε, the Tafel equation was obtained

Fig. 12.15 Illustration of the relationship between the energy of activation (Q) and the energy of adsorption of hydrogen atoms (W) [45]



$$\log i = \frac{(1-\alpha)\varepsilon}{FRT} + \text{const} \qquad (18 \text{ of } [40]) \tag{12.6}$$

In the subchapter "Ionization of hydrogen at electrodes: electrolytic deposition of hydrogen," the effect of the metal–hydrogen interaction, i.e., the adsorption of hydrogen was treated in detail. There is an excellent figure which illustrates the potential energy curves (Fig. 12.14). Curve **a** is that of the adsorbed hydrogen atom, i.e., the Ni–H bond. Curve **b** represents the energy of the H atom in the final state, that is, in the coordinate bonding of the complex $^{+}HOH_2$. The straight line labeled "H_2" indicates the energy level of the gaseous hydrogen. They neglected the dipole character of the Ni–H bond, any change of the electric field causes the increase or a decrease of the energy of hydrogen ions, consequently there will be a perpendicular shift of the parabola **b**, the horizontal shift is minimal and can be neglected. Therefore it can be written

$$\Delta_1 Q' = \alpha\varepsilon, \tag{12.7}$$

and

$$\Delta_2 Q = -(\varepsilon - \alpha\varepsilon) = -(1-\alpha)\varepsilon \tag{12.8}$$

The best available data were used by the authors for calculation of distances, the bond lengths, and energies as well as for the activation and reaction heats for constructing the potential energy curves.

The difference in the adsorption energy (called adsorption potential in [45]) is responsible for the different rate of hydrogen ionization at different metal since the energy of activation changes as it was illustrated in Fig. 12.15.

In respect of electrode processes, the ionization and deposition of hydrogen on Ni were carefully analyzed. They considered Frumkin's results on the double layer structure [63, 64] and the nature of the metal. They recognized that practically no specific adsorption exists for H^+ ions; however, the different metals can be characterized in terms of different adsorption energies of the H atom. Polányi also referred to the tunneling effect. The α coefficient that had appeared as a proportionality factor between the activation energy and the reaction energy, in the case of electrode processes established a connection between the energy of activation and the polarization voltage (electrode potential).

A substitution into the rate equation results in a perfect description of the current–potential function, the rest potential (when $i_{\text{cathodic}} = i_{\text{anodic}}$), and the Tafel equation at higher voltages (overpotentials). It has also been realized that $\alpha_c = \alpha_a = 0.5$ corresponds to the situation in which the potential curves of both the initial and final states have the same slope at their point of intersection.

It was evident for Polányi that they found a fundamental relationship since he wrote in their paper: "It is obvious that this relationship can be generalized even further. Its application to reactions which formally can be treated just like the ionogenic reactions is most obvious." Albeit the theory of electrode processes is the most important in the work of Horiuti and Polányi, they also supplied a theoretical foundation for proton transfer including electrolytic dissociation, prototropy, as well as catalytic hydrolysis of esters. Although they mentioned Nernst's theory, they used the recent ideas of Erdey-Grúz and Volmer as well as of Frumkin. (Frumkin was cited as A. Frumkin as it appeared in the title page of *Acta Physicochim. URSS*.)

A new era in electrochemistry has begun by the paper of Horiuti and Polányi. I would encourage everybody to read Polányi's seminal paper. The reader will be charmed by the intellectual accomplishment and the beauty of science as the hidden laws of the nature suddenly come into light.

An interesting fact is that this pivotal work appeared in *Acta Physicochimica URSS*, while most of Polányi's papers were published in German and English journals.

In the early 1930s, Polányi visited the Soviet Union and became friends with Soviet chemists, especially with Alexander Frumkin and Nikolai N. Semyënov (Semenoff, Semyonov, Semenov). Both of them were members of the Editorial Board of *Acta Physicochimica URSS*. Besides Semyënov (Nobel prize in chemistry, 1956) and Frumkin, some outstanding scientists hallmarked this journal, such as J. Frenkel and N. Kurnakov, and later P. Rehbinder and M. Temkin (Tyëmkin) (Fig. 12.16). Polányi published several papers also in other Soviet scientific journals such as in *Uspekhi Khimii* and *Phys. Z. Sowjetunion* in 1932 and 1933. *Acta Physicochimica URSS* published by the Academy of Sciences of the USSR was an excellent foreign-language journal (cost $4/volume), and Polányi certainly

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Grundlinien einer Theorie der Protonübertragung

Elektrolytische Dissoziation; Prototropie; spontane Ionisation und elektrolytische Abscheidung von Wasserstoff an Elektroden; Wasserstoffionenkatalyse

Von *J. Horiuti* und *M. Polanyi*

Die Anschauungen, die wir in der Folge darlegen, stellen die Resultate unserer Theorie in vereinfachter Form dar. Da die Fertigstellung der genauen Ausarbeitung, welche unter Berücksichtigung aller erfassbaren Faktoren auch eine genauere Begründung unserer Vorstellungen darlegen soll, im Hinblick auf den Umfang des Materials, längere Zeit erfordert, mag es berechtigt erscheinen, hier zunächst die Ergebnisse in abgekürzter Form mitzuteilen.

I. Einleitung

Unsere Methode schliesst sich an die allgemeine Theorie ionogener Reaktionen von Ogg und Polanyi[1] an. Diese Theorie ist bisher angewendet worden auf die Reaktionen „von Alkalimetalldämpfen mit organischen Halogenverbindungen[1], sowie auf die Reaktionen von Alkalimetalldämpfen mit den Halogenen[2] und den Halogenwasserstoffen[2], ferner auf die Reaktionen von Na_2-Molekülen mit Halogenatomen[3]. Ausserdem liegen vor Anwendungen auf eine Gruppe von Ionenreaktionen in Lösungen, nämlich auf die elektrolytische Dissoziation und Hydrolyse organischer Halogenverbindungen und auf die Substitution organischer Halogenverbindungen durch Halogenionen[4]. Weitere Untersuchungen über Substitution orga-

[1] Ogg u. Polanyi, Proc. Manchester. Lit. Phil. Soc., 78, 41 (1933–34)
[2] Unveröffentlichte Resultate von Ogg u. Polanyi.
[3] M. G. Evans u. A. G. Evans, Trans. Farad. Soc. im Druck.
[4] Ogg u. Polanyi, Trans. Farad. Soc., 31, 604 (1935)

Б. Б. Дамаскин,
О. А. Петрий

ВВЕДЕНИЕ
В ЭЛЕКТРОХИМИЧЕСКУЮ
КИНЕТИКУ

§ 33. ТЕОРИЯ ЭЛЕМЕНТАРНОГО АКТА
ГОРИУТИ — ПОЛЯНИ

Fig. 12.16 The title page of Acta Physicochimica URSS, the first page of the famous paper [45], and its citation in [48]

knew that his work would reach the right reading public. Unfortunately, this journal fell victim to the political autocracy and the Cold War in 1947.

Interestingly, the impression on the Soviet system led Polányi to publish his first nonscientific work entitled “U.S.S.R. Economics-Fundamental Data System and Spirit” which was issued in Manchester in 1935. This and other works of Polányi caused serious problems to his friends in the Soviet Union. Both Frumkin and Semyënov wrote him asking to stop his attacks on the Soviet economic policy. (These letters can be found among “The Michael Polányi papers” in the Department of Special Collections of University of Chicago Library. Frumkin and Polányi have exchanged 23 letters between 1929 and 1945, while the correspondence with Semyënov amounts 11 letters.) He continued his chemical studies as a professor in physical chemistry; however, from 1936, his interest turned more and more to the economy, philosophy, and social sciences. Eventually, for a great loss of chemistry and for a great gain of social sciences, Polányi finished his activity in science (he published his last chemical articles in 1949), and he became a major figure in several branches of philosophy especially in philosophy of science and political philosophy. Even a new professorship of social sciences was created for him at the University of Manchester where he stayed until he became a Fellow at Merton College Oxford in 1959. He died on February 22, 1976, in Oxford, UK.

From the many readings available about Polanyi’s life and scientific career, two are recommended herein; one is written by Wigner who became a lifelong friend of Polányi [65], and the other by his son, John C. Polanyi (1929–, Nobel Prize in Chemistry 1986) who continued the family tradition regarding the study of reaction


Fig. 12.17 John Polányi and his father

dynamics [66]. Additional information on Polanyi can be found on the Polanyi Society homepage [67].

If Polányi had worked on in the field of physical chemistry it would have resulted in a Nobel Prize in chemistry as a recognition of his achievements in reaction kinetics including electrode processes. It is noteworthy that his son, John C. Polányi (Fig. 12.17) continued the work and received the 1986 Nobel Prize in chemistry "for his contributions concerning the dynamics of chemical elementary processes." The influence of M. Polányi on his son and evidently on many researches including us, electrochemists, is still enormous.

The words of John C. Polányi about his father adequately express it: "I can attest, however, that he sensed this to be a powerful insight into the mechanism of chemical reactions, since he tried, gently but insistently, to persuade me to make it the subject of my research. Like most of the young, I only heard his voice much later. I am, it would seem, among a number who continue to hear it."

12.2.6 *László Szebellédy and the Elaboration of Coulometric Analysis*

Szebellédy (Fig. 12.18) was born on April 20, 1901, in Rétság, a small village in Nógrád county, Hungary. He earned his M.Sc. and Ph.D. degrees from the University of Budapest. He joined the staff of the same university and started to work under the supervision of Professor Lajos Winkler (1863–1939), who among others helped in the improvement of analytical techniques, elaborated a famous method of determination of oxygen by titration which was named after him. Szebellédy became a professor of inorganic and analytical chemistry in 1939. He also worked with W. D. Treadwell in Zürich and with W. C. Böttger in Leipzig. Szebellédy with

Fig. 12.18 László Szebellédy

Fig. 12.19 Antal Végh (1903–1995) also a pupil of Lajos Winkler, later professor of chemistry of pharmacy, Szebellédy, Erdey-Grúz (standing), Pál Villecz, Magda Berg (future wife of Erdey-Grúz), Éva Schömer, Gyula Bund, Mrs. Végh, Katalin Berg

his coworker Zoltán Somogyi (1915–1945) invented the coulometric titration (analysis) in 1938 [68, 69]. He published also seminal papers on catalytic microreactions. He died on January 23, 1944, Budapest after a short illness.

Szebellédy and, our next hero, Erdey-Grúz were the members of the new generation born already in the twentieth century. We can see in Fig. 12.19 the young, promising scientists in a friendly gathering in 1933. Unfortunately, Szebellédy died young, and we can only follow the course of life of Erdey-Grúz including his career in the divided world.

12.3 Transition and Work Behind the “Iron Curtain”

12.3.1 The Younger Father of Electrode Kinetics: Tibor Erdey-Grúz

Erdey-Grúz (Fig. 12.20) was born on October 27, 1902 in Budapest. He came from affluent backgrounds; his father was a deputy state secretary in the Ministry of Defense until the end of 1919. Because his father served also during Hungarian Soviet Republic in 1919, he was fired from the Ministry. As it has already been mentioned, Erdey-Grúz studied the same Model Gymnasium where Polányi did some years earlier. Tibor Erdey-Grúz earned M.Sc. and Ph.D. degrees from the University of Budapest under the guidance of Buchböck (Fig. 12.21).

Having received his Ph.D. degree in 1924, he joined the staff of the same university (Fig. 12.22).

A Very Successful Scholarship in Germany

The laboratory of Max Volmer (1885–1965) in Berlin was the possible best choice of the 28-year-old Erdey-Grúz. Volmer was an excellent scientist. He got his Ph.D. at the institute of Le Blanc in 1910. Working with Otto Stern (1888–1969), they discovered the equation of fluorescence intensity (Stern–Volmer equation). After a

Fig. 12.20 Tibor Erdey-Grúz in 1970s

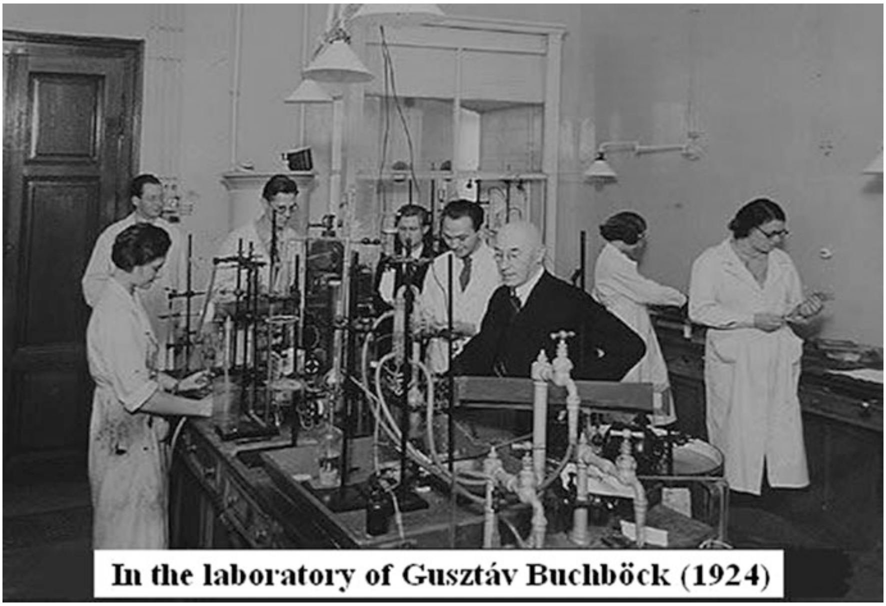
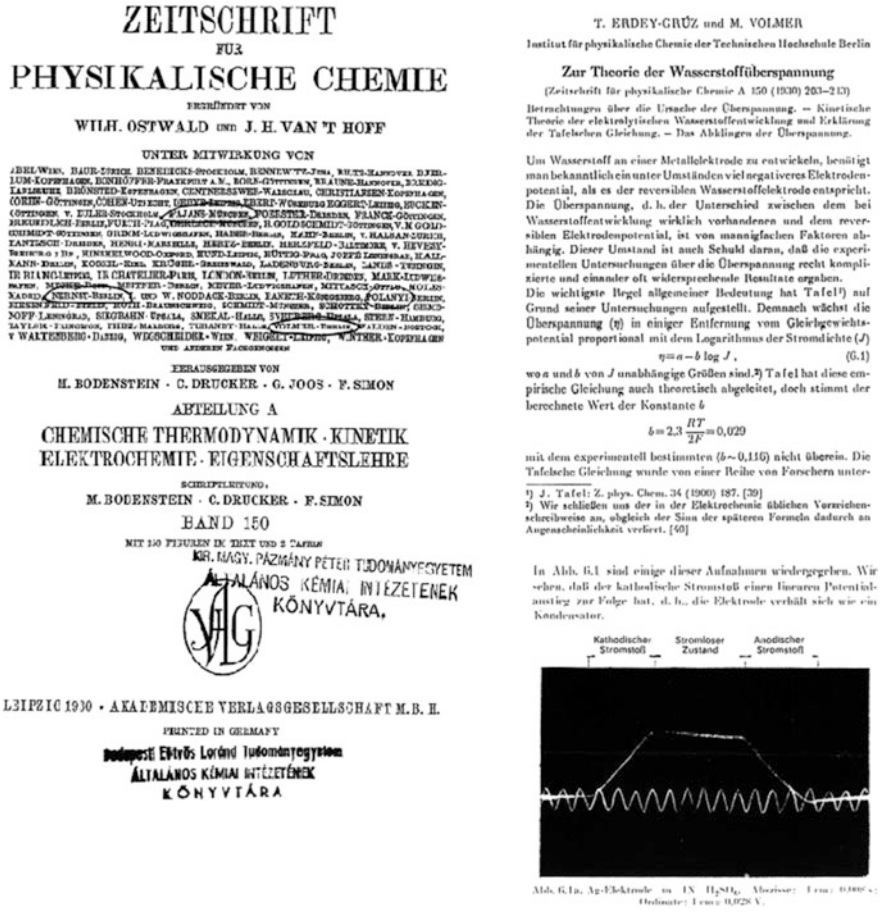


Fig. 12.21 Buchböck and his coworkers, at the rear, close to the door is Erdey-Grúz

Fig. 12.22 Erdey-Grúz works in the laboratory in 1930s

professorship in Hamburg, Volmer became the professor and director of the Physical Chemistry and Electrochemistry Institute of the *Technische Hochschule Berlin* (Berlin-Charlottenburg); the position was previously held by Nernst. In



ZEITSCHRIFT
FÜR
PHYSIKALISCHE CHEMIE
BEGRÜNDET VON
WILH. OSTWALD UND J. H. VAN 'T HOFF
UNTER MITWIRKUNG VON

UND ANDEREN FACHGENOSSEN
HERAUSGEGEBEN VON
M. BODENSTEIN · C. DRUCKER · G. JOOS · F. SIMON
ABTEILUNG A
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MIT 150 FIGUREN IM TEXT UND 2 TAFELN

LEIPZIG 1930 · AKADEMISCHE VERLAGSGESELLSCHAFT M.B.H.
PRINTED IN GERMANY

T. ERDEY-GRÚZ und M. VOLMER

Institut für physikalische Chemie der Technischen Hochschule Berlin

Zur Theorie der Wasserstoffüberspannung

(Zeitschrift für physikalische Chemie A 150 (1930) 203–213)

Betrachtungen über die Ursache der Überspannung. – Kinetische Theorie der elektrolytischen Wasserstoffentwicklung und Erklärung der Tafelschen Gleichung. – Das Abklingen der Überspannung.

Um Wasserstoff an einer Metallelektrode zu entwickeln, benötigt man bekanntlich ein unter Umständen viel negativeres Elektrodenpotential, als es der reversiblen Wasserstoffelektrode entspricht. Die Überspannung, d. h. der Unterschied zwischen dem bei Wasserstoffentwicklung wirklich vorhandenen und dem reversiblen Elektrodenpotential, ist von mannigfachen Faktoren abhängig. Dieser Umstand ist auch Schuld daran, daß die experimentellen Untersuchungen über die Überspannung recht komplizierte und einander oft widersprechende Resultate ergaben.

Die wichtigste Regel allgemeiner Bedeutung hat Tafel[1]) auf Grund seiner Untersuchungen aufgestellt. Demnach wächst die Überspannung (η) in einiger Entfernung vom Gleichgewichtspotential proportional mit dem Logarithmus der Stromdichte (J)

$$\eta = a - b \log J\,, \qquad (6.1)$$

wo a und b von J unabhängige Größen sind.[2]) Tafel hat diese empirische Gleichung auch theoretisch abgeleitet, doch stimmt der berechnete Wert der Konstante b

$$b = 2{,}3\,\frac{RT}{2F} = 0{,}029$$

mit dem experimentell bestimmten ($b \sim 0{,}116$) nicht überein. Die Tafelsche Gleichung wurde von einer Reihe von Forschern unter-

---

[1]) J. Tafel: Z. phys. Chem. 34 (1900) 187. [39]

[2]) Wir schließen uns der in der Elektrochemie üblichen Vorzeichenschreibweise an, obgleich der Sinn der späteren Formeln dadurch an Augenscheinlichkeit verliert. [40]

In Abb. 6.1 sind einige dieser Aufnahmen wiedergegeben. Wir sehen, daß der kathodische Stromstoß einen linearen Potentialanstieg zur Folge hat, d. h., die Elektrode verhält sich wie ein Kondensator.

Fig. 12.23 The title page of *Zeitschrift für Physikalische Chemie* and the first page of the famous paper [62]

1920s, Volmer has published very important papers on the nucleation and growth of new phases as well as on nonpolarizable electrodes.

Erdey-Grúz arrived in Germany in October 1928 with a state scholarship. His study trip that lasted until September, 1931, was very successful. He published very good papers on the problems of hydrogen overvoltage [62, 70], electrocrystallization [71–75], electrode capacitance [76], and at the end of his staying, on adsorption of ions [77] with K. Fajans in Munich.

The paper of Erdey-Grúz and Volmer that appeared in 1930 [62] on the hydrogen overpotential was a seminal one, indeed (Fig. 12.23). It was the first time when the proper relationship between the current and the electrode potential was formulated. This paper can be considered as a landmark since the Nernstian (osmotic) equilibrium theory already hindered the development of electrochemistry. Even almost 20 years later, still the perception of Nernst ruled in the electrochemistry. As Bockris wrote on the occasion of the foundation of the *International Society of Electrochemistry* in 1949: “The atmosphere and background of electrochemistry at this time was dominated by the dead hand of Nernst.” The importance of their contribution has widely been acknowledged. Perhaps Bockris has expressed this view in the most adequate manner [78]: “Erdey-Grúz and Volmer, whom I see as the fathers of electrode kinetics…”

The Breakthrough, the Birth of the Electrode Kinetics

In their pivotal paper entitled “*Zur Theory der Wasserstoffüberspannung*” (“On the theory of hydrogen overvoltage”) [62], Erdey-Grúz and Volmer applied the laws of reaction kinetics and recognized that electrolytic hydrogen overpotential (on the electrodes characterized by large overpotential) was due to the slow neutralization of hydrogen ions which, in turn, was caused by the high activation energy of this process. As shown by Erdey-Grúz and Volmer, the energy of activation can be changed in a controllable manner by varying the potential. The transfer coefficient (α) introduced by them proved to be extremely useful. Based on this kinetic model, the relationship between the reversible (equilibrium) potential and the concentration of the species participating in the electrode reaction, i.e., the Nernst equation, was also derived, and the Tafel relationship [79] was properly elucidated. The essential steps made by Erdey-Grúz and Volmer were as follows.

One of their useful ideas was the splitting of the terms involving the applied potential into two terms, for the anodic (oxidation) and cathodic (reduction) processes, respectively:

$$\frac{J}{F} = k_2 c_+ e^{-\frac{\alpha EF}{RT}} - k_3 c_{\mathrm{H}} e^{+\frac{\alpha EF}{RT}} \tag{12.9}$$

where J is current, F is the Faraday constant, k_2 and k_3 are the rate constants of the neutralization of the hydrogen atom and the ionization of the hydrogen, respectively, c_+ and c_{H} are the concentrations of the hydrogen ions and the hydrogen at the electrode surface, E is the electrode potential, α is the transfer coefficient, R is the gas constant, and T is the thermodynamic temperature.

At equilibrium, i.e., at the reversible potential (E_{r})

$$\frac{J}{F} = k_2 c_+ e^{-\frac{\alpha E_{\mathrm{r}} F}{RT}} - k_3 c_{\mathrm{H}} e^{+\frac{\alpha E_{\mathrm{r}} F}{RT}} \tag{12.10}$$

At overpotential η,

$$J = F k_2 c_+ e^{-\frac{\alpha (E_r + \eta) F}{RT}} - F k_3 c_{\mathrm{H}} e^{+\frac{\alpha (E_r + \eta) F}{RT}} \tag{12.11}$$

At high negative η, $\eta > -0.03$ V,

$$J = Fkc_{+}e^{-\frac{\alpha\eta F}{RT}} \tag{12.12}$$

It soon became clear that the relationships derived from the above concept for the hydrogen overpotential constitute the general basis of the theory of electrode processes with charge transfer as rate-determining step.

Nowadays in most books and papers, the following equation is called Butler–Volmer equation:

$$j = j_{\mathrm{o}}\left\{-\exp\left[-\frac{\alpha_{\mathrm{c}}F\eta}{RT}\right] + \exp\left[\frac{\alpha_{\mathrm{a}}F\eta}{RT}\right]\right\}, \tag{12.13}$$

which gives the description of the polarization curve when the charge transfer step is very sluggish, the standard rate coefficient, $k^{\ominus}$, and the exchange current density, j_{o}, are very small, and large activation overpotential is needed to drive the reaction in any direction. In this case, the anodic and cathodic reactions are never simultaneously significant. This type of kinetics is called irreversible or quasi-reversible in electrochemistry. It is easy to recognize that a linear Tafel plot can be obtained only in this case. This equation is practically identical with the respective equation derived by Erdey-Grúz and Volmer.

R. de Levie [80] wrote: "Erdey-Grúz and Volmer were the first to do this, in 1930, when they derived the corresponding rate expression in a paper on the kinetics of the hydrogen electrode. Recently, this basic law of electrode kinetics has become known as the Butler–Volmer equation. Butler was a leading British electrochemist, who had indeed attempted to find an answer to this question. Butler did not find it. In fact, in his 1940 book on electrocapillarity, Butler specifically refers to Erdey-Grúz and Volmer in this respect. The first time that the name of Erdey-Grúz was replaced by that of Butler appears to be in the 1970 textbook by Bockris and Reddy [81], but it may have an earlier origin. At any rate, subsequent textbook authors simply copied it…".

It is somewhat surprising that Bockris—who recognized the pioneering work of Erdey-Grúz and Volmer—started to use Butler's name and later left out Erdey-Grúz. In his book of 1967, Butler was not mentioned [82]. In his next work, Bockris mentioned that Butler made an attempt to use the kinetic approach regarding the potential dependence of current density (which is in fact incorrect), but the adequate description appeared first in the paper of Erdey-Grúz and Volmer [50]. In 1977, Bockris used the expression that "Butler–Volmer–Erdey-Grúz theory" [50], which determined the post-Nernstian electrochemistry. Most likely three names were too many, and the name of the equation was simplified as Butler–Volmer equation, which was used by Bockris [51] and other authors later on. It is even strange that in the book [51], the name of the chapter is "The Butler–Volmer Equation," however, it starts as follows: "That an exponential relation exists between the shift of the electrode potential from that corresponding to equilibrium to that corresponding to a given rate was established experimentally by Tafel and rationalized properly for the first time by Erdey-Grúz and Volmer in 1930."

In Russian books, the names of Erdey-Grúz and Volmer as well as Frumkin were mentioned in this respect [48]. In a book of French authors, the title of the respective chapter is as follows: "The Theories of Erdey-Gruz, Volmer and Audubert" [49].

In another widely used book [83], it is written that the "slow discharge theory was suggested by Erdey-Grúz and Volmer." Butler was mentioned among the actors who contributed to the further developments, the authors cited a paper of Butler from 1936 [83]. Laidler [53] mentioned only the names Tafel, Erdey-Grúz, and Volmer at the early history of kinetics of electrode processes. Albeit such practice is not unique in the scientific literature, that is theories, equations, and methods were named after scientists working in that field but did not play real role in the establishment of the given achievements. Therefore, in this case, the usage of the name: Erdey-Grúz–Volmer equation has to be proposed.

Erdey-Grúz and Volmer published another important paper in 1931 entitled "*Zur Frage der elektrolytischen Metallüberspannung*" ("On the question of electrolytic overvoltage of metals") [71]. In this paper, they applied the recognition made by them in the previous year, i.e., when the neutralization of the metal ions is the rate determining, the explanation that was given for the slow discharge of hydrogen ions is also valid, and the dependence of the overvoltage on the current density is the same.

Albeit both Volmer and Erdey-Grúz became the president of the respective national academies, their roads leading to it were diagonally different.

While Volmer was not a follower of the Nazi system, and consequently e.g., his election to the Prussian Academy of Science was blocked, he had to spend 10 years in the Soviet Union after 1945. He was "invited" as several other German scientists to the USSR. He worked on deuterium production and nuclear waste processing in the research group of Gustav Hertz (1887–1975, Nobel prize 1925). As many other colleagues, he was released in 1955 and was permitted to return to GDR. He became professor of physical chemistry at Humboldt University (East-Berlin) and president of the East-German Academy of Sciences between 1956 and 1958.

Erdey-Grúz published several papers on electrode kinetics and structure of electrolytes. He also dealt with catalytic hydrogenation [84]. However, after the change of the system, from 1949, his articles almost entirely appeared in Hungarian journals.

Erdey-Grúz wrote several textbooks and books, two of those were excellent compilation of the knowledge on the transport processes [85] and on electrochemical kinetics [47] (Fig. 12.24).

He joined the Party after the change of the system; however, he did not renew his membership after 1956. (The party means the ruling communist party, however, with changing names, such as Hungarian Democratic Party after the forced unification of the communist, the social democratic and the peasant parties in 1950, and after 1956 Hungarian Socialist Workers' Party.) It is not easy to explain why he became a member of the Party and accepted high positions even during the period of the worst years of the system. He became Minister of Higher Education in 1952 and then the Minister of Education between 1953 and 1956. He was the member of the Parliament between 1953 and 1957. It is reasonable to assume that he wanted to defend his family (they had three children), and he wanted to continue his teaching

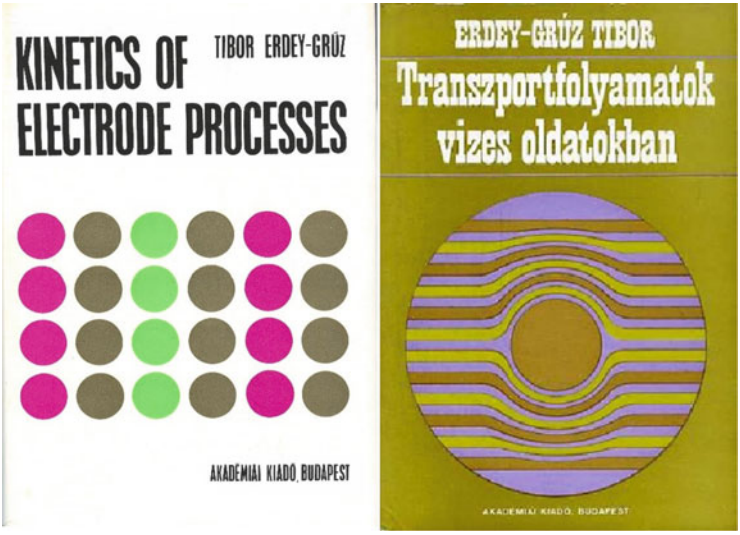

Fig. 12.24 The two most known books of Erdey-Grúz [47, 85]

and research. In fact, they were in danger since the family owned a house in Budapest and also a pharmacy. Albeit those were nationalized with no compensation according to the new laws that were imposed first in 1946 that related to the most important factories, mines, banks, etc. until 1949 when even the small enterprises became involved. However, usually the loss of property was not the only consequence, many of the previous owners were declared to be "capitalists" or because of their high position before the war to enemies of the people, and were expelled from their previous position, sent to the countryside to carry out physical work, or even they were jailed. Erdey-Grúz had a rather introverted personality, he had not revealed the reasons why he became a member of the party and accepted all these high positions in politics. Another professor who was his friend said that albeit they never talked about it, he thought that Erdey-Grúz truly believed that the new system was better than the previous one which maintained social inequalities, entered the war that eventually led to the complete devastation of the country.

Erdey-Grúz was not only an enthusiastic teacher and a successful researcher but he was also very active in the organization of science and education. In fact, the latter were his duties as a minister and at the Hungarian Academy of Sciences. He was the editor in chief of the *Magyar Kémikusok Lapja* (*Journal of Hungarian Chemists*) in 1946, later he held the same position at the *Magyar Kémiai Folyóirat* (*Hungarian Chemical Journal*) between 1949 and 1976.

He has worked for the University of Budapest (presently Eötvös Loránd University, Budapest) from 1941 as an extraordinary and from 1947 as a full professor. He officially retired in 1972, but he continued his research activity. He became a corresponding member of the Hungarian Academy of Sciences in 1943 and a member in 1948. He was the secretary-general of the Academy between 1950

Fig. 12.25 Ernő Pungor (Courtesy of András Pungor)

and 1953, 1956 and 1957, and between 1964 and 1970. He was the president of the Academy from 1970 until his death on August 16, 1976, in Budapest.

12.3.2 The Development of Ion-Selective Electrodes by Ernő Pungor

Ernő Pungor (Fig. 12.25) was born in a peasant family in Vasszécsény (a small village close to the Hungarian–Austrian border) on October 30, 1923.

Pungor studied chemistry in the University of Budapest (then Pázmány Péter University, since 1950 Eötvös Loránd University), where he received his M.Sc. and Ph.D. degrees. He joined the staff of the same university in 1948 and worked there until 1962, when he became the professor of Analytical Chemistry at the University of Veszprém (Fig. 12.26). Pungor introduced the instrumental methods in analytical chemistry in Hungary. In 1970, he was appointed to the Chair of the Department of General and Analytical Chemistry at the Technical University, Budapest. This position was held until his retirement in 1993; however, henceforward he worked as a professor emeritus as well as the director of Bay Zoltán Institute for Applied Research until his death on June 13, 2007, Budapest. He served as the Minister of State responsible for the research and development in Hungary between 1990 and 1994. He became a corresponding member of the Hungarian Academy of Sciences in 1967 and member in 1976. His pioneering work in electroanalytical chemistry was distinguished, among others, with the Hanus Medal, Robert Boyle Gold Medal, and Talanta Gold Medal. He is best known for the development of ion-selective electrodes [86–89] (Fig. 12.27).

Pungor made other important contributions to analytical chemistry, especially to oscillometry and conductometry [90], hydrodynamic voltammetry (flow-cell, flow analysis) [91] (Fig. 12.28), coulometric analysis (coulometric titration) [92], and flame photometry [93] (Fig. 12.29).

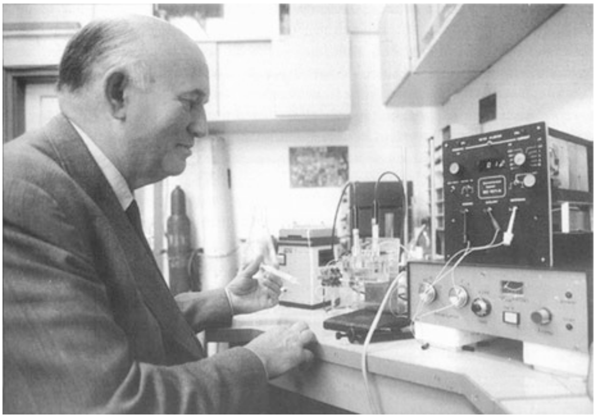

Fig. 12.26 Ernő Pungor in his laboratory in the 1960s

SZABADALMI OKIRAT

AZ ORSZÁGOS TALÁLMÁNYI HIVATAL

152.106

Dr.PUNGOR Ernő egyetemi tanár, budapesti,
HAVAS Jenő okl.vegyészmérnök, fűzfői,
TÓTH Klára egyetemi tanársegéd,veszprémi és
MADARÁSZ Géza okl.vegyészmérnök,fűzfői lakosok

Heterogén felépitésü szelektiv
membránok és eljárás azok előállitására

1963.julius 22.

julius 22.

Budapest 1966. március 28.

ORSZÁGOS TALÁLMÁNYI HIVATAL

/:Tasnádi Emil:/
ELNÖK

ÜBER DIE ANWENDUNG VON MEMBRANELEKTRODEN
BEI DER UNTERSUCHUNG
VON IONENKONZENTRATIONEN

E. Pungor und E. Hollós-Rokosinyi

(Institut für Anorganische und Analytische Chemie der L. Eötvös Universität, Budapest)

Eingegangen am 17. November 1960

In der neueren Literatur begegnet man oft solchen Bestrebungen, die die Herstellung solcher Membranelektroden nach der Form der Glaselektroden bezwecken, die unmittelbar für die Messung der Ionenaktivität bzw. als Bezugselektroden bei potentiometrischen Titrationen angewandt werden können. Solche, für die Messung verschiedener Ionen geeigneten Elektroden können aus anorganischen oder organischen Niederschlägen bzw. aus Ionenaustauschharzen hergestellt werden.

Die Membranelektrode ist eigentlich ein Glasrohr, das am einen Ende mit einer Membran versehen ist. Im Glasrohr befindet sich meistens eine verdünnte Lösung des zu messenden Elektrolyts, eventuell eine Kaliumchloridlösung als innerer Elektrolyt, in den eine Elektrode zweiter Ordnung eingesetzt wird. Das Potential der auf diese Weise hergestellten Membranelektrode wird meistens gegen einer anderen Elektrode zweiter Ordnung, manchmal gegen einer Kalomelelektrode gemessen. Für die Herstellung der Membrane werden in der Literatur verschiedene Verfahren empfohlen.

Nach Shonets und Klebs [1] kann eine Niederschlagmembrane durch Schmelzen des Niederschlages zu Scheibchen von einigen mm Dicke hergestellt werden. Solche, aus 50% Silberjodid und 50% Silberbromid bzw. 90% Silberjodid und 10% Silbersulfid bereitenen Scheiben wurden mittels Piceins am Ende des Glasrohres befestigt. Eine Kaliumchloridlösung diente als innerer Elektrolyt, in den eine Silber-Silberchlorid Elektrode eingetaucht wurde. Die so bereiteten Membranelektroden wurden bei der potentiometrischen Titration von Silber- bzw. Halogenionen angewandt.

Bei ihren ersten Versuchen bereiteten Fischer und Babcock [2] Membrane durch Kompression von Bariumsulfat. Nachdem dieses Verfahren ungeeignet war, stellten sie am Ende des Glasrohres in etwa 1 mm dicke Paraffinschicht eingebettete Membrane her, mit denen sie die Aktivität von Barium- bzw. Sulfationen maßen.

Tendeloo und Krips [3] stellten gleichfalls in Paraffin verteilte Calciumoxalatmembrane mit Zugabe von Arlacel 85 her. Diese Elektrode wurde bei der Bestimmung der Aktivität des Calciums angewandt. Wird Calciumoxalat durch

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Fig. 12.27 The patent and the first paper [86] of the first ion-selective electrode

While Pungor was not a party member during the socialist period, he could carry out his teaching at universities and his research. As we have already seen, the party and the government, which was closely associated with the party, allowed the talented people to work if they were not openly against the system. Even they wanted to show to other nations that it was a democratic system, at least in Hungary no communist

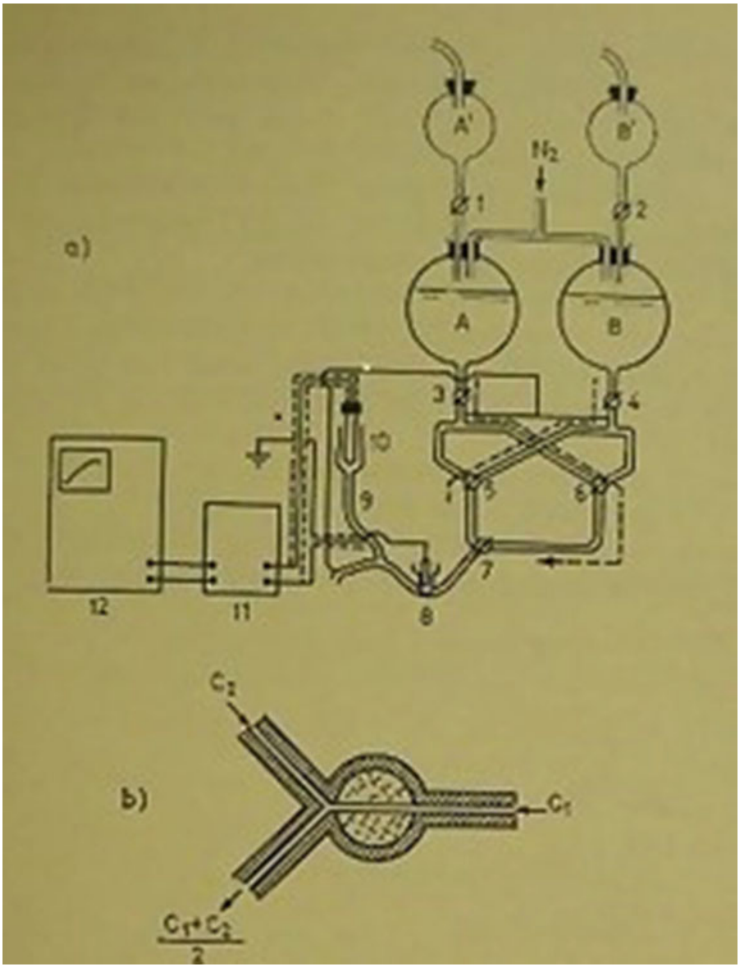


Fig. 12.28 Drawing of the flow-cell

dictatorship existed. In fact, as a result of the uprising in 1956, from the 1960s, it was a benign dictatorship, which was called as “goulash communism.” Pungor also became the head of several important committees, e.g., which decided about the distribution of the expensive instrumentation. He supported the firm Radelkis which produced ion-selective electrodes, pH meters, potentiostats, etc. However, Pungor was not involved directly in politics until the change of the system in 1990.

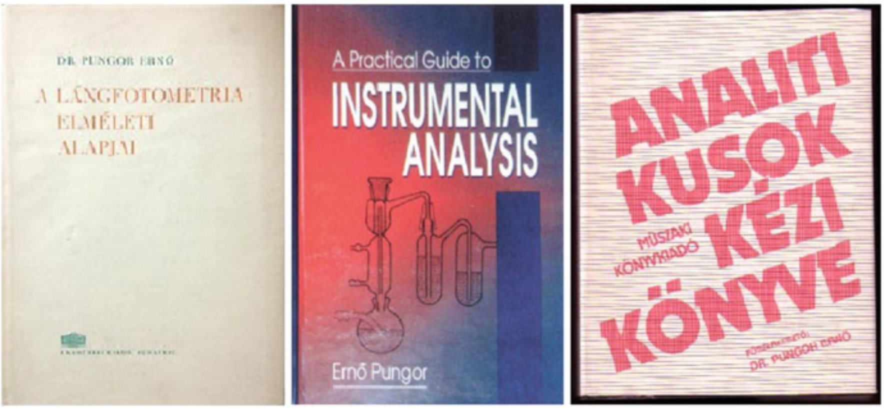


Fig. 12.29 Pungor's books on flame photometry, instrumental analysis, and handbook in analytical chemistry

Fig. 12.30 György Horányi

12.3.3 Application of In Situ Radiotracer Method to Study Electrosorption and Electrocatalysis by György Horányi

György Horányi (Fig. 12.30) was born on July 18, 1934, Budapest. As a child, he survived the persecution during the Second World War. After graduating in a chemistry technical high school, he continued his studies at the Eötvös Loránd University, Budapest, where he graduated in chemistry in 1958 [94]. Although he remained in close contact with the university as a lecturer, later a titular professor, in 1961 he joined the Central Research Institute for Chemistry of the Hungarian Academy of Sciences (RICHAS). Erdey-Grúz invited him to work at the Department of Physical Chemistry. He moved to the university in 1975; however, after the death of Erdey-Grúz, eventually he did not get the professorship. The Party opposed

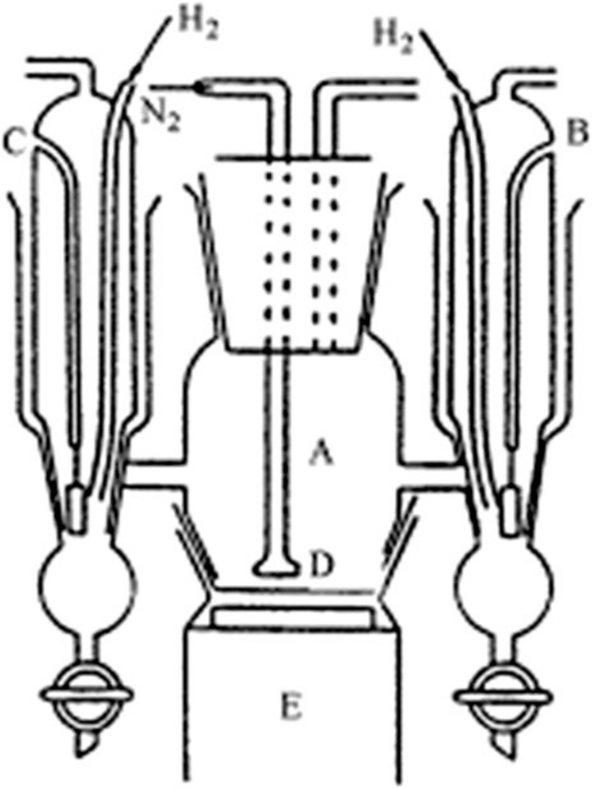


Fig. 12.31 Cell for electrochemical radiotracer experiments with a thin-foil electrode constructed by Horányi in 1971 [94]. Central compartment (A), auxiliary electrode (B), reference electrode (C), working electrode (D), and scintillation counter (E)

it because of his criticism of the system, and the trade union was used to achieve the purpose. They claim that it would cause a "salary tension" if his coworker, Edit Rizmayer—to whom Horányi insisted and it was promised earlier—also would have been hired by the university since at that time the salaries at the research institutes were somewhat higher than at the universities. He maintained his laboratory in the university campus; however, he remained in the staff of RICHAS. (It was a general policy after the uprising in 1956 that scientists were allowed to work—even they were "untrustworthy" politically—in research institutes but not in daily contact with the students at the higher education.)

He developed an in situ radiotracer technique which is called thin-foil radiotracer method [95, 96] (Fig. 12.31). It has been proved to be a very powerful tool for the investigation of electrosorption and electrocatalytic phenomena at solid electrodes, ionic exchange processes in polymer-modified electrodes, and electrochemical oscillations [97–99] (Figs. 12.32, 12.33, and 12.34).

Besides the application of radiotracer labeling, he has studied many systems with traditional and other combined electrochemical techniques [100–104]. Some of his results are considered fundamental ones, e.g., the application of nickel oxide electrodes for the oxidation of organic species, open-circuit electrochemical

A kémia
újabb
eredményei
1971

Szabó Zoltán • Márta Ferenc
Inhibiciós jelenségek gázreakciókban

Nagy Ferenc • Horányi György
A vizesfázisú kontakt
katalitikus hidrogénezés mechanizmusa

Fejes Pál
A kemiszorpció elektronelmélete
és reakciókinetikai jelentősége

Akadémiai Kiadó • Budapest

INTERFACE SCIENCE AND TECHNOLOGY

Radiotracer Studies
of Interfaces

G. Horányi
Editor

Fig. 12.32 Horányi's monograph on catalytic hydrogenation and a book edited by him [96]

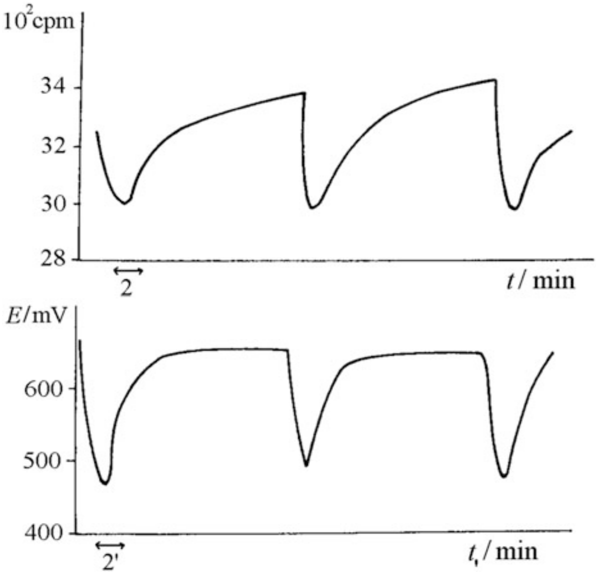
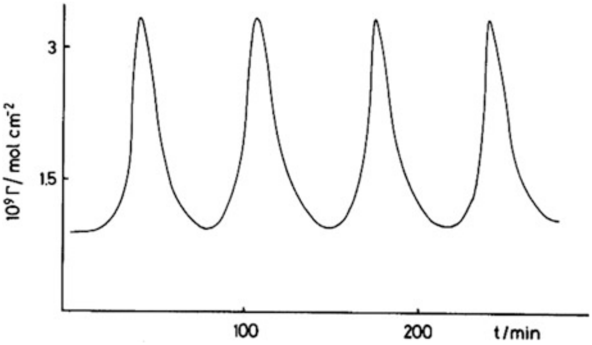


Fig. 12.33 Simultaneous changes of the radiation intensity (cpm) proportional to the amount of adsorbed chloride ions and the electrode potential (E) with time during galvanostatic ($I = 0.3$ mA) potential oscillations. Electrolyte: 0.4 mol dm^{-3} glyoxal, 1 mol dm^{-3} $HClO_4$, and 10^{-4} mol dm^{-3} ^{36}Cl labeled HCl [99]

Fig. 12.34 The changes of the surface concentration of labeled chloride counterions sorbed in a polypyrrole film calculated from the radiation during consecutive voltammetric cycles. Electrolyte: 2×10^{-4} mol dm^{-3} ^{36}Cl labeled HCl



oscillations proving that the periodic changes are in connection with the nature of the electrochemical reactions and not with the electrical circuit reduction of perchlorate and nitrate ions, reductive splitting of C–OH and C–Cl bonds, the application of tungsten carbide as a hydrogenation catalyst, and the clarification of the properties of platinized platinum electrodes. He extended the application of radiotracer technique to the investigation of powered oxide surfaces. These studies contributed to the better understanding of the overall adsorption phenomena in the course of corrosion and constituted a link between electrochemistry and colloid chemistry.

He had a deep and wide knowledge in electrochemistry. He was always helpful but also critical if he found something wrong scientifically. He published the first paper criticizing the validity of the cold fusion as reported by Fleischman and Pons. He sent the manuscript to the Journal of Electroanalytical Chemistry where the first report on cold fusion appeared with unusual advertising in the cover. However, it was rejected. Eventually, it appeared in the same year in Electrochimica Acta [105].

Although he was very stern in scientific and moral matters, he was the most benevolent and supporting person. If I think of Professor Horányi, a saying of Juvenalis comes to my mind: "Vitam impendere vero." It can be translated as "To dedicate one's life to truth." In the last 50 years, he has fought for the improvement and justice especially in the scientific life. He fought for the reform of the Hungarian Academy of Sciences. The prevailing potentates never and nowhere liked it. He maintained his critical attitude toward the actual politics in Hungary even after the change of the system in 1990. When the extremist right-wing movement appeared in the early 1990 and there was a danger that they could seize the power within the ruling right-wing coalition, he took part as one of the founding members of the civil organization called Democratic Charter and acted as one of the spokesmen of the movement from the very beginning. He donated the archives of Democratic Charter to Open Society Archives in the summer of 2002. He passed away on September 3, 2006 in Budapest.

The history teaches us that the struggle of brave men is not in vain and serves as an example for the next generations which eventually leads to a better world.

We have seen that several outstanding scientists left Hungary in 1920s; then in 1940s, before the war and after the war; and also after 1956. We have already mentioned from the first wave of emigration Hevesy, Kármán, Polányi, Wigner but, for example, Dénes (Dennis) Gábor (Nobel Prize 1971), Leo Szilárd, Ede (Edward) Teller, and János (John) von Neumann also belonged to this group. It is interesting that albeit these scientists became famous in physics and mathematics, many of them started to study chemistry, e.g., Szilárd and Neumann listened the lectures of Nernst and Haber in Berlin. Albert Szent-Györgyi (Nobel Prize in 1937) and György (George) Békésy (Nobel Prize in 1961) left the country in 1947. Zoltán Bay emigrated in 1948. He worked with Max Bodenstein and used electrochemical method, a hydrogen coulometer, in his lunar radar experiment. György (George) Oláh (Nobel Prize 1994) left Hungary in 1956. There were also electrochemists or future electrochemists among the emigrants. For instance, I mentioned Gileadi and Tobias among the participants of the ISE Meeting that was held in Budapest in 1978. Eliezer (György) Gileadi was born in Hungary in 1932 and escaped as a child from Hungary to Israel. It was a surprise for me that both Gileadi and Tobias still spoke Hungarian without any accent. Charles (Károly) W. Tobias (1920–1996), who is considered as the founding father of electrochemical engineering, left Hungary after obtaining his Ph.D. from the Technical University, Budapest in 1946. He was a postdoc at the University of California, Berkeley, then an assistant professor in 1950. He became a full professor in 1960, and served as president both of the Electrochemical Society (1970–1971) and the International Society of Electrochemistry (1977–1978).

We can imagine that what Hungary (and other countries in this region because similar emigration took place from other countries) lost by the emigration of these excellent scientists both in respect of research and education of the next generation.

There was a saying in Hungary: “I stay in the country because of love of adventure.” Of course, the motivation of the emigrants are understandable, because of the persecution of different sorts, the lack of research opportunity, the low life standard, and other reasons, but we have to express our thanks to those who stayed in Hungary, and despite all difficulties maintained a high level science including electrochemistry education, and could contribute the development of electrochemistry.

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Chapter 13
Contributions from Electrochemists in Bulgaria

Alexander A. Milchev

13.1 Zakhari Velichkov Karaoglanov

Zakhari Karaoglanov (Fig. 13.1.1) was born on 24 June 1878 in the city of Shumen, Bulgaria, in an artisan's family. He finished his secondary school education in the State Boy's School "Prince Ferdinand I" in the city of Varna and received an "Excellent Rate" Certificate on 29 June 1898. After working for 1 year as a teacher in the village of Brest[1], Nikopol region, Z. Karaoglanov studied chemistry at the Faculty of Physics and Mathematics of Sofia University where he graduated in 1902 and was appointed teacher in Sofia Classical Gymnasium.

Specializing for 2 years in Leipzig University under the supervision of Wilhelm Ostwald, in December 1907 Z. Karaoglanov was appointed assistant in chemistry at the Faculty of Physics and Mathematics of Sofia University. In 1910 he was elected docent and since 1911 was already a lecturer in analytical chemistry (Fig. 13.1.2). In 1920 Z. Karaoglanov was elected professor, and being a member of the Bulgarian Chemical Society, he was elected also member of the first editorial board of its journal *Chemistry and Industry* in 1922.

Zakhari Karaoglanov worked intensively in the field of inorganic and analytical chemistry as well as in electrochemistry and published a large number of scientific papers in national and international scientific journals. His most significant and worldwide recognized scientific achievement consists in the derivation of the chronopotentiometric formula for the electrode potential E [1, 2] when a constant current is applied to an electrochemical system containing *Red* species, transported

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[1] The Bulgarian word "brest" means "elm."

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Fig. 13.1.1 Zakhari V. Karaoglanov (1878–1943)

Fig. 13.1.2 Chemistry lecturers and students at the Sofia High School, 1914. Zakhari Karaoglanov, first from the *left*, sitting; Asen Zlatarov, first from the *left*, upright

to the electrode surface by planar diffusion (see also [3, 4] and the references cited therein):

$$E = E^{\mathrm{h}} - \frac{RT}{nF} \ln\left(\sqrt{\frac{\tau}{t}} - 1\right)$$

In this formula E^{h} is the Nernst halfway potential, n is the electron number, and $\tau = \pi D_{\mathrm{R}} \left(nFAc_{\mathrm{R}}^{\mathrm{b}}/2I\right)^2$ is the so-called *transition time*, D_{R} and $c_{\mathrm{R}}^{\mathrm{b}}$ being the diffusion coefficient and the bulk concentration of the reduced species, respectively, A being the electrode surface area, I being the current, and F, R, and T having their usual meanings.

Z. Karaoglanov was elected Rector of Sofia University in 1922 and in 1932 and was also head of its Analytical Chemistry Department till the end of his life on 21 June 1943. Readers may find valuable and more detailed information on Zakhari Karaoglanov and his scientific achievements in [5, 6].

13.2 Ivan Nikolov (Nikola) Stranski

Ivan Nikolov (Nikola) Stranski (Fig. 13.2.1) was born on 2 January 1897 in Sofia, Bulgaria. His father Nikola Ivanov Stranski was a court pharmacist and dentist. His mother Maria Krohn was a German, from the Baltic part of the country. The family name *Stranski* comes from the Bulgarian word *strannik* meaning *stranger* or *foreigner*.

Ivan Stranski finished the primary and secondary school in Sofia and then studied chemistry in Vienna and in Sofia University where he graduated in 1922. In the same year Stranski joined the *Friedrich-Wilhelms-Universität* (since 1946

Fig. 13.2.1 Ivan Nikolov (Nikola) Stranski

Humboldt-Universität) in Berlin and till 1925 worked on his doctoral thesis on X-ray structural analysis under the supervision of Prof. Paul Günther.

In 1926 Ivan Stranski was elected docent in the Chemistry Faculty of Sofia University; in 1929 he was elected associate professor and in 1937 a full professor (Figs. 13.2.2 and 13.2.3). He was the first lecturer in physical chemistry at the Sofia University, and here it is necessary to mention also the names of his co-workers and later close friends Rostislav Kaischev and Lubomir Krastanov.

Fig. 13.2.2 Ivan Stranski (first row, second from the *right*) and Rostislav Kaischev (last row, first from the *right*) with professors and assistants of Sofia University in front of the Chemistry Faculty (early 1930s)

Fig. 13.2.3 Ivan Stranski giving a lecture in the Chemistry Faculty of Sofia University (middle 1930s)

In 1930 Stranski received a Rockefeller fellowship and worked with Max Volmer in the *Technische Hochschule* (now *Technische Universität*), Berlin. In 1935 he joined the Ural Physical-Technical Institute in Sverdlovsk, Russia (at that time Soviet Union), and developed, together with E. K. Paped, the method of growing metal single crystals from a vapor phase.

Invited by Walther Kossel, in 1941 Ivan Stranski left Bulgaria for Germany and worked firstly at the University of Breslau (now Wroclaw, Poland) and then at the *Kaiser-Wilhelm-Institut für Physikalische Chemie und Elektrochemie* in Berlin-Dahlem (now *Fritz-Haber-Institut der Max-Planck-Gesellschaft*). In 1945 Stranski was elected director of the Institute of Physical Chemistry at the *Technische Hochschule* (now *Technische Universität*) of Berlin and was a rector and a vice rector of this University during the period 1951–1953. In 1953 he joined the *Freie Universität* of Berlin and worked there till 1963, and in 1954 he became also a deputy director of the *Fritz-Haber-Institut*.

Ivan Stranski was elected foreign member of the Bulgarian Academy of Sciences (BAS) in 1966 when Lubomir Krastanov and Rostislav Kaischev held the positions president and vice president of BAS. In 1969 Stranski participated in the celebration of the 100th anniversary of the Bulgarian Academy of Sciences in Sofia, and later he visited his father's country several times (Fig. 13.2.4).

Certainly, the most important contribution of Ivan Stranski to the modern theory of nucleation and crystal growth phenomena is the definition of the concept *half-crystal position*. The concept was defined simultaneously and independently by Walther Kossel [7] and Ivan Stranski [8, 9] (Fig. 13.2.5) in 1927, and the reader may find more information on this unique coincidence of bright scientific ideas in [10].

Fig. 13.2.4 Rostislav Kaischev, Ivan Stranski, and Lubomir Krastanov in R. Kaischev's study at the Institute of Physical Chemistry, BAS, 1975

Fig. 13.2.5 Walther Kossel and Ivan Stranski, Germany, the 1950s

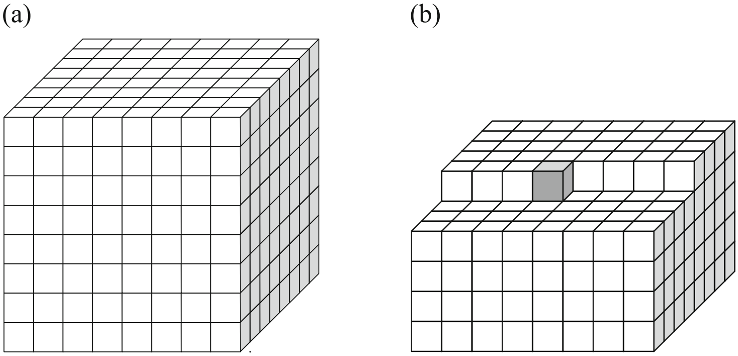

Fig. 13.2.6 Kossel's cubic crystal (**a**) and the atom in the "half-crystal position" (**b**) [10–12]

In an infinitely large crystal (Fig. 13.2.6), the atom in the half-crystal position is bonded with a semi-infinite crystal row, with a semi-infinite crystal plane, and with a semi-infinite crystal block. Attaching or detaching a single building unit (atom, molecule, ion) from the half-crystal position results in a new half-crystal position, and this is what makes this position a repeatable step in the building and disintegration of the infinitely large crystal lattice (see [10–12] and the references cited therein).

Figure 13.2.7 shows four pages from Stranski's Bulgarian notebook, and the text in (b) reads: "The work of separation of a dipole from a given ion", and further, "The work of separation of 1 dipole from a lattice point with respect to the next closest ionic plane".

Three most significant scientific papers of Ivan Stranski devoted to the equilibrium forms of homeopolar crystals were published in coauthorship with Rostislav

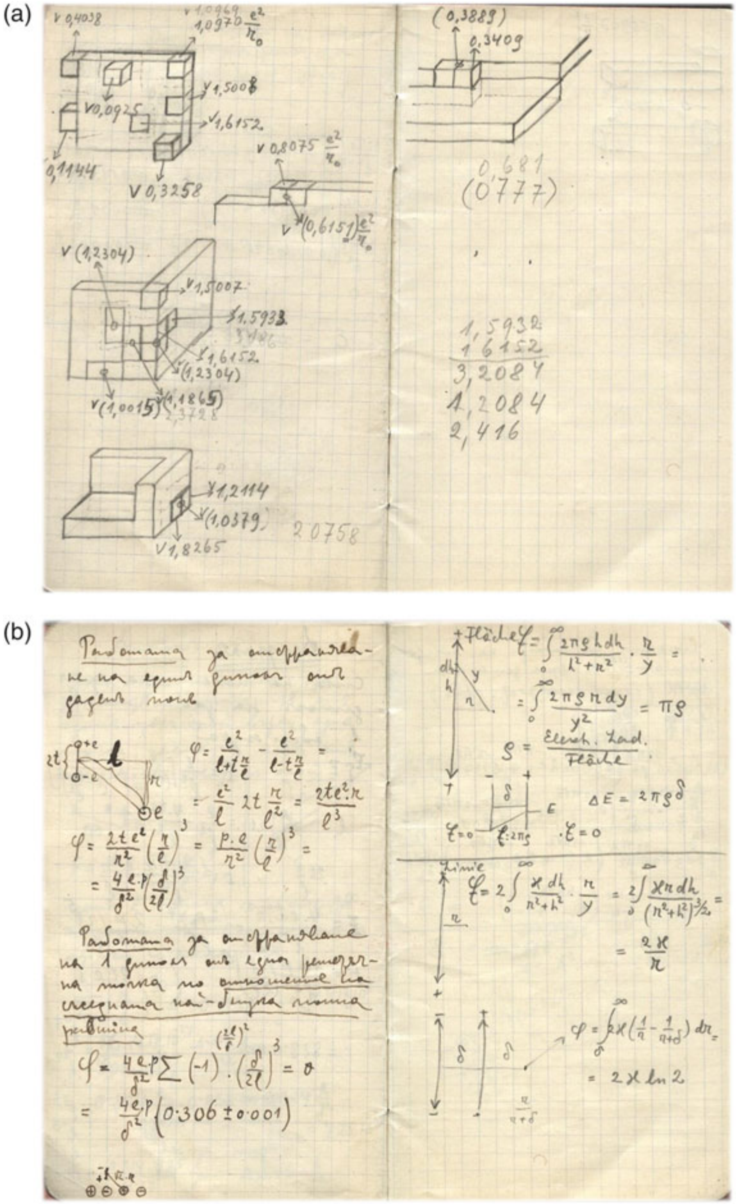

Fig. 13.2.7 Pages from Ivan Stranski's Bulgarian notebook

Kaischev and Lubomir Krastanov within the period 1931–1933 [13–15]. In 1934 I. Stranski and R. Kaischev developed also the so-called theory of mean separation works [11, 16–18], thus shedding, for the first time, light on the interrelation between the thermodynamic and the molecular-kinetic approach to the nucleation and crystal growth phenomena (see also [10, 12] and the references cited therein).

To my knowledge, Ivan Stranski never contributed directly to the field of electrochemical science. However, his definitions of the fundamental concepts *half-crystal position* and *separation work* $\varphi_{1/2}$ of a single atom therefrom [8, 9], as well as the definition of the concept of *mean separation work* $\overline{\varphi}$ of the atoms from a crystal face in contact with a vapor phase [16–18], were used by R. Kaischev [19], who in 1946 proposed definitions of these quantities applicable also to the more complex case of crystals in contact with an ionic electrolyte solution (see also [12]).

No doubt, Ivan Stranski and Rostislav Kaischev are, the two of them (see [20]), extremely good examples of how well international scientific cooperation worked in Europe before the Second World War. Unfortunately, things changed dramatically afterward, when contacts between Eastern and Western Europe scientists were essentially reduced for purely political reasons. It was, namely, during this period of Cold War when Ivan Stranski did his best to make the iron curtain a bit more transparent for his Bulgarian colleagues, helping and recommending them always when it was necessary.

Back to Ivan Stranski's biography, I should mention that he was a member also of the Göttingen Academy of Sciences, Bavarian Academy of Sciences and Humanities, New York Academy of Sciences, German Academy of Sciences Leopoldina, and Swedish Academy of Sciences. In Germany, an institute at the Technical University, Berlin, and the Metallurgical Institute in Oberhausen were named after him, and in 2005 Bulgarian National Television telecasted the movie *The master of crystal growth* devoted to Ivan Stranski and directed by S. Stefanov the son of the physicist S. Stoyanov, member of the Institute of Physical Chemistry, BAS. More information about Ivan Stranski's biography and his scientific career can be found also in [21–24].

Ivan Stranski died in Sofia on 19 June 1979 and was buried in Berlin. Nowadays a street in Sofia is named after him. Certainly, his name will remain forever among the names of those scientists who laid the foundations of the modern theory of crystal growth phenomena.

Acknowledgments Thanks are due to Prof. Chr. Nanev, Ing. A. Mirev, and Dr. K. Girginov, who gave me some of the photos included in this article.

13.3 Rostislav Atanassov Kaischev

Rostislav Atanassov Kaischev (Fig. 13.3.1) was born on 29 February 1908 in Saint Petersburg, Russia, where at that time his father, Captain Atanass Petkov Kaischev, studied at the Russian Military Academy (Fig. 13.3.2). His mother Anastassia Hadzhimarinova descends from the family of landowners and merchants.

Rostislav Kaischev finished the primary and secondary school in Sofia and then studied chemistry at Sofia University where he met for the first time Ivan Stranski,

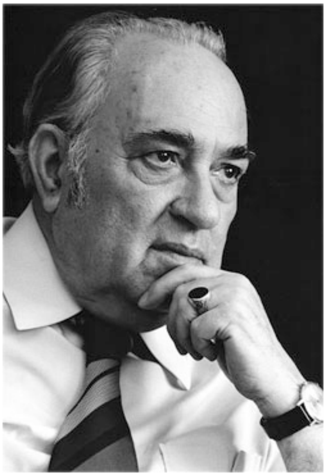

Fig. 13.3.1 Rostislav Atanassov Kaischev

Fig. 13.3.2 Kaischev's family: (**a**) Atanass and Anastassia, 1901; (**b**) Rostislav and his brother Marin, 1910

the professor in physical chemistry with whom he started his scientific researches already in 1929, as a student.

In June 1930 R. Kaischev graduated in chemistry and following Ivan Stranski's advice left for Germany to work on his doctoral thesis under the supervision of Professor Franz Eugen Simon (later in the UK, Sir Francis Simon) (Fig. 13.3.3),

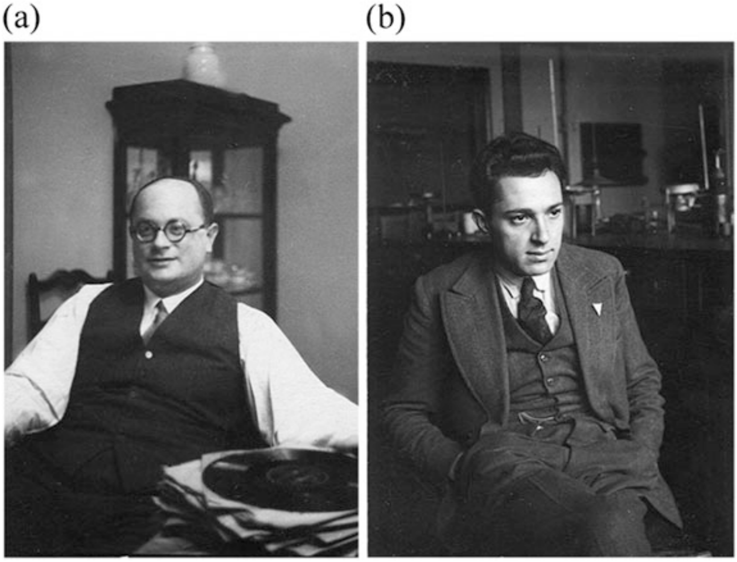

Fig. 13.3.3 Professor Franz Simon (**a**) and Rostislav Kaischev (**b**), Breslau, November 1931

firstly in Berlin and then in Breslau (now Wroclaw, Poland). Kaischev studied the properties of solid and liquid helium and was among the first Bulgarian fellows of the Alexander von Humboldt Foundation receiving a fellowship for the period October 1930–September 1931. Since in that time Ivan Stranski worked in the *Technische Hochschule* (now *Technische Universität*), Berlin, they both completed their first joint scientific study by telephone and published the obtained results in the same year [13].

Kaischev defended his doctoral thesis [25, 26] on 7 November 1932 (Fig. 13.3.4), and his excellent evaluation was *summa cum laude* meaning academic degree received *with highest honor*.

In 1933 Kaischev became an assistant of Stranski at the Chemistry Faculty of Sofia University, and they both developed the theory of mean separation works [16–18]. In 1934 Kaischev was invited to visit the Ukrainian Physical-Technical Institute, in Kharkiv, Ukraine, and worked for 3 months in the laboratory for physics of low temperatures. In the autumn of 1937 he joined the Munich University for 1 year, again as a fellow of the Alexander von Humboldt Foundation. Two of his papers from this period related to the physics at low temperatures were published in *Zeitschrift für Physikalische Chemie* [27, 28].

In 1939 R. Kaischev married Milka Chakalova with whom he stayed together all his life (Fig. 13.3.5). Their daughter, Docent Anastassia Kaischev, was an electrochemist.

In 1944 Kaischev became a docent at Sofia University, in 1947 professor and also corresponding member of BAS, and in 1961 academician (regular member of BAS). In 1958, Kaischev founded the Institute of Physical Chemistry, BAS, and

Fig. 13.3.4 Professor Franz Simon (first row, first from the *left*) and Rostislav Kaischev (first row, third from the *left*) at the celebration on the occasion of R. Kaischev's successful defense of his doctoral thesis, Breslau, November 1932

Fig. 13.3.5 Rostislav and Milka Kaischev, Sofia, 1940

took the position of his director till the end of 1988. He was the vice president of BAS during the period 1962–1968. For him, Ivan Stranski remained forever both a teacher and a remarkable person (Fig. 13.3.6).

Fig. 13.3.6 Visit of Ivan Stranski to the Institute of Physical Chemistry, BAS, 1975. First row, *left* to *right:* G. Bliznakov, D. Nenov, R. Kaischev, I. Stranski, and B. Kurtev. Second row, *left* to *right:* I. Markov, S. Stoyanov, A. Gittis, S. Neykova, and A. Milchev

Kaischev's first two electrochemical papers were devoted to the theory of electrocrystallization [29] and to the electrochemical potential of small electrodes [30] and shed for the first time light on the difference between the separation works of a single atom from a crystal face when the latter was in contact with a vapor phase or in contact with an ionic electrolyte solution. Considering the equilibrium state of a small crystal in contact with an ionic electrolyte solution, Kaischev derived also the Gibbs-Thomson equation accounting for the dependence of the specific free surface energy σ on the electrode potential E. Part of his considerations are demonstrated in Fig. 13.3.7, which shows a draft of R. Kaischev's paper on the theory of electrocrystallization published in 1945 [29] (see also [11]).

Electrocrystallization was certainly among Kaischev's favorite subjects, and I suppose that this is the reason why he directed to this scientific field his first Bulgarian co-workers and later also eminent scientists E. Budevski, J. Malinovski, A. Scheludko, G. Bliznakov, and B. Mutaftchiev. They all started their most successful scientific careers, namely, in the field of electrochemical science [31–33]. In 1974, R. Kaischev participated also in the development of the atomistic theory of electrochemical phase formation [34, 35], which accounts for the specific properties of small clusters of atoms and molecules (see also [10, 12]).

Rostislav Kaischev was an open-minded, fascinating, and most respectable person. He had many friends all over the world, among them M. Volmer, A. N. Frumkin, J. B. Zeldovich, P. Rebinder, H. Bethge (Fig. 13.3.8), and many others. What follows is a short story revealing Kaischev's opinion on A. N. Frumkin, the famous Russian electrochemist.

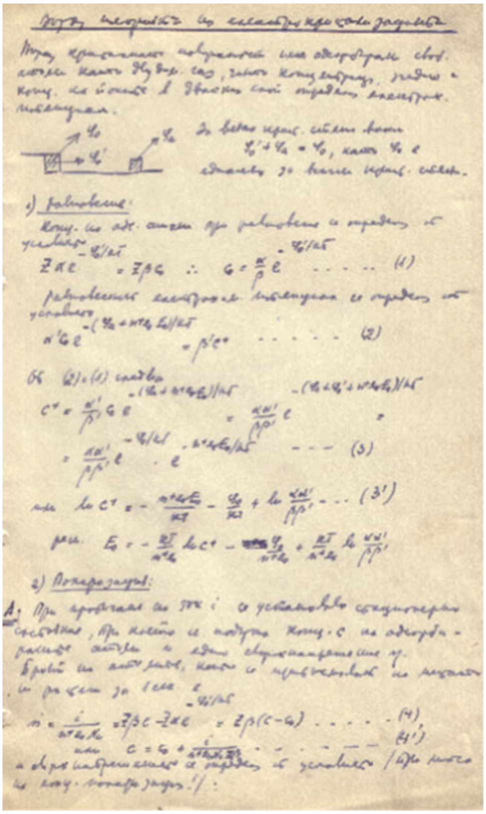

Fig. 13.3.7 Page from Rostislav Kaischev's notebook devoted to the theory of electrocrystallization [29]

Fig. 13.3.8 Heinz Bethge, president of *Deutsche Akademie der Naturforscher Leopoldina* within the period 1974–1990, and Rostislav Kaischev, 1982

It was in the early 1970s when A. N. Frumkin visited the Institute of Physical Chemistry, BAS, in Sofia. The day before his arrival, Kaischev came into my Lab and said to me: "Listen, I will arrive with Prof. Frumkin tomorrow, and you can tell him everything that you are doing here. But be careful how you say it, because

Alexander Naumovich is an extremely intelligent person. He looks at you with his penetrating eyes, and immediately decides if your research has some value!"

Well, I'm afraid that A. N. Frumkin didn't place too much value on my work: I was far too young at the time.

R. Kaischev was a member of the German Academy of Sciences, Czechoslovakian Academy of Sciences, Saxonian Academy of Sciences, as well as the German Academy of Sciences "Leopoldina." He was also the vice president of the International Union of Pure and Applied Physics (IUPAP) within the period 1975–1980. More information about him can be found in the book containing his recollections of the remote past [23].

Rostislav Kaischev died on 19 November 2002 in Sofia. Now the Institute of Physical Chemistry of the Bulgarian Academy of Sciences is named after him.

13.4 Stefan Georgiev Christov

Stefan Christov (Fig. 13.4.1) was born on 12 December 1910 in Sofia. Finishing the secondary school, he studied chemistry and graduated from Sofia University "Saint Kliment Ohridski." Recommended by Ivan Stranski, Stefan Christov specialized in physical chemistry at the Technische Hochschule (now Technical University), Berlin, within the period 1934–1936. Back to his home country, S. Christov worked as an assistant professor both at the Institute of Analytical Chemistry and at the Institute of Physical Chemistry of the Bulgarian Academy of Sciences (BAS). In 1947 he was elected professor in physical chemistry and founded the Physical Chemistry Department at the Sofia Polytechnic.

During the period 1952–1977, S. Christov was head of the Physical Chemistry Department of the Higher Institute of Chemical Technology[2] and took the position of its rector within the period 1964–1966. He was certainly among the best lecturers in the field of physical chemistry and electrochemistry science and was also an extremely tolerant and charming person.

Stefan Christov performed and also promoted profound scientific studies in the field of quantum electrochemistry, physical chemistry, theory of chemical reactions, and solid-state physics [36–43]. His contributions related to hydrogen evolution reactions, corrosion phenomena, and electron transfer reactions are well known to those who work in these particular scientific fields. The same is valid also for the so-called Christov's characteristic temperature related to the transition rate of over- and under-barrier tunneling reactions.

Concerning Stefan Christov's scientific achievements, it might be worth citing also the concluding remark of the famous Russian electrochemist Alexander Naumovich Frumkin, reviewer of S. Christov's DSc thesis: *The scientific studies of S. G. Christov characterize him as a fully independent and original scientist*

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[2] Now the University of Chemical Technology and Metallurgy (UCTM), Sofia

Fig. 13.4.1 Stefan G. Christov (1910–2002)

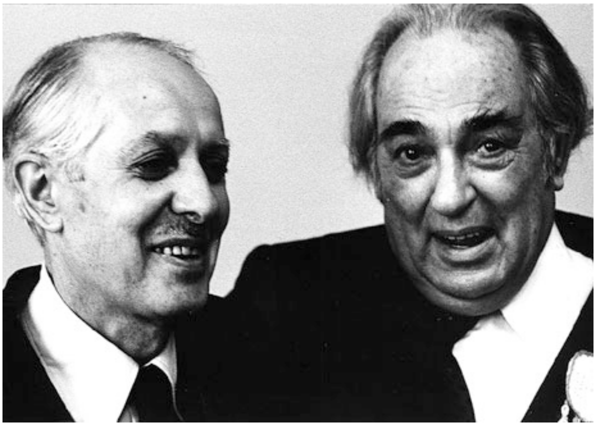

Fig. 13.4.2 Stefan Christov and Rostislav Kaischev at the Institute of Physical Chemistry, Bulgarian Academy of Sciences (BAS), 28 February 1978

extremely skilful at the methods of contemporary physical chemistry and mathematical physics science, 24 06 1959.

Stefan Christov was among the colleagues and close friends of Rostislav Kaischev (Fig. 13.4.2) [23], and I still remember how he introduced himself at the celebration of Kaischev's 70th birthday. He said: "When I joined the Physical Chemistry Department of Sofia University, there were four persons there: one professor—it was Ivan Stranski; one assistant—it was Rostislav Kaischev; one doctorant—it was Ljubomir Krastanov;[3] and one student, preparing his diploma work—it was me!"

Professor S. Christov was elected corresponding member of BAS in 1961 and regular member of BAS (academician) in 1984. He was also a president of the

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[3] President of the Bulgarian Academy of Sciences within the period 1962–1968

Bulgarian Chemical Society and president of the Bulgarian National Committee for the International Union of Pure and Applied Chemistry (IUPAC). S. Christov was also a council member of CITCE (Comité International de Thermodynamique et de Cinétique Electrochimiques), now the International Society of Electrochemistry (ISE), and was its secretary for Bulgaria within the period (1959–1972). He was a winner of many national and international awards.

Stefan Christov died in Sofia on 27 September 2002.

Acknowledgments Thanks are due to Prof. M. Machkova, head of the Physical Chemistry Department, UCTM, Prof. A. Girginov, Prof. M. Christov, Dr. K. Girginov, and Ing. A. Mirev for the valuable information.

13.5 Alexey Dimitrov Scheludko

Alexey Scheludko (Fig. 13.5.1) was born on 18 May 1920 in Halle, Germany, where his father the Ukrainian philologist Dimitri Scheludko worked on his doctoral thesis [44]. His mother Nora (Fig. 13.5.2), born in the city of Sliven, Bulgaria, was a daughter of a Russian Jewish physician, Dr. Joachim Tranen. She studied firstly music in Switzerland and then Slavonic philology in Sofia University "Saint Kliment Ohridski."

Alexey Scheludko finished the primary and secondary school in Sofia and in 1938 started studying chemistry in Sofia University where he had the chance to listen Prof. Ivan Stranski's lectures of physical chemistry.

Fig. 13.5.1 Alexey D. Scheludko (1920–1995)

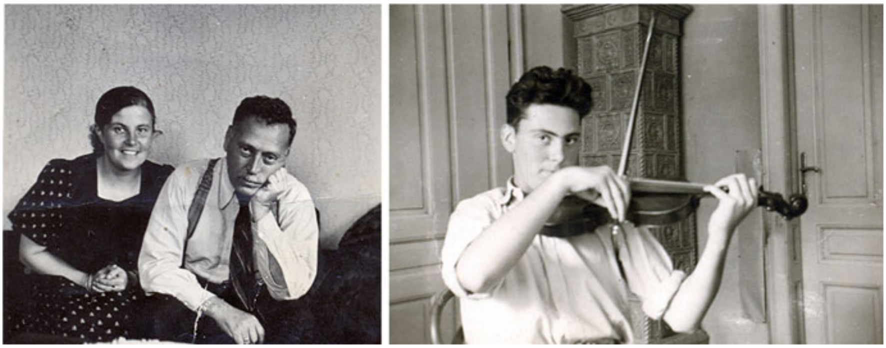

Fig. 13.5.2 Nora and Dimitri Scheludko (**a**) and their son Alexey (**b**) as a student in Sofia University, the early 1940s

In 1943 Alexey Scheludko married his fellow student Gena Hristova, and they had two daughters—Nora, a physicist in the Faculty of Physics of Sofia University, and Anna, a philologist, who died, unfortunately, too young.

Alexey Scheludko graduated in chemistry in 1948 and in 1949 joined the Physical Chemistry Department of the Chemistry Faculty of Sofia University as an assistant. In 1957 he received there his PhD degree, and in 1961 he received also a Doctor of Science degree from the Institute of Physical Chemistry of the Russian Academy of Sciences (RAS).

In 1962 Alexey Scheludko was already professor and head of the Physical Chemistry Department of the Chemistry Faculty of Sofia University, succeeding his teacher Prof. Rostislav Kaischev (Figs. 13.5.3 and 13.5.4). In the same time he headed also the Department of Colloid and Interface Science founded by himself at the Institute of Physical Chemistry of the Bulgarian Academy of Sciences (BAS) in 1958. He was elected corresponding member of BAS in 1967 and a regular member of BAS (academician) in 1984 (for more biographic details, see [45, 46]).

In October 2010 the Physical Chemistry Department of the Chemistry Faculty of Sofia University celebrated the 90th anniversary of Alexey Scheludko's birthday, and I was invited to talk about his contributions to the field of electrochemical science. What follows is based on this lecture of mine [47].

Alexey Scheludko started his scientific experimental and theoretical studies in the field of electrochemical phase formation and published six scientific papers on this subject in the period (1950–1956) [48–53]. Four of them [48, 50, 52, 53] were devoted to the nucleation kinetics and, in my opinion, a most significant achievement described in these articles was the development of the pulse potentiostatic method.

In its initial version, the method was simple and ingenious. A constant external voltage, sufficiently high to initiate a process of nucleus formation, was applied to a two-electrode electrochemical cell containing a solution of metal ions. Then, the current of the growing metal clusters led to a sharp voltage decrease due to the ohmic drop in the electrolyte solution (Fig. 13.5.5), and, namely, the time moment

Fig. 13.5.3 Visit of Academician P. Rebinder (RAS) to the Physical Chemistry Department of Sofia University, 1959. First row, *left* to *right*: E. Budevski, G. Bliznakov, P. Rebinder, R. Kaischev. Second row, *left* to *right*: S. Budurov, A. Scheludko, R. Polikarova, D. Platikanov

Fig. 13.5.4 Alexey Scheludko in his study at the Physical Chemistry Department of Sofia University, the early 1970s

τ_0 of the voltage drop was considered as the time of appearance of the first new-phase nuclei on the electrode surface. As is known, if nonstationary effects can be neglected, the average value of τ_0 is inversely proportional to the stationary rate I_{st} of nucleus formation ($\tau_0 = 1/I_{st}$), and this is the way in which Kaischev, Scheludko, and Bliznakov [48] determined for the first time this important physical quantity in the case of silver electrodeposition on a platinum electrode. The data for

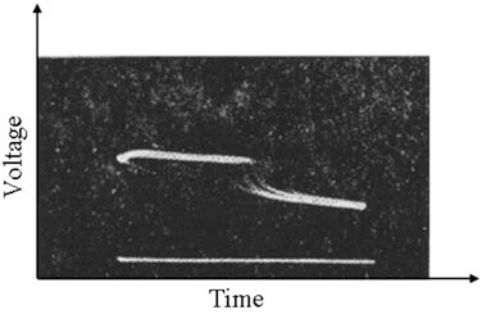

Fig. 13.5.5 Original oscillogram registered in the case of silver electrodeposition on a platinum electrode [48]

I_{st} were interpreted in terms of the classical nucleation theory [54]. Later, the pulse potentiostatic method was modified and refined applying after the first pulse a second, lower one, during which the nuclei grew to sizes visible in an optical microscope and could be easily counted [50, 52, 53] (see also [11, 12, 55, 56]). Nowadays, the pulse potentiostatic method is widely used for studying electrochemical nucleation kinetics (see, e.g., [12, 57, 58] and the references cited therein).

The next significant contribution of Alexey Scheludko to the field of electrochemical science was the development, together with R. Kaischev and G. Bliznakov[4] [49], of the capillary method for studying the electrochemical growth of single metal crystals (Fig. 13.5.6). In this case, silver single crystals were formed and grew within a glass capillary with a cross section of about 2.5×10^{-5} cm^2 and the dynamic changes of the crystal growth forms were observed by means of an optical microscope.

Later, the method was refined by E. Budevski et al. [58] who succeeded to isolate a single face of a silver crystal growing in a glass capillary and to study precisely its growth mechanism.

The description of A. Scheludko's contributions to the field of electrochemical science would not be complete without mentioning the theoretical study of the electrochemical growth of single hemispherical clusters of the new phase performed in 1952 [51]. Considering the case of a constant external voltage applied to the electrochemical system, A. Scheludko and G. Bliznakov derived expressions for the "current-time" and the "radius-time" relationships in three particular cases: (1) complete diffusion, (2) complete ohmic, and (3) complete charge transfer limitations of the growth process. Later, the more complex cases of electrochemical growth under combined charge transfer and diffusion limitations [59] and under combined charge transfer, diffusion, and ohmic limitations [60] have been considered, too.

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[4] Georgi Bliznakov (1920–2004) graduated in chemistry in Sofia University in 1943 and was elected docent in 1954, professor in 1960, corresponding member of BAS in 1967, and regular member of BAS in 1979. He was head of the General and Inorganic Chemistry Department of Sofia University within the period 1960–1989 and director of the General and Inorganic Chemistry Institute of BAS within the period 1960–1990.

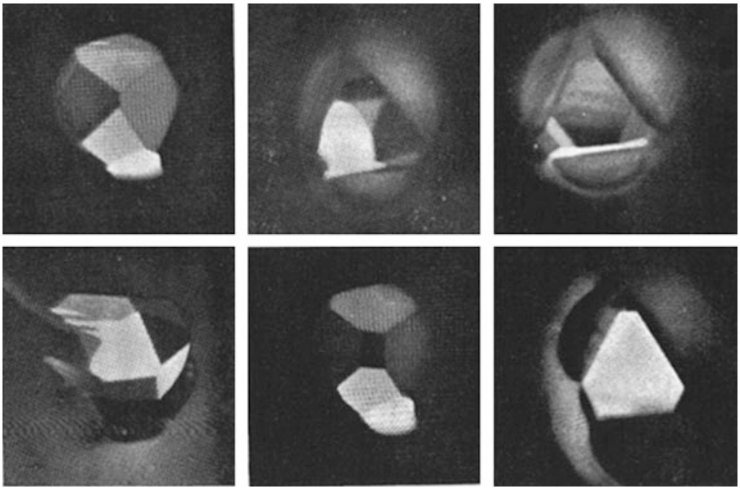

Fig. 13.5.6 Silver crystals grown in a glass capillary [49]

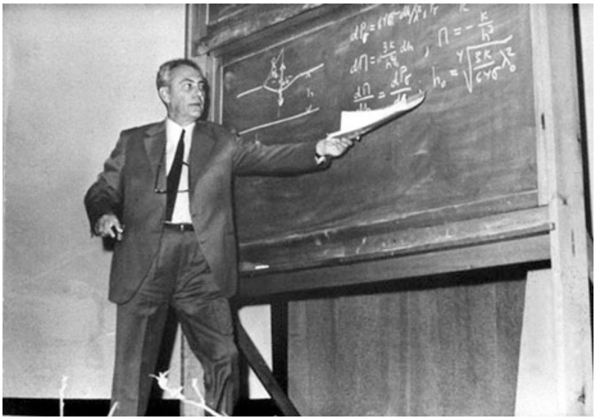

Fig. 13.5.7 Alexey Scheludko giving a lecture

The scientific interests of Alexey Scheludko (Fig. 13.5.7) soon changed, and he directed his efforts to studies of colloids and surfaces, a scientific field in which his theoretical and experimental achievements were internationally recognized. In particular, his book on colloid chemistry was translated in several languages, among them English, Japanese, Polish, and Russian.

Concluding, I would like to mention Alexey Scheludko's unique intuition, particularly when new, sometimes questionable scientific results were discussed and also his sharp, often scathing sense of humor. What follows is a short story, which confirms this talent of his.

In one of the Institute of Physical Chemistry Seminars, a colleague from another Institute presented his not very convincing theoretical model, confirmed by a single experiment performed in his Laboratory. After about 1 hour of bitter discussion A. Scheludko stood up and smiling sarcastically declared: “To me, the theory of our colleague resembles a damaged watch, which obligatory shows the correct time once daily!” I think that the laugh of the audience after these words was may be condign but still a too severe punishment!

Alexey Scheludko was a member of the German Academy of Sciences “Leopoldina,” New York Academy of Sciences, Faraday Society in England, and the Kolloid-Gesellschaft in Germany. He was among the founders of the International Association of Colloid and Interface Scientists and a member of the IUPAC Commission on Colloid and Surface Chemistry. He died in Sofia on 8 May 1995.

Acknowledgements Thanks are due to Docent N. Scheludko, Prof. E. Staycheva and Prof. B. Radoev for the photographs and for the valuable information.

13.6 Evgeni Bogdanov Budevski

Evgeni Budevski (Fig. 13.6.1) was born on 29 July 1922 in Sofia. His father Bogdan Budevski was a chemist and his mother Dima (Fig. 13.6.2) studied architecture in Switzerland but did not finish her education due to the First World War.

Figure 13.6.3 shows E. Budevski’s ancestors and was made in the beginning of the twentieth century. Budevski’s grandfather Gancho was a pyrotechnician, his son Stefan studied engineering in Germany, Peter was a lawyer, and Karan was a chemist, too. The sister of Gancho Budevski, the famous Bulgarian actress Adriana

Fig. 13.6.1 Evgeni B. Budevski (1922–2008)

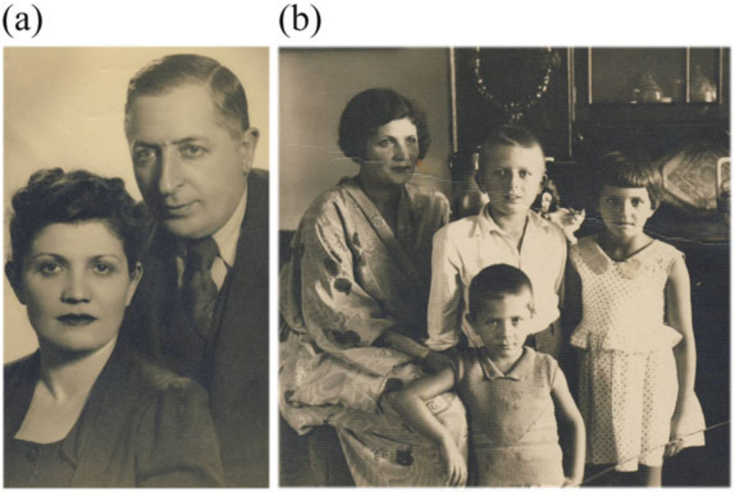

Fig. 13.6.2 (**a**) Dima and Bogdan Budevski, (**b**) Dima and her children, Evgeni, Nadia, and Omurtag (the 1930s)

Fig. 13.6.3 The old Budevski family: (sitting) Gancho and Gergina Budevski and their children, (standing, from *left* to *right*) Bogdan, Galina, Stefan, Peter, and Karan

Budevska (Fig. 13.6.4), was among the founders of the professional Bulgarian theater and was considered as the best performer of tragic roles.

Evgeni Budevski graduated in chemistry from Sofia University "Saint Kliment Ohridski" and within the period 1949–1959 worked as an assistant in the Physical

Fig. 13.6.4 Adriana Budevska (1878–1955)

Fig. 13.6.5 Rostislav Kaischev (the second from the *left*) and his co-workers and later also close friends Stefan Rashkov, Evgeni Budevski, and Jordan Malinovski at the celebration of R. Kaischev's 70th birthday on 28 February 1978 (Rostislav Kaischev was born on 29 February 1908 and in non-leap years celebrated his birthday either on 28th of February or on 1st of March)

Chemistry Department where he started his scientific career studying the electrocrystallization phenomena in close collaboration with R. Kaischev and J. Malinovski (Fig. 13.6.5) [61–66]. Those three Bulgarian scientists were among the first who in 1949 [61] observed the electrochemical spiral growth of crystals, but, as R. Kaischev commented in his *Selected works* [11], considered it as an accidental curiosity since in that time the theoretical studies of F. C. Frank et al. [67–69] were still not well known.

In 1959 Evgeni Budevski habilitated and founded the Electrochemistry Department of the Institute of Physical Chemistry at the Bulgarian Academy of Sciences (BAS). In 1964 he was elected professor, in 1984 corresponding member of BAS, and in 1995 regular member of BAS, academician. In 1967 Evgeni Budevski founded the Central Laboratory of Electrochemical Power Sources (CLEPS, BAS), which in 2003 changed to the Institute of Electrochemistry and Energy Systems (IEES, BAS), nowadays world well-known scientific institution with significant achievements in the field of electrochemical science.

Undoubtedly, the most important contribution of Budevski et al. [58, 70–72] to the field of electrocrystallization consists in the refinement of the capillary method developed in 1951 by Kaischev, Bliznakov, and Scheludko [49] for studying the crystal growth phenomena. What Evgeni Budevski and his co-workers did was to isolate a single, defect-free crystallographic face of a silver crystal in a glassy capillary and to record the current due to the formation and spread of single and multiple two-dimensional (2D) clusters on its surface at a constant electrochemical overpotential η [71, 72].

Evgeni Budevski participated also in detailed studies of electrochemical spiral growth of crystals (Fig. 13.6.6) taking place in the presence of screw dislocations on the crystal surface [73–76] (see also [12, 77, 78] and the references cited therein). His contributions to the field of electrochemical underpotential deposition phenomena (UPD) should be noticed, as well [79–82].

At the end of his most successful scientific career, E. Budevski inspired and also participated in studies related to electrochemical hydrogen energy conversion [83–86] and purification of atmosphere polluted by chemical and metallurgical plants [87–89].

Evgeni Budevski was elected foreign member of the Saxonian Academy of Sciences in 1974 and was the vice president of the International Society of

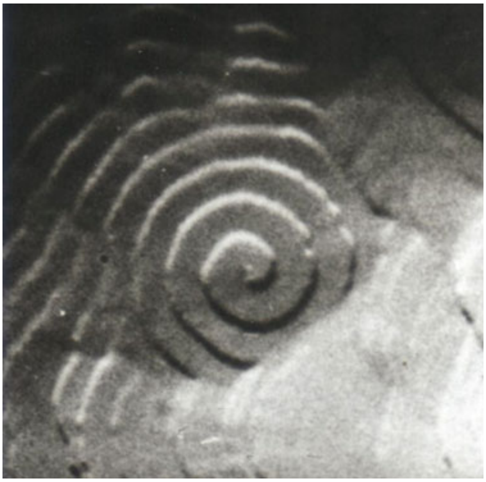

Fig. 13.6.6 Circular macro-spiral electrochemically formed and spreading on the cubic face of a silver crystal growing in an aqueous 6 M $AgNO_3$ solution (Courtesy of V. Bostanov, unpublished result)

Electrochemistry (ISE) within the period 1974–1978. He was also member of the IUPAC Committee of Electrochemistry within the period 1980–1987; member of the editorial boards of *Electrochimica Acta*, *Journal of Applied Electrochemistry*, and *Journal of Power Sources*; member of the Advisory Committee of UNESCO-EPS on Energy Saving and Storage; as well as member of the Advisory Committee of the President of Republic Bulgaria within the period 1997–2001. Evgeni Budevski was also winner of many prestigious national and international awards. He died in Sofia on 13 October 2008.

Acknowledgments Thanks are due to Docent N. Budevska, L. Krusheva, Docent W. Obretenov, Prof. D. Vladikova (Director of IEES, BAS), Prof. E. Slavcheva and Prof. Z. Stoynov for the valuable information.

13.7 Jordan Petrov Malinovski

Jordan Malinovski (Fig. 13.7.1) was born on 3 June 1923 in the city of Sliven, Bulgaria. His mother, Ivanka, was a housewife, and his father, Peter Malinovski, studied pharmacy in Sofia University "Saint Kliment Ohridski" but later worked as a representative of the Ford Company in Bulgaria. Jordan Malinovski had two brothers, Georgy and Alexander, who studied radio engineering and then continued working in the same field (Fig. 13.7.2).

In 1943 Malinovski finished the secondary school in the American College of Sofia and in 1948 graduated in chemistry from the Sofia University "Saint Kliment Ohridski." During the next 10 years, Malinovski worked as a research associate in the Institute of Physics at the Bulgarian Academy of Sciences (BAS). In 1958 he received a PhD degree in chemistry and in 1969 he received also a DSc degree. Jordan Malinovski was elected senior research associate (now docent) at the Institute of Physical Chemistry, BAS, in 1959, professor at the same institute in 1964, corresponding member of BAS in 1979, and regular member of BAS (academician) in 1989.

Jordan Malinovski's first scientific papers related to electrochemical science were published in coauthorship with R. Kaischev and E. Budevski [62–66] and were devoted to electrocrystallization of silver providing valuable information on both the growth forms of single silver crystals and the spiral growth mechanism of individual crystallographic faces as predicted by Burton, Cabrera, and Frank [68].

In 1967 J. Malinovski founded the Central Laboratory of Photographic Processes,[5] BAS, and since that time his scientific interests were entirely directed to the photographic science and, particularly, to studies of the "latent image" formation during illumination of photographic materials. J. Malinovski was the first who revealed the role of the photoholes in the photographic process, and his scientific

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[5] Now *Institute of Optical Materials and Technologies* "Acad. Jordan Malinovski," BAS

Fig. 13.7.1 Jordan P. Malinovski (1923–1996)

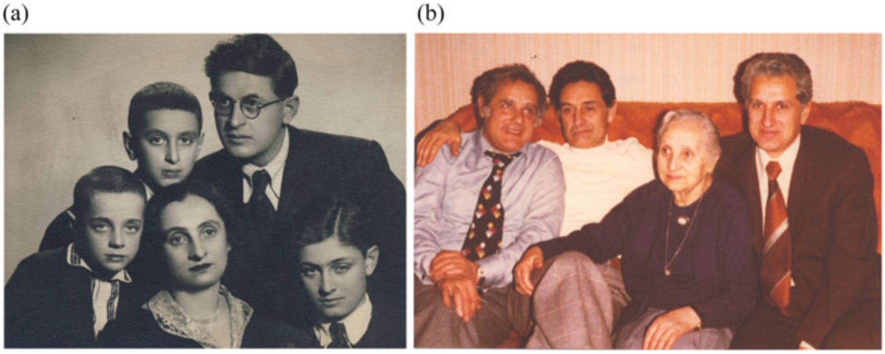

Fig. 13.7.2 Malinovski's family, (**a**) (first row, *left* to *right*) Alexander, Ivanka, and Jordan; (second row, *left* to *right*) Georgy and Peter, the 1930s. (**b**) Alexander, Jordan, Ivanka, and Georgy, 1978

studies [90–95] lead to the creation of a new theory, nowadays well known as Malinovski's "symmetric scheme." Figure 13.7.3 shows him together with his co-workers V. Platikanova and R. Veleva.

Undoubtedly, another most important contribution of Malinovski to the photographic and electrochemical science was a profound model study of the photographic development, which is a typical process of electroless metal plating [96–99] (see also [10, 100, 101]). Evaporating silver crystals on a carbon film, treating them with photographic developers having different electrochemical driving forces, and comparing the crystals' size distribution before and after the electrochemical treatment, the authors succeeded to determine the critical radius[6] r_c and to register

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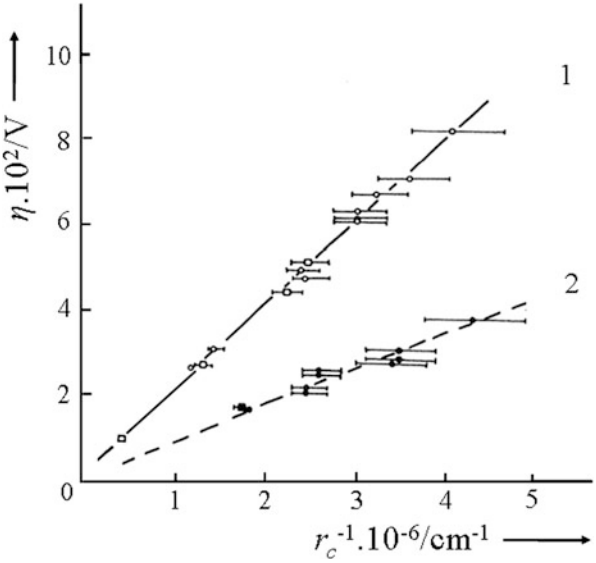
[6] In this paper silver crystals are considered as spherical clusters.

Fig. 13.7.3 J. Malinovski and two of his co-workers V. Platikanova and R. Veleva

Fig. 13.7.4 Overpotential η vs. r_c^{-1} relationships (Eq. 13.1) in the absence (1) and in the presence (2) of a gelatin overlayer (after [93–95, 98])



its overpotential dependence (Fig. 13.7.4). The latter turned out to confirm the validity of the famous Gibbs-Thomson equation

$$\eta = \frac{2\sigma v_M}{zFr_c} \tag{13.1}$$

in an unambiguous and most convincing way. In Eq. 13.1 σ is the specific free surface energy at the "crystal-developer" interface boundary, v_M is the molar

Fig. 13.7.5 Jordan Malinovski giving a keynote lecture at the International Congress of Photographic Science, Rochester, NY, 1978

volume of silver, *z* is the valence, and *F* is the Faraday number. It is my personal opinion that such direct, incontestable experimental proofs of the Gibbs-Thomson equation are not frequently published in the international scientific literature.

Academician Jordan Malinovski (Fig. 13.7.5) was a world-famous Bulgarian scientist. He was an honorary fellow of the Royal Photographic Society of Great Britain; fellow of the American and Japanese Photographic Societies; member of the European Academy of Sciences, Art, and Literature; member of the Academy of Wallonia in Belgium; and others. He was a winner of many national and international awards.

In 1992 Academician Jordan Malinovski was elected president of the Bulgarian Academy of Sciences and took this position till the end of his life in 1996.

Acknowledgements Thanks are due to Prof. V. Platikanova, Prof. N. Malinovski and D. Malinovska for the photographs and for the valuable information.

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Chapter 14
Hans-Heinrich Möbius and the Development of Electrochemistry with Solid Electrolytes

Ulrich Guth

14.1 How Did Electrochemistry with Solid Electrolytes Reach Eastern Germany (Rostock and Greifswald)?

The development of the electrochemistry using solid electrolytes at high temperatures is very closely connected with the name of Hans-Heinrich Möbius [1]. This field of electrochemistry is relatively young and has developed after Carl Wagner's discovery (for the first time mentioned in 1943) of the unipolar mobility of oxide ions in the Nernst's glower (stabilized zirconia) [2]. In some mixed oxides with fluorite structure, the conductivity increases exponentially with increasing temperature due to the migration of oxide ions via oxide ion vacancies. Karl Haufe made his doctor thesis under Wagner's supervision. Haufe, in turn, was Professor from 1948 to 1952 at the University of Greifswald and inspired his student Horst Peters to investigate the structure of mixed oxide based on zirconia by X-ray diffraction. Peters defended his doctoral thesis at the University of Rostock. Based on his ideas, Horst Peters together with Hans-Heinrich Möbius started the investigation on fuel cells based on solid electrolytes like zirconia in Rostock in 1954. Later, in 1960 Möbius moved as a senior assistant to the University of Greifswald because for this research the scientific conditions at the Institute of Physical Chemistry in Greifswald, where the director, Prof. H. Witzmann, worked on luminescence and catalysis of solids [3] were more attractive.

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14.2 Biography

Hans-Heinrich Möbius (*14. Oktober 1929 †14. Oktober 2011)

Hans-Heinrich Möbius, born in 1929 in Ostrau (Saxony, Germany), studied chemistry at Rostock University from 1949 to 1954. In his diploma thesis, supervised by U. von Weber, he has studied a topic of classical thermodynamics, the “Heats of mixing in the benzole-acetone-water system.”His PhD thesis was devoted to “Theoretical and experimental investigations of fuel cell elements with solid electrolytes.” In 1966, H.-H. Möbius qualified as a university lecturer (Habilitation) in physical chemistry. The title of his thesis “On oxygen ion-conducting solid electrolytes and their application possibilities” was also the title of a total of 85 publications published in series. In 1967, he started lecturing in physical chemistry and continued a systematic research on systems with solid electrolytes at Greifswald University. After the reunification of Germany in 1990, he was appointed as professor [4].

Up to 1995, the year in which he became Professor emeritus, and even thereafter he was active in different fields of solid state electrochemistry (solid electrolytes, sensors, SOFC). His pioneering work encompasses contributions to solid oxide fuel cells, theoretical considerations regarding electrochemical phenomena in solid electrolyte cells, basic discoveries in solid electrolyte gas cells, and their applications as gas sensors in different branches of industry. Without any doubt, the discovery of the fuel-oxygen titration curve by means of solid electrolyte cells on which the lambda probe is based is his most memorable contribution to electrochemistry. At the Second European Solid Oxide Fuel Cell Forum, which took place in Oslo on May 1996, Prof. Dr. Hans-Heinrich Möbius was awarded the Christian Friedrich Schönbein Medal of Honor in recognition of his outstanding contributions to the fundamentals and the technology of solid electrolyte fuel cells [1].

14.3 The Development of Solid State Electrochemistry

Although the term "solid state electrochemistry" is used for all electrochemical cells with solid components (besides metals), in a more narrow sense, it means electrochemistry with solid electrolytes. Because of their high operation temperatures, this field of electrochemistry is often called "high temperature electrochemistry." In the 1950s, solid oxide fuel cells were developed for application in space flights. The basic idea was to use oxygen and hydrogen for continuous production of electric energy. Although the Gibbs energy for the oxidation of hydrogen and methane decreases with increasing temperature and subsequently also the open circuit voltage, solid oxide fuel cells (SOFC) were preferred because it was assumed that no kinetic restrictions hinder the electrochemical processes at high temperatures (800–1000 °C).

Closely connected with the development of fuel cells was, on one hand, the investigation of solid electrolytes with respect to their ionic and electronic conductivity, their defect structures, and phase and mechanical stability. On the other hand, it was important which cell voltage can be reached theoretically. That led to thermodynamic consideration of gas equilibria which are operative in hydrogen and carbon oxide containing fuels and furthermore to the in situ determination of single components in hot gases. Today, zirconium dioxide solid electrolyte sensors rank first among all electrochemical sensors, which include lambda sensors in motor vehicles and oxygen probes for steelmaking.

14.3.1 Electrochemical Thermodynamics

Based on Carl Wagner's scientific work after the 2nd Word War in the USA, Kiukula and Wagner published in 1957 first studies in electrochemical high temperature thermodynamics. They used solid electrolytes based on thoria and zirconia and could measure the equilibrium oxygen partial pressure of metal, metal oxide mixtures in nitrogen gas flow [5]. But they could not determine oxygen partial pressures in gas mixtures because their solid electrolytes were not gastight.

In his doctoral thesis, Möbius prepared chemically pure thorium-lanthanum mixed oxides, pressed the obtained powders into disks, and sintered these in a Tammann oven (carbon tube) to produce gastight ceramics. Thereby he could construct gas concentration cells using platinum layers as electrode material. In a self-made high temperature oven, the cell was installed by means of alumina tubes so that each electrode could be fed with a separate gas. In such a way, he could measure the open circuit voltage (emf) not only in oxygen concentration cells but also in CO_2, CO and C, CO_2, CO equilibria [6, 7]. In several publications, he has shown that oxygen partial pressure of free oxygen and equilibrium oxygen (also in H_2O, H_2) could be measured according to the Nernst equation from 400 to 1500 °C [8, 9]. By that means it was possible to determine directly the thermodynamically

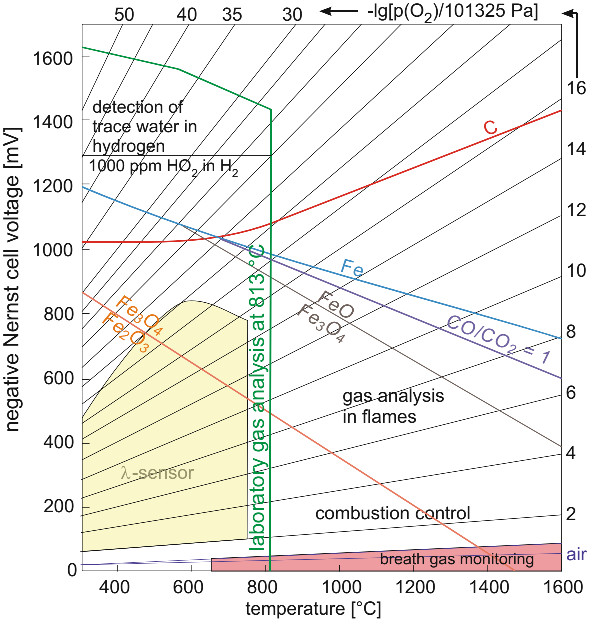

Fig. 14.1 Diagram emf vs. temperature for potentiometric solid electrolyte sensors [10, 11]

expected voltages in a wide range of temperatures for various gas and solid gas equilibria. Möbius extended the well-known Ellingham-Richardson diagram (ΔG vs. T) by the U [E (emf)]-T-diagram (Fig. 14.1) with areas of sensor applications which was published several times [10, 11].

What is less known is the fact that as early as in November 1955, in Rostock, H.-H. Möbius had carried out the first gas analyses with solid electrolyte cells according to thermodynamic principles, i.e., about 2 years before employees of Westinghouse had started to develop the first commercial oxygen sensors [12]. In 1958, together with Dr. Peters, Möbius has applied for the basic world patent for his gas analysis probes using solid electrolyte cells (H. Peters, H.-H. Möbius: "Methods for gas analysis at higher temperatures by means of galvanic solid electrolyte elements" in German: "Verfahren zur Gasanalyse bei erhöhten Temperaturen mit Hilfe galvanischer Festelektrolytelemente") [13]. Unfortunately, Prof. Schwabe (Dresden University of Technology) who was responsible for the application of GDR patents in Western countries did not recommend the application in West Germany. He did not recognize the potential of the high temperature electrochemistry. Möbius' priority claim has been approved in a patent dispute between the Canadian company Babcock & Wilcox and Westinghouse Company, who claimed that the first measurements of oxygen with solid electrolytes were made in the USA in May 1958. Möbius could show that the first measurements of oxygen by means of a solid electrolyte cells took place in November 1955 documented in his lab diary so that his priority had to be recognized according to the US patent regulations [14]. Both companies accepted a settlement out of court and therefore

Westinghouse withdrew the action and could not avoid that other companies produce such oxygen sensors.

Möbius's most important discovery was that reducing gases can be titrated by adding oxygen and vice versa, that oxygen can be titrated with reducing gases. He reported for the first time the *E* (emf)-lambda curve [15]. Möbius was truly ahead of the times, which were not yet ripe for the Lambda Probe and oxygen sensors. Doubtless, he is one of the fathers of the Lambda Probe.

14.3.2 Basic Research in Solid Electrolytes

As early as 1958, Möbius has reviewed the knowledge of mixed oxides which are able to conduct electricity by oxide ions via oxide ion vacancies [16]. In basic research, he investigated a series of mixed oxides regarding conductivity and phase stability [17]. Möbius used a geometric model to explain why in the fluorite lattice (CeO_2, stabilized ZrO_2, ThO_2) the much larger oxygen ions are much more mobile than the smaller multi valent cations (like Zr^{4+}, Th^{4+}) [18, 19]. He could also show by experiments with radio isotopes that the cation diffusion in calcia stabilized zirconia is much smaller than the anion diffusion [20]. He investigated the gas permeability of solid electrolytes by means of solid electrolyte cells [21] and with it connected the electronic (hole) conductivity [22].

14.3.3 Solid Oxide Fuel Cells

In his thesis, Möbius was concerned with the four main problems of solid oxide fuel cells which are important until now [23–25]: (a) The ionic conductivity of the solid electrolyte has to be high. (b) The electronic conductivity of solid electrolyte has to be low. (c) Single cells have to be connected in series because due to the *IR* drop, the electrode area cannot be increased arbitrarily. (d) It was essential to substitute platinum as electrode material by oxide materials which are stable towards oxygen (cathode) and fuel (anode), and which minimize the polarization loss. The last demand became important after the discovery of polarization even at high temperatures by Russian scientists in 1959 which was first reported in an international journal 1964 [26]. As a result of his thesis, Möbius proposed a solid electrolyte fuel cell [23, 27]. His thesis was an inspiration for many scientists in different countries after 1960, which can be seen in a rapidly increasing number of papers. In the 1960s, the group of Möbius has published essential contributions to the abovementioned problems, e.g., the development of less expensive solid electrolytes [28], the development of new electrode materials [25], and interlayers to diminish polarization [29]. He investigated the polarization behavior of solid electrolyte electrodes by ac measurements [30] 2 years before Bauerle has published his frequently cited paper [31]. The international state of the art in

SOFC development, which was to a large extend also the work of Möbius and his coworkers, was presented at a conference in Brussels [32]. At the end of the 1960s, the conditions for fuel cell research in the former GDR became worse due to a forced reform of the system of higher education. Möbius had to shift his research to the industrially interesting water vapor electrolysis and to oxygen generators using solid electrolytes. Although these were tempting tasks, their realization was not possible due to technological deficiencies. In the late 1970s and 1980s, the main research of the Greifswald group was focused on the application of solid electrolyte sensors in different fields of industry, e.g., combustion control, steel hardening, and ceramic production [10, 11].

14.4 International Contacts and Perception

Although Möbius published the first results in thermodynamic measurement of gas equilibria [6, 7] and solid oxide fuel cells [3], the international perception and reputation was limited. One reason was that he published his papers in German mostly in journals of the former GDR so that his results were not noticed in the Western world to the extend they deserved. Although publications in Western journals were not forbidden for East German scientists, there were restrictions and a general discouragement. Until the Second World War, and even in the 1950s, German was a generally accepted language in science. The other reason was a lack of exchange between scientists of GDR with those of other countries. This was true not only for the western countries like the USA (Westinghouse, General Electric), Battelle Institute (Geneva, Switzerland, and Frankfurt a. M., West Germany) but also for the exchange with the Karpachëv's group in USSR (Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, Sverdlovsk, now Yekaterinburg). Sergey Karpachëv (1906–1987) was the first who discovered and investigated kinetic phenomena on solid electrolyte cells at high temperatures. There were in fact few contacts and even a proposed contract. Leading electrochemist from the USSR (Prof. Frumkin, Prof. Bagotskiy [33] and Prof. Karpachëv [26]) visited Möbius in the 1960s. However, the fuel cell research in Soviet Union was of military interest so that beside short visits, further discussions and exchanges with scientists in the former USSR did not take place. Nevertheless, in the late 1970s, some more intensive contacts to scientists in Vilnius (now Lithuanian) Prof. A. Orliukas, and Minsk (now Belarus) Prof. A. A. Vecher (1933–2011) became possible.

Visit of Prof. S.V. Karpachëv (*left*) and Prof. A.N. Frumkin in April 1967 in Greifswald, during trip to Rügen island

Prof. A. Prof. A. Vecher (Minsk, *left*) together with the author Ulrich Guth in Möbius's lab

Prof. A. Orlukas (*middle*) with members of the Möbius's group Dr. P. Shuk (*left*) and Dr. S. Jakobs (*right*) in Vilnius 1988

Especially with Vecher's group, there were several visits, an exchange of young scientists and joint publications [e.g., 33, 36]. Vecher was the head of the Physical Chemistry Department at the Belarus State University Minsk from 1967 to 1998. In the 1970s, he has initiated research on the properties of conductive oxide ceramics as a high temperature fuel cell cathode.

Prof. T. Takahashi and his wife on the market place in Greifswald

Prof. P. Hagenmüller (Bordeaux, France) together with members of Möbius's group October 1989

Nevertheless in the 1980s, Möbius's work was increasingly recognized by the international western community and this lead to a number of visits of leading scientists to Greifswald. For example, the former presidents of the International Society of Solid State Ionics, Prof. T. Takahashi (Nagoya University; Japan) and Prof. H. Iwahara (Nagoya University; Japan) and the well-known solid state scientist Prof. Hagenmuller (Bordeaux, France) visited Möbius in Greifswald.

Last but not least, Möbius is also remembered as a committed teacher. Together with Wolfgang Dürselen (Jena), he wrote the textbook "Chemische Thermodynamik," "Chemical Thermodynamics" [34], which was one of the best valued volumes of the so-called "Lehrwerk Chemie," the standard textbook series for chemistry students in the former GDR. Besides this, he wrote also an important part in the textbook "Elektrolytgleichgewichte und Elektrochemie" for the "Lehrwerk" [35]. Both the research and teaching of Möbius showed his deep admiration and understanding of the great power of classical thermodynamics and electrochemistry. He supervised about 100 graduate, doctoral, and postdoctoral students and published more than 120 scientific papers. He was owner of approximately 50 patents.

Prof. H. Iwahara (Japan) visited Greifswald after The Solid Sate Ionics Meeting in Garmisch 1987

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Chapter 15
Electrochemistry in Saxony, East Germany, Before 1989: Kurt Schwabe in Dresden and Meinsberg

Heiner Kaden

Electrochemical research and electrochemical apprenticeship since decades played an important role in the East of Germany. In Leipzig, electrochemical research was conducted by Wilhelm Ostwald at the Institute of Physical Chemistry [1]. He was the author of the highly respected book "Electrochemistry. Their history and teaching" (1896 published). Max LeBlanc (1865–1943) was Ostwald's successor in Leipzig [1]. He also wrote a textbook of electrochemistry (in German: Lehrbuch der Elektrochemie, 1925); furthermore, Le Blanc developed among others the hydrogen electrode for pH measurements and a capillary for the measurement of electrode potentials. Among the physical chemists in Leipzig in the twentieth century, Wolfgang Lorenz (1925–2007) was particularly well known in the field of electrochemistry. He has worked as a full professor of Physical Chemistry in Leipzig early about electrode kinetics (see [2]).

The East German electrochemist Kurt Schwabe, whose work is discussed here, studied in Dresden (Fig. 15.1).

A scientific school of electrochemistry in Dresden had existed since the late nineteenth century [3]. Some pioneers of electrochemistry from the end of the nineteenth century and the beginning of the twentieth century are mentioned here: Franz Stenger (1859–1893), professor of electrical engineering at the Dresden Royal Saxon Polytechnic, has already held a lecture course on electrochemistry by the year 1892. After his departure from Dresden, the physicist Wilhelm Hallwachs (1859–1922) took over in 1895, lecturing on "Electrochemistry and Electrometallurgy." Walter Hempel (1851–1916), Professor of Chemical Engineering at the Royal Saxon Technical College, before 1890, founded the Dresden Technical College, worked on technical chemistry, and introduced for the first time the use of a diaphragm in the technical chlor-alkali electrolysis one. Fritz

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Fig. 15.1 Kurt Schwabe (1905–1983). Bronze relief in the Institute of Physical Chemistry and Electrochemistry, Dresden University of Technology

Foerster (1866–1931) was the founder of a regular course of electrochemistry at the Dresden Technical University. The establishment of this program in Dresden had been promoted by Wilhelm Ostwald. Foerster's textbook "Electrochemistry of Aqueous Solutions" has long been a standard work of electrochemistry. Foerster laboratory soon became a center of the electrochemical research and teaching in Germany. Since 1896, he was an Associate Professor and, since 1900, a Full Professor of Electrochemistry, Physical Chemistry, and Electrometallurgy at the Technische Hochschule (TH) Dresden. In 1900, Erich Müller (1870–1948) habilitated at the TH Dresden. Following some years in Braunschweig and Stuttgart, he was appointed as full Professor of Electrochemistry, Physical Chemistry, and Electrometallurgy at the TH Dresden in 1912. His research concerned copper electrolysis, electroplating, chlor-alkali electrolysis, as well as the passivity of metals. Successor to Erich Müller at the chair of electrochemistry was his former graduate student Friedrich Müller (1896–1953). He worked mainly on potentiometry and the electrochemistry of metals in aqueous media. In the aftermath of WW II, he went to Switzerland and did not return to Dresden.

Kurt Schwabe was from 1949 to 1970 director of the Institute of Electrochemistry and Physical Chemistry, Dresden Technical University, respectively, from 1961 and from 1949 until his death, also the owner and director of a private electrochemical research institute in Meinsberg, Saxony (Fig. 15.2).

This article aims at appraising Schwabe's scientific achievements from today's point of view. First, a short description of Schwabe's curriculum vitae is given:

Kurt Schwabe was born in Reichenbach, Vogtland. From 1924 to 1927 he studied chemistry at the TH Dresden, where as early as 1927, his interest in electrochemistry was already apparent in his diploma thesis. In 1928, he was awarded his doctorate. In 1933, he habilitated on the subject of anodic behavior of metals in saline solutions. From 1933, he was a private docent (university lecturer), and from 1939 to 1940 professor in Dresden. In 1933, for political reasons, he gave up his whole-time job at the TH Dresden, and he took on a practice employment. After a temporary job with IG Farben in Bitterfeld, from 1928 to

Fig. 15.2 Plaque in memory of Kurt Schwabe on the building of the Research Institute Meinsberg (unveiled in 2013)

1929, he became head chemist at the Kübler & Niethammer paper mill in Kriebstein, Saxony, where he was concerned with tasks of applied chemistry (Fig. 15.3).

15.1 Scientific Work

Schwabe initially turned a great deal of his attention to chemical/technological tasks of interest to the cellulose industry. This is reflected by his publications and patents [4]; only a few of which can be mentioned here. Evidently he also became aware of electrochemical problems at that time. A book [5] on the significance and execution of pH measurement in papermaking, annotated and with margin notes by Schwabe, probably was the starting point for his research into pH measurement, which he continued over many decades. However, there are also patents which document his early interest in fuel cells, corrosion processes, and questions of technical electrolysis which he was to continue to pursue later on when he was appointed as a professor at the TH Dresden. In 1944 Schwabe founded the "Research Institute for Chemical Technology" in Meinsberg, Saxony. This institute was at the center of much of his scientific work for 50 years, right up to the end of his life. In 1949, he was appointed as a full professor of Electrochemistry and Physical Chemistry at TH Dresden, as already mentioned. He took over as director of the Institute for Electrochemistry and Physical Chemistry at the TH without appreciably reducing his work in Meinsberg. Of the numerous positions and appointments which he held during his professional life, several others need to be

Fig. 15.3 Schwabe with the Indian electrochemist Dr. Shashikanth N. Joshi in the laboratory in Meinsberg in 1981. Joshi is now working in a large Indian company in battery research (Green Vision Technologies Pvt. Ltd., Bangalore). (With the approval of Photo Designer Gerhard Weber, Grimma)

mentioned: From 1959 to 1969, he was director of the Institute of Radiochemistry at the Central Institute for Nuclear Research in Rossendorf near Dresden. In Rossendorf, Schwabe took advantage of the opportunity to employ the use of radiochemical methods for electrochemical studies. From 1961 to 1965, vice chancellor of the Technical University of Dresden (in 1961, the TH Dresden was given the status of a University), from 1965 to 1980, President of the Saxon Academy of Sciences in Leipzig, from 1965 to 1971, director of the Central Office for Corrosion Protection in Dresden (which he founded), and vice president of the International Society of Electrochemistry. Supervision of 545 diploma theses, 414 doctoral theses, and 51 habilitation theses bears witness of his prolific activity. Schwabe's curriculum vitae and a list of almost all his publications can be found in a yearbook [6]. In total, Schwabe produced about 530 publications and patents. These will be discussed in the following sections with the main focus on an assessment of Schwabe's lasting achievements.

15.2 pH Measurement

Schwabe's earliest known publication on pH measurement dates from 1935, which was acknowledged by the famous analytical chemist and author Kordatzky in 1949 as being a fundamental work on pH measurement. In 1940, Schwabe applied for his first patent relating to glass electrodes [7]. pH measurement and the development of glass electrodes became a field of research which was to occupy Schwabe until the end of his life. He is rightly known as one of the pioneers of pH measurement, advancing the methodology of liquid analysis more than almost anyone else in Germany and adapting it for use in numerous branches of industry such as sewage control, sugar production, biotechnology, and process engineering. Schwabe's best known publication, giving a comprehensive review of his research results, is his book "pH Measurement Techniques," which was published and then republished in revised editions in 1953, 1958, 1963, and 1976.

In total, Schwabe published about 50 works on how glass electrodes work and on the development of new types of electrode glass. Only some of these can be given prominence here, namely those to which reference is still often made today: At an early stage, Schwabe set out to develop glass with a high electrical conductivity for use as electrode glass. Electrode glass, with both low resistance and favorable electrode characteristics for pH values up to $\mathrm{pH} = 13$, is discussed in his publication of 1957. He has improved the well-known and widely used MacInnes glass (72 % by weight SiO_2, 22 % Na_2O, and 6 % CaO) by adding uranium oxide and other heavy metal oxides. The works on the theory of glass electrodes and how they function, published in the 1960s, have been widely influential, particularly on the introduction of radioactive indicators. Schwabe was also concerned with the investigation of the alkali error in glass electrodes. Recently Cheng [8] has cited several works of Schwabe as evidence for modern theories on how glass electrodes function. Baucke et al. [9] too cited Schwabe's works on pH measurement but in a more critical light, discussing a hypothesis on how electrodes work, which differs from Schwabe's interpretation. Nonetheless, Schwabe's basic initial thesis—that hydronium ions are replaced by the alkali ions of the glass when electrode glass comes into contact with an aqueous phase of the solution—is still true today. Moreover, it has been explicitly corroborated in recent studies by Thomas et al. [10] using nuclear magnetic resonance (NMR) analysis.

Despite its early date of publication, one of Schwabe's most important publications till today concerns pH measurements under extreme conditions. It discusses extremely acidic and extremely alkaline solutions. It goes into measurements at high and low temperatures and under increased pressure. Finally nonaqueous solutions and the use of metal electrodes are discussed. For certain technical applications, particularly with extremely alkaline solutions, glass electrodes are not suitable as the glass surface is too severely affected; this led to Schwabe's successful investigations into the use of bismuth electrodes for pH measurement.

15.3 Corrosion

A second important pillar of Kurt Schwabe's scientific work was his research on corrosion and the passivity of metals. His fundamental knowledge was based on studies by K. Schwabe, G. Kreysa, and U. Ebersbach [11]. According to these authors, even the build-up of a single layer of oxide on the "pure" surface already creates an important barrier to the passage of metal ions through the phase boundary. He summed up his views jointly with the authors in their joint Chemisorption Theory of Passivity. Schwabe took the results of studies regarding the behavior of water in the course of the formation of passive layers as additional proof of this theory. As Ya. M. Kolotyrkin had done before him, Schwabe also provided evidence that passivity without water could not exist. These studies were carried out in nonaqueous sulphuric acid. Due to the lack of a suitable test method, there has been no direct evidence to support the chemisorption theory to the present day. The theory of the passivity of metals and the structure of the passive layer of iron—stating that these consist of an Fe_3O_4 layer on the metal side and an Fe_2O_3 layer on the solvent side, derived in particular from thermodynamics by K. Vetter—while known to Schwabe were not used by him to extend his own investigations because an immediate practical connection to the chemisorption theory could not be made, in particular where the development of new materials was the main objective. The chemisorption theory today has diminished in significance. Nonetheless, various reference to it have appeared in recent papers on corrosion (for example, F. Mansfeld [12] on Schwabe's work concerning the influence of neutral salts on kinetics of corrosion).

Schwabe's pupil and the successor to his chair, Wolfgang Forker, together with Hartmut Worch and other scientists of the Technical University of Dresden, has developed a concept of corrosion theory strongly influenced by thermodynamic and following the approach of K. Vetter and K.-F. Bonhoeffer. In close cooperation between electrochemists and materials scientists, the active dissolution of the iron was investigated, augmented by crystallographic investigations (at atomic level) of the surface finish of iron and of the general metal surfaces. It was shown that both the binding state of the hydroxo-complexes or oxo-complexes and the charge of the cations have an effect on the forming passive layer. From this, a crystallographic model theory of passivity was derived which was compatible with the thermodynamics-based approach. For alloys—especially Fe–Cr alloys—this provided an explanation for the much discussed limit condition of 13 % Cr (by weight) for the resistance of steel to corrosion under atmospheric conditions. This led to the development of a new corrosion resistant steel, free of copper, with ~1 % by weight of silicon.

This presentation shows that the scientific achievements of Kurt Schwabe in the field of corrosion were of great significance at the time and had a wide influence and seminal effect on research, both in East Germany and beyond. In contrast to the field of pH measurement described earlier, the state of scientific research in this field has meanwhile advanced so far that the current relevance of his achievements now takes second place to the undiminished historical importance of his contribution to passivity and corrosion. Despite this, many of his experimental results still attract attention even today, for example, his discovery that for the formation of a passive layer of iron and nickel in acetonitrile, dimethyl formamide, and dimethyl sulfoxide, a very small amount of water is absolutely necessary. Contributions on instruments for corrosion measurement are also still of interest, such as the development of a multichannel potentiostat for checking up to six samples of the same material in a common solution under simultaneous polarization. And, finally, Schwabe also made fundamental contributions to the theory and practice of understanding the kinetics of corrosion processes. He was also the first one to use coulometric measurements in corrosion research.

In 1975, the International Symposium on "Problems of the Passivity of Metals" was organized by the Saxon Academy of Sciences in Leipzig in Schwabe's honor, as a tribute to his international reputation. The international elite in the field of corrosion research from Germany, Belgium, France, Poland, Hungary, and Russia gathered in Dresden for Schwabe's 70th birthday and paid tribute to him in scientific lectures by M. Pourbaix, I. Epelboin, M. Karšulin, M. Prazák, W. Forker, C. Weißmantel, M. Smiałowski, H.-J. Engell, V. Spitzin, I. Rosenfeld, N. D. Tomaschow, L. Kiss, and others.

15.4 Books

The monographs on pH measurement referred to above are outstanding under Schwabe's books, as well as the updated paperback edition of "pH Measurement." The three-volume "Physical Chemistry" published as a "late work" and subsequently republished in two volumes; the third edition, edited by H. Kelm, was published posthumously. Schwabe also wrote books on Polarography (1957) and an Introduction to Statistic Thermodynamics (1971), together with H. Kammer, as well as on the Thermodynamics of Irreversible Processes (1984, published posthumous). For more information, see the bibliography [4, 6].

15.5 Concentrated Electrolytic Solutions

A third dominant field in Schwabe's work concerns his investigations of the behavior of concentrated electrolytic solutions, on acidity measurement, and on the activity of single ions. Some of the applications and results in this area are to be found again in his corrosion research and research into pH measurement: for example, the investigations of corrosion in nonaqueous media and in trifluoroacetic acid. Schwabe's main message was the conclusion that "in principle no single ion activities (beyond the Debye-Hückel range) can be determined" or calculated. In a number of more theoretical publications, Schwabe demonstrates that the solvation energy of ions is responsible for the formation of a short-range order structure of the solvent. One of the most important publications on this topic contains a review of the basic experimental principles and theoretic derivations. Measurements of the medium activity coefficient in galvanic cells of electrochemical chains in solution with differing or equal anions are investigated. The findings showed that the medium activity coefficient of anions and cations varies greatly, which can be explained by a modification of the specific inductive capacity, especially in the case of small ions. Besides potentiometric measurements, he also tried out other measurement methods such as the isopiestic method. According to Schwabe's measurements, the polarization of zinc is practically independent of the anion in pure aqueous zinc salt solutions and low H^+ ion activity, while it clearly depends on the anion for the existence of other inhibitors (ethyl alcohol and dibenzyl sulfoxide among others). This shows that Schwabe constantly aimed at connecting different research fields, such as here electroplating and the theory of electrolytic solutions.

The last publication which Schwabe was able to hold in his own hands in 1983, shortly before he died, was dedicated to the electrochemist A. J. Parker, who died in Australia in 1982. (Several other works by K. Schwabe were published posthumously). It demonstrated once again—by measuring the free standard energy of the transition of ions in organic solvents—that single ion activities cannot be achieved without non-thermodynamic assumptions. In addition, it strengthened the evidence that a pH shift, detected when water is replaced by organic solvents, can be explained by a diminution of the dielectric constant and an increase in coulomb attraction. As two references show, even today many of the above works are still cited.

15.6 Further Fields of Work and Summary

Kurt Schwabe worked for about five decades in the field of electrochemistry. He devoted his time both to a university institute and a private research institute cooperating with industry, and for a while, also to a corrosion research institute. In the present overview, only the main fields in which he produced results of lasting value could be discussed in more detail. In the following, I want to touch briefly on some other areas of his activities. Schwabe worked for several years in the field of polarography, leading to about ten individual publications and an anthology. After the Czech physical chemist, Jaroslav Heyrovský (1890–1967), received the Nobel Prize for chemistry in 1959 for his invention of polarography, Schwabe cannot have expected any more future-oriented development opportunities at his Dresden institute for polarography.

With regard to new developments in instrumental analysis, even outside electrochemistry Schwabe was always open-minded. Thus in 1964, his pupil, Reiner Radeglia, was able to use a tool with a proton frequency of 25 MHz built at the Dresden Institute for his doctoral thesis entitled, "Study of the behavior of strong inorganic acids in solvent mixtures using nuclear magnetic resonance."

At an early stage, Schwabe drew attention to environmental protection problems, both in general and in his own field of electrochemical analysis.

Concerning Schwabe's works on fuel cells, on which he published about ten papers, I would like to recall his then ground-braking investigations into the activation of oxygen electrodes by radiation. In particular, he researched the difficulties of establishing a three-phase gas/electrolyte/electrode boundary when gaseous reactants (H_2, O_2) are used. He achieved this using carbon with optimum grain-size distribution and by making the carbon electrodes water-repellent. In doing this, he took up an idea of Wilhelm Ostwald, the founder of physical chemistry in Leipzig, who long ago had proposed burning carbon in a galvanic element.

Schwabe felt committed to yet another field of technical electrochemistry, chloralkali electrolysis, perhaps because of the brief period he spent at IG Farben in Bitterfeld from 1928 to 1929 and because a number of his pupils also had gone to work at Bitterfeld as industrial chemists. This led to several papers on the development of amalgam and diaphragm electrode processes.

15.7 Summary

Schwabe was a versatile and prolific electrochemist who was always highly interested in the latest developments in electrochemistry. A detailed assessments of Schwabe's scientific work can be found elsewhere [4, 6]. Geographically, Schwabe has worked at the very division between East and West, and his Institute was attractive for foreign researchers and students. This can also bee seen from the long list of visitors of Kurt Schwabe, both in Dresden and Meinsberg; e.g., John O'Mara Bockris, Manfred Eigen, Alexander Naumovich Frumkin, Ewald Heitz, Erika Kalman, Florian Mansfeld; Iosif Lvovich Rozenfeld, Victor Ivanovich Spitsyn, Giordano Trabanelli, and Ernest B. Yeager. During the time of political division of the world, it was a great achievement of Schwabe that he achieved an effective exchange of knowledge across the border, which was normally almost impermeable. It is also part of his legacy that many of his students came in prestigious scientific positions at home and abroad (see Table 15.1).

Table 15.1 Especially successful graduates of Kurt Schwabe in electrochemistry, colloid chemistry, and polymer chemistry

Name	Year of the doctorate	Speciality
Burghardt Philipp	1952	Professor, Polymer chemistry (Academy of Sciences of the GDR, Teltow by Berlin)
Wolfgang Forker	1953	Professor, electrochemistry, electrochemical kinetics (Dresden University of Technology)
Hermann Berg	1953	Professor, Co-founder of bioelectrochemistry (Academy of sciences of the GDR, Jena)
Gottfried Glöckner	1954	Professor, Polymer chemistry (Dresden University of Technology)
Siegfried Ziegenbalg	1956	Professor, Technical Chemistry (Freiberg, Research Institute of nonferrous metals)
Hans-Joachim Bär	1956	Lecturer, Polarography, AC Polarography (Dresden University of Technology)
Hans Sonntag	1958	Professor, Colloid chemistry (Academy of Sciences of the GDR, Berlin)
Klaus Wiesener	1961	Professor, Technical electrochemistry, galvanic cells (Dresden University of Technology)
Lothar Franke	1962	Professor, technical electrochemistry (Dresden University of Technology)
Irmgard Garz	1963	Professor, Corrosion (Magdeburg University of Technology)
Eberhard Schmidt	about 1963 (?), Bern	Student of K. Schwabe; Electrochemistry, Metal under potential deposition (University of Bern, Switzerland)
Wolfgang Lorenz	about 1963 (?), Karlsruhe	Electrochemistry of interfaces (Institute of physical chemistry, University of Karlsruhe)
Helmut Harzbecker	1965	Director, Institute of corrosion prevention Dresden (formerly Central Office for corrosion prevention)
Klaus Müller	about 1966 with J. O'M. Bockris, University of Pennsylvania	Thesis by K. Schwabe about 1960; Coauthor of the Bockris-Müller-Devanathan-Model; Müller recorded and written up in the USA lectures of Bockris as basis of "Modern electrochemistry," famous book of J. O'M. Bockris
Heiner Kaden	1967	Professor; Ion exchange membranes, electrolysis, electrochemical sensors (Director of Meinsberg research institute, Honorary Professor Mining Academy Freiberg)
Helmut Ullmann	1967	Professor, Solid electrolytes (Dresden University of Technology)
Georg Reinhard	1967	Professor, Corrosion (Dresden University of Technology)
Jürgen Garche	1970	Professor, Galvanic and fuel cells (Center of Solar Energy and Hydrogen Research, Ulm, and University Ulm, Germany)

(continued)

Table 15.1 (continued)

Name	Year of the doctorate	Speciality
Erika Kalmán	1970	Professor, Corrosion Engineering (Head of the Department of Surface Modification and Nanostructures of Chemical Research Center of Hungarian Academy of Sciences, Budapest); President of the International Society of Electrochemistry (2001/2002)
Gerhard Kreysa	1970	Professor, Technical electrochemistry and corrosion (Manager of DECHEMA Gesellschaft für Chemische Technik und Biotechnologie, Frankfurt/Main)

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Chapter 16
Publishing in a Divided World

Kh'yena Zalmanovna Brainina and Alexander A. Milchev

16.1 Some Personal Recollections About Publishing During the Soviet Time

Kh'yena Zalmanovna Brainina

What you will read here is not a historical review, but I like to share some personal reflections which I have written down for this book on request of the editor. Now one remembers the Soviet time already as something unreal, and the only idea which comes up is the wish that this will never happen again.

I remember my first attempt, still being a student, to see a Western chemistry journal, and my surprise when I was told in the library that I need a special permission for this. This was at the beginning of the 1950s. For many years, practically until the *Perestroyka* (middle of the 1980s), science in the West and in the USSR was developing on parallel roads, without much interaction. Just as an example, the ideas about the noosphere came up independently on both sides, sometimes with time gaps of several years. Privileged were those people who had access to information from the West.

Western scientists usually did not know much about what was done in the USSR: only a few could read Russian, and for us it was very difficult to publish abroad. Further, in USSR, the scientists had a rather limited knowledge of foreign languages, and it was necessary to get special permissions for the legal publication of papers in

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foreign journals, which normally took on average half a year. I will give here only one example from my own life: In 1990 I met in Australia Dr. Florence who is famous for having introduced what is now known as the "Florence electrode." This electrode (and methodology) played a revolutionary role in stripping voltammetry. We had a long discussion. Meeting him was very rewarding and pleasant. I still remember it as very enjoyable. When we departed, I gave him a reprint of a paper where we have given a very detailed account of the mechanisms and the methodology of working with such electrode, published in the journal "Elektrokhimiya" in 1969 [1]. The paper has been submitted on October 26th 1966, i.e., 3 years before printing! The paper of Florence [2] appeared in 1970. Dr. Florence was very surprised, expressed his thanks and we departed as friends. This example shows how Soviet scientists suffered from extraordinary long review and publication times.

Despite the fact that translations of the main Soviet journals started to be published, on both sides of the divide did not develop a habit to receive and read each others work. By the way, this tendency has not yet been overcome on the Western side, which can be easily seen by comparing the quoting of the same scientists in Western and Russian journals and also from the impact factors of the journals. This is very unfortunate for both, the Soviet and Western scientists. Probably, science would have developed much faster and perhaps more fruitful if it were not for these limitations. I remember a conference on polarography (First All Union Conference on Polarographic Analysis, Kishinev, 1959) where the first talks were given on stripping voltammetry. The authors of the talks were A. G. Stromberg, Ye. N. Vinogradova, and Yu. I. Vaynshteyn. They have shown a peak of lead after its accumulation on a mercury hanging electrode, and the term "nakoplenie" (Russian for accumulation) was introduced as a new term (in Russian, stripping voltammetry is frequently called "voltamperometriya s nakopleniem," i.e., voltammetry with accumulation). So it was, although the papers of Barker and Jenkins [3], Kemula and Kublik [4], Rogers et al. [5], and Delahay et al. [6] have been published before, these were not known to our scientists at that time.

16.2 Recollections of a Bulgarian Scientist

Alexander Milchev

I graduated in Chemistry at Sofia University "St. Kliment Ohridski" in June 1968 and immediately joined the Institute of Physical Chemistry at the Bulgarian Academy of Sciences (BAS). At that time, the Director was Rostislaw Kaischew, professor and regular member of BAS, the first student and coworker of the famous physical chemist Iwan Stranski. Both Stranski and Kaischew laid the foundations of the Bulgarian School in the field of crystal growth phenomena.

My first scientific paper was based on the results of my diploma work and appeared in English, in *Comptes Rendus de l'Académie Bulgare des Sciences* in 1969. How did we publish our scientific studies at that time is certainly an interesting question and in what follows I will provide some information on this subject.

The first, most important and, sometimes, dangerous step was the presentation of the scientific results at the Institute's Seminar. We called it *Colloquium* but if one thinks that it was just a simple *preliminary oral examination* as written in the dictionaries for this word it would be a serious mistake. The audience consisted of the scientific staff of the Institute of Physical Chemistry with Rostislaw Kaischew at the first row and behind him his first students and coworkers: Alexey Scheludko, Jordan Malinovski, Evgeni Budevski, and Georgi Bliznakov, professors and later also regular members of BAS. They were all extremely clever, intelligent, and competent not only in electrocrystallization but also in other fields of the physical chemistry science. What followed was the rest of the Institute's staff consisting of younger chemists and physicists with different scientific degrees. Often we had also guests from other Institutions of BAS and different Universities, and I must say that this was the most competent and, also, the most merciless audience that I have ever met!

The speaker was interrupted with questions, comments, and critical remarks and the procedure was the same for everybody, does not matter whether male or female and communist party member or not! I remember how once a colleague of mine getting nervous of this critical atmosphere exclaimed: "Would you let me finish my presentation and then I will answer all your questions?!" "No"—Kaischew said—"impossible, and if you don't like this, it is entirely your problem."

After about 1 hour, it was clear to everybody whether the results must be published or not and, also, whether all or part of them had to be patented beforehand. We did not vote. Kaischew just summarized the Seminar decision, and the speaker was allowed to go and lick his/her wounds.

The next step was sending the manuscript in the language it was written together with a Bulgarian translation to the Security Department of BAS. After about a week or so the corresponding author was informed about the final decision and if it was positive he/she was provided with an official permission to send it abroad. Without such a stamped certificate, no post office would accept it. Of course, all this refers to the publication procedure accepted at the Institute of Physical Chemistry of BAS, and I am not sure whether the situation was exactly the same in other Institutes of BAS, as well as in Sofia University.

Writing all this, I got interested in how many scientific papers I, myself, published and submitted for publication within the period 1969–1989. The result was 1 patent and 41 papers—3 of them in Bulgarian, 3 in Russian (2 with English translation), and 35 in English (1 in a Bulgarian and 34 in western journals, among them Electrochimica Acta, Journal of Electroanalytical Chemistry, Journal of Crystal Growth, Thin Solid Films, etc.). I suppose that readers might also be interested in how many times those papers were cited in the international scientific literature because the number of citations is, in my opinion, more indicative than the number of papers published. The answer is 1263 till now and I think that for my field of competence this is not a bad result.

Concerning publishing original scientific papers in Bulgarian language, I should say that nowadays it is, perhaps, not worth doing that, unfortunately. The main reason is that it makes sense presenting our scientific results in a readable, understandable, and, also, usable way, and it seems that English language is more suitable for the purpose. Just a simple example in support of this statement: In my case, the average number of citations per article is approximately 31, and my first scientific paper, which is published in English, in a Bulgarian journal, is cited 29 times, which is close to this value. At the same time, the three papers, which I published only in Bulgarian language, were cited 23 times altogether, although their scientific level is, in my opinion, even higher. I wonder if scientists from the English speaking countries realize what a great advantage they have nowadays.

Of course, if one day I decide to make a contribution to the *belles-lettres*, it will be in my own Bulgarian language!

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Erratum to: The Development of Voltammetric Electroanalysis in the Former USSR

Fritz Scholz, El'za Arminovna Zakharova, Nina A. Kolpakova, Julia D. Sister, and Victor G. Mairanovsky

Erratum to:
Chapter 5 in: Fritz Scholz, *Electrochemistry in a Divided World: Innovations in Eastern Europe in the 20th Century*, DOI 10.1007/978-3-319-21221-0_5

On page 160, 10th line text should read as “end of a drop life and for recording *i*–*t*-curves (cf. ref [254]). The inventive talent and”

On page 161, 10th line text in the first paragraph should read as “plant for Vitamin A production was nearby (see Fig. 9.13). I was particularly”

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On page 163, 4th line text in the second paragraph should read as “the curves on the screen (cf. Fig. 9.16). When the first computers appeared, Bryksin”

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Erratum to: Organic Electrochemistry in the USSR

Victor G. Mairanovsky

Erratum to:
Chapter 9 in: Fritz Scholz, *Electrochemistry in a Divided World: Innovations in Eastern Europe in the 20th Century*, DOI 10.1007/978-3-319-21221-0_9

On page 294, the second sentence under the equation should read as “It should be noted that the coefficient $\alpha' = 0.018$ V·mol/kJ in Eq. (9.16) is almost the same as the values of slops in a set of particular experimental dependencies $E_{1/2} = C - BD_{\mathrm{RX}}$ found earlier by Evans and Hush for AlkX with different halogens X = Cl, Br, and I: $B = 0.013$, 0.0173 and 0.018 V·mol/kJ, accordingly [239].”

On page 307, second line text should as “G.A. Tedoradze, L.I. Krishtalik, A.B. Ershler, D.I. Dzhaparidze, and others. The”

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