GAS-PHASE THERMAL REACTIONS

GAS-PHASE THERMAL REACTIONS

Chemical Engineering Kinetics

by

Guy-Marie CÔME
UMR CNRS 7630
ENSIC
Nancy, France

Springer-Science+Business Media, B.V.

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 978-90-481-5834-8 ISBN 978-94-015-9805-7 (eBook)
DOI 10.1007/978-94-015-9805-7

Printed on acid-free paper

Original title: Réactions Thermiques en Phase Gazeuse

Originally published by Kluwer Academic Publishers in 2001.
Softcover reprint of the hardcover 1st edition 2001

To my wife, Michelle

CONTENTS

CHAPTER I — ENERGY, PROCESSES, ENVIRONMENT

CHAPTER II — FUELS, ENGINES, BURNERS, INDUSTRIAL REACTORS

CHAPTER III — MACROSCOPIC DESCRIPTION OF A REACTING GAS MIXTURE

CHAPTER IV — THERMODYNAMIC LAWS

CHAPTER V — ESTIMATION OF THERMODYNAMIC DATA

CHAPTER VI — ELEMENTARY REACTIONS

CHAPTER VII — ESTIMATION OF KINETIC PARAMETERS

CHAPTER VIII — KINETIC MORPHOLOGY

CHAPTER IX — GENERATION OF REACTION MECHANISMS

CHAPTER X — MOLECULAR TRANSPORT LAWS

CHAPTER XI — ESTIMATION OF MOLECULAR TRANSPORT DATA

CHAPTER XII — LABORATORY REACTORS

CHAPTER XIII — ANALYSIS AND REDUCTION OF REACTION MECHANISMS

CHAPTER XIV — TABLES OF THERMODYNAMIC AND KINETIC DATA AND OF MOLECULAR PARAMETERS

NOTATIONS

PREFACE TO THE ENGLISH EDITION

This book is devoted to Gas-Phase Thermal Reactions (GPTRs), and especially combustion reactions, which take place in engines, burners and industrial chemical reactors to produce mechanical or thermal energy to incinerate pollutants or to manufacture chemical substances, and which play an important part due to the consequences they have on the environment : fires and explosions, tropospheric pollution, greenhouse effect, hole in the stratospheric ozone layer.

The design and running of engines, burners, incinerators, industrial reactors, both economical in fuels, raw materials and energy, efficient, safe and clean, as well as the scientific evaluation of the causes and the effects of atmospheric pollutions with a view to taking rational environmental decisions, which necessitate an understanding of the fundamental mechanisms of these reactions and an access to models allowing numerical simulations of the phenomena being studied to be carried out. The analysis of the results of the simulations then allows an optimal solution to be found to the industrial problem or to extrapolate the natural phenomena.

Keeping this in mind, the main object of the book is to suggest a methodology for the kinetic modelling of GPTRs[1] : generation and reduction of reaction mechanisms, estimation of the kinetic data of elementary reactions, estimation of the thermodynamic data and transport data of molecules and free radicals, analysis and validation of the mechanisms by comparison of the calculated results with the experimental results obtained using laboratory reactors. The complete reaction model thus obtained can then be incorporated into a calculation code of a reactor or a computer program of reacting fluid dynamics (CFD).

The book is therefore situated at the interface between physical chemistry (classical thermodynamics and statistical mechanics, chemical kinetics, transport phenomena) and the theory of reactors, themselves at the heart of chemical reaction engineering. It therefore possesses a marked pluridisciplinary character. However, in order to keep this book readable by newcomers to the fields both of GPTRs and the kinetic modelling of reactions, basic concepts, theories and laws of the underlying scientific disciplines are given. The main equations are illustrated by simple numerical applications in order to show how the data tables are used.

The scientific content, the methodological pattern and the pedagogical form of the book result from research work which I have supervised in the framework of industrial

---

[1] In the preface of the collective work which he edited (Gas-Phase combustion Chemistry, Springer, 2000), the late Professor GARDINER thought that a book of this kind should be written on combustion.This book is an attempt to reply to this suggestion.

contracts, of national or European programmes for the supervision of Ph.D. students and lectures given both in University and Chemical Engineering Schools as well as in professional education.

Due to its characteristics, the book applies both to scientists in industrial research and development, research scientists, to graduate students preparing a Ph.D. or a Master's degree, to the undergraduate students in the last stages of their studies, working or destined to work in areas of research involving GPTRs.

This preface gives me the opportunity of thanking my scientific masters : Professor Maurice Letort (1907-1972), Member of the Academy of Sciences, Professor Michel Niclause (1923-1997), director of my own thesis, and Professor Sidney Benson, of Stanford University, USA, whose so fertile ideas have impregnated a whole generation of kineticists. It allows me also to thank all those with whom I have worked : colleagues, teachers and research workers, Ph.D. students, graduates, technicians, administrative staff.

The translation of the book, after updating, has been carried out by Sheena Bouchy, who is a physical chemist of Welsh origin, assisted by her husband, my colleague Professor Michel Bouchy. John Griffiths, Professor at Leeds University (GB), himself co-author of a book in the same field, very kindly suggested reading the translation which allowed us to benefit from his very pertinent comments. I thank all three warmly.

This book has been rendered possible by the constant support of my wife, Michelle, both in my job as University Professor and Research Director, and by the warm environment she creates. I dedicate this work to her, as well as to our elder daughter Catherine and to Luc Grivel, to our younger daughter Agnès, to her husband Frédéric Charreaux and their five children : Camille, Coline, Guillaume, the twins Pierre and Thomas. I pay a filial tribute to my parents, Abel (1899-1994) and Marie (1904-1998).

Guy-Marie CÔME
Nancy (Lorraine) and Port-La-Forêt (Bretagne)

PREFACE TO THE FRENCH EDITION

The level of civilisation is very closely related to the energy consumption and both evolve in a parallel manner.

At the turn of the nineteenth century Man used primarily the energy provided by his food, the additional contribution from animals and mills being very limited. But in the space of two centuries, his consumption has increased more than a hundredfold, that is to say that nowadays he has at his disposal (albeit on average) the equivalent of a hundred "mechanical slaves".

Half of these slaves are *gas-phase thermal reactions*.

They are used to produce an important part of mechanical (engines), thermal (burners) and electrical (turbines) energies, as well as to manufacture chemical substances.

But these slaves also have their weaknesses : these reactions cause atmospheric pollutions and are involved in explosions and fires.

As far as natural gas, crude oil, energy, primary chemical substances and pollution are concerned, which are major geopolitical issues, gas-phase thermal reactions have acquired a major role in the world economy. The knowledge and command of these are of primary importance in the constant search for better performances and profitability.

Now, although these reactions cause numerous and difficult problems, the spectacular progress in experimental, theoretical and computational methods obtained over the last twenty years has resulted in a thorough knowledge of their mechanisms.

To take stock of these methods, and of the results obtained, required a researcher who was personally involved as well as an experienced teacher.

Guy- Marie CÔME has set himself this task.

Graduate engineer of the Ecole Nationale Supérieure des Industries Chimiques and Doctor of Philosophy, Guy-Marie CÔME is a Professor at the Université Henri Poincaré (Nancy I). In the Département de Chimie Physique des Réactions, Unité Mixte Associée au CNRS, at the INP of Lorraine (ENSIC) and at The University of Nancy, he conducts research carried out within the framework of European and national research programmes and of industrial contracts with major firms. More particularly this research has been carried out within the scope of the valorization of natural gas, the reformulation of petrol and diesel fuel for limiting the production of pollutants and computational kinetics for generating more and more complex models on a computer.

Guy-Marie CÔME's book is a synthesis of multidisciplinary elements which contribute to the comprehension of gas-phase thermal reactions.

His main aim is to develop a methodology for the modelling of all aspects of these reactions : thermodynamic, kinetic, reaction mechanisms, molecular transport.

He also suggests a methodology for the validation of these models from the experimental results obtained using laboratory reactors.

This true methodological aspect renders this work applicable to the varied topics encountered both in industrial research and development centres and public laboratories.

The account, which is always clear and detailed, is completed by numerical data tables and a list of computer programs.

This work will be a reference book for University undergraduate and postgraduate students and will be just as useful for those graduate engineers and research fellows who are working on engines, fuels, industrial reactors, chemical safety, atmospheric pollution...

It has neither its equivalent in the French language nor in the English language.

Claude CHEZE
Former University Professor,
Graduate Engineering School Director
and University Institute of Technology Director .

INTRODUCTION

1 - THE IMPORTANCE OF GAS-PHASE THERMAL REACTIONS

Gas-Phase Thermal Reactions (abbreviated as GPTRs) greatly influence our daily lives in three main areas :

- **the production of mechanical energy** for two-wheeled vehicles, cars, lorries, tractors, heavy-plant vehicles, barges, boats, planes, missiles and launchers ;
- **the production of thermal energy** to heat food, houses and offices, to produce electricity and steam, to make industrial ovens and incinerators work ;
- **the manufacture of chemical substances** :
  - by steamcracking to produce alkenes, butadiene and BTX, from which most chemical compounds and organic materials are derived ;
  - by oxidation to make synthesis gas which leads namely to the manufacture of fertilizers and explosives for use in mines and quarries ;
  - by various pyrolysis, oxidation and chlorination reactions...

GPTRs consume an average of 750 g natural gas and 1 500 g crude oil per human being per day. By comparison, an adult eats two and a quarter kilos of food every day.
The GPTRs are therefore at the heart of the geopolitical issues about the optimal management of the resources in fossil hydrocarbon raw materials and in fossil, nuclear or renewable energies.
But the problems about which public opinion has been most sensitive have turned out to be concerns about the environment and more particularly atmospheric pollution, owing to their consequences on human health : genetic mutations and cancers, decrease in the effectiveness of the immune system, diseases of the respiratory system, the eyes, the skin.

GPTRs are involved in the following environmental phenomena :

- **chemical safety**, which concerns the use of gases and organic liquids likely to cause fires and explosions by mixing with air, as well as the prevention and extinction of the fires ;
- **tropospheric pollution** by ozone, the oxides of carbon, nitrogen and sulphur, VOCs

(volatile organic compounds), PAHs (polycyclic aromatic hydrocarbons), solid particles, photochemical smog, acid rains ;

- **the greenhouse effect** partly due to the carbon dioxide produced by combustions ;
- **the depletion of the stratospheric ozone** by the CFCs (chlorofluorocarbons) and the halons (halogenated hydrocarbons).

These different themes are treated in more detail in Chapters I (Energy, processes, environment) and II (Fuels, engines, burners, industrial reactors) of the book.

The ecodevelopment of the planet in the next decades of the XXIst century will therefore depend to a large extent on the mastering of the GPTRs, including two main areas of research :

- the conception of engines and fuels, of burners and incinerators, of industrial reactors which are **efficient, economic, clean and safe** ;
- the scientific evaluation of the causes and effects of **atmospheric pollutions**, with a view to taking rational environmental decisions and to finding optimum or alternative solutions.

2 - AIMS OF THE BOOK

The conception, optimization, extrapolation or mastering of a GPTR necessitates first of all **the elaboration of a reaction model**, then its incorporatation into a **code of Computational Fluid Dynamics (CFD)** in order to carry out **simulations** of the phenomenon being studied under different operating conditions of composition, of pressure, of temperature, with different reactant loads, and for different reactor geometries. **The analysis** of the results of the simulations then allows the optimum reactant-reaction-reactor-product configuration to be determined or the phenomenon to be extrapolated.

The present work deals essentially with the first problem, that is **the elaboration of fundamental models for the GPTRs**.

Figure 1 describes the main steps of this approach which consists of three main phases.

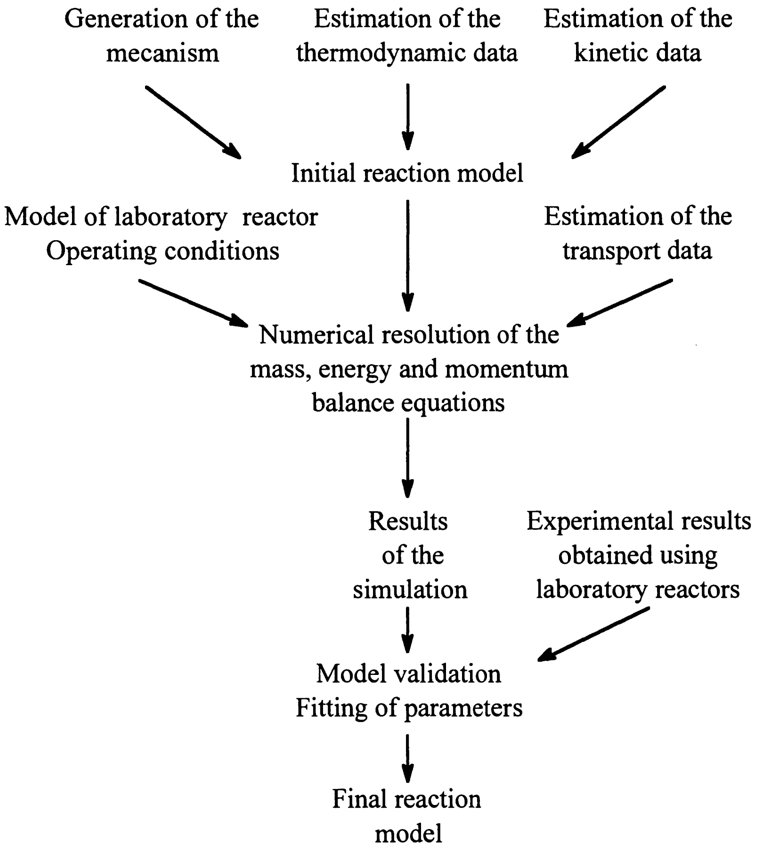
- The elaboration of the initial reaction model ; it consists of generating a mechanism for the reaction, by hand or using a computer program, of estimating the thermodynamic data of the species involved in the mechanism and the kinetic data of the elementary reactions constituting the mechanism.
- The numerical resolution of the balance equations of the laboratory reactor with which the experiments were carried out ; the input data in the corresponding code are the initial model of reaction, the operating conditions (temperature, pressure, composition of the reaction mixture, reaction duration...), as well as, possibly,

transport data for the species.

- The validation of the reaction model by comparison of the results of simulations with experimental results and adjustment where necessary of certain thermodynamic, kinetic or transport parameters.

The final reaction model is then used in the simulations.

Figure 1 : Elaboration and validation of a model of a gas-phase thermal reaction.



3 - CONTENTS AND ORGANIZATION OF THE BOOK

The contents and organization of the core of the book are described in Table 1.
This table consists of three columns giving for each discipline (thermodynamics, chemical kinetics, molecular transport phenomena, laboratory reactors) the numbers of

the chapters or appendices where the following are described :

- the laws, the concepts and corresponding models,
- the methods of estimation of physico-chemical data of the species and of the reactions, of generation, of analysis and of reduction of reaction mechanisms,
- a representative sample of numerical data allowing the use of the proposed methods to be illustrated with numerous real examples.

Table 1 : Architecture of the book.

	Laws, concepts and models	Methods	Numerical data
Thermodynamics	IV	V	XIV-1
Chemical kinetics			
• elementary reactions	VI	VII	XIV-2
• reaction mechanisms	VIII	IX XIII	
Molecular transport	X	XI	XIV-3
Laboratory reactors	XII		

The Roman numbers refer to the chapters.

FURTHER READING

The reading of the book, and above all the study of a particular case, leads necessarily to a search for complementary information, of a scientific or technological nature. A progressive approach is advised.

a) Consultation of general textbooks

Every scientist should have **at his disposal** a few basic textbooks in chemistry, physics, thermodynamics, chemical kinetics, physical kinetics and fluid mechanics, chemical reaction engineering, industrial chemistry... A choice of such books is proposed at the end of the introduction and, more generally, under the heading "further reading" in each chapter.

b) Consultation of encyclopedias

The choice will be limited to the recommendation of one general encyclopedia and a specialized series.

— **Ullmann's Encyclopedia of Industrial Chemistry**

The completely revised fifth edition of this encyclopedia dates from the year 1995. The references placed at the end of each chapter are exhaustive. As an addition to this work, the following volumes could be more readily consulted.

Volume B1 "Fundamentals of Chemical Engineering" contains chapters on mathematical and numerical methods, modelling, transport phenomena, fluid mechanics, the estimation of physical properties, combustion.

Volume B4 entitled "Principles of Chemical Reaction Engineering and Plant Design" treats general topics of Chemical Reaction Engineering and also contains two chapters dealing with industrial and laboratory reactors.

Volumes B7 and B8 refer to the protection of the environment and industrial safety. Volume B7 contains a chapter entitled "Air" treating all aspects of tropospheric pollution. Volume B8 tackles the issues relating to the raw materials and basic energies, to the products of reaction and to chemical safety.

The corpus, consisting of volumes A1 to A28, tackles more specialized subjects, classed in alphabetical order. An index allows appropriate articles to be found. For example, the article "Motor Fuels" (vol. A16, p. 719) treats spark-ignition engines and Diesel engines from different points of view : technology, fuels, emissions.

— The series **"Comprehensive Chemical Kinetics"** is dedicated, as its name suggests, to chemical kinetics, which is the main subject of this work. Numerous volumes, even relatively old, are still of interest today. Volume 35, published in 1997, and entitled "Low-temperature combustion and autoignition" constitutes a reference book in this area.

c) Search for specialized information

This can be found in monographs, articles in periodicals or proceedings from congresses, patents, theses, reports, paper databases, computer databases and computer codes.

The search for information can be carried out in different ways, which are more or less systematic :

- *Chemical Abstracts* allow references to be found by theme, by subject, by key-word, by chemical formula... ; they constitute a quasi-exhaustive source of chemical documentation.
- The references in textbooks, in review papers, in plenary lectures or in recently published specialized articles can be exploited.

Amongst the main periodicals dedicated in part to gas-phase reactions, the following can be listed :

- International Journal of Chemical Kinetics,
- Combustion and Flame,

- Combustion Science and Technology,
- SAE (Society of Automotive Engineers).

The Symposium Proceedings organized by "The Combustion Institute" and entitled "Symposium (International) on Combustion" constitute an endless source of information. Thus the two volumes of the 28th congress, held in Edinburgh (Scotland) in 2000, contain 3000 pages which tackle all the problems of combustion.

These documents and information can be obtained from libraries (Congress Library, British Library,...), institutes specialized in scientific and technical information or the technological centres (NIST, NASA,...),or from centres of computational calculations.

- The World Wide Web or Internet allows a huge mass of information to be obtained on line, in particular computer databases and computer codes which can be used directly. The book gives addresses (URLs) of some relevant sites, with no claim to exhaustivness or perenniality.
- Apart from the Internet forums, the information acquired by the usual paper sources treats completed works. Obtaining information on what is being done, or even better, on what is about to be done in the following years, occurs by direct contact with the research workers and engineers : laboratory and industrial exhibition visits, participation in scientific congresses and in professional training courses. These contacts also allow postdoctoral fellows to look for a job, and research workers and industrial scientists to establish collaborations.

GENERAL BIBLIOGRAPHY

a) Physical Chemistry

ALBERTY R.A., *Physical Chemistry*, 7th edition, Wiley (1985).
ATKINS P.W., *Physical Chemistry,* 5th edition, Oxford University Press (1994).
DUFFEY G.H., *Modern Physical Chemistry*, Kluwer (2000)
LAIDLER K.J., *Chemical Kinetics*, 3rd edition, Harper Collins (1987).

b) Chemical Reaction Engineering

BIRD R., STEWART W.E., LIGHTFOOT E.N., *Transport Phenomena*, Wiley (1960).
FROMENT G.F., BISCHOFF K.B., *Chemical Reactor Analysis and Design*, 2nd edition, Wiley (1990).
LEVENSPIEL O., *The Chemical Reactor Omnibook*, 2nd edition, OSU (1989).
LEVENSPIEL O., *Engineering Flow and Heat Exchange*, Kluwer (1998).
LIBBY P.A., WILLIAMS F.A., *Turbulent Reacting flows*, Academic Press (1994).
ORAN E.S., BORIS J.P., *Numerical Simulations of Reactive Flow*, Elsevier (1987).

SLATTERY J.C., *Advanced Transport Phenomena*, Cambridge University Press (1999).

THOENES D., *Chemical Reactor Development-From Laboratory Synthesis to Industrial Production*, Kluwer (1998).

c) Combustion

BAUKAL C.E.Jr., GERSHTEIN V., LI X., *Computational Fluid Dynamics in Industrial Combustion*, CRC Press (2000).

BORGHI R., DESTRIAU M., *Combustion and Flames*, Technip (1998).

GLASSMAN I. (Editor), *The next 25 years*, Combustion Science and Technology, Vol. 98, N° 4-6 (1994).

GLASSMAN I., *Combustion*, 3rd edition, Academic Press (1996).

GRIFFITHS J.F., BARNARD J.A., *Flame and Combustion*, 3rd edition, Blakie Academic & Professional (1995).

PILLING M. (Editor), *Low-Temperature Combustion and Auto-ignition*, Comprehensive Chemical Kinetics, Vol. 35, Elsevier (1997).

WARNATZ J., MAAS U., DIBBLE R.W., *Combustion*, Springer (1996).

CHAPTER I

ENERGY, PROCESSES, ENVIRONMENT

The aim of this chapter is to show both the part played by and the importance of gas-phase thermal reactions in the consumption of raw materials, the production of mechanical and thermal energy, the manufacture of chemical substances, the chemical safety, the atmospheric pollution, and, more generally, in the ecodevelopment of the planet.

GPTRs[1] are strictly speaking **homogeneous** reactions involving reactants, inert substances and products, **all of which are gases** (molecules, free radicals), and resulting exclusively from a **thermal activation**, which means that the reaction takes place as soon as the temperature level reached by the reaction medium is high enough.
A suitable temperature is established and maintained by an external supply of thermal energy in the case of **endothermic** reactions.
For **exothermic** reactions, which is especially the case in combustion reactions for example, the triggering off of the reaction can be induced by a very small energy contribution. An electric spark for the petrol engine, an auxiliary flame for burners are examples of this. The reaction continues afterwards on its own, either in an adiabatic way, or with heat or mechanical energy transfer towards or from the surrounding medium. The diesel engine exploits an endogenous mechanical energy to reach the temperature and pressure levels required to trigger off the reaction.
But GPTRs also occur to an important extent in more complicated chemical transformations, concomitantly with **photochemical** reactions (urban smog, stratospheric ozone), **heterogeneous catalysis** reactions (oxidizing coupling of methane), non-catalytic **heterogeneous reactions** (CVD/CVI) or involving various **electrical discharges** (HÜLS process, plasmas).

1 - RAW MATERIAL AND ENERGY

Table 1 gives a summary of the worldwide consumption of fossil raw material (natural gas, crude oil, coal), fissile raw material (uranium), commercialized renewable energies

---

[1] Gas-phase thermal reactions.

(hydroelectricity, geothermal and aeolian energies, thermal electricity made from lignocellulosic wastes) and non-commercialized renewable energies. The latter consist mainly of the combustion of biomass (wood, lignocellulosic wastes from hay, cow-pats...) for domestic use, in the heating of houses and food.

Table1 : Worldwide consumption of fossil raw material and renewable energies.

a) Fossil raw material	Mtoe/yr*	%
Natural gas	1 750	19
Crude oil	3 150	34
Coal	2 200	23
b) Fissile raw material		
Uranium	460	5
c) Commercialized renewable energies		
Hydroelectricity	540	6
Geothermal energy	8	0.09
Aeolian energy	1	0.01
Electricity from the biomass	13	0.10
d) Non-commercialized renewable energies		
Domestic heating from the biomass	1 248	13
Total	9 370	100

* 1 Mtoe represents the energy equivalent of 1 million tons of crude oil. The following equivalences can be used :

1 ton of crude oil, of diesel fuel or of domestic fuel oil = 1 toe
1 ton of petrol or of turbojet fuel $\simeq$ 1.048 toe
1 ton of LPG $\simeq$ 1.095 toe
1 ton of heavy fuel = 0.952 toe
1 ton of coal = 0.619 toe
1 ton of natural gas = 1.2 toe

Based on the extrapolation of the consumptions given in Table 1 and on the technologies available today, the so-called proven reserves of natural gas, crude oil and uranium will last for approximately fifty years, and those of coal for several thousand years.

Table 2 indicates the distribution of use of the fossil raw material in large sectors : thermal, electrical and mechanical energy production, chemical and parachemical industries, metallurgical industries.

From the figures given in Tables 1 and 2, the global importance of GPTRs for the production of primary energy and for the manufacture of the major primary chemicals can be assessed. If the reaction really is a GPTR, the reactants must be gaseous, which is true of natural gas, or vaporized before the real reaction takes place, which is the case of oil fractions, but which therefore excludes coal and biomass from the range of so-called GPTRs.

Natural gas

The worldwide consumption of natural gas reaches 1 750 Mtoe/yr, that is an average of 750 g per person per day. This consumption represents a fifth of the consumption of raw material and primary energies (Table 1).

93 % of natural gas is used by combustion GPTRs to produce domestic and industrial heat (68 %) and electricity (25 %) (Table 2). The remaining 7 % are used as raw material for the large-scale chemical industry.

Table 2 : Use of fossil raw material (%).

	Natural gas	Crude oil	Coal
Thermal energy	68	35	—
Electrical energy	25	10	61
Mechanical energy	ε	40	ε
Chemical industry	7	7	1
Metallurgical industry	ε	ε	20
Various	ε	8	18

Crude oil

The worldwide consumption of crude oil reaches 3150 Mt per year, that is an average of 1650 g per day per person. This consumption represents a third of the global consumption of raw material and primary energies.

85% of the crude oil, the oil fractions which are obtained by refining, engine and heating fuels derived from oil is used in combustion GPTRs, in engines and burners, and up to 7 % by the chemical industry.

Combustion

The combustion GPTRs therefore use up a total of 1 630 Mtoe/yr of natural gas and 2680 Mtoe/yr of crude oil, which, taking into account the equivalences given in Table 1, corresponds to an average for the total number of inhabitants of the planet to a daily consumption of 750 g natural gas and 1500 g crude oil, that is a total of 2.25 kg. For comparison, an adult eats almost exactly the same weight, that is two and a quarter kilogrammes of solid food a day. These average figures must not disguise the dramatic reality of the undernourishment or of the malnutrition of a large part of mankind, which is correlated with an insufficient energy consumption. On these two points, and on many others, there remain enormous differences between the rich and poor countries.

2 - ENERGY PRODUCTION

Table 3 gives the energy applications of GPTRs ; they can be divided into two important categories.

Table 3 : Energy production by GPTRs.

NG : natural gas ; CNGV : compressed natural gas for vehicles ;
LPG : liquefied petroleum gas.

a) Mechanical energy production

Engines	*Fuels*	*Applications*
Spark-ignition engines	Petrols LPG, CNGV, alcohols	Mopeds, motorcycles, motor bikes, cars
Diesel engines	Diesel fuel, Diesel fuel oil Heavy fuels	Cars, lorries, agricultural tractors, heavy plant vehicles, barges, ships, locomotives
Fixed turbines	NG, LPG, kerosene, diesel fuel	Power plants
Turbojet engines	Turbojet fuels	Aircraft
Launchers	Ergols	Earth and ballistic missiles, Earth satellites, space probes

b) Thermal energy production

Burners	*Fuels*	*Applications*
Domestic burners	NG, LPG	Heating of food and houses
Industrial burners	NG, LPG, fuel oil	Industrial ovens, Steam for processes Heating of buildings Thermal power plants Incineration
Blow-torches	NG, LPG, C_2H_2, H_2	Welding and cutting of metals

a) Mechanical energy

GPTRs are largely involved in the production of mechanical energy for road, river, sea, air and space transport, as well as for the production of electricity by fixed turbines (Table 3a).

The operating principles of the various **thermal engines**, as well as the characteristics of the **fuels** used and the **reactions**, which take place, will be described in Chapter II.

b) Thermal energy

GPTRs are also used for the production of heat by exothermic combustion reactions. This heat is used domestically, industrially, environmentally (burning of wastes), and for the production of electricity from steam (Table 3b).

The burners used in these reactions, the characteristics of the different fuels used and the corresponding reactions are described in Chapter II.

3 - CHEMICAL INDUSTRIES

a) Manufacture of primary chemicals

Table 2 states that around 7 % natural gas and 7 % crude oil are used to produce so-called primary chemicals. Apart from heterogeneous catalysis and acid-base catalysis processes, two main GPTRs transform raw material into primary chemicals (Table 4a).

— *Steamcracking of hydrocarbons*

Steamcracking produces the primary chemicals which are at the basis of nearly all the large-scale industrial organic chemistry of today, from crude oil fractions, mainly ethane, propane, naphtha, obtained during oil refining : alkenes (C_2H_4, C_3H_6, C_4H_8), butadiene (C_4H_6), benzene, toluene, xylenes (BTX), as well as small quantities of petrol are obtained.

This process will be described in Chapter II.

— *Oxidation of hydrocarbons*

The partial homogeneous oxidation (without catalyst) in the gaseous phase of different hydrocarbons derived from crude oil, from natural gas or from refinery gas, by air, by oxygen-enriched air, or by pure oxygen, allows different synthesis gases to be obtained. This name is primarily given to the CO/H_2 mixture obtained by oxidation by pure **oxygen** ; but the name synthesis gas is also given to the N_2/H_2 mixture obtained in two important steps : homogeneous oxidation of hydrocarbons by **air** to make a $CO/H_2/N_2$ mixture, followed by a conversion of CO into H_2 by a catalytic reaction with steam.

The synthesis gas N_2/H_2 is then converted into ammonia NH_3 by a catalytic reaction.

Ammonia is itself converted into **fertilizers**, and also into nitric acid, from which **explosives** used in mines and quarries and for military use, are derived.
The world food production can only be maintained at its present level thanks to the use of fertilizers derived from ammonia. This explains the development of homogeneous oxidation processes, which have supplanted the catalytic process of steam reforming.
This process will be described in Chapter II.

b) Manufacture of secondary chemicals

The term secondary chemicals is given to the chemicals and materials derived in one or several chemical operations from the primary chemicals obtained in particular by steamcracking or by gasification.

The GPTRs used belong to one of the four main categories (Table 4b).
— True pyrolysis reactions, alone or concomitant with a deposit by Continuous vapor deposition (CVD) or infiltration (CVI).
— The reactions involving hydrogen and which consist mainly of a hydrogenolysis.
— Reactions with oxygen which can either be mainly homogeneous and lead to synthesis gas, to acetylene (BASF process), or involve a catalytic part (oxidizing coupling of methane in the presence of metal oxides), or be at the starting point of a deposition reaction.
— Reactions with chlorine are very varied and lead either to the final chemicals, or to important intermediates. Reactions involving other halogens (fluorine, bromine, iodine) must also be mentioned.

Compared with the number of industrial processes using heterogeneous or acid-base catalysis, the number of processes involving GPTRs appears to be relatively small. This is due to several reasons :

- when a reaction is **exothermic**, the thermodynamic laws (cf. Chapter IV) indicate that the reaction must be carried out at **"low" temperature**. But it often happens that the **rate** of a **homogeneous** gas-phase reaction is insufficient, which leads to the use of a catalyst. This has another beneficial effect which is that it increases the **selectivity** of the reaction with respect to that of the gas-phase radical reactions.
- when a reaction is **endothermic**, the thermodynamic laws indicate that the reaction must be carried out at **"high" temperature**. Apart from the technological difficulties involved when the temperatures are really very high, as often happens, for the reasons of selectivity mentioned above, it is often necessary to use a catalyst.

The outcome of this brief discussion is that it is understood that the **mastering of the selectivity of the GPTRs** is the key to success when using them. The same conclusion will be drawn when discussing the reactions of formation of pollutants.

Table 4: Manufacture of chemicals by GPTRs.

a) Primary chemicals		
Reaction	*Reactants*	*Products*
Steamcracking	Ethane, propane, naphtha	Alkenes, butadiene, C_4 fraction, BTX, petrol
Partial oxidation	Heavy crude oil fractions, NG, refinery gas	Synthesis gas
b) Secondary chemicals		
Reaction	*Reactants*	*Products*
Pyrolysis	1,2 dichloroethane	Vinyl chloride
	Acetic acid	Ketene
	Methyl-2 pentene-2	Isoprene
	Chlorodifluoromethane	Tetrafluoroethylene
	Alkanes, aromatics	CVD/CVI of pyrocarbon
	Silicon and gallium compounds...	Computer components, VHF tubes...
Reactions with hydrogen	Toluene	Benzene
	Methyl acetate	Methanol, ethanol
Reactions with oxygen	Natural gas	Acetylene
		Diamond
Reactions with chlorine	Methane	Chloromethanes
	Ethylene, ethane	Ethyl chloride
	Ethylene, chloroethanes	Vinyl chloride, chlorinated solvents
	Propene	Allyl chloride
		Tetrachloroethylene
		Carbon tetrachloride

4 - CHEMICAL SAFETY

The most direct manner in which chemical reactions affect our environment are fires and explosions which are the most violent examples of GPTRs.

a) Phenomenology

When a large quantity of organic substances, in the gas or liquid phase (hydrogen, natural gas, liquefied petroleum gases...), is accidentally exposed to air, the ignition of this mixture of air and gas or organic vapours leads to several types of situations.

— Gas fires (flash fires)

These are fires, where the quantity of gas is limited, these are not accompanied by an explosion. The damage is only due to the heat given off.

— Explosion of a cloud of organic vapours (Vapour Cloud Explosion = VCE)

These are gas fires accompanied by an explosion, which causes mechanical damage as well as thermal damage. The nature of the explosion is different according to whether it takes place in a confined space, which is the general case of domestic gas explosions in buildings, or in an unconfined environment, when organic vapours spread in the atmosphere (UVCE = Unconfined Vapour Cloud Explosion) ; an example of this is the FLIXBOROUGH accident which is described below.

— Explosion of a vapour emanating from a boiling liquid (Boiling Liquid Expanding Vapour Explosion = BLEVE)

This phenomenon occurs when an organic liquid (hydrocarbon, alcohol, ketone...) stored under its vapour pressure at the temperature conditions of the process, escapes accidentally from the apparatus and catches fire.

— Fires of organic liquids

These fires occur when a mixture of organic liquids, in contact with the surrounding air, catches fire. The flame is kept burning by the evaporation of the liquid, which is itself caused by part of the heat of combustion in the gas phase.

b) Causes and consequences of fires and explosions

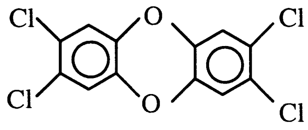
The most frequent causes of fires and explosions involving GPTRs are the breaks in joints and solders, of taps, the bad handling of an exothermic reaction... Some examples will help to better understand the problem.

— The FLIXBOROUGH accident (UK) in 1972

The plant manufactured cyclohexanone by the reaction of cyclohexane with oxygen, at 155 °C and at about 9 atm. The reaction took place in a series of six reactors, corresponding to a capacity of 45 m^3 and 35 t of cyclohexane. Following a breakage, a leak of cyclohexane estimated at 1 t/s led to the formation of a cloud of gas and aerosol of the order of 200 m × 100 m. The ignition occurred in less than a minute and caused the deaths of 28 people, burnt and injured 89 people, destroyed the plant and the houses within a radius of 1 km, as well as causing damage to buildings within a radius of 3 km around the plant.

— The SEVESO accident (Italy) in 1972

Following a malfunction of the heat exchanger, there was an explosion in the reactor, and a loss to the atmosphere of 1 to 2 kg of polychlorodibenzodioxins (PCDD). There are 75 isomers of the PCDDs. 2,3,7,8 tetrachlorodibenzodioxin



is considered to be the most toxic for animals. A similar loss of "dioxin" also happened in Missouri, in the United States. A controversy arose to estimate the effect on the health of the people contaminated ("simple" chloracne, carcinogenic or teratogenic risks).

— In 1990, in the USA, an explosion occurred which was caused by peroxides which had accumulated in a plant for the treatment of styrene and propylene oxide which resulted in the deaths of 17 people and extensive damage to the plant.

— In 1992, in Great Britain, an oil tanker transporting 33 t petroleum products caught fire as the result of a road accident. Although there was no explosion, 6 people were badly burnt and 70 others were treated after having inhaled the gases which were given off. It was necessary to evacuate the houses surrounding the accident zone.

c) Prevention of fires and explosions

Studies on the prevention of chemical accidents (Hazard and Operability studies : HAZOP) constitute an important part of the setting up of an operational chemical process. They necessitate the accumulation of a large amount of physico-chemical data : the self-inflammation and flammability limits, the delays of self-inflammation, the speeds of flame propagation, the conditions under which combustion or detonation occur.

Safe working conditions must be defined to avoid leaks of gases and organic vapours, dispersing possible leaks using ventilation, decreasing their confinement, forbidding sources of ignition (welding, electrical switches, traffic), minimizing the possible effect of explosions using safety valves.

Volumes which normally contain air and are likely to receive hydrocarbons accidentally, and vice-versa, can be rendered inert. These applications concern certain parts of the wings or of the fuselages of aeroplanes, or helicopters, and offshore gas and oil production platforms. This is carried out by the introduction of small amounts of the order of about 5% by volume, of a gaseous agent such as CF_3Br (Halon 1301)[1], into the volume to be rendered inert.

---

[1] Due to the adverse effect of CF_3Br on the stratosperic ozone layer, the production of this halon has been banned by the MONTREAL protocol (cf. § 5.4).

d) Fire extinction

The extinction of a fire involving GPTRs can be obtained using different agents, solid (Na_2CO_3), liquid (H_2O), gaseous (CO_2, N_2, CF_3Br). These agents intervene in three main ways :

- by heat absorption due to their decomposition, to their vaporization, or to their heat capacity. The absorption of part of the heat of combustion causes an endogenous decrease of the temperature and consequently of the rate of reaction.
- by dilution of the reactants, fuel and combustion agent. Lowering the concentrations also decreases the rate of reaction, but this effect is much less sensitive than the previous one.
- by a homogeneous or hetero-homogeneous mechanism of chemical inhibition. The additive acts as a free-radical trap and lowers the concentration of the latter below the critical level for the flame to continue. The chemical mechanism requires only a very short time to be effective, as the absolute rate of radical reactions is very high. This accounts for the ability of CF_3Br to prevent a fire started by firing a bazooka into the fuel tank of an army tank.

These three means of action can of course be combined, to different extents, according to the conditions.

5 - ATMOSPHERIC POLLUTION

5.1 -The atmosphere

a) Chemical composition

The chemical composition of the Earth's atmosphere has changed considerably since its original formation up to its composition today.

For meterological needs, an international agreement for the composition of dry, unpolluted atmospheric air (without water vapour) near the Earth's surface has been reached (Table 5). Amongst other constituents in this table, the three most important are nitrogen, oxygen and argon ; three constituents have a level which varies according to the place and time, these are carbon dioxide, ozone and radon.

Apart from the gases mentioned in Table 5, the atmosphere contains water in different forms (vapour, liquid, solid) as well as numerous other chemical compounds, which will be called by the general name atmospheric **pollutants**.

Although pollutants can be found in the atmosphere at very low concentrations, of the order of ppm or of ppb[1], they nevertheless have **the** crucial role to play in the major

---

[1] Parts per million (10^6) and per billion (10^9) by volume, respectively.

ecological phenomena which determine not only the quality of life on Earth, but also quite simply the survival of all mankind. The origin, the part played by and the fate of these different pollutants is itself the subject of paragraph 5.

Table 5 : Composition of unpolluted atmospheric air at the Earth's surface.

Gas	N_2	O_2	Ar	CO_2
% mol	78.09	20.95	0.93	0.03
Gas	Ne	He	Kr	H_2
% mol	$1.8x10^{-3}$	$5.24x10^{-4}$	$1.0x10^{-4}$	$5.0x10^{-5}$
Gas	Xe	O_3	Rn	
% mol	$8.0x10^{-6}$	$1.0x10^{-6}$	$6.0x10^{-18}$	

b) Vertical structure (Figure 1)

Four main regions of the atmosphere can be distinguished. The **troposphere** is the lowest region and is limited by the tropopause ; the latter is situated at an altitude of 9 km at the poles and 17 km in the tropics. The **stratosphere** extends from the tropopause to the stratopause at an altitude of 50 km. Next comes the **mesosphere**, which stops at the mesopause, at an altitude of around 80 km. Above 80 km, the **thermosphere** starts.

Figure 1 shows the variations in the temperature and the air pressure as functions of the altitude.

The **temperature** decreases in the troposphere ; it increases very little in the tropopause up to 25 km, then increases following the absorption of the solar radiation by the stratospheric ozone ; it decreases in the mesosphere and increases constantly in the thermosphere, but this increase depends on the sun's activity. The chemical reactions, which occur in the troposphere and in the stratosphere and which are those of interest from an ecological point of view, therefore take place at temperatures of between 150 and 300 K.

The **pressure** decreases in an approximately exponential manner with the altitude. It is of the order of $1.013x10^5$ Pa at the Earth's surface and 80 Pa at an altitude of 50 km.

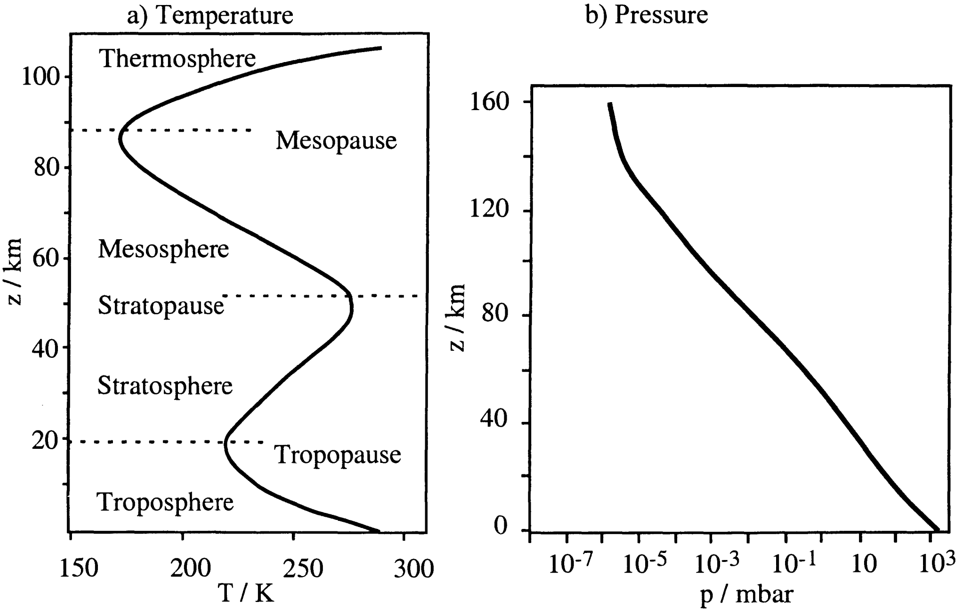
c) Winds

The atmosphere is subject to convective movements which transport the pollutants both horizontally and vertically. These convective movements are due to the thermal gradients which themselves result from the surface heating of the land and the oceans by the sun.

The characteristic times of the horizontal convective transport are of several weeks for

the zonal transport (along the longitude), and of several months for the meridional transport (along the latitude) and of one to two years for the transport between the hemispheres. Those of vertical convective transport vary from several days to several weeks for the troposhere, and from five to seven years for the stratosphere.
These orders of magnitude for the durations of transport should be compared with the lifetimes of the pollutants in order to evaluate the effectiveness of their transport.

Figure 1 : Vertical structure of the atmosphere.
T : temperature ; p : pressure; z : altitude.



5.2 - Tropospheric pollution

a) Primary tropospheric pollutants

The global system Earth-atmosphere is the seat of complicated exchange of matter between the stratosphere, the troposphere, the Earth's biosphere, the sea's biosphere and the lithosphere. Uncertainties in much of the data do not allow the global cycle of carbon to be correctly established today. The best known facts concern the atmosphere.
The troposphere is fed by **pollutants of natural origin** resulting from the respiration and oxidation of the biomass, from the oceans (300 Mt NaCl per year) and from volcanoes (10 Mt HCl per year), for example. As sodium chloride and hydrochloric acid are soluble in water they are mainly leached out by the rain and contribute little to

the transfer of chlorine in the stratosphere. Photosynthesis uses up carbon dioxide which also dissolves in the oceans.

The troposphere is also fed by **pollutants of anthropogenic origin**, that is to say which are due specifically to the activity of mankind. These pollutants result on the one hand from the industrial activities and the combustion of natural gas, petroleum products, and coal, which started in the middle of the XVIIIth century with the industrial revolution, and on the other hand from agricultural activities, with the burning of tropical vegetation to create arable land, the growing of rice and the rearing of livestock which produce methane by anaerobic fermentation in the digestive systems of ruminants, and the use of fertilizers containing nitrogen which generate N_2O.

Table 6 shows the states of the anthropogenic outputs and the total outputs of the main primary pollutants : carbon oxides, methane, nitrogen oxides, sulphur dioxide, chlorofluorocarbons (CFCs) and halons (halogenated hydrocarbons), as well as the resulting concentrations.

It can be observed that the part of the anthropogenic emissions is large if not preponderant in all cases, and even the sole outputs when discussing CO_2, the CFCs and the halons.

It is also surprising that such low concentrations, for example 3 atoms of chlorine to 10^9 molecules of air, can have such an important impact : the reason lies in a complicated combination of photochemical reactions, of chain reactions and of heterogeneous reactions.

Table 6 : Primary tropospheric pollutants.

	Anthropogenic outputs in Mt/yr	Total outputs	Concentrations in ppb
CO	700	2000	50-200
CO_2	5500	5500	350 000
CH_4	350	550	1700
NO and NO_2	25	40	10^{-3}-50
N_2O	6	25	310
SO_2	120	180	0.03-50
CFC, Halons	1	1	3 (in atoms of chlorine)

Table 7 gives the sources of urban atmospheric pollutants, on the one hand in the USA in the 1970s, and on the other in Great Britain in the 1990s. Note that the means of transport are the main producers of CO, NO_x and solid particles, thermal electricity of

SO_x (this pollution is minimized when nuclear electricity is being used) and industry of organic compounds. Comparison of Tables 7a and 7b shows that the means of transport play an increasing part in the outputs of urban pollutants.

Table 7 : Sources of urban atmospheric pollutants.

a) In the USA in the 1970s (in Mt/yr).

	CO	NO_x	SO_x	Organic compounds	Solid particles
Transports	64	8	0.8	17	1.2
Electricity	2	10	25	0.7	9
Industries	10	0.2	7	5	8
Incineration	8	0.6	0.1	2	1
Diverse and domestic uses	17	2	0.6	9	10
Total	101	20.8	33.5	33.7	29.2

b) In Great Britain in the 1990s (in %).

	CO	NO_x	SO_x	Organic compounds	Solid particles
Transports	90	51	2	37	47
Electricity	1	25	70	—	5
Industries	5	21	25	62	20
Diverse and domestic uses	4	3	3	1	28

Taking into account the effects of the emission of pollutants on the health of human beings, animals and plants, and on the potential climatic consequences of the greenhouse effect, it is not surprising that the emissions should comply with the regulations of the public authorities. These recommendations vary much from country to country, and change constantly with the scientific and technological progress made in techniques of measurement and control, the pressure of public opinion, and economic constraints on car manufacturers, engine designers, the petroleum and chemical industries. As an indication, Table 8 gives typical European limiting values for the exhaust, after possible post-treatment, for cars, lorries, aircraft and thermal units. The main controlled pollutants (CPs) are carbon monoxide CO, unburned hydrocarbons HC, the nitrogen oxides NO_x, particles, sulphur dioxide SO_2, ozone, as well as dioxins from thermal plants.

Pollutants which are as yet uncontrolled (UCPs) include numerous volatile organic compounds (VOCs) which will be gradually added to the list of CPs.

Table 8 : Emission regulations around year 2000.

	CO	HC	NO_x	$HC + NO_x$	Particles
a) Light-duty vehicles (g/km)					
Petrol	2.3	0.2	0.15	—	—
Diesel	0.64	—	0.50	0.56	0.05
b) Heavy-duty vehicles (g/kWh)					
Standard cycle	2.1	0.66	5.0	—	0.1
Transient cycle	5.45	0.78	5.0	—	0.16
c) Subsonic jet planes (g/kN)					
	118	19.6	$32 + 1.6\ M_{oo}$	—	$83.6 \times F_{oo}^{-0.274}$ (Smoke number)
M_{oo} : overall compression ratio at sea level ($15 < M_{oo} < 35$)					
F_{oo} : maximum thrust at take-off (in kN)					
d) Thermal plants	CO	NO_x	SO_2	Dioxins	Particles
		ppm	mg/m^3	mg/m^3	mg/kWh
	—	0.1	0.25	0.1	129

Table 9 gives a list of the principal VOCs, which includes mainly the hydrocarbons and oxygenated molecules, as well as the relative reactivity of these VOCs with the free hydroxyl radical. The reactions which are induced by OH lead to the degradation of the pollutants : OH appears thus to be a cleansing agent for the troposphere ; but the reactions of OH with the primary pollutants can also form other pollutants, which will be called secondary pollutants.

b) Photochemical smog

The gases given off by petrol and diesel fuel stations when vehicle fuel tanks are being filled, the exhaust fumes of vehicles in urban areas, the gases released by domestic and industrial thermal stations, by incineration plants and certain chemical factories are likely to react with air under the action of the sunlight to give rise to photochemical smog.

Table 10 gives an example of the composition of photochemical smog. Smog causes respiratory problems (which can be extremely serious), irritates the eyes, reduces the visibility and causes damage to the vegetation. Peroxyacylnitrates and ozone are amongst the most dangerous compounds.

Table 9 : Volatile organic compounds (VOCs).
The numbers indicate the reactivity of the OH free radical with respect to the species being considered, relative to that of methane.

a) Normal alkanes
- Ethane 44
- Propane 182
- n-Butane 500
- n-Hexane 790

b) Branched alkanes
- Isopentane 420
- 2-Methylpentane 440
- 3-Methylpentane 900

c) Alkenes and unsaturated compounds
- Ethylene 1750
- Propene 5830
- cis-2-Butene 6730
- 2-Methyl-2-butene 10 000
- 2,3-Dimethyl-2-butene 14 000
- 1,3-Pentadiene 9670
- Acetylene 168

d) Aromatics
- Benzene 250
- Toluene 1346
- Ethylbenzene 1000
- n-Propylbenzene 770
- Isopropylbenzene 770
- o-Xylene 1750
- m-Xylene 2920
- p-Xylene 1530
- o-Ethyltoluene 1710
- m-Ethyltoluene 2420
- p-Ethyltoluene 1625
- 1,2,3-Trimethylbenzene 3100
- 1,2,4-Trimethylbenzene 4170
- 1,3,5-Trimethylbenzene 6190

e) Alcohols
- Methanol 225
- Ethanol 765

f) Aldehydes
- Formaldehyde 2475

g) Ketones
- Methylethylketone 440
- Methylisobutylketone 1920

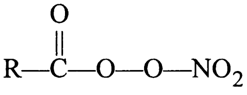
h) Terpenes
- α-Pinene 8750
- d-Limonene 18 800

Table 10 : Photochemical smog.

Pollutant	Concentration in ppb
CO	$2x10^3$-$2x10^4$
NO	10-150
NO_2	50-200
NMHC[1]	200-500
Alkenes	20-60
Aromatics	100-300
Ozone	20-200
Aldehydes and ketones	50-250
PAN[2]	10-40

[1] NMHC : Non-Methane HydroCarbons

[2] PAN : PeroxyAcylNitrates



$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}O\text{—}NO_2$

c) Acid rains

The sulphur contained in fossil fuels, mainly in coal and in mineral ores, is transformed during combustion or firing reactions into sulphur dioxide SO_2. The latter, by reactions involving the hydroxyl radical OH, hydrogen peroxide H_2O_2 and water, forms sulphuric acid and aerosols of sulphates.

The oxides of nitrogen lead to nitric acid and nitrates. Sulphuric and nitric acids are washed by the rains which are therefore called acid rains. They can also be deposited by a dry process or with the aid of solid particles.

These acid rains caused the water of the lakes in Scotland to have pHs of 2.4 in the 1970s, that is an acidity similar to that of vinegar. A fifth of the Swedish lakes have lost a large portion of their fish, in particular trout which cannot survive in pHs lower than 5. The agricultural damage, the corrosion of the metals of buildings, the harmful effects on the respiratory systems must also be attributed to sulphur pollution. Thus the annual cost of the corrosion by acid rains in the USA has been estimated to be worth 10^{11} US dollars.

Sulphate aerosols scatter the light very strongly ; this has the effect not only of reducing the visibility but also of increasing the albedo of the atmosphere, i.e. its power to reflect the sun's rays ; these aerosols therefore contribute, like other particles, to cooling the planet and counterbalancing the greenhouse effect.

5.3 - Greenhouse effect

In order to explain the greenhouse effect, it is necessary to carry out an **energy balance of the Earth-atmosphere system**. The energy received by this system is mainly that due to the sun's rays[1].

a) Incident radiation balance (Table11a)

The radiation from the sun that reaches the Earth is mainly in the visible and the near infrared from 0.2 to 4 µm. Taking into account the inclination of the sun's rays and that half of the Earth is not irradiated, a power of 175 petawatt or 342 W/m^2 is calculated to be received by the atmosphere-Earth system. These 342 W/m^2 can be divided into 4 parts :

- 12 W/m^2 are absorbed in the stratosphere, mainly by stratospheric ozone,
- 64 W/m^2 are absorbed in the troposphere, mainly by tropospheric ozone and water vapour,
- 164 W/m^2 are absorbed by the lithosphere,
- 102 W/m^2 are reflected directly and sent back into space by the stratosphere, the

---

[1] and, for a minuscule fraction, to the moon which is responsible for the tides.

troposphere and the lithosphere ; this is mean albedo, representing about 30 % of the incident flux, but likely to vary between 15 and 85 %.

Of the 342 W/m^2 received, 102 are already sent back into space. If the atmosphere-Earth system is in a steady state, the first principle of thermodynamics states that 240 W/m^2 supplementary energy must go back into space in the form of thermal energy.

b) Balance at the Earth-atmosphere interface (Table 11b)

Assuming that the Earth is a black body, in order to emit 240 W/m^2, the temperature at the surface must be equal to − 18 °C. But in fact, all the radiation emitted does not go back into space. In actual fact, it is absorbed by water vapour at wavelengths shorter than 8 μm, by the carbon dioxide at those higher than 13 μm, by ozone at 9.6 μm, as well as other greenhouse effect gases (CH_4, N_2O, CFCs...).

Table 11 : Energy balance of the Earth-atmosphere system (in W m^{-2}).

a)Incident radiation balance				
Incident solar radiation	342	Albedo	102	
		Stratospheric absorption	12	240
		Tropospheric absorption	64	
		Lithospheric absorption	164	
			342	
b) Balance at the Earth-atmosphere interface				
Solar Energy	240	Thermal radiation of the Earth	400	
Greenhouse effect	274	Evaporation of water	90	
		Winds	24	
Total	514		514	

The radiation absorbed is transformed into heat and then re-emitted, still in the infrared, partly towards the Earth and partly towards space. The Earth must therefore emit a thermal radiation of 400 W/m^2, which is more powerful and corresponds to a mean temperature at the Earth's surface of 16 °C. It also dissipates 90 W/m^2 for the evaporation of water and 24 W/m^2 for turbulent convection, in other words the tropospheric winds.

The total energy dissipated by the surface of the Earth is therefore worth 514 W/m^2. As the Earth receives 240 W/m^2 solar energy directly, the difference, which can be attributed to the greenhouse effect, is equal to 274 W/m^2, which is a considerable amount of energy. In total, the radiation coming from the atmosphere and received by the Earth is equal to 350 W/m^2.

60% of the thermal radiation emitted by the Earth is absorbed in the low atmosphere by water vapour, and 30 % by carbon dioxide and the remaining 10 % by the other greenhouse effect gases.

Now, in Table 6, it was shown that to a large extent, these gases come from anthropogenic sources. Thus the MAUNA LOA observatory in HAWAII observed an average level of CO_2 of 316 ppm in 1960 which increased steadily to 336 ppm in 1980. It is estimated that this level will reach 400 ppm early in the XXIst century as opposed to 280 at the end of the XIXth century. Anthropogenic emissions of CO_2 come from the burning of natural gas, of crude oil, of coal and of the tropical biomass due to the deforestation ; the lack of photosynthetic fixing and the emission of carbon dioxide resulting from the mineralization of the humus thus degraded must be added to this last cause.

On the contrary, other phenomena tend to increase the albedo (this is especially the case of aerosols and dust formed from SO_2) and therefore cool the Earth.

In conclusion, despite the complexity of the phenomena involved, and the uncertainties which arise in the predictive models of the greenhouse effect, it is certain that the pollutants of anthropogenic origin can cause a global modification of the climate of the planet. The consequences of this heating concern the nebulosity, the winds, the melting of the glaciers with a correlated increase in the level of the oceans ... and are themselves difficult to evaluate.

5.4 - Stratospheric ozone

a) Role of the ozone layer

The stratospheric ozone layer is situated at an altitude of between 17 and 50 km. It contains 90 % of the ozone content of the Earth's atmosphere. Ozone absorbs the sun's UVB radiation (280-310 nm) ; this fact can be easily demonstrated in the laboratory. Stratospheric ozone is therefore of major importance as a protective screen for the Earth against the sun's radiations. Thus, in the Antarctic, at each austral spring, a sharp decrease in the total ozone layer is observed with respect to the value in the summer ; correlatively, a significant increase in the UVB radiation at ground level is observed.

Now, the UVB radiation is likely to have harmful effects on the health of human beings causing melanomas, cataracts, erythemas, by decreasing the effectiveness of the immune system and causing genetic mutations ; it also affects animals and plants and is a cause of the ageing of plastics, paints and varnishes.

It is difficult to establish precise relationships on the one hand, between the total quantity of stratospheric ozone and the intensity of the UVB radiation which reaches the Earth's surface, and on the other hand, between the doses of UVB radiation and in particular the effects on human health. Nevertheless, there is an important and lasting decrease in the stratospheric ozone layer which is a subject of worry to planetary ecologists.

b) The experimental facts

Measurements of the local ozone concentration, at a given latitude and altitude, can be integrated to give the total concentrations at a given instant. These measurements are carried out from the Earth, using balloons, aeroplanes or satellites.

The Englishman DOBSON, who gave his name to the unit for measuring quantities of ozone, and his collegues started to measure the ozone over HALLEY bay in the Antarctic in 1956. Measurements in March-April gave values of 450 DU and they were surprised to obtain 300 DU in September, during the austral spring. For two decades, measurements have given the same results at the same periods of the year. It is therefore a seasonal cycle due to the particular conditions prevailing at the south pole each springtime.

But since the beginning of the 1980s, this seasonal phenomenon has worsened. More than 65 % of the ozone disappears in the spring over a surface of 20 million km^2, about 90 % of which is at an altitude of between 18 and 25 km.

c) Interpretation of the observations

This relies on the hypothesis that the hole in the ozone layer is due to reactions induced by **the nitrogen oxides, the CFCs and the halons of anthropogenic origin**. For this interpretation the Nobel Prize for Chemistry was awarded to ROWLAND, MOLINA and CRUTZEN[1] in 1995 who had established that these compounds contributed to the destruction of the stratospheric ozone in the 1970s.

— The CFCs and the halons (Table 12)

The CFCs, or chlorofluorocarbons, are molecules containing chlorine, fluorine and

---

[1] The Royal Academy of Sciences in Sweden which awards this prize indicated that, by explaining the chemical mechanisms which alter the thickness of the stratospheric ozone layer, the three scientists had contributed towards saving the world from a global environmental problem which was likely to have catastrophic consequences for all mankind.

carbon. They are characterized by the letters CFC followed by a two- or three-figure number which allows their basic formula to be identified. The number of carbon atoms is equal to the first figure plus 1, the number of hydrogen atoms that of the second figure minus 1, and that of the fluorine atoms to the third figure. The number of chlorine atoms can be deduced by taking into account the fact that the CFCs are derived from the alkanes by replacing the H atom by Cl or F atoms. When the identifying number of a CFC contains only two figures, this means that the first figure is equal to 0 and that the molecule then contains only one carbon atom. The illustration of this nomenclature is given in the columns a and b of Table 12, which shows the names and molecular formulae of the CFCs which are forbidden by the MONTREAL protocol.

The halogenated hydrocarbons are molecules which contain carbon, fluorine, chlorine and bromine. They are given the word halon followed by a 4-figure number indicating in order the number of C, F, Cl and Br atoms. Table 12 contains the name and the molecular formula of the three halons mentioned in the MONTREAL protocol.

Columns c and d of Table 12 give the tonnages and the principal applications of these eight CFCs and halons. The term **mousse** represents both soft mousses and hard polyurethane mousses ; the term **cold** stands for all domestic and industrial applications to refrigeration, to the air conditioning of buildings and cars ; the term **propellant** can be applied to the gases contained in the cartridges destined for the production of cosmetic and medicinal aerosols, etc... ; the term **solvent** represents the cleaning operation of electronic, electrotechnical or mechanical parts, to remove smears which are soluble in CFC 113 ; lastly, the halons were very often used in the **extinction of fires** occurring in space occupied by people or expensive equipment (civilian and military aircraft, army tanks, aircraft carriers, petroleum platforms, computer rooms, libraries...), as well as rendering them **inert**. These agents can be used locally in portable extinguishers, or by a total flooding using fixed injectors which are conveniently placed within the gaseous volume to be extinguished ; in this case a quantity of halons of the order of 5 % by volume is dispersed, which is quite sufficient to put out the fire within a fraction of a second without causing the occupants of the building to be striken with anoxia and without making them inhale large quantities of toxic vapours.

— ODP

These letters stand for the Ozone Depletion Potential, which designates the capacity of destruction of the stratospheric ozone by a given substance. The ODP is the result of four phenomena :

- The lifetime of the species in the troposphere which depends in particular on its reactivity with free radicals such as OH. Table 12e gives the values of the tropospheric lifetimes of the species singled out by the MONTREAL protocol. It should be noted that they are of the order of 1 century for most of the species concerned.

- This lifetime allows the CFCs and the halons to be transported from the troposphere towards the stratosphere.
- Once in the stratosphere, the potential destruction of the ozone by each of these species depends on their respective reactivities. Table 12f gives the values of the ODPs relative to those of the CFCs 11 and 12 which are taken to be equal to 1 by definition.
- The actual fraction of destruction of the ozone by a given CFC or halon depends also on the absolute quantities emitted (Table 12g). Note that the CFCs 11, 12, 113 and the halon 1301 make up 97 % of the total.

Table12 : CFCs and halons prohibited by the MONTREAL protocol.

a) Name	b) Molecular formula	c) Production 1987 (in kT)	d) Applications
CFC 11	$CFCl_3$	310	Mousse, cold
CFC 12	CF_2Cl_2	444	Mousse, cold, propellants
CFC 113	$C_2F_3Cl_3$	140	Solvent
CFC 114	$C_2F_4Cl_2$	15	Mousse, cold
CFC 115	C_2F_5Cl	—	Cold
Halon 1301	CF_3Br	20	Extinguishing agent
Halon 1211	CF_2ClBr	—	Extinguishing agent
Halon 2402	$C_2F_4Br_2$	—	Extinguishing agent

	e) Tropospheric lifetime (in years)	f) ODP	g) Destruction of the ozone (%)
CFC 11	100	1	{ 75
CFC 12	120	1	
CFC 113	90	0.8	12
CFC 114	185	1	0.9
CFC 115	380	0.6	—
Halon 1301	110	10	10
Halon 1211	25	3	—
Halon 2402	—	6	—

The global phenomenon is extremely difficult to model, as it involves both **photochemical reactions, gas-phase thermal reactions, heterogeneous reactions** (especially with ice particles), phenomena of **convective and diffusive transport** inside the troposphere and **energy** balances between the lithosphere, the troposphere and the stratosphere.

d) Regulations

Taking into account the potential risk of an increase in the UV radiation due to this destruction of the stratospheric ozone, the governments of twenty-four countries met in MONTREAL on 16th September 1987 and signed a protocol meant to restrict the production and use of eight of the CFCs and halons mentioned in Table 12, which are potentially the most dangerous for the ozone layer. Following similar meetings held in London in 1990 and in Copenhagen in 1992, this ban became effective in 1996. They are replaced nowadays by second generation HCFCs and HFCs, i.e. hydrochlorofluorocarbons and hydrofluorocarbons (Table 13). These compounds have tropospheric lifetimes which are shorter than those of the CFCs, as the presence of one or several H atoms favours their attack by the OH radical. The HCFCs therefore have a very much smaller ODP than the CFCs, but which is not equal to zero, as is the case for the HFCs. The use of HCFCs will be forbidden in the long run and they will be replaced by the third generation HFCs (Table 13). The research for substitutes for the halons which are used as extinguishing or inert agents in certain civilian and military applications is being pursued.

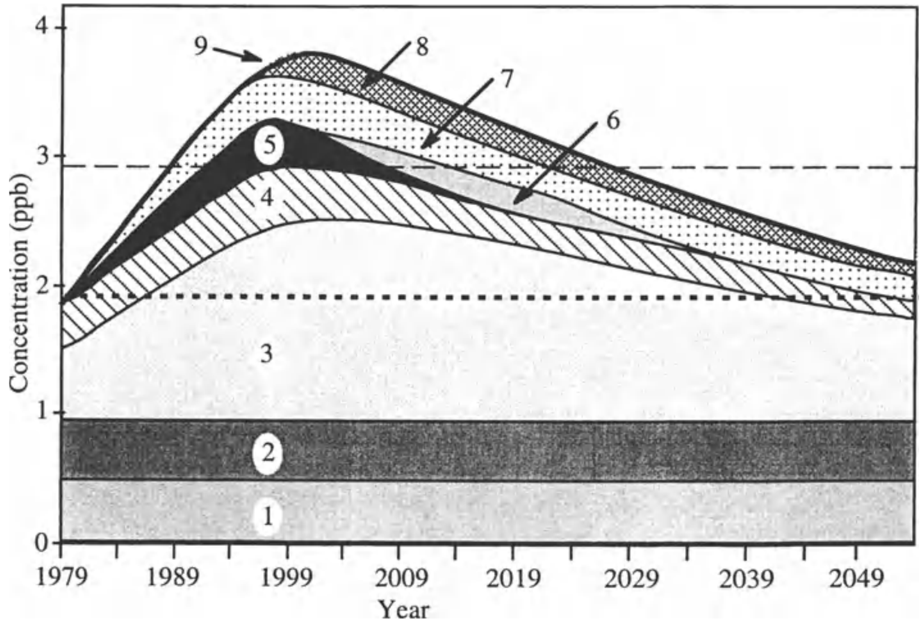
Table13 : HCFCs and HFCs [SOLVAY Live, 1997].

	Present demand	Future demand
Refrigeration	HFC-134a HFC 125/HFC 143a HCFC-22	HFC-134a HFC 125/HFC 143a HFC 125/HFC 32
Mousses	HCFC-141b HCFC-142b HCFC-22	New HFC HFC-134a HFC-152a
Solvents	HCFC-141b	New HFC
Aerosols	HCFC-141b HFC-134a HFC-227ea	HFC-152a HFC-134a HF-227ea

Figure 2 shows the evolution of the stratospheric concentration in chlorine atoms or equivalent species (for brominated compounds) since the period when the hole in the ozone layer first appeared in the 1980s, taking the recommendations of the international agreement protocols into account. The diagram also shows the evolution of the different pollutants of natural or anthropogenic origin which are the cause of this phenomenon. The decrease starts at the beginning of the XXIst century but the level before this crisis, i.e. 2 ppb of atomic chlorine, will only be reached again in around 2060. This is explained by the cumulative effect due to the lifetime of the pollutants, as well as delays caused by the transport time between the troposphere and the stratosphere : pollution phenomena also have an inertia.

Figure 2 : Scenario of the variation of the stratospheric concentration in chlorine atoms or equivalents.
…… Level of appearance of the hole in the ozone layer.

Natural origin : 1 - CH_3Cl ; 2 - CH_3Br. Anthropogenic origin : 3 - CFC ; 4 - CCl_4 ; 5 - $CHCl_3$; 6 - HCFC ; 7 - Halons ; 8 - CH_3Br ; 9 - Cl total.



CONCLUSION : the concept of ecodevelopment

The declaration about the environment given in STOCKHOLM in June 1972 states :
"Man has a fundamental right to freedom, to equality and satisfactory living conditions in an environment whose quality allows him to live in dignity and comfort. He has the

solemn duty to protect and improve the environment for generations present and future".

This declaration has been modified, clarified and extended during the different national or international meetings, such as the United Nations Conference on the environment and development, held in RIO in 1992, or that of KYOTO in Japan in 1997. Some major guidelines evolve from these texts :

a) The first aim is the development of the various regions of the world and especially that of the less favoured countries ;
b) The mastering of this development must take various rightful aspirations into account :
   - the reduction of the inequalities by the integration into the development schemes of the demographic, political, economical, social and cultural differences ;
   - the respect of the human being ;
   - the respect of the local, regional and planetary environment ;
   - the registration of the development in a lasting perspective and solidarity towards future generations.

The combination of these two objectives constitutes the very concept of **PLANETARY ECODEVELOPMENT**, or sustainable development.

Ecodevelopment necessitates the integration of the reflections carried out in different areas : ethics, politics, economics, human and social sciences, life, Earth and space sciences, engineering sciences.

The different themes discussed in this chapter, relating to gas-phase thermal reactions :

Use of fossil raw material,
Production of mechanical, thermal and electrical energy,
Manufacture of chemical substances,
Chemical safety,
Tropospheric and stratospheric pollutions,

make up an integral part of these preoccupations. The scientific and technological mastering of gas-phase thermal reactions therefore opens up a vast field of research and development for research scientists and engineers.

FURTHER READING

FINLAYSON - PITTS B.J., PITTS J.N.J^{r}., *Atmospheric Chemistry - Fundamentals and Experimental Techniques*, Wiley (1986).

GLASSMAN I., *Combustion*, 3rd edition, Academic Press (1996).

GLASSMAN I. (Editor), Combustion Science and Technology 25th Anniversary issue, *The Next 25 Years*, vol. 98 (1994).

GOODY R., *Principles of atmospheric physics and chemistry,* Oxford University Press (1995).

GRAEDEL T.E., CRUTZEN P.J., *Atmospheric Change, an earth system perspective,* Freeman (1993).

GRIFFITHS J.F., BARNARD J.A., *Flame and Combustion*, 3rd edition, Blackie Academic & Professional (1995).

HEWITT C.N., STURGES W.T. (Editors), *Global Atmospheric Chemical Change*, Chapman & Hall (1995).

JONES J.C., *Environmental and safety aspects of combustion technologies,* Whittles (1997).

LEES F.P., *Loss Prevention in the Process Industries,* 2nd edition, 3 volumes, Butterworths (1996).

MIZIOLEK A.W., TSANG W. (Editors), *Halon Replacement - Technology and Science*, ACS Symp. Ser. 611 (1995).

Organisation for Economic Co-operation and Development (OECD) :
- *Energy in The Next Fifty Years* (1999).
- *Climate Change - Mobilising Global Effort* (1997).
- *Environmental Indicators - Towards Sustainable Development* (1998).
- *Environmental Requirements for Industrial Permitting*, 3 vols. (1999).

RICHARDSON M., Coordinator, *Chemical safety,* VCH (1994).

STEINBACH J., *Safety Assessment for Chemical Processes*, Wiley-VCH (1999).

VOVELLE C. (Editor), *Pollutants from Combustion - Formation and Impact on Atmospheric Chemistry*, Kluwer (2000).

WAYNE R., *Chemistry of atmospheres,* 3rd edition, Oxford (2000).

WEISSERMEL K., ARPE J., *Industrial organic chemistry,* 2nd edition, VCH (1993).

CHAPTER II

FUELS, ENGINES, BURNERS, INDUSTRIAL REACTORS

This chapter has three aims :

- *characterization of **engines and heating fuels** on chemical grounds,*
- *description of the working principles of **engines**, **burners** and **industrial reactors**, involving gas-phase thermal reactions,*
- *presentation of the operating conditions under which the **reactions** in these different devices take place.*

1 - ENGINE AND HEATING FUELS

A combustion reaction can be described by the following general equation :

$$\text{Fuel} + \text{Combustion-agent} \longrightarrow \text{Products of combustion} + \text{Energy}$$

The fuel undergoes an oxidation reaction by the combustion-agent, which is therefore an oxidizing agent.

The word fuel indicates both the **engine fuels** used in spark-ignition engines, diesel engines, turbines and turboreactors, the **ergols** used in launchers, or **heating fuels** destined for the production of heat in furnaces and boilers.

In the following discussion, only **gaseous** and **liquid fuels** will be considered. These give rise to gas-phase thermal reactions, following prior or in situ vaporization in the case of liquids. Solid fuels are excluded, as their reaction mechanisms are very different from those of gases.

Table 1 gives the typical chemical compositions of some of the main fuels : by individual molecules[1], by families of molecules or by analysis of the elements. These include natural gases (NG), liquefied petroleum gases (LPG), unleaded petrols, turbojet fuels, diesel fuels and diesel fuel oils, heavy fuels, low-energy gases.

It should be noted that, apart from the low-energy gases, the main constituents of fuels are **hydrocarbons**.

---

[1] The acronym PIONA, which is often used, means : Paraffins (n-alkanes), Isoparaffins (iso-alkanes), Olefins (alkenes), Naphtenes (cyclanes), Aromatics.

Table 1 also gives the number of carbon atoms and the H/C atomic ratio for the more complex hydrocarbon fuels.

Table 2 shows the names and the graphic formulae of model molecules encountered in petrols, turbojet fuels and diesel fuels, belonging to different chemical families.

Table 1 : Chemical composition of fuels.

a) Natural gas (% mol)

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5+	N_2	H_2S	CO_2
Norway (Frigg)	95.7	3.6	-	-	-	0.4	-	0.3
Siberia	85.3	5.8	5.3	2.1	0.2	0.9	-	0.4
New Zealand	45.6	5.8	2.9	1.1	0.8	-	-	43.8

Number of carbon atoms : 1-5

H/C atomic ratio : 2.12-3.95

b) Liquefied petroleum gas (%mol)

	CH_4	C_2H_6	C_3H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	C_4H_8	C_4H_6	C_5+
Europe	-	0.4	9.1	31.8	28.3	19.6	10.6	0.1	ε
California	0.6	6.6	1.1	91.3	ε	0.3	-	-	-

Number of carbon atoms : 1-5

H/C atomic ratio : 2.0-2.67

c) Unleaded petrols (% mass)

	Normal alkanes	Iso alkanes	Alkenes	Cyclanes	Aromatics	Ethers
Europe	8.3	31.1	18.7	2.9	35.5	3.5
California	5.3	44.7	4.9	3.3	30.7	11.1

Number of carbon atoms : 4-13

H/C atomic ratio : 1.7-1.9

d) Turbojet fuels (% mass)

Alkanes	Alkenes	Monocyclic cyclanes	Polycyclic cyclanes	Monocyclic Aromatics	Polycyclic Aromatics	Cyclano-aromatics
58.3	0	23.85	2.4	13.4	0.35	1.7

Number of carbon atoms : 9-13

H/C atomic ratio : 1.9-2.1

e) Diesel fuels and diesel fuel oils (DFO)

Diesel fuels (% mass)

Alkanes	Alkenes	Mono-cyclic cyclanes	Poly-cyclic cyclanes	Mono-cyclic aromatics	Poly-cyclic aromatics	Cyclano-aromatics	Thio-phenes
30.9	0	23.7	15.1	9.2	6.8	12.5	1.8

Diesel fuel oils (% mass)

	C	H	N	S	ρ (kg m^{-3})
Domestic fuels	86	13.5	-	0.5	840

Number of carbon atoms : 7-27

H/C atomic ratio : 1.9-2.1

f) Heavy fuels (% mass)

	C	H	N	S	ρ (kg m^{-3})
Marine fuels	86	10.5	0.3	3.2	992

Number of carbon atoms : 13-40

H/C atomic ratio : 0.8-1.7

g) Low-energy gases (% mol)

	H_2	CO	CH_4	CO_2	N_2	Various
Blast furnaces	4.0	28.0	—	8.0	60.0	—
Coke ovens	50.0	8.0	30.5	2.0	5.5	4.0

1.1 - Natural gas or NG (Table 1a)

The main constituent of natural gas is methane, between 45 and 96 % mol. Other hydrocarbons include mainly ethane, propane and butanes, with small amounts of C_5 and C_6 hydrocarbons. Impurities are N_2, H_2S and CO_2. The amount of CO_2 can be as high as 44 % mol.

1.2 - Liquefied petroleum gases or LPGs (Table 1b)

The main components of LPGs are C_2, C_3 to C_4 alkanes and alkenes.

1.3 - Petrols

Petrol is the main fuel for the spark-ignition engine. Two large categories of petrol can be distinguished : leaded and unleaded petrols, and in addition substitutes for common petrol.

Table 2 : Model molecules for fuels (petrols, turbojet fuels, diesel fuels and diesel fuel oils).

a) Normal-alkanes

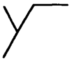
n-Butane 

n-Heptane 

n-Decane 

Cetane 

b) Iso-alkanes

Isopentane 

2-Methylpentane 

Iso-octane 

Heptamethylnonane 

c) Alkenes

Butene-1 

Butene-2 

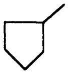
Isobutene 

2-Methylbut-1-ene 

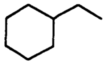
Pent-2-ene 

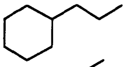
2-Methylbut-2-ene 

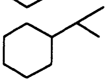
d) Cyclanes

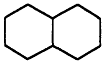
1-Methylcyclopentane 

Cyclohexane 

Ethylcyclohexane 

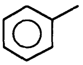
n-Propylcyclohexane 

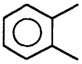
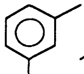
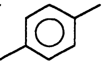
Isopropylcyclohexane 

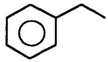
Decalin 

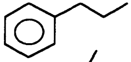
e) Aromatics

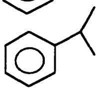
Benzene 

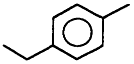
Toluene 

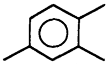
Xylenes   

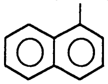
Ethylbenzene 

n-Propylbenzene 

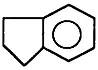
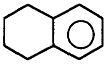
Isopropylbenzene 

3-Ethyltoluene 

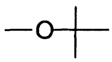
1,2,4-Trimethylbenzene 

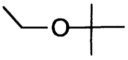
1-Methylnaphthalene 

f) Cyclano-aromatics

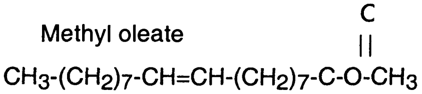
Indane  Tetralin 

g) Ethers

Methyltertbutylether (MTBE) 

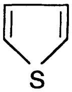
Ethyltertbutylether (ETBE) 

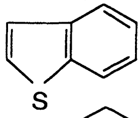
h) Esters

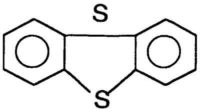
Methyl oleate 

$CH_3\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}\overset{\overset{C}{\|}}{C}\text{-}O\text{-}CH_3$

i) Thiophenes

Thiophene 

Benzothiophene 

Dibenzothiophene 

a) Leaded petrols

These petrols contain anti-knocking additives consisting of lead alkyls (0.3-0.6 g Pb/litre). These compounds are very toxic on their own, and harmful to the environment by the emission of lead compounds. In addition, the lead destroys the catalysts contained in the catalytic converters, which are meant to reduce the amount of tropospheric pollutants emitted by vehicles. For all these reasons, leaded petrols are doomed to disappear ; this will become effective internationally at the beginning of the 21st century.

b) Unleaded petrols (Table 1c)

A detailed analysis of petrols primarily using chromatography, shows that they are made by blending one to three hundred individual molecules. A similar number of molecules is used for turbojet fuels and many more for diesel fuels and diesel fuel oils.

Therefore, it is common practice to group the molecules into major families : alkanes, alkenes, cyclanes, aromatics, cyclano-aromatics.

In the case of alkanes and alkenes, it would be advisable to distinguish between the ***linear** (or **normal**)* molecules and the ***branched** (or **iso**)* molecules, because the octane number, which will be discussed below, is closely dependent on both this characteristic and on the number of carbon atoms.

In the case of cyclic molecules, the number of ***condensed*** or ***fused*** rings could be of major importance when the formation of heavier species is being considered.

In these unleaded petrols, the anti-knocking leaded additives have been replaced by oxygenated compounds, mainly ethers, MTBE and ETBE (Table 1c).

The object of these additives is to maintain the octane number at a level which is high enough, typically 91 (regular), 95 (premium), 98 (superpremium) grades.

The Research Octane Number or RON[1] characterizes the resistance of a fuel to engine knock. This phenomenon, which occurs as a characteristic metallic sound, brings about deteriorations in the cylinder walls, in the valves and in the piston. The RON of the petrols sold in Europe have standard values of 95 or of 98. The use of a petrol of RON lower than those advised by the car manufacturer leads to the destruction of the engine.

The Research Octane Number of a given petrol is measured using specific engines (of the CFR type) according to standardized processes.

The behaviour of a real fuel is compared to that of a mixture of Primary Reference Fuels, denoted by the abbreviation PRF. The two PRFs of petrols are n-heptane CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 of RON = 0 and iso-octane or 2-2-4-trimethylpentene $C(CH_3)_3$-CH_2-$CH(CH_3)_2$ of RON = 100. These mixtures are referred to as PRF

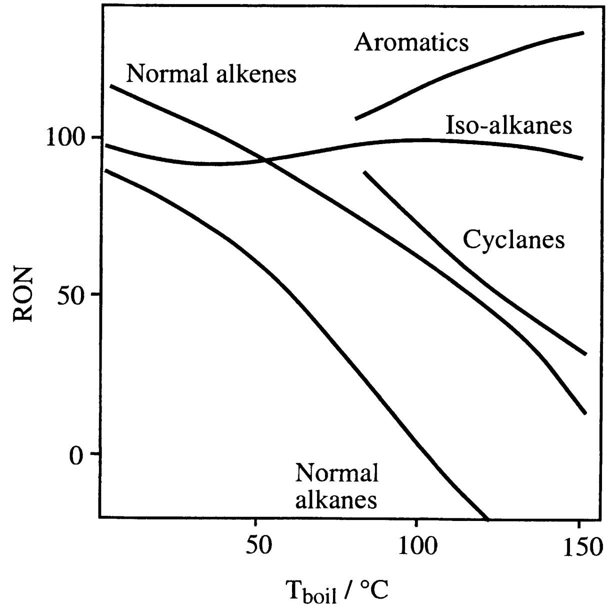
---

[1] Motor Octane Number (MON), Road Octane Number and Anti-Knock Index (AKI) are also used.

followed by the RON. Thus PRF 95 represents a mixture (% vol) of 95% iso-octane and 5% n-heptane.

Figure 1 shows the RON values of the molecules of the main families of hydrocarbons as a function of their boiling points. It should be noted that, at boiling points above 100°C, only the **aromatics** and the **iso-alkanes** have an RON higher than 95. The **iso-alkenes** can be included, e.g. 2-methyl-but-1-ene has a boiling point of 31°C and an RON of 102.5. The usual anti-knocking additives such as the **ethers**, as well as the **alcohols** usually have RONs higher than 95. However, cyclanes, normal alkanes and alkenes are much more likely to cause engine knock, with the exception of the molecules with the lowest boiling points. For example, the RON of methyl-cyclopentane, pent-2-ene and n-butane are 91, 98 and 95 for boiling points of 72, 37 and 0°C, respectively. These trends allow the differences between Californian petrol (Table 1c), reformulated with a view to reducing the emission of pollutants whilst maintaining a suitably high octane value, and standard European petrol (Table 1c) to be understood : the decrease in the iso-alkenes and the aromatics is compensated for by an increase in the iso-alkanes and the ethers.

Figure 1 : Octane number of hydrocarbons.
RON : Research octane number ; T_{boil} : boiling point



Alcohols can be used instead of ethers to replace the leaded additives. Thus the **gasohol** is an unleaded petrol containing 10 % ethanol. The American consumption of gasohol was 30Mm^3/year at the beginning of the 1990s and this represented about 7 % of the market.

Besides octane improvers, petrols contain other additives (antioxidants, detergents,...) designed to ensure a satisfactory use of the fuel and the engine in the long term.

c) Alternative fuels

The possible increasing use of alternative fuels pursues several goals : decreasing the consumption of crude oil, minimizing the greenhouse effect as well as the emissions of pollutants, making use of renewable energies. These non-conventional fuels include :

- the natural gases for vehicles (NGVs),
- the liquefied petroleum gases (LPGs),
- ethanol and other biofuels,
- methanol for producing ethers,
- electricity.

Thus 2 million Brazilian vehicles equipped with suitable engines use 7 Mm^3 ethanol per year, whereas Japan, the USA, the Netherlands and Italy use a total of 5 Mm^3 of LPG-fuel per year.

1.4 - Fuels for turbojets, turbines, missiles and rockets

a) Fuels for turbojets (Table 1d)

The jet A1 fuel is used by the jet-planes of the international civilian lines. The turbojet fuels of the national lines and military planes are very similar to the jet A1.

This fuel is obtained from an atmospheric distillation of crude oil between 140-150 and 240-260°C.

The specifications for the classical composition of jet A1 fuels are the following :
alkenes < 5 % vol., aromatics < 22 % vol., sulphur < 0.3 % mass.

Compared with petrol and diesel fuels, the combustion of jet fuel takes place, not in a batch reactor, but in an open reactor, thus avoiding the occurrence of knock. Therefore, the problems connected with RON or cetane numbers, such as autoignition, do not impose stringent conditions on the chemical composition of jet fuels.

b) Fuels for fixed turbines

These turbines are also called turboengines and they can function with a very large range of fuels e.g. NG, LPG, kerosene, diesel fuel. Kerosene is a middle cut in the atmospheric distillation of crude oil, in between petrol and diesel fuel.

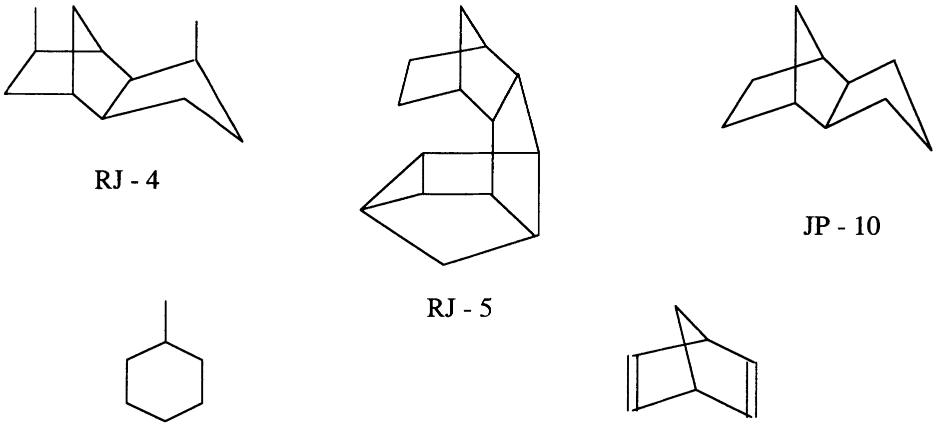
c) Fuels for missiles

Missile turbojet fuels must, for reasons of space economy, possess a very high volume energy. The fuels RJ 4, 5 and 6 are used with the Ramjets, the fuels JP 9 and JP 10 for

Jet propulsion. The fuel RJ 6 is a mixture of RJ 5 and of JP 10 ; the fuel JP 9 is a mixture of RJ 5, JP 10 and methylcyclohexane.

Figure 2 shows the carbon skeletons of the molecules RJ 4, RJ 5 and JP 10 ; the molecule RJ 4 has 8 isomeric forms. The figure also shows the starting molecule, norbornadiene, which is obtained by the Diels-Alder reaction between cyclopentadiene and acetylene.

Figure 2 :Missile fuels.



RJ - 4

RJ - 5

JP - 10

Methylcyclohexane

Norbornadiene

d) Ergols

The term ergol stands for both the fuel and the combustion-agent used in ballistic missile launchers, Earth satellites and spatial probes. The combination fuel/combustion-agent is called **propergol**. Propergols can be in solid or liquid form. In solid propergols, the fuel and the combustion-agent are usually in two distinct phases and the reaction processes differ considerably from those which occur in GPTRs ; these propergols will not therefore be examined here. Liquid propergols, after vaporization, give a GPTR.

There are three main liquid propergols :

- the hydrogen-oxygen propergol RP 1 (Rocket Propellant n°1) is used in the HM7B engine on the third stage of ARIANE IV, which takes in 11 tons of this fuel, and by the SATURN V rockets. This propergol was at the origin of the explosion of the CHALLENGER shuttle ;
- the kerosene-oxygen propergol is used by satellite launchers for telecommunication, teledetection, meteorology and for navigation ;
- the nitrogen peroxide propergol N_2O_4-UDMH is used by ARIANE launchers and has

been used for the APOLLO missions. The abbreviation UDMH means UnsymmetricalDiMethylHydrazine and represents the molecule $N_2H_2(CH_3)_2$.

1.5 - Diesel fuels and diesel fuel oils (Table 1e)

Diesel fuels are used by the diesel engines of cars and lorries. Diesel fuel oils (DFOs) are used for the production of domestic heat and also by agricultural tractors and heavy-plant vehicles, but their use is forbidden for cars and lorries, because they are taxed less than diesel fuels. In order to detect possible frauds, a scarlet colouring agent and two tracers which can be easily identified (diphenylamine and furfural), are added to the DFOs. Otherwise the chemical composition and other characteristics of DFOs are very similar to those of diesel fuel, which will be discussed below.

Comparison of the composition of a diesel fuel (Table 1e) with that of a petrol (Table 1c), shows an increase of cyclanes and a decrease of aromatics in the former. Concerning alkanes, a diesel fuel contains a proportion of normal alkanes higher than that of branched alkanes, contrary to petrols.

This is due to the way in which the diesel engine works, where the ignition of the mixture is caused by a rise in the pressure and temperature, and is then called **autoignition**, in contrast to the petrol engine, where the ignition is caused by a spark-plug.

The capacity of diesel fuels for autoignition is characterized by the cetane number. Commercial diesel fuels have cetane numbers of between 48 and 55. This number is measured with the aid of a CFR diesel engine by comparison with mixtures of primary reference fuels ; cetane or n-hexadecane has a cetane number of 100 (by definition), and heptamethylnonane has a cetane number of 15. A binary mixture of these two species containing X % by volume of cetane has therefore a cetane number equal to $X + 0.15 (100 - X)$.

Diesel fuels also contain sulphur compounds, namely thiophenes. Their combustion leads to sulphur oxides from which acid rains originate. Thus, the sulphur content of diesel fuels is becoming more and more strictly regulated.

Methyl oleate or diester (for diesel ester), which is a methyl ester $R\text{-}CO\text{-}O\text{-}CH_3$ derived from rape-seed, can be added to the diesel fuel. This additive has a cetane number equal to 49 ; diesel fuel can only contain from 5 % to 50 %.

Moreover, specific additives, such as demulsifiers and flow improvers, can improve some specific properties of diesel fuels, especially in cold weather conditions.

1.6 - Heavy fuels (Table 1f)

These fuels are made from distillate residues of crude oil refining. They are mainly used in large diesel engines for the propulsion of high-tonnage marine ships. Other uses include the production of electricity in an emergency, in remote areas, on drilling platforms and also for locomotives.

The molecules of heavy fuels have numbers of carbon atoms ranging between 15 and 40, and an H/C atomic ratio between 0.8 and 1.7. The percentage of carbon atoms pertaining to aromatic structures lies between 55 and 100 %. That means that purely alkanic, cyclanic or aromatic molecules do not exist in heavy fuels, so that their chemical compositions are given in the form of an analysis of the elements.

1.7 - Heating fuels

These fuels are destined for the production of heat. They can be in the gaseous, liquid or solid phase. Only the first two categories, which are the only ones likely to involve GPTRs, will be considered.

— Gaseous fuels include natural gas (Table 1a), the low-energy gases of the blast furnaces and coke ovens (Table 1g), as well as various heating gases, which are produced by steamcrackers and later recycled for heating.

— Low-energy gases can also be used in diesel stationary engines to produce electricity.

— Natural gas, LPG, acetylene and hydrogen are used as fuels for blow-torches.

— Liquid fuels include LPG, domestic fuel oil (DFO) and heavy fuels (Table 1f). They are characterized by different sulphur contents, ranging from several tenths of a percent to several percent, and by different viscosities, amongst other properties.

1.8 - Other characteristics of fuels (Table 3)

Beyond the chemical composition and the octane and cetane numbers of a given fuel, many other physico-chemical characteristics are measured : distillation intervals for given fractions, density, volatility, viscosity, heat of vaporization, etc... Of special interest is the amount of energy released by the combustion of the fuel and due to the exothermiticity of the reaction. This quantity is often tabulated as the Net Heating Value or NHV, i.e. the heat of reaction of a liquid fuel and air giving gaseous combustion products (CO_2 and H_2O) at 25°C.

Of course, some **specifications** of fuels are strongly **regulated** and their **measurements normalized**. This is also true for the specifications of emissions.

Table 3 shows some typical values of densities, viscosities and NHVs of various engine fuels.

1.9 - Characteristics of combustion mixtures

Apart from the propergols, the combustion-agent most frequently used for energy

Table 3 : Physico-chemical characteristics of engine fuels.

Fuel	Petrol	Jet A1	Diesel fuel and DFO	Residue marine fuel
Density at 15°C ($kg\ dm^{-3}$)	0.275 - 0.780	0.775 - 0.840	0.820 - 0.860	0.975 - 1.010
Viscosity ($mm^2\ s^{-1}$)	0.55 - 0.61	< 8 (-20°C)	1.3-4.5 (40°C)	10-55 (100°C)
Net Heating Value at 25°C ($MJ\ kg^{-1}$)	42.7	> 42.8	42.6	39-40

applications is simply air, sometimes enriched with oxygen. Table I-5 gives the molar composition of dry air, i.e. without water vapour but also with neither VOCs nor aerosols or dust, and which has therefore been filtered.

Dry air contains mainly nitrogen and oxygen, as well as small quantities of rare gases, the main one of which is argon.

In order to simplify the calculations of the combustion reactions, approximations of the molar fractions can be made by taking into account only N_2, 0_2, and Ar where :

$$x_{N_2} = 0.781 \quad ; \quad x_{O_2} = 0.210 \quad ; \quad x_{Ar} = 0.009$$

Combining argon and nitrogen gives :

$$x_{N_2} = 0.79 \quad ; \quad x_{O_2} = 0.21$$

a) Stoichiometric combustion

In combustion, specific terms are used to characterize the initial composition of the reaction mixture. The reference taken is the stoichiometric combustion reaction leading to the formation of CO_2 and H_2O :

$$C_xH_yO_z + (x + \frac{y}{4} - \frac{z}{2})\,(O_2 + 3.762\,N_2) \longrightarrow$$

$$x\,CO_2 + \frac{y}{2}\,H_2O + 3.762\,(x + \frac{y}{4} - \frac{z}{2})\,N_2 \qquad (1)$$

Example 1

Write down the stoichiometric combustion equations of CH_4, C_8H_{18} and $C_{16}H_{34}$ in air. Deduce the mole fractions of the hydrocarbon in the initial mixture.

Taking the above relationships into account, the following reaction equations are obtained :

$$CH_4 + 2\,O_2 + 7.524\,N_2 \longrightarrow CO_2 + 2\,H_2O + 7.524\,N_2$$
$$C_8H_{18} + 12.5\,O_2 + 47.025\,N_2 \longrightarrow 8\,CO_2 + 9\,H_2O + 47.025\,N_2$$
$$C_{16}H_{34} + 24.5\,O_2 + 92.169\,N_2 \longrightarrow 16\,CO_2 + 17\,H_2O + 92.169\,N_2$$

From these equations, the values of the mole fractions can be deduced :

$$x_{CH_4} = 9.50\text{x}10^{-2} \; ; \; x_{C_8H_{18}} = 1.65\text{x}10^{-2} \; ; \; x_{C_{16}H_{34}} = 8.50\text{x}10^{-3}$$

b) Equivalence ratio

— Engines

The initial fuel/air mixture introduced into an S.I. engine, an aircraft turbine or a diesel engine is usually characterized by the equivalence ratio :

$$\varphi = \frac{(x_{fuel}/x_{air})_{engine}}{(x_{fuel}/x_{air})_{stoichiometric}} \qquad (2)$$

According to the value of the equivalence ratio φ, three kinds of mixtures and regimes of combustion can be defined. A rich mixture, i.e. rich in fuel, is characterized by an equivalence ratio $\varphi>1$, a stoichiometric mixture by a ratio $\varphi=1$, and a lean mixture by a ratio $\varphi<1$.

S.I. engines run on petrols at equivalence ratios between 0.85 and 1.15. They use lean mixtures which are more economic at cruising speeds and rich mixtures which are more efficient, but also more polluting, for accelerating. Cars with a three way catalytic converter are operated with an equivalence ratio between 0.98 and 1.02.

Turbojet engines and diesel engines are run with lean mixtures with a global equivalence ratio of between 0.6 and 0.9. Their efficiencies are not very sensitive to the equivalence ratio.

Sometimes, the quantity $\lambda = 1/\varphi$ is used, instead of φ. In case of doubt, φ is called fuel equivalence ratio and λ air equivalence ratio.

— Burners

In this case, the quantities $e = (1-\varphi)/\varphi$ and $h = (\varphi-1)/\varphi$ are used and named excess and lack of air, respectively.

Furnaces and boilers usually function with an excess of air of 10 to 40 % to avoid clogging up the exchangers and reducing the formation of atmospheric pollutants.

The following terms are also used.

The combustive power, or stoichiometric air, is the volume of air in m^3 necessary to carry out the stoichiometric combustion of 1 m^3 of gaseous fuel.

The smoke-producing power is the total volume of gas produced by the stoichiometric combustion of 1 m^3 of gaseous fuel.

2 - THERMAL ENGINES

2.1 - Spark-ignition engines

a) Operating principles

Only the four-stroke engines will be discussed.

— Design

Figure 3a shows a basic schematic representation of such an engine. The main part of a car petrol engine is the cylinder and its piston. The most common engines are 4, 6 or 8 cylinder ones. The piston is attached to the crankshaft by a con-rod, which changes the reciprocating motion of the piston into a rotary movement using a crankshaft system.

The piston moves between the top dead centre (TDC) and the bottom dead centre (BDC). At the TDC, the volume of the combustion chamber is equal to v. The volume swept between the TDC and the BDC is the unitary cylinder volume V, which is of the order of 200 to 600 cm^3. V is given by the following formula :

$$V = \frac{\pi d^2}{4} C \qquad (3)$$

where d is the bore of the cylinder and C is the pathlength of the piston.

The compression ratio or the volume ratio is equal to :

$$\varepsilon = \frac{V + v}{v} \qquad (4)$$

It is of the order of 8 to 12 for natural intake engines and 7 to 9 for injection engines. The value of the compression ratio imposes certain characteristics on petrols.

— Theoretical cycle

The theoretical cycle of a four-stroke engine involves the following steps (Figure 3b).

● Intake

The piston moves from TDC to BDC (1) and sucks the air-fuel mixture in by the intake valve, which closes at BDC.

● Compression-ignition

The piston moves from BDC to TDC (2) and compresses the charge to a pressure of about 10 bar. The electric spark provided by the plug triggers off the combustion.

● Combustion-expansion

The heat given out by the reaction and the increase in the number of moles lead to an increase in the pressure to about 50 bar (3), which pushes the piston back towards the BDC (4).

● Exhaust

When the piston is at the BDC, the exhaust valve opens (5) and the burned gases are expelled into the atmosphere by the movement of the piston from BDC to TDC. The exhaust valve closes and the cylinder is ready for another cycle.

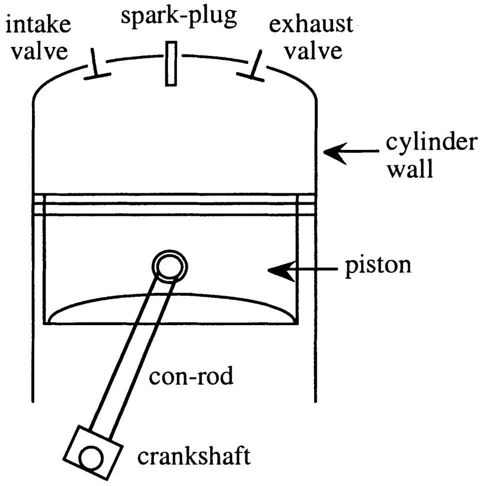
Each cycle corresponds to two turns of the crankshaft. Motorists often use the crank angle (θ) as an independent variable. Thus at 3600 rpm, 1 ° of θ represents on average 4.63×10^{-5} s.

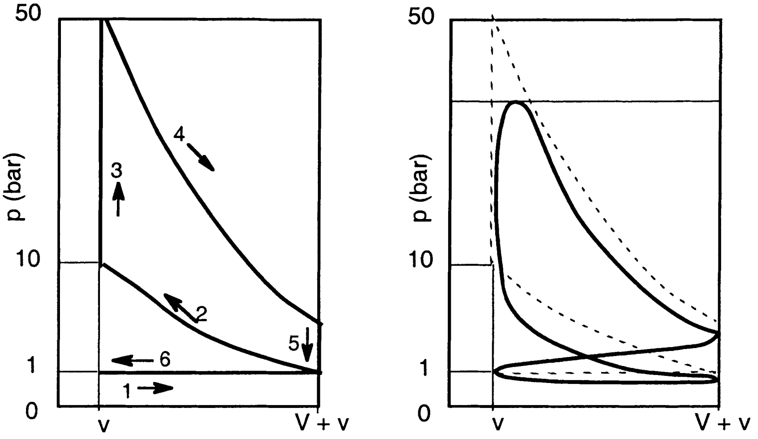
— **Real cycle**

The real cycle (Fig. 3c) differs from the Beau de Rochas cycle for several reasons.

Figure 3 :Spark-ignition engine.

a) Schematic representation




b) Theoretical cycle

c) Real cycle

The combustion (Step 3, Fig. 3b) is not instantaneous and therefore cannot occur at constant volume. Moreover, the charge is ignited before the piston arrives at TDC. This ignition advance falls between 5 and 50 ° of θ.

The cylinder wall is in contact with a cooling liquid, which is itself cooled by the surrounding air. The heat exchanges between the hot gases and the cylinder walls influence the temperature and as a consequence also the pressure prevailing in the cylinder.

The lengths and the starting times of intake and of exhaust can be modified by the advances or the delays in opening and closing the corresponding valves.

The theoretical pressure at intake and at exhaust is equal to the atmospheric pressure. In fact there is a small depression at intake and a slight over-pressure at the exhaust.

b) Normal combustion

The fuel finishes vaporizing during the compression step, and taking the high turbulence generated by the motion of the piston into account, the spark of the spark-plug ignites a practically homogeneous gaseous mixture. The flame is propagated in a turbulent environment and separates the zones, which contain burned gases and unburned gases.

The combustion occurs over 60 to 90° of θ, i.e. several milliseconds ; this is not therefore an explosion.

The flame propagates in the mixture from the zone around the spark-plug at a rate of the order of **50 m s^{-1}**. This is a **rate of turbulent deflagration**, much higher than that of a **laminar** deflagration, which is of the order of **50 cm s^{-1}**, but very much smaller than that of a **detonation**, which is of the order of **2000 m s^{-1}**.

The rate of turbulent deflagration increases rapidly with the intensity of the turbulence, that is with the fluctuations in the local flow rate of the gases.

The properties which define the state of the gases in the cylinder can be identified using three indices : u for unburned gases, f for the gases situated in the flame front, b for the burned gases. The extent of the cycle is generally taken to be an independent variable and this can be given by the crank angle (θ), where zero corresponds to the TDC.

Figure 4a describes the evolution of the pressure and Figure 4b that of the temperature of both the burned and unburned gases. It can be observed that the maximum pressure approaches 40 bar and the maximum temperature 3000 K. The temperature of the unburned gases can reach 1000 K.

c) Engine knock

The temperature and pressure conditions prevailing inside the unburned gas allow it to ignite itself. If this autoignition occurs before the arrival of the flame front, the local pressure increases rapidly and creates vibrations which are expressed as the characteristic knocking noise. These vibrations decrease until the pressure has become homogeneous in all the gaseous volume (Fig. 4c). Severe engine knock can cause the quasi-immediate destruction of the engine and it is therefore important to prevent this phenomenon.

Diagram 4d illustrates the conditions under which engine knock can occur. This diagram shows the variations in the conversion ratio X_b of the fuel as a function of time (curve with a continuous line). The fuel is practically totally converted after a time t_F.

When the moment is reached at which the conditions of pressure and temperature reached allow an autoignition of the unburned gases to take place three situations can occur, according to the length of the **delay of autoignition** δ, i.e. the time difference between the instant when autoignition is possible and that when it actually happens. Diagram 4d shows the variations in the quantity $Y = \int_0^t dt/\delta$ as a function of t as the dashed lines. When this quantity becomes equal to 1, autoignition of the unburned gases occurs. For fuel A, the delay is sufficiently short so that the autoignition occurs before the arrival of the flame front ($t_A < t_F$) and there is severe engine knock. For fuel C ($t_c > t_F$), the opposite situation occurs and there is no engine knock. The critical condition corresponds to a triggering off of the autoignition at the instant t_F. This condition is almost fulfilled for fuel B, for which sporadic engine knock will occur.

For PRF, the delay of autoignition is expressed as follows :

$$\delta = 1.931 \text{x} 10^{-2} \left(\frac{\text{RON}}{100}\right)^{3.4017} p^{-1.7} \exp\left(\frac{3800}{T}\right) \qquad (5)$$

where δ is the delay of autoignition in s,
RON is the research octane number of the fuel,
p is the pressure in bar,
T is the temperature in K.

Example 2

Calculate the delay of autoignition of PRF 98 at 26 bar and 900 K. The following can be written :

$$\delta = 1.931 \text{x} 10^{-2} \times 0.98^{3.4017} \times 26^{-1.7} \times \exp\left(\frac{3800}{900}\right)$$

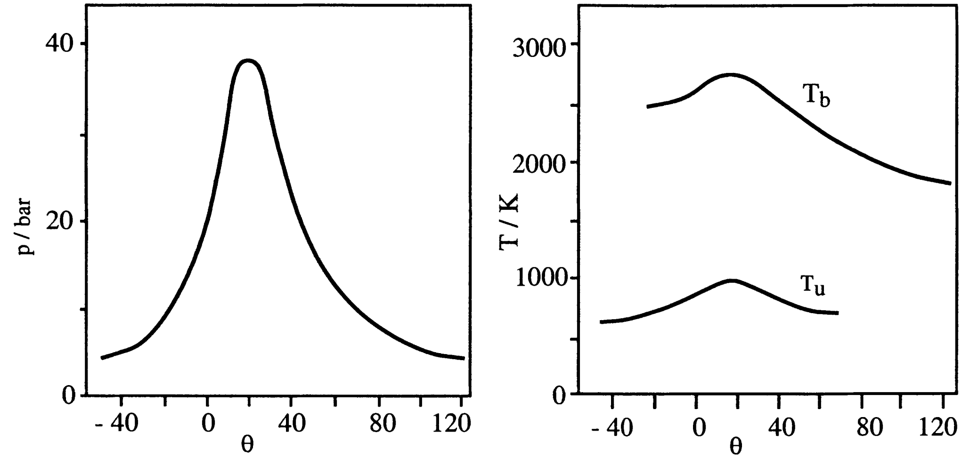
$$\delta = 4.8 \text{ ms}$$

This delay is long enough so that there is no engine knock.

2.2 - Diesel engines

The diesel engine works following a four-stroke cycle analogous to that of a petrol engine. There are however, very important differences, which can be explained using the diagram in Figure 5, which shows the changes in pressure as a function of the crank angle.

Figure 4 : Spark-ignition engine. Change in the state of the gases.



a) Pressure

b) Temperature

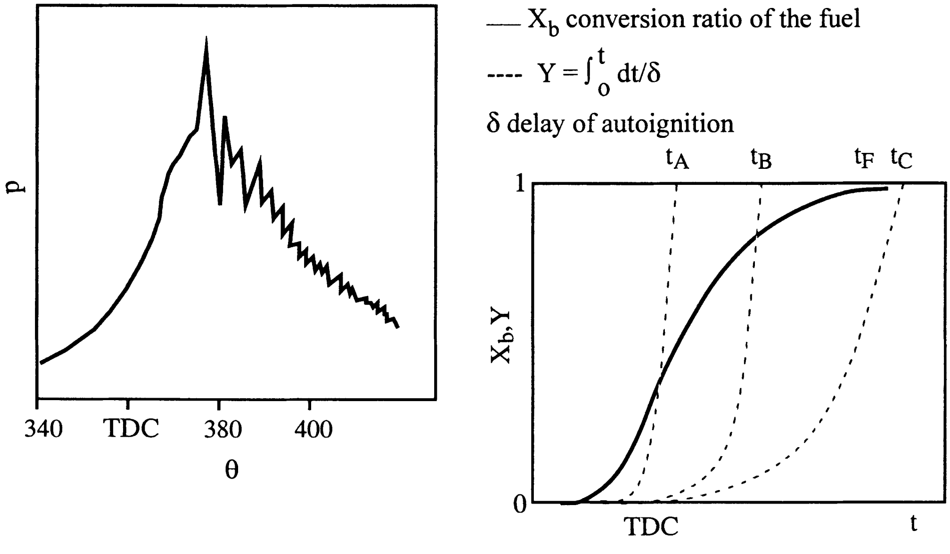
c) Engine knock

d) Conditions under which engine knock occurs

—— X_b conversion ratio of the fuel

---- $Y = \int_0^t dt/\delta$

δ delay of autoignition



Air is introduced during the intake phase and progressively compressed whilst the piston moves from the BDC to the TDC. This compression also causes a significant rise in temperature. The compression ratio of diesel engines is of the order of 15 to 20 for direct injection engines and of 20 to 23 for indirect injection engines.

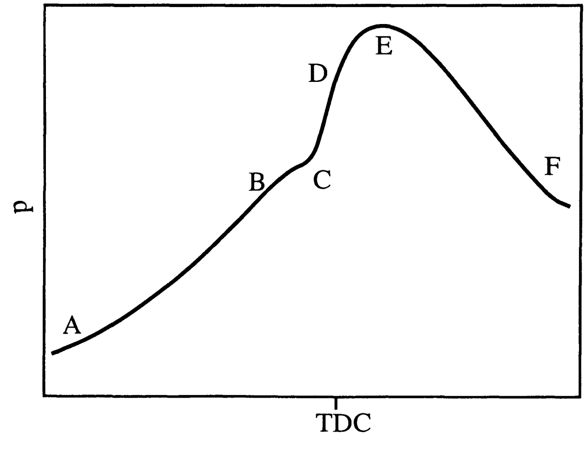
Diesel fuel starts to be atomized (at B) at high pressure in the combustion chamber where it is mixed with compressed air. The mixture obtained is very heterogeneous, containing droplets of unvaporized diesel fuel, in addition to zones which are rich, or lean in vaporized diesel fuel. The injection of diesel fuel continues up to point D.

The movement of the fluids inside the cylinder is, as for the petrol engine, very turbulent.

The ignition of the gaseous mixture occurs by autoignition in all the zones where favourable conditions of pressure, temperature and composition are fulfilled.

The autoignition delay (BC) has a meaning, which is even more global than in the petrol engine, as it results from a **physical delay** caused by heating the diesel fuel droplets, their vaporization and their mixing by turbulent diffusion with air, and an actual **chemical delay**, analogous to that which has been described for autoignition of a homogeneous petrol-air mixture. The physical and chemical delays are of the same order of magnitude.

Figure 5 :Autoignition and combustion in a diesel engine.



— The mass combustion thus started (CDE) lasts for several degrees of θ and creates strong pressure gradients (3-4 bar/°), which are responsible for the characteristic noise of diesel engines. The final diesel fuel intake occurs at high pressure and high temperature, which causes the reaction to be particularly fast.

To sum up, the combustion in a diesel engine occurs in a turbulent flame, which is non-premixed, non-isothermal, non-isobaric, where there is vaporization of the liquids, heat exchanges, variable reaction volume, transient state, a complex and non-homogeneous reaction mixture.

2.3 - Turbojet engines and gas turbine engines

Turbojet engines and gas turbine engines have gradually replaced reciprocating engines for most of the following applications : propulsion of jet planes, production of electricity and industrial compressors. It is fitting to distinguish between gas turbine engines where the main energy produced is that of the jet propulsion, and gas turbines where the main energy is directly transferred from the turbine to an alternator, an engine or a compressor. However, the two categories of engines operate in very similar ways and only turbojet engines will be described here.

a) Principles of operation

Figure 6a shows a schematic representation of a single-pass turbojet engine. The following elements can be identified :

- air intake a,
- the entrance diffuser b in which a first compression takes place,
- the compressor c, driven by the turbine f, which carries out a second compression,
- the fuel injectors d in the reaction chamber e, where the combustion reaction takes place,
- the turbine f, which is moved by a first expansion of the fuel gases,
- the ejection nozzle g, which carries out the thrust by the final expansion of the burned gases.

b) Combustion chamber

Figure 6b shows a schematic representation of an axisymmetrical combustion chamber. The chamber consists of :

- an outside wall, which is in contact with the air coming out of the compressor on the one hand, and the surrounding air on the other,
- a flame tube, which is cooled by air coming from the compressor and inside which the combustion reaction takes place. It is fed with atomized fuel by an injector, and air is supplied gradually by separate primary, secondary and tertiary openings, designed in such a way as to ensure an optimum mixing of the fuel and the combustion-air, as well as the desired temperature profile at the actual entrance to the turbine.

c) Thermodynamic cycle

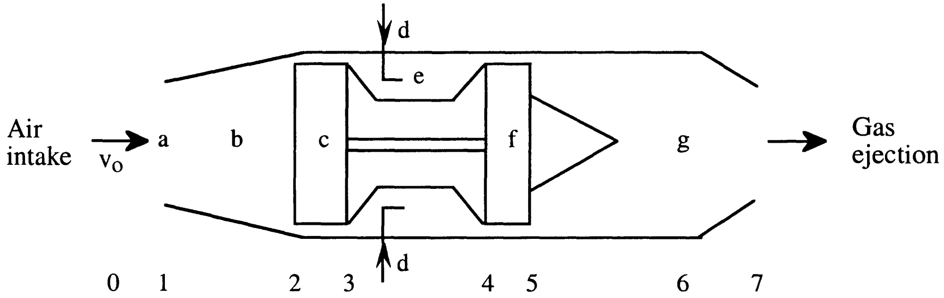
Figure 6c describes the ideal thermodynamic evolution of the gases and the real evolution in an enthalpy-entropy diagram.

Under ideal operating conditions, the compressions 0-2' and 2-3' are supposed to be isentropic, and so are the expansions 4-5' and 5-7'. In practice, the two compressions (0-2 and 2-3) and the two expansions (4-5 and 5-7) are not isentropic. During the actual combustion, there is a pressure drop in the combustion chamber ($p_4 < p_3$). The temperature of the gases feeding the turbine lies between 1000 and 1600 K to avoid it being damaged.

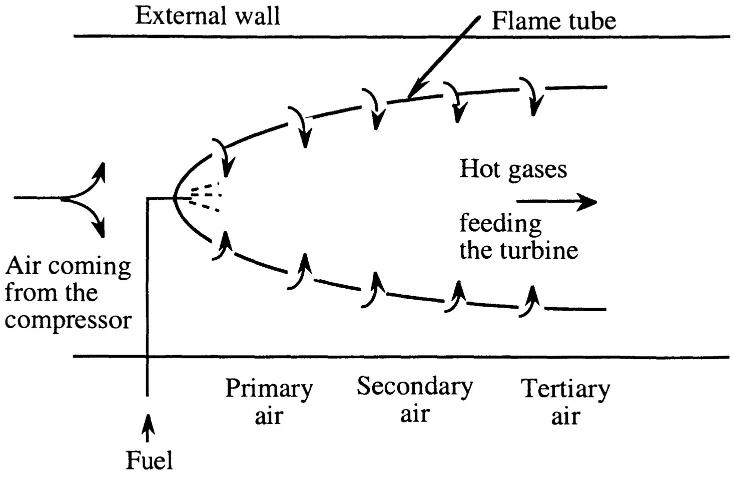
In the **post-combustion** technique, fuel is injected downstream of the turbine ; the temperature of the gases can then rise to 1500-1700°C, and an increase in the useful thrust is obtained in particular during the take-off.

Figure 6 : Turbojet engine.

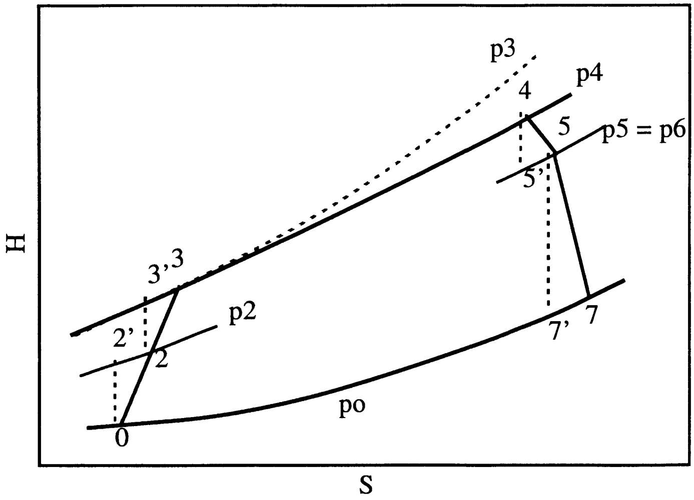
a) Schematic representation



b) Combustion chamber



c) Thermodynamic cycle



A turbojet engine is fed globally with a lean mixture (0.1 < φ < 0.5). However, two main combustion zones can be distinguished ; in a first zone, the mixture is relatively rich (0.3 < φ < 1.5) to obtain a high rate of reaction ; in a second zone, an intake of fresh air leads to a decrease in the richness (0.1 < φ < 0.5) and, correlatively, of the temperature to a level which is tolerated by the turbine.

d) Turboprops and ramjets

In a turboprop, the turbine operates both the compressor and a propeller. The propulsion is ensured by the ejection of gases and by the propeller.

Ramjets, or propelling nozzles, operate with neither compressor nor turbine. The air taken in by the diffuser is compressed due to its rate alone and the expansion of burned gases in the nozzle ensures the propulsion by the reaction. The thrust is equal to zero at rest, and the necessary speed must therefore be reached using an auxiliary engine or a rocket.

2.4 - Launchers

Ballistic missiles, satellite launchers and space launchers are all referred to by the general name of launcher. The difference between these three types of trajectories (Earth-Earth, Earth-stationary orbit, Earth-space) results from the value of the speed reached at the end of the propelling phase : less than 7000 m s^{-1}, falling between 7000 and 11000 m s^{-1},over 11000 m s^{-1}, respectively.

In rockets using liquid propergol, the fuel and the combustion-agent are introduced under high pressure (50 to 200 bar) into a combustion chamber. The combustion gases are ejected at high speed by a nozzle and ensure the propulsion of the rocket. The rate of ejection is of the order of 4100 m s^{-1} for the ergols H_2/O_2, 3000 m s^{-1} for kerosene/O_2 and of 2850 m s^{-1} for nitrogen peroxide/unsymmetrical dimethylhydrazine (UDMH). The temperature reached by the burned gases exceeds 3000°C, which necessitates the cooling of the internal walls of the nozzles. This cooling can be obtained by the circulation of one of the ergols in a jacket which then vaporizes, or by injecting a film of liquid ergol between the combustion gas and the nozzle.

3 - BURNERS

Three main categories of burners can be distinguished according to whether they work using gases, liquids or solids. Only the first two categories of burners give rise to gas-phase thermal reactions and will be discussed here.

Several criteria can be taken into account to characterize a burner :

- the way the fuel/combustion-agent mixture is formed, in particular with, or without mixing prior to the flame,
- the pressures of the supply,
- the flow mode at the exit openings,
- the stabilization technique for the flames,
- the localization of the flame,
- the preheating of the fuel or of the combustion-air.

There therefore exists a very large variety of designs, which will be illustrated by some typical examples.

a) Gas burners

Domestic burners for heating and cooking work with a premixed flame. They produce short flames.

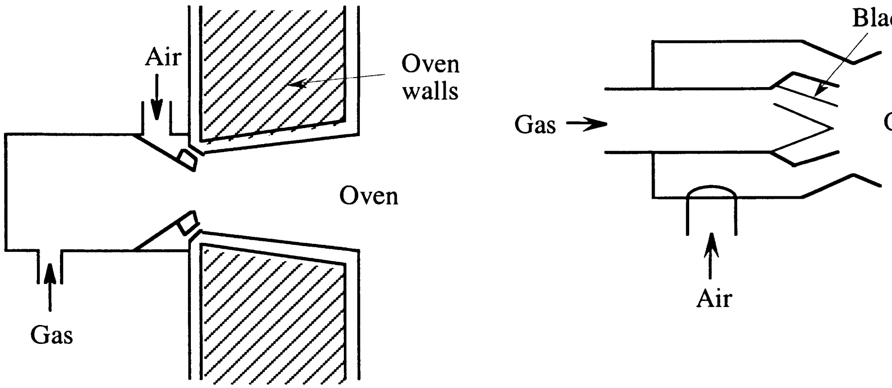
Industrial burners working without premixing of the air and gas are described in Figures 7a and 7b. For the burner in 7a, the mixing is carried out by a convergent-divergent flow and in the case of 7b by the rotation of the gas using blades. It is possible to put the gas on the one hand and the air on the other into rotation by making them arrive at a tangent. Making them rotate in opposite directions favours the mixing.

Torches in refineries and petroleum platforms eject hydrocarbons into the air at a speed close to that of sound. They can burn up to a million cubic metres a day.

b) Liquid fuel burners

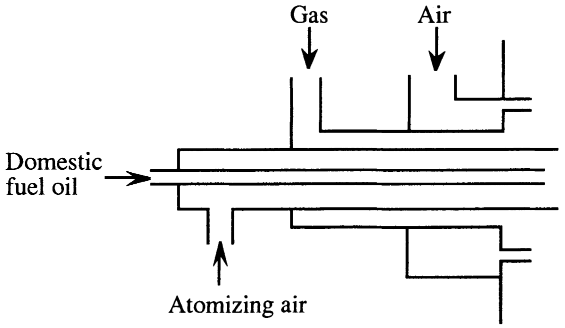
The actual combustion occurs in the gaseous phase, after the evaporation of the fuel and its diffusion in the combustion-air. In order to favour the evaporation, the fuel is atomized into very small droplets, of sizes of between 10 and 150 µm.

Figure 7 : Burners.



a) Convergent-divergent burner

b) Burner with blades



c) Burner using a mixture of gas and domestic fuel oil

This atomization also allows the fuel to be distributed in an optimum way within the combustion-air.

The air supply can be induced by the fall in pressure prevailing in the combustion chamber and by the thrust of the jet of fuel. The burners of this category are called **air-induced** burners.

The air can also be supplied under pressure by a ventilator or a blower ; this type of burner, called **air blown**, allows the flame to be controlled better, as the flows of the fuel and of the combustion-air are relatively independent.

Figure 7c shows a diagram of a mixed burner capable of working either with gas, or with domestic fuel oil, or simultaneously with both. Domestic fuel oil is atomized by air.

The burners described here are meant to obtain temperatures of the order of 1000-1200°C. But a whole range of burners also exists, which are meant to produce lower temperatures of the order of 500 °C, as well as **blow-torches** for very different uses : machine blow-torch, oxy-arc cutting, soldering, glass blowing, jewellery....

4 - INDUSTRIAL CHEMICAL REACTORS

4.1 - The steamcracker

a) The reactor

Figure 8 shows a schematic representation of the steamcracking reactor.
A steamcracking oven has the following approximate dimensions H × L × P = 7.5 m × 3.6 m × 10 m and contains about a hundred radiant burners, which provide a burned gas at a temperature of about 1200 °C. The oven contains 4 to 8 tubes of total length of around 60 m for naphtha and 85 m for ethane, and usually have diameters of between 75 and 115 mm . The space times lie between 0.3 and 0.8 s, which corresponds to a Reynolds number of the order of 300,000. The heat flux furnished to the tubes varies from 55 to 85 kW m^{-2}, the temperature of the tube is lower than 1050 °C.
The energy consumption reaches 2000 kWh heat per ton of load and 7500 kWh per ton of C_2H_4. About 20 % are used up by the endothermicity of the reaction and 80 % can be released as heat.
The preheated reaction feed first goes into a convection zone, which is heated by the burned gases, then into a radiation zone where it is heated by radiation and convection ; it is cooled quickly and fractionated at the exit to the chamber.

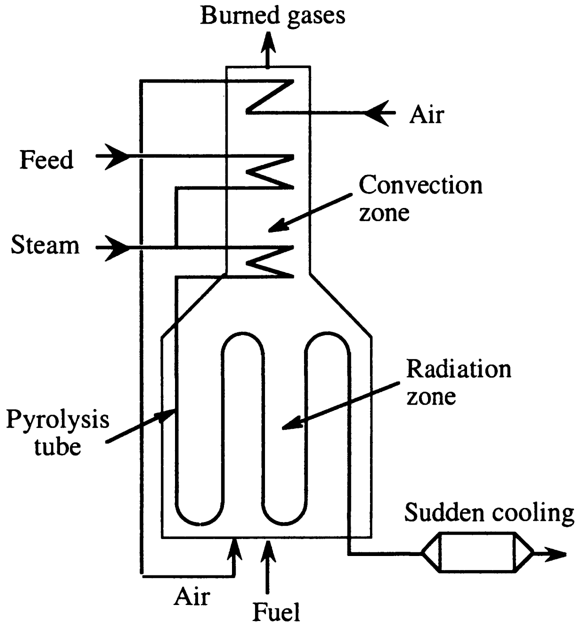
b) Feeds

A steamcracker can be supplied with ethane, propane, naphtha, vacuum distillates, or even crude oil. If the hydrocarbon is liquid, it is vaporized by steam ; if it is gaseous, it is also mixed with steam. Steam acts in different ways : it is a heat carrier, it lowers the partial pressure of the hydrocarbons, it also acts chemically by limiting the formation of coke on the walls of the reactor and favouring the production of ethylene.

Example 3
A steamcracker is supplied with 2500 kg h^{-1} of naphtha distillate collected between 15 and 135°C, of PIONA = 47 : 37 : 0 : 11 : 5 (w/w), which corresponds to hydrocarbons possessing 5 to 10 carbon atoms. Naphtha is mixed with steam, at a ratio of H_2O : naphtha = 0.7 : 1 (w/w).
The temperature of the gases at the entrance of the tube is of the order of 650 °C, and at the exit it is between 830 and 870 °C. The pressure at the entrance is about 3 bar and at

the exit 1.7 bar.

Figure 8 : Steamcracker.



c) Products of reaction

Table 4 gives a typical mass composition of the products formed during the steamcracking of ethane, propane and naphtha. This shows that the alkenes decrease and that the aromatics and the petrols increase when the mean molar mass of the feed increases.

Table 4 : Steamcracking.

Feeds	Ethane	Propane	Naphtha
Products			
Ethylene	80	45.0	36
Propene	1.4	14.5	18
Butadiene	—	2.8	4
BTX	—	3.3	9
C_4 fraction	4.8	2.0	4
Petrol	0.2	4.2	6
Fuel gases	13.6	28.2	20
Feed	—	—	3

4.2 - Synthesis gas

The term synthesis gas is given to mixtures of CO and H_2 of different compositions according to the way in which they are made and also if they are destined for the manufacture of NH_3, of CH_3OH or fuels.

The manufacturing processes of synthesis gases used to be based on the gasification of coke obtained from anthracite or lignite by the action of air and steam. After the Second World War, natural gas and petroleum fractions were mainly used as raw materials. Two very different methods can be used.

- Catalytic steam reforming is an extremely endothermic reaction. The heat necessary is supplied by the burning of natural gas or petroleum distillates.
- The homogeneous partial oxidation in the gas phase which was very much developed in the 1990s, as there were about 150 plants of this type, producing about 2.5×10^{10} m^3 of synthesis gas a year.

a) Reactor

The reactor is a vertical chamber lined on the inside with a silica or alumina refractory ore. The oxygen-steam mixture is introduced through tangential entrances, which creates a gyratory movement of the combustion-agent around the introduction pipe and the atomization of the liquid hydrocarbon feed. The mixture of oxidizing agent and feed is also ensured by a convergent-divergent device. Efficient mixing decreases the amounts of solid by-products formed.

b) Feeds (Table 5a)

The process can cope with very different feeds, which include natural gases and petroleum fractions and ranging from the light naphthas to the asphalts, as well as refinery gases.

The fact that the reaction takes place in the gas phase and without a catalyst means that it is not necessary to eliminate sulphur from the feed.

c) Operating conditions (Table 5b)

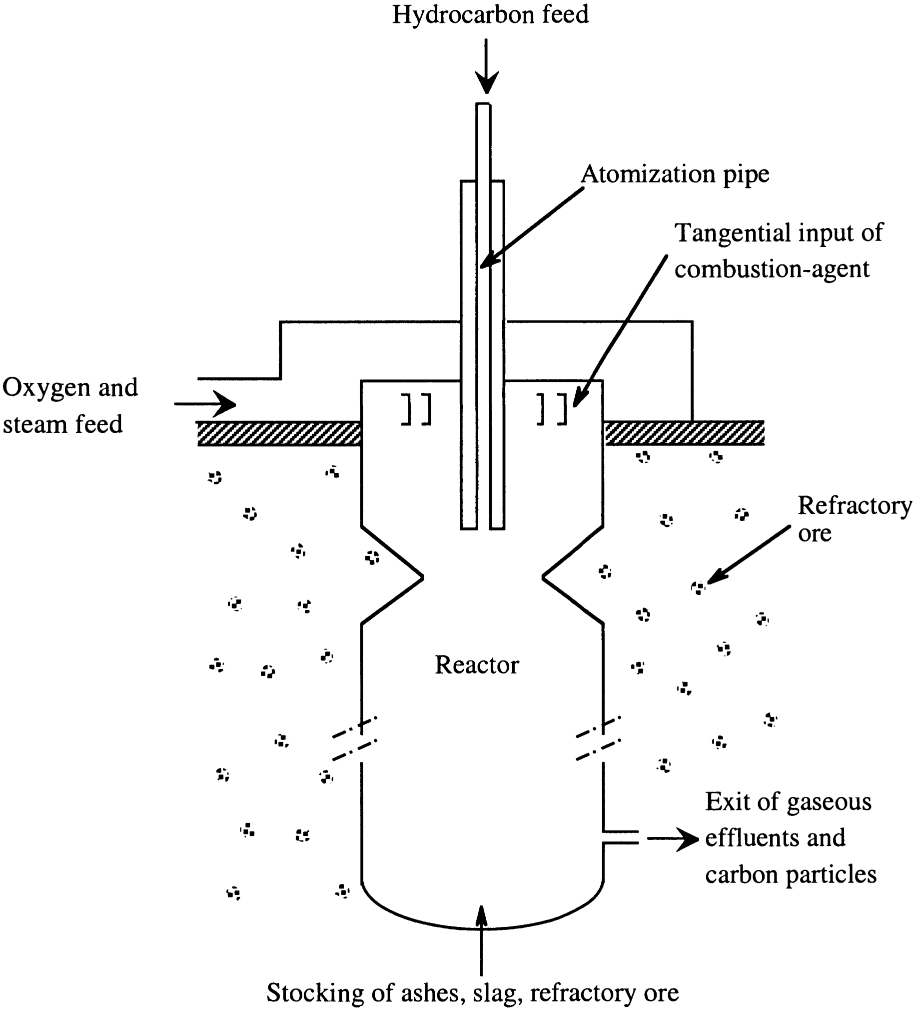
The reactants are preheated to different temperatures according to the nature of the feed. They are mixed with oxygen and steam in proportions which also depend on the type of feed used.

The oxygen produces exothermic reactions, whereas the steam decreases the temperature of the reaction using a heat capacity effect and by endothermic reactions. On the whole, the reaction occurs in a quasi-adiabatic manner at temperatures between 1300 and 1500 °C. The reaction is carried out at pressures from 2 to 6 MPa.

d) Products of the reaction

Table 5 gives the composition of the dry gases obtained. Note that the main products are hydrogen and carbon monoxide. The example shown is that of the gasification by oxygen, it is therefore normal to find nitrogen and argon in negligible amounts. The by-products include carbon dioxide and methane, as well as hydrogen sulphide and carbonyl sulphide ; the formation of carbon particles and of ashes, which can be as high as 2 % w/w for heavy petroleum fractions must be added to this.

Figure 9 : Synthesis gas : schematic representation of the reactor.



An important by-product is steam. Part of this steam is used to lower the temperature of the reaction. Table 5d indicates the net production of steam, once the steam used in the process has been deducted ; this vapour is used for the production of mechanical or electrical energy.

Table 5 : Synthesis gas : Characteristics of the process.

Feeds	Natural gas	Light naphtha	Heavy fuel	Residue under vacuum	Asphalt
a) Characteristics					
Density at 15°C	—	0.67	0.97	1.04	1.09
H/C (% w/w)	0.33	0.19	0.13	0.12	0.10
S (% w/w)	—	0.03	3.50	4.25	4.92
Ashes (% w/w)	—	—	0.07	0.15	0.10
b) Operating conditions					
Preheating temperature (°C)	400	27	260	260	300
O_2/feed	1.10	1.24	1.05	1.01	0.98
H_2O/feed	0.2	0.4	0.45	0.5	0.5
c) Compositions of the dry gases (% v/v)					
H_2	59.8	52.3	46.9	44.9	44.1
CO	35.5	42.5	47.4	48.9	49.9
CO_2	3.8	4.8	4.3	4.6	4.3
CH_4	0.5	0.3	0.3	0.3	0.3
N_2+Ar	0.4	0.1	0.2	0.2	0.3
H_2S	—	0.01	0.8	1.0	1.1
COS	—	—	0.03	0.04	0.05
d) Saturated vapour at 80 bar (in kg H_2O/kg feed)					
	2.7	2.6	2.2	2.1	2.1

FURTHER READING

ALBRIGHT L.F., CRYNES B.L., CORCORAN W.H. (Editors), *Pyrolysis : Theory and Industrial Practice*, Academic Press (1983).

BEJAN A., *Advanced Engineering Thermodynamics*, 2nd edition, Wiley (1997).

BRADLEY D., MORLEY C., *Autoignition in Spark-Ignition Engines*, Compr. Chem. Kin., vol.35, Elsevier (1997).

BUCKMASTER. J., JACKSON. T.L., KUMAR A. (Editors), *Combustion in High-Speed Flows*, Kluwer (1994).

GUIBET J.C., *Fuels and Engines - Technology, energy, environment*, Technip (1999).
MORAN M..J., SHAPIRO H.N., *Fundamentals of Engineering Thermodynamics*, 2nd edition, Wiley (1993).
OWEN K., (Editor), *Gasoline and Diesel Fuel Additives*, Critical Reports on Applied Chemistry, vol. 25, The Society of Chemical Industry, Wiley (1989).
STONE R., *Introduction to Internal Combustion Engines*, 3rd edition, SAE-Macmillian (1999).
SUTTON J.P., *An Introduction to the Engineering of Rockets*, 5th edition, Wiley (1986).
WEISSERMEL K., ARPE J., *Industrial Organic Chemistry*, 2nd edition, VCH (1993).

Ullmann's Encyclopedia of Chemical Technology
COMMICHAU A. et al., *Natural gas*, A 17, 73-124, VCH (1991).
FABRI J. et al., *Motor fuels*, A 16, 719-753, VCH (1990).
GRANTOM R.L., ROYER D.J., *Ethylene*, A 10, 45-93, VCH (1987).
HOCHGESAND G., Coordinator, *Gas production*, A 12, 169-306, VCH (1989).
STRAUSS K.H., *Aviation Turbine Fuels*, A 3, 211-212, VCH (1985).

CHAPTER III

MACROSCOPIC DESCRIPTION OF A REACTING GAS MIXTURE

The primary aim of this chapter is to describe the state of a mixture of gases and the changes in this state due to the chemical reactions which it is undergoing. A second aim is to suggest a way of working out the reaction schemes and the related kinetic laws ; it is an empirical approach, which can in principle be worked out on the basis of experimental data exclusively, and is independent of any mechanistic interpretation.

1 - THE STATE OF A MIXTURE OF GASES

1.1 - Ideal Gases

The description of a mixture of gases starts by making a list of the chemical species contained within it. These species are numbered from 1 to J, where J is the total number of constituents being considered. The constituent n° j is called C_j, x_j is its mole fraction, c_j its concentration, w_j its mass fraction and M_j its molar mass.
The mixture of gases is at temperature T, at pressure p, and of density ρ. First of all it will be assumed that the mixture of gases is ideal (a test for this approximation is given in §1.2).

Table 1 gives definitions of the properties p, x_j, c_j, ρ, w_j for the following two cases :

a) a mixture of gases in an enclosed volume V, with no exchange of matter with the surroundings and containing a quantity n_j mol of constituent C_j ;
b) a mixture of gases undergoing pure convective flow (as the diffusion is considered to be negligible) of volume flow rate Q across a constant cross-section and carrying a molar flow rate F_j of constituent C_j.

In order to simplify the writing of the equations in Table 1, the abbreviated form Σ has been used instead of $\sum_{j=1}^{J}$.

The change from equations a) of Table 1 to equations b) and vice-versa can be carried out by exchanging : volume ↔ volume flow rate, mole ↔ molar flow rate.

Table 1 :State of a mixture of gases.

Property	a) batch reactor	b) convective flow	
pressure	$p = \frac{n\,RT}{V}$	$p = \frac{F\,RT}{Q}$	(1)
mole fraction	$x_j = \frac{n_j}{n}$	$x_j = \frac{F_j}{F}$	(2)
molar concentration	$c_j = \frac{n_j}{V}$	$c_j = \frac{F_j}{Q}$	(3)
density	$\rho = \frac{n\,M}{V}$	$\rho = \frac{F\,M}{Q}$	(4)
mass fraction	$w_j = \frac{n_j\,M_j}{\Sigma\, n_j\,M_j}$	$w_j = \frac{F_j\,M_j}{\Sigma\, F_j\,M_j}$	(5)

The equations given in Table 1 involve the total quantity of matter n and the total molar flow rate F :

$$n = \Sigma\, n_j \tag{6}$$

$$F = \Sigma\, F_j \tag{7}$$

as well as the mean molar mass M :

$$M = \frac{\Sigma\, n_j\,M_j}{n} \tag{8}$$

$$M = \frac{\Sigma\, F_j\,M_j}{F} \tag{9}$$

The sum of mole and mass fractions are equal to 1 :

$$\Sigma\, x_j = \Sigma\, w_j = 1 \tag{10}$$

With total concentration c :

$$c = \Sigma\, c_j \tag{11}$$

equations 1 and 4 can be written :

$$p = c\,RT \tag{12}$$

and :

$$\rho = c\,M \tag{13}$$

From the above, the following relationship between p and ρ can be derived :

$$p = \rho\frac{RT}{M} \tag{14}$$

Expressions (8) and (9) for the mean molar mass M can be changed using equations (2), (3) and (5) into :

$$M = \Sigma\, x_j\, M_j \tag{15}$$

$$M = \frac{1}{c}\, \Sigma\, c_j\, M_j \tag{16}$$

$$M = \frac{1}{\Sigma\, w_j/M_j} \tag{17}$$

The state of a mixture of gases is completely defined when the values of the state variables are known. The number of state variables is equal to 1 +J : the temperature and one state variable per constituent, that is J variables for all of the constituents. Three main choices of state variables exist :

- T, p, x_j	in thermodynamics
- T, c_j	in kinetics
- T, ρ, w_j	in fluid mechanics

The number of state variables is actually equal to 1+J in each case, according to equation (10) between mole and mass fractions.

It is easy to go from one system of state variables to another using equations (1) to (17).

— *Variables T, p, x_j*

$$c_j = x_j \frac{p}{RT} \quad ; \quad M = \Sigma\, x_j\, M_j \quad ; \quad w_j = x_j \frac{M_j}{M} \quad ; \quad \rho = \frac{pM}{RT}$$

— *Variables T, c_j*

$$x_j = \frac{c_j}{c} \quad ; \quad M = \frac{1}{c} \Sigma\, c_j\, M_j \quad ; \quad w_j = \frac{c_j M_j}{c M} \quad ; \quad p = c\,RT \quad ; \quad \rho = c\,M$$

— *Variables T, ρ, w_j*

$$M = \frac{1}{\Sigma\, w_j/M_j} \quad ; \quad p = \rho \frac{RT}{M} \quad ; \quad x_j = w_j \frac{M}{M_j} \quad ; \quad c_j = w_j \frac{\rho}{M_j}$$

Example 1

A steamcracking unit is supplied with 2 kg s^{-1} ethane and 0.7 kg s^{-1} water vapour, at 1100 K and 1.24×10^5 Pa. Calculate the compositions and the flow rates.

Giving j = 1 to C_2H_6 and j = 2 to H_2O, leads to $W_1 = 2$ kg s^{-1}, $W_2 = 0.7$ kg s^{-1}, $M_1 = 30 \times 10^{-3}$ kg mol^{-1}, $M_2 = 18 \times 10^{-3}$ kg mol^{-1}.

Thus $w_1 = 0.741$; $w_2 = 0.259$; $M = 25.6 \times 10^{-3}$ kg mol^{-1} ; $x_1 = 0.632$; $x_2 = 0.368$; $c = 13.6$ mol m^{-3} ; $\rho = 0.347$ kg m^{-3} ; $c_1 = 8.56$ mol m^{-3} ; $c_2 = 5.00$ mol m^{-3} ; $F_1 = 66.7$ mol s^{-1} ; $F_2 = 38.9$ mol s^{-1} ; $F = 105.6$ mol s^{-1} ; $Q = 7.79$ m^3 s^{-1}.

1.2 - The REDLICH and KWONG equation

In Example 1 the ideal gas law was used. To test if this law can be used, another, more accurate law, must be available. The REDLICH and KWONG equation appears to be well adapted for this purpose, both by its simplicity and its ease of application. This analytical state equation relates the pressure p, to the temperature T and the molar volume V :

$$p = \frac{RT}{V-b} - \frac{a}{T^{1/2}\, V\,(V+b)} \tag{18}$$

with :

$$a = \sum_{j,k} (a_j\, a_k)^{1/2}\, x_j\, x_k \tag{19}$$

$$b = \sum_{j} b_j\, x_j \tag{20}$$

$$a_j = 0.4275\, R^2\, T_{cj}^{2.5}/p_{cj} \tag{21}$$

$$b_j = 8.664\text{x}10^{-2}\, RT_{cj}/p_{cj} \tag{22}$$

T_{cj} and p_{cj} are the critical temperature and pressure of C_j .

Example 2

What accuracy can be expected of the ideal gas law for methane at 2000 K and 10^7 Pa ?

The critical values for CH_4 are $T_c = 190$ K and $p_c = 4.60\text{x}10^6$ Pa. It can be deduced that $a = 3.20$ and $b = 2.98\text{x}10^{-5}$. The ideal gas law gives $V = 1.66\text{x}10^{-3}$ m^3. Putting this value into equation (18), gives $p = 1.017\text{x}10^7$ Pa. The error is less than 2%.

2 - CONVERSION, SELECTIVITY, YIELD

2.1 - Continuous chemical unit operation

Industrial reactors using a gas phase thermal reaction handle very large quantities of materials each year. Thus the steamcracker in Example 1 works for about 300 days a year and uses about 50,000 t C_2H_6 and produces 40,000 t C_2H_4. Such processes must operate continuously.

A continuous industrial process requires the following main elements (Figure 1) :

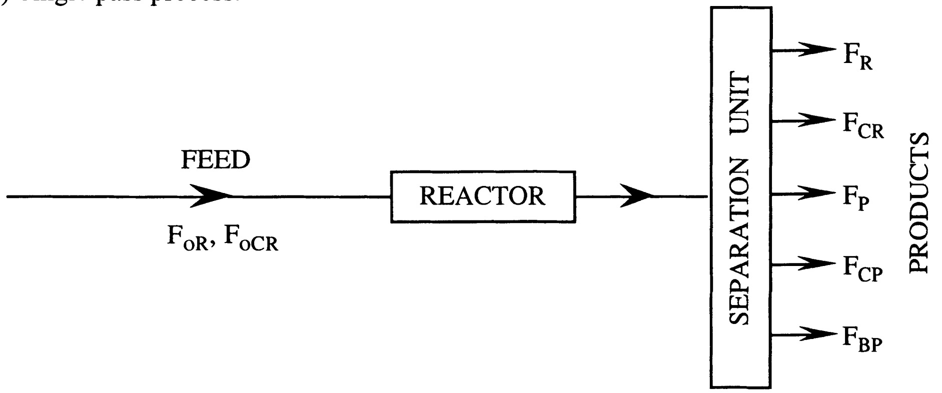
- a continuous supply of reactant R and co-reactant CR,
- a reactor where the transformation of R and CR into the product P, co-product CP

and by-product(s) BP takes place,

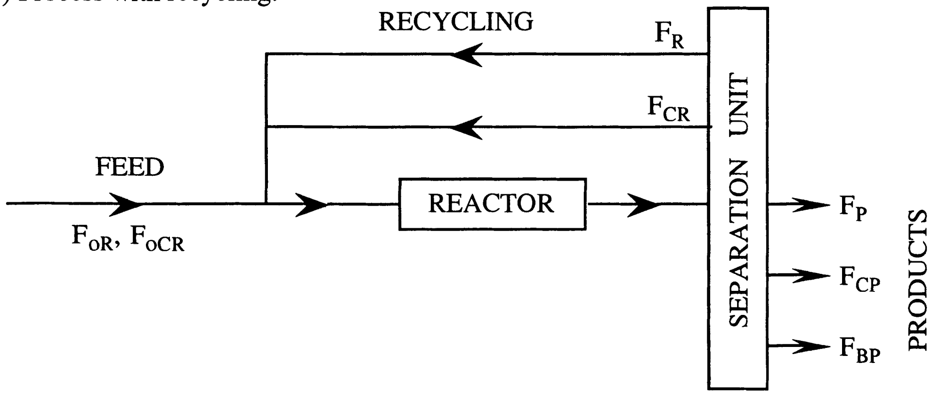
- a separation unit (distillation columns, absorption columns...) which separates the different effluents from the reactor, unused R and CR, P, CP and BP,
- in a single pass process (Figure 1a), the effluents are withdrawn for use or stocking. These effluents are R, CR, P, CP, BP.
- in a process involving recycling (Figure 1b), the reactant R and the co-reactant CR are sent back to the feed of the reactor. Only P, CP and BP are withdrawn ; neither R nor CR leaves the process.

Figure 1 : Schematic representation of a continuous industrial process.

a) Single pass process.



b) Process with recycling.



A certain number of appliances are not shown in scheme 1, such as the means necessary for ensuring the circulation and the mixing of the fluids, the heat exchangers, the instruments for monitoring and controlling the process.

It is assumed that the process is at a **steady state** i.e. all the other characteristic properties of the process are constant with time. In fact, the starting and stopping of the process, as well as its control, belong to a transient state, as the operating properties vary or change with time.

The molar flow rate of the supply of constituent j to the unit (j=R, CR) will be called F_{0j} and the molar flow rate of constituent j leaving the separation unit (j = R, CR, P, CP, BP) will be called F_j. In the petroleum chemical industry, chemically complex reactants are used (naphtha, LPG ...), and it is much more common to carry out mass balances. W_{0j} and W_j are the mass-flows of constituent j supplying the process and leaving the separation unit, respectively.

In Figure 1 note that the molar flow rates of the supply in R and CR of the actual reactor are equal to F_{0R} and F_{0CR} for a single pass process (Figure 1a), and to $F_{0R} + F_R$ on the one hand, $F_{0CR} + F_{CR}$ on the other hand, for a process involving recycling (Figure 1b).

2.2 - Stoichiometric equation for the process

a) When it is possible to give a chemical identity to the species R, CR, P and CP, the stoichiometric equation for the process can be written :

$$\nu_R\, R + \nu_{CR}\, CR = \nu_P\, P + \nu_{CP}\, CP \tag{23}$$

This equation means that, when one mole of R disappears, (ν_P/ν_R) moles of P appear, but also inevitably (ν_{CP}/ν_R) moles of co-product CP appear and (ν_{CR}/ν_R) moles of the co-reactant CR disappear.

The by-products BP need not appear in the stoichiometric equation (23), since they are formed in very much lower quantities than the product and the co-product. Besides, for a totally selective process, no by-products are formed. The amounts of by-products formed depend on the way in which the reaction is carried out, whereas the ratio F_{CP}/F_P depends only on the stoichiometric equation (23) and is equal to (ν_{CP}/ν_P).

b) When several products and co-products are formed, and their chemical formulae are known, several stoichiometric equations must be written. This matter will be dealt with later.

c) When the load or the effluents are too complex, it is no longer possible to describe the chemical transformation using simple stoichiometric equations. Then either representative model species are used, or lumped pseudo-species, which group analogous species together.

2.3 - Conversion

a) Single pass conversion (Figure 1a)

Calling X_R and X_{CR} the fractional conversions per pass of R and CR respectively, gives :

$$F_R = F_{oR}(1 - X_R) \tag{24}$$

$$F_{CR} = F_{oCR}(1 - X_{CR}) \tag{25}$$

b) Conversion with recycling (Figure 1b)

As neither R nor CR leaves the processing unit, the conversions of R and of CR are total. Equations (24) and (25) give the expressions for the recycling flows F_R and F_{CR}.

2.4 - Selectivity

$S_{P/R}$, $S_{CP/R}$ and $S_{BP/R}$ are the fractions of the converted reactant R which are transformed into P, CP and BP, respectively.
These three quantities are the selectivities of P, CP and BP of the process with respect to R. The selectivities with respect to CR are defined in an analogous way.
As the reactant R is only transformed into P, CP and BP, the sum of the selectivities is equal to 1 :

$$S_{P/R} + S_{CP/R} + S_{BP/R} = 1 \tag{26}$$

Calling $F_{R \to P}$ the molar flow rate of the reactant transformed by the process into the product P, the molar flow rate of P, which is withdrawn, can be written from equation (1) as follows :

$$F_P = \frac{\nu_P}{\nu_R} F_{R \to P} \tag{27}$$

a) Single pass process

From equation (24), the molar flow rate of converted R is equal to $X_R F_{oR}$; therefore :

$$F_P = \frac{\nu_P}{\nu_R} S_{P/R} X_R F_{oR} \tag{28}$$

$$F_{CP} = \frac{\nu_{CP}}{\nu_R} S_{CP/R} X_R F_{oR} \tag{29}$$

As there is no stoichiometric equation for the formation of by-products, the mass-flow of by-products W_{BP} can be calculated by applying Lavoisier's law, or mass conservation law :

$$W_{BP} = W_o - (W_P + W_{CP}) \tag{30}$$

with :

$$W_o = W_{oR} + W_{oCR} \tag{31}$$

$$W_P = F_P M_P \tag{32}$$

$$W_{CP} = F_{CP} M_{CP} \tag{33}$$

where M_P and M_{CP} are the molar masses of P and CP.

b) Process with recycling

Equations (28) and (29) apply, with $X_R = 1$:

$$F_P = \frac{\nu_P}{\nu_R} S_{P/R} F_{oR} \tag{34}$$

$$F_{CP} = \frac{\nu_{CP}}{\nu_R} S_{CP/R} F_{oR} \tag{35}$$

2.5 - Yield

In general, the yield of a process is defined as being the fraction of the flow rate of reactant entering the unit which is transformed into a product leaving the unit, that is :

$$Y_{P/R} = \frac{F_{R \to P}}{F_{oR}} \tag{36}$$

a) Single pass process

The yield is equal to the product of the conversion and the selectivity :

$$Y_{P/R} = X_R S_{P/R} \tag{37}$$

b) Process with recycling

The above equation applies with $X_R = 1$:

$$Y_{P/R} = S_{P/R} \tag{38}$$

In a process with recycling, the yield becomes equal to the selectivity, and is therefore larger than the yield in a single pass process.

Example 3

The steamcracker of ethane in Example 1 has an operating cycle of 300 days a year. The conversion per pass is 60%. The mass composition of the hydrocarbon products withdrawn as follows : 80% C_2H_4 ; 1.4% C_3H_6 ; 4.8% C_4H_8 ; 0.2% petrol ; 13.6% fuel gases. Calculate the mass flow rates of the supply, of the withdrawn products and of the recycling of the unit, and the selectivities of the alkenes.

The mass flow rates of the supply are equal to :

$$W_{o,C_2H_6} = (2\ \text{kg s}^{-1}) \,.\, (84\ 600\ \text{s day}^{-1}) \,.\, (300\ \text{day year}^{-1})$$
$$W_{o,C_2H_6} = 5.8\text{x}10^7\ \text{kg/year}$$

$$W_{o,H_2O} = 1.81\text{x}10^7 \text{ kg/year}$$

The recycling flow rate is :

$$W_{C_2H_6} = (1 - X_{C_2H_6})\, W_{o,C_2H_6} = 2.7\text{x}10^7 \text{ kg/year}$$

The exit flow rates can be obtained from the mass composition of the dry products :

$$W_{C_2H_4} = 5.12\text{x}10^7\text{x}0.8 = 4.14\text{x}10^7 \text{ kg/year}$$
$$W_{C_3H_6} = 7.25\text{x}10^5 \text{ kg/year}$$
$$W_{C_4H_8} = 2.49\text{x}10^6 \text{ kg/year}$$
$$W_{petrol} = 1.04\text{x}10^4 \text{ kg/year}$$
$$W_{gas} = 7.05\text{x}10^6 \text{ kg/year}$$

Check that the sum of these flows is equal to W_{o,C_2H_6}. Water can be considered to be almost inert under these conditions, therefore :

$$W_{H_2O} \cong W_{o,H_2O} = 1.81\text{x}10^7 \text{ kg/year}$$

To calculate the selectivities, the corresponding stoichiometric equations must be written :

$$C_2H_6 = C_2H_4 + H_2 \qquad C_2H_6 = 0.67\ C_3H_6 + H_2 \qquad C_2H_6 = 0.50\ C_4H_8 + H_2$$

Therefore :

$$S_{C_2H_4} = \frac{(80/100)}{(28/30)} = 0.857$$

$$S_{C_3H_6} = \frac{(1.4/100)}{\left(\frac{2\text{x}42}{3} / 30\right)} = 0.015$$

$$S_{C_4H_8} = \frac{(4.8/100)}{(0.5\text{x}56/30)} = 0.051$$

In all, 92.3 % of the ethane is changed into olefins, the rest is found mainly in the form of CH_4 and H_2 as fuel gases and to a lesser extent as petrol.

3 - STOICHIOMETRIC ANALYSIS

The main use of stoichiometric equations is to express LAVOISIER'S law in a mathematical form, that is the conservation of the elements (C, H, O...) during a chemical transformation.

First of all, these equations confirm that the experimental results are not impaired by systematic errors, due to erroneous quantitative measurements or the failure to take into account one or other constituent. One can easily imagine that this is an essential prerequisite for the scientific analysis of experimental data and for the design or control of a chemical reaction.

But it will be seen that theory allows the number of equations for the reactions which are strictly necessary to describe the chemical system precisely to be defined in a rigorous way, when the nature and the number of the constituents to be taken into account are themselves well-defined. The theory therefore provides the necessary and sufficient number of chemical variables (or JOUGUET-de DONDER variables) and equations to calculate the composition of the reaction mixture during the transformation. In particular, these equations can be applied to chemical equilibria.

On the contrary, stoichiometric equations do not give any indication about the way in which the chemical changes take place on a molecular level. This task has been assigned to the reaction mechanisms. However, it is possible to incorporate a kinetic meaning into stoichiometric equations ; **kinetic schemes** are then obtained, which make an extremely useful compromise for the modelling of chemical reactions, between a completely empirical approach and a purely fundamental approach.

3.1 - Stoichiometric equations

Consider that a chemical reaction is satisfactorily represented by I reactions involving J constituents. The stoichiometric equation n° i can be written :

$$\text{(i)} \quad \sum_{j=1}^{J} \nu'_{ij}\, C_j = \sum_{j=1}^{J} \nu''_{ij}\, C_j \qquad i = 1, 2, \ldots, I \tag{39}$$

where : C_j is constituent n° j,

ν'_{ij} is the stoichiometric coefficient of reactant C_j,

ν''_{ij} is the stoichiometric coefficient of product C_j.

The generalized stoichiometric coefficients are defined by the relationship :

$$\nu_{ij} = \nu''_{ij} - \nu'_{ij} \tag{40}$$

They are positive for products, negative for reactants, and equal to zero for inert substances.

The development of a representative stoichiometric system involves four steps.

3.2 - The BRINKLEY criterion

This criterion stipulates the number I of stoichiometric equations which are necessary to describe the chemical change :

$$I = J - J' \tag{41}$$

where : J is the total number of constituents in the system, J' is the number of independent constituents.

J' is equal to the rank of the matrix of the indices of the elements in the formulae for the constituents. The rank of a matrix is the order of the determinant of the highest order, which can be extracted from the matrix, which is not equal to zero.

Example 4

Consider the reaction for the decomposition of neopentane (C_5H_{12}) in a stirred flow reactor at very short space time. By extrapolation of the experimental results to a space time equal to zero, the following molar composition for the products which were formed was obtained : 50 % C_4H_8, 28 % CH_4, 11 % C_2H_6 and 11 % H_2. Analyse these results.

Starting by determining the number of independent constituents, the formula matrix can be written as follows :

	C_5H_{12}	C_4H_8	CH_4	C_2H_6	H_2
C	5	4	1	2	0
H	12	8	4	6	1

It is possible to extract a non-zero determinant of order 2 from this matrix. It is deduced that J' = 2. As J = 5, then I = 3. Three stoichiometric equations must therefore be written, for example :

$$C_5H_{12} = CH_4 + C_4H_8 \qquad (1)$$

$$C_5H_{12} = \frac{1}{2}\,C_2H_6 + \frac{1}{2}\,H_2 + C_4H_8 \qquad (2)$$

$$C_5H_{12} = \frac{5}{4}\,C_4H_8 + H_2 \qquad (3)$$

3.3 - The JOUGUET criterion

Each linear combination of stoichiometric equations is itself a stoichiometric equation. This is the reason why the number of stoichiometric equations is fixed, but not their nature. The writing of a complex stoichiometric system is therefore likely to lead to equations which are not independent. One must make certain that this is not the case. JOUGUET's criterion indicates that the equations are independent if the rank of the matrix of the stoichiometric coefficients is equal to I.

Example 5

Apply JOUGUET's criterion to Example 4.

The matrix of the generalized stoichiometric coefficients can be written as follows :

Reaction	C_5H_{12}	C_4H_8	CH_4	C_2H_6	H_2
1	−1	1	1	0	0
2	−1	1	0	0.5	0.5
3	−1	1.25	0	0	1

This matrix is of rank 3 and the equations are actually independent.

3.4 - The JOUGUET- de DONDER equations

Consider a batch reactor containing n_j moles of constituent C_j. The law of definite proportions stipulates that the variation $(dn_j)_i$ in the quantity of C_j due to the reaction i is proportional to the stoichiometric coefficient ν_{ij}. $d\xi_i$ represents the proportionality coefficient, ξ_i is a Jouguet-de Donder chemical variable. The total variation dn_j due to the I reactions (39) can be written as follows :

$$dn_j = \sum_{i=1}^{I} \nu_{ij}\, d\xi_i \tag{42}$$

The integration of this equation between the instant t = 0 ($n_j = n_{oj}$, $\xi_i = 0$) and t gives the following expression :

$$n_j = n_{oj} + \sum_{i=1}^{I} \nu_{ij}\, \xi_i \tag{43}$$

The transposition to a continuous reactor operating under steady-state conditions leads to the following expression :

$$F_j = F_{oj} + \sum_{i=1}^{I} \nu_{ij}\, \zeta_i \tag{44}$$

The calculation of the variables ξ_i or ζ_i from the experimental results can be carried out by solving the sets of equations (43) or (44) for j = 1, 2, ..., J.

Example 6

Calculate the chemical variables of Example 4.

The equations (44) are written for each constituent :

C_4H_8 : $\zeta_1 + \zeta_2 + 1.25\,\zeta_3 = 50$ C_2H_6 : $0.5\,\zeta_2 = 11$

CH_4 : $\zeta_1 = 28$ H_2 : $0.5\,\zeta_2 + \zeta_3 = 11$

The following values are found : $\zeta_1 = 28$; $\zeta_2 = 22$; $\zeta_3 = 0$. Reaction 3 is negligible and the system is suitably represented by equations (1) and (2) alone, of relative weightings

56 and 44 %.The number of stoichiometric equations has become I' = 2.

3.5 - The JOUGUET-de DONDER invariants

A property of the form $\sum_j \lambda_j n_j$ for a batch reactor (or $\Sigma \lambda_j F_j$ for a continuous flow reactor) is invariant if it is constantly equal to $\sum_j \lambda_j n_{oj}$ (or $(\sum_j \lambda_j F_{oj})$ whatever the values of the chemical variables ξ_i (or ζ_i). Taking equations (43) or (44) into account, the numbers λ_j are solutions of the set of equations :

$$\sum_{j=1}^{J} \nu_{ij} \lambda_j = 0 \qquad i = 1, 2, \ldots, I' \tag{45}$$

The solution of the homogeneous set (45) of linear equations gives different sets of coefficients λ_j. For a given set, the number of invariants is well defined, and it can indeed be higher than the number of elements, which gives to this method its optimal character (with respect to a balance of the elements only). On the contrary, the exact nature of the invariants is arbitrary, because, as for the stoichiometric equations, each linear combination of invariants is itself an invariant. This indetermination vanishes by fixing the basic vectors a priori.

Example 7

Identify the invariants of Example 4.

First of all, the constituents are numbered as follows :

Constituent	C_5H_{12}	C_4H_8	CH_4	C_2H_6	H_2
Index j	1	2	3	4	5

The Jouguet-de Donder equations can be written as follows :

$$-\lambda_1 + \lambda_2 + \lambda_3 = 0$$
$$-\lambda_1 + \lambda_2 + 0.5\,\lambda_4 + 0.5\,\lambda_5 = 0$$

As there is no information available about C_5H_{12}, the invariants cannot involve the associated flow rates ; therefore $\lambda_1 = 0$. The following set of equations can then be written :

$$\lambda_2 + \lambda_3 = 0$$
$$\lambda_2 + 0.5\,\lambda_4 + 0.5\,\lambda_5 = 0$$

For example λ_2 and λ_4 can be chosen arbitrarily ; λ_3 and λ_5 are then deduced :

λ_2	λ_4	λ_3	λ_5
0	1	0	−1
1	0	−1	−2

Two invariants are obtained :

$$F_{C_2H_6} = F_{H_2} \qquad\qquad F_{C_4H_8} = F_{CH_4} + 2\,F_{H_2}$$

Note that these equations are compatible with the experimental results. The conclusion can therefore be drawn that the chemical change is well represented by the stoichiometric equations (1) and (2), and that there has been neither error nor omission in the qualitative and quantitative analysis of the products of the reaction.

4 - REACTION SCHEMES

The kinetic modelling of a GPTR using reaction schemes involves the following three main stages :

- the development of a reaction scheme ;
- the assigning of empirical kinetic laws to the reactions of the scheme ;
- the validation and identification of the model from the experimental results.

A reaction scheme is a set of equations, which describes the relationship between the products and the reactants, without involving transient species of very high reactivity, such as free radicals. For this case, reaction mechanisms would have to be dealt with.

4.1 - Development of a reaction scheme

The development of a reaction scheme is based upon the analysis of experimental selectivities[1], which allows those products which are of, for example, a primary, secondary or tertiary nature to be identified amongst the products of the reaction. These classes of constituents will now be defined.

Let A be a constituent of the load introduced into the reactor, B be a primary product, C be a secondary product, D a tertiary product.

Example 8

The following very simple reaction scheme involves these four categories of constituents :

$$A + A \longrightarrow B \qquad\qquad A + B \longrightarrow C \qquad\qquad A + C \longrightarrow D$$

The primary product B results from the initial reactant A ; the secondary product C is formed from the primary product B ; the tertiary product D is derived from the secondary product C.

In order to establish the nature of the different products formed, diagrams must be

---

[1] The experimental selectivity Y_j of product C_j is equal to the mole fraction of C_j with respect to the products of the reaction, excluding the reactants and the inert carrier gases.

drawn which represent the variations in the experimental selectivities as functions of a property related to the extent of the reaction, such as the conversion ratio of a reactant, the duration of the reaction or the space time.

The primary products are those for which the selectivity is extrapolated to a non-zero value at a duration of reaction equal to zero, whereas the selectivity of a secondary product must be extrapolated to zero at zero duration.

Example 9

Figures 2 and 3 show the variations in the experimental selectivities as a function of the space time for the pyrolysis of neopentane in a stirred flow reactor at a temperature of 1008 K and at a neopentane pressure of 2.19×10^3 Pa.

It can be seen in Figure 2 that the primary products of the reaction are iC_4H_8, CH_4, H_2 and C_2H_6 ; Figure 3 shows that the other products are not primary products.

In order to specify the secondary or tertiary nature of these other non-primary products, complementary experiments can be carried out which study the reactions of the primary products systematically, either alone or in the presence of the reactants or of other primary products. The principle of least change of structure could also be used, which states that the structural changes which enable a species to change into another must be as small as possible.

Example 10

Establish a reaction scheme for the pyrolysis of neopentane starting with the results of the analysis of the selectivities shown in Figures 2 and 3.

First of all, the reactions for the formation of the primary products are written as follows :

$$C_5H_{12} \longrightarrow C_4H_8 + CH_4 \tag{46}$$

$$2\,C_5H_{12} \longrightarrow 2\,C_4H_8 + C_2H_6 + H_2 \tag{47}$$

These two reactions form more isobutene than methane and equal quantities of ethane and hydrogen, which agrees with the extrapolation of the results to extent zero.

The secondary reactions of isobutane give rise to two other alkenes :

$$C_4H_8 \longrightarrow \frac{4}{5}\,C_5H_{10} \tag{48}$$

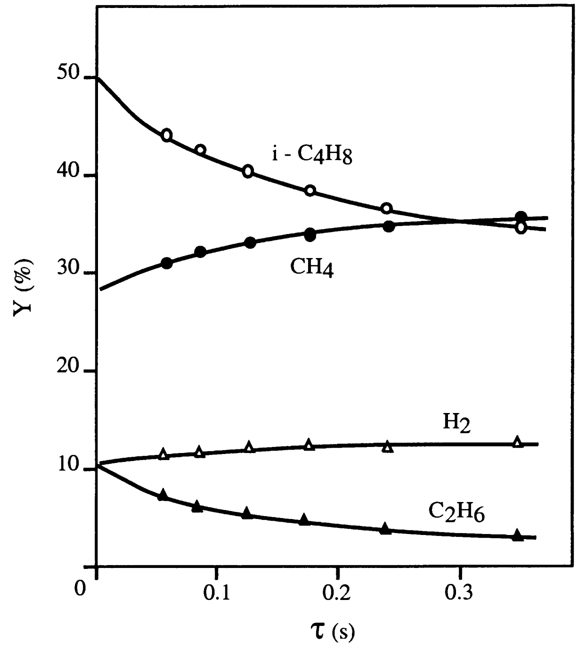
$$C_4H_8 \longrightarrow \frac{4}{3}\,C_3H_6 \tag{49}$$

where C_5H_{10} represents both m_2b_1 and m_2b_2. These reactions explain the relative decrease of C_4H_8 when the extent of the reaction increases.

Three dehydrogenation reactions allow the presence of three other products to be explained :

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \tag{50}$$
$$C_3H_6 \longrightarrow C_3H_4 + H_2 \tag{51}$$
$$C_5H_{10} \longrightarrow C_5H_8 + H_2 \tag{52}$$

Figure 2 : Primary products of the pyrolysis of neopentane.



Ethylene therefore appears as a secondary product, whereas allene and propyne (C_3H_4), as well as isoprene (C_5H_8) are tertiary products. These reactions explain the increase in the relative amount of H_2 when the extent of reaction increases.

The above reactions are otherwise reasonably compatible with the principle of least change of structure as they correspond to likely schemes

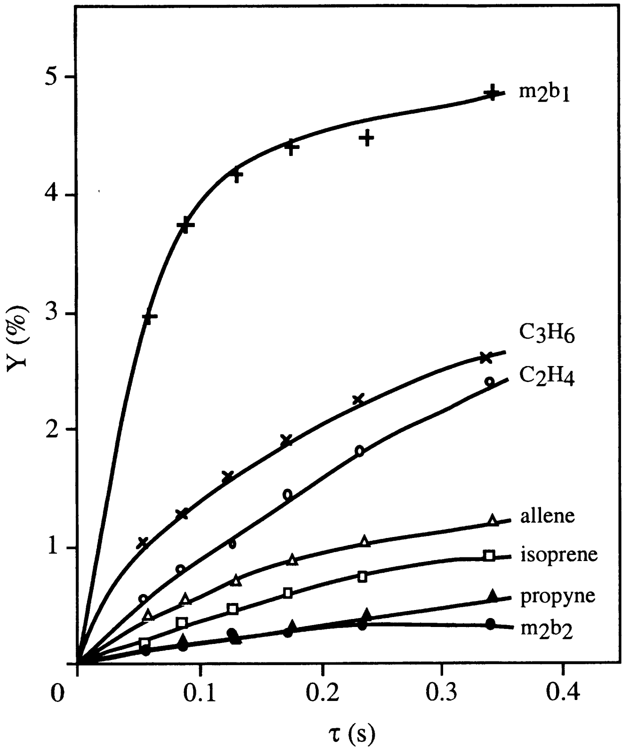
$$\text{alkane} \longrightarrow \text{alkene} \longrightarrow \begin{cases}\text{alkene}\\ \text{alkyne}\\ \text{diene}\end{cases}$$

But, of course, other reactions could be envisaged which are also compatible with the experimental results, such as :

$$C_4H_8 + C_2H_6 \longrightarrow C_5H_{10} + CH_4$$

Here, the intrinsic limits of the empirical methods, which are not based on fundamental physico-chemical principles, are being reached.

Figure 3 : Secondary products of the pyrolysis of neopentane.
m_2b_1 : methyl-2 butene-1 ; m_2b_2 : methyl-2 butene-2.



4.2 - Rate of reaction

The reaction scheme obtained after a kinetic analysis can be expressed in the following general form :

$$\sum_{j=1}^{J} v'_{ij}\, C_j \rightleftarrows \sum_{j=1}^{J} v''_{ij}\, C_j \quad (i) \qquad (53)$$

$$i = 1, 2 \ldots I$$

which is analogous to that used for the stoichiometric equations, with the exception of the reaction symbol. The reaction symbol $\rightleftarrows$ means that the reaction takes place both in the forward direction, from left to right and in the reverse direction, from right to left[1] ; it does not indicate if the reaction is in a state of equilibrium or of quasi-equilibrium.

a) Rate of production of a constituent

Consider a reaction volume where all the state variables (temperature and concentrations for example) have identical values. The molar flow rate of production of the constituent C_j due to this element of volume is therefore well defined.

The rate of production of C_j will be called R_j, and it is equal to the ratio of the molar flow rate of C_j to the volume being considered. The rate R_j is therefore equal to the quantity of C_j produced per unit volume and per unit time. In SI units, R_j is expressed in mol m^{-3} s^{-1}. The rate of production R_j is the difference between two terms :

$$R_j = R'_j - R''_j \tag{54}$$

The terms R'_j and R''_j correspond to a rate of formation and a rate of consumption of C_j, respectively. As a result, R_j is a net rate which can be positive, negative or equal to zero.

The rates R_j are state functions, that is to say functions of the state variables c_j and T, because, as has already been seen, the values of these properties define the state of a uniform gaseous volume perfectly.

b) Rate of reaction

The law of definite proportions dictates that the quantities of each constituent C_j produced by the reaction i be proportional to the stoichiometric coefficients ν_{ij}.

The rate of production R_j must therefore be considered to be the sum of the rates of the reactions r_i multiplied by the stoichiometric coefficients ν_{ij} :

$$R_j = \sum_{i=1}^{I} \nu_{ij}\, r_i \tag{55}$$

The rates r_i possess properties analogous to the rates R_j :

- they are functions of the state variables, temperature T and concentrations c_j ;
- they are net rates, equal to the difference between the rates in the forward and reverse directions.

Example 11

Write the rates of chemical production which correspond to the reaction scheme shown in Example 10.

---

[1] Only in the case of **elementary reactions**, does this symbol trigger off the calculation of the rate constant of the reverse reaction starting with that of the forward reaction using the principle of detailed balancing.

Applying equations (55) gives :

$$R_{C_5H_{12}} = - r_{46} - 2\, r_{47}$$

The negative sign indicates that C_5H_{12} disappears in reactions (46) and (47) ; the coefficient 2 means that 2 moles of C_5H_{12} are used up in reaction (47).

$$\begin{aligned}
R_{C_4H_8} &= r_{46} + 2\, r_{47} - r_{48} - r_{49} \\
R_{CH_4} &= r_{46} \\
R_{C_2H_6} &= r_{47} - r_{50} \\
R_{H_2} &= r_{47} + r_{50} + r_{51} + r_{52} \\
R_{C_5H_{10}} &= 4/5\, r_{48} - r_{52} \\
R_{C_3H_6} &= 4/3\, r_{49} - r_{51} \\
R_{C_2H_4} &= r_{50} \\
R_{C_3H_4} &= r_{51} \\
R_{C_5H_8} &= r_{52}
\end{aligned}$$

4.3 - Empirical kinetic laws

These laws describe the influence the concentrations and the temperature have on the rate of the reactions which form the reaction scheme. Different types of laws which can be applied to the reaction below :

$$\nu_1\, C_1 + \nu_2\, C_2 \longrightarrow \text{products} \qquad (56)$$

will be shown.

Laws which can be applied at a given temperature will be studied first.

a) The Guldberg and Waage law

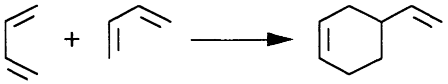
This law can be written as follows :

$$r = k\, c_1^{\nu_1}\, c_2^{\nu_2} \qquad (57)$$

where r is the rate of reaction (56),
c_1 and c_2 are the concentrations of C_1 and C_2,
k is the rate constant of the reaction.

Not only can this law be applied to numerous elementary reactions, but also to certain overall reactions of reaction schemes.

Example 12
The DIELS-ALDER reaction



obeys the following kinetic law :

$$r = k\,[C_4H_6]^2$$

both in the gas and in the liquid phase.

b) Orders of reaction

The Guldberg and Waage law can be generalized in the form :

$$r = k\,c_1^{\omega_1}\,c_2^{\omega_2} \tag{58}$$

The numbers ω_1 and ω_2, which are positive or equal to zero, are called the orders of the reaction with respect to the reactants C_1 and C_2, respectively. They can be equal to the stoichiometric coefficients or differ from them ; they are not necessarily integer nor fractional numbers.

The rate law (58) does not involve the concentrations of the products of the reaction ; it therefore applies more particularly to the kinetic data obtained by extrapolation to zero conversion.

Example 13

Figure 4 shows the variations of log r_0 as a function of log p_0 at two temperatures, r_0 is the rate of the pyrolysis reaction of neopentane in a batch reactor, extrapolated to zero conversion, and p_0 is the initial partial pressure of neopentane in the reactor. Law (58) can be written :

$$r_0 = k\,[C_5H_{12}]_0^{\omega} \tag{59}$$

Putting (59) into a decimal logarithmic form, the following linear relationship can be obtained :

$$\log r_0 = \log k + \omega \log [C_5H_{12}]_0 \tag{60}$$

that is :

$$\log r_0 = \log k - \omega \log RT + \omega \log p_0 \tag{61}$$

Figure 4 shows that this expression is satisfactorily verified for a pressure p_0 higher than about 100 mmHg. The corresponding dotted lines have exactly the same slope at the two temperatures being considered : $\omega = 1.5$.

The rate constants can also be calculated from these straight lines at two temperatures.

c) Accelerating and inhibiting influence of additives

Constituents, which differ from the reactants C_1 and C_2, can have an accelerating or an inhibiting influence on the reaction ; amongst these figure the products of the reaction itself, but potentially all the other constituents involved in the reaction.

Assuming that reaction (56) obeys law (58), in the absence of products of the reaction and of additives, the following law expresses the kinetic influence of a constituent C_3 :

$$r = k\, c_1^{\omega_1}\, c_2^{\omega_2} \left(\frac{1 + a_3\, \varphi_3}{1 + b_3\, \varphi_3} \right)^{\omega_3} \tag{62}$$

where a_3, b_3 are the constants of acceleration and inhibition, respectively,

ω_3 is the overall order of acceleration-inhibition,

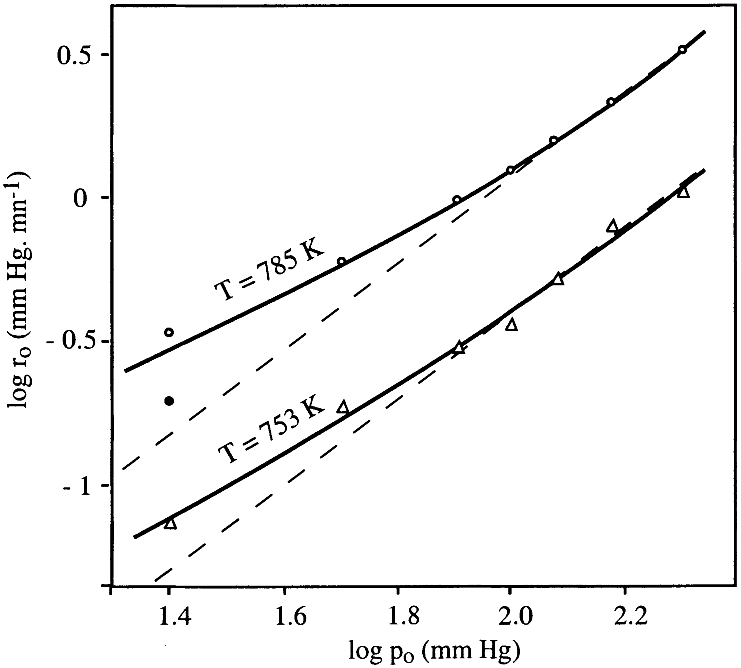
and

$$\varphi_3 = \left(\frac{c_3}{c_1} \right)^{\alpha_3} \left(\frac{c_3}{c_2} \right)^{\beta_3} \tag{63}$$

φ_3 is the relative concentration of the accelerator-inhibitor, α_3 and β_3 are the partial orders.

If $a_3 > b_3$, the constituent C_3 accelerates the reaction ; if $a_3 < b_3$, the constituent C_3 inhibits the reaction. Law (63) actually gives law (58) when $c_3 = 0$.

Figure 4 : Pyrolysis of neopentane in a batch reactor ; reaction order at conversion equal to zero.



Example 14

The oxidation reaction of ethanal in the gaseous phase at low temperature

$$CH_3CHO + O_2 \longrightarrow CH_3CO_3H$$

obeys the following law :

$$r = k\,[CH_3CHO]^{1.5}\,[O_2]^{0.5}\left(1 + a\,\frac{[CH_3CO_3H]}{[O_2]}\right)^{0.5} \tag{64}$$

which is indeed of the same form as (62).

The product of the reaction, which is a peroxide, has an accelerating effect.

Example 15

The pyrolysis of neopentane C_5H_{12} was suspected to be inhibited by isobutene C_4H_8. In order to test this hypothesis, experiments were carried out using an isothermal batch reactor, with various mixtures of C_5H_{12} and C_4H_8. In order to simplify the analysis of experimental results, rate data were extrapolated to zero reaction, i.e. to a zero conversion of C_5H_{12}, which allowed the following kinetic data to be obtained : r_0, the rate of pyrolysis of pure C_5H_{12} at zero conversion of C_5H_{12} and $r_0(C_4H_8)$, the rate of pyrolysis of a C_5H_{12}-C_4H_8 mixture, still at zero conversion of C_5H_{12}.

The simplest empirical kinetic law[1] of the type (62) for this reaction can be written as follows :

$$r_0(C_4H_8) = r_0\,\frac{1 + a\ [C_4H_8]_0/[C_5H_{12}]_0}{1 + b\ [C_4H_8]_0/[C_5H_{12}]_0} \tag{65}$$

From law (65), the following linear relationship can be deduced :

$$\frac{r_0}{r_0 - r_0(C_4H_8)} = \frac{b}{b-a} + \frac{1}{b-a}\,\frac{[C_5H_{12}]_0}{[C_4H_8]_0} \tag{66}$$

Figure 5 shows that this relationship is in good agreement with the experimental results. The following values for the coefficients a and b have been obtained :

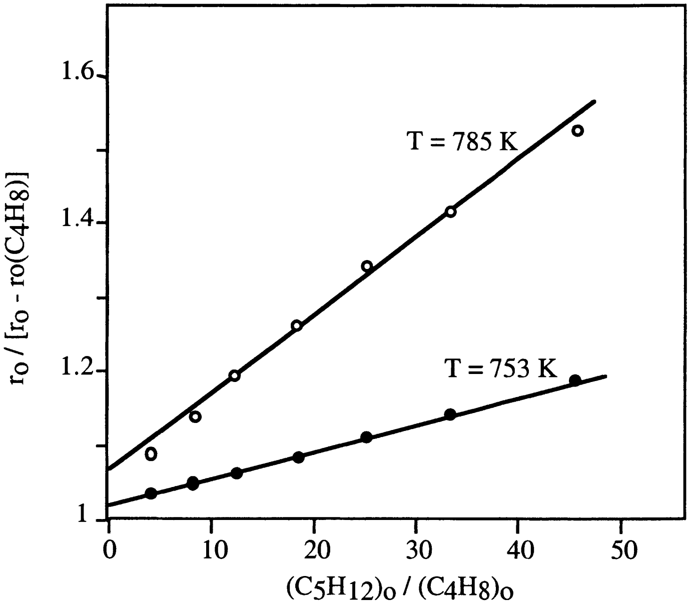
T/K	a	b
753	6	277
785	7	102

The fact that the coefficient b is higher than the coefficient a indicates that the reaction is inhibited by the added isobutene. This inhibition is very marked ; thus an addition of isobutene of about 4 % to the neopentane reduces the rate of reaction at 753 K by a factor of 2.

---

[1] Indeed, this law can also be derived from the reaction mechanism.

Figure 5 : Pyrolysis of neopentane in a batch reactor : kinetic effect of isobutene at conversion equal to zero.



d) Auto-acceleration and auto-inhibition

In Example 15 above, the added isobutene is also the main product of the reaction. Consequently, the reaction is auto-inhibited by the isobutene formed, and its rate decreases very much when the conversion increases. It seems sensible therefore to take these results into account using the following law, of the same type as (62), and combining laws (59) and (65) :

$$r = k\,[C_5H_{12}]^{\omega}\,\frac{1 + a\,[C_4H_8]/[C_5H_{12}]}{1 + b\,[C_4H_8]/[C_5H_{12}]} \qquad (67)$$

The quantities k and ω in equation (66) are the same as those in Example 13 ; on the contrary the coefficients a and b of auto-inhibition (equation 67) are slightly different from the coefficients of inhibition (equation 65). This shows that the two sets of experiments are not rigorously identical due to the kinetic influence of the impurities in the added isobutene or that of other minor products formed during the reaction.

e) The Arrhenius law

The rate constant k is in fact a function of the temperature. ARRHENIUS (1880), suggested the following relationship in order to represent the variations of k with T :

$$k = A \exp(-E/RT) \tag{68}$$

where			
k	is the rate constant,	A	is a pre-exponential factor,
E	is the activation energy,	R	is the gas constant,
T	is the absolute temperature.		

Example 16

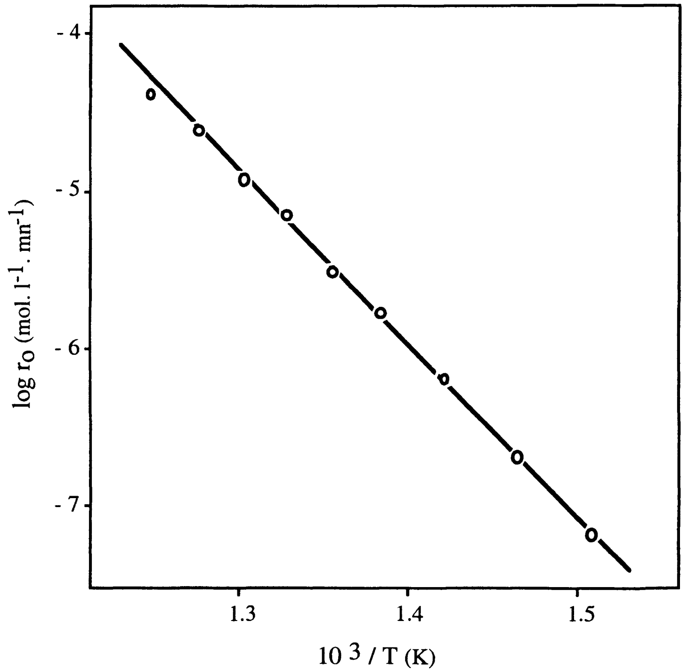
Figure 6 shows the variations of log r_0 as a function of $10^3/T$ for the pyrolysis of neopentane in a batch reactor for the following value of the initial concentration, $[C_5H_{12}]_0 = 2.04\ \mathrm{mol\ m^{-3}}$.

The following relationship can be deduced from equations (59) and (68) :

$$\log r_0 = \log A + 1.5 \log [C_5H_{12}]_0 - \frac{E \log e}{10^3 R} \cdot \left(\frac{10^3}{T}\right) \tag{69}$$

This relationship correlates well with the experimental results (Figure 6). The value $E = 2.1\mathrm{x}10^5\ \mathrm{J\ mol^{-1}}$ can be calculated from the diagram.

Figure 6 : Pyrolysis of neopentane in a batch reactor ; the Arrhenius law.



4.4 - Conclusion

The methodology shown in paragraph 4 above is very important in chemical reaction engineering for several reasons:

a) Indeed, in general, this methodology can be applied not only to gas-phase thermal reactions, but also to heterogeneous catalysis reactions, acid-base or enzymatic, as well as heterogeneous reactions ;

b) It has three conceptual advantages :
  - the conception of reaction schemes leads to a classification of the constituents as reactants, **primary products, secondary products**... This step will be kept for the creation of reaction mechanisms ;
  - in the first place, the elaboration of kinetic laws necessitates the study of the **inhibiting or accelerating influence** of the products of the reaction, of the constituents which figure as impurities in the reaction load, and lastly of the other constituents likely to increase the conversion and/or the selectivity of the chemical process ;
  - the heuristic interest of experiments which are carried out **at low conversion and with additives**.

c) The methodology of reaction schemes exhibits intrinsic limits for two reasons :
  - it is not exactly predictive, as it is totally based on the exploitation of the experimental results. It is more powerful in interpolation, but relatively less so in extrapolation ;
  - kinetic laws of the generalized types (62) and (63) must be given a priori. A screening of many kinetic laws must therefore be carried out, amongst which it is possible to find several different laws which are compatible to an equivalent extent with the experimental results. It is also possible that no satisfactory kinetic laws can be found, if the experimental range being studied is reasonably large.

These characteristics of the methodology of reaction schemes can become self-defeating, in which case a study of the real mechanisms of the reaction would be necessary.

FURTHER READING

ARIS R., *Introduction to the Analysis of Chemical Reactors*, Prentice-Hall (1965).

BARONNET F., DZIERZYNSKI M., CôME G.M., MARTIN R., NICLAUSE M., *The pyrolysis of neopentane at small extents of reaction*, Int. J. Chem. Kin., III, 197 (1971).

CôME G.M., *The Use of Computers in the Analysis and Simulation of Complex Reactions,* in "Modern Methods in Kinetics", Comprehensive Chemical Kinetics, Vol. 24, Elsevier (1983).

KEE R.J., RUPLEY F.M., MILLER J.A., Chemkin II : *A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics,* SANDIA Reports (1993).

LEVENSPIEL O., *Chemical Reaction Engineering,* 2nd edition, Wiley (1962).

POLING B.E., PRAUSNITZ J.K., O'CONNEL J.P., *The Properties of Gases and Liquids*, 5th edition, McGraw Hill (2000).

CHAPTER IV

THERMODYNAMIC LAWS

This chapter has two main aims :
- *to define the standard thermodynamic properties of the chemical species and of the reactions*
- *to set out the laws and the methods of calculating equilibria*

The thermodynamics of the chemical reaction has four main applications :

a) The **heat produced** or **absorbed by a chemical reaction** can be calculated and therefore an energy balance for the reactor can be carried out.

b) It provides expressions for the **equilibrium constants**, which allow the composition at equilibrium to be established.

c) The rate constant k" of an elementary reaction occurring from right to left (reverse direction) is deduced from the constant k' of the reaction in the forward direction using the following relationship : $k''=k'/K_c$ where K_c is the concentration equilibrium constant of the reaction in the forward direction. This relationship is known as the **principle of detailed balancing**.

d) The **activated-complex theory** is based on the hypothesis of a quasi-equilibrium between the reactants and the activated complex. The rate constant of an elementary reaction is then expressed as a function of the constant of this quasi-equilibrium.

1 - THERMODYNAMIC PROPERTIES OF CHEMICAL SPECIES

1.1 - Standard reaction of formation

Consider the reaction of formation of one mole of constituent C_j from the elements E_ℓ, which it contains :

$$\text{(f)} \qquad \sum_{\ell=1}^{L} a_{j\ell} E_\ell \longrightarrow C_j \qquad (1)$$

where ℓ is the subscript of the element,
L is the number of elements,
$a_{j\ell}$ is a formula subscript.

The reactants are the elements E_ℓ at the standard state. The standard state of an element is the most common form of it at 25°C and 1 bar (or 1 atm). For H_2, O_2, N_2, F_2, Cl_2, it is the gas ; for Br_2, it is the liquid and for C, I_2 and S, the solid form.
Each of the reactants, as well as the product, are taken to be at standard pressure $p^o = 1$ bar $= 10^5$ Pa and at temperature T.

1.2 - The standard enthalpy of formation

The enthalpies of substances have no known absolute value. It is therefore necessary to choose a reference. By convention :
the standard enthalpy of formation of an element at the standard state (1 mole of element at 1 bar) is equal to zero at all temperatures.

The standard enthalpy of formation of constituent C_j at temperature T, $\Delta_f H_j^o(T)$, is the enthalpy of the standard reaction of formation of C_j.
The enthalpy of an ideal gas is independent of the pressure, the property $\Delta_f H_j^o(T)$ is therefore the same at the present standard pressure $p^o = 1$ bar and at the previous one, $p^o = 1$ atm $= 1.01325$ bar.
The relationship between the standard enthalpies of formation at temperature T and at 298.15 K can be written as follows :

$$\Delta_f H_j^o(T) = \Delta_f H_j^o\,(298.15) + \int_{298.15}^{T} C_{pj}^o(T)\,dT - \sum_{\ell=1}^{L} a_{j\ell} \int_{298.15}^{T} C_{p\ell}^o(T)\,dT \qquad (2)$$

The apparent standard enthalpy of formation can also be introduced :

$$\Delta_{fa} H_j^o(T) = \Delta_f H_j^o\,(298.15) + \int_{298.15}^{T} C_{pj}^o(T)\,dT \qquad (3)$$

The properties $\Delta_f H_j^o(T)$ and $\Delta_{fa} H_j^o(T)$ are therefore not equal, except of course, at 298.15 K :

$$\Delta_{fa} H^o\,(298.15) = \Delta_f H^o\,(298.15) \qquad (4)$$

Figure 1 shows the way in which the relationships (2) and (3) can be worked out using the principle of initial and final states. **Heat functions** have been used in this diagram, which are also frequently tabulated :

$$H_j^o(T) - H_j^o\,(298.15) = \int_{298.15}^{T} C_{pj}^o(T)\,dT \qquad (5)$$

$$H_\ell^o(T) - H_\ell^o\,(298.15) = \int_{298.15}^{T} C_{p\ell}^o(T)\,dT \qquad (6)$$

Example 1

The following values can be found in JANAF tables (units : J mol^{-1} K^{-1}) :

	C (gr)	H_2 (g)	CH_4 (g)
$\Delta_f H^o_{(298)}$	0	0	- 74873
$H^o_{(3000)} - H^o_{(298)}$	60300	88743	222083

Deduce $\Delta_f H^o$ and $\Delta_{fa} H^o$ for CH_4 at 3000 K.

The standard reaction of formation of CH_4 (g) can be written :

$$C\,(gr) + 2\,H_2\,(g) \longrightarrow CH_4\,(g)$$

Using relationships (1) to (4) or using Figure 1, gives the following :

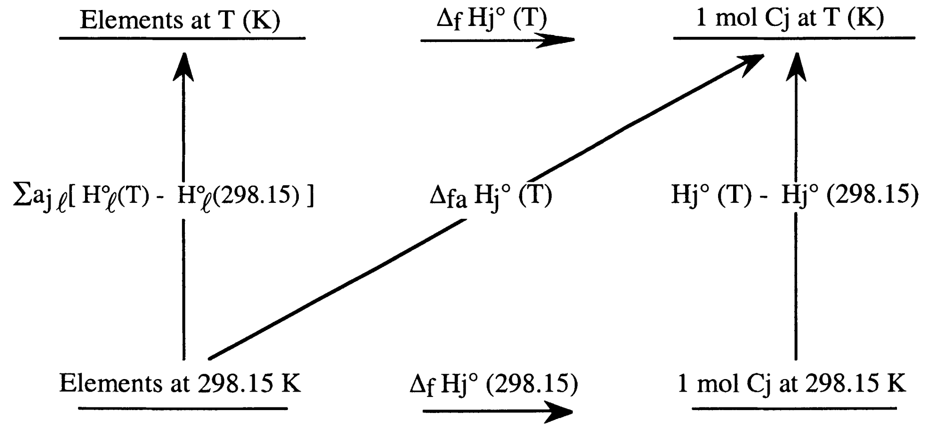
$$\Delta_f H^o_{CH_4}\,(3000) = -\,74873 + 222083 - 60300 - 2\times 88743$$

$$\Delta_f H^o_{CH_4}\,(3000) = -\,90576 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta_{fa} H^o_{CH_4}\,(3000) = -\,74873 + 222083 = 147210 \text{ J mol}^{-1}\text{ K}^{-1}$$

The two quantities are very different.

Figure 1 : Standard enthalpy of formation



1.3 - Standard entropy

The standard entropy[1] of a gaseous species is defined by the following relationship :

---

[1] The standard entropy varies if the standard pressure p^o is changed into p^* according to the following relationship : $S^o = S^* + R \ln p^*/p^o$.

$$S_g^o(T) = S_{cr}^o(0) + \int_0^{T_{mel}} C_{pcr}^o \frac{dT}{T} + \frac{\Delta H_{mel}^o}{T_{mel}} + \int_{T_{mel}}^{T_b} C_{p\ell}^o \frac{dT}{T} + \frac{\Delta H_{vap}^o}{T_b}$$
$$+ \int_{T_b}^{T} C_{pg}^o \frac{dT}{T} \tag{7}$$

where T_{mel} is the melting point,

ΔH_{mel}^o is the standard enthalpy of melting,

T_b is the boiling point,

ΔH_{vap}^o is the standard enthalpy of vaporization,

cr refers to a perfect crystal,

ℓ refers to a liquid,

g refers to a gas.

The third law of thermodynamics states that the standard entropy of a perfect crystal at 0 K is equal to zero :

$$S_{cr}^o(0) = 0 \tag{8}$$

The entropies are therefore **absolute entropies**. If the species is gaseous at 298.15K, formula (7) can be simplified :

$$S_j^o(T) = S_j^o\,(298.15) + \int_{298.15}^{T} C_{pj}^o \frac{dT}{T} \tag{9}$$

1.4 - Standard free enthalpy of formation

This property, $\Delta_f G_j^o$, is also the standard free enthalpy of reaction (f) :

$$\Delta_f G_j^o(T) = \Delta_f H_j^o(T) - T\left(S_j^o(T) - \sum_l a_{jl}\, S_l^o(T)\right) \tag{10}$$

The standard free enthalpy of formation of an element is equal to zero at all temperatures.

The apparent standard free enthalpy of formation can also be introduced :

$$\Delta_{fa} G_j^o(T) = \Delta_{fa} H_j^o(T) - T\, S_j^o(T) \tag{11}$$

Example 2

JANAF tables give the following data (Unit : J mol^{-1} K^{-1}) :

	C (gr)	H_2 (g)	CH_4 (g)
S^o (298.15)	5.686	130.683	186.255
S^o (3000)	50.748	202.887	345.695

Calculate $\Delta_f G^o$ and $\Delta_{fa} G^o$ for CH_4 at 298.15 and at 3000 K.

The following numerical values are obtained with the aid of equations (10) and (11), as well as the results of Example 1 and the above data :

$$\Delta_f G^o_{CH_4}(298.15) = -74873 - 298.15\,(186.255 - 5.686 - 2\times 130.683)$$

$$= -50783 \text{ J mol}^{-1}$$

$$\Delta_{fa} G^o_{CH_4}(298.15) = -74873 - 298.15\times 186.255 = -130405 \text{ J mol}^{-1}$$

$$\Delta_f G^o_{CH_4}(3000) = -90576 - 3000\,(345.695 - 50.748 - 2\times 202.887)$$

$$= 241905 \text{ J mol}^{-1}$$

$$\Delta_{fa} G^o_{CH_4}(3000) = 147210 - 3000\times 345.695 = -889875 \text{ J mol}^{-1}$$

1.5 - NASA polynomials

The calculation of the heat functions [eqns 5 and 6] is not easy from the tabulated values of C_p^o as a function of T. It is therefore desirable to have an analytical expression available. The NASA representation used in the CHEMKIN computer program is a polynomial of degree 4 in T :

$$\frac{C^o_{pj}(T)}{R} = a_{1j} + a_{2j}T + a_{3j}T^2 + a_{4j}T^3 + a_{5j}T^4 \tag{12}$$

Expressions for the apparent standard enthalpy of formation $\Delta_{fa}H^o_j(T)$ and for the standard entropy $S^o_j(T)$ can be deduced using equations (2) and (7), which are written in the following form :

$$\frac{\Delta_{fa}H^o_j(T)}{RT} = a_{1j} + a_{2j}\frac{T}{2} + a_{3j}\frac{T^2}{3} + a_{4j}\frac{T^3}{4} + a_{5j}\frac{T^4}{5} + \frac{a_{6j}}{T} \tag{13}$$

$$\frac{S^o_j(T)}{R} = a_{1j}\ln T + a_{2j}\,T + a_{3j}\frac{T^2}{2} + a_{4j}\frac{T^3}{3} + a_{5j}\frac{T^4}{4} + a_{7j} \tag{14}$$

The five coefficients a_{1j}, a_{2j} ... a_{5j} are calculated from the tabulated values of C^o_{pj}as a function of T. In general, two sets of coefficients are used, one which is valid from 300 to 1000 K, and the other from 1000 to 5000 K.

The constants a_{6j} and a_{7j} are integration constants, which can be calculated from the coefficients a_{1j}, a_{2j} ... a_{5j} and the values of $\Delta_{fa}H^o_j$ (298.15) and S^o_j (298.15), respectively.

Equation (11) allows the following expression to be obtained :

$$\frac{\Delta_{fa}G_j^o(T)}{RT} = \frac{\Delta_{fa}H_j^o(T)}{RT} - \frac{S_j^o(T)}{R} \tag{15}$$

which is useful for the calculation of equilibrium constants.

Example 3

The CHEMKIN recording of the NASA polynomials of ethylene is given in the following form :

```
C2H4        121286    C2H4      G           0300        5000        1000        1
3.5284E+00   1.1485E-02   -4.4184E-06   7.8446E-10   -5.2668E-14   2
4.4283E+03   2.2304E+00   -8.6149E-01   2.7962E-02   -3.3887E-05   3
2.7852E-08   -9.7379E-12  5.5730E+03    2.4212E+01                 4
```

The last column indicates the number of the line. The first line gives, in order : the CHEMKIN name of the constituent (C2H4), the date of creation of the recording (121286), the molecular formula (C2H4), the phase (G for gas), the low temperature (300 K), the high temperature (5000 K), the intermediate temperature (1000 K). Line 2 gives the coefficients a_1-a_5 at low temperature (300-1000 K) ; line 3 the coefficients a_6-a_7 (300-1000 K) and a_1-a_3 (1000-5000 K) ; line 4 the coefficients a_4-a_7 at high temperature (1000-5000 K). The coefficients are shown in computer language. Thus -5.2668E-14 is equivalent to -5.2668×10^{-14}.

1.6 - Chemical potential

a) Non-ideal mixtures

The chemical potential μ_j of the gaseous constituent C_j in a non-ideal gaseous mixture has the following expression :

$$\mu_j = \mu_j^o + RT \ln \frac{f_j}{p^o} \tag{16}$$

where μ_j^o is the standard chemical potential,
f_j is the fugacity,
p^o is the standard pressure.

The actual value of p^o is equal to 1 bar, that is 10^5 Pa. The previous value of p^o was 1 atm, that is 1.01325×10^5 Pa.

The fugacity f_j is related to the partial pressure p_j by the following relationship :

$$f_j = \gamma_j \, p_j \tag{17}$$

γ_j is the fugacity coefficient of constituent C_j in the mixture. Equation (16) becomes :

$$\mu_j = \mu_j^o + RT \ln \gamma_j \frac{p_j}{p^o} \tag{18}$$

Using the following relationship between the partial pressure p_j and the total pressure p :

$$p_j = x_j\, p \tag{19}$$

where x_j is the molar fraction of C_j, gives :

$$\mu_j = \mu_j^o + RT \ln \frac{p}{p^o} + RT \ln \gamma_j\, x_j \tag{20}$$

b) Ideal mixtures

When the total pressure tends towards 0, the behaviour of the gas becomes closer and closer to ideality, and the fugacity coefficients tend towards 1. Expressions (18) and (20) can then be written as follows :

$$\mu_j = \mu_j^o + RT \ln \frac{p_j}{p^o} \tag{21}$$

$$\mu_j = \mu_j^o + RT \ln \frac{p}{p^o} + RT \ln x_j \tag{22}$$

If, in addition, it is assumed that the gas is perfect, then :

$$p_j = c_j\, RT \tag{23}$$

that is :

$$\mu_j = \mu_j^o + RT \ln \frac{c_j}{c^o} \tag{24}$$

where :

$$c^o = \frac{p^o}{RT} \tag{25}$$

The approximation to ideality is not very satisfactory for equilibrium reactions which occur at high pressure, such as the synthesis of ammonia. It is however generally assumed in chemical kinetics.

To check the validity of this approximation, the Redlich and Kwong state equation (cf. Chap. III) will be used. These authors have also suggested correlations which permit the fugacity coefficients to be estimated.

c) Standard chemical potential

Two expressions using this property can be used :

$$\mu_j^o(T) = \Delta_f G_j^o(T) \tag{26}$$

$$\mu_j^o(T) = \Delta_{fa} G_j^o(T) \tag{27}$$

Relationship (26) is handy when tabulated values are available, and relationship (27) when NASA polynomials are being used (§ 1.5).

2 - THERMODYNAMIC PROPERTIES OF REACTIONS

The thermodynamic properties of the reaction system as defined by the following equations will be dealt with :

$$\sum_{j=1}^{J} \nu'_{ij} C_j \rightleftharpoons \sum_{j=1}^{J} \nu''_{ij} C_j \qquad \text{(i)} \tag{28}$$

$$\nu_{ij} = \nu''_{ij} - \nu'_{ij}$$

$$i = 1, \dots I$$

According to LAVOISIER's principle, the elements from which, either the reactants, or the products of the reaction (i) are obtained, are rigorously identical. As a result, by applying the principle of the initial and final states, either the standard properties of formation, or the apparent standard properties of formation of the species can be used for the calculation of the thermodynamic properties of the reaction.

The following equations are thus obtained :

a) Standard enthalpy of reaction :

$$\Delta_i H^o(T) = \sum_i \nu_{ij}\, \Delta_f H_j^o(T) \tag{29}$$

$$\Delta_i H^o(T) = \sum_i \nu_{ij}\, \Delta_{fa} H_j^o(T) \tag{30}$$

b) Standard entropy of reaction :

$$\Delta_i S^o(T) = \sum_j \nu_{ij}\, S_j^o(T) \tag{31}$$

c) Standard free enthalpy of reaction :

Therefore :

$$\Delta_i G^o(T) = \Delta_i H^o(T) - T\Delta_i S^o(T) \tag{32}$$

i.e. :

$$\Delta_i G^o(T) = \sum_j \nu_{ij}\, \Delta_f G_j^o(T) \tag{33}$$

$$\Delta_i G^o(T) = \sum_j \nu_{ij}\, \Delta_{fa} G_j^o(T) \tag{34}$$

Expressions (30) and (34) are particularly handy to use with NASA polynomials (§ 1.5).

Example 4

The JANAF tables give the following values at 1000 K (units : J, mol, K) :

	CH_4	H_2O	CO	CO_2	H_2
Δ_fH^o	−89881	−247885	−112010	−394639	0
S^o	247.555	232.706	234.530	269.524	166.222
Δ_fG^o	19460	−192579	−200294	−395924	0

Calculate Δ_iS^o, Δ_iH^o and Δ_iG^o for the following gas -phase reactions :

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2 \qquad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

These reactions of heterogeneous catalysis are used to make hydrogen, starting from natural gas ; hydrogen is necessary for the manufacture of NH_3.
Applying relationships (29), (31) and (33) gives :

Reaction	Δ_iH^o	Δ_iS^o	Δ_iG^o
i = 1	225756	252.935	-27175
i = 2	−34744	−31.49	-3051

Reaction (1) is **endothermic**, whereas reaction (2) is **exothermic**.

3 - EQUILIBRIA LAWS

3.1 - The law of mass action

The free enthalpy of the reaction i can be expressed as :

$$\Delta_iG(T) = \sum_j \nu_{ij}\, \mu_j(T) \qquad (35)$$

Using expression (18) for the chemical potential, gives :

$$\Delta_iG(T) = \sum_j \nu_{ij}\, \mu_j^o(T) + RT \ln \prod_j \left(\gamma_j \frac{p_j}{p^o}\right)^{\nu_{ij}} \qquad (36)$$

Besides, using equations (26) and (33), gives :

$$\Delta_iG^o(T) = \sum_j \nu_{ij}\, \mu_j^o \qquad (37)$$

When the reaction is at equilibrium, the quantity Δ_iG is equal to zero. The relationship between partial pressures at equilibrium can be deduced from equations (36) and (37) :

$$\prod_j \left(\gamma_j \frac{p_j}{p^o}\right)^{\nu_{ij}} = \exp\left(-\frac{\Delta_iG^o(T)}{RT}\right) \qquad (38)$$

a) Standard equilibrium constant

By definition, the equilibrium constant K_i^o of the reaction i is equal to :

$$K_i^o(T) = \exp\left(-\frac{\Delta_i G^o(T)}{RT}\right) \tag{39}$$

This equilibrium constant is a pure number, and is a function of the temperature only.

Example 5

Calculate the standard equilibrium constants of the reactions given in Example 4 at 1000 K.

This gives : $K_1^o = \exp\left(\frac{27175}{8.3145 \times 1000}\right) = 26.3$

$$K_2^o = \exp\left(\frac{3051}{8.3145 \times 1000}\right) = 1.44$$

b) Pressure equilibrium constant

Relationship (38) can be written in the following form :

$$\prod_j (\gamma_j\, p_j)^{\nu_{ij}} = K_{pi}(T) \tag{40}$$

where :

$$K_{pi}(T) = K_i^o(T)\, (p^o)^{\Delta_i \nu} \tag{41}$$

and :

$$\Delta_i \nu = \sum_i \nu_{ij} \tag{42}$$

K_{pi} is the pressure equilibrium constant, which is expressed in $Pa^{\Delta_i \nu}$ and which is a function of the temperature only.

Example 6

Calculate the pressure equilibrium constants of the reactions given in Example 4 at 1000 K.

If the following values are taken into account :

$$\Delta_1 \nu = (1+3) - (1+1) = 2 \;\; ; \;\; \Delta_2 \nu = (1+1) - (1+1) = 0,$$

it can be deduced that : $K_{p1} = 26.3 \times (10^5)^2 = 2.63 \times 10^{11}$ Pa^2 and $K_{p2} = 1.44$.

c) Mole fraction equilibrium constant

Using relationship (19) : $p_j = x_j\, p$, the law of mass action (38) becomes :

$$\prod_j (\gamma_j\, x_j)^{\nu_{ij}} = K_{xi}(T,p) \tag{43}$$

where : $$K_{xi}(T,p) = K_i^o(T) \times \left(\frac{p^o}{p}\right)^{\Delta_i\nu} \tag{44}$$

K_{xi} is the mole fraction equilibrium constant. It is a pure number which is not only a function of the temperature but also of the pressure.

Example 7

Calculate the mole fraction equilibrium constants of the reactions described in Example 4 at 1000 K, 10^5 and 10^6 Pa.

This gives : K_{x1} (1000 K, 10^5 Pa) = K_1^o = 26.3

$$K_{x1}\ (1000\ K,\ 10^6\ Pa) = 26.3 \times \left(\frac{1}{10}\right)^2 = 0.263$$

$$K_{x2}\ (1000\ K,\ 10^5\ Pa) = K_{x2}\ (1000\ K,\ 10^6\ Pa) = K_2^o = 1.44$$

Note that the constant K_{x1} decreases when the pressure increases.

d) Concentration equilibrium constant

If the perfect gas law (23) is applied : $p_j = c_j\ RT$, the law of mass action (38) becomes :

$$\prod_j (\gamma_j\, c_j)^{\nu_{ij}} = K_{ci}(T) \tag{45}$$

where : $$K_{ci}(T) = K_i^o(T) \times \left(\frac{p^o}{RT}\right)^{\Delta_i\nu} \tag{46}$$

K_{ci} is the concentration equilibrium constant. K_{ci} is expressed in $(\text{mol m}^{-3})^{\Delta_i\nu}$ and is a function of the temperature only.

Example 8

Calculate the concentration equilibrium constants of the reactions given in Example 4 at 1000 K.

This gives : $K_{c1} = 26.3 \times \left(\frac{10^5}{8.3145 \times 1000}\right)^2 = 3.80\text{x}10^3\ \text{mol}^2\ \text{m}^{-6}$

$$K_{c2} = 1.44$$

e) The law of mass action for ideal gases

In this case, the fugacity coefficients are equal to 1, and the law of mass action takes the following different forms :

$$\prod_j \left(\frac{p_j}{p^o}\right)^{\nu_{ij}} = K_i^o \tag{47}$$

$$\prod_j p_j^{\nu_{ij}} = K_{pi} \tag{48}$$

$$\prod_j x_j^{\nu_{ij}} = K_{xi} \tag{49}$$

$$\prod_j c_j^{\nu_{ij}} = K_{ci} \tag{50}$$

Of course, the relationships (41), (44) and (46) between K_{pi}, K_{xi}, K_{ci} and K_i^o remain valid.

3.2 - The Le Châtelier laws

These are qualitative laws concerning the effect of changes in temperature, in pressure, of the addition of reactants, of products or inert substances on a chemical system at equilibrium.

Le Châtelier has given a very general statement of these laws, which is sometimes called the **law of moderation** : when an independent variable of a chemical system at equilibrium is modified, the system evolves in the direction which opposes such a change.

The two most important applications concern the effect of the temperature and of the pressure.

a) Effect of the temperature

When heat is applied to a system at equilibrium, that is when its temperature is raised, the system evolves in an endothermic direction.

The demonstration of this law can be carried out using equations (32) and (39). The following relationship is deduced :

$$\ln K_i^o = \frac{\Delta_i S^o}{R} - \frac{\Delta_i H^o}{RT} \tag{51}$$

If small changes in temperature are considered, then the properties $\Delta_i S^o$ and $\Delta_i H^o$ can be assumed to be constant. The diagrams in Figure 2a are obtained. When the temperature is increased, the quantity 1/T decreases.

For the endothermic reaction ①, the equilibrium constant decreases, and the equilibrium is shifted to the left, in the endothermic direction. For the athermal reaction ②, the change in temperature has no effect. For the endothermic reaction ③, the increase in T brings about an increase in K^o and the reaction is shifted to the right.

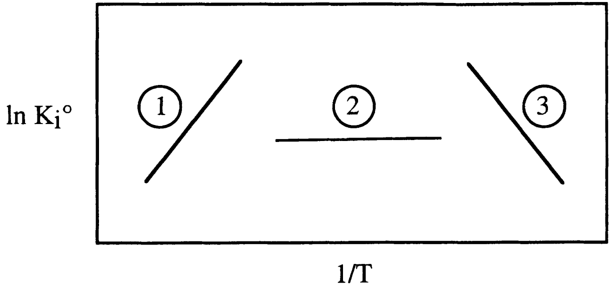
Example 9

In which direction must the temperature be changed in order to favour the reactions given in Example 4 ?

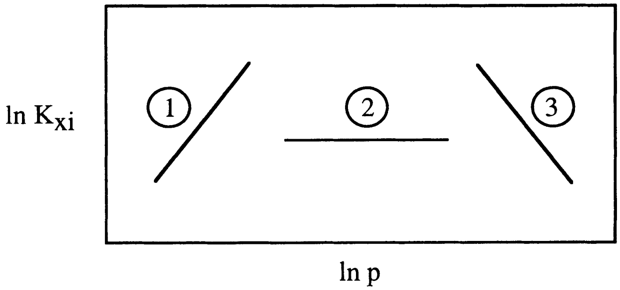
Reaction (1) is endothermic, the temperature must be increased. Reaction (2) is exothermic, therefore the temperature must be decreased, But the rate of reaction is then likely to be too low, even when using a catalyst.

Figure 2 : Le Châtelier's laws

a) Effect of the temperature



b) Effect of the pressure



b) Effect of the pressure

When the pressure is increased, the system evolves so that the total number of moles decreases.

Starting with equation (44), the following relationship is obtained :

$$\ln K_{xi} = \ln K_i^o \,.\, (p^o)^{\Delta_i\nu} - \Delta_i\nu \,.\, \ln p \qquad (52)$$

At a given temperature, K_i^o is constant and the diagrams in Figure 2b are obtained.

The reaction ① ($\Delta_i\nu < 0$) is favoured by an increase in pressure and the reaction ③ ($\Delta_i\nu > 0$) is not. Pressure variations have no effect on reaction ②.

Example 10

In which way must the pressure change in order to favour the reactions given in Example 4 ?

To favour reaction (1), the pressure must be decreased. The pressure has no thermodynamic effect on reaction (2).

c) The effects of the addition of a reactant, of a product or of an inert substance are treated as well as possible by calculating the equilibria as will be explained below.

4 - CALCULATION OF EQUILIBRIA

Three main methods allow an equilibrium to be calculated : the direct application of the law of mass action, the minimization of the free enthalpy of the system and the simulation of a kinetic model. This last approach has the advantage of providing the time necessary to reach equilibrium.

4.1 - Law of mass action

When the overall chemical equilibrium is reached, all the chemical reactions are themselves at equilibrium. The law of mass action can then be applied to them and the system of non-linear equations arising from it can be solved.

a) Isothermal batch reactor of constant volume

The JOUGUET-de DONDER equations can be written as follows :

$$n_j = n_{oj} + \sum_{i=1}^{I} \nu_{ij}\, \xi_i$$

Dividing both sides by the volume V of the reactor, which is assumed to be constant, gives :

$$c_j = c_{oj} + \sum_{i=1}^{I} \nu_{ij}\, \xi_i/V \qquad (53)$$

Putting this into equation (50), gives :

$$\begin{cases} \prod_{j=1}^{J} \left(c_{oj} + \sum_{i=1}^{I} \nu_{ij}\, \xi_i/V \right)^{\nu_{ij}} = K_{ci} \\ i = 1, 2 \ldots I \end{cases} \qquad (54)$$

The solution of this set of I non-linear equations with I unknowns $\xi_1, \xi_2 \ldots \xi_I$ is usually only possible using numerical methods.

Example 11

The pyrolysis of methane at temperatures of about 1200 °C leads mainly to the formation of ethylene, acetylene, benzene and hydrogen. n_o moles of CH_4 are introduced into a batch reactor of constant volume V at a given temperature T_o. Establish the equations at equilibrium.

Using the Brinkley criterion, there are three equations for the reaction :

$$(1) \qquad 2\,CH_4 \rightleftharpoons C_2H_4 + 2\,H_2$$

$$(2) \qquad 2\,CH_4 \rightleftharpoons C_2H_2 + 3\,H_2$$

$$(3) \qquad 6\,CH_4 \rightleftharpoons C_6H_6 + 9\,H_2$$

The JOUGUET-de DONDER equations can be written as follows :

$$n_{CH_4} = n_o - 2\,\xi_1 - 2\,\xi_2 - 6\,\xi_3$$

$$n_{C_2H_4} = \xi_1 \;;\; n_{C_2H_2} = \xi_2 \;;\; n_{C_6H_6} = \xi_3$$

$$n_{H_2} = 2\,\xi_1 + 3\,\xi_2 + 9\,\xi_3$$

The law of mass action gives the following three equations :

$$\frac{\xi_1\,(2\,\xi_1 + 3\,\xi_2 + 9\,\xi_3)^2}{V\,(n_o - 2\,\xi_1 - 2\,\xi_2 - 6\,\xi_3)^2} = K_{c1}$$

$$\frac{\xi_2\,(2\,\xi_1 + 3\,\xi_2 + 9\,\xi_3)^3}{V^2\,(n_o - 2\,\xi_1 - 2\,\xi_2 - 6\,\xi_3)^2} = K_{c2}$$

$$\frac{\xi_3\,(2\,\xi_1 + 3\,\xi_2 + 9\,\xi_3)^9}{V^4\,(n_o - 2\,\xi_1 - 2\,\xi_2 - 6\,\xi_3)^6} = K_{c3}$$

The numerical solution of this set of non-linear equations permits ξ_1, ξ_2 and ξ_3 to be calculated as functions of n_o, T_o and V.

b) Isothermal, isobaric, isochoric continuous flow reactor, under steady-state conditions

The JOUGUET-de DONDER equations can be written as follows :

$$F_j = F_{oj} + \sum_i \nu_{ij}\,\zeta_i$$

The total molar flow rate has the following expression :

$$F = F_o + \sum_{i,j} \nu_{ij}\,\zeta_i \qquad (55)$$

The mole fractions can be obtained by dividing the F_j term by the F term :

$$x_j = \frac{F_{oj} + \sum_i \nu_{ij}\,\zeta_i}{F_o + \sum_{i,j} \nu_{ij}\,\zeta_i} \tag{56}$$

The law of mass action (49), along with expression (44) for K_{xi} gives the following relationships :

$$\begin{cases} \prod_j \dfrac{F_{oj} + \sum_i \nu_{ij}\,\zeta_i}{F_o + \sum_{i,j} \nu_{ij}\,\zeta_i} = K_i^o \left(\dfrac{p^o}{p}\right)^{\Delta_i \nu} \\ i = 1, 2 \ldots I \end{cases} \tag{57}$$

In general, system (57) is solved using numerical methods.

Example 12

Consider the gas-phase reaction A $\rightleftharpoons$ B + C at equilibrium, carried out at $3\text{x}10^5$ Pa. Consider a molar flow rate of pure A of $F_o = 100$ mol s^{-1}. Calculate the composition at equilibrium at the exit of a continuous flow reactor, knowing that $K^o = 1$.

First of all the mass-balance equations are written :

$$F_A = F_o - \zeta \;\; ; \;\; F_B = F_C = \zeta \;\; ; \;\; F = F_o + \zeta$$

The following expressions can be deduced :

$$x_A = \frac{F_o - \zeta}{F_o + \zeta} \;\; ; \;\; x_B = x_C = \frac{\zeta}{F_o + \zeta}$$

The law of mass action leads to the following expression :

$$\frac{\left(\dfrac{\zeta}{F_o + \zeta}\right)^2}{\dfrac{F_o - \zeta}{F_o + \zeta}} = \frac{\zeta^2}{F_o^2 - \zeta^2} = K^o \frac{p^o}{p}$$

When $F_o = 100$ mol s^{-1}, $K^o = 1$, $p^o = 10^5$ Pa, $p = 3\text{x}10^5$ Pa, the following equation must be solved : $\zeta^2 = (10^4 - \zeta^2)/3$. The following value is obtained $\zeta = 50$ mol s^{-1}, i.e. $F_A = F_B = F_C = 50$ mol s^{-1} and $x_A = x_B = x_C = 1/3$.

4.2 - Minimization of the free enthalpy

Consider a batch reactor containing n_j mol of constituent C_j ($j = 1, 2 \ldots J$). The constituent C_j contains a_{jl} atoms of the element E_l ($l = 1, 2 \ldots L$). The reaction system contains b_l moles of element E_l at the initial time. LAVOISIER's law indicates that these elements are conserved during the reaction :

$$\begin{cases} \sum_j a_{jl}\, n_j - b_l = 0 \\ l = 1, 2 \ldots L \end{cases} \qquad (58)$$

The free enthalpy of the mixture of gases can be expressed as follows :

$$G = \sum_j n_j\, \mu_j \qquad (59)$$

where, if the gaseous mixture is ideal :

$$\mu_j = \mu_j^o + RT \ln \frac{p}{p^o} + RT \ln \frac{n_j}{n} \qquad (60)$$

and

$$n = \sum_j n_j \qquad (61)$$

finally :

$$\frac{G}{RT} = \sum_{j=1}^{J} n_j \left(\frac{\mu_j^o}{RT} + \ln \frac{p}{p^o} + \ln \frac{n_j}{n} \right) \qquad (62)$$

At equilibrium, the property G must be at a minimum.
At this stage, there are two main possibilities.

a) A numerical search for the minimum of G/RT

The problem here is a non-linear optimization one with constraints :

- equations (58) of conservation of the elements,
- the quantities n_j are positive or equal to zero.

b) The method of LAGRANGE multipliers

The Lagrange function is written :

$$L = \sum_j n_j\, \mu_j + \sum_l \lambda_l \left(\sum_j a_{jl}\, n_j - b_l \right) \qquad (63)$$

The numbers λ_l are the Lagrange multipliers.

Taking equations (58) into account, the second term of L is equal to zero. The minimum of L is therefore the same as that of G. The L function simply integrates the LAVOISIER constraints.

- It is possible then, as in a), to look for the minimum of L by an optimization method with constraints, these are reduced to $n_j \geq 0$.
- It is also possible to set up the normal equations, which are the necessary conditions for the existence of a minimum for a function with several variables :

$$\begin{cases} \dfrac{\partial L}{\partial n_j} = \mu_j + \sum\limits_{l} a_{jl}\,\lambda_l = 0, j = 1, 2 \ldots J \\ \dfrac{\partial L}{\partial \lambda_l} = \sum\limits_{j} a_{jl}\,n_j - b_l = 0, l = 1, 2 \ldots L \end{cases} \tag{64}$$

The J + L equations with J variables n_j and with L variables λ_l are solved by numerical methods.

c) Standard chemical potential

Whatever the method used, there are two ways of calculating the values μ_j^o :

$$\mu_j^o = \Delta_f G_j^o \tag{26}$$

or :

$$\mu_j^o = \Delta_{fa} G_j^o \tag{27}$$

Example 13

Consider the reaction at 1000 K and 10^5 Pa of a mol of CH_4 and b mol of H_2O leading to CO, CO_2 and H_2. Write the Lagrange equations (64) for this problem.

The JANAF tables give the following values (in kJ mol^{-1}) :

Substance	CH_4	H_2O	CO	CO_2	H_2
$\Delta_f G^o$ (1000)	19.460	−192.579	−200.294	−395.924	0

As p = p^o, the term RT ln(p/p^o) in equations (60) is equal to zero ; therefore :

CH_4 : $$\mu_{CH_4}^o + RT \ln\frac{n_{CH_4}}{n} + \lambda_C + 4\,\lambda_H = 0$$

H_2O : $$\mu_{H_2O}^o + RT \ln\frac{n_{H_2O}}{n} + 2\,\lambda_H + \lambda_O = 0$$

CO : $$\mu_{CO}^o + RT \ln\frac{n_{CO}}{n} + \lambda_C + \lambda_O = 0$$

CO_2 : $$\mu_{CO_2}^o + RT \ln\frac{n_{CO_2}}{n} + \lambda_C + 2\,\lambda_O = 0$$

$$\begin{aligned}
&H_2: && \mu^{o}_{H_2} + RT \ln \frac{n_{H_2}}{n} + 2\,\lambda_H = 0 \\
&C: && n_{CH_4} + n_{CO} + n_{CO_2} = a \\
&H: && 4\,n_{CH_4} + 2\,n_{H_2O} + 2\,n_{H_2} = 4a + 2b \\
&O: && n_{H_2O} + n_{CO} + 2\,n_{CO_2} = b
\end{aligned}$$

In order to be able to solve the system numerically, the following values are used (units : J mol^{-1}) :

$\mu^{o}_{CH_4} = 19460$; $\mu^{o}_{H_2O} = -192579$; $\mu^{o}_{CO} = -200294$; $\mu^{o}_{CO_2} = -395924$;
$\mu^{o}_{H_2}$: 0 ; $RT = 8314.5$

The method of free enthalpy minimization does not necessitate writing the stoichiometric equations which represent the system.

4.3 - Kinetic calculation

The methods for calculating the equilibria described in paragraphs 3 and 4 are purely thermodynamic and do not require a knowledge of the mechanism of the reaction.

If this mechanism is known, it is possible to use it to compute an ideal reactor.

By increasing the time of reaction, a stable limit for the concentrations of the different species can be reached.

For this numerical limit to be the same as the one, which corresponds to thermodynamic equilibrium, several conditions must be obeyed :

- all of the reactions of the mechanism must be written in the forward and reverse directions. Indeed, if a single reaction were to be written in the forward direction only, it could be of concern that the products of this reaction would become the major products ;
- the rate constants must be compatible with the thermodynamic data, or in other words the relationship $k'_i/k''_i = K_{ci}$ must hold ;
- the rate of reaction must be high enough so that equilibrium is reached within a time which is compatible with a reasonable computer time.

In practice, if this last condition is not satisfied, it means that the reaction does not reach thermodynamic equilibrium for kinetic reasons.

In fact, the main interest of this method of calculation of the equilibrium lies in the fact that it provides essential process data, which is the time of reaction necessary to approch equilibrium.

From a numerical point of view, the methods used for the computing of reactors could turn out to be more effective than the two preceding methods. But on the contrary, the kinetic model is much more complex and stiff than the stoichiometric equations.

FURTHER READING

ALBERTY R.A., *Physical Chemistry*, 7th edition, Wiley (1987).
CHASE M.W., Jr., DAVIES C.A., DOWNEY J.R., Jr., FRURIP D.J., McDONALD R.A., SYVERUD A.N., JANAF Thermochemical Tables, 2 vol., 3rd edition, *J. Phys. Chem. Ref. Data*, Vol. 14, Suppl. n°1, ACS (1985)
KEE R.J., RUPLEY F.M., MILLER J.A., CHEMKIN-II : A FORTRAN Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics, SANDIA Report SAND89-8009 B (1993)
MORAN M.J., SHAPIRO H.N., *Fundamentals of Engineering Thermodynamics*, 2 vol., 2nd edition, Wiley (1993).

COMPUTER PROGRAMS

CHEMKIN REAL-GAS, EQUIL, FITDAT, STANJAN.

CHAPTER V

ESTIMATION OF THERMODYNAMIC DATA

This chapter discusses methods of estimating the standard enthalpy of formation, entropy and heat capacity of molecules and free radicals, using both BENSON's method and those of statistical mechanics.
The application of the above to the calculation of CHETAH safety criteria is also given.

The thermodynamic data of molecules and free radicals in the gas phase can be found in specialized tables, in databases and in journals.
They can be estimated using structural correlations, by methods of statistical mechanics and by those of quantum chemistry. The latter approach will not be discussed in this book.
In the techniques of structural correlations, a property ($\Delta_f H^o$, S^o, C_p^o) of a chemical species is considered to be equal to the sum of the contributions of the different sub-structures which constitute the species.
POLING, PRAUSNITZ and O'CONNEL have compared five methods of contributions of sub-structures, those of BENSON, YONEDA, JOBACK, THINH and CARDOZO.
Amongst these methods, BENSON's possesses several advantages : its accuracy is amongst the best, it can be applied to numerous families of compounds and it permits the thermodynamic properties of free radicals to be calculated. It has been extended by BENSON to the estimation of kinetic data, and has been called **thermochemical kinetics**. Finally, this method is still much used and continues to give rise to the publication of updated tables. These advantages clearly outweigh a certain difficulty of application, an inconvenience, that is minimized by the existence of fully automatic computer programs for the calculations.

1 - BENSON's METHOD

This method consists of a first phase using the additivity of group properties. The values of $\Delta_f H^o$, S^o and C_p^o obtained during this first phase are then improved by different corrections. Values of $\Delta_f H^o_{298}$, S^o_{298} and C_p^o are thus obtained from 300 to 1500 K, for both molecules and free radicals.

1.1 - The additivity of group properties

A BENSON group consists of an atom of valency of at least 2 and of atoms or certain groups of atoms which are bound to it.

a) Notations

In order to represent these groups, first of all the polyvalent atom is indicated followed by a hyphen, and it is followed by the atoms or the groups of bound atoms in brackets with an index which indicates the number of times each ligand occurs.
The BENSON groups are shown using the following notations :

- C indicates a carbon atom with four simple bonds ;
- C_d represents a carbon atom which is bound to another carbon atom by a double bond. C_d is considered to be divalent ;
- C_t represents a carbon atom which is bound to another carbon atom by a triple bond. C_t is monovalent ;
- C_a represents an allenic carbon >C=C=C< ; the terminal carbon atoms are treated like the atoms C_d ;
- C_B represents a carbon atom in an aromatic ring. C_B is trivalent ;
- C_{BF} represents a carbon atom which belongs to at least two joined aromatic rings. C_{BF} is trivalent .

b) Equivalences

The following equivalences are permitted between certain groups of hydrocarbons and other groups :

$$
\begin{array}{lllll}
\mathrm{C\text{-}(H)_3(C)} & \mathrm{=C\text{-}(H)_3(C_d)} & \mathrm{=C\text{-}(H)_3(C_t)} & \mathrm{=C\text{-}(H)_3(C_B)} & \mathrm{=C\text{-}(H)_3(O)} \\
 & \mathrm{=C\text{-}(H)_3(CO)} & \mathrm{=C\text{-}(H)_3(N)} & \mathrm{=C\text{-}(H)_3(N_A)} & \mathrm{=C\text{-}(H)_3(N_I)} \\
 & \mathrm{=C\text{-}(H)_3(S)} & \mathrm{=C\text{-}(H)_3(S)} & \mathrm{=C\text{-}(H)_3(SO_2)} & \\
\mathrm{C\text{-}(H)(C)_3} & \mathrm{=C\text{-}(H)(C)(C_d)_2} & & & \\
\mathrm{C_d\text{-}(H)} & \mathrm{=C_d\text{-}(H)(O)} & \mathrm{=C_d\text{-}(H)(S)} & & \\
\mathrm{C_d\text{-}(H)(C_d)} & \mathrm{=C_d\text{-}(H)(C_t)} & \mathrm{=C_d\text{-}(H)(C_B)} & \mathrm{=C_d\text{-}(O)(C_d)} & \\
\mathrm{C_B\text{-}(H)(C_B)_2} & \mathrm{=C_B\text{-}(H)(O)(C_B)} & \mathrm{=C_B\text{-}(H)(N)(C_B)} & \mathrm{=C_B\text{-}(H)(N_I)(C_B)} & \\
 & \mathrm{=C_B\text{-}(H)(S)(C_B)} & \mathrm{=C_B\text{-}(C)(O)(C_B)} & \mathrm{=C_B\text{-}(C)(N)(C_B)} & \\
 & \mathrm{=C_B\text{-}(C)(S)(C_B)} & & & \\
\mathrm{C_B\text{-}(C_d)(C_B)_2} & \mathrm{=C_B\text{-}(C_t)(C_B)_2} & & &
\end{array}
$$

CO represents a carbonyl group, N a trivalent nitrogen atom, N_A a monovalent atom of nitrogen of the azo type, N_I a monovalent nitrogen of the type imino, O a divalent oxygen, S a divalent sulphur, SO_2 a monovalent group.

1.2 - Corrections

The values of $\Delta_f H^o$, S^o, C_p^o obtained in the above step by the additivity of groups must undergo corrections to obtain a better accuracy. Certain corrections are tabulated, others are calculated.

a) Tabulated corrections

- CH_3 tert : correction for each methyl group attached to a tertiary carbon.
- CH_3 quat : correction for each methyl group attached to a quaternary carbon.
- CH_3 tert-quat : correction for each methyl group attached to the longest hydrocarbon chain possessing both a tertiary carbon and a quaternary carbon.
- CH_3 quat-quat : correction analogous to the tert-quart, but applied when the chain possesses two quaternary carbons.
- cis : correction applicable to cis compounds.
- ortho : correction due to a substituent on an aromatic ring in an ortho position.
- meta : correction analogous to the precedent for a meta position.
- correction for ring strain. These are corrections which are specific for each ring.

b) Calculated corrections

Statistical mechanics (cf. § 2) indicates that the entropy is equal to R ln Ω, where Ω is the number of distinct configurations of a chemical species. Two corrections to the values of the entropy obtained previously result from this.

— *Symmetry correction*

If the total number of symmetries is denoted by σ, the **entropy must be decreased by Rlnσ** :

$$\delta S^o_{sym} = - R \ln \sigma \qquad (1)$$

As it happens, all the independent permutations of atoms or groups of identical atoms obtained by symmetry operations correspond to a unique configuration, as identical atoms are indiscernible.

It is convenient to separate σ into two terms σ_{ext} and σ_{int} :

$$\sigma = \sigma_{ext} \times \sigma_{int} \qquad (2)$$

σ_{ext} is the number of external symmetries. This number is equal to the independent permutations of the identical atoms or groups of atoms, which can be obtained by rotation of the molecule as a whole, if it were rigid.

σ_{int} is the number of internal symmetries. It results from the possibilities of internal rotation about a single bond of atoms which themselves have a symmetry axis.

Example 1

Calculate the entropy correction of the neopentane molecule due to symmetry.

The neopentane molecule has the following formula $C(CH_3)_4$.

The external symmetry is equal to $\sigma_{ext} = 4\times3 = 12$, as the molecule possesses 4 axes of order 3, binding the central carbon to each of the methyl groups ; a rotation about such an axis permutes identical methyl groups.

The internal symmetry is equal to $\sigma_{int} = 3^4 = 81$, as there are 4 methyl groups each of which has an internal symmetry equal to 3 (axis of order 3).

The total number of symmetries is therefore equal to $\sigma = 12\times81 = 972$. The entropy correction which follows from this equals $\delta S^o = -\ 8.315\times\ln 972 = -\ 57.2$ J mol^{-1} K^{-1}. Forgetting this correction for very symmetrical chemical species would therefore result in a catastrophic error.

— *Optical isomerism correction*

If a molecule contains n_{io} optical isomers, **the entropy must be increased by R ln n_{io}** :

$$\delta S^o_{io} = +\ R \ln n_{io} \tag{3}$$

As it happens, each optical isomer corresponds to a different configuration.

The number of optical isomers n_{io} is equal to twice the number of asymmetric carbons, which carry 4 different substituents.

Example 2

Calculate the optical isomerism entropy correction for $CH(CH_3)(C_2H_5)(C_3H_7)$.

As the four substituents bound to the central carbon are distinct, these are two optical isomers. The entropy correction is therefore equal to $\delta S^o = R \ln 2 = 5.8$ J mol^{-1} K^{-1}.

1.3 - Examples

Taking the importance of BENSON's method into account, several examples of its application to cyclic and non-cyclic molecules will be treated in this paragraph.

The linear notation of chemical species is explained in the appendix Notations. The data tables of the groups and corrections can be found in Chapter XIV.1.

Example 3

Calculate $\Delta_f H^o$, S^o and C^o_p at 298.15 K for iso-octane $C(CH_3)_3/CH_2/CH(CH_3)_2$.

The tables give the following data :

— Groups	Number	$\Delta_f H^o$	S^o	C_p^o
$C\text{-}(C)_4$	1	19.2	− 149.5	16.5
$C\text{-}(H)_3(C)$	5	− 42.3	127.3	25.7
$C\text{-}(H)_2(C)_2$	1	− 20.6	39.2	22.9
$C\text{-}(H)(C)_3$	1	− 1.2	− 53.6	20.1
— Corrections				
CH_3 tert-quat	5	− 1.8	0	0
Total		− 223.1	472.6	188.0

There is a symmetry correction for S^o :

$\sigma_{ext} = 1$; $\sigma_{int} = 3^6 = 729$; $n_{io} = 1$

$\delta S^o = - R \ln \sigma = - (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times \ln 729$

$\delta S^o = - 54.8 \text{ J mol}^{-1} \text{ K}^{-1}$

Finally, this gives :

$\Delta_f H^o = - 223.1 \text{ kJ mol}^{-1}$

$S^o = 417.8 \text{ J mol}^{-1} \text{ K}^{-1}$

$C_p^o = 188.0 \text{ J mol}^{-1} \text{ K}^{-1}$

Example 4

Calculate $\Delta_f H^o$ at 298.15 K for the $CH_3/CH//CH/C(CH_3)_3$, cis isomer.

The tables give the following values :

— Groups	Number	$\Delta_f H^o$
$C\text{-}(C_d)(H)_3$	1	− 42.26
$C_d\text{-}(C)(H)$	2	36.32
$C\text{-}(C_d)(C)_3$	1	22.13
$C\text{-}(H)_3(C)$	3	− 42.26
— Corrections		
CH_3 quat	3	− 4.56
t butyl cis	1	17.24
Total		− 70.7

$$\Delta_f H^o_{298.15} = - 70.7 \text{ kJ mol}^{-1}$$

Example 5

Calculate S^o at 298.15 K for dimethyl 1,2-cyclopentane.

The tables give the values :

— Groups	Number	S^o_{298}
$C\text{-}(H)_3(C)$	2	127.32
$C\text{-}(H)(C)_3$	2	- 53.60
$C\text{-}(H)_2(C)_2$	3	39.16
CH_3 tert	2	0
— Corrections		
ring	1	118.39
Total		383.3

— Symmetry correction :

$\sigma_{ext} = 2$; $\sigma_{int} = 3^2 = 9$; $\sigma = 18$

$\delta S^o = - 8.3145 \times \ln 18 = - 24.0$

— Final value :

$S^o = 359.3$ J mol^{-1} K^{-1}

Example 6

Calculate $\Delta_f H^o$, S^o and C^o_p for methyl-1 ethyl-2 benzene at 298.15 K.

The tables give the following values :

— Groups	Number	$\Delta_f H^o$	S^o	C^o_p
$C_B\text{-}(C)$	2	23.64	- 35.61	9.75
$C_B\text{-}(H)$	4	13.81	48.31	13.61
$C\text{-}(C_B)(H)_3$	1	- 42.26	127.32	25.73
$C\text{-}(C_B)(C)(H)_2$	1	- 21.34	42.59	25.61
$C\text{-}(C)(H)_3$	1	- 42.26	127.32	25.73
— Corrections				
ortho	1	1.26	- 2.50	6.40
ring	1	0	0	0
Total		- 2.08	416.75	157.4

— Symmetry correction :

$\sigma_{ext} = 1$; $\sigma_{int} = 9$; $n_{io} = 1$; $\delta S^o = - 18.27$ J mol^{-1} K^{-1}

— Final values :

$\Delta_f H^o_{298} = - 2.1$ kJ mol^{-1} ; $S^o = 398.5$ J mol^{-1} K^{-1} ; $C^o_p = 157.4$ J mol^{-1} K^{-1}

2 - STATISTICAL MECHANICS

The standard entropy S^o and the molar heat capacity at constant volume C_V^o of a molecule or a free radical are the sums of the translational (tr), external rotational (rot), vibrational (vib) and electronic (el) terms :

$$S^o = S^o_{tr} + S^o_{rot} + S^o_{Vib} + S^o_{el} \tag{4}$$

$$C^o_V = C^o_{V\,tr} + C^o_{V\,rot} + C^o_{V\,Vib} + C^o_{V\,el} \tag{5}$$

The molar heat capacity at constant pressure can be calculated using the following relationship :

$$C^o_p = C^o_V + R \tag{6}$$

The calculation of the different terms of equations (4) and (5) requires a prior definition of the degrees of freedom of a chemical species and of the corresponding different movements.

2.1 - Degrees of freedom

Consider a molecule or free radical made up of N atoms. Each atom can move in the three directions in space ; it therefore has three degrees of freedom. The molecule or the radical possesses a total of 3N degrees of freedom. Table 1 gives the details of these degrees of freedom for atoms (example : H), linear molecules (example : H-C≡C-H), non-linear molecules with a linear skeleton (example : C_2H_6) or non-linear molecules (example : isobutane). The skeleton is made up of the heavy atoms (C, O, N, S...), to the exclusion of the light atoms (essentially H).

Table1 : Degrees of freedom of a molecule.
N : number of atoms of the molecule.
P : number of heavy atoms of the molecule (skeleton).

	Atom	Linear molecule	Non-linear molecule
Translation	3	3	3
External rotation	0	2	3
Skeletal vibrations	0	3P-5	3P-5^a 3P-6^b
Vibrations of H atoms	0	3(N-P)	3(N-P)-1^a 3(N-P)^b

a : linear skeleton ; b : non-linear skeleton

a) Translation

There are 3 translational degrees of freedom.

b) External rotations

These are rotations of the molecule as a whole, if it were assumed to be rigid. The atoms have no external rotational degrees of freedom, linear molecules 2, non-linear molecules 3.

c) Vibrations

Therefore there remain 3N-5 degrees of vibrational freedom (generally speaking) for the linear molecules and 3N-6 for the non-linear molecules. This distribution is carried out by distinguishing the P heavy atoms of the skeleton and the (N-P) hydrogen atoms.

— There are 3P-5 degrees of vibrational freedom for a linear skeleton and 3P-6 for a non-linear skeleton.

— As the sum of the degrees of freedom is equal to 3N-6, the number of degrees of freedom possessed by the H atoms (Table 1) can be easily deduced.

2.2 - Fundamental vibrations

Generally speaking, vibrations, in the extended sense of the word used up to now, can be classed into four main categories which are defined and illustrated in Figure 1. These vibrations are classed according to the importance of their contribution to S^o and C_v^o, which vary in the opposite manner to the frequency of vibration v or the wavenumber $\tilde{v}$.

a) Internal rotations

An internal rotation consists of the rotation of a group of atoms, like the methyl group (Figure 1), around a single bond. The total number of internal rotations is equal to n-1, n being the number of single bonds between polyvalent atoms.

b) Torsions

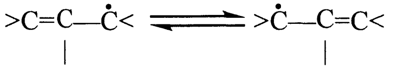
There are two main categories.

— *Torsions of double bonds*

These torsions can be encountered in the case of alkenes.

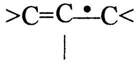
— *Torsions of three electron bonds*

The free electron of a free radical stabilized by resonance is delocalized :



$$>C{=}\underset{|}{C}{-}\dot{C}< \;\rightleftharpoons\; >\dot{C}{-}\underset{|}{C}{=}C<$$

BENSON considers a unique form of this radical, characterized by a three-electron bond which is intermediate between a single and a double bond :



$$>C=\underset{|}{C}\overset{\bullet}{-}C<$$

The following rule is recommended by BENSON : the torsion frequency of a three-electron bond is equal to half that of the corresponding double bond.

Example 7

Calculate the wavenumber of the three-electron torsion of the allyl radical. The torsion of the double bond of propene has a wavenumber $\tilde{\nu} = 800\ \mathrm{cm}^{-1}$.

Propene has the formula $CH_3\text{-}CH=CH_2$. Following BENSON's rule, the torsion frequency of the three-electron bond of $CH_3\text{-}CH\overset{\bullet}{-}CH_2$ is deduced to be equal to $400\ \mathrm{cm}^{-1}$.

The allyl radical $CH_2=CH\overset{\bullet}{-}CH_2$, as it has a very similar structure, therefore has a torsion frequency of $400\ \mathrm{cm}^{-1}$ for the three-electron bond.

c) Bends (changes in the angle between two bonds)

These bends can take place in the plane of the two bonds and are then called i.p., or out of the plane and are called o.p..

d) Global movements of atoms or groups of atoms with respect to the rest of the molecule

According to whether these movements happen in the plane, out of the plane, or include a torsion, they are called by the evocative names, rock, wag and twist. Eight cases will be considered.

α) $-CH_3$ group

The three H atoms give rise to $3 \times 3 = 9$ fundamental vibrations :

1 internal rotation ; 2 rocks ; 3 bends H-C-H ; 3 stretches C-H

β) $>CH_2$ group

The 2 H give rise to $2 \times 3 = 6$ fundamental vibrations :

1 rock ; 1 twist ; 1 wag ; 1 bend H-C-H, 2 stretches C-H

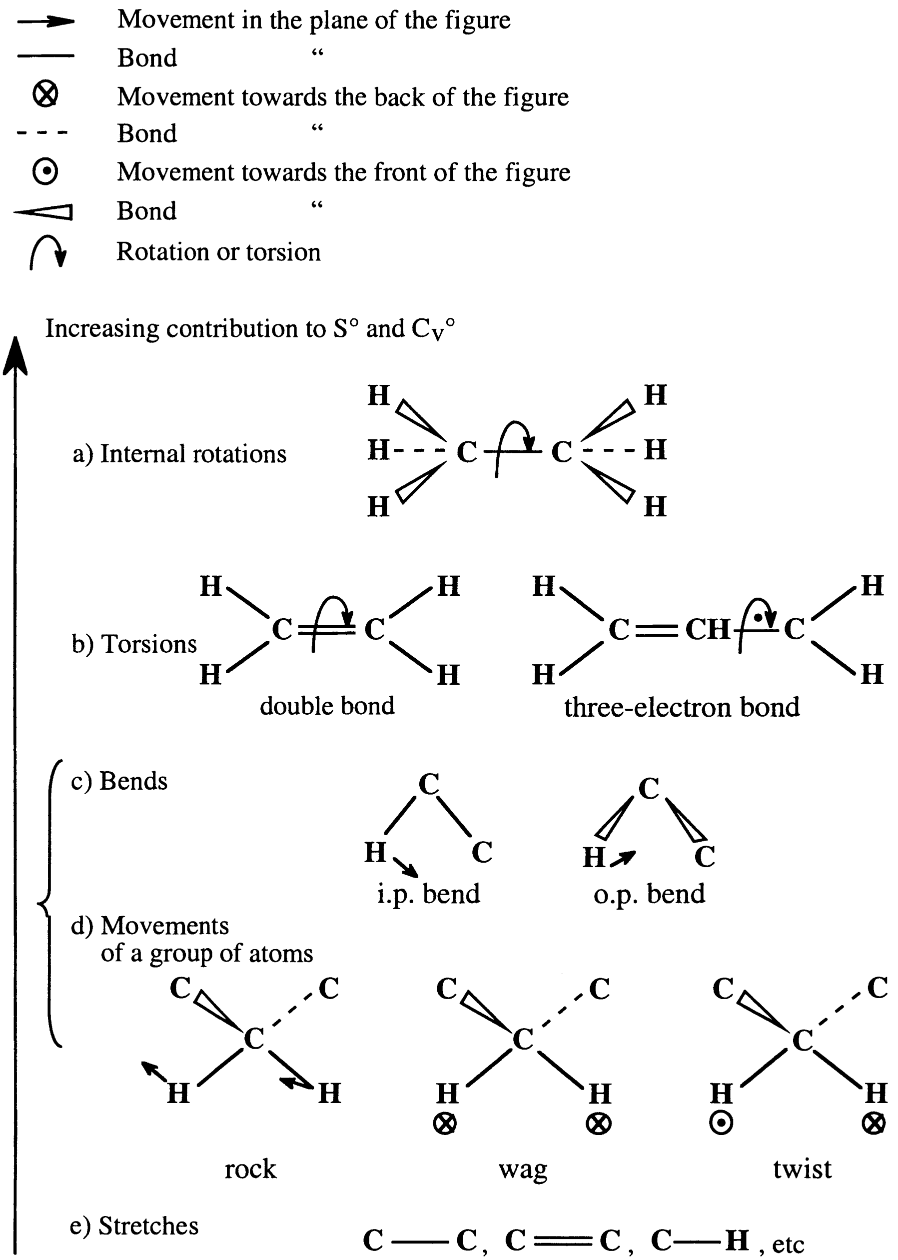
γ) $-\dot{C}H_2$ free radical

The analysis is the same as in ß), except that the rock is replaced by an internal rotation.

δ) $-\dot{C}H_2$ free radical stabilized by resonance

The analysis remains the same as in ß), except that the rock is replaced by a torsion with three electrons.

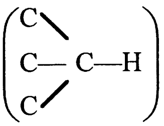
Figure 1 : Fundamental vibrations.



ε) Vinylic=CH$_2$ group

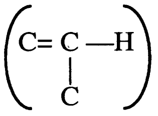
Analysis identical to ß) : the rock is replaced by a torsion of the double bond.

ζ) Tertiary H atom



The H atom gives rise to three independent vibrations : 2 bends H-C-C, 1 stretch C-H.

η) Vinylic H atom



The three fundamental vibrations include : 1 i.p. bend H-C-C, 1 o.p. bend H-C=CH, 1 stretch C-H.

θ) Rings

A ring containing P heavy atoms has P stretches and 2P-6 bends which are distributed between P-3 i.p. bends of "standard" frequency$\tilde{\nu}$ = 550 cm^{-1} and P-3 o.p. bends of standard frequency $\tilde{\nu}$ = 225 cm^{-1}. The values of the "standard" frequencies are those of cyclohexane. Corrections are therefore necessary for less strained rings : thus we have δS^o = 16.3 J mol^{-1} K^{-1} and δC_v^o = 3.3 J mol^{-1} K^{-1} for the pentene ring.

e) Stretches (bond elongations)

A molecule made up of N atoms possesses N-1 stretching vibrations if it is not cyclic and N if it is cyclic.

2.3 - Vibrational analysis

The identification of the nature and of the number of fundamental vibrations of a molecule or of a free radical can be carried out starting with the carbon backbone and ending with the H atoms. The procedure will be shown using an example. The frequencies of vibration are given in Chapter XIV.

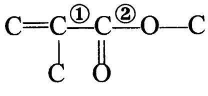
Example 8

Carry out a vibrational analysis for the molecule CH$_2$=C(CH$_3$)-CO-O-CH$_3$.

a) This molecule contains N = 15 atoms. As it is non-linear it has $3\times15-6=39$ fundamental vibrations.

b) Vibrations of the skeleton.

The skeleton is composed of the atoms C and O :



$$\mathrm{C{=}\underset{\displaystyle C}{\underset{|}{C}}\overset{①}{-}\underset{\displaystyle O}{\underset{\|}{C}}\overset{②}{-}O{-}C}$$

The skeleton contains P = 7 atoms, it has therefore a total of $3\times7-6$ = 15 vibrations.

— Stretches

There are 6 of these :

Vibration	Number	$\tilde{\nu}$ (cm^{-1})
C—C	2	1000
C—O	2	1200
C═C	1	1650
C═O	1	1700

— Internal rotations

There are 2 of these, one about the C—C n° ① bond and the other about the C—O n° ② bond.

— Bends

7 bends remain :

Vibration	Number	$\tilde{\nu}$ (cm^{-1})
C═C—C	2	420
C—C—C	1	420
C—C═O	1	420
C—C—O	1	400
C—O—C	1	400
O═C—O	1	420

c) Vibrations of the H atoms.

There are 8 H atoms, i.e. 24 fundamental vibrations .

— CH_2 group:

There are $2 \times 3 = 6$ fundamental vibrations :

Vibration	Number	$\tilde{\nu}$ (cm^{-1})
Torsion	1	700
$(H—C—C)_{t,w}$	2	1150
H—C—H	1	1450
$(C—H)_{stretch}$	2	3100

— CH_3 *groups*

There are $3 \times 3 = 9$ fundamental vibrations :

Vibration	Number	$\tilde{\nu}$ (cm^{-1})
Internal rotation	1	cf. § 2.4.c
Rock	2	1150
H—C—H	3	1450
C—H	3	3100

2.4 - Calculation of the entropy and of the heat capacity of a molecule

From the preceding vibrational analysis, the translational, rotational, vibrational and electronic contributions to S^o and C_v^o can be calculated (eqns 4 and 5).

a) Translation

The expressions are :

$$S^o_{tr} = 154.8 + \frac{5}{2} R \ln \frac{T}{298} + \frac{3}{2} R \ln \frac{M}{40} + R \ln n_{io} \qquad (7)$$

$$C^o_{v\,tr} = \frac{3}{2} R \qquad (8)$$

where S^o_{tr} and $C^o_{v\,tr}$ are in J mol^{-1} K^{-1},
R = 8.31451 J mol^{-1} K^{-1},
⚠ M is the molar mass in amu,
n_{io} is the number of optical isomers.

Example 9

Calculate S^o_{298} and $C^o_{v\,298}$ for O_2.
Knowing M = 32 amu, n_{io} = 1, the following values are therefore obtained :
S^o_{tr} = 154.5 J mol^{-1} K^{-1} ; C^o_v = 12.5 J mol^{-1} K^{-1}.

b) External rotations

— Atoms

There is no rotational term.

— Linear molecule

In this case there are two degrees of freedom for the rotation of the molecule as a whole :

$$S^o_{rot\,2} = 28.9 + R \ln \frac{T}{298} + R \ln \frac{I}{\sigma_{ext}} \qquad (9)$$

$$C^o_{V\,rot\,2} = R \qquad (10)$$

where $S^o_{rot\,2}$ and $C^o_{v\,rot\,2}$ are in J mol^{-1} K^{-1} ; R = 8.1451 J mol^{-1} K^{-1},
⚠ I is the moment of inertia of the molecule with respect to its centre of gravity in amu.Å^2,
σ_{ext} is the number of external symmetries,
T is the temperature in K.

Example 10

Calculate $S^o_{rot\,2}$ and $C^o_{v\,rot\,2}$ for O_2 at 298.15 K.

Knowing : I = 11.67 amu Å^2 and σ_{ext} = 2, equations (9) and (10) give the following values :

$S^o_{rot\,2}$ = 43.6 J mol^{-1} K^{-1} and $C^o_{v\,rot\,2}$ = 8.3 J mol^{-1} K^{-1}

— Non-linear molecule :

There are three degrees of freedom here :

$$S^o_{rot\,3} = 48.5 + \frac{3}{2} R \ln \frac{T}{298} + \frac{R}{2} \ln (I_1\, I_2\, I_3) - R \ln \sigma_{ext} \qquad (11)$$

$$C^o_{v\,rot\,3} = \frac{3}{2} R \tag{12}$$

where $S^o_{rot\,3}$ and $C^o_{v\,rot\,3}$ are in J mol^{-1} K^{-1},
R = 8.31451 J mol^{-1} K^{-1},

⚠ I_1, I_2, I_3 are the principal moments of inertia, in amu Å^2,
σ_{ext} is the number of external symmetries of the molecule,
T is the temperature in K.

Example 11

Calculate $S^o_{rot\,3}$ and $C^o_{v\,rot\,3}$ for H_2O at 3000 K.
Knowing $I_1I_2I_3$ = 1.259 amu^3 Å^6 and $\sigma_{ext} = 2$, equations (11) and (12) give :

$$S^o_{rot\,3} = 72.5 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{and} \quad C^o_{v\,rot\,3} = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

c) Internal rotations

These are rotations about single bonds. The calculation is carried out first for the rotation which is assumed to be free (subscript f), then the fact that the rotation is not free, but hindered (subscript h) by the other atoms of the molecule is taken into account.

—Free internal rotation
This is a rotation with one degree of freedom :

$$S^o_f = 19.5 + \frac{R}{2} \ln \frac{T}{298} + R \ln I_r^{1/2} - R \ln \sigma_{int} \tag{13}$$

$$C^o_{vf} = \frac{R}{2} \tag{14}$$

where S^o_f and C^o_{vf} are in J mol^{-1} K^{-1} ; R = 8.3145 J mol^{-1} K^{-1} ; T is in K,

⚠ I_r is the reduced moment of inertia in amu Å^2,
σ_{int} is the number of symmetries of the rotor.

The reduced moment of inertia I_r of two rotors A and B bound by a single bond is given by the following relationship :

$$I_r = \frac{I_A\, I_B}{I_A + I_B} \tag{15}$$

I_A (I_B respectively) is the moment of inertia of the rotor A (B respectively) with respect to an axis which is parallel to the axis of the A—B bond and passes through the centre of gravity of the rotor A (B respectively).

Example 12

Calculate S^o_f and C^o_{vf} of C_2H_6 at 298.15 K, using the following values :
d(C—H) = 1.09 Å and θ(C—C—H) = 109.5°.

The two CH_3 rotors are symmetrical with respect to the axis of internal rotation. The moment of inertia of a CH_3 rotor is equal to :

$$I_{CH_3} = 3 \times (1 \text{ amu}) \times [1.09\text{Å} \times \sin(180 - 109)]^2$$

$$I_{CH_3} = 3.19 \text{ amu Å}^2$$

Relationship (15) gives $I_r = 1.59$ amu Å^2.

The internal symmetry of the free rotation is equal to 3. Equations (13) and (14) give :

$$S^o_f = 12.3 \text{ J mol}^{-1} \text{ K}^{-1} \text{ and } C^o_{vf} = 4.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

— Hindered internal rotation

The correction to be made to S^o_f to obtain S^o_h is a function of three properties : the temperature T, the potential energy barrier V of the hindered internal rotation and the partition function q_f of the free internal rotation.

The partition function q_f can be calculated using the following relationship :

$$q_f = \frac{6.2}{\sigma_{int}} \left[I_r\left(\frac{T}{298}\right)\right]^{1/2} \qquad (16)$$

where : ⚠ I_r in amu Å^2.

Tables XIV give the potential energy barriers as well as the values of the corrections to these barriers $\delta S^o_f = S^o_f - S^o_h$ as functions of V/RT and $1/q_f$, which allow S^o_h to be calculated from the relationship :

$$S^o_h = S^o_f - \delta S^o_b \qquad (17)$$

⚠ Concerning C^o_{vh}, the table gives the values directly as functions of the same parameters V/RT and $1/q_f$. **This is not a correction.**

Example 13

Calculate S^o_h and C^o_{vh} for C_2H_6 at 298.15 K, using the results of Example 12.

Table 1.5 gives V = 12.1 kJ mol^{-1}, i.e. V/RT = 4.88. Equation (16) gives $q_f = 2.61$ i.e. $1/q_f = 0.38$. Table 1.6 gives the correction $\delta S^o_b = 5.0$ J mol^{-1} K^{-1}. Therefore, using equation (17) gives : $S^o_h = 7.4$ J mol^{-1} K^{-1}. By interpolation, Table 1.7 gives $C^o_{vh} = 8.2$ J mol^{-1} K^{-1}.

d) Vibrations

Considered here are the fundamental vibrations described in Figure 1, excluding the internal rotations, which have been treated in the paragraph above.

Each of the fundamental vibrations is characterized by its wavenumber $\tilde{\nu}$, which can be found in Table 1.8.

⚠ The wavenumbers $\tilde{\nu}$ are expressed in cm^{-1}.

The temperature T_{Vib}, which is characteristic of a given vibration, is defined by the following relationship :

$$T_{Vib} = 1.438\,\tilde{v} \tag{18}$$

where $\tilde{v}$ is in cm^{-1} and T_{Vib} is in K.

The reduced temperature is introduced :

$$u = T_{Vib}/T \tag{19}$$

The contributions S^o_{vib} and $C^o_{v\ vib}$ of a given vibration are expressed as functions of this reduced temperature :

$$S^o_{vib} = R\left[\frac{u}{e^u - 1} - \ln(1 - e^{-u})\right] \tag{20}$$

$$C^o_{v\ vib} = R\frac{u^2\,e^u}{(e^u - 1)^2} \tag{21}$$

Example 14

Calculate T_{Vib} and the properties u, S^o_{vib} and $C^o_{v\ vib}$ at 1000 K of the three electron torsion of isobutene, of the $(H—C—C)_r$ bend and the C—C, C=C and C—H stretches. The wavenumber of the twisting of the double bond of isobutene is 700 cm^{-1} (Table 1.8), that of the twisting of a corresponding three-electron bond is therefore 350 cm^{-1} (§ 2.2.b). The wavenumbers of other vibrations can be found directly in Table 1.8. The following table can therefore be established using equations (18) to (21) :

Vibration	$\frac{\tilde{v}}{cm^{-1}}$	$\frac{T_{Vib}}{K}$	u	$\frac{S^o_{vib}}{J\ mol^{-1}\ K^{-1}}$	$\frac{C^o_{v\ vib}}{J\ mol^{-1}\ K^{-1}}$
$C(CH_3)_2\overset{\bullet}{-}CH_2$	350	503	0.503	14.2	8.2
$(H—C—C)_r$	700	1007	1.007	8.8	7.6
C—C	1000	1438	1.438	5.9	7.0
C=C	1650	2373	2.373	2.9	5.3
C—H	3100	4458	4.458	0.4	2.0

e) Electronic terms

In general these terms are negligible, even for radical species.

3 - THERMODYNAMIC DATA FOR FREE RADICALS

BENSON's method allows $\Delta_f H^o_{298}$ and S^o_{298} to be calculated, as well as C^o_p from 300 to 1500 K, mainly for molecules. As it happens, the data relating to radical groups are scarce (only about forty groups). BENSON developed a means of calculation based on

the results of statistical mechanics, which have just been shown in paragraph 2.
This method consists of calculating the properties of a free radical •R from those of the parent molecule RH by carrying out appropriate corrections.
This technique consisting of estimating the thermodynamic data of a compound from those of a similar compound is also applicable to two molecules, but mainly to a molecule and an activated complex ; this last approach constitutes the thermochemical kinetics created by BENSON.

3.1 -Standard enthalpy of formation

The calculation of $\Delta_f H^o_{298}$ (•R) from $\Delta_f H^o_{298}$ (RH) necessitates a knowledge of the standard dissociation energy D^o_{298}(R—H) of the RH bond. This property D^o_{298} has been determined or estimated for numerous categories of free radicals. When it is not tabulated for a given free radical, the value D^o_{298} is chosen which is the value of a radical whose chemical structure near the radical centre is similar.
Consider the reaction of breaking the R—H single bond :

$$\text{R—H} \longrightarrow {}^\bullet\text{R} + {}^\bullet\text{H}$$

By definition, the D^o_{298}(R—H) dissociation energy of the R—H bond at 298.15 K is equal to the standard enthalpy of this reaction at 298.15 K :

$$D^o_{298}(\text{R—H}) = \Delta_f H^o_{298}({}^\bullet\text{R}) + \Delta_f H^o_{298}({}^\bullet\text{H}) - \Delta_f H^o_{298}(\text{RH}) \qquad (22)$$

$\Delta_f H^o_{298.15}$(•R) can be calculated from the following relationship :

$$\Delta_f H^o_{298.15}({}^\bullet\text{R}) = D^o_{298.15}(\text{R—H}) + \Delta_f H^o_{298.15}(\text{RH}) - \Delta_f H^o_{298.15}({}^\bullet\text{H}) \quad (23)$$

Typical values of $D^o_{298.15}$(R—H) are given in Table 1.3., in addition :

$$\Delta_f H^o_{298.15}({}^\bullet\text{H}) = 218.0 \text{ kJ mol}^{-1} \qquad (24)$$

Example 15
Calculate $\Delta_f H^o$ at 298.15 K for the iso-octyl radical from the value of iso-octane $\Delta_f H^o = -223.1$ kJ mol^{-1} (Ex. 3).

Table 1.3 gives : $D^o = 418.4$ kJ mol^{-1} for the equivalent R—H bond, •R being C(CH3)3/CH2(•). The following expression can be deduced using formula (23) :

$$\Delta_f H^o = 418.4 - 223.1 - 218.0 = -22.7 \text{ kJ mol}^{-1}$$

3.2 - Entropy and heat capacity

Starting with the values of S^o and C^o_v for the RH molecule, which is the parent of the •R free radical, δS^o and $\delta\, C^o_v$ corrections are carried out :

$$S^o(^\bullet R) = S^o(RH) + \delta S^o \tag{25}$$

$$C_v^o(^\bullet R) = C_v^o(RH) + \delta C_v^o \tag{26}$$

The overall correction δS^o is the sum of the corrections due to the optical isomerism, translation, symmetry, external rotations, internal rotations, vibrations and spin :

$$\delta S^o = \delta S_{oi}^o + \delta S_{tr}^o + \delta S_{sym}^o + \delta S^o_{ext.rot.} + \delta S^o_{int.rot.} + \delta S^o_{vib} + \delta S^o_{spin} \tag{27}$$

Correction δC_v^o has only two terms :

$$\delta C_v^o = \delta C^o_{v\ int.rot.} + \delta C^o_{v\ vib} \tag{28}$$

a) Optical isomerism correction

It is convenient to take this term out of the translational term in equation (7). Applying equation (7) to, $^\bullet$R and RH and subtracting, gives :

$$\delta S_{oi}^o = R \ln \frac{n_{oi}(^\bullet R)}{n_{oi}(RH)} \tag{29}$$

There is no correction of this kind for C_v^o.

b) Translational correction

It follows from equation (7) that :

$$\delta S_{tr}^o = \frac{3}{2} R \ln \frac{M(^\bullet R)}{M(RH)} \tag{30}$$

$$\delta C^o_{v\ tr} = 0 \tag{31}$$

Example 16

Calculate δS_{tr}^o for the tert-butyl radical $^\bullet C(CH_3)_3$.

$$\delta S_{tr}^o = \frac{3}{2} \times (8.315\ J\ mol^{-1}\ K^{-1}) \times \ln \frac{57}{58} = -\ 0.2\ J\ mol^{-1}\ K^{-1}$$

This correction becomes negligible for larger free radicals.

c) Symmetry correction

The terms σ_{ext} are taken out of equation (11) and σ_{int} out of equation (12), giving :

$$\delta S_{sym}^o = -\ R \ln \frac{\sigma(^\bullet R)}{\sigma(RH)} \tag{32}$$

where : $\sigma = \sigma_{ext} \times \sigma_{int}$ (33)

σ is the total symmetry.

There is no symmetry correction for C_v^o.

Example 17

Calculate δS^o_{sym} for the tert-butyl radical. The radical is assumed to be planar.

The parent molecule isobutane has an external symmetry axis of order 3 ($\sigma_{ext} = 3$) and 3 internal rotors CH_3 ($\sigma_{int} = 3^3$). The total symmetry is $\sigma = 81$.

The free radical also has an external symmetry $\sigma_{ext} = 3$ and an internal symmetry $\sigma_{int} = 2 \times 3^3$, i.e. $\sigma = 162$. Therefore :

$$\delta S^o_{sym} = -\,8.3145 \ln \frac{162}{81} = -\,5.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

d) External rotation correction

Equations (11) and (12) give the following relationships, for non-linear molecules :

$$\delta S^o_{ext.rot.} = \frac{R}{2} \ln \frac{(I_1\, I_2\, I_3)_{^\bullet R}}{(I_1\, I_2\, I_3)_{RH}} \qquad (34)$$

$$\delta C^o_{v\ ext.rot.} = 0 \qquad (35)$$

The rigorous calculation of the moments of inertia I_1, I_2, I_3 of $^\bullet R$ and of RH is not essential, as the addition of an H barely alters the mass and the geometry. Therefore, the following approximation will be adopted :

$$I \simeq M\, d^2 \qquad (36)$$

where M is the mass of $^\bullet R$ or RH,
d is a characteristic distance.

The distance d is practically the same for $^\bullet R$ and RH, therefore equation (34) becomes :

$$\delta S^o_{ext.rot.} = \frac{3}{2} R \ln \frac{M(^\bullet R)}{M(RH)} \qquad (37)$$

The correction due to the external rotation is the same as that of the translation.

e) Free internal rotation correction

The subscript f is used to describe a free internal rotation. Equations (13) and (14) applied to $^\bullet R$ and RH give the following expressions :

$$\delta S^o_f = \frac{R}{2} \ln \frac{I_r(^\bullet R)}{I_r(RH)} \qquad (38)$$

$$\delta C^o_{vf} = 0 \qquad (39)$$

Example 18

Calculate δS^o_f for the ethyl and tert-butyl radicals.

From $I_r(\text{—}\dot{C}H_2) = 1.8$ amu Å^2 and $I_r(\text{—}CH_3) = 3.0$ amu Å^2 (Table 1.4), the following values are deduced :

$$I(^{\bullet}C_2H_5) = \frac{3.0x1.8}{4.8} = 1.13 \text{ amu Å}^2 \quad \text{and} \quad I(C_2H_6) = \frac{3.0\times3.0}{6.0} = 1.50 \text{ amu Å}^2$$

Using equation (38), $\delta S^o_f = -1.2 \text{ J mol}^{-1} \text{ K}^{-1}$ is found for the ethyl radical.
This correction is even smaller for the tert-butyl radical, as the missing H atom changes practically nothing whereas the moment of inertia decreases, therefore $\delta S^o_f = 0$.

f) Correction due to the internal rotation barrier

Most internal rotations are hindered and it is therefore necessary to take this potential barrier to rotation into account, which can be different for $^{\bullet}$R and RH. The subscript h will be given to a hindered internal rotation. Applying equation (17) to $^{\bullet}$R and RH :

$$S^o_h(^{\bullet}R) = S^o_f(^{\bullet}R) - \delta S^o_b(^{\bullet}R) \tag{40}$$

$$S^o_h(RH) = S^o_f(RH) - \delta S^o_b(RH) \tag{41}$$

The following relationship can be deduced by subtracting the two equations :

$$\delta S^o_h = \delta S^o_f + \delta S^o_b(RH) - \delta S^o_b(^{\bullet}R) \tag{42}$$

The correction δS^o_f is calculated using equation (38) and the values of the barrier corrections $\delta S^o_b(RH)$ and $\delta S^o_b(^{\bullet}R)$ are tabulated as functions of the rotation barrier V and of the partition function q_f of the internal rotation, which is assumed to be free (eqn 16).

For the calculation of the correction δS^o_{Vh}, the values of $C^o_{Vh}(^{\bullet}R)$ and $C^o_{Vh}(RH)$ as functions of V and q_f can be found in the tables, and the following simple relationship is used :

$$\delta C^o_{Vh} = C^o_{Vh}(^{\bullet}R) - C^o_{Vh}(RH) \tag{43}$$

BENSON has suggested the following rules for the evaluation of V($^{\bullet}$R) :

- When $\sigma_{int}(^{\bullet}R) < 6$, then $V(^{\bullet}R) \simeq 2/3\ V(RH)$ is assumed. Calculation then shows that, whatever V(RH), this modification to the internal rotation barrier leads to a correction to S^o of 2 J mol^{-1} K^{-1} and to C^o_V of 0.5 J mol^{-1} K^{-1}.
- When $\sigma_{int}(^{\bullet}R) \geq 6$, then it is assumed that $V(^{\bullet}R) = 0$, so that the internal rotation of $^{\bullet}$R can be considered to be free. As a result, the correction $\delta S^o_b(^{\bullet}R)$ is equal to zero.

Example 19
Calculate δS^o_h and δC^o_{Vh} for the tert-butyl radical at 298 K.

It was shown in Example 18 that $\delta S^o_f = 0$.
The molecule iC_4H_{10} (RH) and the radical tC_4H_9 ($^{\bullet}$R) each have three internal rotations of the methyl groups. The calculation is started with **one** internal rotation as they are

rigorously equivalent in the two cases.

The rotation barrier of a methyl group in iC_4H_{10} has a value of V(RH) = 15.1 J mol^{-1} K^{-1} (Table 1.5). The value of q_f of the rotor CH_3—C_3H_7 will be taken to be that of the rotor CH_3—∞, i.e. $q_f = 3.7$ (Table 1.4). It is deduced that $V/RT = 6$ and $1/q_f = 0.3$. Tables 1.6 and 1.7 give $\delta S^o_b(RH) = 6.3$ J mol^{-1} K^{-1} and $C^o_{Vh}(RH) = 8.4$ J mol^{-1} K^{-1}.

The internal rotation symmetry of a —CH_3 group in tC_4H_9 is equal to 6, as there is a rotation axis of order 3 and another of order 2. V(•R) is taken to be equal to zero according to the rule stated above, therefore $\delta S^o_b(^\bullet R) = 0$. The value of q_f (equal to 3.7) for the rotor iC_4H_{10} is taken for the rotor CH_3—C_3H_6. Therefore, the following values can be found in Table 1.7 : $C^o_{Vh}(^\bullet R) = 4.2$ J mol^{-1} K^{-1} (for each methyl group).

The properties δS^o_b and C^o_{Vh} are now calculated for RH and •R taking the 3 internal rotations into account, then :

$$\delta S^o_b(RH) = 3\times 6.3 = 18.9 \text{ J mol}^{-1}\text{ K}^{-1} \;;\; C^o_{Vh}(RH) = 3\times 8.4 = 25.2 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\delta S^o_b(^\bullet R) = 0 \;;\; C^o_{Vh}(^\bullet R) = 3\times 4.2 = 12.6 \text{ J mol}^{-1}\text{ K}^{-1}$$

Equations (42) and (43) give the values of the desired corrections :
$\delta S^o_h = 18.9$ J mol^{-1} K^{-1} and $\delta C^o_{Vh} = -12.6$ J mol^{-1} K^{-1}.

g) Vibrational corrections

The missing three vibrations in •R, with respect to RH, due to the H atom, introduce the corrections δS^o_{vib} and $\delta C^o_{V\,vib}$ which are calculated using equations (20) and (21). These calculations necessitate a prior analysis of the vibrational differences between •R and RH.

Example 20

Calculate δS^o_{vib} and $\delta C^o_{V\,vib}$ for $^\bullet C(CH_3)_3$ at 298 K.

The analysis of the vibrational differences in going from RH to •R allow the following table to be drawn up :

Vibration	$\tilde{\nu}$/cm^{-1}	Variation (RH→•R)	δS^o_{vib} J mol^{-1} K^{-1}	$\delta C^o_{V\,vib}$ J mol^{-1} K^{-1}
C—H	3100	− 1	0	0
H—C—C	1150	− 2	− 2×0.2	− 2×1.0

The following values are obtained :
$\delta S^o_{vib} = -0.4$ J mol^{-1} K^{-1} and $\delta C^o_{V\,vib} = 2.0$ J mol^{-1} K^{-1}.

h) Overall correction

Equations (27) and (28) are applied.

Example 21

Calculate S^o_{298} and $C^o_{p\,298}$ for the free radical $^\bullet C(CH_3)_3$.

The following values are given :

$S^o_{298}(iC_4H_{10}) = 294.75$ J mol^{-1} K^{-1} and $C^o_p(iC_4H_{10}) = 96.82$ J mol^{-1} K^{-1}.

The results of paragraphs a) to h) are gathered in the table below :

Correction	δS^o J mol^{-1} K^{-1}	δC^o_V J mol^{-1} K^{-1}
Optical isomerism	0	–
Translation	– 0.2	0
Symmetry	– 5.8	–
External rotation	– 0.2	0
Free internal rotation	0	0
Rotation barriers	+ 18.9	– 12.6
Vibrations of H	– 0.4	– 2.0
Spin	+ 5.8	0
Total	+ 18.1	– 14.6

The following values are obtained, after correction :

$S^o_{298}(tC_4H_9) = 312.9$ J mol^{-1} K^{-1} and $C^o_{p\,298}(tC_4H_9) = 82.2$ J mol^{-1} K^{-1}.

4 - EXTRAPOLATION TO HIGH TEMPERATURE

BENSON's tables have been established for temperatures between 300 and 1500 K. The calculation of the heat capacity C^o_p at temperatures above 1500 K necessitates an extrapolation technique.

4.1 - Calculation of $C^o_{p\infty}$

The formulae allowing C^o_{pT} to be calculated have been given in paragraph 2 :

$$C^o_V = C^o_{V\,tr} + C^o_{V\,rot} + C^o_{V\,vib} \tag{5}$$

$$C^o_p = C^o_V + R \tag{6}$$

$$C^o_{V\,tr} = \frac{3}{2}R \tag{8}$$

$$C^o_{V\,rot\,2} = R \tag{10}$$

$$C^o_{V\,rot\,3} = \frac{3\,R}{2} \tag{12}$$

$$C^o_{V\,vib} = R\frac{u^2\,e^u}{(e^u - 1)^2} \tag{21}$$

In equation (5), the term $C^o_{V\,el}$ has been neglected. Equations (10) and (12) relate to linear and non-linear molecules, respectively.

In equation (21), the variable u has the following expression :

$$u = \frac{T_{Vib}}{T} \tag{19}$$

When T → ∞, u → 0, therefore :

$$e^u \approx 1 + u$$

and equation (21) gives the following value for $C^o_{V\infty}$ per vibration :

$$C^o_{V\infty} = R \tag{44}$$

A linear molecule has 3N-5 degrees of vibrational freedom and a non-linear molecule 3N-6, N being the number of atoms in the molecule. The following results can be deduced :

— Atom $\quad C^o_{p\infty} = 2.5\,R \quad$ (45)

— Linear molecule $\quad C^o_{p\infty} = (3N - 1.5)\,R \quad$ (46)

— Non-linear molecule $\quad C^o_{p\infty} = (3N - 2)\,R \quad$ (47)

Example 22

Calculate $C^o_{p\infty}$ for H, H_2, CH_4.

Formulae (45-47) give :

$C^o_{p\infty}(H) = 20.8$ J mol^{-1} K^{-1}

$C^o_{p\infty}(H_2) = 4.5\,R = 37.4$ J mol^{-1} K^{-1}

$C^o_{p\infty}(CH_4) = 13\,R = 108.1$ J mol^{-1} K^{-1}

For comparison, these properties take the following values at 3000 K :

$C^o_p(H) = 20.8$, $C^o_p(H_2) = 37.1$ and $C^o_p(CH_4) = 101.4$ J mol^{-1} K^{-1}

The difference comes from the vibrational terms.

4.2 - Extrapolation formula

It can be noticed in formula (21) that $C^o_{V\,vib}$ increases with temperature. This variation can be represented in the following form [YUAN S.C., MOCK Y.I. - *Hydrocarbon Processing*, 47, 133 (1968)] :

$$C^o_{pT} = C^o_{p\infty}\,[1 - a\exp(-bT)] \tag{48}$$

Putting :

$$y = 1 - \frac{C^o_{pT}}{C^o_{p\infty}} \tag{49}$$

gives :

$$y = a\exp(-b\,T) \tag{50}$$

and the following expressions for b and a can be deduced :

$$b = \frac{\ln(y_2/y_1)}{T_1 - T_2} \tag{51}$$

$$a = y_1\exp(b\,T_1) \tag{52}$$

Example 23

Knowing $C^o_{p\,1000}(CH_4) = 71.8$ and $C^o_{p\,1500}(CH_4) = 86.6$, calculate $C^o_{p\,3000}(CH_4)$.

$C^o_{p\infty}(CH_4) = 108.1$ J mol^{-1} K^{-1} was obtained in Example 22. Using equations (51) and (52), for $T_1 = 1000$ K and $T_2 = 1500$ K, the following values are obtained :

$y_1 = 0.3358$; $y_2 = 0.1989$; $b = 1.0474.10^{-3}$; $a = 0.9571$

Equation (48), applied to T = 3000 K, gives :

$C^o_{p\,3000} = 108.1\,[1 - 0.9571\exp(-1.0474\times3)] = 103.6$ J mol^{-1} K^{-1}

The error with respect to the tabulated value (Ex. 22) is of the order of 2 %.

Formula (48) allows the values of C^o_p to be calculated at several temperatures between 1000 and 5000 K for example, and the corresponding NASA polynomials to be deduced.

5 - CHETAH SAFETY CRITERIA

The number of molecules known nowadays is of the order of 20 million and increases by about 500,000 annually. The manufacture, storing and transport of these molecules and their mixtures cause safety problems.

The American Society for Testing and Materials (ASTM) has developed a computer program called "Chemical Thermodynamics and Energy Hazard Evaluation" (CHETAH), which is designed to evaluate the potential risks of instability, of sensitivity to knocks , of auto-inflammation or of spontaneous explosion of substances, or of mixtures of substances , from their chemical formulae.

The level of risk is deduced from the values of the four criteria denoted C_1, C_2, C_3 and C_4. The levels of risk have been established from the study of about 200 compounds, which are representative of the different families of chemical substances.

a) Criterion C_1

The criterion C_1 is the standard enthalpy of decomposition of the substance into small stable molecules : H_2O, CO_2, N_2, C...

$$C_1 = \Delta H_d^o \tag{53}$$

The CHETAH computer program looks for molecules leading to the highest possible value of $|\Delta H_d^o|$, i.e. of the exothermicity of the reaction. The levels of risk associated with C_1 are shown in Figure 2a.

⚠ C_1 is calculated in kcal g^{-1}.

Example 24

Evaluate the level of risk C_1 for CH_3—CH_2—$CH(NO_2)_2$.

The decomposition reaction of this compound can be written :

$$CH_3—CH_2—CH(NO_2)_2 \longrightarrow 3\ H_2O + \frac{1}{2}\ CO_2 + \frac{5}{2}\ C + N_2$$

The following values can be found in Tables XIV :

$\Delta_f H^o_{300}(H_2O) = -\ 241.8$ kJ mol^{-1} ; $\Delta_f H^o(CO_2) = -\ 395\ 4$ kJ mol^{-1} ;

$\Delta_f H^o(C) = \Delta_f H^o(N_2) = 0$

The value of $\Delta_f H^o_{300}$ for the reactant RH being considered, is calculated using BENSON's method ; it follows that : $\Delta_f H^o(RH) = -\ 125.5$ kJ mol^{-1}. The following value is deduced : $\Delta H_d^o = -\ 797.9$ kJ mol^{-1}. The molar mass of the reactant is 134 g mol^{-1} ; thus $C_1 = -\ 1.4$ kcal g^{-1}. Note in Figure 2a that the corresponding level of risk is high.

b) Criterion C_2

The criterion C_2 can be expressed as follows :

$$C_2 = \Delta H_c^o - \Delta H_d^o \tag{54}$$

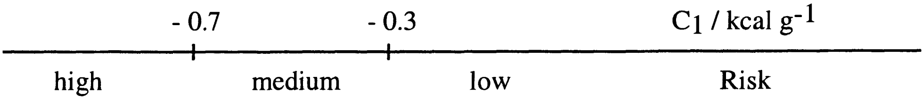
ΔH_c^o is the standard enthalpy of combustion of the substance.

The levels of risk associated with criterion C_2 are indicated in Figure 2b.

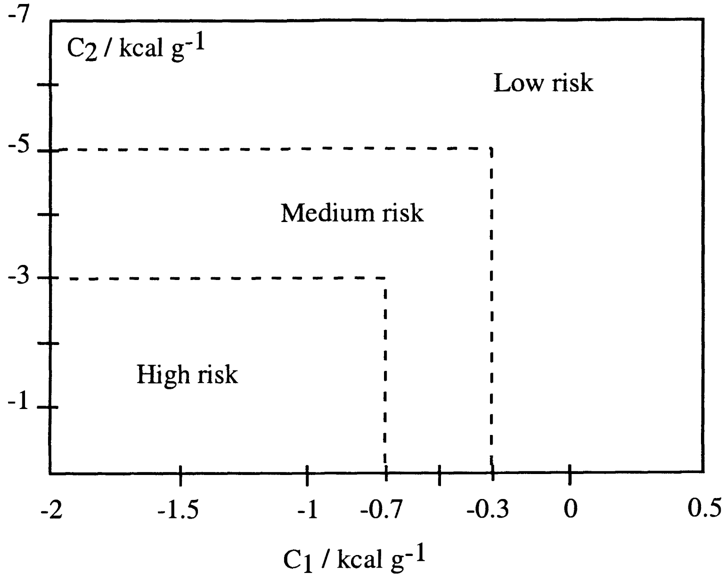
⚠ ΔH_c^o and ΔH_d^o are in kcal g^{-1}.

Figure 2 : CHETAH level of risk.

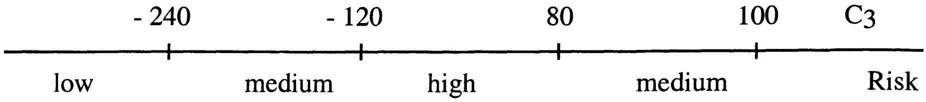
a) Criterion C_1



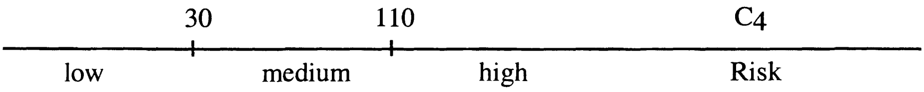
b) Criterion C_2



c) Criterion C_3



d) Criterion C_4



Example 25

Calculate C_2 for $CH_3—CH_2—CH(NO_2)_2$ and evaluate the associated risk.

The combustion equation can be written :

$$CH_3—CH_2—CH(NO_2)_2 + 2.5\ O_2 \longrightarrow 3\ H_2O + 3\ CO_2 + N_2$$

so that : $\Delta H_c^o = -3\times241.8 - 3\times395.4 + 125.5 = -1786.1\ \text{kJ mol}^{-1}$

also : $\Delta H_c^o = -3.2$ kcal g^{-1}, which gives : $C_2 = -1.8$ kcal g^{-1}.

This lies within the zone of high risk of Diagram 1b ($C_1 = -1.4$; $C_2 = -1.8$).

c) Criterion C_3

For a molecule of molecular formula $C_xH_yO_zN_u$, the criterion C_3 can be expressed as follows :

$$C_3 = 100\left(z - 2x - \frac{y}{2}\right)\frac{16}{M} \tag{55}$$

where M is the molar mass of the reactant in g mol^{-1}.

C_3 is the mass percentage of oxygen, which must be added to a mole of reactant in order to have complete combustion.

The level of risk associated with C_3 is indicated in Figure 2c.

Example 26

Evaluate the criterion C_3 and the associated risk for the following molecule :
$CH_3—CH_2—CH(NO_2)_2$.

The value $C_3 = 100\left(4 - 2\times3 - 6/2\right) \times 16/134 = -59.7$ is found. The risk C_3 is high.

d) Criterion C_4

This criterion can be expressed as follows :

$$C_4 = 10\,C_1^2\,\frac{M}{N} \tag{56}$$

where C_1 is in kcal g^{-1},

M is the molar mass in g mol^{-1},

N is the number of atoms of the reactant.

The levels of risk associated with criterion C_4 are indicated in Figure 2d.

Example 27

Evaluate the criterion C_4 and the associated risk for the following molecule :
$CH_3—CH_2—CH—(NO_2)_2$.

The value $C_1 = 10\ (-1.4)^2 \times (134/15) = 175$ is found. The associated risk is high.

e) Global evaluation of the risk

According to CHETAH's rules, a substance must be considered to be dangerous if any one of the first three criteria is in the medium or high-risk zone. This is the case for the molecule dealt with in the examples above.

Applying this rule, it is found that certain non-dangerous compounds are considered in fact to present a risk. The opposite situation, i.e. a substance known to be dangerous experimentally, but which is declared to be of low risk by CHETAH's method, has not yet been found.

FURTHER READING

BENSON S.W., *Thermochemical Kinetics*, 2nd edition, Wiley (1976).

DAVIS C.A., FREEDMAN E., FRURIA D.J., HERTEL G.R., SEATON W.H., TREWEEK D.N., *Chetah, Version 4.4*, 2nd edition, ASTM Data Series Publication DS 51 A (1990).

MULLER C., MICHEL V., SCACCHI G., CôME G.M., *A computer program for the evaluation of thermochemical data of molecules and free radicals in the gas phase*, J. Chim. Phys., 92, 1154 (1995).

ONKEN V., PAUL H.I., *Estimation of physical properties*, Ullmann's Enc. Ind. Chem., B1, chap. 6.

POLING B.E., PRAUSNITZ J.M., O'CONNEL J.P., *The Properties of Gases and Liquids*, 5th edition, McGraw Hill (2000).

COMPUTER PROGRAMS

BAC MP 4, NIST DB 25, RADICALC, THERGAS, THERM, THERMDAT.

CHAPTER VI

ELEMENTARY REACTIONS

This chapter has two aims:

- *To describe the different categories of elementary reactions from which reaction mechanisms will be elaborated,*
- *To describe the kinetic laws used in the tables and in the simulations for the calculation of the rate constants of elementary reactions.*

1 - GENERIC ELEMENTARY REACTIONS

The **free radical reactions** below have been classified into three main categories: those which increase the number of free radicals, those which conserve, and those which decrease the number of free radicals. A two-letter index has been given beside the descriptive term of the reaction which will be used when generating mechanisms. The meaning of the symbols +M and (+M) will be commented on in paragraph 2. The examples are presented with the NANCY linear chemical notation described in the appendix NOTATIONS at the end of the book.

Some types of **molecular reactions** are also given.

1.1 - Initiation and branching

a) Unimolecular initiation (ui)

A molecule gives rise to two free radicals by the breaking of a single bond.

Example 1

Write down the unimolecular initiation reactions of normal butane.

Butane CH3/CH2/CH2/CH3 possesses two distinct types of C—C bonds and also two types of C—H bonds. There are therefore four possible unimolecular initiations :

$$
\begin{array}{llll}
\text{CH3/CH2/CH2/CH3} & \longrightarrow & 2\ \bullet\text{CH2/CH3} & (1)\\
 & \longrightarrow & \bullet\text{CH3} + \bullet\text{CH2/CH2/CH3} & (2)\\
 & \longrightarrow & \bullet\text{CH(/CH3)/CH2/CH3} + \bullet\text{H} & (3)\\
 & \longrightarrow & \bullet\text{CH2/CH2/CH2/CH3} + \bullet\text{H} & (4)
\end{array}
$$

b) Bimolecular initiation (bi)

Two molecules react to give two free radicals by atom transfer. One of the molecules is therefore unsaturated.

Example 2

Write down the bimolecular initiation reaction of normal butane with oxygen.

There are two classes of H atom, therefore there are two reactions (bi) :

CH3/CH2/CH2/CH3 + O//O → •CH(/CH3)/CH2/CH3 + •O/OH (5)
→ •CH2/CH2/CH2/CH3 + •O/OH· (6)

c) Branching

A free radical reacts with a molecule to give two free radicals. One of the reactions of this type, which plays a major part in the theory of combustion, is the following :

•H + O2 → •OH + •O• (7)

Example 3

Write down the reactions of the •O• biradical with normal butane.

There are two possible reactions :

•O• + CH3/CH2/CH2/CH3 → •OH + •CH(/CH3)/CH2/CH3 (8)
→ •OH + •CH2/CH2/CH2/CH3 (9)

Note that the branching reactions in these examples are metatheses, these will be classed with the metatheses in the mechanisms, although their kinetic consequences have nothing in common with them.

1.2 - Propagations

These reactions propagate the reaction whilst conserving the number of free radicals. They can be unimolecular or bimolecular.

a) Addition of free radicals to oxygen (ad)

This reaction leads to a peroxy radical.

Example 4

Write down the addition reactions of n-butyl radicals to oxygen :

•CH(/CH3)/CH2/CH3 + O//O → •O/O/CH(CH3)/CH2/CH3 (10)
•CH2/CH2/CH2/CH3 + O//O → •O/O/CH2/CH2/CH2/CH3 (11)

b) Isomerization of free radicals (is)

This reaction consists in the internal abstraction of an H atom by an atom carrying the free electron. The atom, which is abstracted, can be in position 3, 4, 5 or 6 with respect to the radical atom ; the corresponding activated complexes are rings of 4, 5, 6 or 7 atoms, respectively.

Example 5

Write down the isomerization reactions of the •O/O/CH2/CH2/CH3 radical.

There are three different classes of H atoms, in positions 3, 4, and 5, which lead to three isomerizations :

•O/O/CH2/CH2/CH3 ⟶ •CH2/CH2/CH2/O/OH (12)
⟶ CH3/CH(•)/CH2/O/OH (13)
⟶ CH3/CH2/CH(•)/O/OH (14)

c) Unimolecular decomposition of free radicals by beta-scission (bs)

This reaction occurs by the breaking of a single bond in the ß position with respect to the radical point with the concomitant formation of a double bond.

Example 6

Write down the decomposition reactions of n-butyl radicals.

•CH(/CH3)/CH2/CH3 ⟶ CH3/CH//CH2 + •CH3 (15)
⟶ CH2//CH/CH2/CH3 + •H (16)
⟶ CH3/CH//CH/CH3 + •H (17)
•CH2/CH2/CH2/CH3 ⟶ CH2//CH2 + •CH2/CH3 (18)
⟶ CH2//CH/CH2/CH3 + •H (19)

d) Cyclization of hydroperoxyalkyl free radicals (cy)

The radical carbon atom forms a covalent bond with the oxygen atom attached to the carbon chain, which leads to the formation of a cyclic ether with the elimination of a hydroxy free radical.

Example 7

Write down the cyclization reactions of the hydroperoxybutyl radicals :
CH2(•)/CH2/CH2/O/OH, CH3/CH(•)/CH2/CH2/O/OH, CH3/CH2/CH(•)/CH2/O/OH.

CH2(•)/CH2/CH2/CH2/O/OH ⟶ CH2(#1)/CH2/CH2/CH2/O/1+•OH (20)
CH3/CH(•)/CH2/CH2/O/OH ⟶ CH3/CH(#1)/CH2/CH2/O/1+•OH (21)
CH3/CH2/CH(•)/CH2/O/OH ⟶ CH3/CH2/CH(#1)/CH2/O/1+•OH (22)

e) Oxidation of free radicals (ox)

A molecule of oxygen abstracts an H atom situated in the ß position with respect to the radical point with the formation of the •O/OH free radical and an unsaturated molecule.

Example 8

Write down the oxidation reactions of the secondary n-butyl radical.

$$\text{•CH(/CH3)/CH2/CH3 + O//O} \longrightarrow \text{CH3/CH2/CH//CH2 + •O/OH} \quad (23)$$

$$\longrightarrow \text{CH3/CH//CH/CH3 + •O/OH} \quad (24)$$

f) Metatheses (me)

A free radical abstracts an H atom from a molecule giving another free radical and another molecule.

Example 9

Write down the metatheses reactions of the hydroxy radical with n-butane.

$$\text{•OH + CH3/CH2/CH2/CH3} \longrightarrow \text{OH2 + •CH(/CH3)/CH2/CH3} \quad (25)$$

$$\longrightarrow \text{OH2 + •CH2/CH2/CH2/CH3} \quad (26)$$

1.3 - Terminations

a) Combination of free radicals (co)

Two free radicals give rise to a molecule by the formation of a covalent bond. Three cases must be considered :

- the combination of two free atoms always involves a third body M :

$$\text{•H + •H + M} \longrightarrow \text{H2 + M} \quad (27)$$

- the combination of two free radicals of small size has a rate constant, which varies with the pressure, which is indicated by the symbol (+M), for example :

$$\text{•H + •CH3 (+M)} \longrightarrow \text{CH4 (+M)} \quad (28)$$

- the combination of two large-sized free radicals is a reaction of overall order equal to 2, except at very low pressures, where the behaviour is similar to the preceding case. For example, the reaction :

$$\text{2 •CH2/CH3} \longrightarrow \text{CH3/CH2/CH2/CH3} \quad (29)$$

has a rate constant, which is independent of the pressure, and is equal to $1.1\text{x}10^{13}$ $\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ for a total concentration higher than $2\text{x}10^{-8}$ mol cm^{-3}, that is a pressure of $2\text{x}10^2$ Pa at 1000 K. Below this pressure, the rate constant decreases when the pressure decreases.

b) Disproportionation of two free radicals (di)

Two free radicals react exchanging a labile atom to give two molecules.

Example 10

Write down the disproportionation reactions of the •O/OH and •CH2/CH3 free radicals.

The H atom exchanged can come from one or other of the radicals :

$$^{\bullet}\text{O/OH} + {}^{\bullet}\text{O/OH} \longrightarrow \text{OH/OH} + \text{O//O} \qquad (30)$$

$$^{\bullet}\text{O/OH} + {}^{\bullet}\text{CH2/CH3} \longrightarrow \text{OH/OH} + \text{CH2//CH2} \qquad (31)$$

$$\longrightarrow \text{O//O} + \text{CH3/CH3} \qquad (32)$$

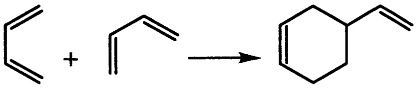
$$^{\bullet}\text{CH2/CH3} + {}^{\bullet}\text{CH2/CH3} \longrightarrow \text{CH3/CH3} + \text{CH2//CH2} \qquad (33)$$

1.4 - Molecular reactions

The reactants as well as the products of this type of reaction are molecules.

a) The DIELS-ALDER reaction

This is a concerted reaction at six centres leading to the formation of a ring. The reverse reaction is called retro- DIELS-ALDER. Therefore, starting with butadiene the following reaction is obtained :



(34)

Analogous reactions can occur by a biradical mechanism.

b) Four-centre elimination

This reaction is encountered with heteroatoms:

$$CH_3{-}CH_2Cl \longrightarrow C_2H_4 + HCl \qquad (35)$$

$$C(CH_3)_3{-}O{-}CH_3 \longrightarrow CH_3OH + iC_4H_8 \qquad (36)$$

2 - KINETIC LAWS

2.1 - Influence of concentrations

Six categories of elementary reactions will be considered.

a) $C_1 \longrightarrow$ products (37)

The rate of this unimolecular reaction is expressed as follows :

$$r_{37} = k_{37}\,[C_1] \qquad (38)$$

The rate constant k_{37} is expressed in s^{-1}.

b) $C_1 + C_2 \longrightarrow$ products (39)

The rate of this bimolecular reaction is expressed as follows:

$$r_{39} = k_{39}\,[C_1]\,[C_2] \qquad (40)$$

The rate constant k_{39} is expressed in $mol^{-1}\ m^3\ s^{-1}$ in basic SI units.

c) $C_1 + M \longrightarrow \text{products} + M$ (41)

This is a unimolecular reaction whose rate can be written as follows :

$$r_{41} = k_{41}\ [C_1]\ [M] \tag{42}$$

The concentration of the pseudo-species M can be calculated using the following relationship :

$$[M] = \sum_{j=1}^{J} \alpha_j\ [C_j] \tag{43}$$

In the absence of values for the coefficients α_j, they are taken to be equal to 1 ; in this case, the concentration of M is simply the total concentration. The rate constant k_{41} is expressed in $mol^{-1}\ m^3\ s^{-1}$, in basic SI units.

d) $C_1 + C_2 + M \longrightarrow \text{products} + M$ (44)

The rate of this reaction is of the following form :

$$r_{44} = k_{44}\ [C_1]\ [C_2]\ [M] \tag{45}$$

The expression for [M] is the same as in c) (eqn 43). The rate constant k_{44} is expressed in $mol^{-2}\ m^6\ s^{-1}$.

e) $C_1(+M) \longrightarrow \text{products}\ (+M)$ (46)

Three cases can be distinguished, according to the "pressure", actually according to the concentration of the pseudo-species M, which is calculated using relationship (43).

- At "high pressure", denoted by the exponent ∞, the rate is independent of the concentration [M] :

  $$r_{46} = k_{46}^{\infty}\ [C_1] \tag{47}$$

  k_{46}^{∞} is a rate constant of order 1, which is expressed in s^{-1}.
- At "low pressure", denoted by the exponent o, the rate is proportional to [M] :

  $$r_{46} = \overset{o}{k}_{46}\ [C_1]\ [M] \tag{48}$$

  $\overset{o}{k}_{46}$ is a rate constant of order 2, which is expressed in $mol^{-1}\ m^3\ s^{-1}$.
- At "fall-off pressures " , the rate is written in the following form :

  $$r_{46} = k_{46}\ [C_1] \tag{49}$$

  The rate constant k_{46} is of order 1 and is therefore expressed in s^{-1}.

  The rate constant k_{46} varies with [M] according to the following law, given by TROE :

$$k_{46} = k_{46}^{\infty} \frac{[M]/[M]_c}{1 + [M]/[M_c]} F \tag{50}$$

where :

$$[M]_c = \frac{k_{46}^{\infty}}{\overset{o}{k}_{46}} \tag{51}$$

$$\log F = \frac{\log F_c}{1 + \left[\dfrac{\log \left([M]/[M]_c \right)}{0.75 - 1.27 \log F_c} \right]^2} \tag{52}$$

$$F_c = a \exp\left(-\frac{T}{T_1} \right) + (1-a) \exp\left(-\frac{T}{T_2} \right) + \exp\left(-\frac{T_3}{T} \right) \tag{53}$$

In order to be able to calculate k_{46} using these relationships, six parameters must be known : k_{46}^{∞}, $\overset{o}{k}_{46}$, a, T_1, T_2 and T_3. In default of a value for F, it is taken to be equal to 1, which is equivalent to using the original law by LINDEMANN and HINSHELWOOD :

$$k_{46} = \frac{\overset{o}{k}_{46} [M]}{1 + \overset{o}{k}_{46} [M]/k_{46}^{\infty}} \tag{54}$$

When using law (54) it is only necessary to know $\overset{o}{k}_{46}$ and k_{46}^{∞}.

It can be seen that when the ratio $[M]/[M]_c$ becomes very large with respect to 1, the rate constant k_{46} tends towards k_{46}^{∞}. On the contrary, when this ratio becomes very small with respect to 1, the constant k_{46} becomes equivalent to $\overset{o}{k}_{46}$ [M]. The laws of "high pressure" (47) and of "low pressure" (48) are effectively found again. The "fall-off pressures " correspond therefore to values of [M] which are close to the critical concentration $[M]_c$.

Remark

The LINDEMANN-HINSHELWOOD theory for unimolecular reactions is based on the following mechanism :

$$A + M \rightleftarrows A^* + M \tag{55}$$

$$A^* \longrightarrow \text{products} \tag{56}$$

A is the stable reactant, transformed into a more energetic species A* by collision with a species M which gives up part of its energy to it [forward reaction (55)]. This activated species A* can either be deactivated by collision with M [reverse reaction (55)], or be transformed into products by the reaction (56). The quasi-stationary-state approximation gives the following relationship when applied to species A* :

$$k'_{55}\,[A]\,[M] = k''_{55}\,[A^*]\,[M] + k_{56}\,[A^*] \qquad (57)$$

The rate of product formation is that of the reaction (56) :

$$r = k_{56}\,[A^*] \qquad (58)$$

The expression for [A*] is given by relationship (57) which finally gives :

$$r = \frac{k'_{55}\,k_{56}\,[M]}{k''_{55}\,[M] + k_{56}}\,[A] \qquad (59)$$

The LINDEMANN and HINSHELWOOD law has been improved by RICE, RAMPSPERGER, KASSEL and MARCUS and is known by the name RRKM theory. Law (50) constitutes an approximation to the RRKM laws.

f) $C_1 + C_2\ (+M) \longrightarrow$ products (+M) (60)

The rate of this reaction has the following expression :

$$r_{60} = k_{60}\,[C_1]\,[C_2] \qquad (61)$$

The rate constant k_{60} obeys TROE 's law (eqns 50 to 53). The constants k^0_{60} and k^∞_{60} are expressed in $mol^{-2}\ m^6\ s^{-1}$ and $mol^{-1}\ m^3\ s^{-1}$, respectively.

2.2 - The ARRHENIUS-KOOIJ law

The expression, which is most commonly used in tables to represent the variations of a rate constant k with the absolute temperature, is the ARRHENIUS-KOOIJ law :

$$k = A\,T^b \exp(-E/RT) \qquad (62)$$

where A is an exponential factor, in the units of k/T^b,
b is the temperature exponent,
E is the activation energy in $J\ mol^{-1}$,
R is the gas constant : $R = 8.3145\ J\ mol^{-1}\ K^{-1}$,
T is the absolute temperature, in K.

The ARRHENIUS law corresponds to a value $b = 0$:

$$k = A \exp(-E/RT) \qquad (63)$$

A so-called **ARRHENIUS diagram** is the representation of the variations of log k as a function of 1/T. For ARRHENIUS' law (63), gives :

$$\log k = \log A - \frac{E \log e}{R} \times \left(\frac{1}{T}\right) \qquad (64)$$

The corresponding ARRHENIUS diagram is linear. The term T^b of the ARRHENIUS-KOOIJ law (62) introduces a curvature into the ARRHENIUS diagram. This curvature, which is observed experimentally if the temperature range is wide enough, is interpreted on the one hand by the variations in the entropy and enthalpy of activation with the temperature and on the other hand, by the tunnelling effect.

2.3 - Examples

Using the relationships given in paragraphs 2.1 and 2.2 above can cause some practical difficulties, as the systems of units used in the tables are rather ill-assorted. When in doubt it is advisable to return to basic SI units : mol, m, s, J, K. The values given below will be useful for this:

$$1\ \text{cal} = 4.184\ \text{J} \quad ; \quad R = 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} = 1.987\ \text{cal mol}^{-1}\ \text{K}^{-1}.$$

In Anglo-Saxon tables the molecule is considered to be a unit of quantity of matter, which is not recommended by the IUPAC, but turns out to be very handy when changing the units. With this in mind, Avogadro's number is written $N_A = 6.022\text{x}10^{23}$ molecule mol^{-1} and not $N_A = 6.022\text{x}10^{23}$ mol^{-1}, which is recommended by the IUPAC.

Example 11

Calculate the rate of the following reaction :

$$H_2 + M \longrightarrow 2H + M$$

for $[H_2] = 10^{-6}$ mol cm^{-3}, $[M] = 10^{-5}$ mol cm^{-3}, T = 1000 K .Taking the following values into account :

$$A = 2.2\text{x}10^{14}\ \text{mol}^{-1}\ \text{cm}^3\ \text{s}^{-1} \quad ; \quad b = 0 \quad ; \quad E = 95.7\text{x}10^3\ \text{cal mol}^{-1}.$$

The rate constant is calculated using relationship (62) :

$$k = 2.2\text{x}10^{14} \exp\left(-\frac{95\ 700}{1.987 \times 1000}\right) = 2.66\text{x}10^{-7}\ \text{mol}^{-1}\ \text{cm}^3\ \text{s}^{-1}$$

Relationship (42) gives the following rate :

$$r = 2.66\text{x}10^{-7} \times 10^{-6} \times 10^{-5} = 2.66\text{x}10^{-18}\ \text{mol cm}^{-3}\ \text{s}^{-1}$$

Example 12

Calculate the rate of the following reaction :

$$CH_3 + CH_3\ (+M) \longrightarrow C_2H_6\ (+M)$$

using the formulae of LINDEMANN-HINSHELWOOD on the one hand, and TROE on the other, for $[CH_3] = 10^{-13}$ mol cm^{-3}, T = 800 K and (a) $[M] = 4\text{x}10^{-4}$ mol cm^{-3}, (b) $[M] = 4\text{x}10^{-7}$ mol cm^{-3}, (c) $[M] = 4\text{x}10^{-10}$ mol cm^{-3}.

This gives :

- for k_∞ : $A = 1.5\text{x}10^{14}$ mol^{-1} cm^3 s^{-1} ; b = 0 ; E = 0

- for k_0, assigned the keyword LOW : $A = 5.2x10^{41}$ mol^{-2} cm^6 s^{-1} K^b ; $b = -7$; $E = 3.0x10^3$ cal mol^{-1}
- for the TROE parameters : $a = 0.62$; $T_1 = 73$ K ; $T_2 = 1180$ K ; there is no value for T_3, therefore the corresponding term of equation (53) will not be taken into account.

$k_\infty$and k_0 are calculated first:

$$k_\infty = 1.5x10^{14} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

$$k_0 = 5.2x10^{41} \times \left(800^{-7}\right) \times \exp\left(-\frac{3000}{1.987 \times 800}\right) = 3.756x10^{20} \text{ mol}^{-2} \text{ cm}^6 \text{ s}^{-1}$$

The value of $[M]_c$ can be deduced (eqn 51) :

$$[M]_c = 1.5x10^{14}/3.756x10^{20} = 3.994x10^{-7} \text{ mol cm}^{-3}$$

The $[M]/[M]_c$ ratios can be calculated :

a) $[M]/[M]_c \simeq 10^3$; b) $[M]/[M]_c \simeq 1$; c) $[M]/[M]_c \simeq 10^{-3}$

Applying the LINDEMANN and HINSHELWOOD formula (eqn 54) gives the following values for the rate constant of order 2 :

a) $k \simeq k_\infty = 1.5x10^{14}$ mol^{-1} cm^3 s^{-1}

$r = 1.5x10^{14} \times 10^{-26} = 1.5x10^{-12}$ mol cm^{-3} s^{-1}

b) $k \simeq k_\infty/2 = 0.75x10^{14}$ mol^{-1} cm^3 s^{-1}

$r = 0.75x10^{-12}$ mol cm^{-3} s^{-1}

c) $k \simeq k_0 [M] = 3.756x10^{20} \times 3.994x10^{-10} = 1.5x10^{11}$ mol^{-1} cm^3 s^{-1}

$r = 1.5x10^{-15}$ mol cm^{-3} s^{-1}

More accurate values can be calculated using the TROE formulae (50) to (53), this gives :

$F_c = 0.62 \exp(-800/73) + 0.38 \exp(-800/1180) = 0.1929$, i.e. $\log F_c = -0.7147$

therefore :

a) $\log F = -0.1672$; $F = 0.6805$; $k = 1.5x10^{14} \times 0.6805 = 1.02x10^{14}$ mol^{-1} cm^3 s^{-1}

$r = 1.0x10^{-12}$ mol cm^{-3} s^{-1}.

b) $\log F = -0.7147$; $F = F_c = 0.1929$

$k = 1.5x10^{14} \times 0.1929/2 = 1.4x10^{13}$ mol^{-1} cm^3 s^{-1}

$r = 1.4x10^{-13}$ mol cm^{-3} s^{-1}

c) $\log F = -0.1672$; $F = 0.6805$

$k = 1.0x10^{11}$ mol^{-1} cm^3 s^{-1}

$r = 1.0x10^{-15}$ mol cm^{-3} s^{-1}

In each case a significant difference is observed, due to the introduction of the F factor, between the values calculated using the TROE formulae and those of LINDEMANN-

HINSHELWOOD. This difference is most marked at fall-off pressures, for $[M]/[M]_c \simeq 1$, and decreases at higher and lower pressures, as expected.
Using only the LINDEMANN-HINSHELWOOD formula, it is observed that the rate constant of order two varies over three orders of magnitude between the highest and the lowest pressure. It is, therefore, not satisfactory to neglect the effect this pressure has on the rate constants ; in the case being discussed, it is apparent for $[M] \simeq [M]_c$, i.e. for a pressure :

$$p_c = (0.4 \text{ mol m}^{-3}) \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (800 \text{ K}) = 2.66 \text{ kPa}$$

For example, these pressures are encountered industrially in CVD processes.

2.4 - Principle of detailed balancing

The principle of microscopic reversibility at equilibrium, which comes from classical mechanics, states that the reaction paths in the forward direction and in the reverse direction are identical, apart from the direction, which corresponds to an inversion of time in mechanics equations. This principle therefore forbids the following reaction sequence :

$$A \longrightarrow B \longrightarrow C \longrightarrow A$$

and requires the sequence to be written as follows :

$$A \rightleftarrows B \qquad (65)$$

$$B \rightleftarrows C \qquad (66)$$

$$C \rightleftarrows A \qquad (67)$$

According to this mechanism, an equilibrium state would be observed if the following conditions were obeyed (the superscripts ' and " refer to the forward and reverse reactions, respectively) :

$$r'_{65} - r''_{65} = r'_{66} - r''_{66} = r'_{67} - r''_{67} = r \qquad (68)$$

and this is true whatever the net rate r.

The principle of detailed balancing states that this rate r is equal to zero when the overall equilibrium is reached, that is to say that the forward and reverse elementary reactions are themselves at equilibrium : the global equilibrium is therefore a consequence of the detailed equilibria.
The kinetic principle of detailed balancing dictates the relationships between the kinetic parameters and the thermodynamic properties of an elementary reaction.
The net rate of the elementary reaction :

$$\nu'_1 C_1 + \nu'_2 C_2 \rightleftarrows \nu''_3 C_3 + \nu''_4 C_4 \qquad (69)$$

is expressed as follows :

$$r = k' c_1^{\nu'_1} c_2^{\nu'_2} - k'' c_3^{\nu''_3} c_4^{\nu''_4} \tag{70}$$

where k' and k" are the rate constants of the forward and reverse reactions, respectively. At equilibrium, according to the principle of detailed balancing, r = 0 and therefore :

$$\frac{k'}{k''} = \frac{c_{3\,eq}^{\nu''_3} \, c_{4\,eq}^{\nu''_4}}{c_{1\,eq}^{\nu'_1} \, c_{2\,eq}^{\nu'_2}} \tag{71}$$

where the subscript eq stands for concentrations at equilibrium. The right hand side of equation (71) can be recognized as the expression for the concentration equilibrium constant K_c, therefore :

$$\frac{k'}{k''} = K_c \tag{72}$$

i.e.

$$\frac{k'}{k''} = \left(\frac{p^o}{RT}\right)^{\Delta\nu} K^o = \left(\frac{p^o}{RT}\right)^{\Delta\nu} \exp\left(\Delta S^o/R - \Delta H^o/RT\right) \tag{73}$$

The ARRHENIUS-KOOIJ laws give :

$$k' = A' \, T^{b'} \exp\left(- E'/RT\right) \tag{74}$$

$$k'' = A'' \, T^{b''} \exp\left(- E''/RT\right) \tag{75}$$

The identification of the k'/k" ratio given by equation (73) on the one hand, and equations (74) and (75) on the other, lead to the following relationships :

$$\left\{ \begin{array}{ll} A'/A'' = (p^o/R)^{\Delta\nu} \exp\left(\Delta S^o/R\right) & (76) \\ b' - b'' = -\Delta\nu & (77) \\ E' - E'' = \Delta H^o & (78) \end{array} \right.$$

Relationships (76) to (78) allow the kinetic parameters of a reverse reaction to be calculated from those of the forward reaction and the thermodynamic properties ΔS^o and ΔH^o of the forward reaction. An example of their application will be treated in Chapter VII.

When relationships (76) to (78) are obeyed, it is said that there is **consistency** between the kinetic parameters and the thermodynamic properties. When an **adjustment** of the kinetic parameters is carried out, in order to obtain a better agreement between the results calculated using the kinetic model and the experimental results, it is advisable that this consistency will remain within limits, which are compatible with the ranges of uncertainty of the different quantities involved in relationships (76) to (78).

FURTHER READING

BAULCH D.L., *Kinetics Databases*, Comprehensive Chem. Kin., vol. 35, chap. 3 (1997).

GARDINER W.C., Jr., *Gas-Phase Combustion Chemistry*, Springer (2000).

GILBERT R.G., SMITH S.C., *Theory of Unimolecular and Recombination Reactions*, Blackwell (1990).

KEE R.J., RUPLEY F.M., MILLER J.A., Sandia Report SAND89-8009 B (1993).

LAIDLER K.J., *Chemical Kinetics*, 3rd edition, Harper Collins (1987).

ROBERTSON S.H., SEAKINS P.W., PILLING M.J., *Elementary reactions*, Comprehensive Chem. Kin., vol. 35, chap. 2 (1997).

CHAPTER VII

ESTIMATION OF KINETIC PARAMETERS

Chapter VII discusses the three main methods for estimating the kinetic parameters of elementary reactions : collision theory, thermochemical kinetics, structure-reactivity correlations.

1 - COLLISION THEORY

The collision theory, which has been modified by BENSON, allows the pre-exponential factor A for the combination of two free radicals, to be calculated.

$$^{\bullet}R_1 + {}^{\bullet}R_2 \longrightarrow R_1 - R_2 \qquad \text{(co)}$$

KOOIJ 's coefficient b and the activation energy E are assumed to be equal to zero. Consequently, A is simply the rate constant of the reaction (co). The A factor is given by the following relationship :

$$A = \frac{1}{4} P\, Z \qquad (1)$$

- The factor 1/4 represents the probability of obtaining R_1–R_2 in a stable singlet state.
- P is a steric factor which can be estimated from geometric considerations related to the activated complex.
- Z is the collision frequency between the two free radicals.

a) For two different free radicals $^{\bullet}R_1$ and $^{\bullet}R_2$:

$$Z_{12} = N_A\, \sigma_{12}^2 \left(\frac{8\,\pi\, RT}{M_{12}}\right)^{1/2} \qquad (2)$$

where $N_A = 6.022\text{x}10^{23}\ \text{mol}^{-1}$

$$\sigma_{12} = 2.8 \left(\frac{300}{T}\right)^{0.17} l_{12} \qquad (3)$$

$R = 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}$

$$M_{12} = \frac{M_1\, M_2}{M_1 + M_2} \qquad (4)$$

- σ_{12} is the molecular diameter (in m) of the molecule R_1-R_2.
- The factor 2.8 corresponds to the stretching of the R_1-R_2 bond in the activated complex with respect to that of the stable molecule.
- The term $(300/T)^{0.17}$ is an empirical term.
- l_{12} is the length (in m) of the R_1-R_2 bond. This length l_{12} is the sum of the covalent radii (Table XIV-2.2).
- M_{12} is the reduced molar mass of R_1-R_2, M_1 and M_2 are the molar masses (in kg mol^{-1}) of $^\bullet R_1$ and $^\bullet R_2$.

b) For the combination of two identical free radicals $^\bullet R_1$:

$$Z = 2\,N_A\,\sigma_{11}^2\left(\frac{\pi\,RT}{M_1}\right)^{1/2} \tag{5}$$

where :

$$\sigma_{11} = 2.8\left(\frac{300}{T}\right)^{0.17} l_{11} \tag{6}$$

l_{11} is the length (in m) of the R_1-R_1 bond. In both a) and b), the collision frequency Z is expressed in mol^{-1} m^3 s^{-1}.

The rate constant k_{di} of a disproportionation reaction can be deduced from the combination constant k_{co} by applying a correcting factor. Table XIV gives the average values of the ratio k_{di}/k_{co} for some hydrocarbon free radicals.

Example 1

Calculate the rate constants at 700 K for the following combination and disproportionation reactions :

CH3(•)+CH3/CH(•)/CH2/CH2/C(CH3)3 ⟶ CH(CH3)2/CH2/CH2/C(CH3)3 (co)

⟶ CH4+CH2//CH/CH2/CH2/C(CH3)3 (di)

Deduce the kinetic parameters for the unimolecular initiation reaction (ui) and the reverse reaction (co) by applying the principle of detailed balancing. Take the following values : $\Delta_{co}H^o_{700} = -358.3$ kJ mol^{-1} ; $\Delta_{co}S^o_{700} = -169.7$ J mol^{-1} K^{-1}.

a) Calculation of k_{co}

Using formulae (1) to (4), gives :

$$l_{12} = 2\,r_c = 2\times 0.77\ \text{Å i.e. } \sigma_{12} = 3.734\text{x}10^{-10}\ \text{m}$$

The molar masses have the following values :

$$M_1 = 15\text{x}10^{-3}\ \text{kg mol}^{-1}\ ;\ M_2 = 113\text{x}10^{-3}\ \text{kg mol}^{-1}$$

therefore :

$$M_{12} = 13.24\text{x}10^{-3}\ \text{kg mol}^{-1}$$

The collision frequency is equal to:

$$Z_{12} = 2.791\text{x}10^8 \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}$$

The steric factor P , ($^\bullet R_1 + {}^\bullet CH_3$) is estimated to be 0.22 from Table XIV-2.1. The following value is deduced :

$$A_{co} = \frac{1}{4} \times 0.22 \times 2.791\text{x}10^8 = 1.54\text{x}10^7 \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}.$$

and : $b_{co} = 0$; $E = 0$.

b) Calculation of k_{di}

Table XIV-2.3 gives $k_{di}/k_{co} = 0.2$ for the analogous termination $^\bullet CH_3 + {\bullet}sC_3H_7$; therefore $A_{di} = 3.07\text{x}10^6 \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}$; $b_{di} = 0$; $E_{di} = 0$.

c) Calculation of k_{ui}

Reaction (ui) is the reverse of reaction (co) ; the equations derived from the principle of detailed balancing can therefore be applied taking care that the forward reaction is now (ui), i.e. $\Delta\nu = +1$:

$$\frac{A_{ui}}{A_{co}} = \left(\frac{p^o}{R}\right)^1 \exp\left(-\frac{\Delta_{co}S^o_{700}}{R}\right) \;;\; b_{ui} - b_{co} = -1 \;;\; E_{ui} - E_{co} = -\Delta_{co}H^o_{700}$$

$$A_{ui} = 1.35\text{x}10^{20} \text{ s}^{-1} \text{ K} \;;\; b_{ui} = -1 \;;\; E_{ui} = 358.3 \text{ kJ mol}^{-1}$$

i.e. $$k_{ui} \text{ s}^{-1} = 1.35\text{x}10^{20} \text{ T}^{-1} \exp\left(-\frac{353\,300}{8.3145 \text{ T}}\right)$$

gives : $$k_{ui} \text{ (700 K)} = 8.36\text{x}10^{-10} \text{ s}^{-1}$$

2 - BENSON'S METHOD

BENSON's thermochemical kinetics takes the **transition-state theory** as a starting point for the calculation of a rate constant. It will be shown that this theory introduces two properties, the standard entropy and the standard enthalpy of activation $\Delta_\ddagger S^o$ and $\Delta_\ddagger H^o$, which are the thermodynamic properties of the reaction :

$$\text{Reactants} \rightleftharpoons \text{Activated complex } C_\ddagger$$

The calculation of $\Delta_\ddagger S^o$ and, in certain cases, of $\Delta_\ddagger H^o$ is based upon two main principles.

- The activated complex is considered, with the exception of the bond, which is being formed or broken, to be a normal species. It is therefore possible to calculate $S^o_\ddagger$ and, even, $\Delta_f H^o_\ddagger$ by the additivity methods described in Chapter V, as long as its structure is known.

- In fact, the calculations are carried out not in an absolute way, but with respect to a model molecule, to whose data are applied analogous corrections to those which allowed the calculation of the properties of a free radical $^\bullet$R using those of the parent molecule RH.

2.1 - Transition-state theory

Consider the following gas-phase elementary reaction :

$$\nu_1\, C_1 + \nu_2\, C_2 \Rightarrow \text{products} \qquad (7)$$

According to the transition-state theory, this elementary reaction is described by the following model :

$$\nu_1\, C_1 + \nu_2\, C_2 \rightleftarrows C_\ddagger \qquad (8)$$

$$C_\ddagger \longrightarrow \text{products} \qquad (9)$$

$C_\ddagger$ represents the transition state or activated complex, denoted by the subscript ‡.
It is assumed that reaction (8) is at quasi-equilibrium and that reaction (9) has the following rate :

$$r = \nu^\ddagger\, c_\ddagger \qquad (10)$$

$\nu^\ddagger$ is the frequency of decomposition of the activated complex into the products of the reaction.
$c_\ddagger$ is the concentration of the activated complexes, calculated using the quasi-equilibrium hypothesis :

$$c_\ddagger = K^o \left(\frac{p^o}{RT}\right)^{1-\nu_1-\nu_2} c_1^{\nu_1}\, c_2^{\nu_2} \qquad (11)$$

Equation (11) also assumes that the reaction is ideal, i.e. that the fugacity coefficients are equal to 1. The equilibrium constant K^o contains a partition function corresponding to the vibrational frequency $\nu^\ddagger$. Transition-state theory assumes that the vibration has a very low frequency, so that the corresponding partition function can be factorized in the following form :

$$K^o = \frac{k_B T}{h\nu^\ddagger} K^o_\ddagger \qquad (12)$$

$K^o_\ddagger$ is a pseudo-constant of equilibrium. The rate of reaction is therefore finally written :

$$r = k\, c_1^{\nu_1}\, c_2^{\nu_2} \qquad (13)$$

with the following expression for the rate constant :

$$k = \frac{k_B T}{h}\left(\frac{p^o}{RT}\right)^{1-\nu_1-\nu_2} K^o_{\ddagger} \qquad (14)$$

The equilibrium constant $K^o_{\ddagger}$ can be expressed as follows :

$$K^o_{\ddagger} = \exp\left(-\,\Delta_{\ddagger}G^o/RT\right) \qquad (15)$$

$\Delta_{\ddagger}G^o$ is the standard free enthalpy of activation, which can itself be divided up into two terms :

$$\Delta_{\ddagger}G^o = \Delta_{\ddagger}H^o - T\,\Delta_{\ddagger}S^o \qquad (16)$$

$\Delta_{\ddagger}H^o$ is the standard enthalpy of activation and $\Delta_{\ddagger}S^o$ is the standard entropy of activation.

Putting into equations (14) and (15), gives :

$$k = \frac{k_B}{h}\left(\frac{p^o}{R}\right)^{1-\nu_1-\nu_2} \exp\left(\frac{\Delta_{\ddagger}S^o}{R}\right) T^{\nu_1+\nu_2} \exp\left(-\frac{\Delta_{\ddagger}H^o}{RT}\right) \qquad (17)$$

This relationship is of the ARRHENIUS-KOOIJ type :

$$k = A\,T^b \exp\left(-\,E/RT\right) \qquad (18)$$

where : $$A = \frac{k_B}{h}\left(\frac{p^o}{R}\right)^{1-\nu_1-\nu_2} \exp\left(\frac{\Delta_{\ddagger}S^o}{R}\right) \qquad (19)$$

$$b = \nu_1 + \nu_2 \qquad (20)$$

$$E = \Delta_{\ddagger}H^o \qquad (21)$$

In basic SI units, the relationships (18) to (21) apply where :

$k_B = 1.380658\text{x}10^{-23}$ J K^{-1} ; $h = 6.626076\text{x}10^{-34}$ J s ;

$R = 8.314510$ J K^{-1} mol^{-1} ;

$p^o = 10^5$ Pa ; T in K ; $\Delta_{\ddagger}S^o$ in J mol^{-1} K^{-1} ; $\Delta_{\ddagger}H^o$ in J mol^{-1}

2.2 - Free radical isomerization

The isomerization of a free radical takes place by the internal transfer of a hydrogen atom. The activated complex is a cyclic intermediate whose size is equal to 4 for a 1–3 transfer, to 5 for a 1–4 transfer, to 6 for a 1–5 transfer...

a) Entropy of activation

The property $\Delta_{\ddagger}S^o$ is equal to the difference between the entropy of the activated complex and that of the free radical. It consists mainly of two terms.

- The entropy of activation due to the number of possible reaction paths, which is here the number n_H of hydrogen atoms concerned by the transfer :

$$\Delta_{\ddagger}S^{o}_{sym} = R \ln n_H \tag{22}$$

- The entropy of activation coming from the variation in the number of internal rotations $\Delta_{\ddagger}n_{int.rot..}$ between the activated complex and the free radical :

$$\Delta_{\ddagger}S^{o}_{int.rot.} \simeq 1.75\, R\, \Delta_{\ddagger}n_{int.rot.} \tag{23}$$

The translation term is equal to zero, as the mass of the activated complex and of the free radical is the same, the terms due to external rotations, vibrations and the electronic terms are negligible ; therefore, finally :

$$\frac{\Delta_{\ddagger}S^{o}}{R} = \ln n_H + 1.75\, \Delta_{\ddagger}n_{int.rot.} \tag{24}$$

b) Enthalpy of activation

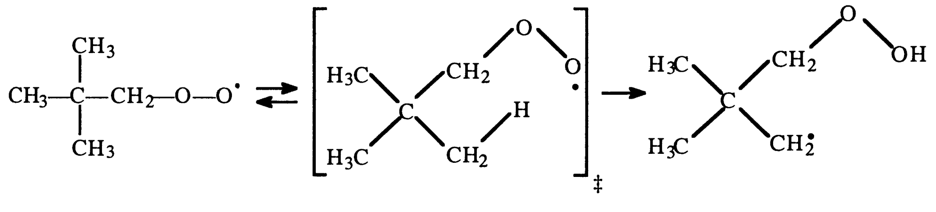
The property $\Delta_{\ddagger}H^{o}$ is calculated by adding the activation energy E_{me} of the reaction of internal metathesis to the tension energy $E_{tension}$ of the ring formed during the passage from a free radical to an activated complex :

$$\Delta_{\ddagger}H^{o} = E_{me} + E_{tension} \tag{25}$$

Example 2

Calculate the rate constant for the isomerization reaction of the neopentylperoxy radical by a 1–5 internal transfer of an H atom at T = 1000 K.

The elementary reaction is described by the following scheme :



The 9 H atoms of the three methyl groups are equivalent for the reaction ; therefore $n_H = 9$. The free radical has 5 internal rotations and only 2 remain in the activated complex, the three others being blocked by the ring ; thus : $\Delta_{\ddagger}n_{int.rot..} = -3$.
Equation (24) gives the following : $\Delta_{\ddagger}S^{o}/R = \ln 9 - 5.25 = -3.053$.
The transferred Hs are primary, the free radical is of the alkylperoxy type and the activated complex has a size equal to 6. Table XIV-2.4 gives : $E_{me} = 84$ kJ mol^{-1} and $E_{tension} = 36$ kJ mol^{-1}, i.e. $\Delta_{\ddagger}H^{o} = 120$ kJ mol^{-1}.
This gives finally :

$$A = \frac{1.381\text{x}10^{-23}}{6.626\text{x}10^{-34}} \exp(-3.053) = 9.841\text{x}10^{8} \;\; ; \;\; b = 1 \;\; ; \;\; E = 120\text{x}10^{3}\ \text{J mol}^{-1}$$

The value of the rate constant at 1000 K can be deduced :

$$k = 5.3x10^5 \ s^{-1}$$

BENSON's methods allow the pre-exponential factors to be calculated and, in certain rarer cases, the activation energies of other categories of reactions.

3 - STRUCTURE-REACTIVITY CORRELATIONS

The simple idea which determines the derivation of correlations between the kinetic parameters of a reaction and the structure of the reactants consists in identifying the **minimum sub-structures** which permit the characterization of the bonds broken and formed, neglecting the effects of the atoms or groups of atoms far removed from the site of the reaction.

Tables XIV.2 show such correlations used for calculating the kinetic parameters of the elementary reactions involved in pyrolysis mechanisms, in the oxidation and combustion of hydrocarbons.

3.1 - Initiations

a) Unimolecular initiations

Table XI-2.5.a gives the kinetic parameters for the initiations obtained by the breaking of a single C—C bond between two primary (p), secondary (s) or tertiary (t) carbons, and by that of a peroxidic O—O bond.

Example 3

Calculate the kinetic parameters for the unimolecular initiation reactions of normal butane.

For symmetry reasons, only two reactions are considered :

$$CH3/CH2/CH2/CH3 \longrightarrow \bullet CH3 + \bullet CH2/CH2/CH3 \qquad (1)$$

$$\longrightarrow 2\bullet CH2/CH3 \qquad (2)$$

Reaction (1) occurs by the breaking of a C_p—C_s bond ; two possibilities must be taken into account ; thus :

$$\log A_1 \ (s^{-1}) = 17.3 \quad ; \quad E_1 = 369 \ kJ \ mol^{-1}$$

Reaction (2) occurs by the breaking of a C_s—C_s bond, i.e. :

$$\log A_2 \ (s^{-1}) = 16.35 \quad ; \quad E_2 = 358 \ kJ \ mol^{-1}$$

b) Bimolecular initiations

At "low" temperature, abstracting an H atom from a hydrocarbon molecule RH by

oxygen O_2 becomes easier than a unimolecular initiation, provided of course, that the oxygen concentration is high enough.
Table XIV-2.5.b gives the kinetic parameters of five categories of bimolecular initiation reactions concerning primary (p), secondary (s), tertiary (t), allylic (a) and vinylic (v) H atoms. The A factor is relative to one H atom.

Example 4
Calculate the kinetic parameters for the bimolecular initiation reactions of propane.

There are two reactions :

$$\text{CH3/CH2/CH3+O2} \longrightarrow \text{•CH2/CH2/CH3+HO2•} \tag{1}$$

$$\longrightarrow \text{•CH(CH3)2+HO2•} \tag{2}$$

Reaction (1) involves 6 equivalent primary H atoms ; therefore :

$$\log A_1\ (\mathrm{mol^{-1}\ cm^3\ s^{-1}}) = 13.4 \quad \text{and} \quad E_1 = 205\ \mathrm{kJ\ mol^{-1}}$$

Reaction (2) involves 2 equivalent secondary H atoms ; thus :

$$\log A_2\ (\mathrm{mol^{-1}\ cm^{-3}\ s^{-1}}) = 12.3 \quad \text{and} \quad E_2 = 201\ \mathrm{kJ\ mol^{-1}}$$

3.2 - Unimolecular decompositions of free radicals

Three main categories of unimolecular decompositions of free radicals exist.

a) Reactions which occur by the breaking of a single bond between the C atom situated in the ß position with respect to the radical point (and which will be called beta-scissions, for this reason) and the atom which is bound to it. Three cases must then be distinguished, according to whether they form an $^\bullet$H, $^\bullet CH_3$ or a larger $^\bullet$R radical (Table XIV-2.6.a).

Example 5
Determine the kinetic parameters for the decomposition of the n-butyl radical.

There are two possible reactions:

$$\text{•CH2/CH2/CH2/CH3} \longrightarrow \text{CH2//CH2+•CH2/CH3} \tag{1}$$

$$\longrightarrow \text{•H+CH2//CH/CH2/CH3} \tag{2}$$

The values of the parameters are : $\log A_1\ (\mathrm{s^{-1}}) = 13.3 \ ;\ E_1 = 120\ \mathrm{kJ\ mol^{-1}}$

$$\log A_2\ (\mathrm{s^{-1}}) = 13.34 \ ;\ E_2 = 182\ \mathrm{kJ\ mol^{-1}}$$

b) Reactions which occur by the breaking of a single bond situated in a ß position with respect to the radical point of a hydroperoxyalkyl •QOOH or a dihydroperoxyalkyl •U(OOH)2 radical, with the formation of an HO2• or an •OH radical (Table XIV 2.6.b).

Example 6
Determine the kinetic parameters for the decomposition of the CH3/CH2/CH2/•CH/O/OH radical.

The reaction leads to the, formation of the aldehyde CH3/CH2/CH2/CHO and the •OH radical. The values of the parameters are as follows :

$$\log A\ (s^{-1}) = 9.00 \quad ; \quad E = 31\ \text{kJ mol}^{-1}$$

c) Hydroperoxyalkyl •QOOH and dihydroperoxyalkyl •U(OOH)2 radicals can also give rise to a molecule of cyclic ether with the concomitant elimination of a hydroxy radical (Table XIV-2.6.b).

Example 7
Determine the kinetic parameters for the formation of a cyclic ether from the •CH2/CH2/CH2/CH2/O/OH radical.

The reaction leads to furane and a hydroxy radical, therefore :

$$\log A\ (s^{-1}) = 11.3 \quad ; \quad E = 24\ \text{kJ mol}^{-1}$$

3.3 - Reactions of free radicals with molecular oxygen

These reactions are of two types.

a) The additions of alkyl or hydroperoxyalkyl radicals lead to a peroxy radical. The same values of A, b and E are given to these two generic reactions (Table XIV-2.7.a).

b) The oxidation of a hydrocarbon radical by oxygen occurs by the abstraction of an H atom situated in a ß position with respect to the radical point (Table XIV-2.7.b).

Example 8
Determine the kinetic parameters for the oxidation reaction of the secondary n-butyl radical.
There are two reactions :

CH3/•CH/CH2/CH3+O2 ⟶ CH2//CH/CH2/CH3+•O/OH (1)
⟶ CH3/CH//CH/CH3+•O/OH (2)

Reaction (1) involves 3 H_p atoms and reaction (2) 2 equivalent H_s atoms, thus :

$$\log A_2\ (\text{mol}^{-1}\ \text{cm}^3\ \text{s}^{-1}) = 11.85 \quad ; \quad E_1 = 20.9\ \text{kJ mol}^{-1}$$

$$\log A_2\ (\text{mol}^{-1}\ \text{cm}^3\ \text{s}^{-1}) = 12.2 \quad ; \quad E_2 = 20.9\ \text{kJ mol}^{-1}$$

3.4 - Metatheses

These reactions consist in the abstraction of an H atom of an alkane R'H molecule by a free radical •R to give a molecule RH and a free radical •R'. The kinetic parameters of a metathesis reaction depend on the nature of the attacking radical and on that of the transferred H atom (Table XIV.2.8). The pre-exponential factors are related to one transferred H atom.

Example 9

Determine the kinetic parameters for the metathesis reaction of the n-butyl radical with n-butane.

There is only one possible reaction :

•CH2/CH2/CH2/CH3+CH3/CH2/CH2/CH3

$\longrightarrow$ CH3/CH2/CH2/CH3+CH3/•CH/CH2/CH3

as the other reaction regenerates the reactants. The attacking radical is a primary radical which can abstract 4 equivalent H_s atoms, therefore :

$$\log A\ (\text{mol}^{-1}\ \text{cm}^3\ \text{s}^{-1}) = 11.6 \quad ; \quad E = 46.8\ \text{kJ mol}^{-1}$$

FURTHER READING

BENSON S.W., *Thermochemical Kinetics*, 2^{nd} edition, Wiley (1976).
ROBERTSON S.H., SEAKINS P.W., PILLING M.J., *Elementary Reactions*, Comprehensive Chem. Kin., vol. 35, chap. 2, p. 125 (1997).
WARTH V., STEF N., GLAUDE P.A., BATTIN-LECLERC F., SCACCHI G., CÔME G.M., *Computer-Aided Derivation of Gas-Phase Oxidation Mechanisms : Application to the Modelling of the Oxidation of n-Butane*, Comb. & Flame, 114, 81-102 (1998).

COMPUTER PROGRAMS

BAC MP 4, CHEMACT, KERGAS, KINBEN, KINCOR, RADICALC, UNIMOL.

CHAPTER VIII

KINETIC MORPHOLOGY

Gas-phase thermal reactions and, more particularly, the oxidation of hydrocarbons exhibit a wide variety of **macroscopic behaviour patterns** : slow reactions which are strongly inhibited or accelerated by the addition of small quantities of additives, cool flames and oscillations, isothermal explosions, two stage autoignitions, thermal explosions and flames.

Transitions from one behaviour pattern to another, which is completely different, can be provoked by minimum changes in the operating conditions, so giving them the character of a true **catastrophe** in the mathematical and in the practical sense of the term, as in the case of natural gas explosions or of firedamp triggered off by the smallest spark.

The **chemistry** associated with these different regimes is itself very varied depending on the experimental conditions, especially the temperature and the equivalence ratio of the mixture, and is often very complex, with the formation of numerous unsaturated hydrocarbons, aromatics and polyaromatics and of oxygenated molecules (aldehydes, ketones, alcohols, cyclic ethers...), all of these species are likely to be atmospheric pollutants.

This macroscopic morphology is based on the ***general structures of the reaction schemes.*** *The first aim of this chapter is to describe these and thus to trace the framework within which the detailed reaction mechanisms likely to account for the resulting chemistry will be developed.*

A second, more technical aim of this chapter, consists in the setting up of the ***quasi-stationary-state approximation (QSSA)*** *and of the method of* ***limiting cases,*** *for establishing the kinetic laws from the mechanisms.*

1 - QUASI-STATIONARY-STATE APPROXIMATION

The idea behind the QSSA is the following. If an **intermediate species** is much more reactive than the other species present in the reaction medium, it is, consequently, at a lower concentration with respect to the other species. This is the case, in general, of most free radicals. The net rate of production of this intermediate must therefore be negligible with respect to the other rates. The QSSA consists in carrying out kinetic calculations assuming that this rate is equal to zero.

The essential aspects of the QSSA can be demonstrated using the following simple mechanism :

$$C_1 \longrightarrow C_2 \tag{1}$$

$$C_2 \longrightarrow C_3 \tag{2}$$

It is assumed that the reactions obey the law of mass action, therefore :

$$r_1 = k_1\, c_1 \tag{3}$$

$$r_2 = k_2\, c_2 \tag{4}$$

The reaction is assumed to occur in a continuous flow, perfectly stirred, isothermal, isochoric, isobaric reactor working under steady-state conditions and fed by a pure reactant C_1.

The net rates of production of the three species can be written as follows :

$$R_1 = -\, r_1 = -\, k_1\, c_1 \tag{5}$$

$$R_2 = r_1 - r_2 = k_1\, c_1 - k_2\, c_2 \tag{6}$$

$$R_3 = r_2 = k_2\, c_2 \tag{7}$$

The rate R_2 is the difference between a **rate of appearance** r_1 and a **rate of disappearance** r_2. The structure of equation (6) therefore actually indicates that C_2 is a reactive intermediate. The QSSA consists in putting $R_2 = 0$, i.e. :

$$r_2 = r_1 \tag{8}$$

Equations (5)-(7) can then be written as follows :

$$R_1 = -\, k_1\, c_1 \tag{9}$$

$$c_2 = \frac{k_1}{k_2}\, c_1 \tag{10}$$

$$R_3 = k_1\, c_1 \tag{11}$$

a) Rigorous mass balance

Using expressions (5) to (7) for the rates, gives :

$$\frac{c_1}{c_{o,1}} = \frac{1}{1 + k_1\tau} \tag{12}$$

$$\frac{c_2}{c_{o,1}} = \frac{k_1\tau}{\left(1 + k_1\tau\right)\left(1 + k_2\tau\right)} \tag{13}$$

$$\frac{c_3}{c_{o,1}} = \frac{k_1 k_2 \tau^2}{\left(1 + k_1\tau\right)\left(1 + k_2\tau\right)} \tag{14}$$

$c_{o,1}$ is the concentration of C_1 at the input of the reactor ;
c_1, c_2, c_3 are the concentrations of C_1, C_2, C_3 at the exit to the reactor ;
τ is the space time.

b) Quasi-stationary mass balance

Using the rate equations (9) to (11), gives :

$$\frac{c_1}{c_{o,1}} = \frac{1}{1 + k_1\tau} \tag{15}$$

$$\frac{c_2}{c_{o,1}} = \frac{k_1}{\left(1 + k_1\tau\right) k_2} \tag{16}$$

$$\frac{c_3}{c_{o,1}} = \frac{k_1\tau}{1 + k_1\tau} \tag{17}$$

c) Conditions of validity of the QSSA

These are obtained by comparing the approximate solutions with the rigorous ones.

— The comparaison of equations (16) and (13) leads to the following first condition :

$$k_2\tau >> 1 \tag{18}$$

i.e. :

$$\tau >> 1/k_2 \tag{19}$$

The time of reaction (here the space time τ) must be very much higher than $1/k_2$. This quantity is called the **true induction period** of the reaction and therefore corresponds to the establishment of the QSS. The QSSA is not applicable during the induction period. This induction period is **the opposite of the reactivity** of the intermediate C_2, which is also called mean lifetime of the intermediate. The mean lifetime of the reactant C_1 is equal to $1/k_1$.

— Moreover, so that the QSSA can be applied, the concentration of the intermediate must be negligible with respect to that of the reactant. Taking equations (15) and (16) into account, the inequality $c_2 << c_1$, is equivalent to :

$$k_2 >> k_1 \tag{20}$$

or :

$$1/k_1 << 1/k_2 \tag{21}$$

Equation (20) means that the reactivity of the intermediate species C_2 is much higher than that of the reactant C_1. Equation (21) indicates that the mean lifetime $1/k_1$ of the reactant, which is also the **characteristic time of the reaction**, is very much higher than that of the intermediate species.

These differences of reactivity are at the basis of the **stiffness** of the mathematical equations encountered in chemical kinetics and the consequent difficulties involved in obtaining a numerical solution.

In the example discussed in this paragraph, there is only one very reactive intermediate to which the QSSA can be applied. For complex reaction mechanisms, there are obviously many very reactive intermediates, and especially atoms and free radicals. In general, the QSSA will be applied to all these radical species.

2 - MOLECULAR REACTIONS

A molecular reaction occurs in only one reaction step. Of course, it is usually not known before having studied the reaction experimentally, if the reaction effectively takes place in one or several steps.

Several experimental characteristics provide indications in favour of the hypothesis that this is in fact an elementary reaction.

a) The orders of reaction are equal to the stoichoimetric coefficients, i.e. the law of mass action can be applied.
b) The ratio k'/k" of the rate constants of the forward and reverse reactions is equal to K_c, the concentration equilibrium constant of the reaction.
c) The reaction does not depend on the nature and on the relative area of the reactor walls.
d) The same can be said of the addition of substances, such as inhibitors or accelerators of radical chain reactions, which have no effect here.
e) Incident radiation does not change the molecular reaction, but it can start off competitive photochemical reactions.
f) Some molecular reactions occur in solution in the same way as in the gas phase, i.e. they obey the same kinetic laws, with the same rate constants and the same activation energies. As a rule, changes of solvent have no effect, but very polar solvents can favour ionic mechanisms.

a) The DIELS-ALDER reaction

The DIELS-ALDER reaction for the formation of cyclohexane from 1,3 butadiene and ethylene :

$$C_4H_6 + C_2H_4 \longrightarrow C_6H_{10} \qquad (22)$$

obeys the following kinetic law :

$$r = k_{22}\,[C_4H_6]\,[C_2H_4] \tag{23}$$

where :

$$k_{22} = 3\mathrm{x}10^{10}\exp(-27500/RT) \tag{24}$$

(units : mol, cm^3, s, cal)

The reverse reaction :

$$C_6H_{10} \longrightarrow C_4H_6 + C_2H_4 \tag{25}$$

obeys the following kinetic law :

$$r = k_{25}\,[C_6H_{10}] \tag{26}$$

where :

$$k_{25} = 1.6\mathrm{x}10^{15}\exp(-66200/RT) \tag{27}$$

(units : mol, cm^3, s, cal)

The values of k_{22} and k_{25} are in reasonable agreement with thermochemical data. This actually gives :

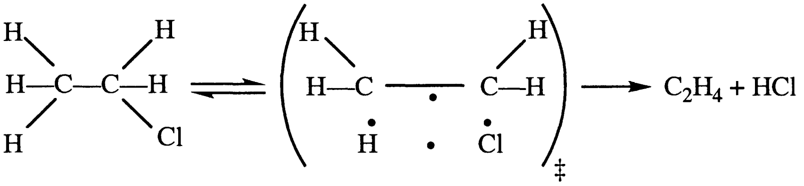
$$\Delta_f H^o_{(C_2H_4)} = 12.5 \;;\; \Delta_f H^o_{(C_4H_6)} = 26.3 \;;\; \Delta_f H^o_{(C_6H_{10})} = -0.3$$

i.e. : $\Delta H^o = -40.1$ kcal mol^{-1}, which is a value very close to $E_{22} - E_{25} = -38.7$ kcal mol^{-1}.

This DIELS-ALDER reaction appears to be a six-centred concerted molecular reaction. Other reactions, which seem to be similar to the DIELS-ALDER reaction, actually occur by a biradical mechanism.

b) Pyrolysis of halogenated hydrocarbons

The pyrolysis of ethyl chloride probably occurs by a concerted reaction at four centres :



(28)

Several arguments can be put forward in favour of a molecular reaction in this case : the reaction order is equal to 1, it does not depend on the nature of the walls, the pre-exponential factor A, calculated by BENSON's methods, is very close to the experimental factor $A = 3\mathrm{x}10^{13}$ s^{-1}.

The pyrolysis of CH_2Cl–CH_2Cl is of great industrial importance, as it is a method of manufacturing vinyl chloride monomer $CH_2{=}CHCl$. The experimental kinetic characteristics of this reaction (sensitivity to the nature of the walls, existence of an induction period...) permit this reaction to be classed as a straight chain radical reaction.

From these two examples involving molecules, which are very similar in appearance, it can be easily understood that the elucidation of a mechanism, even a simple one, necessitates both experimental and theoretical arguments.

3 - NON-CHAIN REACTIONS

Non-chain reactions are also called **open sequence** reactions, this adjective possibly better indicates their fundamental difference with **closed sequence** reactions, to which category so-called chain reactions and catalytic reactions belong, whether they are homogeneous or heterogeneous.

In an open sequence radical reaction, the free radicals created in one step disappear in another, later step, but never regenerate a free radical involved in a previous step. In general, the rate of reaction is therefore determined by the most difficult step.

As a result, non-chain reactions possess a certain number of kinetic characteristics which are analogous to those of molecular reactions, that is a certain insensitivity to the nature and the relative area of the walls of the reactor and to the addition of substances which inhibit radical reactions.

3.1 - The pyrolysis of tertiary dibutyl peroxide

This reaction, carried out in the gas phase between about 120 and 300 °C, gives mainly acetone and ethane according to the following stoichiometric equation :

$$(CH_3)_3C\text{–}O\text{–}O\text{–}C(CH_3)_3 \longrightarrow 2\,CH_3COCH_3 + C_2H_6 \qquad (29)$$

The experimental study has permitted the following kinetic law, of order 1, to be established :

$$r_{29} = k_{29}\,[\text{peroxide}] \qquad (30)$$

The rate constant k_{29} has an activation energy $E_{29} \simeq 155$ kJ mol^{-1}.

The following mechanism has been proposed to take these observations into account :

$$(CH_3)_3C\text{–}O\text{–}O\text{–}C(CH_3)_3 \longrightarrow 2\,(CH_3)_3CO^{\bullet} \qquad (31)$$

$$(CH_3)_3CO^{\bullet} \longrightarrow CH_3COCH_3 + {}^{\bullet}CH_3 \qquad (32)$$

$$2\,{}^{\bullet}CH_3 \longrightarrow C_2H_6 \qquad (33)$$

First of all, it is obvious that this is really an open sequence reaction mechanism, as the two free radicals involved in this mechanism are not regenerated in the step following the one in which they first appear.

The mechanism really is compatible with the stoichiometric equation. In fact, if the sum of the equations (31) + 2×(32) + (33) is carried out, equation (29) is found again.

In order to obtain the kinetic law, the QSSA is applied to the two free radicals ; the following relationships are thus obtained :

$$2\,r_{31} - r_{32} = 0 \tag{34}$$

$$r_{32} - 2\,r_{33} = 0 \tag{35}$$

i.e. :

$$r_{32} = 2\,r_{31} = 2\,k_{31}\,[\text{peroxide}] \tag{36}$$

$$r_{33} = r_{31} = k_{31}\,[\text{peroxide}] \tag{37}$$

The expression for the rate r of consumption of peroxide, is deduced :

$$r = r_{31} = k_{31}\,[\text{peroxide}] \tag{38}$$

Law (30) is effectively found to be of order 1.

The activation energy E_{31} is close to the peroxide bond dissociation energy, that is 155 kJ mol^{-1}, which is reasonably compatible with the experimental activation energy E_{29}. Note lastly that $R_{\text{acetone}} = 2\,r_{31}$ and $R_{\text{ethane}} = r_{31}$, which effectively indicates that reaction (31) is the rate-determining step.

Reaction (31) is not affected by the presence of acetone or ethane, and the reaction therefore has no auto-accelerating or auto-inhibiting character. The addition of inhibitors of radical chain reactions has no effect, which is normal for a non-chain reaction, controlled by the initiation step. On the contrary, the addition of tertiary dibutyl peroxide accelerates chain reactions by the creation of free radicals at low temperature. This property is used to start off radical polymerizations ; it is also the source of degenerate branching (§ 6) likely to lead to explosions. The accumulation of peroxides in a reaction mixture undergoing recycling constitutes a potential cause of industrial accidents. Taking all these arguments into account, the proposed mechanism appears to be reasonably well established.

3.2 - The thermal decomposition of ozone

As was discussed earlier, ozone plays an important part in the chemistry of the troposphere, where its excess is harmful, and in stratospheric chemistry, where its shortage is also detrimental. Ozone can decompose by several mechanisms : thermal, photochemical, homogeneous catalysis reactions and under the action of solid surfaces. In the laboratory, the latter effect can be controlled by a suitable treatment of the reactor walls, as well as by a study of the rate of reaction as a function of the surface/volume ratio. In order to eliminate photochemical and homogeneous catalysis reactions, the chemical reaction must be carried out in the absence of radiations and catalytic additives, such as halogenated substances. The mechanism put forward to interpret the thermal reaction, can be written as follows :

$$O_3 + M \rightleftharpoons O + O_2 + M \qquad (39)$$

$$O + O_3 \longrightarrow 2\,O_2 \qquad (40)$$

This is an open sequence reaction, as the O atom produced by reaction (39) disappears in reaction (40) without being regenerated later on.

In order to establish the kinetic laws of the reaction, the QSSA is applied first of all to the very reactive intermediate O :

$$r'_{39} - r''_{39} - r_{40} = 0 \qquad (41)$$

The following expression for the quasi-stationary concentration of the O atom is deduced :

$$[O] = \frac{k'_{39}\,[O_3]\,[M]}{k''_{39}\,[O_2]\,[M] + k_{40}\,[O_3]} \qquad (42)$$

The rate of consumption of ozone can be written as follows :

$$r = r'_{39} - r''_{39} + r_{40} = 2\,r_{40} \qquad (43)$$

Two limiting cases of this law can be considered :

a) If $[O_3]/[O_2] << k''_{39}\,[M]/k_{40}$, i.e. when the ozone is very much diluted in oxygen, the following expression can be written :

$$[O] \simeq \frac{k'_{39}\,[O_3]}{k''_{39}\,[O_2]} = K_{c39}\,\frac{[O_3]}{[O_2]} \qquad (44)$$

Equation (44) means that reaction (39) is at quasi-equilibrium. The rate of reaction can be written :

$$r \simeq 2\,k_{40}\,K_{c39}\,\frac{[O_3]^2}{[O_2]} \qquad (45)$$

The rate has an order of 2 with respect to O_3 and of -1 with respect to O_2.

b) If $[O_3]/[O_2] >> k''_{39}\,[M]/k_{40}$, the following relationships can be written :

$$[O] \simeq k'_{39}\,[M]/k_{40} \qquad (46)$$

and :

$$r \simeq 2\,k'_{39}\,[O_3]\,[M] \qquad (47)$$

Therefore, when the ozone concentration becomes very high, the rate-determining step is the forward reaction (39). The rate is of order 1 with respect to O_3 ; moreover, it is proportional to the total pressure, characterized by the quantity [M]. **The rate can** therefore, under these conditions, **be increased by the addition of an inert substance**. Experimental observations confirm the above limiting laws, this gives the mechanism a suitable plausibility.

4 - STRAIGHT CHAIN REACTIONS

In a straight chain reaction, free radicals are created by **the initiation** reactions and destroyed by the **termination** reactions. Certain free radicals called chain carriers **propagate** the overall reaction by a set of elementary reactions forming at least one **closed sequence**, i.e. a given free radical reacting at the beginning of the sequence is regenerated at the end of the sequence. Consequently, starting with only one free radical created during the initiation, the closed sequence can be repeated a large number of times, like the links in a chain, before the chain is stopped by a termination.

The closed sequence radical reaction introduces a multiplicative kinetic factor with respect to the initiation so that there is a certain analogy with homogeneous and heterogeneous catalysis, which is also characterized by the existence of closed sequences. However, a big difference exists between chain reactions and so-called catalytic reactions. In fact, in catalytic reactions, the total number of active centres is fixed, whereas that of chain reactions is determined by the competition between the initiation and termination reactions. The rate of a chain reaction is therefore a function of both the kinetic characteristics of the initiation, propagation and termination reactions.

In what follows, the principal characteristics of straight chain reactions will be discussed for the case of the pyrolysis of neopentane, which will then allow the kinetic rules ß μ Y, which are useful for the generation of reaction mechanisms to be discussed.

4.1 - The pyrolysis of neopentane : experimental facts

a) Experimental studies

This reaction has been studied using batch reactors, perfectly stirred continuous reactors, tubular continuous reactors, BENSON type reactors, wall-less reactors and shock tubes. The reaction has been carried out at temperatures between 700 and 1300 K, at pressures of 0.1 Pa to 10^7 Pa and at reaction times of 10^{-5} s to 10^3 s. The effects of the nature and of the area of the reactor walls as well as those of various additives have also been studied. The diversity of the studies carried out by a dozen teams throughout the world, the particularly widespread range of operating conditions (600 K for the temperature, which represents 11 orders of magnitude for the rate of initiation, 8 orders of magnitude for the pressure and reaction duration) make the pyrolysis of neopentane into a **model radical reaction**.

The main experimental results given in Chapter III and especially in Figures 2 to 6 will be summarized in the following two sub-paragraphs, and some complementary observations will be added.

b) Products of the reaction

There is a quasi-general agreement amongst all the experimentalists about the identity of the products of the reaction and about their primary or secondary nature. The primary products include isobutene, methane, hydrogen and ethane, the secondary products include methyl-2 butene-1, propene, ethylene, allene, isoprene, propyne and methyl-2 butene-2, classed by decreasing order of importance.

The relative importance of the primary products varies much with the temperature :

— At "low" temperatures (around 500 °C), essentially isobutene and methane are formed in approximately equal quantities, the proportions of hydrogen and of ethane are much lower.

— At "high" temperatures (above 700 °C), primarily more isobutene than methane is formed and hydrogen and ethane are formed in equal proportions, the latter two substances being no longer miner products with respect to the first two.

c) Kinetic laws

The reaction has been studied by changing the nature and the surface/volume ratio of the reactor walls. The effects of these factors on the chemistry or on the kinetics are not very pronounced. Therefore, the reaction must be considered to be essentially homogeneous. The agreement between the results obtained using very different reactors confirms this.

The overall order of the reaction at about 500 °C at a conversion equal to zero, is close to 3/2 at a high enough pressure and falls a little when the pressure decreases. The overall activation energy is approximately equal to 210 kJ mol^{-1}. At higher temperatures, at about 700 °C, the overall order of reaction becomes lower than 3/2 and the activation energy tends progressively towards 345 kJ mol^{-1}.

The rate of pyrolysis of neopentane is strongly decreased by the addition of propene or of isobutene. The reaction is therefore believed to be strongly auto-inhibited by the isobutene formed, this is expressed in particular, by a current order of reaction which varies with the extent of the reaction and is much higher than the order at conversion equal to zero.

4.2 - Primary mechanism for the pyrolysis of neopentane

A **primary** mechanism uses as reactants the molecules included in the reaction load, i.e. neopentane in the present case, and free radicals arising from it, with the exclusion of the products which are formed. If the reactions of the primary products are taken into account, this is then a secondary mechanism, which is necessarily more complicated. On principle, a primary mechanism only takes the experimental results at **conversion equal to zero** into account, which can therefore only be obtained by **extrapolation**. It is advisable to be extremely careful about the choice of the extrapolation technique, which is likely to introduce large errors.

a) Mechanism

The mechanism includes the following elementary reactions :

$$\textbf{Initiation}\quad\left\{\begin{array}{rcl} C_5H_{12} & \longrightarrow & {}^\bullet C(CH_3)_3 + {}^\bullet CH_3 \\ {}^\bullet C(CH_3)_3 & \longrightarrow & iC_4H_8 + {}^\bullet H \\ {}^\bullet H + C_5H_{12} & \longrightarrow & H_2 + {}^\bullet C_5H_{11} \\ {}^\bullet C(CH_3)_3 + C_5H_{12} & \longrightarrow & iC_4H_{10} + {}^\bullet C_5H_{11} \end{array}\right. \qquad \begin{array}{r} (48) \\ (49) \\ (50) \\ (51) \end{array}$$

$$\textbf{Propagation}\quad\left\{\begin{array}{rcl} {}^\bullet C_5H_{11} & \longrightarrow & iC_4H_8 + {}^\bullet CH_3 \\ {}^\bullet CH_3 + C_5H_{12} & \longrightarrow & CH_4 + {}^\bullet C_5H_{11} \end{array}\right. \qquad \begin{array}{r} (52) \\ (53) \end{array}$$

$$\textbf{Termination}\quad 2\,{}^\bullet CH_3\ (+M) \longrightarrow C_2H_6\ (+M) \qquad (54)$$

This mechanism involves a closed sequence, or chain, consisting of reactions (52) and (53). The two free radical chain carriers are the neopentyl radical ${}^\bullet C_5H_{11}$ and the methyl radical ${}^\bullet CH_3$. The chain propagation reactions do not change the number of free radicals. Free radicals are formed by the open reaction sequence (48) to (51). Each time that this sequence occurs, two free radical chain carriers appear. The free radicals disappear by the termination reaction (54). The propagations result in the formation of iC_4H_8 and CH_4, the initiation sequence (48)-(51) in iC_4H_8, H_2 and iC_4H_{10}, and the termination in C_2H_6.

b) Quasi-stationary kinetic laws

Applying the QSSA globally to the radicals gives the following relationship :

$$2\,k_{48}\,[C_5H_{12}] = 2\,k_{54}\,[{}^\bullet CH_3]^2 \qquad (55)$$

The factors 2 indicate that the initiation (48) creates 2 free radicals and that the termination (54) makes 2 disappear. The following expression for the concentration of the methyl radicals is thus obtained :

$$[{}^\bullet CH_3] = \left(\frac{k_{48}}{k_{54}}\right)^{1/2} [C_5H_{12}]^{1/2} \qquad (56)$$

It is important not to forget that the rate constant k_{54} varies with the pressure, which is indicated by the notation (+M) in equation (54).

The rates of formation of CH_4 and C_2H_6 are deduced from the above :

$$R_{CH_4} = r_{53} = k_{53} \left(\frac{k_{48}}{k_{54}}\right)^{1/2} [C_5H_{12}]^{3/2} \tag{57}$$

$$R_{C_2H_6} = k_{48} [C_5H_{12}] \tag{58}$$

Applying the QSSA to the $^\bullet C_4H_9$, $^\bullet H$ and $^\bullet C_5H_{11}$ radicals gives the following expressions :

$$[^\bullet C_4H_9] = \frac{k_{48} [C_5H_{12}]}{k_{49} + k_{51} [C_5H_{12}]} \tag{59}$$

$$[^\bullet H] = \frac{k_{48}}{k_{50}} \frac{k_{49}}{k_{49} + k_{51} [C_5H_{12}]} \tag{60}$$

$$[^\bullet C_5H_{11}] = \frac{k_{48} [C_5H_{12}]}{k_{52}} \frac{k_{49}}{k_{49} + k_{51} [C_5H_{12}]} + \frac{k_{53}}{k_{52}} \left(\frac{k_{48}}{k_{54}}\right)^{1/2} [C_5H_{12}]^{3/2} \tag{61}$$

The following kinetic laws are deduced from the above expressions :

$$R_{C_4H_{10}} = k_{48} [C_5H_{12}] \frac{k_{51} [C_5H_{12}]}{k_{49} + k_{51} [C_5H_{12}]} \tag{62}$$

$$R_{H_2} = k_{48} [C_5H_{12}] \frac{k_{49}}{k_{49} + k_{51} [C_5H_{12}]} \tag{63}$$

$$R_{C_4H_8} = k_{48} [C_5H_{12}] \left(1 + \frac{k_{49}}{k_{49} + k_{51} [C_5H_{12}]}\right) + k_{53} \left(\frac{k_{48}}{k_{54}}\right)^{1/2} [C_5H_{12}]^{3/2} \tag{64}$$

The above kinetic laws can be simplified for two **limiting cases** : at "low" temperature (around 500 °C) and at "high" temperature (above 700 °C).

c) Long chain reaction

This case is encountered when the principal products of the reaction come from the chain and the minor products from the initiation and termination reactions. The chain length can be defined by the following ratio :

$$\lambda = \frac{R_{CH_4}}{R_{C_2H_6}} = \frac{k_{53} [C_5H_{12}]^{1/2}}{(k_{48} k_{54})^{1/2}} \tag{65}$$

CH_4 being a product which is characteristic of the chain and C_2H_6 of the termination. The activation energy of the chain length has the following expression :

$$E_\lambda = E_{53} - \frac{1}{2} (E_{48} + E_{54}) \tag{66}$$

Now, it is known that $E_{53} \simeq 40$ kJ mol^{-1}, $E_{48} \simeq 345$ kJ mol^{-1}and $E_{54} \simeq 0$, therefore :

$$E_\lambda \simeq -133 \text{ kJ mol}^{-1}$$

which implies that the chain length increases very much when the temperature is decreased. Moreover, as $E_{49} > E_{51}$, the value of the ratio $k_{49}/k_{51}[C_5H_{12}]$ decreases when the temperature decreases.

The following consequences are deduced :

- the principal primary products of the reaction are CH_4 and iC_4H_8 ; C_2H_6, C_4H_{10} and H_2 are minor primary products ;
- the rates of appearance of CH_4 and iC_4H_8 are practically equal and the order is close to 3/2. This order decreases when the pressure decreases due to the variation in the constant k_{54} ;
- the activation energy for the formation of methane is as follows :

$$E = E_{53} + \frac{1}{2} E_{48} = 212 \text{ kJ mol}^{-1}$$

These consequences of the mechanism are in good agreement with the experimental results recalled above and already described in Chapter III.

d) Short chain reaction

This occurs at temperatures which are high enough : the chain length decreases and, moreover, the ratio $k_{49}/k_{51}[C_5H_{12}]$ increases. The following consequences are deduced from the kinetic laws (57) to (64) :

- the principal primary products of the reaction include, as well as CH_4 and iC_4H_8, C_2H_6 and H_2 ; trace quantities of C_4H_{10} are found ;
- the rates of appearance of C_2H_6 and H_2 are practically equal, and of order 1 with respect to neopentane ;
- the rate of formation of C_4H_8 is higher than that of CH_4 ; the order of formation of CH_4 is equal to or a little lower than 3/2, whereas that of C_4H_8 is a little lower than that of CH_4 ; however, it remains higher than 1 ;
- the rate laws (63) and (58) allow the rate constant k_{48} to be determined. The study of the variations of this constant as a function of the temperature allows A_{48} and E_{48} to be estimated. The value $E_{48} \simeq 345$ kJ mol^{-1} is found. This activation energy is also equal to the dissociation energy of the C–C bond of neopentane. When the chains become especially short, i.e. in fact, when the reaction becomes practically a non-chain reaction, the overall activation energy tends to the value of 345 kJ mol^{-1}.

The experimental results at conversion nearly equal to zero confirm all these conclusions which have been deduced from the mechanism.

4.3 - Mechanism of inhibition by isobutene

When a mixture of neopentane and isobutene is pyrolysed, the primary mechanism of reaction includes a metathesis reaction analogous to (53), but involving isobutene, as well as reactions (48) to (54) :

$$^{\bullet}CH_3 + C_4H_8 \longrightarrow CH_4 + {}^{\bullet}C_4H_7 \qquad (67)$$

The isobutenyl free radical $^{\bullet}CH_2{-}C(CH_3){=}CH_2$ is stabilized by resonance and, consequently, is much less reactive than the neopentyl or the methyl radical. Two consequences result from this :

- as a first approximation, the decomposition or metathesis reactions of this radical can be neglected ;
- on the contrary, due to its high concentration, it can be involved in termination processes :

$$^{\bullet}CH_3 + {}^{\bullet}C_4H_7 \longrightarrow C_5H_{10} \qquad (68)$$

$$^{\bullet}C_4H_7 + {}^{\bullet}C_4H_7 \longrightarrow C_8H_{14} \qquad (69)$$

The new rate laws, which take the reactions (67) to (69) into account, can be established using the global QSSA :

$$2\,k_{48}\,[C_5H_{12}] = 2\,k_{54}\,[^{\bullet}CH_3]^2 + 2\,k_{68}\,[^{\bullet}CH_3]\,[^{\bullet}C_4H_7] + 2\,k_{69}\,[^{\bullet}C_4H_7]^2 \qquad (70)$$

and applying it to the $^{\bullet}C_4H_7$ radical :

$$k_{67}\,[^{\bullet}CH_3]\,[C_4H_8] = k_{68}\,[^{\bullet}CH_3]\,[^{\bullet}C_4H_7] + 2\,k_{69}\,[^{\bullet}C_4H_7]^2 \qquad (71)$$

Relationships (70) and (71) can be simplified using the so-called crossed-constants approximation, coming from the kinetic theory of gases :

$$k_{68} \simeq 2\left(k_{54} \times k_{69}\right)^{1/2} \qquad (72)$$

The rate of production of CH_4 has the following expression :

$$r = k_{53}\,[^{\bullet}CH_3]\,[C_5H_{12}] + k_{67}\,[^{\bullet}CH_3]\,[C_4H_8] \qquad (73)$$

Using relationships (70) to (72), gives, finally :

$$r = r_o\,\frac{1 + a\,[C_4H_8]/[C_5H_{12}]}{1 + b\,[C_4H_8]/[C_5H_{12}]} \qquad (74)$$

where :

$$r_o = k_{53}\left(\frac{k_{48}}{k_{54}}\right)^{1/2}[C_5H_{12}]^{3/2} \qquad (75)$$

$$a = k_{67}/k_{53} \qquad (76)$$

$$b = \frac{k_{67}\,[C_5H_{12}]^{1/2}}{2\left(k_{48}\,k_{54}\right)^{1/2}} \qquad (77)$$

r_0 is the rate of formation of CH_4, at conversion of C_5H_{12} equal to zero, in the absence of C_4H_8, whereas r is the rate, still at zero conversion of C_5H_{12}, but in the presence of C_4H_8.

The coefficient a expresses the accelerating influence of C_4H_8, due to reaction (67) and the coefficient b the inhibiting influence of the terminations (68) and (69). The overall influence of C_4H_8 is inhibiting if $b > a$, i.e. :

$$\frac{k_{53}\,[C_5H_{12}]^{1/2}}{2\left(k_{48}\,k_{54}\right)^{1/2}} > 1 \qquad (78)$$

This relationship is actually verified here, as the term on the left of the equation is nothing other than $\lambda/2$ (eqn 65).

In Chapter III it was shown that the relationship (74) was suitably verified by experiment.

The inhibition mechanism of the pyrolysis of neopentane in the presence of isobutene can be used to explain the auto-inhibition of the pyrolysis of neopentane by the isobutene formed during the reaction.

4.4 - Kinetic rules ß µ Y

a) µH mechanism

The primary mechanism of the pyrolysis of neopentane can be generalized to the case of an organic substance µH possessing a **labile H atom**. The mechanism proposed by GOLDFINGER, LETORT and NICLAUSE is the following :

$$\begin{array}{lcll}
\mu H & \longrightarrow & 2 \text{ free radicals} & (ui) \\
\left\{\begin{array}{l} {}^\bullet\mu \\ {}^\bullet\text{ß} + \mu H \end{array}\right. & \begin{array}{c} \longrightarrow \\ \longrightarrow \end{array} & \begin{array}{l} {}^\bullet\text{ß} + m \\ \text{ß}H + {}^\bullet\mu \end{array} & \begin{array}{l} (bs) \\ (me) \end{array} \\
\left\{\begin{array}{l} {}^\bullet\text{ß} + {}^\bullet\text{ß} \\ {}^\bullet\text{ß} + {}^\bullet\mu \\ {}^\bullet\mu + {}^\bullet\mu \end{array}\right. & \begin{array}{c} \longrightarrow \\ \longrightarrow \\ \longrightarrow \end{array} & \vdots\ \text{products} & \begin{array}{l} (\text{ßß}) \\ (\text{ß}\mu) \\ (\mu\mu) \end{array}
\end{array}$$

It includes a unimolecular initiation reaction (ui) leading, by transfer reactions, which have not been written, to the free radical chain carriers •ß or •µ. The chain is propagated by the reactions (bs) and (me) and gives rise to products m and ßH. The free radical •µ decomposes by a **m**onomolecular reaction, whereas the free radical •ß reacts in a **b**imolecular reaction ; the initial letters of these two adjectives have given their Greek symbols to the two types of radical. The free radicals •ß and •µ are called **chain carriers**. The termination reactions include the two by two recombination or disproportionation of two chain-carrier free radicals. The products of termination, as well as the products of transfer, are not given, which is the same as implying that the chains are long. The main stoichiometry of the reaction can therefore be written :

$$\mu H \longrightarrow m + ßH \tag{79}$$

The products formed during the initiation and termination reactions are in quantities which are negligible with respect to m and ßH.

The kinetic laws deduced from this mechanism are calculated using the QSSA and the LCA.

The global QSSA gives the following relationship :

$$2\,k_{ui}\,[\mu H] = 2\,k_{ßß}[^{\bullet}ß]^2 + 2\,k_{ß\mu}[^{\bullet}ß][^{\bullet}\mu] + 2\,k_{\mu\mu}[^{\bullet}\mu]^2 \tag{80}$$

The approximation using crossed termination constants can be written :

$$k_{ß\mu} \approx 2\left(k_{ßß} \cdot k_{\mu\mu}\right)^{1/2} \tag{81}$$

Equation (80) can then be written more simply :

$$k_{ui}^{1/2}\,[\mu H]^{1/2} = k_{ßß}^{1/2}\,[^{\bullet}ß] + k_{\mu\mu}^{1/2}\,[^{\bullet}\mu] \tag{82}$$

The long chain approximation (LCA) consists in applying the QSSA to the propagations only :

$$k_{me}\,[^{\bullet}ß]\,[\mu H] = k_{bs}\,[^{\bullet}\mu] \tag{83}$$

Two limiting cases are deduced :

— *1st limiting case:*

$$k_{bs} >> k_{me}\,[\mu H] \tag{84}$$

This inequality means that beta-scission is much easier than metathesis. As a result, the concentration of the $^{\bullet}\mu$ radicals is much lower than the $^{\bullet}ß$ radicals. The term $k_{\mu\mu}^{1/2}[^{\bullet}\mu]$ in equation (82), can then be neglected with respect to $k_{ßß}^{1/2}[^{\bullet}ß]$, as the rate constants $k_{\mu\mu}$ and $k_{ßß}$ are of the same order of magnitude (i.e.10^{13} mol^{-1} cm^3 s^{-1}), therefore :

$$[^{\bullet}ß] = \left(\frac{k_{ui}}{k_{ßß}}\right)^{1/2}\,[\mu H]^{1/2} \tag{85}$$

and the rate of reaction can be expressed by the following :

$$r_{79} = k_{me}\,[^{\bullet}ß]\,[\mu H] = k_{me}\left(\frac{k_{ui}}{k_{ßß}}\right)^{1/2}\,[\mu H]^{3/2} \tag{86}$$

This law is of order 3/2, if the rate constants k_{ui} and $k_{ßß}$ do not depend on the pressure. The **determining propagation** reaction is the bimolecular reaction (me), as it is the rate constant k_{me} which appears in law (86). In the same way, the **determining termination** reaction is the reaction (ßß), as it is the rate constant $k_{ßß}$ which appears in equation (86). The **free radical $^{\bullet}$ß is** said to be **determining**, as this radical is involved in the

terminations, and is the most abundant in the reaction medium.
It is fitting to remark that the LCA (83) can be written as follows :

$$r_{bs} = r_{me} \tag{87}$$

which means that the two propagation reactions take place at the same rate. This can appear surprising a priori, in so far as it is the (me) reaction which determines the global rate. In fact, it is the most **difficult** reaction which determines the rate. It is therefore erroneous to speak of a "slow" reaction for (me) and a "fast" reaction for (bs).
The law for the pyrolysis of neopentane is again found, but it also applies to the pyrolysis of ethanal and numerous other organic substances.

— *2nd limiting case:*

$$k_{bs} << k_{me}\,[\mu H] \tag{88}$$

This inequality means that the decomposition of the $^\bullet\mu$ radical is more difficult than the reaction of the $^\bullet\beta$ radical with μH. As a result, the determining radical is the $^\bullet\mu$ radical, i.e. the least reactive and the most abundant radical, the determining termination is the ($\mu\mu$) termination and the determining propagation is the (bs) decomposition. The calculation is carried out in an analogous way to that used in the 1st limiting case and gives the following rate law :

$$r_{79} = k_{bs}\left(\frac{k_{ui}}{k_{\mu\mu}}\right)^{1/2} [\mu H]^{1/2} \tag{89}$$

This is a kinetic law of order 1/2. In particular, this law can be applied to the pyrolysis of ethane :

Initiation

$$C_2H_6\ (+M) \longrightarrow 2\ ^\bullet CH_3\ (+M) \tag{90}$$

$$^\bullet CH_3 + C_2H_6 \longrightarrow CH_4 + {}^\bullet C_2H_5 \tag{91}$$

Propagation

$$^\bullet C_2H_5 \longrightarrow {}^\bullet H + C_2H_4 \tag{92}$$

$$^\bullet H + C_2H_6 \longrightarrow H_2 + {}^\bullet C_2H_5 \tag{93}$$

Termination

$$2\ ^\bullet C_2H_5 \longrightarrow n\ C_4H_{10} \tag{94}$$

b) Free radicals β, μ and $\beta\mu$

The mechanism μH involves two types of radicals which react in two very different ways in the propagation reactions.

— The ß radicals react only by bimolecular reactions of metathesis, i.e. they are not supposed to decompose at all by monomolecular reactions. Stricto sensu, this is the case for the free atoms $^{\bullet}H$, $^{\bullet}O^{\bullet}$, $^{\bullet}Cl$... This remains true for small free radicals such as $^{\bullet}OH$, $^{\bullet}CH_3$, $^{\bullet}NH_2$... which decompose with great difficulty, except at the very high temperatures encountered in flames for example (1800 K and over).

— The μ radicals decompose easily by monomolecular reactions, even at low temperatures (lower than 800 K). This is especially so of the alkyl radicals which are likely to decompose by the breaking of a C–C bond, for example :

$$CH_3-CH_2-CH_2^{\bullet} \longrightarrow {}^{\bullet}CH_3 + CH_2=CH_2 \qquad (95)$$

$$^{\bullet}CH_2-CH(CH_3)_2 \longrightarrow {}^{\bullet}CH_3 + CH_2=CH-CH_3 \qquad (96)$$

$$^{\bullet}CH_2-C(CH_3)_3 \longrightarrow {}^{\bullet}CH_3 + CH_2=C(CH_3)_2 \qquad (52)$$

Reaction (52) occurs in the pyrolysis of neopentane (§ 4.3).

The μ radicals are therefore at a low concentration and their bimolecular metathesis reactions are negligible with respect to those of the ß radicals which are at a much higher concentration. This is also due to the fact that the metathesis reactivities of the μ radicals are of the same order of magnitude as, or lower than, those of the ß radicals.

— A third category of free radical exists, called ßμ, whose behaviour pattern changes with the temperature. The ßμ radicals have a ß behaviour at "low" temperature and a μ behaviour at "high" temperature. This arises from the fact that the decomposition occurs by the breaking of a stronger bond than that of the usual μ radicals and weaker than that of the ß radicals. This is particularly the case of the $^{\bullet}CH_2-CH_3$, $CH_3-{}^{\bullet}CH-CH_3$, $^{\bullet}C(CH_3)_3$, $^{\bullet}CH=CH_2$...radicals which can only decompose by the breaking of a C–H bond which is stronger than the C–C bond :

$$^{\bullet}CH_2-CH_3 \longrightarrow {}^{\bullet}H + CH_2=CH_2 \qquad (92)$$

$$CH_3-{}^{\bullet}CH-CH_3 \longrightarrow {}^{\bullet}H + CH_3-CH=CH_2 \qquad (97)$$

$$^{\bullet}C(CH_3)_3 \longrightarrow {}^{\bullet}H + CH_2=C(CH_3)_2 \qquad (98)$$

Reaction (92) occurs in the mechanism of pyrolysis of ethane (§ 4.5).

The comparison of reactions (52) and (92) allows the deep-seated origin of the difference between the mechanisms of pyrolysis of neopentane (eqns 48 to 54) and of ethane (eqns 90 to 94), at "low" temperatures (lower than 800 K) to be understood.

The neopentyl radical is a very reactive μ radical at negligible concentration with respect to the methyl radical of type ß ; the main termination is therefore of the ßß type. The ethyl radical is a ßμ radical, therefore of the ß type at "low" temperatures, but much less reactive than the H atom ; the main termination is therefore of the ßμ–ßμ type.

c) Kinetic rules ßμ

Taking the relative reactivities of the radicals of types μ, ßμ and ß as a function of the temperature into account, the following rules can be stated, which are useful for the a priori simplification of the reaction mechanisms.

— At "high" temperatures, in flames for example, it is assumed that the radicals ßμ and μ decompose very easily and consequently that the ß radicals are determining. They are therefore the only ones to be involved in the termination reactions and in the bimolecular reactions.

— At "intermediate" temperatures, the determining radicals become the ß and ßμ radicals.

— Lastly, at "low" temperatures (slow oxidation, cool flames...), the μ radicals can be involved in certain categories of bimolecular reactions, such as additions to oxygen.

d) μH, YH mechanism

The pyrolysis mechanism of a substance μH in the presence of an additive YH includes the following reactions, as well as the reactions of the μH mechanism alone (§ a) :

$$\begin{array}{lll} \mathrm{YH} & \longrightarrow 2\ \text{free radicals} & \text{(ui')} \end{array}$$

$$\left\{\begin{array}{lll} {}^\bullet\beta + \mathrm{YH} & \longrightarrow \beta\mathrm{H} + {}^\bullet\mathrm{Y} & \text{(me')} \\ {}^\bullet\mathrm{Y} + \mu\mathrm{H} & \rightleftharpoons \mathrm{YH} + {}^\bullet\mu & \text{(me'')} \end{array}\right.$$

$$\left\{\begin{array}{lll} {}^\bullet\beta + {}^\bullet\mathrm{Y} & \longrightarrow \beta\mathrm{Y} & (\beta\mathrm{Y}) \\ {}^\bullet\mu + {}^\bullet\mathrm{Y} & \longrightarrow \mu\mathrm{Y} & (\mu\mathrm{Y}) \\ {}^\bullet\mathrm{Y} + {}^\bullet\mathrm{Y} & \longrightarrow \mathrm{YY} & (\mathrm{YY}) \end{array}\right.$$

This supplementary mechanism includes a unimolecular initiation reaction (ui'), two (me') and (me") reactions which form, with the (bs) reaction a new chain with an identical stoichiometric equation to that of the pure substance ($\mu\mathrm{H} \rightarrow \mathrm{m} + \beta\mathrm{H}$), and three termination reactions involving the $^\bullet$Y radical.

The calculation of the kinetic law from the complete mechanism is very complicated and it appears reasonable to treat the limiting case already discussed in the § 4.4 dealing with the inhibition of the pyrolysis of neopentane by isobutene. The following hypotheses can be made :

- the reaction of μH in the absence of YH occurs by a long chain mechanism with preponderant (ßß) termination,
- the addition of YH induces the negligible initiations (ui') ,
- the $^\bullet$Y radical formed is not very reactive so that the forward reaction (me") is negligible ; the (me") reverse reaction is negligible with respect to the (me') reaction, as the $^\bullet\mu$ radical is less abundant than the $^\bullet$ß radical,

- the new terminations (ßY) and (YY) are the only ones taken into account, in agreement with the fact that the terminations involving the μ radical are negligible.

With these hypotheses, kinetic laws analogous to the laws (74) to (78) are found again :

$$r = r_o \frac{1 + a\,[YH]/[\mu H]}{1 + b\,[YH]/[\mu H]} \tag{99}$$

$$r_o = k_{me} \left(k_{ui}/k_{ßß}\right)^{1/2} [\mu H]^{3/2} \tag{100}$$

$$a = k_{me'}/k_{me} \tag{101}$$

$$b = \frac{k_{me'}\,[\mu H]^{1/2}}{2\left(k_{ui}\,k_{ßß}\right)^{1/2}} \tag{102}$$

where $b > a$.

These equations simply mean that the additive YH inhibits the pyrolysis reaction of the substance µH, due to the disappearance of the $^{\bullet}$Y radicals by termination.

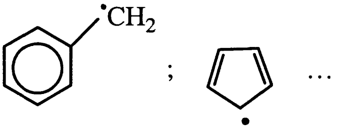
e) Kinetic rules Y

The following rules are deduced from the above.

When a gas-phase thermal reaction involves molecules of the type YH which are likely to form free radicals of the allylic type $^{\bullet}$Y, which are stabilized by resonance, by the abstraction of an H atom, the terminations involving these radicals must be taken into account, i.e. :

- at high temperatures, the terminations (ßY),
- at intermediate temperatures, the terminations ßY and (ßµ, Y).

Typical types of $^{\bullet}$Y radicals are the allyl •CH2/CH//CH2, the isobutenyl radical •CH2/C(CH3)//CH2, the propargyl radical •CH2/C///CH, and the following radicals :



5 -BRANCHED CHAIN REACTIONS

Straight chain reactions include three main categories of elementary reactions :

- the **initiation** reactions which create free radicals from molecules of the reactants ;
- the **propagation** reactions which conserve the number of free radicals ;
- the reactions of **quadratic termination** which destroy two free radicals by combination or gas-phase disproportionation.

Branched chain reactions involve two new classes of elementary reactions :

- **branching** reactions which create two free radicals from only one free radical. It can be easily understood that this reaction causes an exponential growth in the concentration of the radicals, which can cause so-called **isothermal explosions**. It is precisely due to this chemical explanation of explosions that C. HINSHELWOOD and N. SEMENOV won their NOBEL Prize in 1956 ;
- **linear termination** reactions which cause the disappearance of a free radical by interaction with the reactor wall, and which cancel out the effects of branching[1].
  The rate of these heterogeneous terminations can be limited by the **diffusion** of the free radicals towards the walls, which itself depends on the **pressure**. The effectiveness of the linear terminations is also a function of the **surface/volume ratio** and of the **nature** of the reactor walls. All these operating parameters must therefore be clearly stated when describing an experiment.

The reaction system $H_2{-}O_2$ has been greatly studied by the works of HINSHELWOOD and SEMENOV in around 1930, and even more with the spatial applications and due to the fact that its mechanism is an integral part of any hydrocarbon oxidation or combustion mechanism. It will therefore be taken as an example to illustrate the theory of branched chain reactions.

5.1 - Explosion limits of the $H_2{-}O_2$ system in a batch reactor

Figure 1 shows a T_0, p_0 diagram, in which there is a Z-shaped curve separating a zone on the left where the reaction is slow from a zone on the right where the reaction becomes explosive. T_0 and p_0 are the initial temperature and pressure of the reaction mixture introduced into the batch reactor. Three parts can be distinguished on this curve, called 1st, 2nd and 3rd limits, respectively. At a given temperature (at 750 K for example) and for a given composition of the initial mixture (stoichiometric, for example), the reaction goes successively, when the initial total pressure p_0 increases, from a slow reaction ($p_0 < p_1$) to an explosive reaction ($p_1 < p_0 < p_2$), then to a slow reaction ($p_2 < p_0 < p_3$), to become an explosive reaction again at very high pressures ($p_0 > p_3$). The critical pressure p_1 decreases when the temperature increases, like the limit p_3, whereas the critical pressure p_2 increases.

Moreover, the limits p_1, p_2, p_3 depend on other operating parameters ; this is not indicated in the "mean" diagram shown in Figure 1.

The limit p_1 decreases when the dimensions of the reactor increase, i.e. when the S/V ratio decreases, and when an inert gas is added. It depends strongly on the nature of the

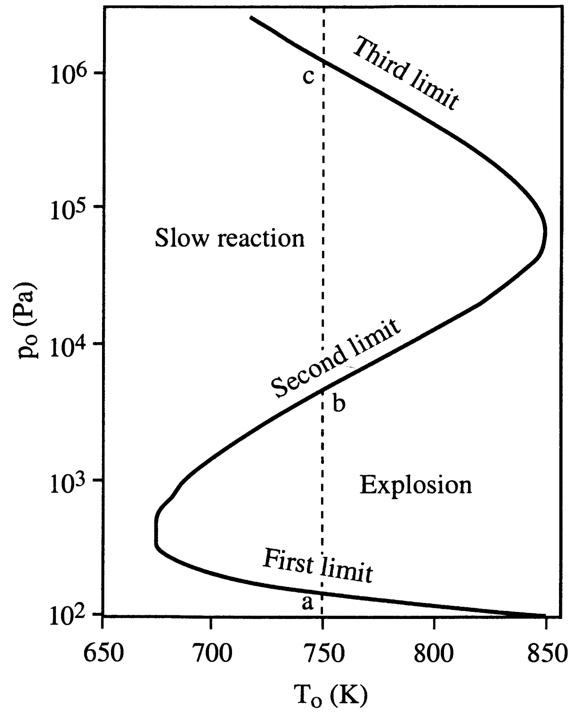
---

[1] This type of reaction allows the way in which the DAVY lamp for miners works, to be explained : the grid blocks the exit of the free radicals present in the flame.

reactor walls. Therefore a treatment of the walls by KOH or K_2HPO_4 gives a limit p_1, which is two orders of magnitude higher than the limit obtained by treatment with B_2O_3, or an acid wash, whereas a treatment with KCl or NaCl gives intermediate limits. At a given initial pressure p_0, the initial composition of the mixture has a decisive impact on the limit p_1, the explosion is triggered off as soon as the mole fraction of oxygen exceeds a critical threshold.

The limit p_2, unlike the limit p_1, is not very sensitive to the nature and the relative area of the reactor walls.

Figure 1 : Explosion limits of an H_2/O_2 mixture in a batch reactor.



5.2 - Interpretation of the limits

a) First limit

The simplest possible reaction mechanism likely to take the experimental observations relative to the first limit into account, is the following :

$$H_2 + O_2 \longrightarrow {}^{\bullet}H + HO_2^{\bullet} \qquad (103)$$

$$\left\{\begin{array}{lcl} {}^\bullet H + O_2 & \longrightarrow & {}^\bullet OH + {}^\bullet O^\bullet \quad (104) \\ {}^\bullet OH + H_2 & \longrightarrow & H_2O + {}^\bullet H \quad (105) \\ {}^\bullet O^\bullet + H_2 & \longrightarrow & {}^\bullet OH + {}^\bullet H \quad (106) \end{array}\right.$$

$$\left\{\begin{array}{lcl} {}^\bullet H & \longrightarrow & \text{products} \quad (107) \\ HO_2^\bullet & \longrightarrow & \text{products} \quad (108) \end{array}\right.$$

This mechanism includes an initiation (103), propagation reactions (104) to (106) and linear termination reactions at the reactor walls (107) and (108). The propagation reactions (104) and (106) are **branching** reactions, as they multiply the number of free radicals by 2 each time they occur. The $HO_2^\bullet$ radical does not play a kinetic role, which means that it is not very reactive, and its chemical role is minor, if the long chain approximation is assumed, which is the same as saying that the reactants are consumed and the products formed essentially by the reactions (104) to (106).

In order to be able to calculate the kinetic laws from the mechanism, as well as using the LCA, the hypothesis that the ${}^\bullet O^\bullet$ and ${}^\bullet OH$ free radicals are much more reactive than the ${}^\bullet H$ ones will be made. The following quasi-stationary equations are deduced :

$$ {}^\bullet OH \qquad r_{104} - r_{105} + r_{106} = 0 \tag{109}$$

$$ {}^\bullet O^\bullet \qquad r_{104} - r_{106} = 0 \tag{110}$$

and, in addition :

$$\frac{d[{}^\bullet H]}{dt} = r_{103} - r_{104} + r_{105} + r_{106} - r_{107} \tag{111}$$

Taking equations (109) and (110) into account, gives :

$$\frac{d[{}^\bullet H]}{dt} = r_{103} + 2\, r_{104} - r_{107} \tag{112}$$

i.e., finally :

$$\frac{d[{}^\bullet H]}{dt} = k_{103}\, [H_2]\, [O_2] + \left(2\, k_{104}\, [O_2] - k_{107}\frac{S}{V}\right) [{}^\bullet H] \tag{113}$$

Reaction (107) occurs on the surface S of the reactor walls, whereas the balance is carried out for the volume V of the gaseous phase, which necessitates introducing the S/V ratio.

The branching factor is defined by the following relationship :

$$\varphi = 2\, k_{104}\, [O_2] - k_{107}\frac{S}{V} \tag{114}$$

The integration of the equation (113), assuming that the concentrations of H_2 and O_2 are constant, gives the following relationship :

$$[{}^\bullet H] = \frac{k_{103}\, [H_2]\, [O_2]}{\varphi} \left\{\exp(\varphi t) - 1\right\} \tag{115}$$

Two limiting regimes can be distinguished, according to the sign of the branching factor :

— $\varphi < 0$

When the time t increases, the term exp (φt) becomes negligible with respect to -1, and the concentration of the •H atoms has a limiting value :

$$[{}^{\bullet}H] = \frac{k_{103}\,[H_2]\,[O_2]}{|\varphi|} \tag{116}$$

This is a slow reaction.

— $\varphi > 0$

The term exp (φt) increases indefinitely, so that the rate of reaction, which is that of step (2), also increases indefinitely in principle, but the consumption of the reactants has to be taken into account. However, in this situation, the reaction is explosive.

— The critical condition which separates these two regimes is obtained for $\varphi = 0$, i.e. :

$$p_1 = RT\,\frac{k_{107}\,(S/V)}{2\,k_{104}\,x_{O_2}} \tag{117}$$

The activation energy difference ($E_{104} - E_{107}$) is of the order of 70 kJ.mol^{-1}, which means that p_1 decreases when the temperature T increases. The critical pressure also decreases if the mole fraction x_{O_2} of oxygen increases, if the S/V ratio decreases, and if the effectiveness of the walls (characterized by the constant k_{107}) decreases. Equation (117) does not take the effect of the addition of an inert gas into account directly, as the decrease in p_1, which results from this, arises from diffusional limitations.

The proposed mechanism appears therefore to be remarkably compatible with the experimental observations.

b) Second limit

As the pressure is much higher in the neighbourhood of the second limit than at that of the first, the H radicals react in the gaseous phase before reaching the reactor walls :

$${}^{\bullet}H + O_2 + M \longrightarrow HO_2^{\bullet} + M \tag{118}$$

The $HO_2^{\bullet}$ radical is assumed to remain inactive, it therefore has the time to diffuse towards the walls and to disappear by the linear termination reaction (108). Due to this, reaction (118) can be considered to be a radical termination reaction and gives the following expression for the branching factor :

$$\varphi = 2\,k_{104}\,[O_2] - k_{118}\,[O_2]\,[M] \tag{119}$$

The critical conditions are obtained for $\varphi = 0$:

$$p_2 = 2\,RT\,\frac{k_{104}}{k_{118}} \tag{120}$$

The activation energy difference ($E_{104} - E_{118}$) is of the order of 70 kJ mol^{-1} ; consequently, the pressure p_2 increases when the temperature increases, which agrees with the diagram in Figure 1.

c) Third limit

Up to now, the $HO_2^\bullet$ radical was considered to be so poorly reactive that it disappeared only by reactions at the walls. When the pressure nears the third limit, the diffusion of the $HO_2^\bullet$ radicals towards the walls becomes more difficult and they could end up reacting in bimolecular reactions such as :

$$HO_2^\bullet + H_2 \longrightarrow H_2O_2 + {}^\bullet H \qquad (121)$$

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2 \qquad (122)$$

Reaction (121) boosts the propagation (104)-(106), whereas reaction (122) is a termination. But, in fact, both reactions form hydrogen peroxide which can decompose giving two very reactive free radicals :

$$H_2O_2 + M \longrightarrow 2\,{}^\bullet OH + M \qquad (123)$$

Reaction (123) is a **degenerate** branching reaction, as it occurs starting with a product of the primary reaction, and not from the reactants themselves. This topic will be discussed in § 6.

In conclusion, the **simplified** reaction mechanism shown in Paragraphs 5.2 to 5.4 above allows the experimental observations to be taken into account in a semi-quantitative way. The model can be improved in two different ways :

- the development of the techniques for measuring the rate constants of elementary reactions has allowed **detailed** mechanisms of the reaction to be elaborated ;
- it has been implicitly assumed in the preceding calculations that the phenomena were isothermal, i.e. the effects due to the **heats of reaction** and possible **heat transfers** between the reaction medium and the surroundings have been neglected.

Concerning this last point, it is effectively not completely unreasonable to consider that the explosions between the first and second limits occur in a quasi-isothermal manner. In fact, the application of the LCA and the QSSA for the OH and O radicals (eqns 109 and 110) leads to the following global equation for the branching reaction :

$${}^\bullet H + O_2 + 3\,H_2 \longrightarrow 3\,{}^\bullet H + 2\,H_2O \qquad (124)$$

Reaction (124) is very weakly exothermic ($\Delta H^o \simeq -50$ kJ mol^{-1}), which would lead to an adiabatic temperature of reaction of the order of 300 °C. This result validates the approximation of a quasi-isothermal explosion. But, of course, a more or less important fraction of the H radicals recombine, in a homogeneous or heterogeneous way, thus releasing an important amount of heat (435 kJ mol^{-1} for the $2H \rightarrow H_2$ reaction). For example, the reaction :

$$^{\bullet}H + O_2 + 3\,H_2 \longrightarrow {}^{\bullet}H + H_2 + 2\,H_2O \qquad (125)$$

has an exothermicity of 485 kJ mol^{-1}, which would lead to an adiabatic temperature of the order of 3500 °C. For the equation of reaction (125), the explosion would no longer be due to the branching reactions, but indeed to a thermal effect. These are then called **thermal explosions** ; the theory will be developed in Paragraph 7.

Accounting simultaneously for detailed mechanisms and for thermal phenomena constitutes the **unified theory** of explosions.

6 - CHAIN REACTIONS WITH DEGENERATE BRANCHING

The oxidation of hydrocarbons at low temperatures, between 500 and 900 K, is of great importance as these reactions are responsible for the engine knock in spark-ignition engines and the autoignition of diesel fuel in Diesel engines and contribute to the formation of pollutants.

Besides the straight chains and branched chains seen previously, the mechanisms of these oxidations include degenerate branching reactions, which are in fact secondary initiations. This confers a very wide variety of behaviour patterns to these reactions : cool flames, autoignitions, to which must be added a particular phenomenon, the negative temperature coefficient, which consists in a lowering of the rate when the temperature is increased in a region situated around 700 K.

6.1 - The main experimental facts

a) Pressure-temperature diagram

Figure 2 shows a T_0–p_0 diagram for a propane-oxygen mixture of stoichiometric composition introduced into a batch reactor at an initial temperature T_0 and initial pressure p_0. First of all, it must be observed that this diagram is very different from that shown in Figure 1, for a H_2–O_2 mixture.

The following facts can be remarked upon about Diagram 2, by fixing the initial temperature T_0 at 600 K for example, and by increasing the pressure gradually :

- for $p < p_a$, the reaction is slow ;
- for $p_a < p < p_b$, the reaction exhibits one cool flame called CF. A cool flame is characterized by a pulsation of the temperature and of the pressure and by a quasi-simultaneous luminous emission of short duration ;
- for $p_b < p < p_c$, the reaction shows 2 cool flames ;

- for $p_c < p < p_d$, it shows 3 or more of them (Figure 3) ;
- lastly, for $p > p_d$, a second-stage autoignition is observed, which starts with one or more cool flames and ends with the usual autoignition (Figure 4).

To sum up, the T_0–p_0 diagram of propane shows three main zones, one of slow reaction, one of cool flames and one of autoignition, the same is also found for the heavier hydrocarbons, as well as for a large variety of organic substances (ethers, aldehydes, alcohols...).

b) Autoignition delays

When a reaction mixture is under the same conditions of temperature and pressure as in Figure 2, where an autoignition is likely to develop, there is a certain time lapse, called the autoignition delay, before this becomes effective. This delay is important in the Diesel engine but also in the safety of industrial combustion reactions. The measurement of these delays is carried out mainly using batch reactors, rapid compression machines and shock tubes.

The precise experimental definition of a delay depends on the reactor being used and on the properties it is possible to measure. Thus, for a batch reactor, the recording of the pressure increase as a function of time allows the time for which the global rate $d(\Delta p)/dt$ is at a maximum, to be determined. The intersection of the tangent to the curve $\Delta p(t)$ at this point with the horizontal $\Delta p = 0$ gives the value of the delay.

Figure 2 : Pressure-temperature diagram of a propane-oxygen mixture. CF : cool flame.

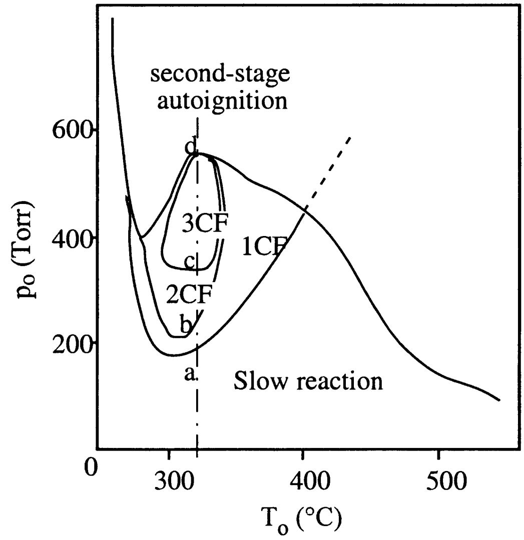


Figure 3 : Cool flames during the oxidation of propane in a perfectly -stirred batch reactor.
$V = 500\ cm^3$; $T_o = 580$ K.

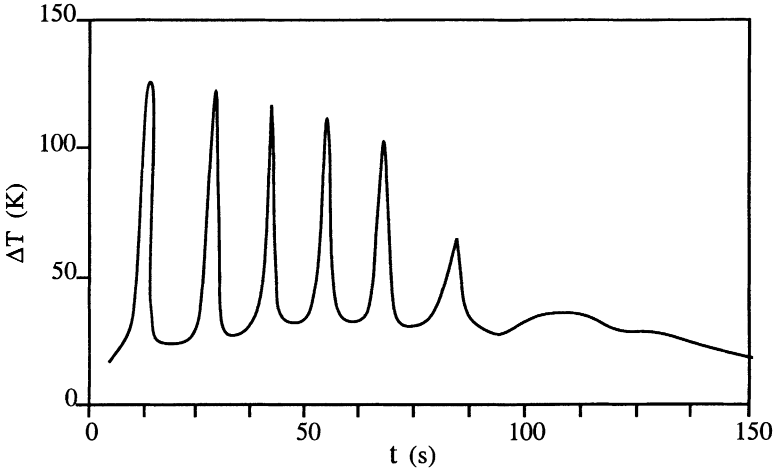


Figure 4 : Autoignition preceded by two cool flames during the oxidation of propane in a batch reactor. $T_o = 543$ K.

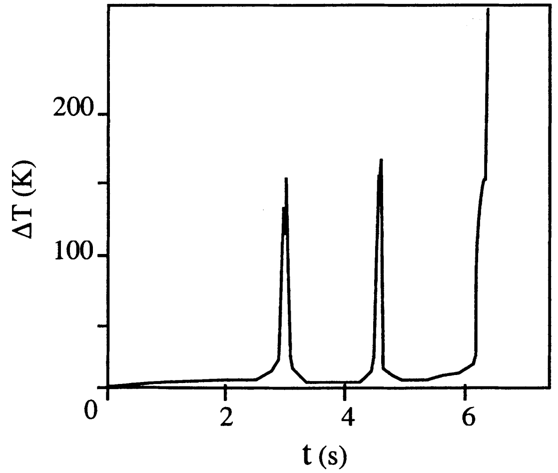
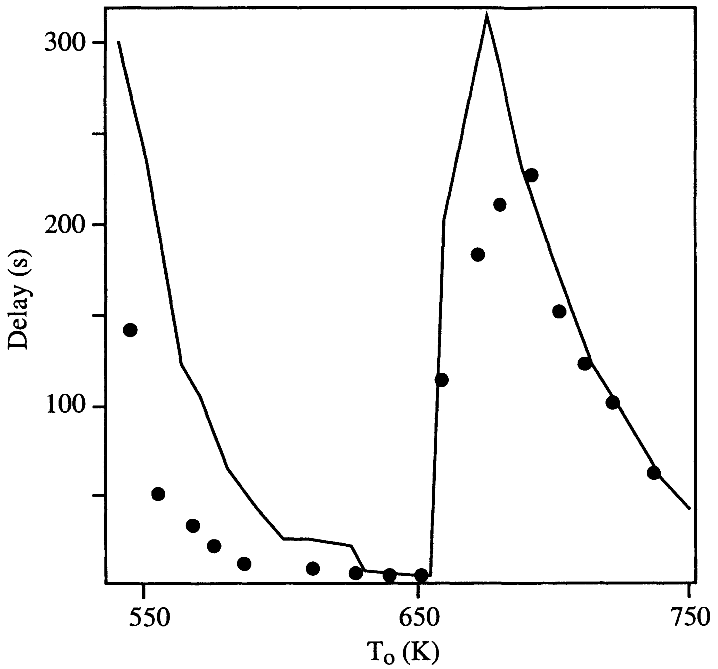


Figure 5 shows the variations in the delay of autoignition as a function of the temperature for the oxidation of n-butane in a batch reactor. The delay is observed to decrease from 550 to 650 K, increase from 650 to 700 K only to decrease afterwards. The delay constitutes an indicator related to the global rate of the reaction. It can therefore be deduced that the rate of the reaction decreases when the temperature increases between about 650 and 700 K. This anomaly in the behaviour is called the **region of negative temperature coefficient.**

Figure 5 : Variations in the delay of autoignition as a function of the temperature. Oxidation of n-butane in a batch reactor.
p_o = 73 kPa ; nC_4H_{10} : O_2 : N_2 = 1 : 2 : 20.33 ; • experimental points ; —— theoretical model.



c) Nature and quantities of the products formed

The preceding experimental data can be classed as **macroscopic** ; others exist which are equally interesting like the speed of a premixed laminar flame. It is possible to take this into account using globalized mechanisms.

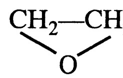
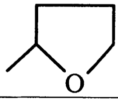
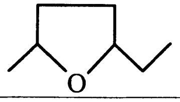
As regards chemical information about the nature and quantity of the products formed, this necessitates the development of detailed mechanisms which permit an explanation of the influence of the chemical structure of the reactant and of the operating conditions, in particular of the temperature, on the results.

Table 1 draws up a list of the main products formed during the oxidation of the two reference molecules n-heptane and iso-octane, for experiments carried out in a continuous flow stirred tank reactor (CFSTR) at 1 MPa between 500 and 1200 K. The temperature range has itself been divided up into three sub-ranges : 500-800, 800-850 and 850-1200 K. The products formed can be classed into two large categories :

- the hydrocarbons : hydrogen, methane, alkenes, dienes, alkynes ;
- oxygenated molecules : carbon oxides, aldehydes, alcohols, ketones, cyclic ethers.

Table 1 : Products of oxidation of alkanes in a continuous flow stirred tank reactor at 1 MPa.

a) Oxidation of n-heptane

Mole fraction	$500 < T < 800$ K	$800 < T < 850$ K	$850 < T < 1200$ K
10^{-2}			CO, CO_2, H_2, C_2H_4
10^{-3}	CO	CH_4, C_3H_6, HCHO	
10^{-4}	CO_2, HCHO, CH_3OH, CH_3CHO, C_2H_5CHO		
10^{-5}	C_7H_{14}, CH_3COCH_3, 	$CH_2{=}CH{-}CH_2{-}CH_3$, $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$ C_2H_2	C_3H_8
10^{-6}	 		

b) Oxidation of iso-octane

Mole fraction	$500 < T < 800$ K	$800 < T < 850$ K	$850 < T < 1200$ K
10^{-2}			CO, CO_2, H_2
10^{-3}		$CH_2{=}C(CH_3)_2$ CH_4, C_2H_4, C_3H_6, C_2H_6 HCHO	
10^{-4}			
10^{-5}	$CH_2{=}CH{-}CH_2{-}CH_3$ CO_2	C_2H_2 C_4H_6	C_5H_{10}
10^{-6}			

The analysis and comparison of Tables 1a and 1b allow several simple observations to be made : the chemistry of n-heptane is more complicated than that of iso-octane, the temperature has a major influence on the nature of the products formed and of course, on their quantities.

6.2 - Globalized mechanisms for the oxidation of alkanes

So that the fundamental structures of the reaction mechanisms involving degenerate branchings can be demonstrated, only two globalized reaction mechanisms will be discussed here ; the detailed reaction mechanisms will be described in the following chapter. Moreover, the interaction of real chemical phenomena with thermal phenomena must not be forgotten (cf. § 7).

a) The parrot mechanism

This scheme includes five reactions :

$$F + 12.35\,O_2 \longrightarrow P \tag{126}$$

$$F + O_2 \longrightarrow X \tag{127}$$

$$X \longrightarrow 2\,X \tag{128}$$

$$2\,X \longrightarrow P \tag{129}$$

$$X \longrightarrow P \tag{130}$$

F is the fuel , P are the products of the reaction and X is an intermediate species.
Reaction (126) describes the combustion of the fuel ; this is therefore a strongly exothermic reaction. Its rate law has been deduced from experimental data and is expressed in the following form :

$$r_{126} = k_{126}\,[F]^{0.25}\,[O_2]^{1.50} \tag{131}$$

Reaction (127) forms an intermediate X likely to give rise to the branching reaction (128) or to quadratic (129) and linear (130) terminations. The rates of these reactions are assumed to obey the law of mass action :

$$\begin{aligned} r_{127} &= k_{127}\,[F]\,[O_2] \\ r_{128} &= k_{128}\,[X] \\ r_{129} &= k_{129}\,[X]^2 \\ r_{130} &= k_{130}\,[X] \end{aligned} \tag{132}$$

The net rates of chemical production of each of the constituents are deduced from the kinetic laws (131) and (132) :

$$\begin{aligned} R_F &= -\,r_{126} - r_{127} \\ R_{O_2} &= -\,12.35\,r_{126} - r_{127} \\ R_X &= r_{127} + r_{128} - 2\,r_{129} - r_{130} \\ R_P &= r_{126} + r_{129} + r_{130} \end{aligned} \tag{133}$$

The kinetic laws thus established allow the design of a reactor to be carried out by solving the mass and energy balance equations. The parrot scheme can be shown to account for the delays of autoignition and the negative temperature coefficient. However, the main chemical objection that could be made of this model results from the fact that the concentration of the intermediate X does not intervene directly in the kinetic laws of the reactions (126) and (127) which consume both the fuel and the combustion agent, but indirectly, by thermal effects. The scheme mimics the macroscopic phenomena fairly well, like a parrot with the human voice, but without going into the essentials of their interpretation. Of course, such a scheme can neither explain the influence of the chemical structure of the fuel on the delay of autoignition, nor even more so, the nature and the quantities of the products formed.

b) The COX and COLE mechanism (Table2)

This mechanism contains the main generic reactions that can be found also in the detailed primary mechanisms for the oxidation of the alkanes at low temperatures ($T < 750$ K) in Chapter IX. It is also very similar to the reduced mechanisms obtained by the "lumping" of the detailed mechanisms. Its analysis therefore gives information about the structure of oxidation mechanisms, but also demonstrates the limits of this approach.

Putting this clearly, the primary reactions, which only involve the starting alkane RH, oxygen O_2 and the resulting free radicals as reactants have been gathered together in Table 2a, and, in Table 2b, the secondary reactions, where at least one of the reactants is a primary product.

— *The primary mechanism*

It contains the three large categories of elementary reactions : an initiation (134) which creates free radicals, propagations (135) to (142) which do not change the total concentration of the free radicals, and two terminations (143) and (144) which make the two main radicals ($^\bullet$R and $^\bullet$OOH) disappear. The absence of true branching reactions must be noted and also the fact that the $^\bullet$OOH radical is considered to be non-reactive for the propagation of the chains. The primary mechanism therefore appears at first, to be a straight chain reaction analogous to the mechanisms of pyrolysis discussed earlier. However, it differs from them in many ways.

The central reaction of the mechanism is the reversible addition (135) of the alkyl radical $^\bullet$R to oxygen O_2 to give an alkyl-peroxy radical $^\bullet$OOR. Assuming that this reaction is at quasi-equilibrium, gives the following relationship :

$$[^\bullet\mathrm{OOR}]/[^\bullet\mathrm{R}] = 10^{-2.53} \exp(13950/T) \times [O_2] \qquad (149)$$

When the temperature increases, the relative concentration of the $^\bullet$OOR radicals with respect to the $^\bullet$R radicals becomes negligible, so that all the reactions related to the existence of the •OOR radical (135, 136, 137, 139-141) disappear. This means going from an oxidation mechanism at low temperature to a combustion mechanism at high temperature. The decrease in the importance of reactions (139) to (141), when the temperature increases, is also responsible for the negative temperature coefficient.

— *Secondary mechanism*

This mechanism involves two propagation reactions (145) and (146) which lead to the formation of a hydroperoxide ROOH and hydrogen peroxide H_2O_2. It is important to note that these two products are also formed in the primary mechanism by reactions (141) and (144). The primary formation of the peroxide is due to the second addition of oxygen (137) and that of hydrogen peroxide to the formation of •OOH free radicals by the radical oxidation (138).

Table 2 : COX and COLE mechanism.
Nomenclature
RH : alkane ; Q : alkene ; QO : cyclic ether; RCHO : aldehyde ; ROOH : hydroperoxide.
Units
Pre-exponential factor A : mol, cm^3, s ; Activation energy E : kJ mol^{-1}

a) Primary mechanism

— Initiation	log A	E	
$RH + O_2 \longrightarrow {}^{\bullet}R + {}^{\bullet}OOH$	13.73	166	(134)
— Propagations			
${}^{\bullet}R + O_2 \rightleftharpoons {}^{\bullet}OOR$	12.00	0	(135)
	14.53	116	
${}^{\bullet}OOR \rightleftharpoons {}^{\bullet}QOOH$	11.88	80.5	(136)
	10.79	49.1	
${}^{\bullet}QOOH + O_2 \rightleftharpoons {}^{\bullet}OOQOOH$	8.98	0	(137)
	13.12	116	
${}^{\bullet}R + O_2 \longrightarrow Q + {}^{\bullet}OOH$	12.18	42	(138)
${}^{\bullet}QOOH \longrightarrow Q + RCHO + {}^{\bullet}OH$	14.40	129	(139)
${}^{\bullet}QOOH \longrightarrow QO + {}^{\bullet}OH$	11.04	66	(140)
${}^{\bullet}OOQOOH \longrightarrow ROOH + {}^{\bullet}OH$	10.81	90	(141)
${}^{\bullet}OH + RH \longrightarrow H_2O + {}^{\bullet}R$	14.00	8.3	(142)
— Terminations			
${}^{\bullet}R + {}^{\bullet}R \longrightarrow RH$	15.30	0	(143)
$2\,{}^{\bullet}OOH \longrightarrow H_2O_2 + O_2$	12.18	0	(144)

Table 2 (continued)

b) Secondary mechanism

— Propagations				
$^{\bullet}OOR + RCHO \longrightarrow ROOH + {}^{\bullet}R$	11.50	36.2	(145)
$^{\bullet}OOH + RCHO \longrightarrow H_2O_2 + {}^{\bullet}R$	11.50	36.2	(146)
— Initiations			
$ROOH \longrightarrow {}^{\bullet}R + {}^{\bullet}OH$	17.00	167	(147)
$H_2O_2 + M \longrightarrow 2\,{}^{\bullet}OH + M$	12.18	0	(148)

The peroxide ROOH and hydrogen peroxide H_2O_2 are at the basis of the **degenerate branching** reactions (147) and (148) which are therefore secondary initiations. These two branching agents accumulate progressively in the reaction medium whilst the primary reaction is taking place, so that the rates of secondary initiations increase also with the reaction time, conferring an auto-accelerated behaviour to this reaction. The proposed mechanism therefore takes both the possibility of autoignition and the delay associated with the formation of the peroxides into account.

In conclusion, the COX and COLE kinetic scheme possesses a structure which is reasonably compatible with macroscopic experimental observations relating to the oxidation of alkanes at low temperature. It also gives some indication about the distribution of the families of products formed (alkenes, aldehydes, cyclic ethers) as a function of the operating conditions and especially of the temperature. Its structure can be found in the detailed mechanisms of oxidation of the alkanes which will be discussed in Chapter IX.

7 - THERMAL EXPLOSIONS

Already at the end of the 19th century, Van't HOFF had understood that the heat given out by an exothermic reaction was likely to raise the temperature of the reaction medium, and as a consequence to increase the rate of reaction, this increase accelerates in turn the heat production and so on until there is an explosion. The main factor, which allows this type of explosion to be avoided, consists in the elimination of the heat of reaction by transfer using a heat exchanger.

SEMENOV developed a model of this phenomenon in about 1930, which is still used in studies on industrial safety. A batch reactor of volume V equipped with a heat exchanger of area S is considered. The reaction medium is assumed to be perfectly-stirred and an exothermic chemical reaction ($\Delta_r H^o < 0$) with the following kinetic law is assumed to take place :

$$r = A \exp(-E/RT) \, . \, c^{\omega} \tag{150}$$

where c is the concentration of the reactant, ω is the order of the reaction, and T the temperature of the reaction medium.

The quantity of heat Q_V produced per unit time by the chemical reaction is given by the following relationship :

$$Q_V = - r \, \Delta_r H^o \, . \, V \tag{151}$$

i.e. :

$$Q_V = V \, |\Delta_r H^o| \, A \exp\left(- E/RT\right) c^{\omega} \tag{152}$$

The quantity of heat Q_S withdrawn per unit time by the walls of the heat exchanger is given by the following relationship :

$$Q_S = h \, S \left(T - T_o\right) \tag{153}$$

where h is the transfer coefficient,
S is the surface area of thermal exchange,
T_o is the temperature of the heat-carrying fluid.

The SEMENOV diagram (Figure 6) consists of a representation of the variations in Q_V and Q_S as functions of T. The variations of Q_V seem to be approximately exponential, whereas those of Q_S are approximately linear. The three curves, represented by the letters a, b and c, represent the variations in Q_V at three increasingly high concentrations $c^{(a)}$, $c^{(b)}$ and $c^{(c)}$.

a) The curve $Q_V^{(a)}$ cuts the curve Q_S at two points ST and UN at temperatures T_{st} and T_{un}.

— The point ST is a stable point. Indeed, for $T = T_{st}$: $Q_V = Q_S$ and the temperature remains constant ; for $T < T_{st}$: $Q_V > Q_S$ and T increases to T_{st} ; for $T > T_{st}$: $Q_S > Q_V$ and T decreases to T_{st}.

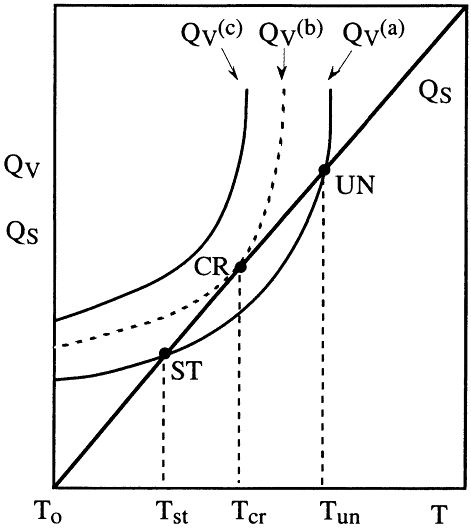
— The point UN is an unstable point, although $Q_V = Q_S$ for $T = T_{un}$. Indeed, when $T < T_{un}$, $Q_S > Q_V$, and the temperature decreases to the stable limit T_{st}. On the contrary, if $T > T_{un}$, then $Q_V > Q_S$ and the temperature increases indefinitely. T_{un} is called the autoignition temperature.

b) For the critical concentration $c^{(b)}$ of the reactant, the curve Q_V is tangent to the straight line Q_S at CR. The corresponding critical temperature T_{cr} is the maximum temperature above which no stable point ST is observed. The point CR is itself unstable, as $Q_V > Q_S$, except at CR.

c) If the concentration is high enough, then it is always true that $Q_V > Q_S$ and autoignition occurs as soon as the reactant is introduced into the reactor.

Summarizing, the critical point CR of the SEMENOV diagram separates the regions of slow reaction and of autoignition where the reaction is explosive.

Figure 6 : SEMENOV diagram.



The relationships established above have more qualitative than quantitative value. The empirical kinetic law (150) in particular should be replaced by a globalized or detailed reaction mechanism. This would be part of the framework of the **unified theory** of autoignitions, which takes into account both the interaction between the branching and the degenerate branching mechanisms and the thermal phenomena. Such models can only be treated by numerical methods.

FURTHER READING

ALBRIGHT L.F., CRYNES B.L., Editors, *Industrial and Laboratory Pyrolysis*, ACS Symp. Series, vol. 32 (1976).

ALBRIGHT L.F., CRYNES B.L., CORLORAN W.H., Editors, *Pyrolysis : Theory and Industrial Practice*, Academic Press (1983).

BARONNET F., DZIERZYNSKI M., CÔME G.M., MARTIN R., NICLAUSE M., *The Pyrolysis of Neopentane at Small Extents of Reaction*, Int. J. Chem. Kin., 111, 197 (1971).

GLASSMAN I., *Combustion*, 3rd edition, Academic Press (1996).

GRAY P., SCOTT S.K., *Chemical oscillations and instabilities,* Clarendon (1990).

GRIFFITHS J.F., BARNARD J.A., *Flame and combustion*, 3rd edition., Blakie Acad. & Profess. (1995).

ORNINSKI A., *Catastrophe theory*, Comprehensive Chemical Kinetics, vol. 33, Elsevier (1992).

PILLING M.J., Editor, *Low-temperature Combustion and Autoignition*, Comprehensive Chemical Kinetics, vol. 35, Elsevier (1997).

CHAPTER IX

GENERATION OF REACTION MECHANISMS

This chapter aims to describe the methods of automatic generation of the ***detailed mechanisms*** *of the oxidation and combustion reactions of alkanes, as well as the techniques of* ***reduction*** *of these mechanisms by the* ***lumping*** *of the species and of the* reactions.

INTRODUCTION

a) Description of the problem

Two **a priori lumped** kinetic models were discussed in Chapter VIII : the **µH, YH** model for pyrolyses and the **COX and COLE** model for oxidations. These models are basic models as they have the morphology which must be obeyed by all detailed reaction mechanisms of pyrolysis and oxidation.

As has already been seen, these a priori lumped kinetic models account for the macroscopic properties of the reactions, such as cool flames, the delays of auto-ignition... but without being able to relate them to the chemical structure of the reactants. In other words, they are incapable of describing both qualitatively and quantitatively the formation of individual molecules, such as the toxic substances (carbon monoxide, aldehydes, butadiene, aromatics, PAHs, soot) or the tropospheric pollutants (nitrogen and sulphur oxides, unburnt hydrocarbons, various oxygenated compounds), produced by the burning of fuels. There is therefore a strong requirement to develop detailed reaction mechanisms, likely to predict both the kinetic and chemical characteristics of these reactions.

The manual writing out of mechanisms involves several hundred chemical species and several thousand reactions, and presents, other than its tedious aspect, high risks of material errors and, more inacceptable still, it necessitates tackling again in entirety the generation for each new molecule. Resorting to the computer is therefore unavoidable.

The generation of reaction mechanisms assisted by the computer has been rendered possible due to experimental and theoretical knowledge accumulated over the last three decades about the thermodynamic properties of molecules and free radicals, about elementary reactions and about the morphology of the reaction mechanisms themselves. All of this knowledge has been described in the preceding chapters.

The interest of these detailed mechanisms from a chemical point of view must not be allowed to overshadow their incorporation into the CFD (Computational Fluid Dynamic) codes for the calculation of three-dimensional turbulent reacting flows. Despite the increased power of computers and the constant improvements in numerical programs, these codes can only accept that the reaction schemes involve at most a dozen species. Two complementary approaches allow this objective to be reached :

- the **a posteriori lumping** of the detailed mechanisms, which will be discussed in this chapter, allows the size of the models to be reduced substantially, whilst protecting the chemical information and the fundamental kinetic characteristics which they carry ;
- the techniques of **mathematical reduction** provide a potential answer to this problem ; they will be discussed in Chapter XIII.

b) The strategies of conception

The first approach to be checked industrially for the development of detailed mechanisms and the technique of chemical lumping has been worked out at the Polytechnic Institute in Milan for steamcracking[1]. The modelled hydrocarbon loads include ethane, propane, the naphthas and even vacuum-distilled diesel fuel, i.e. complex mixtures of hydrocarbons possessing from two to forty carbon atoms.

The first task consists in describing the load from the chemical analyses and the physico-chemical properties. Concerning the last point, it is necessary to establish correlations between the global physico-chemical properties and the chemical composition in terms of the individual molecules or families of molecules. So that the number of individual molecules to be treated can be reduced, a first lumping is carried out for the species belonging to the same chemical family.

Example 1

The 12 n-alkylbenzenes from C_9 to C_{20} are represented as being combinations of C_9AR, $C_{15}AR$ and $C_{20}AR$, for example :

$$C_{16}AR = 0.8\ C_{15}AR + 0.2\ C_{20}AR$$

The actual reaction mechanism consists of two important parts :

- a basic set of elementary reactions including reactions of hydrocarbons containing from 1 to 4 carbon atoms (C_1–C_4). This basic set is the nucleus of the system ;
- the reaction mechanisms of hydrocarbons containing n carbon atoms, where $n \geq 5$,

---

[1] SPYRO model.

are successively created and fitted one inside the other like Russian dolls. Indeed, the detailed mechanism of a species in C_5 leads to the formation of species in C_4, C_3... whose reactions are already included in the basic set C_1–C_4 and which therefore do not have to be rewritten. The C_5 detailed mechanism is then lumped using the techniques which will be described in paragraph 5 of this chapter, then checked taking the available experimental results into consideration.

Then the modelling of the reactions of the C_6 hydrocarbons will be treated using the same technique, and so on up to a maximum value fixed by the number of carbon atoms. The validation of successive interlinked mechanisms depends on the preceding validations, each depending itself on the experimental facts on which it is founded. This procedure therefore reduces the transparency of the models thus created.

The same approach has been used by the team from MILAN for the oxidation of alkanes. The basic set of reactions C_1–C_4 is then much more important than for pyrolyses, more especially as all the reactions of the species C_0 (H, O, OH...) must be added to it.

The approach adopted in NANCY will be discussed in the following, this possesses both an algorithmic aspect, using an iterative method based on a systematic activation of generic reactions, and an expert system aspect, as the user can define the type of kinetic model which he or she wishes to generate.

1 - GENERAL DESCRIPTION OF THE EXGAS SYSTEM

Figure 1 shows the general organization of the system. It consists of three main modules :

- EXGAS for the automatic generation of reaction mechanisms,
- THERGAS for the calculation of thermochemical data,
- KINGAS for the calculation of kinetic data.

The input data to the system consists of the developed formulae of the reactants and the output data is the reaction model, made up from the mechanism and the associated numerical data. The three parts are connected by the links shown in Figure 1 : THERGAS sends thermochemical data to EXGAS, but also to KINGAS, in order to apply the principle of detailed balancing ; KINGAS sends kinetic data to EXGAS.

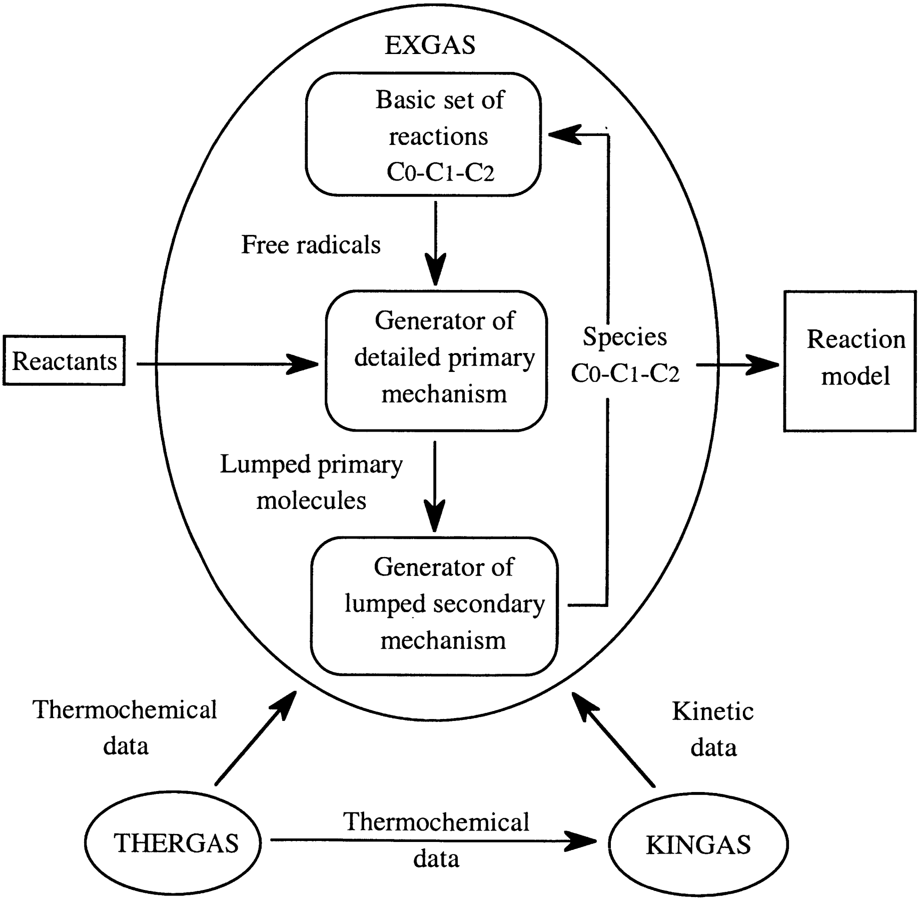
The EXGAS module is itself made up of three sections :

- a basic set of reactions involving molecules and free radicals containing 0, 1 or 2 carbon atoms,
- a generator of detailed primary mechanisms, of which the reactants are on the one

hand the initial reactants entered by the user, and on the other hand the free radicals from the basic set of reactions C_0–C_1–C_2,

- a generator of lumped secondary mechanisms, the reactants of which are the lumped primary molecules coming from the primary generator, the products of which are the species of the C_0–C_1–C_2 basic set.

Figure 1 : General organization of the system.



The development of the system is such that the primary products as well as the secondary products must systematically undergo reaction and can therefore, because of this, accumulate in an unwarranted manner in the reaction medium.

2 - THE C_0–C_1–C_2 BASIC SET OF REACTIONS

This basic set makes up the heart of the system, as it contains the unimolecular, bimolecular and trimolecular elementary reactions, of the molecular chemical species and radicals containing 0, 1 or 2 carbon atoms, as well as hydrogen and oxygen atoms. It was created using the method proposed by TSANG.

First of all, an organized list of the 42 C_0–C_1–C_2 species containing 24 free radicals and 18 molecules has been drawn up (Figure 2).
Secondly, a systematic inventory of the possible reactions of each species has been established from the literature, by considering successively the unimolecular reactions of the species (column 0 in Figure 1), the reactions of the species with the species n° 1 (column 1), 2 (column 2)..., stopping at the reaction of the species with itself.

Two cases are observed, according to whether a reaction can be found in the literature, in which case it is introduced into the basic set, or it is improbable and is not to be found in the literature, in which case it is not considered. This method has led to the creation of a basic set of about 800 reactions. The kinetic data have mainly been taken from the critical compilations of BAULCH *et al.*, and of TSANG *et al.* (cf. Chapter XIV).

The basic set of reactions has finally been validated by simulating various oxidation and combustion reactions of hydrocarbons, in particular of methane and of ethane, in different laboratory reactors (stirred flow reactor, plug-flow reactor...) carried out using very varied operating conditions.

Example 2
Generate an exhaustive model for the reaction of H_2 with Br_2 using TSANG's method.

The following species are considered ; Br_2, Br, H_2, H and HBr. The following table can be written :

		0	1	2	3	4	5
1	Br_2	+	-				
2	Br	-	-	+			
3	H_2	+	-	+	-		
4	H	-	+	+	-	+	
5	HBr	+	-	+	-	+	-

The following mechanism is thus obtained :

$$Br_2 + M \longrightarrow 2\,Br + M$$

$$Br + Br + M \longrightarrow Br_2 + M$$

$$H_2 + M \longrightarrow 2\,H + M$$

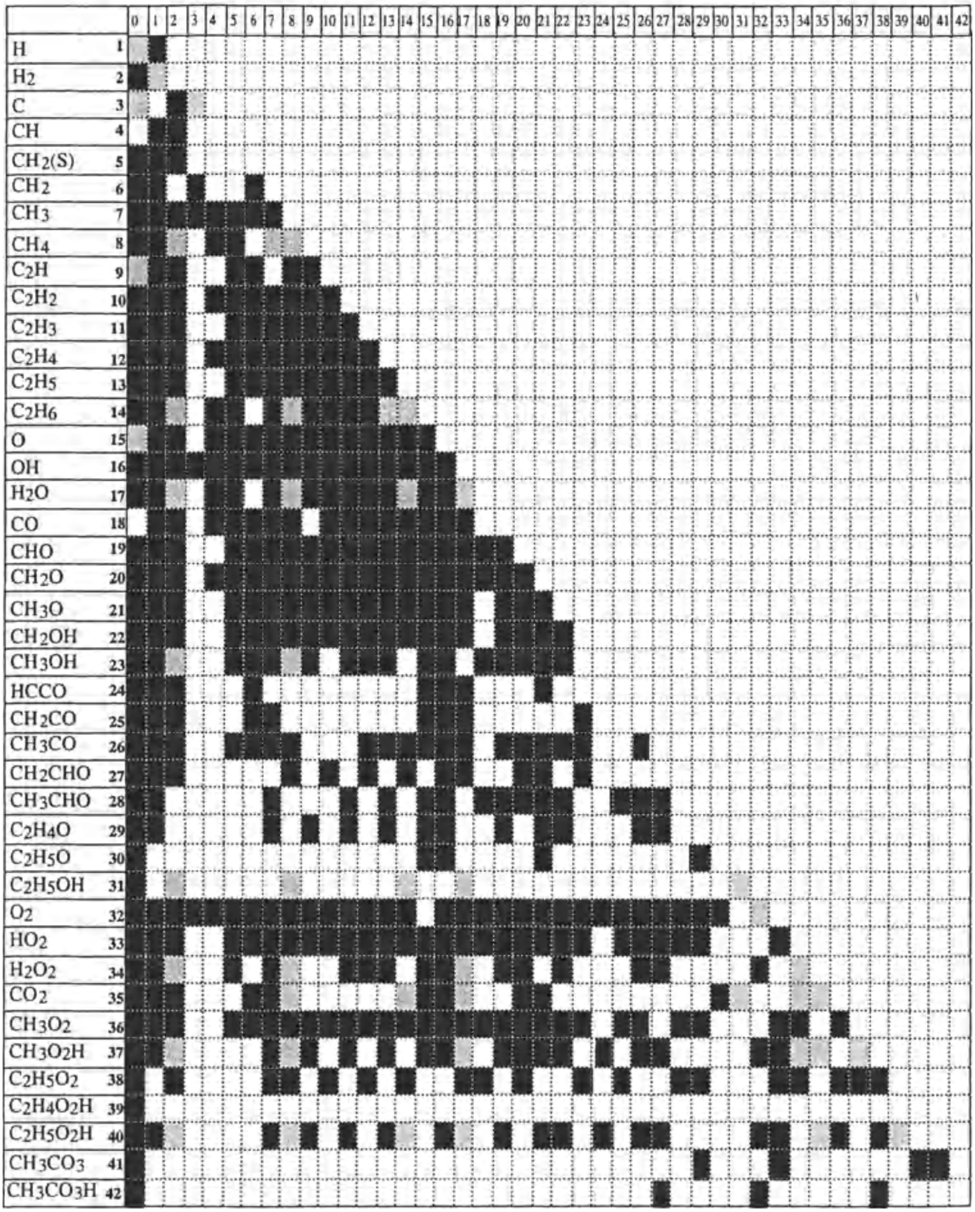
$$H_2 + Br \longrightarrow H + HBr$$

Figure 2 : *Basic set of reactions C_0–C_1–C_2*

■ Reaction considered in the basic set

▨ Improbable reaction

☐ Absence of kinetic data in the literature



$$H + Br_2 \longrightarrow HBr + Br$$
$$H + Br + M \longrightarrow HBr + M$$
$$H + H + M \longrightarrow H_2 + M$$
$$HBr + M \longrightarrow H + Br + M$$
$$HBr + Br \longrightarrow H + Br_2$$
$$HBr + H \longrightarrow H_2 + Br$$

This technique has the advantage of writing all the possible reactions, but necessitates the subsequent elimination of the reactions which are negligible under the given experimental conditions.

3 - THE GENERATION OF DETAILED PRIMARY MECHANISMS

3.1 - Algorithm for the generation of an exhaustive primary mechanism

The structure of the algorithm is shown in Figure 3. Three main classes of **generic reactions** are used in a systematic manner and are illustrated in Table 1.

a) Initiation reactions

The alkane molecule undergoes unimolecular (ui) and bimolecular (bi) initiations which result in the formation of two free radicals.

b) Propagation reactions

Any free radical enters into the reactions of addition to oxygen (ad), of isomerization (is), of decomposition by beta-scission (bs) or by cyclization (cy), of oxidation (ox) and of metathesis (me). Some of these propagation reactions (bs, cy, ox, me) contribute to the formation of the primary products of the reaction.
Starting with a given radical •R, the propagation reactions generate other free radicals •R which in their turn systematically undergo generic propagation reactions, until no new free radical, or no free radical included in the basic set, appears. This iterative process ensures the exhaustiveness of the mechanism.

c) Termination reactions

All the free radicals created previously by initiation and propagation reactions enter into two by two combination (co) and disproportionation (di) reactions.

d) Structure of the mechanism

Figure 4 shows the structure of the primary mechanism for the oxidation of an alkane obtained by the application of the propagation of generic reactions. A certain analogy with that of the COX and COLE mechanism (Chap. VIII, Table 2) can be observed.

Figure 3 : Algorithm for the generation of an exhaustive primary mechanism.

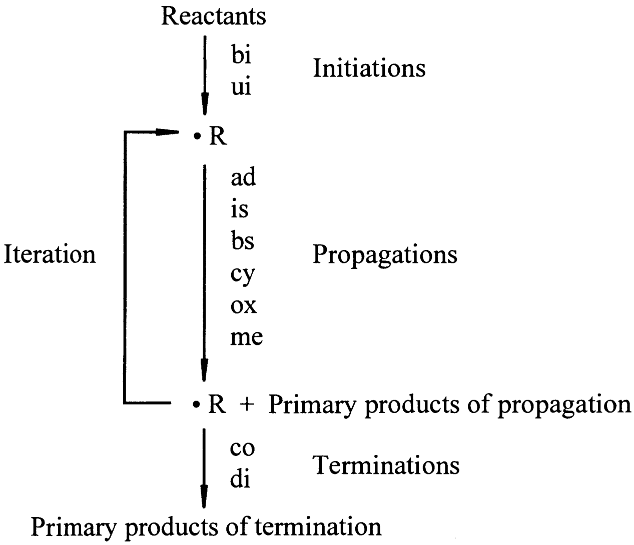
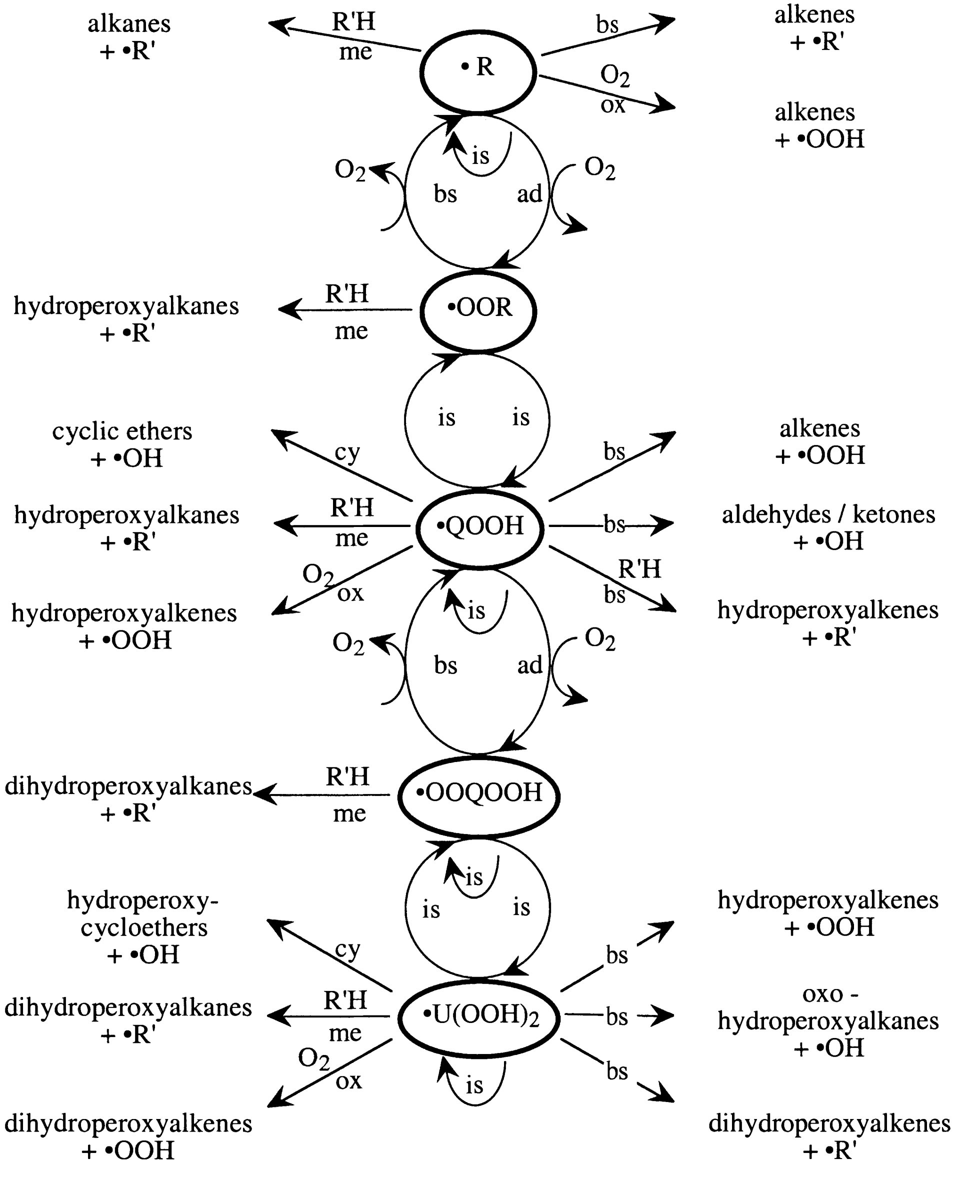


Table1 : Typical primary generic reactions (units : mol, cm^3, s, kJ).

	log A	b	E
Unimolecular initiation (ui)			
ch3/ch2/ch2/ch3 → 2•ch2/ch3	16.34	0.00	358.4
Bimolecular initiation (bi)			
ch3/ch2/ch2/ch3+o2 → •o/oh+•ch(ch3)/ch2/ch3	12.60	0.00	200.6
Addition of free radicals to oxygen (ad)			
•ch(ch3)/ch2/ch3+o2 → •o/o/ch(ch3)/ch2/ch3	19.34	−2.50	0.0
Isomerization of free radicals (is)			
•o/o/ch(ch3)/ch2/ch3 → •ch2/ch(o/oh)/ch2/ch3	12.60	0.00	148.4
Unimolecular decomposition of free radicals by beta-scission (bs)			
•ch(ch3)/ch2/ch3 → •ch3+ch3/ch//ch2	13.30	0.00	129.6
Unimolecular decomposition of hydroperoxyalkyl free radicals to cyclic ethers (cy)			
•ch2/ch(o/oh)/ch2/ch3 → c(#1)h(ch2/ch3)/ch2/o/1+•oh	11.30	0.00	74.0
Oxidation of free radicals (ox)			
•ch(ch3)/ch2/ch3+o2 → ch3/ch2/ch//ch2+•o/oh	11.85	0.00	20.9
Metathesis (me)			
•oh+ch3/ch2/ch2/ch3 → oh2+•ch(ch3)/ch2/ch3	6.71	2.00	-3.2
Combination of free radicals (co)			
•ch3+•ch(ch3)2 → ch(ch3)3	13.19	0.00	0.0
Disproportionation of free radicals (di)			
•o/o/ch(ch3)/ch2/ch3+•o/oh → ch3/ch(ooh)/ch2/ch3+o2	11.30	0.00	−5.43

Figure 4 : Detailed primary mechanism of oxidation of an alkane : the propagation reactions.



The framework of the mechanism involves alkyl •R, alkylperoxy •OOR, hydroperoxyalkyl •QOOH, hydroperoxyalkylperoxy •OOQOOH and dihydroperoxyalkyl $\bullet U(OOH)_2$ radicals which are obtained from the •R radical parent of the RH molecule by a first addition of oxygen, followed by an isomerization, and then a second addition of oxygen also followed by an isomerization. This framework will of course be found in the lumped primary mechanism.

3.2 - A priori simplification of the primary mechanism

The exhaustiveness of the mechanism has an obvious drawback, i.e. the large number of species and of reactions. The application of the kinetic laws ßμ given in Chapter VIII allows the size of the mechanism to be reduced a priori by **inactivating** certain generic reactions.

a) Combustion reactions at high temperature

When the temperature is high enough, which is the case of flames, the μ and ßμ radicals easily decompose by beta-scission reactions, so that their concentrations become negligible with respect to those of the ß radicals.
This fact has two consequences.

- The addition reactions to oxygen of the $^\bullet$R free radicals coming from the starting alkane RH, can be neglected. This causes the disappearance of the $^\bullet$OOR, $^\bullet$QOOH, $^\bullet$OOQOOH, $^\bullet$U(OOH)$_2$ radicals and of their reactions (Figure 4). The only reactions left for the $^\bullet$R radicals are those of beta-scission, of oxidation and of metathesis.
- In the combination and disproportionation reactions of free radicals, only the ß radicals will be taken into account. These reactions are already written in the C_0–C_1–C_2 basic set.

b) Oxidation reactions at low temperature

Of course, there is no question that a single propagation reaction of Figure 4 will be neglected here, and in particular those which arise from a second addition of oxygen and which lead to the formation of degenerate branching agents. It is however possible to envisage reducing the number of termination reactions by writing only those which involve the ß or ßμ radicals. It is possible to check if this approximation is justified by taking note if the concentrations of the μ radicals are effectively negligible with respect to those of the ß and ßμ radicals in the results of a simulation of the simplified mechanism.

4 - THE GENERATION OF SECONDARY MECHANISMS

The primary products formed from the starting alkane will react in their turn to produce secondary products. Taking the large number of primary products which are generated into account, it is not possible to write a detailed mechanism analogous to that of the initial alkane for each of these. It is therefore necessary to fall back on lumping techniques.

4.1 - Lumping of the species

The species which intervene in the secondary mechanism are lumped according to the following rules : the molecules and free radicals which have the same basic formula, the same functional groups and rings of the same size are grouped together into a single species, with no distinction between the different isomers, as was the case in the detailed primary mechanism. Table 2 gives a list of the elements which constitute a lumped chemical formula of a molecule or free radical.

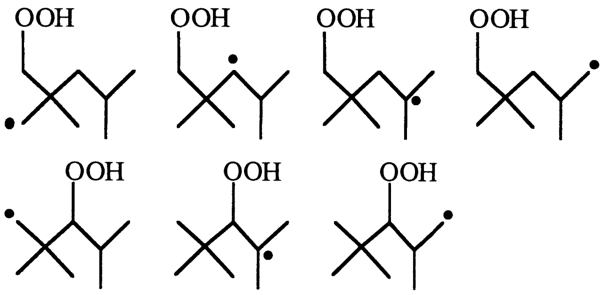
Table 2 : Lumping of the species.

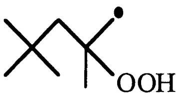
cxhy	hydrocarbon molecule or hydrocarbonated part of a molecule or of a free radical where x : is the number of carbon atoms ; y : is the number of hydrogen atoms
(co)	ketone
(cho)	aldehyde
(oh)	alcohol
(o@n)	cyclic ether where n : is the ring size
(ooh)	hydroperoxide
•cxhy	hydrocarbonated free radical
•(oo)	peroxy free radical
•(co)	ketonic free radical

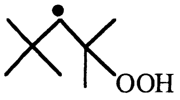
Example 3

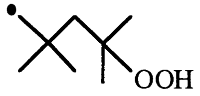
Write down the developed formulae of the hydroperoxyalkyl •c8h16(ooh) radical for iso-octane.

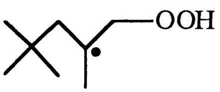
There are 14 isomers :

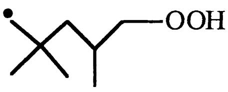


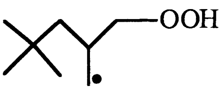












4.2 - Lumping of the secondary reactions

According to the scheme shown in Figure 1, the products formed by the secondary reactions are the molecules and the free radicals of the C_0–C_1–C_2 basic set. The secondary reactions of different species will be examined below ; they are illustrated in Table 3 by examples taken from the mechanism for the oxidation of butane.

a) Degenerate branching reactions

The first step consists in breaking the peroxydic O–O bond of the hydroperoxyalkanes, hydroperoxyalkenes, dihydroperoxyalkanes, dihydroperoxyalkenes, oxohydroperoxyalkanes, hydroperoxycycloethers formed primarily. This step leads to the formation of an •OH radical and a large radical which is assumed to decompose in a second step into a free radical and one or several molecules of the C_0–C_1–C_2 basic set. The grouping together of these two steps constitutes the lumped reaction of degenerate branching (Table 3a).

b) Reactions of the alkanes

The first step is an abstraction of an H atom by a radical of the ß type, followed by a decomposition of the alkyl radical formed into a radical and one or several molecules of the basic set (Table 3b).

c) Reactions of the alkenes

Alkenes can react according to two main classes of reactions (Table 3c) :

- by the addition of a small free radical, followed by a decomposition of the radical formed into alkenes, aldehydes, alcohols and cyclic ethers ;
- by metathesis leading to a free radical of the Y type which is stabilized by resonance. The Y radical is not very reactive and can either add on to an alkene to give a free radical which is likely to decompose into smaller species, or enter into termination reactions with the ß or ßμ radicals.

d) Reactions of the alcohols

Alcohols undergo first of all a metathesis reaction followed by a decomposition of the radical formed into a small radical and an alkene, an aldehyde or a ketone (Table 3d).

e) Reactions of the aldehydes

Aldehydes undergo first of all an abstraction reaction of an aldehydic hydrogen, which leads to the formation of a ketonic radical. These radicals react in two ways (Table 3e) :

- by decomposition giving carbon monoxide,
- by addition of oxygen to form alkylketoperoxy radicals which, either react with the initial alkane, or isomerize into ketohydroperoxyalkyl radicals which give rise to a degenerate branching reaction. It is observed that the addition of oxygen ends finally in the formation of CO_2.

f) Reactions of the epoxides

These cyclic ethers undergo a metathesis reaction, followed by a decomposition reaction of the radical formed into species of the basic set (Table 3f).

g) Reactions of cyclic ethers

Cyclic ethers react first of all by metathesis reactions giving rise to a cyclic radical. This radical can either decompose into products from the basic set, or add on to an oxygen molecule and generate the classical sequence of isomerization, secondary addition of oxygen, formation of ketohydroperoxides, degenerate branching reactions (Table 3g).

Table 3 : Typical secondary generic reactions. Units : mol, cm^3, s, kJ.

a) Degenerate branching reactions	log A	b	E
c4h9(ooh) $\longrightarrow$ •oh+ch3(cho)+•c2h5	14.85	0.00	175.6
b) Reactions of the alkanes			
•oh+c3h8 $\longrightarrow$ oh2+•ch3+c2h4	6.88	2.00	−3.2
c) Reactions of the alkenes			
— Addition followed by decomposition			
•h+c4h8 $\longrightarrow$ c2h4+•c2h5	0.85	4.00	5.4
•ch3+c4h8 $\longrightarrow$ 2c2h4+•ch3	10.98	0.00	33.4
•oh+c4h8 $\longrightarrow$ •ch3+c2h5(cho)	0.30	4.00	−4.2
$\longrightarrow$ •ch3+c3h5(oh)	0.30	4.00	−4.2
•ooh+c4h8 $\longrightarrow$ c4h8(o@3)+•OH	12.00	0.00	60.2
— Formation and reactions of allylic radicals			
•oh+c4h8 $\longrightarrow$ •c4h7+oh2	6.49	2.00	−1.3
•c4h7+c4h8 $\longrightarrow$ •c2h3+2c2h4	9.78	0.00	47.7
•c4h7+•oh $\longrightarrow$ c4h7(oh)	13.00	0.00	0.0

Table 3 (continued)

d) Reactions of the alcohols			
•oh+c4h9(oh) → oh2+•oh+c4h8	9.11	1.25	2.9
→ oh2+•ch3+c2h5(cho)	12.60	0.00	1.9
→ oh2+•ch3+c2h6(co)	12.60	0.00	1.9
e) Reactions of the aldehydes			
— Formation of a ketonic radical			
•oh+c3h7(cho) → oh2+•(co)c3h7	12.67	0.00	2.1
— Decomposition of the ketonic radical			
•(co)c3h7 → co+•ch3+c2h4	13.30	0.00	120.0
— Addition of oxygen			
•(co)c3h7+o2 → •(oo)(co)c3h7	12.38	0.00	0.0
•(oo)(co)c3h7+c4h10 → •c4h9+•oh+co2+•ch3+c2h4	12.95	0.00	73.2
•(oo)(co)c3h7 → c3h6+•oh+co2	11.65	0.00	104.5
f) Reactions of the epoxides			
•oh+c4h8(o@3) → oh2+ch2(co)+•c2h5	6.88	2.00	−3.2
g) Reactions of the cyclic ethers			
— Metathesis			
•oh+c4h8(o@5) → oh2+•c4h7(o@5)	6.95	2.00	−5.7
— Decomposition of the cyclic radical			
•c4h7(o@5) → •ch2(cho)+c2h4	13.0	0.00	120.00
— Addition of oxygen			
•c4h7(o@5)+o2 ↔ •(oo)c4h7(o@5)	19.34	−2.50	0.0
	22.70	−2.50	150.0
•(oo)c4h7(o@5) ↔ •c4h6(o@5)(ooh)	13.90	0.00	106.6
	12.69	0.00	81.2
•c4h6(o@5)(ooh)+o2 ↔ •(oo)c4h6(o@5)(ooh)	19.34	−2.50	0.0
	22.70	−2.50	0.0
•(oo)c4h6(o@5)(ooh) → •oh+c3h5(o@5)(co)(ooh)	9.00	0.00	31.3
c3h5(o@5)(co)(ooh) → •oh+co2+•(cho)+c2h4	14.85	0.00	175.6

4.3 - Estimation of the kinetic parameters of the lumped secondary mechanism

The kinetic parameters which are taken for a lumped secondary mechanism are those of the determining elementary reaction amongst those which constitute the lumped reaction. This determining reaction is, as a general rule, the first in the sequence being considered : this is a consequence of the quasi-stationary-state approximation.

Concerning the estimation of the kinetic parameters of the determining reactions, the same methods are used as for the primary generic reactions, that is the structure-reactivity correlations.

5 - LUMPING OF THE DETAILED PRIMARY MECHANISMS

5.1 - Lumped primary mechanism

The lumping of the propagation reactions of the detailed primary mechanism described in Figure 4 can be carried out by considering effectively only four lumped free radicals, parents of the initial alkane molecule RH , i.e. :

$$^\bullet R,\ ^\bullet OOR,\ ^\bullet QOOH,\ ^\bullet OOQOOH$$

and by lumping the reactions of these intermediates. The corresponding reaction scheme is given in Table 4, with the orders of magnitude of the ARRHENIUS parameters A and E.

Table 4 : Lumped primary mechanism for the oxidation of an alkane: propagation reactions. Units : mol, cm^3, s, kJ.

	log A	E
$^\bullet R \longrightarrow \text{alkenes} + {}^\bullet R'$	13.50	117-134
$^\bullet R + O_2 \longrightarrow \text{alkenes} + {}^\bullet OOH$	11.30*	13
$^\bullet R + O_2 \rightleftharpoons {}^\bullet OOR$	12.18	0
	13.48	126
$^\bullet OOR \rightleftharpoons {}^\bullet QOOH$	10.60-11.80*	84-119
	10.00-11.26	50-80
$^\bullet QOOH \longrightarrow \text{alkenes} + {}^\bullet OOH$	13.48	96
$^\bullet QOOH \longrightarrow \text{cyclic ethers} + {}^\bullet OH$	10.30-11.60	29-84
$^\bullet QOOH \longrightarrow \text{alkenes} + \text{aldehydes} + {}^\bullet OH$	13.48	103
$^\bullet QOOH + O_2 \rightleftharpoons {}^\bullet OOQOOH$	12.18	0
	13.48	126
$^\bullet OOQOOH \longrightarrow OQOOH + {}^\bullet OH$	10.60-11.80	75-109

* per H atom

As well as the propagation reactions mentioned in Table 4, the following reactions must be taken into account in order to obtain a lumped mechanism which is complete :

— Initiation :

$RH \longrightarrow {}^\bullet R' + {}^\bullet R''$

$RH + O_2 \longrightarrow {}^\bullet R + {}^\bullet OOH$

— Metathesis :

$^\bullet \beta + RH \longrightarrow \beta H + {}^\bullet R$

— Degenerate branching

$OQOOH \longrightarrow {}^\bullet OQO + {}^\bullet OH$

${}^\bullet OQO \longrightarrow {}^\bullet ß$ + oxygenated molecules

— Termination

Combinations and disproportionations of the ${}^\bullet ß$ and ${}^\bullet ß\mu$ radicals

Table 5 gives the propagation reactions (not including metatheses) of the lumped primary mechanism of the oxidation of n-pentane. It must be noted that this scheme only includes 4 free radicals instead of 24 for the detailed mechanism : 3 pentyl radicals, 3 peroxy radicals, 9 hydroperoxypentyl radicals and 9 hydroperoxypentyl-peroxy radicals ; the dihydroperoxypentyl radicals have not been considered.

Table 5 : Lumped primary mechanism for the oxidation of n-pentane ; propagation reactions. Units : mol, cm^3, s, kJ.

	log A	E
${}^\bullet C_5H_{11} \longrightarrow 0.25\,(C_2H_4 + {}^\bullet C_3H_7)$		
$+ 0.55\,(C_3H_6 + {}^\bullet C_2H_5)$	13.52	126
$+ 0.20\,(C_4H_8 + {}^\bullet CH_3)$		
${}^\bullet C_5H_{11} + O_2 \longrightarrow C_5H_{10} + {}^\bullet OOH$	12.23	13
${}^\bullet C_5H_{11} + O_2 \rightleftharpoons {}^\bullet OOC_5H_{11}$	12.00	0
	13.48	126
${}^\bullet OOC_5H_{11} \rightleftharpoons {}^\bullet C_5H_{10}OOH$	12.11	109
	9.97	80
${}^\bullet C_5H_{10}OOH \longrightarrow C_5H_{10}(O@) + {}^\bullet OH$	10.95	62
$\longrightarrow C_5H_{10} + {}^\bullet OOH$	13.18	100
$\longrightarrow {}^\bullet OH + 0.10\,(CH_2O + C_4H_8)$		
$+ 0.65\,(CH_3CHO + C_3H_6)$		
$+ 0.25\,(C_2H_5CHO + C_2H_4)$	13.18	100
${}^\bullet C_5H_{10}OOH + O_2 \longrightarrow {}^\bullet OOC_5H_{10}OOH$	12.0	0
	13.48	128
${}^\bullet OOC_5H_{10}OOH \longrightarrow {}^\bullet OH + OC_5H_9OOH$	12.00	109

5.2 - Estimation of the fractional stoichiometric coefficients and of the kinetic parameters of the lumped primary mechanism

The principle of the method will be discussed for the pyrolysis of n-butane, then generalized for the oxidation of any alkane.

a) The pyrolysis of n-butane

The propagation reactions of the detailed mechanism are the following :

$$
\begin{array}{lll}
{}^\bullet C_2H_5 + C_4H_{10} & \longrightarrow C_2H_6 + {}^\bullet R_1 & (1) \\
 & \longrightarrow C_2H_6 + {}^\bullet R_2 & (2) \\
{}^\bullet CH_3 + C_4H_{10} & \longrightarrow CH_4 + {}^\bullet R_1 & (3) \\
 & \longrightarrow CH_4 + {}^\bullet R_2 & (4) \\
{}^\bullet R_1 & \longrightarrow C_2H_4 + {}^\bullet C_2H_5 & (5) \\
{}^\bullet R_2 & \longrightarrow C_3H_6 + {}^\bullet CH_3 & (6)
\end{array}
$$

where $\quad {}^\bullet R_1 = {}^\bullet CH_2{-}CH_2{-}CH_2{-}CH_3$
$\qquad\quad {}^\bullet R_2 = {}^\bullet CH(CH_3){-}CH_2{-}CH_3$

The decompositions of the ${}^\bullet R_1$ and ${}^\bullet R_2$ radicals by the breaking of a C–H bond in the ß position with respect to the radical point, have been neglected in this mechanism.
First of all, the long chain approximation is applied to the four radical chain carriers :

$$
\left.
\begin{array}{ll}
{}^\bullet C_2H_5 & -r_1-r_2+r_5 = 0 \\
{}^\bullet CH_3 & -r_3-r_4+r_6 = 0 \\
{}^\bullet R_1 & r_1+r_3-r_5 = 0 \\
{}^\bullet R_2 & r_2+r_4-r_6 = 0
\end{array}
\right. \qquad (7)
$$

The following relationship between the concentrations of the $[{}^\bullet R_1]$ and $[{}^\bullet R_2]$ radicals is deduced :

$$
\frac{[{}^\bullet R_1]}{[{}^\bullet R_2]} = \frac{k_6}{k_5} \frac{k_1 + k_2}{k_2} \frac{k_3}{k_3 + k_4} \qquad (8)
$$

The lumped mechanism deduced from the detailed mechanism (1-6) can be written as follows :

$$
\begin{array}{lll}
{}^\bullet C_2H_5 + C_4H_{10} & \longrightarrow C_2H_6 + {}^\bullet C_4H_9 & (9) \\
{}^\bullet CH_3 + C_4H_{10} & \longrightarrow CH_4 + {}^\bullet C_4H_9 & (10) \\
{}^\bullet C_4H_9 & \longrightarrow C_2H_4 + {}^\bullet C_2H_5 & (11) \\
{}^\bullet C_4H_9 & \longrightarrow C_3H_6 + {}^\bullet CH_3 & (12)
\end{array}
$$

where : $[{}^\bullet C_4H_9] = [{}^\bullet R_1] + [{}^\bullet R_2]$ (13)

The rates of production of the products of propagation must be the same for the lumped mechanism and for the detailed mechanism :

$$\begin{aligned} r_9 &= r_1 + r_2 \\ r_{10} &= r_3 + r_4 \\ r_{11} &= r_5 \\ r_{12} &= r_6 \end{aligned} \tag{14}$$

The following relationships between the lumped rate constants and the real rate constants are obtained :

— for metatheses :

$$\begin{cases} k_9 = k_1 + k_2 \\ k_{10} = k_3 + k_4 \end{cases} \tag{15}$$

— for beta-scissions :

$$\begin{cases} k_{11} = k_5\ [{}^\bullet R_1]/[{}^\bullet C_4H_9] \\ k_{12} = k_6\ [{}^\bullet R_2]/[{}^\bullet C_4H_9] \end{cases} \tag{16}$$

Taking equation (8) into account, relationships (15) have the following form :

$$\begin{aligned} k_{11} &= k_5 \frac{1}{1 + \dfrac{k_5}{k_6}\dfrac{k_2}{k_1+k_2}\dfrac{k_3+k_4}{k_3}} \\ k_{12} &= k_6 \frac{1}{1 + \dfrac{k_6}{k_5}\dfrac{k_1+k_2}{k_2}\dfrac{k_3}{k_3+k_4}} \end{aligned} \tag{17}$$

Relationships (17) can be simplified for the two limiting cases :

— $[{}^\bullet R_1] >> [{}^\bullet R_2]$, then gives : $k_{11} \approx k_5$ and $k_{12} \approx 0$

— $[{}^\bullet R_1] << [{}^\bullet R_2]$, then gives : $k_{11} \approx 0$ and $k_{12} \approx k_6$.

For an intermediate case :

— $[{}^\bullet R_1] \approx [{}^\bullet R_2]$, would give : $k_{11} \approx k_5/2$ and $k_{12} \approx k_6/2$.

This is a good approximation to start with as $k_1 \approx k_2$, $k_3 \approx k_4$, $k_5 \approx k_6$.

The lumping of reactions (11) and (12) can be carried further by introducing the fractional stoichiometric coefficients as in the example in Table 5 :

$${}^\bullet C_4H_9 \longrightarrow a_{11}\ (C_2H_4 + {}^\bullet C_2H_5) + a_{12}\ (C_3H_6 + {}^\bullet CH_3) \tag{18}$$

where : $a_{11} + a_{12} = 1$ (19)

The rate constant k_{18} and the coefficients a_{11} and a_{12} are calculated by writing the equality for the production of C_2H_4 and C_3H_6 by reaction (18) on the one hand, and by the reactions (11) and (12), on the other :

$$\begin{aligned} a_{11}r_{18} &= r_{11} \\ a_{12}r_{18} &= r_{12} \end{aligned} \tag{20}$$

From equations (19) and (20) the following relationships can be deduced :

$$\begin{aligned} k_{18} &= k_{11} + k_{12} \\ a_{11} &= k_{11}/(k_{11} + k_{12}) \\ a_{12} &= k_{12}/(k_{11} + k_{12}) \end{aligned} \tag{21}$$

These three quantities can be evaluated from the rate constants of the detailed mechanism by replacing the constants k_{11} and k_{12} by their expressions (17) in relationships (21). Using the approximation $k_{11} \approx k_5/2$ and $k_{12} \approx k_6/2$, gives :

$$\begin{aligned} k_{18} &\approx (k_5 + k_6)/2 \\ a_{11} &\approx k_5/(k_5 + k_6) \\ a_{12} &\approx k_6/(k_5 + k_6) \end{aligned} \tag{22}$$

Equations (22) point out an interesting fact : **the coefficients a_{11} and a_{12} are weakly dependent on the temperature**, as the activation energies E_5 and E_6 have values which are very close to one another. These coefficients will therefore be calculated only once at a temperature in the middle of the range being studied. On the contrary, it is clear that the rate constant k_{18} depends strongly on the temperature, as is the case for k_5 and k_6.

b) General case

The calculation is carried out in two stages.
— Long chain approximation
First of all, the equations for the long chain approximation as applied to the detailed mechanism, i.e. to the totality of the propagation reactions, excluding the initiation and termination reactions, are solved numerically. Calling one of the J free radicals involved in the propagation reactions ${}^{\bullet}R_j$, a system of linear equations of the following form is obtained :

$$\sum_{j=1}^{J} b_{ij}\,[{}^{\bullet}R_j] = 0,\ i = 1, J \tag{23}$$

The coefficients b_{ij} are functions of the concentrations of the reactants and of the temperature. Equations (23) are not independent so that the following equation can be added :

$$\sum_{j} [{}^{\bullet}R_j] = [{}^{\bullet}R_p] \tag{24}$$

where $[^\bullet R_p]$ stands for the total concentration of free radicals of propagation. The solution of the system of equations (23-24) allows the relative importance of each of the free radicals of the detailed mechanism to be calculated :

$$\alpha_j = [^\bullet R_j] / [^\bullet R_p] \tag{25}$$

— Estimation of the lumped rate constants

Calling $^\bullet L$ a lumped free radical, relationship (13) can be generalized in the following form :

$$[^\bullet L] = \sum [^\bullet R_L] \tag{26}$$

where $^\bullet R_L$ stands for a free radical of the detailed mechanism belonging to the $^\bullet L$ family. Taking relationship (25) into account, gives :

$$[^\bullet L] = \sum \alpha_L \, [^\bullet R_p] \tag{27}$$

Calling k_L the rate constant of the radical $^\bullet R_L$ for a given class of reaction and $\tilde{k}_L$ the corresponding lumped rate constant, the generalization of equations (16), gives :

$$\tilde{k}_L \, [^\bullet L] = \sum k_L \, [^\bullet R_L] \tag{28}$$

that is, finally:

$$\tilde{k}_L = \sum \alpha_L \, k_L \, / \sum \alpha_L \tag{29}$$

The lumped rate constant is the average of the rate constants of the elementary reactions which it groups together, weighted by the relative importance of the free radicals involved in these.

If the propagation reactions are lumped using the fractional stoichiometric coefficients a_L, the generalized relationships (21) are used, i.e. :

$$\begin{aligned} \tilde{k} &= \sum \tilde{k}_L \\ a_L &= \tilde{k}_L / \sum \tilde{k}_L \end{aligned} \tag{30}$$

As has already been said, the coefficients a_L vary little with the temperature, as the rate constants $\tilde{k}_L$ have activation energies whose values are close to one another.

As far as metatheses are concerned, the rate constants can be calculated using the following relationship, which generalizes relationships (15) :

$$k_{me} = p \, k_p + s \, k_s + t \, k_t \tag{31}$$

where k_p, k_s, k_t are the rate constants of abstraction of one primary, secondary and tertiary H atom,

p, s, t are the numbers of primary, secondary and tertiary H atoms.

The constants k_p, k_s and k_t are themselves evaluated using structure-reactivity correlations.

Example 4

Calculate the rate constant of the lumped metathesis reaction :

$$^\bullet OH + C_4H_{10} \longrightarrow H_2O + {}^\bullet C_4H_9 \qquad (1)$$

Reaction (1) groups together the following two elementary reactions :

$$^\bullet OH + C_4H_{10} \longrightarrow H_2O + {}^\bullet 1\text{-}C_4H_9 \qquad (2)$$

$$^\bullet OH + C_4H_{10} \longrightarrow H_2O + {}^\bullet 2\text{-}C_4H_9 \qquad (3)$$

therefore : $k_1 = k_2 + k_3$.

k_2 and k_3 can be calculated using structure-reactivity correlations for the metathesis reactions : $k_2 = 6\ k_p$, $k_3 = 4\ k_s$.

Example 5

Calculate the rate constants and the fractional stoichiometric coefficients of the lumped oxidation reactions :

$$^\bullet C_4H_9 + O_2 \longrightarrow 1\text{-}C_4H_8 + {}^\bullet OOH \qquad (1)$$

$$^\bullet C_4H_9 + O_2 \longrightarrow 2\text{-}C_4H_8 + {}^\bullet OOH \qquad (2)$$

$$^\bullet C_4H_9 + O_2 \longrightarrow a_1\ 1\text{-}C_4H_8 + a_2\ 2\text{-}C_4H_8 + {}^\bullet OOH \qquad (3)$$

The lumped reactions (1) and (2) group together the following elementary reactions :

$$^\bullet CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_3 + O_2 \longrightarrow CH_2\text{=}CH\text{–}CH_2\text{–}CH_3 + {}^\bullet OOH \qquad (4)$$

$$CH_3\text{–}{}^\bullet CH\text{–}CH_2\text{–}CH_3 + O_2 \longrightarrow CH_2\text{=}CH\text{–}CH_2\text{–}CH_3 + {}^\bullet OOH \qquad (5)$$

$$\longrightarrow CH_3\text{–}CH\text{=}CH\text{–}CH_3 + {}^\bullet OOH \qquad (6)$$

therefore :

$$k_1 = \frac{k_4\ [{}^\bullet 1\text{-}C_4H_9] + k_5\ [{}^\bullet 2\text{-}C_4H_9]}{[{}^\bullet C_4H_9]}$$

$$k_2 = \frac{k_6\ [{}^\bullet 2\text{-}C_4H_9]}{[{}^\bullet C_4H_9]}$$

$$k_3 = k_1 + k_2$$

$$a_1 = \frac{k_1}{(k_1 + k_2)}$$

$$a_2 = \frac{k_2}{(k_1 + k_2)}$$

The constants k_4, k_5 and k_6 are calculated using the structure-reactivity correlations for the oxidations : $k_4 = 2\ k_s$, $k_5 = 3\ k_p$ and $k_6 = 2\ k_s$.

FURTHER READING

BARBE P., BATTIN-LECLERC F., CôME G.M., *Experimental and modelling study of methane and ethane oxidation between 773 and 1573 K*, J. Chim. Phys., 92, 1666 (1995).

CôME G.M., WARTH V., GLAUDE P.A., FOURNET R., BATTIN-LECLERC F., SCACCHI G., *Computer-aided design of gas-phase oxidation mechanisms. Application to the modeling of n-heptane and iso-octane oxidation*, 26th Symp. (Int.) on Combustion, 755 (1996).

CURRAN H.J., GAFFURI P., PITZ W.J., WESTBROOK C.K., *A comprehensive modeling study of n-heptane oxidation*, Combustion and Flame, 114, 149 (1998).

DENTE M., RANZI E., *Mathematical modeling of hydrocarbon pyrolysis reactions*, in "Pyrolysis : theory and industrial practice", Academic Press (1983).

FOURNET R., WARTH V., GLAUDE P.A., BATTIN-LECLERC F., SCACCHI G., CÔME G.M., *Automatic Reduction of Detailed Mechanisms of Combustion of Alkanes by Chemical Lumping*, Int. J. Chem. Kin., 32, 36 (2000).

GLAUDE P.A., WARTH V., FOURNET R., BATTIN-LECLERC F., SCACCHI G., CÔME G.M., *Modelling of the Oxidation of n-Octane and n-Decane Using an Automatic Generation of Mechanisms*, Int. J. Chem. Kin., 30, 949 (1998).

GLAUDE P.A., BATTIN-LECLERC F., JUDENHERC B., WARTH V., FOURNET R., CÔME G.M., SCACCHI G., DAGAUT P., CATHONNET M., *Experimental and Modelling Study of the Gas-Phase Oxidation of Methyl and Ethyl Tertiary Butyl Ethers*, Comb. & Flame, 121, 345 (2000).

RANZI E., FARAVELLI T., GAFFURI P., SOGARO A., *Low-temperature combustion: automatic generation of primary oxidation reactions and lumping procedures*, Combustion and Flame, 102, 179 (1995).

RANZI E., DENTE M., GOLDANIGA A., BOZZAVO G., FARAVELLI T., *Lumping Procedures in Detailed Kinetic Modelling of Gasification, Pyrolysis, Partial Oxidation and Combustion of Hydrocarbon Mixtures*, Prog. Energy & Comb. Sc., 27, 99 (2001).

TOMLIN A.S., TURANYI T., PILLING M.J., *Mathematical tools for the construction, investigation and reduction of combustion mechanisms*, Comprehensive Chem. Kin., vol. 35, chap. 4, p. 293 (1997).

WARTH V., STEF N., GLAUDE P.A., BATTIN-LECLERC F., SCACCHI G., CôME G.M., *Computer-aided derivation of gas-phase oxidation mechanisms: application to the modeling of the oxidation of n-butane*, Combustion and Flame, 114, 81 (1998).

WARTH V., BATTIN-LECLERC F., FOURNET R., GLAUDE P.A., CÔME G.M., SCACCHI G., *Computer Based Generation of Reaction Mechanisms for Gas-Phase*

Oxidation, Comp. & Chem., 24, 541 (2000).

COMPUTER PROGRAMS

EXGAS, KERGAS, KINBEN, KINCOR, LUMPGAS, SPYRO, THERGAS.

CHAPTER X

MOLECULAR TRANSPORT LAWS

The aim of this chapter is to discuss the molecular transport laws of matter, of heat and of momentum, and to define the properties which characterize them : diffusion coefficient , thermal conductivity and viscosity.

1 - MOLECULAR TRANSPORT PHENOMENA

When concentration, temperature or flow velocity gradients exist in a gas, the Brownian movement of the molecules tends to reduce these differences. Table 1 shows an inventory of these phenomena and of the corresponding laws.

Table1 : Molecular transport phenomena

	Gradient		
Flux	Concentration	Temperature	Flow velocity
Matter	FICK's law	SORET effect	
Heat	DUFOUR effect	FOURIER's law	
Momentum			NEWTON's law

Diffusion is the transport of matter caused by a concentration gradient. Matter is transported from areas of high concentration towards those of low concentration, i.e. in the opposite direction to the concentration gradient. The corresponding law is **FICK**'s law. Two other phenomena of molecular transport of matter exist ; one results from a temperature gradient, this is the **SORET** effect ; the other is due to a pressure gradient and is called **barodiffusion**. These two diffusion fluxes are negligible with respect to FICK's diffusion in most cases.
Thermal conduction is the molecular transport of heat energy caused by a temperature gradient. The heat is transported from regions of high temperature towards those at lower temperatures, i.e. in the opposite direction to the temperature gradient. The corresponding law is **FOURIER**'s law. The same phenomenon of transport of energy

can be the result of a concentration gradient, it is then called the **DUFOUR effect** and can be negligible to a first approximation with respect to FOURIER conduction.
The **viscosity** of gases is such that, if there is a flow velocity gradient between two adjacent filaments, the faster tends to accelerate the slower, and the slower to slow down the faster ; in other words, there is transport of momentum from regions of high velocity towards those of low velocity, i.e. in the opposite direction to the velocity gradient. The corresponding law is **NEWTON**'s law.

2 - MOLECULAR TRANSPORT OF MATTER

2.1 - FICK's law

a) Binary diffusion

A mixture of two gases A and B is considered whose concentrations c_A and c_B are functions of the space variables, all other variables, especially the pressure and the temperature, being constant. FICK's law states that the flux density of A is proportional to the concentration gradient of A :

$$\vec{\varphi}_{AB} = - D_{AB} \overrightarrow{\text{grad}}\, c_A \qquad (1)$$

where $\vec{\varphi}_{AB}$ is the molar flux density of species A, in mol m^{-2} s^{-1},

D_{AB} is the binary diffusion coefficient of A in B, in m^2 s^{-1},

c_A is the concentration of A, in mol m^{-3},

$\overrightarrow{\text{grad}}\, c_A$ is the concentration gradient of A, in mol m^{-4}.

The negative sign indicates that the matter is transported from regions of high concentration towards those of lower concentration in A.

b) Diffusion of a gas in a mixture

FICK's law takes the following more general form :

$$\vec{\varphi}_j^{\,c} = - D_j^c \overrightarrow{\text{grad}}\, c_j \qquad (2)$$

where $\vec{\varphi}_j^{\,c}$ is the molar flux density of constituent C_j, in mol m^{-2} s^{-1},

D_j^c is the diffusion coefficient of C_j in the gas mixture, in m^2 s^{-1},

c_j is the concentration of C_j, in mol m^{-3},

$\overrightarrow{\text{grad}}\, c_j$ is the concentration gradient of C_j, in mol m^{-4}.

The superscript c indicates that the transport of matter results from a concentration gradient.

Law (2) can be rewritten introducing the mass flux density :

$$\vec{\psi}_j^c = \vec{\varphi}_j^c M_j \tag{3}$$

where $\vec{\psi}_j^c$ is in kg m^{-2} s^{-1},

M_j is the molar mass of C_j, in kg mol^{-1}.

Now, the following relationships have been established in Chapter III :

$$c_j = x_j c \tag{4}$$

$$M_j = \frac{\rho}{c} \frac{w_j}{x_j} \tag{5}$$

where x_j is the mole fraction of C_j,

c is the total concentration, in mol m^{-3},

ρ is the density, in kg m^{-3},

w_j is the mass fraction of C_j.

The following law can be deduced :

$$\vec{\psi}_j^c = - D_j^c \rho w_j \overrightarrow{\text{grad}} \ln x_j \tag{6}$$

The velocity of diffusion $\vec{V}_j$ as defined by the following relationship, can be introduced :

$$\vec{\psi}_j^c = \rho \vec{V}_j \tag{7}$$

where $\vec{V}_j$ is in m s^{-1}.

The following expression for the velocity of diffusion can be deduced :

$$\vec{V}_j = - D_j^c w_j \overrightarrow{\text{grad}} \ln x_j \tag{8}$$

This velocity of diffusion must be added to the velocity of convection.

2.2 - SORET effect

The SORET effect, or thermal diffusion, obeys the following law :

$$\vec{\varphi}_j^T = - D_j^T \overrightarrow{\text{grad}} \ln T \tag{9}$$

where $\vec{\varphi}_j^T$ is the molar flux density of C_j, in mol m^{-2} s^{-1},

D_j^T is the thermal diffusion coefficient, in mol m^{-1} s^{-1},

$\overrightarrow{\text{grad}} \ln T$ is the gradient of the Napierian logarithm of the temperature T, in m^{-1}.

The superscript T indicates that the matter transport due to the SORET effect is the result of a temperature gradient.

The thermal diffusion intervenes mainly at low temperature for light species, like H and H_2.

2.3 - Barodiffusion

This phenomenon obeys the following law :

$$\vec{\varphi}_j^{\,p} = - D_j^p \,\overrightarrow{\text{grad}} \ln p \tag{10}$$

where $\vec{\varphi}_j^{\,p}$ is the molar flux density of C_j, in mol m^{-2} s^{-1},

D_j^p is the coefficient of barodiffusion, in mol m^{-1} s^{-1},

$\overrightarrow{\text{grad}} \ln p$ is the gradient of the Napierian logarithm of the pressure, in m^{-1}.

The superscript p indicates that the phenomenon is the result of a pressure gradient.

In general, this flux is negligible except in the case of the very high pressure gradients which occur in detonations, for example.

2.4 - General law

This law results from the addition of the three phenomena :

$$\vec{\varphi}_j = \vec{\varphi}_j^{\,c} + \vec{\varphi}_j^{\,T} + \vec{\varphi}_j^{\,p} \tag{11}$$

It can be written as follows : $\vec{\varphi}_j = - D_j^c \,\overrightarrow{\text{grad}}\, c_j - D_j^T \,\overrightarrow{\text{grad}} \ln T - D_j^p \,\overrightarrow{\text{grad}} \ln p$ (12)

3 - MOLECULAR TRANSPORT OF HEAT

3.1 - FOURIER's law

A pure gas whose temperature T is a function of the spatial coordinates is considered. The temperature gradient causes a molecular transport of heat energy which obeys the following relationship :

$$\vec{\varphi}_q^{\,T} = - \lambda \,\overrightarrow{\text{grad}}\, T \tag{13}$$

where $\vec{\varphi}_q^{\,T}$ is the heat flux density, in J m^{-2} s^{-1},

λ is the thermal conductivity, in J m^{-1} K^{-1} s^{-1},

$\overrightarrow{\text{grad}}\, T$ is the temperature gradient, in K m^{-1}.

The superscript T indicates that the cause of the heat transport is the temperature gradient.

3.2 - Diffusional transport

The molecules which are transported as a result of a concentration gradient transport also a quantity of heat :

$$\vec{\varphi}_q^{\,c} = \sum_j \varphi_j^c H_j \tag{14}$$

where $\vec{\varphi}_q^{\,c}$ is the heat flux density, in J m^{-2} s^{-1},
H_j is the enthalpy of C_j, in J mol^{-1}.

The superscript c indicates that the cause of the transport is the concentration gradient.

3.3 - DUFOUR effect

Remember that this is a heat flux resulting from a concentration gradient. The corresponding law can be written as follows :

$$\vec{\varphi}_q^{\,D} = MRT \sum_j \sum_{k \neq j} \frac{D_j^T}{\rho\, D_{jk}\, M_k} \left(\frac{w_k}{w_j} \vec{\psi}_j^{\,c} - \vec{\psi}_k^{\,c} \right) \tag{15}$$

where $\vec{\varphi}_q^{\,D}$ is the heat flux density, in J m^{-2} s^{-1},
M is the mean molar mass, in kg mol^{-1},
R is the gas constant, in J mol^{-1} K^{-1},
T is the temperature, in K,
D_j^T is the thermal diffusion coefficient, in mol m^{-1} s^{-1},
ρ is the density, in kg m^{-3},
D_{jk} is the binary diffusion coefficient of C_j in C_k, in m^2 s^{-1},
M_j, M_k are the molar masses of C_j and C_k, respectively, in kg mol^{-1},
w_j, w_k are the mass fractions of C_j and C_k, respectively,
$\vec{\psi}_j^{\,c}$, $\vec{\psi}_k^{\,c}$ are the flux densities of mass diffusion of C_j and C_k, respectively, in kg m^{-2} s^{-1}.

3.4 - General law

It is the result of the three phenomena :

$$\vec{\varphi}_q = \vec{\varphi}_q^{\,T} + \vec{\varphi}_q^{\,c} + \vec{\varphi}_q^{\,D} \tag{16}$$

In general, the DUFOUR effect is negligible, therefore :

$$\vec{\varphi}_q = -\lambda\, \overrightarrow{\text{grad}}\, T + \sum_j \vec{\varphi}_j^{\,c} H_j \tag{17}$$

4 - MOLECULAR TRANSPORT OF MOMENTUM

This type of transport obeys NEWTON's law.

4.1 - Unidimensional case

Viscosity is the measure of the resistance that a fluid offers to an applied shearing force. A gas whose velocity v_y in the direction Oy is a function of the spatial coordinates z, is considered. NEWTON's law states that the flux density of momentum in the direction Oz perpendicular to Oy is proportional to the velocity gradient :

$$\varphi_{mv} = -\eta \frac{\partial v_y}{\partial z} \tag{18}$$

where φ_{mv} is the flux density of momentum, in kg m^{-1} s^{-2},

η is the dynamic viscosity, in kg m^{-1} s^{-1},

$\partial v_y/\partial z$ is the velocity gradient in the direction Oz, in s^{-1}.

The SI unit of viscosity is the Pascal s. A fluid has a viscosity of 1 Pa s if a force of 1 N is required to move a plane of 1 m^2 at a velocity of 1 m s^{-1} with respect to a plane surface 1 m away and parallel to it.

4.2 - Three-dimensional case

NEWTON's law can be expressed in tensorial form :

$$\overline{\overline{p}} = p\,\overline{\overline{e}} + \overline{\overline{P}} \tag{19}$$

where $\overline{\overline{p}}$ is the pressure tensor,

p is the hydrostatic pressure,

$\overline{\overline{e}}$ is a unit tensor,

$\overline{\overline{P}}$ is a term describing the viscosity effect.

The term $\overline{\overline{P}}$ can be calculated using the kinetic theory of gases :

$$\overline{\overline{P}} = -\eta \left[(\overrightarrow{\text{grad}}\ \vec{v}) + (\overrightarrow{\text{grad}}\ \vec{v})^t\right] + \left(\frac{2}{3}\eta - \kappa\right)(\text{div}\ \vec{v})\ \overline{\overline{e}} \tag{20}$$

where η is the mean dynamic viscosity,

$\vec{v}$ is the rate of convection,

κ is the volume viscosity.

As a first approximation, a volume viscosity $\kappa=0$ will be assumed, which is only rigorously true of monoatomic gases.

5 - ANALOGIES BETWEEN THE PHENOMENA OF MOLECULAR TRANSPORT

The laws which govern the phenomena of molecular transport of quantities of matter, of heat and of momentum, seen in the paragraphs above, can be presented in the following general form :

$$\begin{pmatrix}\text{flux density}\\ \text{of the quantity}\end{pmatrix} = -\,(\text{conductivity}) \times \begin{pmatrix}\text{potential}\\ \text{gradient}\end{pmatrix} \tag{21}$$

These laws are summarized in Table 2a.
Law (21) can be written in another form involving the quantity concentration defined by the relationship :

$$\begin{pmatrix}\text{quantity}\\ \text{concentration}\end{pmatrix} = (\text{capacity}) \times (\text{potential}) \tag{22}$$

Relationship (21) can then be written as follows :

$$\begin{pmatrix}\text{flux density}\\ \text{of the quantity}\end{pmatrix} = -\,(\text{diffusivity}) \times \begin{pmatrix}\text{quantity concentation}\\ \text{gradient}\end{pmatrix} \tag{23}$$

Table 2b shows the corresponding different laws, with the concomitant definition of the diffusivities :

$$\alpha = \lambda/\rho\, c_p^o \tag{24}$$

$$\nu = \eta/\rho \tag{25}$$

The diffusivities D, α, ν characterize the ease of the molecular transports of the three quantities : matter, heat and momentum, respectively. These diffusivities can be expressed in the same units, i.e. $m^2\ s^{-1}$ in basic SI units.

The ratio of two diffusivities is therefore a non-dimensional number which represents the relative efficiency of the two modes of transport. Three non-dimensional numbers have been defined, the Schmidt numbers (Sc), the Prandtl numbers (Pr) and the Lewis numbers (Le) :

$$Sc = \nu/D \tag{26}$$

$$Pr = \nu/\alpha \tag{27}$$

$$Le = \alpha/D \tag{28}$$

For gases, where the molecular collisions are less numerous than for liquids, the transports of the three quantities (mass, heat, momentum) occur with efficiencies which are very close to one another. It is concluded that the Schmidt numbers, the Prandtl numbers and the Lewis numbers are close to 1 :

$$Sc \simeq Pr \simeq Le \simeq 1 \qquad (29)$$

Moreover, under usual conditions, the following orders of magnitude have been observed for gases : D, α, $\nu \simeq 10^{-5}$ m^2 s^{-1}.

Table2 : Analogies between the phenomena of molecular transport.

a) Conductivities

Law	Quantity transported	Potential	Conductivity
FICK	Matter (mol)	Concentration (mol m^{-3})	Diffusion coefficient D (m^2 s^{-1})
FOURIER	Heat (J)	Temperature (K)	Thermal conductivity λ (J m^{-1} K^{-1} s^{-1})
NEWTON	Momentum (kg m s^{-1})	Velocity (m s^{-1})	Dynamic viscosity η (kg m^{-1} s^{-1})

b) Diffusivities

Law	Quantity transported	Quantity concentration	Diffusivity
FICK	Mass (kg)	Density ρ (kg m^{-3})	D (m^2 s^{-1})
FOURIER	Heat (J)	$\rho\, c_p^o\, T$ (J m^{-3})	$\alpha = \lambda/\rho c_p^o$ (m^2 s^{-1})
NEWTON	Momentum (kg m s^{-1})	$\rho\, v$ (kg m^{-2} s^{-1})	$\nu = \eta/\rho$ (m^2 s^{-1})

Example

Evaluate the order of magnitude of the diffusion coefficients D, of thermal conductivity λ and of dynamic viscosity η of a gas of heat capacity $C_p^o = 10^2$ J mol^{-1} K^{-1}, of molar mass $M = 0.1$ kg mol^{-1}, at a pressure $p = 10^5$ Pa and a temperature $T = 1000$ K.

Taking :	$D = \alpha = \nu = 10^{-5}$ m^2 s^{-1}
and :	$\lambda = \alpha\, \rho\, c_p^o$; $\eta = \rho\, \nu$ (eqns 24 and 25).
the density can be calculated :	$\rho = pM/RT = 1.2$ kg m^{-3}
and the specific heat :	$c_p^o = C_p^o/M = 10^3$ J kg^{-1} K^{-1}
finally :	$D \sim 10^{-5}$ m^2 s^{-1} ; $\lambda \sim 1\text{x}10^{-2}$ J m^{-1}K^{-1} s^{-1}
	$\eta \sim 1.2\text{x}10^{-5}$ kg m^{-1} s^{-1}

FURTHER READING

BIRD R.B., STEWART W.E., LIGHTFOOT E.N., *Transport Phenomena*, Wiley (1960).

FLUMERFELT R.W., GLOVER C.J., *Transport Phenomena*, Ullmann's Encyclopedia of Industrial Chemistry, vol. B1, chap. 4 (1995).

HIRSCHFELDER J.O., CURTISS C.F., BIRD R.B., *Molecular Theory of Gases and Liquids*, John Wiley, New York (1954).

SLATTERY J.C., *Advanced Transport Phenomena*, Cambridge Univ. Press (1999).

CHAPTER XI

ESTIMATION OF MOLECULAR TRANSPORT DATA

This chapter suggests methods of estimating the diffusion coefficients, the viscosity and the thermal conductivity of pure substances and gaseous mixtures.

The molecular transports of matter and of momentum depend mainly on the translational energy of the molecules, which allows the diffusion coefficients and the dynamic viscosities to be calculated using the kinetic theory of gases, improved so that the potential energy of interaction between the molecules e.g. of the LENNARD-JONES type, can be taken into account. The theory is rigorous for monatomic gases, but can also be considered to be a satisfactory approximation for polyatomic gases, as the internal movements (vibrations and rotations) of the molecules do not intervene to a significant extent.

The same cannot be said of the thermal conductivity, for which the energies of vibration and rotation intervene to a significant extent. The theory must therefore take these supplementary factors into account, otherwise erroneous values may be found.

1 - DIFFUSION COEFFICIENT

1.1 - Binary diffusion coefficient

A gas A, which diffuses in a gas B, is considered. The expression for the binary diffusion coefficient D_{AB} can be written as follows :

$$D_{AB} = 5.8755x10^{-24} \frac{T^{3/2}}{p\, M_{AB}^{1/2}\, \sigma_{AB}^{2}\, \Omega_d} \qquad (1)$$

where D_{AB} is the binary diffusion coefficient, in $m^2\ s^{-1}$,

T is the absolute temperature, in K,

p is the pressure, in Pa,

M_{AB} is the reduced molar mass of AB, in kg mol^{-1},

$$M_{AB} = \frac{M_A M_B}{M_A + M_B} , \qquad (2)$$

M_A, M_B are the molar masses of A and B, in kg mol^{-1},

σ_{AB} is the collision diameter of A and B, in m,

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2 , \qquad (3)$$

σ_A, σ_B are the molecular diameters of A and B, in m,

Ω_d is the reduced integral of collision.

The reduced integral of collision Ω_d differs according to whether the species A and B are polar or non-polar. The polarity of a species is characterized by a non-dimensional parameter δ which can be expressed as follows :

$$\delta = 3{,}622.10^{-27} \frac{\mu^2}{\sigma^3 \, (\varepsilon/k_B)} \qquad (4)$$

where μ is the dipolar moment of the species, in Debye (D),

σ is the LENNARD-JONES collision diameter, in m,

ε/k_B is the depth of the LENNARD-JONES potential well, in K.

The polarity parameter of the binary species AB can be calculated using the following relationship :

$$\delta_{AB} = (\delta_A \cdot \delta_B)^{1/2} \qquad (5)$$

a) If at least one of the two species A and B is not polar, then : $\delta_A = 0$ or $\delta_B = 0$ and $\delta_{AB} = 0$; the integral of diffusion can be obtained using the following correlation :

$$\begin{aligned} \Omega_d (\delta_{AB} = 0) = {} & 1.06036 \, (T^*_{AB}{}^{-0{,}1561} + 0.19300 \exp(-\,0.47635 \, T^*_{AB}) \\ & + 1.03587 \exp(-\,1.52996 \, T^*_{AB}) \\ & + 1.76474 \exp(-\,3.89411 \, T^*_{AB}) \qquad (6) \end{aligned}$$

where T^*_{AB} is the reduced temperature :

$$T^*_{AB} = T/(\varepsilon_{AB}/k_B) \qquad (7)$$

$$\varepsilon_{AB}/k_B = \left[(\varepsilon_A/k_B) \cdot (\varepsilon_B/k_B)\right]^{1/2} \qquad (8)$$

Values of ε/k_B, σ and μ are given in Tables XIV.3.

Example 1

Calculate the diffusion coefficient of the system CO_2—N_2 at 590 K and 1 bar.

Tables XIV.3 give the following values :

	ε/k_B (K)	σ (m)	μ (D)
CO_2 (A)	244	3.76×10^{-10}	0
N_2 (B)	97.5	3.62×10^{-10}	0

The two constituents have a dipolar moment μ which is equal to zero and consequently a non-dimensional polarity parameter δ equal to zero ; as a result $\delta_{AB} = 0$. Equation (6) can therefore be applied to calculate Ω_d ; thus :

$M_{AB} = 17.11 \times 10^{-3}$ kg mol^{-1} ; $\sigma_{AB} = 33.69 \times 10^{-10}$ m ; $\varepsilon_{AB}/k_B = 154$ K ; $T^*_{AB} = 3.825$;

$\Omega_d = 0.8942$; $D_{AB} = 5.29 \times 10^{-5}$ m^2 s^{-1}

A measurement of this property gave the value : $D_{AB} = 5.83 \times 10^{-5}$ m^2 s^{-1}.

b) If the two species are polar, the integral Ω_d has the following form :

$$\Omega_d = \Omega_d (\delta_{AB} = 0) + 0{,}19\ \delta^2_{AB}/T^*_{AB} \tag{9}$$

Example 2

Calculate the diffusion coefficient of methyl chloride in sulphur dioxide at 323 K and 1 atm.

CH_3Cl is called A and SO_2 is called B. The following values can be found in Tables XIV.3 :

	ε/k_B (K)	σ (m)	μ (D)
(A)	320	4.14×10^{-10}	1.87
(B)	347	4.04×10^{-10}	1.63

therefore :

$M_{AB} = 28.25 \times 10^{-3}$ kg mol^{-1} ; $\sigma_{AB} = 4.09 \times 10^{-10}$ m ; $\delta_A = 0.5578$; $\delta_B = 0.4206$;
$\delta_{AB} = 0.4844$; $\varepsilon_{AB}/k_B = 333.2$ K ; $T^*_{AB} = 0.9694$; $\Omega_d (\delta_{AB} = 0) = 1.462$;
$D_{AB} = 7.96 \times 10^{-6}$ m^2 s^{-1}

An experimental value of 7.69×10^{-6} m^2 s^{-1} has been published.

1.2 - Diffusion coefficient in a mixture

The global diffusion coefficient D^c_j of the species C_j in the mixture of the species C_k can be calculated from the binary diffusion coefficients D_{jk} of C_j in C_k : k≠j;

$$D^c_j = \frac{1 - w_j}{\sum\limits_{k \neq j} x_k/D_{jk}} \tag{10}$$

where w_j is the mass fraction of C_j,
x_k is the molar fraction of C_k.

2 - VISCOSITY

2.1 - Dynamic viscosity of a pure gas

This can be calculated using the following formula :

$$\eta = 8.441\text{x}10^{-25} \frac{(MT)^{1/2}}{\sigma^2 \Omega_v} \tag{11}$$

where η is the dynamic viscosity, in kg m^{-1} s^{-1},
M is the molar mass, in kg mol^{-1},
T is the temperature, in K,
σ is the diameter of the molecule, in m,
Ω_v is the reduced integral of collision.

The integral of collision Ω_v is obtained from the following correlations :

a) Non-polar gases ($\delta = 0$)

$$\Omega_v = 1.16145(T^*)^{-0.14874} + 0.52847 \exp(-0.77320\,T^*) + 2.16178 \exp(-2.43787\,T^*) \tag{12}$$

b) Polar gases ($\delta \neq 0$)

$$\Omega_v = \Omega_v(\delta = 0) + 0.20\,\delta^2/T^* \tag{13}$$

The properties T* (reduced temperature) and δ (polarity parameter) have the same meaning as in Paragraph 1 and can therefore be calculated using the following equations :

$$T^* = \frac{T}{(\varepsilon/k_B)} \tag{14}$$

$$\delta = 3.622\text{x}10^{-27} \frac{\mu^2}{\sigma^3 \times (\varepsilon/k_B)} \tag{15}$$

where T is in K ; ε/k_B in K ; μ in D and σ in m.

Example 3

Calculate the dynamic viscosity of CH_3OH at 550 K and 1 bar.

The following values can be found in Tables XIV.3 :

$\varepsilon/k_B = 417$ K ; $\sigma = 3.69\text{x}10^{-10}$ m ; $\mu = 1.7$ D

therefore :

$\delta = 0.4996$; $T^* = 1.319$; $\Omega_v(\delta = 0) = 1.392$; $\Omega_v = 1.430$;

$\eta = 1.82\text{x}10^{-5}$ kg m^{-1} s^{-1}

An experimental value $\eta_{exp} = 181$ μP has been published.

The poise (P) has the value 0.1 N s m^{-2} ; consequently 1μP = 10^{-7} kg m^{-1} s^{-1}, i.e. $\eta_{exp} = 1.81\text{x}10^{-5}$ kg m^{-1} s^{-1}.

The agreement is excellent.

2.2 - Dynamic viscosity of a mixture of gases

The following empirical approximation gives satisfactory values :

$$\eta = \frac{1}{2}\left[\sum x_j \eta_j + \left(\sum \frac{x_j}{\eta_j}\right)^{-1}\right] \tag{16}$$

where x_j is the molar fraction of constituent C_j.

Of course other correlations exist which allow more precise values to be obtained.

Example 4

TANAKA *et al.* have measured the dynamic viscosity of a mixture :

$CHF_2Cl : N_2 = 0.714 : 0.286$ (mol) at 323 K and $1.013\text{x}10^5$ Pa.

They found :

$\eta = 1.45\text{x}10^{-5}$ kg m^{-1} s^{-1}

Calculate the viscosity of the mixture knowing that $\eta(CHF_2Cl) = 1.34\text{x}10^{-5}$ and $\eta(N_2) = 1.88\text{x}10^{-5}$ kg m^{-1} s^{-1}.

Formula (15) gives :

$$\eta = 0.5\left[(0.714\times1.34+0.286\times1.88) + \left(\frac{0.714}{1.34}+\frac{0.286}{1.88}\right)^{-1}\right]\times10^{-5}$$

$\eta = 1.48\text{x}10^{-5}$ kg m^{-1} s^{-1}

The agreement with the experimental value is not quite as good as that obtained for example using the REICHENBERG method.

3 - THERMAL CONDUCTIVITY

3.1 - Thermal conductivity of a monoatomic gas

This can be calculated using the following formula :

$$\lambda = 2.632\text{x}10^{-23}\frac{T^{1/2}}{M^{1/2}\,\sigma^2\,\Omega_v} \tag{17}$$

where λ is the thermal conductivity, in J s^{-1} m^{-1} K^{-1},
T is the absolute temperature, in K,
M is the molar mass, in kg mol^{-1},
σ is the diameter of the atom, in m,
Ω_v is the reduced integral of collision.

The integral Ω_v can be calculated using equation (11).
Note the analogy between the expressions for the dynamic viscosity η and the thermal conductivity λ. EUCKEN has introduced the non-dimensional number :

$$f_{tr} = \frac{\lambda M}{\eta C_V^o} \qquad (18)$$

where λ is in J m^{-1} K^{-1} s^{-1},
M is in kg mol^{-1},
η is in kg m^{-1} s^{-1},
C_V^o is the heat capacity at constant volume, in J mol^{-1} K^{-1}.

For a monoatomic gas, which has only three degrees of translational freedom, then :

$$C_V^o = C_{V\,tr}^o = \frac{3}{2} R \qquad (19)$$

Putting expressions (11), (17) and (19) into equation (18), gives :

$$f_{tr} = \frac{5}{2} \qquad (20)$$

i.e. :

$$\lambda = \frac{\eta R}{M} \times \frac{15}{4} \qquad (21)$$

3.2 - Thermal conductivity of a polyatomic gas

Formula (21) does not give good results for polyatomic gases, due to the participation of the internal movements of the molecules (vibrations and rotations) to the thermal conductivity. It is therefore necessary to generalize relationship (21) in the following form :

$$\lambda = \frac{\eta R}{M}\left[\frac{15}{4} + f_p\, f_{int}\left(\frac{C_p^o}{R} - \frac{5}{2}\right)\right] \qquad (22)$$

where

$$f_{int} = 1 + (Sc^{-1} - 1) \exp(-10\, h^*/T^{*1/2}) \qquad (23)$$

$$h^* = \frac{1{,}384.10^{-10}}{\sigma M^{1/2} (\varepsilon/k_B)^{1/2}} \qquad (24)$$

$$Sc = \frac{\eta}{\rho D} = \frac{5}{6}\frac{\Omega_d}{\Omega_v} \qquad (25)$$

Sc is the SCHMIDT number for a pure gas. The value of Sc^{-1} is close to 1.32.
For a **non-polar gas**, the following value is taken :

$$f_p = 1 \qquad (26)$$

and for a **polar gas** :

$$f_p = \exp\left(-\ 11\ h^{*2}\delta/T^{*}\right) \qquad (27)$$

The polarity parameter δ is calculated using equation (4).
Note that formula (22), which is meant for polyatomic gases, can also be applied to monoatomic gases, for which $C_p^o/R = 5/2$, which gives formula (21) again.
Expressions (22) to (27) will be used with basic SI units :

λ	$J\ m^{-1}\ K^{-1}\ s^{-1}$
η	$kg\ m^{-1}\ s^{-1}$
$R = 8.3145$	$J\ mol^{-1}\ K^{-1}$
M	$kg\ mol^{-1}$
C_p^o	$J\ mol^{-1}\ K^{-1}$
σ	m
ε/k_B	K

Example 5

Calculate the thermal conductivity of isopentane at 10^5 Pa and 373 K. An experimental value $2.2\text{x}10^{-2}$ $J\ m^{-1}\ K^{-1}\ s^{-1}$ has been published.

The following values are taken : $\eta = 8.77\text{x}10^{-6}\ kg\ m^{-1}\ s^{-1}$, $C_p^o = 144\ J\ mol^{-1}\ K^{-1}$, $M = 7.2\text{x}10^{-2}\ kg\ mol^{-1}$, $\sigma = 6.03\text{x}10^{-10}$ m, $\varepsilon/k_B = 293$ K.

It is assumed that isopentane is a non-polar gas, i.e. $f_p = 1$, and a value of 1.32 is taken for Sc^{-1}, therefore :

$$h^* = 5.00\text{x}10^{-2}\ ;\ T^* = 1.27\ ;\ f_{int} = 1.1\ ;\ \lambda = 2.19\text{x}10^{-2}\ J\ m^{-1}\ K^{-1}\ s^{-1}$$

The calculated value is in better agreement with the measured value than those obtained by the methods tested by Poling *et al.* : Eucken ($1.88\text{x}10^{-2}$), modified Eucken ($2.36\text{x}10^{-2}$), Stiel and Thodos ($2.11\text{x}10^{-2}$), Roy and Thodos ($2.30\text{x}10^{-2}$), Chung *et al.* ($2.3\text{x}.10^{-2}$), Ely and Hanley ($2.25\text{x}10^{-2}$).

Example 6

Calculate the thermal conductivity of ammonia at 716 K and 10^5 Pa.

The following values are taken : $\eta = 2.53\text{x}10^{-5}\ kg\ m^{-1}\ s^{-1}$ and $C_p^o = 48.1\ J\ mol^{-1}\ K^{-1}$. Tables XIV.3 give $\varepsilon/k_B = 481$ K, $\sigma = 2.92\text{x}10^{-10}$ m, $\mu = 1.47$ D. Relationship (4) gives the value of the polarity parameter $\delta = 0.654$; NH_3 is therefore a polar substance and relationship (27) must be used. This gives $h^* = 0.166$, $T^* = 1.49$, $f_{int} = 1.08$ (with

$Sc^{-1} = 1.32$), $f_p = 0.875$, $\eta R/M = 1.237.10^{-2}$. Relationship (22) finally gives : $\lambda = 8.52 \times 10^{-2}$ J m^{-1} K^{-1} s^{-1}. This calculated value is in better agreement with the experimental value ($\lambda = 8.54 \times 10^{-2}$), than that which is obtained using the method used in the CHEMKIN computer program.

3.3 - Thermal conductivity of a mixture of gases

A formula analogous to that used for the viscosity is used :

$$\lambda = \frac{1}{2}\sum x_j \lambda_j + \frac{1}{2}\left(\sum \frac{x_j}{\lambda_j}\right)^{-1} \tag{28}$$

where x_j is the molar fraction of constituent C_j.
As for the viscosities, more complicated formulae exist which give more precise results.

Example 7
BENNETT and VINES have measured a thermal conductivity

$$\lambda = 1.92 \times 10^{-2} \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$$

for a mixture C_6H_6 : Ar = 0.25 : 0.75 (mol) at 374 K and 10^5 Pa.
Calculate the thermal conductivity of the mixture taking $\lambda(C_6H_6) = 1.66.10^{-2}$ and $\lambda(Ar) = 2.14 \times 10^{-2}$ J m^{-1} K^{-1} s^{-1}.

Formula (28) gives :

$$\lambda = \frac{1}{2}(0.25 \times 1.66 + 0.75 \times 2.14) \times 10^{-2} + \frac{1}{2}\left(\frac{0.25}{1.66 \times 10^{-2}} + \frac{0.75}{2.14 \times 10^{-2}}\right)^{-1}$$

$$\lambda = 2.01 \times 10^{-2} \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$$

The difference with respect to the experimental value is 4 to 5 %, which is analogous to that obtained by the methods of SAXON and MASENA, but lower than that resulting from the CHUNG *et al.* method.

4 - LENNARD-JONES PARAMETERS

The calculation of diffusion, viscosity and thermal diffusion coefficients, requires a knowledge of the values of the LENNARD-JONES parameters σ and ε/k_B. Tables XIV.3 give these values for a few species. Other compilations in the literature allow the values of supplementary species to be obtained. However, it is useful to have correlations between these properties and other properties of the molecules most frequently tabulated, which is especially true of the critical pressure and temperature (p_c and T_c) and of the PITZER (ω) acentric factor, which constitutes a macroscopic measurement of the difference with respect to a spherical geometry of the force field around the molecule.

a) Non-polar gases

The following correlations are available :

$$\varepsilon/k_B = T_c\left(0.753 - 0.468\,\omega - 0.277\,\omega^2 + 0.462\,\omega^3\right) \qquad (29)$$

$$\sigma = 4.722\text{x}10^{-9}\left((T_c/p_c)\times(13.56 + 9.60\,\omega + 6.26\,\omega^2 - 10.0\,\omega^3)\right) \qquad (30)$$

where ε/k_B is the depth of the potential well in K,

T_c is the critical temperature, in K,

ω is the acentric factor,

σ is the molecular diameter, in m,

p_c is the critical pressure, in Pa.

Of course, $\mu = 0$ for a non-polar gas.

Example 8

Calculate ε/k_B and σ for isopentane. The following values are available $T_c = 460.4$ K, $p_c = 3.39\text{x}10^6$ Pa, $\omega = 0.227$.

It is assumed that isopentane has a negligible dipolar moment ; formulae (29) and (30) give the following $\varepsilon/k_B = 293.7$ K and $\sigma = 6.11\text{x}10^{-10}$ m.

b) Polar gases

Corrections are carried out on values for molecules which are assumed to be non-polar :

$$[(\varepsilon/k_B)/T_c] = [(\varepsilon/k_B)/T_c]_{\mu=0} + 2.290\text{x}10^{-2}\,(0.476 + 3.82\,\omega)\,\mu\,p_c^{1/2}/T_c \qquad (31)$$

$$[\sigma^3 p_c/T_c] = [\sigma^3 p_c/T_c]_{\mu=0} - 1.856\text{x}10^{-26}\,(1+10\omega)\,\mu\,p_c^{1/2}/T_c \qquad (32)$$

where ε/k_B and T_c are in K ; μ in D ; p_c in Pa and σ in m.

Example 9

Calculate ε/k_B and σ for ethyl acetate. The following values are obtained from tables :

$T_c = 523.2$ K, $p_c = 3.83\text{x}10^6$ Pa, $\mu = 1.9$ D, $\omega = 0.362$.

The "non-polar" properties are calculated using equations (29) and (30) ; which gives :

$[(\varepsilon/k_B)/T_c]_{\mu=0} = 0.5692$ and $[\sigma^3 p_c/T_c]_{\mu=0} = 1.830\text{x}10^{-24}$

The corrections given by relationships (31) and (32) are carried out, which gives :

$$(\varepsilon/k_B)/T_c = 0.5692 + 2.290\text{x}10^{-2}\times1.859\times1.9\times(3.83\text{x}10^6)^{1/2}/523.2 = 0.8718$$

$$\sigma^3 p_c/T_c = 1.830\text{x}10^{-24} - 1.856\text{x}10^{-26}\times4.62\times1.9\times(3.83\text{x}10^6)^{1/2}/523.2 = 1.221\text{x}10^{-24}$$

This finally gives :

$$\varepsilon/k_B = 456 \text{ K} \quad \text{and} \quad \sigma = 5.50\text{x}10^{-10} \text{ m}$$

5 - LIMITS OF VALIDITY

The methods of estimation proposed in this chapter are applicable to gases whose pressure is higher than that of the KNUDSEN regime (where the molecular collisions with the reactor walls become more frequent than the collisions in the gas phase), and lower than a pressure defined by the following relationship :

$$p/p_c < 0.061\ T/T_c - 0.003 \qquad (33)$$

with the following temperature constraint :

$$0.5 < T/T_c < 4.5 \qquad (34)$$

Example 10

Define the limits of validity of the formulae for the calculation of D, η, λ for the case of iso-octane at 1800 K. Knowing the following values :

$T_c = 544$ K and $p_c = 2.57\text{x}10^{6}$ Pa

The ratio $T/T_c = 3.31$ actually obeys constraint (34). The pressure must therefore respect the inequality (33) :

$$p < 2.57\text{x}10^{6}\,(0.061\times 3.31 - 0.003) = 5.1\text{x}10^{5}\ \text{Pa}$$

FURTHER READING

GARDINER W.C. Jr, Coordinator, *Combustion Chemistry*, 2nd edition, Springer-Verlag (1994).

KEE R.J., MILLER J.A., *A Structured Approach to the Computational Modelling of Chemical Kinetics and Molecular Transport in Flowing Systems*, Sandia Report SAND 86-8841 (1992).

KEE R.J., DIXON-LEWIS G., WARNATZ J., COLTRIN M.E., MILLER J.A., *A Fortran Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties*, SANDIA Report SAND 86-8246. VC-401 (1993).

ONKEN V., PAUL H.I., *Estimation of physical properties*, Ullmann's Enc. Ind. Chem., B1, chap. 6 (1995).

POLING B.E., PRAUSNITZ J.M., O'CONNEL J.P., *The Properties of Gases and Liquids*, 5th edition, McGraw Hill (2000).

WANG H., FRENKLACH M., *Transport properties of polycyclic aromatic hydrocarbons for flame modeling*, Comb. & Flame, 96, 163 (1994).

COMPUTER PROGRAMS

TRANDAT, TRANFIT, TRANLIB.

CHAPTER XII

LABORATORY REACTORS

The primary aim of Chapter XII is to describe the ***technology*** *of the main kinds of reactors used in the laboratory to study complex gas-phase thermal reactions.*
The second aim is to establish the mass, energy and momentum ***balance equations****, to simulate these reactors so that it is possible to determine the rates of reaction directly.*

1 - GENERAL CHARACTERISTICS

a) Area of study

The essential operating conditions which characterize the setting up of a GPTR are the time of the reaction t_r, the temperature T_r and the pressure p_r. Table 1 gives the areas of study which can be explored by the six main laboratory reactors ; this table therefore allows the reactor best adapted to the study being envisaged, to be chosen.

Table1 : Laboratory reactors for GPTRs

	t_r (s)	T_r (K)	p_r (Pa)
Batch reactor	$10–10^6$	300–1400	$10^3–10^9$
Stirred flow reactor	1–10	300–1400	$10^{-1}–10^6$
Tubular reactor	$10^{-3}–1$	300–1400	$10^3–10^6$
Rapid compression machine	$10^{-3}–0.1$	600-1100	$1–2\text{x}10^6$
Premixed laminar flames	$10^{-4}–10^{-2}$	1500–3000	$10–10^5$
Shock tube	$10^{-6}–10^{-3}$	900–3000	$10^5–10^7$

— *Times of reaction*

These go from 10^6 s, that is several weeks, for the slowest reactions to 10^{-6} s for those studied using a shock tube, which corresponds to a spread over **twelve** orders of magnitude, that is a factor of 10^{12}.

— *Temperatures*

These go from room temperature, that is 300 K to about 3000 K. For a rate constant which has an activation energy of 10^5 J mol^{-1}, this corresponds to a variation of **fifteen** orders of magnitude, that is a factor of 10^{15}. The high temperatures can be limited by the resistance of the materials.

— *Pressures*

Certain reactors can be used in the KNUDSEN mode, i.e. at pressures of the order of 0.1 Pa, up to very high pressures of 10 000 atm, characteristic of those which can occur in some oil-fields. The ratio of these two extreme pressures is 10^{10}, that is **ten** orders of magnitude.

b) Ideal reactors

Certain reactors function under conditions such that the rate of reaction can be calculated easily from the experimental results. These reactors are called ideal reactors ; this is particularly the case of :

- the batch reactor at constant volume operating under isothermal conditions,
- the well-stirred flow reactor at constant volume operating under steady-state conditions, at constant temperature and pressure,
- the plug-flow reactor at constant volume operating under steady-state conditions, at constant temperature and pressure.

For the laboratory reactors which do not function according to one of these ideal conditions, it is generally necessary to proceed by solving the mass, energy and momentum balance equations by numerical methods. These equations can be simplified with respect to those, which can be applied to three-dimensional reactant flows, for two reasons :

- the flow of the fluids is treated in the same way as a one-dimensional flow as in the case of a tubular reactor, of the flat-flame burner and of the shock tube ; it is even zero-dimensional for the well-stirred flow reactor ;
- the reactors are made to work under one or other of the following working conditions, so that the balance equations can be treated more easily : reactor at constant volume, isothermal or temperature profile mode, adiabatic mode, isobaric mode, steady- state mode, unique residence time or an exponential distribution of the residence times. In particular, an isothermal operating mode causes the thermodynamic properties to vanish from the models ; for some reactors, the phenomena of molecular transport can be neglected.

c) Balance equations

The mass, energy and momentum balance equations can be written for an element of volume which is homogeneous in temperature, pressure and concentrations in the following general form :

$$\begin{pmatrix}\text{accumulation}\\ \text{rate}\end{pmatrix}=\begin{pmatrix}\text{input}\\ \text{flow rate}\end{pmatrix}-\begin{pmatrix}\text{output}\\ \text{flow rate}\end{pmatrix}+\begin{pmatrix}\text{chemical production}\\ \text{rate}\end{pmatrix} \qquad (1)$$

The fact that a homogeneous element of volume is considered results in the fact that the rate of reaction, which is a function of the concentrations, of the temperature and of the pressure, is the same at each point within the volume element ; which causes the rate of chemical production to be proportional to the volume of the element.

This general equation can be simplified, as has already been stated, for the following two particular cases :

- for a closed element of volume which does not exchange matter with the surroundings, the input and output flow rates are equal to zero, which gives :

$$\begin{pmatrix}\text{accumulation}\\ \text{rate}\end{pmatrix}=\begin{pmatrix}\text{chemical production}\\ \text{rate}\end{pmatrix} \qquad (2)$$

- for a stirred flow reactor working under steady-state conditions, all the properties remain constant with time, and consequently the accumulation rate is equal to zero, therefore :

$$\begin{pmatrix}\text{output}\\ \text{flow rate}\end{pmatrix}=\begin{pmatrix}\text{input}\\ \text{flow rate}\end{pmatrix}+\begin{pmatrix}\text{chemical production}\\ \text{rate}\end{pmatrix} \qquad (3)$$

As has already been seen in Chapter III, which was dedicated to the general study of reaction systems, the balance equations can either be written in **molar quantities**, or in **mass quantities**. The first approach will be used for ideal reactors, as they demonstrate well their interest from the point of view of the **measurement of the rate of reaction** ; the second approach is better adapted to the **modelling of reacting flows**.

2 - BATCH REACTOR

In a batch reactor, the reactants are introduced into the reaction chamber at the instant t = 0 and the reaction mixture is analysed after a time lapse t_r of reaction.

2.1 - Experimental aspects

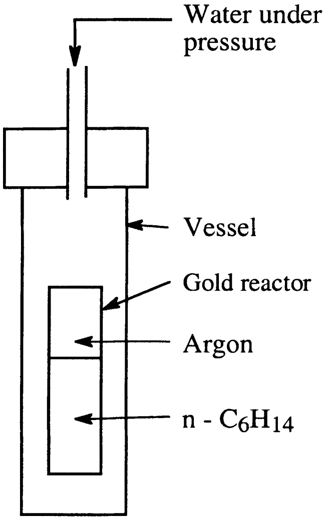
a) Design

Figure 1 shows a schematic representation of the operating principle of a batch reactor likely to be used at very high pressures.

This type of reactor has been used for the study of the pyrolysis of normal hexane under supercritical conditions, at temperatures of between 290 and 365 °C and at pressures of between 210 and 15 600 bar (the critical values for hexane are 234 °C and 29.3 bar). These studies are interesting for understanding the evolution of oil-fields.

A reactor consisting of a gold tube of 3.8 (or 3) mm diameter, of 0.2 mm thickness and of 40 (or 16) mm length is used. The tube is sealed at one extremity, then filled with hexane under an atmosphere of argon to avoid having oxygen present, then electrically soldered at the other extremity. A reactor contains about 100 to 150 (or 20) μL hexane.

Figure 1 : Batch reactor for very high pressures



The reactor is placed in a vessel filled with water, and is itself inside an autoclave which is put in an oven the temperature of which is regulated.

At the instant t = 0, the reactor is put under pressure by the water, the pressure being applied by a movable piston in a cylinder. At the instant $t = t_r$, lying between 14 h and 1 month, the gold capsule is removed from the apparatus, placed in a recipient which is emptied ; the ampoule is then pierced, the products are taken out and analysed by gas-phase chromatography and GCMS (Gas Chromatograph coupled to a Mass Spectrometer).

b) Effects of the walls

The batch reactor is convenient for the study of the sensitivity of the reaction to the nature and the relative extent of the reactor walls. Three types of experimental tests are carried out.

- The reactor can be **conditioned** by carrying out the reaction under conditions which are more severe than normal, i.e. at reaction times, at initial concentrations of the reactants and at temperatures higher than those of the study.

- The reactor can be **treated** with different gases or liquids, which differ both from the reactants and from the products.

  Thus, carbon deposits on the reactor walls can possibly be burned by using air or oxygen. The initial treatment of a "new" reactor consists in successive washings by bases and acids, by oxidizing mixtures, by organic solvents, followed by rinsing using distilled water and vacuum pumping. More specific treatments aim at easing or inhibiting such and such a reaction ; for example, the treatment of Pyrex by lead nitrate leads, after heating, to the formation of lead oxide, which can favour heterogeneous termination reactions.
- The **S/V ratio** of the surface S of the reactor walls to the volume of gas V **can be modified** by placing some pellets, cylinders or small-sized tubes into the reactor, made of the same material and having undergone the same conditionings and treatments as the original reactor walls. It is also possible to test packings made of materials which differ from those used for the reactor.

Example 1

The pyrolysis of isopentane has been studied in a batch reactor at constant volume at the temperature T = 480 °C, at an initial isopentane pressure of p_0 = 25 mmHg. Figure 2 shows the variation of the partial pressures of the products formed as a function of the reaction time. Very different results are observed according to the operating conditions.

- Curves A were obtained for an empty, untreated reactor, of S/V ratio = 0.8 cm^{-1}, and in the absence of oxygen.
- Curves B were obtained for a reactor filled with small Pyrex cylinders, of S/V ratio = 11 cm^{-1}, treated with PbO and in the presence of 1 % oxygen.

It is obvious that the addition of oxygen in the presence of important and effective reactor walls has a very strong inhibiting effect on the reaction, whereas it has a very strong accelerating effect on the empty, untreated reactor (the latter effect is not shown in Figure 2).

The acceleration of the reaction is interpreted by a homogeneous initiation involving oxygen, the inhibition being due to the heterogeneous terminations involving oxygenated free radicals coming from the reactions of alkyl radicals with oxygen.

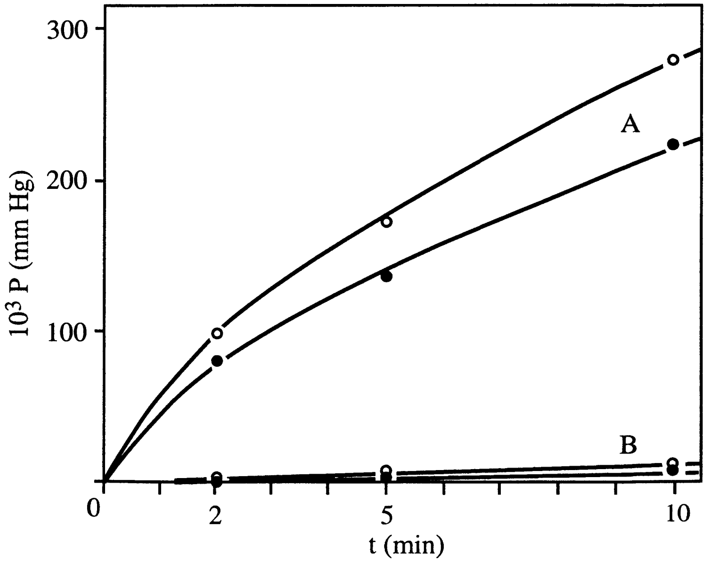
The existence of such heterogeneous terminations is very important in oxidation and combustion reactions.

As could have been expected from this interpretation, the oxygen is consumed by the reactions responsible for the acceleration or inhibition ; the latter decreases with time.

c) Experimental procedure

An experiment is carried out as follows. The reactor is pumped out until a satisfactory level of vacuum is obtained. The fact that the vacuum remains reasonably good is checked by measuring the increase in pressure of the reactor, without pumping. The treatments discussed above are then carried out on the reactor walls. Once these treatments have been completed, a given reaction mixture is introduced, at a given pressure, the reactor being regulated at a fixed temperature. A gaseous sample is taken in an ampoule for analysis ; this operation is carried out by expansion, the reaction mixture is destroyed. The cycle described above is then started again for a new experiment.

Figure 2 : Pyrolysis of isopentane in a batch reactor. $T = 480$ *°C,* $p_o = 25$ *mmHg, sample pressure = 10 mmHg.*
A - Without oxygen, in a Pyrex reactor of ratio $S/V = 0.8\ cm^{-1}$.
B - With 1 % oxygen, in a Pyrex reactor of ratio $S/V = 11\ cm^{-1}$, *treated with PbO.*
○ $C_2H_4 + C_3H_6$ + *butenes* ; ● $CH_4 + C_2H_6 + C_3H_8$



d) Experimentation programme

First of all, the ranges of initial concentrations, of temperatures and of reaction times which will be studied must be defined, as well as the concentrations which will be measured.

A **plan of experiments**, as defined by the statisticians, can then be drawn up. However, kineticists prefer an approach oriented towards the validation and identification of the **experimental kinetic laws** discussed in Chapter III. The **experimentation programme** which results from this is based on the separation of the kinetic factors and involves the following phases :

- The concentration c_j measured at a given temperature T, is plotted versus the reaction time t, for given values of the initial concentrations c_{0j} of the reactants.
- The above procedure is repeated at different initial concentrations.
- The preceding experiments are repeated at different temperatures.

A very simple rule allows the number of experiments of a given type, which are to be carried out, to be fixed. Knowing that the simplest graphic verification consists in making a linear plot of one property as a function of another, therefore **at least four experiments** must be carried out for each category.
For example, the validation of the ARRHENIUS law, $k = A \exp(-E/RT)$, necessitates the determination of the value of the rate constant k at four temperatures to check the linearity of the relationship between log k and 1/T. If this linearity is proved, and only then, it is possible to calculate the values of the kinetic parameters A and E.
A second important aspect of an experimentation programme consists in **repeating the same experiment at regular intervals**. This operation allows the checking of the correct functioning of the apparatus (flow-meters, thermocouples, pressure gauges...), of the methods of sampling and analysis ; it allows the evolution of the reactants and of the reactor in the long term to be tested, as well as the influence of the modifications carried out on the apparatus, and on the analytical and experimental procedures ; moreover, it furnishes an evaluation of the overall error in the measurement.
For all these reasons, the **cost** of an experimentation programme is much higher than that of a plan of experiments, but the benefit is much higher from the point of view of interpretation.

It is clear that most of the observations made above, concerning the experimental procedure and the experimentation programme, can be transposed to the operating of other laboratory reactors.

2.2 - Balance equations

a) Batch reactor of constant volume operating under isothermal conditions

This type of reactor is used for kinetic studies of weakly exothermic reactions, or at low reaction extent, or in a dilute medium.
The balance equation of constituent C_j, derived from the general equation (2), can be written as follows :

$$\frac{dn_j}{dt} = R_j V \tag{4}$$

where n_j is the number of moles of C_j in the reactor,
t is the reaction time,

R_j is the rate of production of C_j,
V is the volume of the reactor.

The following concentration has been introduced : $c_j = \frac{n_j}{V}$

Assuming that V is constant, equation (4) becomes :

$$R_j = \frac{dc_j}{dt} \tag{5}$$

To obtain R_j, the variations in the concentration c_j are plotted as a function of the reaction time t. The slope of the tangent to the curve gives the rate.

Example 2

A gas-phase reaction is being studied using a batch reactor of constant volume $V = 100\ \mathrm{cm}^3$ at temperature $T = 770$ K. A mixture of reactants of given composition and at a given pressure, is introduced at the instant $t = 0$, and the reaction mixture is analysed after a reaction time t. The following results have been obtained, where c_B designates the concentration of a product B of the reaction :

t /min	1	2	3	4
c_B /mol m^{-3}	0.22	0.39	0.53	0.63

Calculate the rate of production of the product B for t = 2 min.

The smoothed curve $c_B(t)$ is plotted, as well as the tangent to this curve at t = 2 min. The slope of this tangent gives the rate $R_B = 0.15$ mol m^{-3} min^{-1}. Note that it was neither necessary to know which were the reactants nor to know the other products and therefore, *a fortiori*, the stoichiometries.

b) Batch reactor at constant volume operating under adiabatic conditions

This is the case for example of a **combustion bomb**.

— *Mass balance*

By multiplying both sides of equation (4) by the molar mass M_j of the constituent C_j, the following equation is obtained :

$$\frac{dm_j}{dt} = R_j M_j V \tag{6}$$

where m_j is the mass of C_j in the reactor at the instant t.

This equation can be rewritten by introducing the mass fractions :

$$w_j = \frac{m_j}{m} \tag{7}$$

and the specific volume :

$$v = \frac{V}{m} \tag{8}$$

where m is the total mass of the reaction mixture :

$$\frac{dw_j}{dt} = R_j\, M_j\, v \tag{9}$$

As the reactor is closed, the total mass is constant, and as the volume is constant, the specific volume is also constant.

— *Energy balance*

The application of the first law of thermodynamics gives the following relationship, as this is operating at constant volume and under adiabatic conditions :

$$du = \delta q - p\, dv = 0 \tag{10}$$

where u is the specific internal energy of the reaction mixture with respect to unit mass :

$$u = \sum_{j=1}^{J} w_j\, u_j \tag{11}$$

where u_j is the specific internal energy of C_j and J is the total number of constituents.

Hereafter, the following notation will be adopted: $\sum = \sum\limits_{j=1}^{J}$.

Relationship (11) is differentiated : $du = \sum \left(u_j\, dw_j + w_j\, du_j\right)$ (12)

For an ideal gas, the following expression can be written : $du_j = c_{Vj}\, dT$ (13)

where c_{Vj} is the specific heat of C_j at constant volume.

The following relationship can be obtained from relationships (9) to (13) :

$$v \sum R_j\, M_j\, u_j + \sum w_j\, c_{Vj} \frac{dT}{dt} = 0 \tag{14}$$

Introducing the following expression for the mean specific heat at constant volume of the reaction mixture :

$$c_V = \sum w_j\, c_{Vj} \tag{15}$$

gives :

$$c_V \frac{dT}{dt} = -v \sum R_j\, M_j\, u_j \tag{16}$$

c) Batch reactor operating under isobaric and adiabatic conditions

The mass balance equations are still the equations (9) :

$$\frac{dw_j}{dt} = v\, R_j\, M_j \tag{9}$$

Applying the first law of thermodynamics gives the following relationship :

$$dh = \delta q + v\, d\, p \tag{17}$$

where h is the specific enthalpy of the reaction mixture :

$$h = \sum w_j h_j \tag{18}$$

where h_j is the specific enthalpy of C_j.
Under isobaric and adiabatic conditions, dp = 0 and dq = 0, therefore :

$$dh = 0 \tag{19}$$

Differentiating relationship (18), gives :

$$\sum \left(w_j\, dh_j + h_j\, dw_j\right) = 0 \tag{20}$$

For an ideal gas, the following relationship can be written : $dh_j = c_{pj}\, dT$ (21)
where c_{pj} is the specific heat of C_j at constant pressure.
Relationships (9), (17) to (20), give :

$$c_p \frac{dT}{dt} = -\, v \sum R_j\, M_j\, h_j \tag{22}$$

where :

$$c_p = \sum w_j\, c_{pj} \tag{23}$$

where c_p is the mean specific heat of the reaction mixture at constant pressure.

3 - STIRRED FLOW REACTOR

A **perfectly**-stirred flow reactor is characterized by a homogeneous state of the reaction mixture throughout the entire volume of the reactor, i.e. the concentration of each constituent, the temperature and the pressure have the same value at each point of the reactor. There are two consequences of this :

- the concentrations at the exit to the reactor are the same as those of the gases within the reactor, on condition that the **cooling** of the effluents is effective ;
- the rates of chemical production are identical at all points of the reactor, as these are functions of the concentrations of the species making up the reaction mixture, of the temperature and of the pressure.

3.1 - Experimental aspects

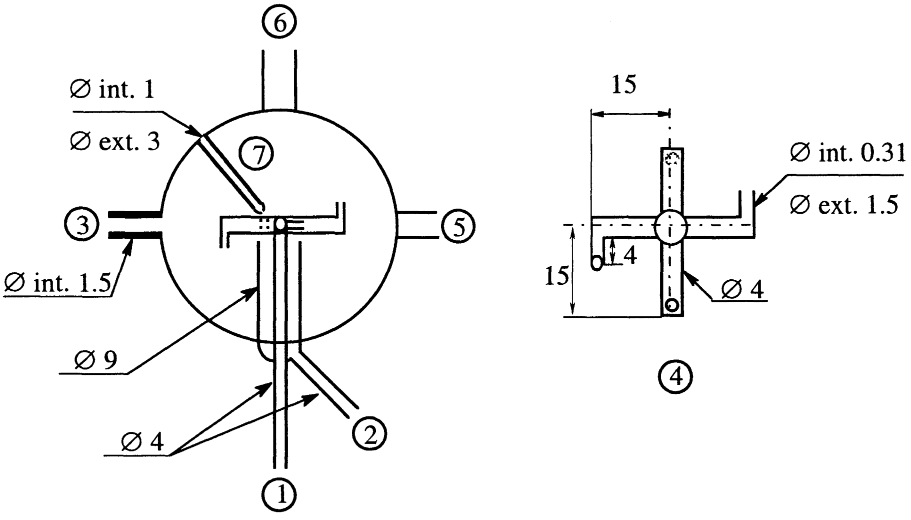
a) Flow reactor stirred by jets of gases

Good mixing can be obtained by mechanical means, but these techniques are not very suitable for gas reactions at high temperatures. A set-up will therefore be described here where the stirring of the gases is obtained by the jets of the gases themselves.

Figure 3 gives the characteristics of the reactor.

The reactants arrive through a pipe ① and are injected into the spherical reaction chamber by 4 nozzles in the shape of a twisted swastika ④. The reaction mixture leaves by a tube ② situated in the centre of the reactor. The reactor is equipped with pressure ③ and temperature ⑤ ⑥ ⑦ gauges.

Figure 3 : Flow reactor stirred by jets of reactants. The diameters are given in mm. 1 : gas input; 2 : gas exit ; 3 : pressure gauge ; 4 : detailed view of the cross carrying the injectors ; 5 and 6 : appendices which permit the positioning of the two thermocouples and the holding of the reactor ; 7 : thermometer well.



The mixing of the gases in this reactor occurs for various reasons :

- the jets of gases coming out of the nozzles are **turbulent,** due to their small diameter,
- these jets of gases cause two currents of **internal recycling** to occur within the reactor and these propel the rest of the gaseous volume,
- as these two recycling currents are situated in perpendicular planes, they generate a supplementary turbulence when they **cross** one another.

There are three geometrical characteristics of this reactor which are necessary so that the macromixing of the gases is quasi-perfect :

- the jets of gases coming out of the nozzles must be turbulent,
- their speed must be less than the speed of sound,
- the fraction of recycling must be higher than 30.

If in addition, it is necessary to guarantee a good homogeneity of the temperature, the reactants must be **preheated** to a temperature close to that at which the reaction will take place.

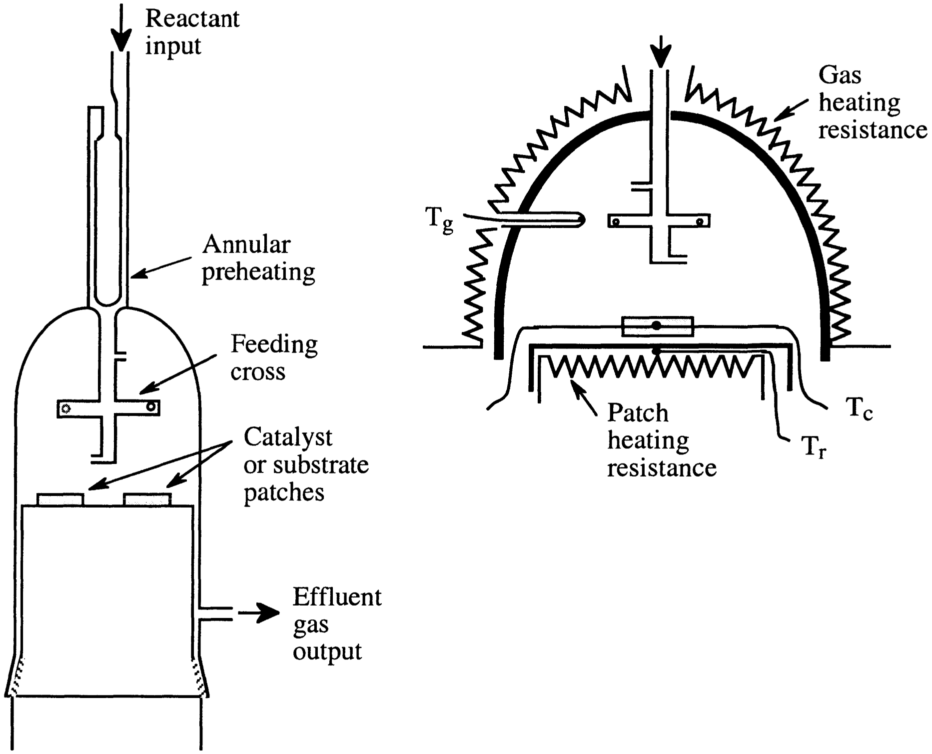
For the reactor in Figure 3, the reaction volume is equal to 87 cm^3 and the diameter of the nozzles is 0.31 mm. According to the mixing criteria, the gases are assumed to be well macromixed for space times of between 0.6 and 6 s.

b) Stirred flow reactor for a GPTR catalysed by a solid or for a CVD reaction

The above concept was extended to a reactor in which the gas phase is stirred by the same type of jets as in the preceding case, but which also has a plane surface to which a variable number of patches of catalyst or of substrate can be attached.

Figure 4 shows a schematic representation of such a reactor.

Figure 4 :Stirred flow reactor for the study of a GPTR catalysed by a solid or of a CVD reaction.



a) General scheme

b) Temperature controls

The surface onto which the patches are stuck can be heated independently of the walls which heat the gases ; in this way, a catalyst temperature T_c can be obtained which is different to the temperature of the gases T_g.

This reactor possesses two ways of separating the gas-phase reaction from the reactions involving the catalytic surface.

It has been used to study the oxidizing coupling of methane in the presence of lanthanum oxide, with a view to the direct formation of ethylene. This is one of the reactions likely to be used to convert natural gas into higher hydrocarbons without the intervention of synthesis gas CO/H_2 whose manufacture is very costly in energy. It has also been used for the CVD of pyrocarbon.

c) Operating principles

As will be seen in § 3.2, when setting out the equations for the stirred flow reactor, in order to gain a maximum kinetic information, it is advisable to make it work under isothermal, isobaric and steady-state conditions. The mass flow rates W_{oj} of each constituent C_j fed into the reactor, the temperature T_r and the pressure p_r of the gases within the reactor are measured. The volume V_r open to the gas within the reactor must be determined, for example by filling the reactor with mercury and weighing it.

The following can therefore be deduced :

– the molar flow rates of the feed in C_j :

$$F_{oj} = \frac{W_{oj}}{M_j} \tag{24}$$

– the total molar flow rate of the feed :

$$F_o = \sum F_{oj} \tag{25}$$

– the volume flow rate of the feed under the conditions of the reaction :

$$Q_o = \frac{F_o R T_r}{p_r} \tag{26}$$

– the space time :

$$\tau_r = V_r/Q_o \tag{27}$$

– the concentrations of the reactants at the entrance to the reactor :

$$c_{oj} = F_{oj}/Q_o \tag{28}$$

The concentrations c_{rj} of the different constituents C_j and the volume flow rate Q_r are measured at the exit to the reactor under the conditions of the reaction, the following can therefore be deduced :

– the molar flow rates at the exit to the reactor of the constituents C_j :

$$F_{rj} = Q_r\, c_{rj} \tag{29}$$

– the volume expansion coefficient due to the chemical reaction :

$$\chi_r = Q_r/Q_o \tag{30}$$

3.2 - Balance equations

a) Stirred flow reactor at constant volume under isothermal, isobaric and steady-state conditions

The steady-state conditions permit equations (3) to be used and to be applied only to the balance of the species, as the conditions are isothermal and isobaric :

$$\begin{cases} F_{rj} = F_{oj} + R_{rj}\, V_r \\ j = 1, \ldots, J \end{cases} \tag{31}$$

where F_{rj} is the molar flow rate of C_j leaving the reactor,
F_{oj} is the molar flow rate of C_j entering the reactor,
R_{rj} is the molar rate of chemical production of C_j,
V_r is the reaction volume,
J is the number of constituents.

A first expression for the rate can be deduced as follows :

$$R_{rj} = \frac{(F_{rj} - F_{oj})}{V_r} \tag{32}$$

Introducing the variables τ_r and χ_r (eqns. 27 and 30), gives :

$$R_{rj} = \frac{(\chi_r\, c_{rj} - c_{oj})}{\tau_r} \tag{33}$$

If the reaction occurs without an increase in the volume flow rate, therefore $\chi_r = 1$; if it occurs at very low conversion or in a very dilute medium, then $\chi_r \simeq 1$. In all these cases, relationship (33) can be simplified as follows :

$$R_{rj} = \frac{(c_{rj} - c_{oj})}{\tau_r} \tag{34}$$

Example 3

A stirred flow reactor of volume $V_r = 2\text{x}10^{-4}$ m^3 working under steady-state conditions and at pressure $p_r = 10^5$ Pa and temperature $T_r = 1100$ K is fed with a molar flow rate $F_{0A} = 8.89\text{x}10^{-4}$ mol s^{-1} of a pure reactant A. The volume flow rate $Q_r = 9.54\text{x}10^{-5}$ m^3 and the concentration of a product B, $c_{rB} = 1.61$ mol m^{-3} are measured at the exit to the reactor.

Calculate the rate of chemical production of the product B under these conditions, as

well as the volume expansion coefficient χ_r and the space time τ_r.
Relationship (29) gives $F_{rB} = 9.54\text{x}10^{-5} \times 1.61 = 1.54\text{x}10^{-4}$ mol s^{-1}. The rate $R_{rB} = 1.54\text{x}10^{-4}/2\text{x}10^{-4} = 0.77$ mol m^{-3} s^{-1} can be deduced using relationship (32). Relationship (26) permits $Q_o = 8.89\text{x}10^{-4} \times 8.3145 \times 1100/10^5 = 8.13\text{x}10^{-5}$ m^3 s^{-1} to be calculated. $\tau_r = 2.46$ s and $\chi_r = 1.17$ are deduced from this (eqns 27 and 30). Taking this value of χ_r into account, it is obvious that the approximate relationship (34) cannot be applied.

b) Stirred flow reactor at constant volume, under isobaric, non-isothermal and steady-state conditions

It is assumed here that the reactor undergoes a heat exchange with the surrounding medium to which it gives up a heat flux q, expressed for example in J s^{-1}. The gases enter at temperature T_o and leave at temperature T.

— *Continuity equation*

Under steady-state conditions, the total mass flow rate W at the exit is equal to that at the entrance W_o :

$$W = W_o \tag{35}$$

— *Mass balance*

The following expression can be written under steady-state conditions :

$$W\, w_j = W_o\, w_{oj} + R_j\, M_j\, V \tag{36}$$

where w_j, w_{oj} are the mass fractions at the exit and at the entrance, respectively
M_j is the molar mass of C_j

— *Energy balance*

As these are isobaric conditions, an enthalpy balance is carried out :

$$W \sum w_j\, h_j = W_o \sum w_{oj}\, h_{oj} - q \tag{37}$$

where h_j, h_{oj} are the specific enthalpies of C_j at the exit and at the entrance, respectively.

Combining equations (35) to (37), gives :

$$W \sum w_{oj}\, h_j = W \sum w_{oj}\, h_{oj} - q - V \sum R_j\, M_j\, h_j \tag{38}$$

The following relationship can be written for an ideal gas :

$$h_j = h_{oj} + \int_{T_o}^{T} c_{pj}\, dT \tag{39}$$

where c_{pj} is the specific heat of C_j at constant pressure.

c) Stirred flow reactor at constant volume, under isobaric, non-isothermal and transient-state conditions

The solution of the above equations can necessitate, for reasons of numerical convergence, the study of an associated transient problem.

— *Mass balance*

$$\rho V \frac{dw_j}{dt} = W\left(w_{oj} - w_j\right) + V R_j M_j \tag{40}$$

where ρ is the density of the mixture.

— *Energy balance*

$$\rho V \frac{dh}{dt} = W \sum \left(w_{oj} h_{oj} - w_j h_j\right) - q \tag{41}$$

where h is the mean specific enthalpy

$$h = \sum w_j h_j \tag{42}$$

Differentiating gives :

$$\frac{dh}{dt} = c_p \frac{dT}{dt} + \sum h_j \frac{dw_j}{dt} \tag{43}$$

where c_p is the mean specific heat of the mixture at constant pressure

$$c_p = \sum w_j c_{pj} \tag{44}$$

Combining equations (41)to (44), finally gives:

$$\rho V c_p \frac{dT}{dt} = W \sum w_{oj}\left(h_{oj} - h_j\right) - V \sum R_j M_j h_j - q \tag{45}$$

The density is calculated using the ideal gas law :

$$\rho = \frac{pM}{RT} \tag{46}$$

where M is the mean molar mass of the mixture :

$$M = \frac{1}{\sum \left(w_j/M_j\right)} \tag{47}$$

4 - PLUG-FLOW REACTOR

A plug-flow reactor is characterized by a gas flow which is analogous to the movement of a piston in a cylinder. Each differential volume element dV of gas therefore flows through the reactor without exchange of matter with either the preceding or following element ; the molecules in this volume element thus evolve as if they were in a batch reactor. Under steady-state conditions, all these segments of gas stay for the same length of time in the reactor. The plug-flow reactor is therefore characterized by a

unique residence time, contrary to the perfectly-stirred flow reactor, which has an exponential-type distribution of the residence times.

4.1 - Experimental aspects

The laboratory reactor which is closest to the plug-flow reactor is made up of a long cylindrical tube. So that all the molecules stay for the same length of time in the reactor, the flow rate must be the same at each point of any given cross-section of the reactor. This is obtained in the case of turbulent flow, with the exception of the laminar layer, but of course not in the case of a laminar flow. A flat rate profile can also be obtained by introducing a packing into the reactor, if it is possible to avoid preferential channels ; this technique causes an increase in the S/V ratio of the surface area of the walls to the volume of gas. Obtaining a turbulent flow on a laboratory scale is not easy, as this necessitates high flow rates, which can cause excessive pressure gradients.

Perturbations in the plug-flow due to the entrance and the exit of the reactor must also be limited. This is the case if the ratio of the length to the diameter of the tube is sufficiently high, at least equal to 100, for example. The situation can be improved, if it is not practically possible to reach this value, by dividing up the input and output fluxes using packing, or discs with holes.

The most important point concerns the temperature T of the gases as a function of the distance z along the tube. This temperature is likely to vary with the actual design of the oven in which the tube is placed, at the entrance to the oven when the gases go progressively from the preheating temperature to the given temperature, then lastly due to the thermicity of the reaction. It is therefore sensible, wherever possible, to measure the temperature along the tube in order to obtain the profile T(z).

It is also advisable to measure the pressure at the entrance and at the exit to the reactor, in order to make sure that it is working under isobaric conditions.

The assumption made for the plug-flow reactor means that the diffusion phenomena are negligible. In order to take these into account it is necessary to evaluate the molecular transport properties ; this will be explained for the case of a flat-flame premixing burner.

4.2 - Balance equations

The plug-flow reactor works in the most advantageous way under steady-state, isobaric and isothermal conditions, at constant volume ; the pressure, the temperature and the reaction volume will be represented by the symbols p_r, T_r, V_r, respectively (Figure 5a). The reactor is fed by mass flow rates W_{oj} of the reactants C_j ; these mass flow rates are measured using mass flow meters and are constant during the experiment, therefore :

– the molar flow rates of the feed in C_j are :

$$F_{oj} = W_{oj}/M_j \tag{48}$$

– the total molar flow rate of the feed is :

$$F_o = \sum F_{oj} \tag{49}$$

– the volume flow rate of the feed is :

$$Q_o = F_o RT_r/p_r \tag{50}$$

– the space time is :

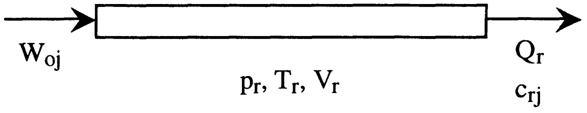
$$\tau_r = V_r/Q_o \tag{51}$$

– the concentrations at the entrance are :

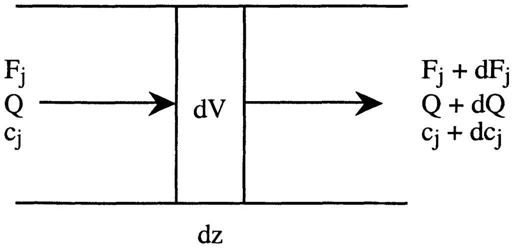
$$c_{oj} = F_{oj}/Q_o \tag{52}$$

Figure 5 : Plug-flow reactor

a) Measured properties



b) Balance equations on a differential element of volume



The volume flow rate Q_r and the concentrations c_{rj} of the different constituents C_j of the reaction mixture at the exit to the reactor are also measured.

As the concentrations are constantly changing along the reactor, the same is true of the rate of chemical production R_j of the constituent C_j. A mass balance on a differential element of volume dV must therefore be carried out, in which the rates R_j can be considered to have well-defined values.

At the steady state, the number of moles of C_j contained in the element of volume dV is constant, so that the mass balance equation (3) can be put into the following form :

$$F_j + dF_j = F_j + R_j\,dV \tag{53}$$

i.e., more simply :

$$dF_j = R_j\,dV \tag{54}$$

where F_j is the local molar flow rate of C_j.

The molar flow rate F_j is expressed as a function of the local concentration c_j and of the local volume flow rate Q by the following relationship :

$$F_j = Q\, c_j \tag{55}$$

Differentiating gives :

$$dF_j = Q\, dc_j + c_j\, dQ \tag{56}$$

The two variables τ and χ which are defined by the following relationships, are introduced:

$$dV = Q_o\, d\tau \tag{57}$$

$$dQ = Q_o\, d\chi \tag{58}$$

The following relationships are obtained by integrating these equations, at fixed volume flow rate Q_o, between the entrance and the exit of the reactor :

$$V_r = Q_o\, \tau_r \tag{59}$$

and :

$$Q_r = Q_o\, \chi_r \tag{60}$$

and also :

$$\tau_r = V_r/Q_o \tag{61}$$

$$\chi_r = Q_r/Q_o \tag{62}$$

τ_r is the space time and χ_r is the volume expansion coefficient due to the chemical reaction ; it is possible to calculate these values from the measured properties.
The integration of equation (58) gives :

$$Q = Q_o\, \chi \tag{63}$$

Using relationships (56) to (58) and (63), equation (54) becomes :

$$R_j = \chi \frac{dc_j}{d\tau} + c_j \frac{d\chi}{d\tau} \tag{64}$$

Taking the sum of all the constituents (reactants, inert substances, products) present in the reaction medium, the following expression is obtained :

$$\sum R_j = \chi \frac{dc}{d\tau} + c \frac{d\chi}{d\tau} \tag{65}$$

where c is the total concentration.

The perfect gas law gives :

$$c = p_r/R\, T_r \tag{66}$$

Under assumed isobaric and isothermal conditions, the total concentration c is constant ; consequently, $dc/d\tau = 0$, and equation (66) can then be put into the following form :

$$\frac{d\chi}{d\tau} = \frac{RT_r}{p_r} \sum R_j \tag{67}$$

Putting into equation (65) gives :

$$\begin{cases} \dfrac{dc_j}{d\tau} = \dfrac{R_j}{\chi} - \dfrac{c_j}{\chi}\dfrac{RT_r}{p_r}\sum R_j \\ j = 1, \ldots, J \end{cases} \tag{68}$$

where J is the total number of constituents.

Under isobaric and isothermal conditions, the rates R_j are only functions of the current concentrations c_j. Equations (68) and (69) therefore constitute a system of J+1 ordinary differential equations with J+1 initial conditions :

$$\begin{cases} \chi\,(\tau = 0) = 1 \\ c_j\,(\tau = 0) = c_{oj} \\ j = 1, \ldots, J \end{cases} \tag{69}$$

Integrating these equations from $\tau = 0$ to $\tau = \tau_r$, the quantities χ_r and c_{rj} are obtained at the exit to the reactor :

$$\begin{cases} \chi_r = \chi_r\left(\tau_r\,;\, c_{o1}, \ldots, c_{oJ}\,;\, T_r, p_r\right) \\ c_{rj} = c_{rj}\left(\tau_r\,;\, c_{o1}, \ldots, c_{oJ}\,;\, T_r, p_r\right) \\ j = 1, \ldots, J \end{cases} \tag{70}$$

Equations (70) indicate the kind of experimental programme that must be carried out in the case of the plug-flow reactor. A reactor of given volume V_r is used at a given pressure p_r and at a given temperature T_r. The reactor is fed with a mixture of reactants at concentrations c_{oj} (at given p_r and T_r). A first experiment is carried out with a given volume flow rate $Q_o^{(1)}$ for the feed, then a second experiment at a given flow rate $Q_o^{(2)}$ ... ; Q_r and c_{rj} are measured for each case.

It is then possible to follow the variations in c_{rj} and in $\chi_r = Q_r/Q_o$ as a function of $\tau_r = V_r/Q_o$ for the whole set of experiments. The value of the rate of production of C_j under the conditions at the exit to the reactor is deduced using equation (64) :

$$R_{rj} = \chi_r \frac{dc_{rj}}{d\tau_r} + c_{rj}\frac{d\chi_r}{d\tau_r} \tag{71}$$

A particularly interesting case of relationship (71) occurs if the reaction takes place without a change in the number of moles, in which case $\chi_r = 1$, or if the reaction takes place at low conversion or in a medium which is highly diluted by an inert carrier gas, in which case $\chi_r \simeq 1$; the term $c_{rj}\, d\chi_r/d\tau_r$ becomes negligible, therefore :

$$R_{rj} \simeq \frac{dc_{rj}}{d\tau_r} \tag{72}$$

This is the same equation as that which applies to a batch reactor, the evolution in time being replaced by a spatial evolution.

Example 4

A plug-flow reactor of volume $V_r = 2\text{x}10^{-4}$ m^3 working under steady-state conditions at pressure $p_r = 10^5$ Pa and at temperature $T_r = 1100$ K is fed by a molar flow rate F_{oA} of pure reactant A. The volume flow rate Q_r and the concentration c_{rB} of a product B are measured at the exit to the reactor. Four experiments have been carried out :

F_{oA} (mol s^{-1})×10^4	19.9	8.89	5.29	3.52
Q_r (m^3 s^{-1})×10^4	1.98	0.976	0.629	0.451
c_{rB} (mol m^{-3})	0.994	1.82	2.52	3.12

Calculate the rate of chemical production of B for $c_{rB} = 1.82$ mol m^{-3}.

In order to be able to use equation (71), the curves $c_{rB}(\tau_r)$ and $\chi_r(\tau_r)$ must first be plotted. The volume flow rate at the entrance Q_o is calculated using equation (50), the space time τ_r can then be calculated using equation (61) ; the volume expansion coefficient can then be calculated using equation (62), therefore :

Q_o (m^3 s^{-1})×10^5	18.2	8.13	4.84	3.22
τ_r (s)	1.10	2.46	4.13	6.21
χ_r	1.09	1.20	1.30	1.40

Curves $c_{rB}(\tau_r)$ and $\chi_r(\tau_r)$ can now be plotted, as well as the tangents to these curves at $\tau_r = 2.46$ s.

The slopes of the tangents give the values

$$dc_{rB}/d\tau_r = 0.504 \text{ mol m}^{-3} \text{ s}^{-1}, \; d\chi_r/d\tau_r = 6.93\text{x}10^{-2} \text{ s}^{-1}.$$

Relationship (71) allows the rate to be calculated :

$$R_{rB} = 1.20 \times 0.501 + 1.83 \times 6.93\text{x}10^{-2} = 0.605 + 0.127 = 0.73 \text{ mol m}^{-3} \text{ s}^{-1}$$

It must be noted that the term $c_{rB}\, d\chi_r/d\tau_r = 0.13$ is not negligible with respect to the term $\chi_r dc_{rB}/d\tau_r = 0.60$; this is normal as the reaction is accompanied by a non-negligible volume expansion ($\chi_r = 1.2$). By applying relationship (72), which would have been wrong in this case, $R_{rB} = 0.50$ would have been found instead of 0.73.

5 - RAPID COMPRESSION MACHINE

5.1 - Experimental aspects

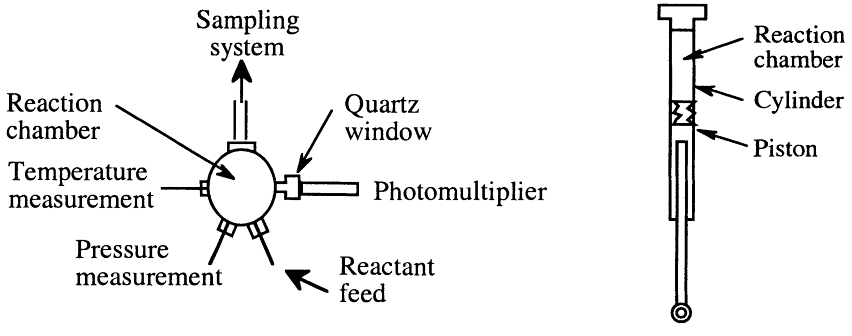
Figure 6 describes schematically an example of a rapid compression machine. It is composed of the following elements :

- A reaction chamber into which the reacting gases are introduced by an injector. This chamber is 2.2 cm long and has a diameter of 5 cm.

- The pressure in the chamber is measured by a piezo-electric sensor.
- The temperature is measured before compression using a thermocouple.
- A quartz window is set into the chamber and allows the luminous emissions to be detected by a photomultiplier fitted with a blue filter.
- A cooling device and a sampling system for the gases is connected to the reaction chamber. A diaphragm made out of aluminium foil 50 μm thick is pierced with a needle after a well-defined length of reaction ; the reaction mixture then expands into a chamber of volume 1530 cm^3, that is about 40 times as big as the chamber, which ensures the cooling of the mixture. It is then possible to take samples to be analysed.
- The compression of the gases is carried out in this machine by two pistons fixed at an angle of ninety degrees to one another and connected by a cam. The engine piston is put into motion by the expansion of a gas ; this then displaces the actual piston via the cam ; the latter has a path of 19.9 cm and the compression ratio reaches 9.8. The duration of the compression is adjusted to a value between 20 and 80 ms by changing the pressure of the driving gas.

The temperature reached by the gases at the end of the compression is modified in two ways ; on the one hand, by changing the initial temperature T_0 of the reaction mixture, on the other hand, either by diluting the actual reactant gases with different kinds of inert gases of different values for γ (= C_p/C_v) or by using these in variable proportions.

Figure 6 : Rapid compression machine.

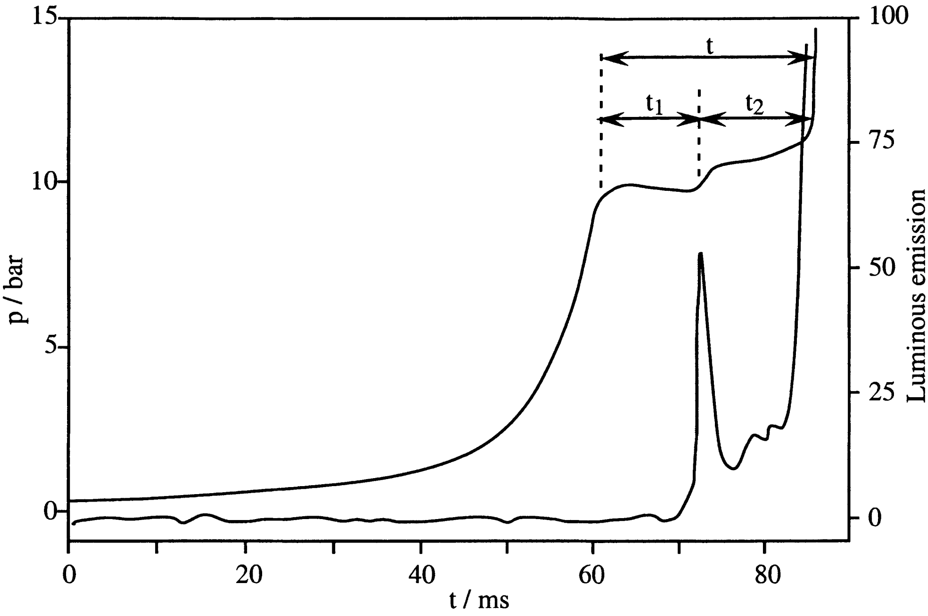


Example 5

Figure 7 shows an example of a recording of the pressure and of the light intensity as a function of time for a stoichiometric mixture of normal butane and air. A two-step autoignition can be observed in this figure. After a time t_1, a slight increase in pressure, of the order of 1 bar and a light emission mean that a cool flame was produced.

After a length of time t_2, this is transformed into a real, so-called second stage, autoignition.

Figure 7 : Evolution of the pressure and light emission during the compression and autoignition of a mixture of normal butane and air. Equivalence ratio = 1, T_0 = 355 K, T_1 = 749 K, density of the compressed load: 180 mol m^{-3}.



5.2 - Balance equations

a) Compression temperature

The temperature T_1 reached by the adiabatic compression of a gaseous mixture going from a pressure p_0 and a temperature T_0 to a pressure p_1 and a temperature T_1 can be evaluated in the following way. For an infinitesimal transformation, the following expressions can be written :

$$dU = -p\, dV = n\, c_V\, dT \tag{73}$$

$$dH = V\, dp = n\, c_p\, dT \tag{74}$$

i.e. :

$$\frac{dV}{V} = -\frac{1}{\gamma}\frac{dp}{p} \tag{75}$$

where :

$$\gamma = c_p/c_V \tag{76}$$

Differentiation of the law of ideal gases gives :

$$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T} \tag{77}$$

i.e. :
$$\left(1-\frac{1}{\gamma}\right)\frac{dp}{p}=\frac{dT}{T} \tag{78}$$

The temperature T_1 can therefore be calculated using the following equation :

$$\int_{T_o}^{T_1}\frac{\gamma}{\gamma-1}\frac{dT}{T}=\ln\frac{p_1}{p_o} \tag{79}$$

b) Batch reactor of variable volume operating adiabatically

The balance equations in this case are close to those which were established in § 2.2.b, except that now the change in volume must be taken into account.
The balance equation of species C_j can be written as follows :

$$\frac{dw_j}{dt}=v\,R_j\,M_j \tag{80}$$

and the energy balance equation is :

$$c_V\frac{dT}{T}=-v\sum R_j\,M_j-p\frac{dv}{dt} \tag{81}$$

where :
$$\frac{dv}{dt}=\frac{1}{m}\frac{dV}{dt}=\frac{1}{\rho V}\frac{dV}{dt} \tag{82}$$

and :
$$p=\rho\frac{RT}{M} \tag{83}$$

where V is the volume of the gases,
ρ is the density,
M is the mean molar mass,
v is the specific volume.

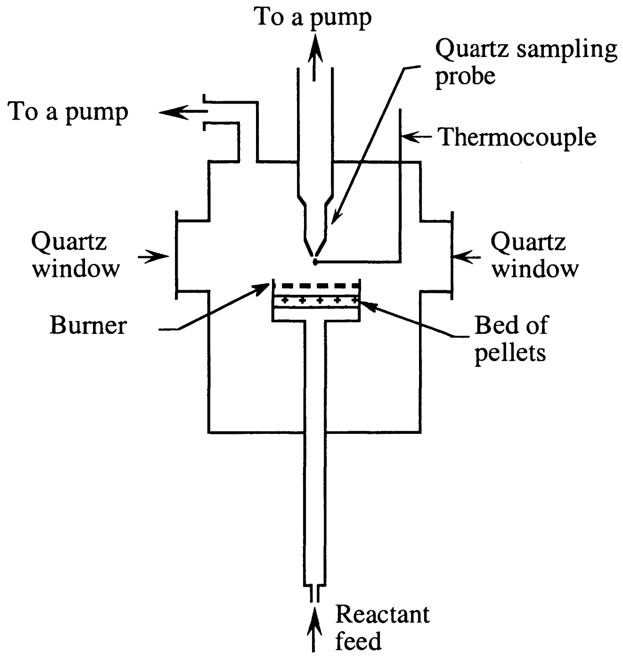
6 - FLAT-FLAME BURNER

6.1 - Experimental aspects

Figure 8 shows a schematic representation of a typical burner with premixing of the reactants, with a flat flame, working at pressures below atmospheric pressure. The apparatus is composed of the following elements :

- An airtight vessel of diameter 150 mm and of length 200 mm , cooled by the circulation of thermostated water at 343 K.
- A tube which feeds the burner in **premixed** reactants ; it is for this reason that this type of flame is called a premixed flame and possesses very different characteristics to diffusion flames.

Figure 8 : Flat flame burner.



- A bed of pellets which ensures that the gas flow spreads over the entire surface of the burner.
- The burner consists of a stainless steel disc of diameter 65 mm pierced with several hundred holes of internal diameter 0.8 mm ; the burner is cooled by water circulating in an annulus at 343 K.
- Samples are taken using a fixed probe. The probe consists of a quartz tube of diameter 25 mm and of length 360 mm, ending in a smaller tube of diameter 11 mm and of length 40 mm, which itself ends in a conical nozzle of angle 40° with a sampling hole, of the order of 100 µm. The pressure in the probe is measured using a capacitive gauge ; it is of the order of 2.6 Pa.
- The probe is attached by a tube, to a pumping system consisting of a primary two-stage pump of flow rate 80 m^3/h and a secondary pump of the ROOTS type of flow rate 500 m^3/h. The attachments are carried out using tubes of diameter 40 mm in order to avoid pressure drops.
- The continuous drawing off of about 300 L/h of effluents from the chamber is carried out using a tube attached to a rotary pump of 25 m^3/h flow rate. This pumping allows a pressure of the order of 5 kPa measured with the aid of a capacitive gauge, to be

obtained within the vessel. A series of traps and filters is placed between the burner and the pump to limit the emission of polluting substances.

- The distance between the burner and the probe can be adjusted using a knurled screw. A micrometric comparator allows the position of the burner to be ascertained.
- The temperature of the gases is measured using a thermocouple which can be moved.
- The positions of the burner, of the flame front, of the thermocouple and of the extremity of the probe are ascertained using a cathetometer through the quartz windows.
- The lighting of the flame is carried out using an electrical discharge.

Remark

The change in pressure between the walls and the probe brings about a decrease in temperature from 1500 to 300 K which quenches most reactions. However, this change of pressure is not high enough to obtain a supersonic gaseous flux in the probe and to cause a molecular beam. Side-reactions involving free radicals can therefore occur in the sampling probe.

6.2 - Balance equations

A laminar flat flame with premixing under steady-state, isobaric conditions can be modelled as a unidimensional reactant flow involving thermal conductivity and diffusion phenomena.

— Mass flow rate

$$W = \rho\, u\, A \tag{84}$$

— Balance of the constituents

$$\begin{cases} W \dfrac{dw_j}{dz} = -A\, R_j\, M_j - \dfrac{d}{dz}\left(A\, \rho\, w_j\, V_j\right) \\ j = 1, \ldots, J \end{cases} \tag{85}$$

— Energy balance

$$c_p\, W \frac{dT}{dz} = -A \sum R_j\, M_j\, h_j - A \sum \rho\, w_j\, c_{pj}\, V_j \frac{dT}{dz} + \frac{d}{dz}\left(A\, \lambda \frac{dT}{dz}\right) \tag{86}$$

where W is the mass flow rate,
ρ is the density,
u is the velocity of the fluid,
A is the cross-section of the flame,
w_j is the mass fraction of species C_j,
z is the spatial coordinate,
R_j is the rate of chemical production of C_j,
M_j is the molar mass of C_j,
V_j is the rate of diffusion of C_j,

c_p is the specific heat of the mixture at constant pressure,
T is the absolute temperature,
h_j is the specific enthalpy of C_j,
c_{pj} is the specific heat of C_j at constant pressure,
λ is the thermal conductivity of the mixture.

The sign $\sum$ is an abbreviation of $\sum_{j=1}^{J}$, where J is the number of constituents.

The density ρ is calculated using the ideal gas law :

$$\rho = \frac{pM}{RT} \tag{87}$$

where M is the mean molar mass of the mixture.

7 - SHOCK TUBE

7.1 - Experimental aspects

a) The reactor

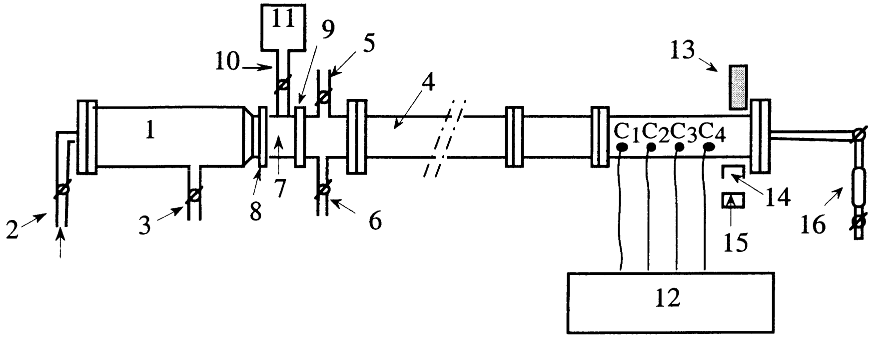
Figure 9 shows a schematic representation of a typical shock tube.

The apparatus consists of the following elements :

- A tube (1) for high pressure of internal diameter 120 mm and of length 90 cm. This tube is supplied with helium by a pipe (2) and emptied by a pipe (3) attached to a pumping system.
- A tube (4) for low pressure of internal diameter 78 mm and of length 9 m. This tube is supplied with reactants by a pipe (5) and emptied by a pipe (6) attached to a pumping system.
- Tubes (1) and (4) are separated by a chamber (7) equipped with 2 terphane diaphragms (8) and (9). The chamber (7) is attached by a tube (10) to an expansion chamber (11).
- Four piezo-electric sensors C1, C2, C3, C4 of diameter 0.8 mm are placed at the extremity of the tube and are separated from one another by 150 mm. The pressures measured by these sensors are recorded on a digital oscilloscope (12).
- A set-up for measuring the concentration of the reactant by UV absorption at a wavelength of 250 nm is placed near the end of the low pressure tube. This set-up consists of a deuterium lamp (13), a monochromator (14) and a photomultiplier (15). The corresponding signal is picked up by the two-track oscilloscope.
- The end of the tube is equipped with a system for taking samples in a phial (16). The

gases are analysed by quadruple mass-spectrometry. The tubes (1) and (4) are made of stainless steel and their walls have been carefully polished.

Figure 9 : Shock tube



b) Operating procedure

An inert gas, generally helium, is introduced into high pressure chamber (1), at pressure p_4 and at temperature T_4. This gas is called driving gas or piston gas.

The reactant or the mixture of reactants is introduced into low pressure chamber (4) at pressure p_1 and at temperature T_1. In general, the temperatures T_4 and T_1 are equal to room temperature.

Chamber (11) is evacuated and chamber (7) is filled with helium. When the tap (10) joins these two chambers together, the pressure drop causes the successive rupture of membranes (8) and (9). The piston gas expands suddenly and a set of compression waves form and propagate along in the reaction mixture.

c) Propagation of waves (fig. 10)

— Incident shock wave

After having travelled along a distance equal to several diameters of the tube, the compression waves join to form an **incident shock wave**, which looks like a discontinuity surface, of thickness of the order of a nanometre, separating the fresh reaction mixture (index 1) from the reaction mixture shocked by the incident wave (index 2).

This shock wave makes the reaction mixture go from pressure p_1 and temperature T_1 to pressure p_2 and temperature T_2 which are higher. The shock wave propagates at constant velocity U_I ; this velocity U_I is determined from recordings of the pressures by sensors C_1 to C_4 as a function of time.

— Reflected shock wave

When the incident shock wave arrives on the end wall of the tube, it gives rise to a

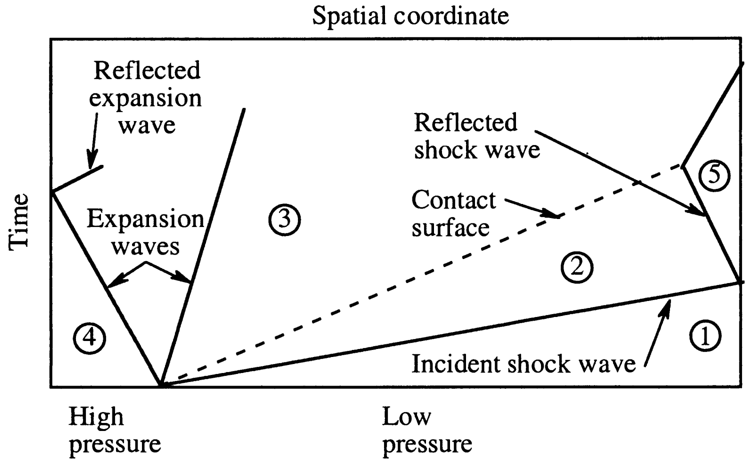
reflected shock wave which crosses the reaction mixture in the opposite direction to the incident shock, making its pressure go from the value p_2 to the value p_5, and its temperature from T_2 to T_5. The index 5 therefore stands for the state of the reaction mixture after the reflected shock wave has passed. It propagates at a constant velocity U_R which can also be determined from the measurements of the sensors C_1 to C_4.

The pressure p_5 and the temperature T_5 are the **initial conditions** of the reaction.

— *Expansion waves*

Meanwhile, **expansion waves** propagate in the piston gas and cause a decrease in its pressure and in its temperature. Index 3 is given to the piston gas between the progressive expansion wave and the contact surface with the reaction mixture, and index 4 to the piston gas after the regressive expansion wave has passed ; this wave is itself reflected. The reflected shock wave also enters into interaction with the **contact surface** which separates the gas shocked by the incident wave from the piston gas.

Figure 10 : Propagation of waves.



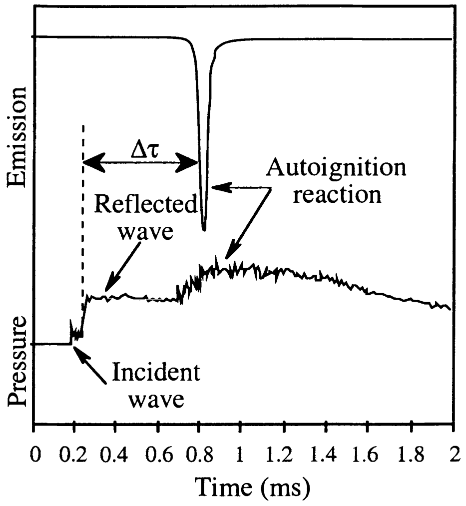
Example 6

Figure 11 shows an example of the recordings of the variations in the pressure and in the emission of the OH free radicals as a function of time in a shock tube experiment. The initial mixture has the following molar composition : Ar : O_2 : C_2H_4 = 96 : 3 : 1

An initial increase is observed on the pressure diagram due to the incident wave, then a second increase due to the reflected wave. The pressure reached is 7.28×10^5 Pa and the temperature 1280 K.

The pressure thus stays constant and the emission of OH is negligible up to the moment when the autoignition reaction occurs, after a **measured** delay $\Delta\tau = 560$ μs.

Figure 11 : Recording of the variations in the pressure and in the emission of the OH free radicals as a function of the time in a shock tube experiment.



7.2 - RANKINE-HUGONIOT equations

These equations, established in the 19th century, allow the **initial values p_5 of the pressure and T_5 of the temperature** at which the reaction will start to be calculated, as functions of **three measured experimental properties** : the pressure p_1 and the temperature T_1 of the fresh reaction mixture and the velocity U_I of the incident shock wave.

Figure 12 shows the nomenclature of the properties which describe on the one hand the state of the gases and on the other the velocities before and after the passage of the incident (fig. 12a) then reflected (fig. 12b) shock waves. This description can be carried out in two types of references :

- a fixed reference system linked to the laboratory, the velocities are shown in capital letters,
- a reference system linked to the shock wave, the velocities are represented by small letters.

a) Incident shock wave (fig. 12a)

Before the passage of the incident shock wave, the reaction mixture is at rest ($U_1 = 0$) at pressure p_1 and at temperature T_1. The shocked mixture has a velocity U_2, a pressure p_2 and a temperature T_2.

As the velocity of the incident wave measured by the sensors is equal to U_I, the fresh mixture moves relatively to the shock front with a velocity :

$$u_1 = U_I \tag{88}$$

and the shocked mixture with a velocity :

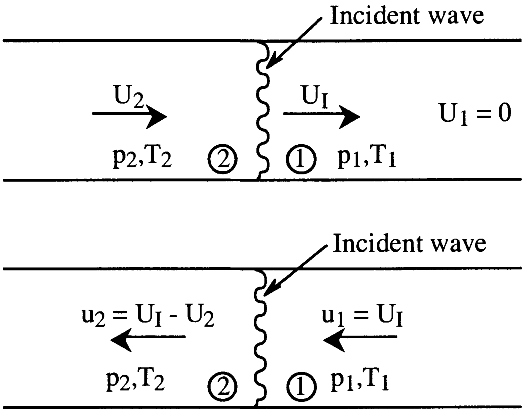
$$u_2 = U_I - U_2 \tag{89}$$

Figure 12 : Shock waves.

a) Incident shock wave

— Fixed reference

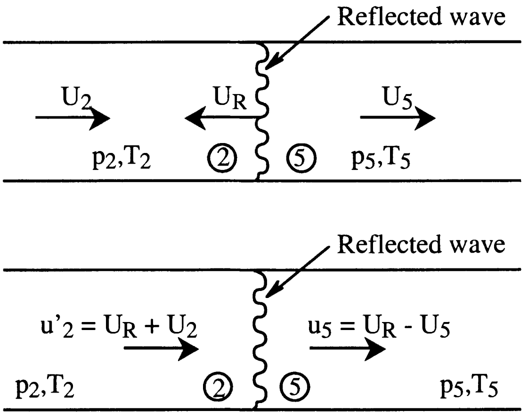
— Reference linked to the shock wave



b) Reflected shock wave

— Fixed reference

— Reference linked to the shock wave



The equations of conservation of mass, of energy and of momentum can be written as follows, in the shock wave reference system :

$$\rho_2 u_2 = \rho_1 u_1 \tag{90}$$

$$h_2 + u_2^2/2 = h_1 + u_1^2/2 \tag{91}$$

$$p_2 + \rho_2 u_2^2 = p_1 + \rho_1 u_1^2 \tag{92}$$

where ρ_1, ρ_2 are the densities.

ρ_1 and ρ_2 are expressed as follows, using the ideal gas law :

$$\rho_1 = \frac{p_1 M}{R T_1} \tag{93}$$

$$\rho_2 = \frac{p_2 M}{R T_2} \tag{94}$$

therefore :

$$\frac{p_2}{T_2} u_2 = \frac{p_1}{T_1} u_1 \tag{95}$$

$$h_2 + u_2^2/2 = h_1 + u_1^2/2 \tag{96}$$

$$p_2\left(1 + \frac{M u_2^2}{RT_2}\right) = p_1\left(1 + \frac{M u_1^2}{RT_1}\right) \tag{97}$$

This is a system of three equations with three unknowns : p_2, T_2, u_2. Indeed, p_1, T_1 and u_1 are measured properties, the specific enthalpy h_1 is a function of the temperature T_1, h_2 a function of T_2, and the mean molar mass M of the mixture is known since its composition is fixed.

In fact, u_2 can easily be eliminated using equation (95) and the system reduced to two equations with two unknowns p_2 and T_2 :

$$h_2 + \frac{1}{2}\left(\frac{p_1 T_2}{p_2 T_1}\right)^2 u_1^2 = h_1 + \frac{1}{2} u_1^2 \tag{98}$$

$$p_2\left[1 + \frac{M u_1^2}{RT_2}\left(\frac{p_1 T_2}{p_2 T_1}\right)^2\right] = p_1\left(1 + \frac{M u_1^2}{RT_1}\right) \tag{99}$$

In order to be able to solve this system, it is necessary to have a satisfactory initial approximation to the solution p_2 and T_2. This is done by assuming that the specific heats c_p and c_V of the reaction mixture are constant and independent of the temperature.

Two auxiliary properties are introduced :

— the speed of sound in the fresh reaction mixture :

$$a_1 = \left(\frac{\gamma R T_1}{M}\right)^{1/2} \tag{100}$$

where

$$\gamma = c_p/c_V \tag{101}$$

— the MACH number of the incident shock wave :

$$M_1 = \frac{u_1}{a_1} = u_1 \left(\frac{M}{\gamma R T_1}\right)^{1/2} \qquad (102)$$

The following initial estimations for T_2 and p_2 are deduced :

$$T_2^{(o)} = T_1 \frac{\left(\gamma M_1^2 - \frac{\gamma-1}{2}\right)\left(\frac{\gamma-1}{2} M_1^2 + 1\right)}{\left(\frac{\gamma+1}{2} M_1\right)^2} \qquad (103)$$

$$p_2^{(o)} = p_1 \frac{2\gamma M_1^2 - (\gamma-1)}{\gamma+1} \qquad (104)$$

b) Reflected shock wave (fig. 12b)

The notations are analogous to those in Figure 12a. The velocity of the reflected wave is designated by U_R, the velocity of the mixture in state 2 by u_2 and that of the mixture in state 5 with respect to the reflected wave by u_5, therefore :

$$u'_2 = U_R + U_2 = U_R + U_I - u_2 \qquad (105)$$

$$u_5 = U_R - U_5 \qquad (106)$$

If the reaction mixture remains at rest, which is the case of an ideal gas, $U_5 = 0$ and therefore :

$$u_5 = U_R \qquad (107)$$

The following three conservation equations can be written :

$$\rho_5 u_5 = \rho_2 u'_2 \qquad (108)$$

$$h_5 + u_5^2/2 = h_2 + u'^2_2/2 \qquad (109)$$

$$p_5 + \rho_5 u_5^2 = p_2 + \rho_2 u'_2 \qquad (110)$$

The calculations can be continued in two ways. If the velocity U_R of the reflected wave is measured, u'_2 can be calculated using relationship (105), if not, the approximate relationship (107) can be used. Applying the same technique of calculation as before, the following set of two equations with two unknowns p_5 and T_5, is obtained :

$$h_5 + \frac{1}{2}\left(\frac{p_2 T_5}{p_5 T_2}\right) u'^2_2 = h_2 + \frac{1}{2} u'^2_2 \qquad (111)$$

$$p_5 \left[1 + \frac{M u'^2_2}{R T_5}\left(\frac{p_2 T_5}{p_5 T_2}\right)^2\right] = p_2 \left(1 + \frac{M u'^2_2}{R T_2}\right) \qquad (112)$$

The following initial approximations for p_5, T_5 and U_R, are obtained by assuming that the specific heats c_p and c_V are constant :

$$\frac{p_5^{(o)}}{p_1} = 1 + \frac{\gamma_1 (\eta-1)(\xi-1) M_1^2}{\xi - \eta} \tag{113}$$

$$\frac{T_5^{(o)}}{T_1} = 1 + \frac{(\gamma_1-1)(\eta-1)(\xi-1) M_1^2}{\eta(\xi-\eta)} \tag{114}$$

$$\frac{U_R^{(o)}}{U_I} = \frac{\eta - 1}{\xi - \eta} \tag{115}$$

where :

$$\eta = \frac{(\gamma_1 + 1) M_1^2}{(\gamma_1 - 1) M_1^2 + 2} \tag{116}$$

$$\xi = \frac{\eta\,[\gamma_1 (\eta-1) M_1^2 + \eta]}{\eta + (\gamma_1 - 1)(\eta - 1) M_1^2} \tag{117}$$

Example 7

An experiment in a shock tube is carried out with air of molar mass $M = 29\text{x}10^{-3}$ kg mol^{-1}. The fresh gas is at pressure $p_1 = 6.67\text{x}10^2$ Pa and at temperature $T_1 = 296$ K. The incident shock wave has a velocity of $U_I = 2800$ m s^{-1}. Estimate the values of the pressure p_2 and of the temperature T_2 after the incident wave has passed. The following value is taken $\gamma = 1.33$.

The speed of sound is calculated (eqn 100) : $a_1 = (1.33\times8.3145\times296/29\text{x}10^{-3})^{1/2}$, $a_1 = 336$ m s^{-1}. The Mach number of the incident shock wave is deduced (eqn 102) : $M_1 = 8.334$. Relationships (103) and (104) give the following :

$$T_2^{(o)} = 296\,\frac{\left(1.33\times8.334^2-0.33/2\right)\left(0.33\times8.334^2/2+1\right)}{(2.33\times8.334/2)^2} = 3608 \text{ K}$$

$$p_2^{(o)} = 6.67\text{x}10^2\left(2\times1.33\times8.334^2 - 0.33\right)/2.33 = 5.28\text{x}10^4 \text{ Pa}$$

7.3 - Balance equations

In order to be able to write the mass, energy and momentum balance equations, a certain number of simplifying assumptions must be made :

- the flow is one-dimensional ; its position is given by the spatial coordinate z along the tube,
- the flow is adiabatic,
- the transport phenomena due to diffusion, to the thermal conductivity and to the

viscosity are negligible ; the length of an experiment is actually less than a millisecond,

- the influence of the laminar limiting layer is negligible ; in fact, this layer brings about a slowing down of the shock, an acceleration of the contact surface and, in a general way, causes the flow in the wake of the shock to be non-uniform. This effect can be taken into account by considering that the cross-sectional area of the tube changes with the spatial coordinate.

a) Continuity equation

This equation expresses LAVOISIER's law, that is that the mass flow rate across a cross-section of the tube is constant :

$$W = \rho\ v\ A = \text{Constant} \tag{118}$$

where W is the mass flow rate,
ρ is the density,
v is the flow velocity of the fluid,
A is the cross-sectional area of the tube.

Assuming that the area A is constant, differentiation of equation (118) leads to the following relationship :

$$\frac{d\rho}{\rho} + \frac{dv}{v} = 0 \tag{119}$$

i.e.:

$$\frac{dv}{dt} = -\frac{v}{\rho}\frac{d\rho}{dt} \tag{120}$$

where t is the time.

b) Species balance equations

The following relationship can be written :

$$\begin{cases} \rho\ v \dfrac{dw_j}{dz} = R_j\ M_j \\ j = 1, \ldots, J \end{cases} \tag{121}$$

where w_j is the mass fraction of C_j,
R_j is the rate of production of C_j,
M_j is the molar mass of C_j,
J is the number of constituents.

It is suitable to take the time t as an independent variable instead of the abscissa z. The following relationship is used to carry out this change of variable :

$$\frac{d}{dt} = v \frac{d}{dz} \tag{122}$$

where :

$$v = \frac{dz}{dt} \tag{123}$$

Equation (121) can therefore be written as follows :
$$\begin{cases} \dfrac{dw_j}{dt} = \dfrac{R_j M_j}{\rho} \\ j = 1, \ldots, \end{cases} \tag{124}$$

c) Energy conservation

The following relationship can be written for an adiabatic flow :

$$h + \frac{1}{2} v^2 = \text{Constant} \tag{125}$$

This becomes, by differentiation :

$$\frac{dh}{dz} + v \frac{dv}{dz} = 0 \tag{126}$$

i.e., taking equation (120) into account :

$$\frac{dh}{dt} = - v \frac{dv}{dt} = - \frac{v^2}{\rho} \frac{d\rho}{dt} \tag{127}$$

where h is the specific enthalpy of the mixture :

$$h = \sum_{j=1}^{J} w_j h_j \tag{128}$$

where h_j is the specific enthalpy of C_j.
Differentiating relationship (128), gives :

$$\frac{dh}{dt} = \sum h_j \frac{dw_j}{dt} + \sum w_j \frac{dh_j}{dt} \tag{129}$$

The term dw_j/dt is given by equation (124) and the thermodynamic law for an ideal gas can be written as follows : $dh_j = c_{pj}\, dT$

where c_{pj} is the specific heat of C_j at constant pressure.

Equation (129) becomes :
$$\frac{dh}{dt} = \sum \frac{R_j M_j h_j}{\rho} + \sum w_j c_{pj} \frac{dT}{dt} \tag{130}$$

The following relationship can be written : $c_p = \sum w_j c_{pj}$
where c_p is the mean specific heat of the mixture at constant pressure.

The combination of equations (127) and (130) leads to the energy balance equation :

$$\frac{dT}{dt} = - \sum \frac{R_j M_j h_j}{\rho c_p} + \frac{v^2}{\rho c_p} \frac{d\rho}{dt} \tag{131}$$

d) Momentum conservation

This law can be written as follows :

$$p + \rho v^2 = \text{Constant} \tag{132}$$

The above equation is differentiated, taking into account that the product ρv is constant :

$$\frac{dp}{dz} + \rho\, v\, \frac{dv}{dz} = 0 \tag{133}$$

i.e., changing to the independent variable t and taking equation (120) into account, gives :

$$\frac{dp}{dt} = -\rho\, v\, \frac{dv}{dt} = v^2 \frac{d\rho}{dt} \tag{134}$$

The variables p and ρ are related by the ideal gas equation :

$$p = \rho \frac{RT}{M} \tag{135}$$

where M is the mean molar mass of the reaction mixture :

$$M = \frac{1}{\Sigma\left(w_j/M_j\right)} \tag{136}$$

where M_j is the molar mass of C_j.

Differentiating equation (135) gives :

$$\frac{dp}{dt} = \frac{RT}{M}\frac{d\rho}{dt} + \frac{\rho R}{M}\frac{dT}{dt} - \frac{\rho RT}{M^2}\frac{dM}{dt} \tag{137}$$

The term dM/dt is obtained by differentiating (136) and taking relationship (124) into account, gives :

$$\frac{dM}{dt} = -M^2 \sum \frac{1}{M_j}\frac{dw_j}{dt} = -M^2 \sum \frac{R_j}{\rho} \tag{138}$$

Using relationships (137) and (138), equation (137) becomes :

$$\frac{dp}{dt} = \frac{RT}{M}\frac{d\rho}{dt} + \frac{\rho R}{M}\left(-\frac{1}{\rho c_p} \sum R_j M_j h_j + \frac{v^2}{\rho c_p}\frac{dp}{dt} \right) + RT \sum R_j \tag{139}$$

Combining equations (134) and (139) gives the final form of the momentum balance :

$$\frac{d\rho}{dt} = \frac{\dfrac{\rho R}{M c_p} \sum R_j\, M_j \left(h_j - M\, c_p\, T/M_j\right)}{p + p v^2/c_p T - \rho\, v^2} \tag{140}$$

The evolution of the test-gas is therefore represented by the system of ordinary differential equations (120), (124), (131) and (140). The initial conditions of this system are given by the RANKINE-HUGONIOT equations.

e) Particle time and measured time

Figure 13 shows the paths taken :

— by a gas particle between the instant when it was hit by the incident shock wave and that at which it undergoes observation : $U\Delta t$,

— by the incident shock wave during the same time interval : $U_I\Delta t$,

— by the incident shock wave during a time interval Δt_m measured on a recorder and counted from the moment when the shock wave goes past the observation point.

This gives the following expression :

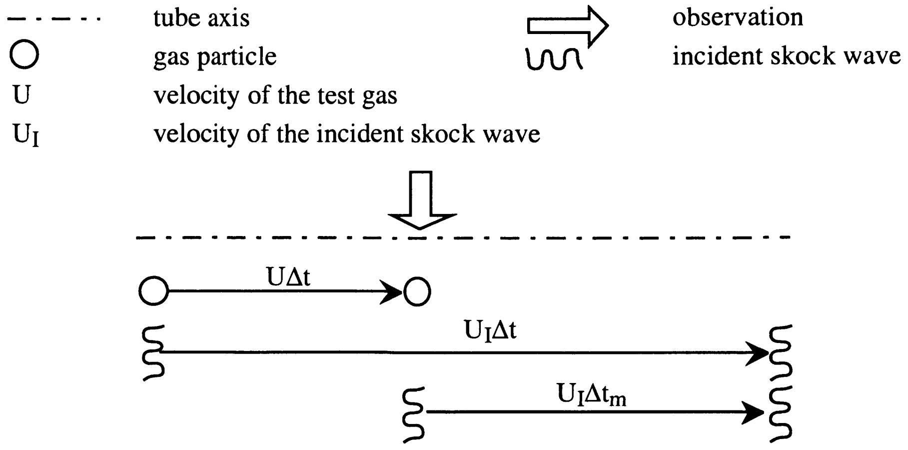
$$(U_I - U)\,\Delta t = U_I\,\Delta t_m \tag{141}$$

i.e., by extending to the limit :

$$\frac{dt_m}{dt} = 1 - \frac{U}{U_I} \tag{142}$$

This differential equation must be added to the preceding ones in order to obtain the time measured as a function of the particle time. This correction is far from being negligible.

Figure 13 : *Particule time and measured time.*



FURTHER READING

AZAY P., CôME G.M., *Temperature gradients in a continuous flow stirred tank reactor*, Ind. Eng. Chem. Process Des. Dev., 18, 754 (1979).

BARBÉ P., LI Y., MARQUAIRE P.M., CôME G.M., BARONNET F., *Competition* *between the gas and surface reactions for the oxidative coupling of methane - 1. Non-isothermal results in catalytic jet-stirred reactor,* Catalysis Today, 21, 409 (1994).

CôME G.M., *Laboratory Reactors for Pyrolysis Reactions*, in "Pyrolysis: Theory and Industrial Practice", Academic Press (1983).

DAGAUT P., CATHONNET M., ROUAN J.P., FOULATIER R., QUILGARS A., BOETTNER J.C., GAILLARD F., JAMES H., *A jet-stirred reactor for kinetic studies of homogeneous gas-phase reactions at pressures up to ten atmospheres*, J. Phys. E.: Sci. Instrum., 19, 207 (1986).

HLAVACEK V., PUSZYNSKI J.A., VILJOEN H.J., GATICA J.E., *Model Reactors and their Design Equations*, Ullmann's Enc. Ind. Chem., vol. B 4, 121 (1995).

LEVENSPIEL O., *Chemical Reaction Engineering*, Wiley (1972).

MARQUAIRE P.M., CôME G.M., React. Kin. Cat. Letters, 9, 165 (1978).

MINETTI R., RIBAUCOUR M., CARLIER M., FITTSCHEN C., SOCHET L.R., *Experimental and modeling study of oxidation and autoignition of butane at high pressure*, Comb. Flame, 96, 201 (1994).

THOENES D., *Chemical Reactor Development-From Laboratory Synthesis to Industrial Production*, Kluwer (1998).

CHAPTER XIII

ANALYSIS AND REDUCTION OF REACTION MECHANISMS

This chapter gives two methods of analysing complex reaction mechanisms :

- *the sensitivity analysis allows the negligible and the determining reactions to be detected, and also to find links between determining kinetic parameters;*
- *the analysis of the chemical fluxes leads to the generation of reaction schemes which are useful for an intuitive understanding of the way in which the reaction takes place.*

It also describes the two main methods of reduction of complex mechanisms : quasi-stationary state and partial equilibria approximations and eigenvalue analysis. These two methods give kinetic models which may be used in the computer codes for calculating three-dimensional turbulent reacting flows.

1 - ANALYSIS OF REACTION MECHANISMS

1.1 - Sensitivity Analysis

In order to simplify the presentation, the reaction will be considered to take place in a batch reactor of constant volume, working under isothermal conditions. The mass balance equations can be written as follows :

$$\begin{aligned} \frac{dc_j}{dt} &= R_j\left(c_1, c_2, \ldots, c_J\right) \\ c_j(o) &= c_{oj}\ ;\ j = 1, J \end{aligned} \tag{1}$$

where c_j is the concentration of the species C_j at the instant t,

t is the reaction time,

c_{oj} is the initial concentration of C_j,

R_j is the net rate of production of C_j,

J is the number of constituents.

The rate R_j is a function of the concentrations of all the species present in the reaction medium.

The numerical integration of equations (1) gives the values of the concentrations as functions of the reaction time, t :

$$c_j = c_j\left(t\,;c_{o1},\ldots,c_{oJ}\,;k_1,\ldots,k_I\right) \qquad j=1,J \tag{2}$$

The calculated concentrations c_j are functions of the reaction time t and of the initial concentrations $c_{o1}, \ldots, c_{oJ}$. It will be assumed in what follows that these values are given. Under these conditions, the calculated concentrations depend on the parameters of the model (1), that is the I rate constants $k_1, k_2, \ldots, k_I$ of the I elementary reactions or lumped reactions which constitute the reaction mechanism.

a) Sensitivity coefficients

If the rate constants k_i are varied, for fixed initial concentrations c_{oj} and reaction time t, the concentrations c_j calculated from equations (1) vary. For small variations, the following equations can be written :

$$dc_j = \sum_{i=1}^{I}\left(\frac{\partial c_j}{\partial k_i}\right)dk_i \tag{3}$$

The quantity :

$$s_{ji} = \left(\frac{\partial c_j}{\partial k_i}\right) \tag{4}$$

is called the absolute sensitivity coefficient of the concentration c_j with respect to the rate constant k_i.

A normalized sensitivity coefficient is also introduced, as follows :

$$\sigma_{ji} = \frac{k_i}{c_j}\frac{\partial c_j}{\partial k_i} = \frac{\partial \ln c_j}{\partial \ln k_i} \tag{5}$$

Numerous methods of calculating the sensitivity coefficients exist.

The method of brute force consists in varying each rate constant individually, carrying out a simulation and calculating the sensitivity coefficient using the following relationship :

$$s_{ji} \simeq \frac{\Delta c_j}{\Delta k_i} \tag{6}$$

This method is very costly in calculation time.

The most commonly used method, which is used in particular in the SENKIN computer program, is the **direct decoupled method**. It consists of differentiating the equations (1) with respect to k_i :

$$\frac{d}{dt}\frac{\partial c_j}{\partial k_i} = \frac{\partial R_j}{\partial k_i} + \sum_{l=1}^{I}\frac{\partial R_j}{\partial c_l}\times\frac{\partial c_l}{\partial k_i} \qquad j=1,\ldots,J\,;\,i=1,\ldots,I \tag{7}$$

Equations (1) and (7) are simultaneously integrated taking into account the fact that the

Jacobian of the two systems is the same. The initial condition for the vector $\partial c_j/\partial k_i$ is the zero vector.

b) Negligible, non-determining and determining reactions

— *Negligible reactions*

If one or several negligible reactions in the mechanism are eliminated, only very small differences between the concentrations $\tilde{c}_j$ calculated with the simplified mechanism and the concentrations c_j calculated with the complete mechanism, must be observed.

— *Non-determining reactions*

By definition, these are non-negligible reactions, which have been eliminated during the previous step. A reaction i is considered to be non-determining if the **global sensitivity** of the reaction i :

$$b_i = \sum_j |\sigma_{ji}| \tag{8}$$

is much lower than 1, the sum being over all the constituents present in the reaction medium. It is possible, of course, to calculate the global sensitivity of a set of reactions :

$$b = \sum_i b_i \tag{9}$$

the sum being over certain well-specified reactions, and to identify a group of non-determining reactions in one calculation.

— *Determining reactions*

Determining reactions are neither negligible nor non-determining. A determining reaction therefore has a global sensitivity coefficient which is not close to zero, for example :

$$b_i > 0.1 \tag{10}$$

This necessitates that at least one of the individual sensitivity coefficients has a value which is not close to zero :

$$|\sigma_{ji}| > 0.1 \tag{11}$$

According to equation (5), the relative variation dc_j/c_j is equal to the relative variation dk_i/k_i multiplied by σ_{ji}. For example, for $dk_i/k_i = 0.5$ and $\sigma_{ji} = 0.5$, $dc_j/c_j = 0.25$ is obtained. In a very general way, the variations in the determining rate constants bring about variations of the same order in the calculated concentrations. Conversely, it is possible to adjust the determining kinetic parameters in order to reduce the differences between the calculated concentrations and the measured experimental concentrations.

Example 1

Identify in the following mechanism the negligible, non-determining and determining reactions for the limiting case $k_2[\mu H] << k_3$. Assume that the chains are long.

$$\mu H \longrightarrow 2\,{}^\bullet ß \quad (12)$$

$$^\bullet ß + \mu H \longrightarrow ßH + {}^\bullet\mu \quad (13)$$

$$^\bullet\mu \longrightarrow {}^\bullet ß + m \quad (14)$$

$$^\bullet ß + {}^\bullet ß \longrightarrow ßß \quad (15)$$

$$^\bullet ß + {}^\bullet\mu \longrightarrow ß\mu \quad (16)$$

$$^\bullet\mu + {}^\bullet\mu \longrightarrow \mu\mu \quad (17)$$

Taking the hypotheses which have been made into account, it is possible to establish the following kinetic laws :

$$R_{ßH} \simeq R_m \simeq -R_{\mu H} \simeq k_{13}\left(k_{12}/k_{15}\right)^{1/2}[\mu H]^{3/2} \quad (18)$$

$$R_{ßß} \simeq k_1[\mu H] \quad (19)$$

$$R_{ß\mu}, R_{\mu\mu} << R_{ßß} \quad (20)$$

Reactions (16) and(17) are negligible. In actual fact, their rate constants have not been included in equations (18) and (19) and, in addition, the rates of formation of the $ß\mu$ and $\mu\mu$ products are negligible with respect to those of the ßß products.

Reaction (14) is not negligible, as, if it were eliminated, the product m would no longer be formed. It is not a determining reaction either, as the rate constant k_{14} does not appear in the kinetic laws (18) and (19). This is therefore typically a non-determining reaction.

Consequently, the determining reactions are the initiation (12), propagation (13) and termination (15) reactions, whose rate constants appear in the kinetic laws (18) and (19).

It can be noted that the kinetic law (18) actually involves the group of three determining parameters $k = k_{13}(k_{12}/k_{15})^{1/2}$. Consequently, if, during experiments, only the rates of appearance of the main products ßH and m have been measured, only the value of the global constant k can be determined, and not of the individual constants k_{12}, k_{13} and k_{15}. The existence of links between the parameters of a model can be demonstrated by the principal component analysis of a suitable objective function.

c) Search for the links between kinetic parameters

From equation (2), an **objective function** is defined which is the sum of the squares of the relative variations of the calculated concentrations resulting from variations in the rate constants :

$$E = \sum_j \left[\frac{c_j(\alpha) - c_j(\alpha_o)}{c_j(\alpha_o)}\right]^2 \quad (21)$$

where $$\alpha_i = \ln k_i \ ; i = 1, I \quad (22)$$

and $$\alpha^T = (\alpha_1, \alpha_2, \ldots, \alpha_I) \quad (23)$$

Carrying out a limited development of order 1 of $c_j(\alpha)$ about α_o, the following approximation is obtained :

$$E \simeq (\Delta\alpha)^T S^T S (\Delta\alpha) \quad (24)$$

where $$\Delta\alpha = \alpha - \alpha_o \quad (25)$$

S is the matrix of the normalized sensitivity coefficients.

An analysis of the principal components of the objective function is carried out. The matrix of normalized eigenvectors of S^TS is called U, so that :

$$U^TU = I \quad (26)$$

where I is the identity matrix.

The new parameters defined by the following relationship : $\beta = U^T\alpha$ (27)

are eigenvectors of S^TS and are called principal components. The objective function takes the following form :

$$E = \sum_i \lambda_i (\Delta \beta_i)^2 \quad (28)$$

The quantities λ_i are eigenvalues of S^TS. They can be divided into two groups. The larger eigenvalues obviously correspond to determining kinetic parameters. The smaller eigenvalues allow relationships between determining parameters to be found, of the form $k_1^{\gamma_1} k_2^{\gamma_2} \ldots k_I^{\gamma_I}$.

During the fitting process of the kinetic parameters, in particular when using a numerical optimization computer program, it is important to bear in mind the possible existence of these links between the parameters.

1.2 - Analysis of the chemical fluxes

Consider the following reaction mechanism : $$\sum_{j=1}^{J} \nu'_{ij} C_j \rightleftharpoons \sum_{j=1}^{J} \nu''_{ij} C_j \quad (29)$$

$$i = 1, 2, \ldots, I$$

The net rate of production of C_j has the following expression :

$$R_j = \sum_i \nu_{ij} r_i \quad (30)$$

where r_i is the net rate of the reaction (i).

R_j can be divided into two terms :

— a rate of appearance :

$$R_j^+ = \sum_i (\nu''_{ij} r'_i + \nu'_{ij} r''_i) \quad (31)$$

— a rate of disappearance :

$$R_j^- = \sum_i \left(v'_{ij}\, r'_i + v''_{ij}\, r''_i\right) \tag{32}$$

where r'_i is the rate of reaction i from left to right,

r''_i is the rate of the reverse reaction.

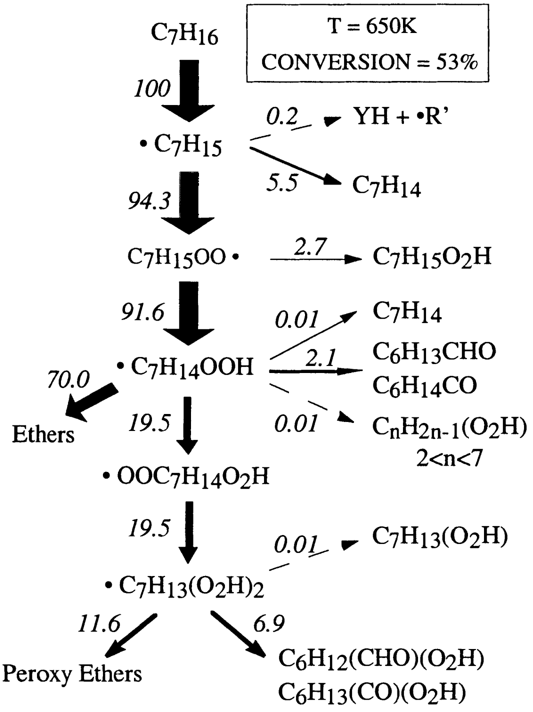
It then becomes possible to define the relative importance of the reaction route (i) :

— for the formation of C_j
$$\alpha_{ij}^+ = \frac{\left(v''_{ij}\, r'_i + v'_{ij}\, r''_i\right)}{R_j^+} \tag{33}$$

— for the consumption of C_j
$$\alpha_{ij}^- = \frac{\left(v'_{ij}\, r'_i + v''_{ij}\, r''_i\right)}{R_j^-} \tag{34}$$

Figure 1 illustrates the presentation of equations (33) and (34) in a graphic form, for the case of the oxidation of n-heptane at high conversion (53 %).

Figure 1 : Analysis of the chemical fluxes.
Oxidation of n-heptane in a stirred flow reactor.
$T = 650$ K, $\varphi = 1$, $\tau = 1$ s, conversion = 53 %.



The scheme shown constitutes an analysis of the primary mechanism, although the secondary reactions have an important part to play. The thickness of an arrow is approximately proportional to the flux, the latter being specified by a number.
A few simple observations can be made about this scheme.
— The main products of the reaction are on the one hand, cyclic ethers and on the other, hydroperoxides (ethers, aldehydes, ketones) ; the latter come from the addition of oxygen which is therefore very largely the cause of degenerate branchings.
— This kinetic scheme constitutes a reduced model of the reaction deduced from the detailed mechanism.

2 - REDUCTION OF REACTION MECHANISMS

2.1 -Quasi-stationary-state and partial equilibria approximations

a) Quasi-stationary-state approximation (QSSA)

This technique has already been defined and used for simple mechanisms (Chapter VIII). A complex reaction mechanism which is described by the following system of ordinary differential equations is considered here :

$$\frac{dc_j}{dt} = R_j \quad ; \quad c_j(o) = c_{oj} \quad ; \quad j = 1, J \tag{1}$$

The QSSA consists of replacing (1) by the following system :

$$\begin{cases} R_j = 0 \quad ; \quad j = 1, J_f & (35) \\ \dfrac{dc_j}{dt} = R_j \quad ; \quad c_j(o) = c_{oj} \quad ; \quad j = J_f + 1 \quad , \quad J = J_f + J_s & (36) \end{cases}$$

where J_f is the number of fast variables,
J_s is the number of slow variables .

The system of equations therefore includes J_f algebraic equations (35) for which the initial conditions have been eliminated ; these are the quasi-stationary equations which define a manifold of dimension J_f of the phase space $(c_1, c_2, ..., c_J)$. The trajectories of the system are therefore situated on this manifold, and their dynamics are described by the system of differential equations with initial conditions (36) of dimension $J_s = J - J_f$.
The differential system (36) has lost the **stiffness** which characterized the initial system (1). It can therefore be integrated by **explicit** algorithms which are a lot less costly in calculation time than **implicit** algorithms which are indispensable for solving system (1). Some specific numerical codes have been adapted to the solution of these systems of mixed algebraic-differential equations. This gives a very significant gain.

It is possible to go further in this approach and proceed to eliminate the quasi-stationary species by solving equations (35).

Example 2

Reduce the sub-mechanism :

$$H + O_2 \longrightarrow OH + O \qquad (37)$$

$$O + H_2 \longrightarrow OH + H \qquad (38)$$

$$OH + H_2 \longrightarrow H_2O + H \qquad (39)$$

by applying the QSSA to the species O and OH.

The QSSA gives 2 relationships ($J_f = 2$) :

$$\begin{aligned} O &: r_{37} - r_{38} = 0 \\ OH &: r_{37} + r_{38} - r_{39} = 0 \end{aligned} \qquad (40)$$

The solution of this system gives the equations of the reduced manifold of dimension $J_s = 1$:

$$\begin{aligned} [O] &= \frac{k_1}{k_2} \frac{[O_2]}{[H_2]} [H] \\ [OH] &= \frac{2\,k_1}{k_3} \frac{[O_2]}{[H_2]} [H] \end{aligned} \qquad (41)$$

The corresponding lumped reaction can be obtained by multiplying each reaction by a coefficient λ_i, and adding them and stating that the quasi-stationary species do not appear in the lumped equation for the reaction ; the following system is then obtained :

$$\begin{aligned} O &: \lambda_{37} - \lambda_{38} = 0 \\ OH &: \lambda_{37} + \lambda_{38} - \lambda_{39} = 0 \end{aligned} \qquad (42)$$

Putting $\lambda_{37} = 1$; it follows that $\lambda_{38} = 1, \lambda_{39} = 2$, which gives the following equation :

$$H + O_2 + 3\,H_2 \longrightarrow 3\,H + 2\,H_2O \qquad (43)$$

This reaction shows clearly the fact that the mechanism (37)-(39) is that of a branching chain reaction.

The dynamics of the system on the manifold (41) is given by the following equation :

$$\frac{d\,[H]}{dt} = -\,r_{37} + r_{38} + r_{39} = 2\,r_{37} = 2\,k_{37}\,[H]\,[O_2] \qquad (44)$$

It can be observed that the kinetic law (44) which applies to reaction (43) bears no resemblance to the one which would have been written if reaction (43) had been an elementary reaction. This is a very common concept.

The writing of equations (35) and (36) assumes that it was possible, either to suggest a priori the identity of the quasi-stationary species (free radicals, for example) and then to check that the QSSA can be applied, or to look for them in a systematic way.

The quasi-stationary species are characterized by a net rate of production R_j which is practically equal to zero, which is the case if the quantity :

$$\alpha_j = \frac{R_j}{\left(R_j^+ + R_j^-\right)} \tag{45}$$

has an absolute value very much lower than 1.

b) Partial equilibria approximation (PEA)

This approximation consists in assuming that a reaction is in quasi-equilibrium, which is the same as writing :

$$r_i = 0 \tag{46}$$

An analogous test to test (45) is carried out to detect if the reactions are in quasi-equilibrium ; the following quantity is calculated :

$$ß_i = \frac{r_i}{\left(r_i' + r_i''\right)} \tag{47}$$

The reactions for which $|ß_i| << 1$ are in quasi-equilibrium.

Example 3

Apply the partial equilibrium approximation to the mechanism (37)-(39) assuming that the three reactions are at quasi-equilibrium.

Calling K_{37}, K_{38} and K_{39} the concentration equilibrium constants of the reactions (37)-(39), gives the following relationships :

$$\begin{aligned}
[O] &= K_{37}\,K_{39}\,[O_2]\,[H_2]\,/\,[H_2O] \\
[OH] &= \left(K_{37}\,K_{38}\right)^{1/2}\,[O_2]^{1/2}\,[H_2]^{1/2} \\
[H] &= \left(K_{37}\,K_{38}\right)^{1/2}\,K_{39}\,[O_2]^{1/2}\,[H_2]^{3/2}\,/\,[H_2O]
\end{aligned} \tag{48}$$

The relationships (48) are only suitably checked if the temperature is high enough (T > 1800 K). Note that in this case the PEA is strictly equivalent to the QSSA applied to the three radicals O, OH and H. This is simply a consequence of relationship (30) :

$$R_j = \sum \nu_{ij}\, r_i$$

It is of course possible to combine the two approximations (QSSA and PEA) so that a maximum reduction of the mechanism can be obtained. It is also necessary to take the relationships dictated by the conservation of the elements into account.

2.2 - Analysis using eigenvalues

The linear differential system which describes the local behaviour in the vicinity of a point $(c_1^*, c_2^*, \ldots, c_J^*)$, is associated with the system (1) :

$$\frac{dc_j}{dt} = R_j\left(c_1^*, \ldots, c_J^*\right) + \sum_{l} \frac{\partial R_j}{\partial c_l}\left(c_1^*, \ldots, c_J^*\right) \times \left(c_l - c_l^*\right) \tag{49}$$

Let the following matrices be defined :

$$z = \begin{pmatrix} c_1 \\ \vdots \\ c_J \end{pmatrix} \; ; \; f(z) = \begin{pmatrix} R_1 \\ \vdots \\ R_J \end{pmatrix} \; ; \; J = \begin{pmatrix} \dfrac{\partial R_1}{\partial c_1} \cdots \dfrac{\partial R_1}{\partial c_J} \\ \cdots\cdots\cdots\cdots\cdots \\ \dfrac{\partial R_J}{\partial c_1} \cdots \dfrac{\partial R_J}{\partial c_J} \end{pmatrix} \tag{50}$$

therefore :

$$\frac{dz}{dt} = f(z^*) + J^* \left(z - z^*\right) \tag{51}$$

where J^* is the Jacobian of $f(z)$ for $z = z^*$. Calling the eigenvectors and the eigenvalues of the Jacobian J^*, V and Λ, gives :

$$J^* = V \Lambda V^{-1} \tag{52}$$

Putting into equation (51) and multiplying the left-hand side by V^{-1}, gives :

$$\frac{dZ}{dt} = A + \Lambda Z \tag{53}$$

where

$$A = V^{-1} \left[f(z^*) - J^* z^*\right] \tag{54}$$

$$Z = V^{-1} z \tag{55}$$

As the matrix of eigenvalues Λ is diagonal, the differential system (53) is completely uncoupled, which allows the differential equations associated with the shortest characteristic times to be replaced by algebraic equations, which define an Intrinsic Low-Dimension Manifold : ILDM. The dynamics of the system can thus be described by the dynamics on this manifold.

With respect to the previous methods, it can be remarked that an eigenvalue analysis allows the fast and the slow variables to be defined, without having to identify the quasi-stationary species or the reactions at quasi-equilibrium.

Example 4

Carry out the analysis of the following mechanism, using eigenvalues :

$$C_1 \longrightarrow C_2 \tag{56}$$

$$C_2 \longrightarrow C_3 \tag{57}$$

The mass balance equations of a batch reactor at constant volume working under isothermal conditions can be written as follows, as the orders are equal to 1 :

$$(dz/dt) = J\,z \tag{58}$$

where $$z = \begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} \text{ and } J = \begin{pmatrix} -k_{56} & 0 & 0 \\ k_{56} & -k_{57} & 0 \\ 0 & k_{57} & 0 \end{pmatrix} \tag{59}$$

Letting λ be an eigenvalue and $\begin{pmatrix} a \\ b \\ c \end{pmatrix}$ the associated eigenvector, gives :

$$\begin{cases} -(k_{56}+\lambda)a & & & = 0 \\ k_{56}a & -(k_{57}+\lambda)b & & = 0 \\ & k_{57}b & -\lambda c & = 0 \end{cases} \tag{60}$$

This system has three eigenvalues as solutions :

$$\lambda_1 = 0 \;;\; \lambda_2 = -k_{57} \;;\; \lambda_3 = -k_{56} \tag{61}$$

with the associated eigendirections :

$$V_1 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \;;\; V_2 = \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} \;;\; V_3 = \begin{pmatrix} k_{56}-k_{57} \\ -k_{56} \\ k_{57} \end{pmatrix} \tag{62}$$

Using general nomenclature, gives :

$$\Lambda = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -k_{57} & 0 \\ 0 & 0 & -k_{56} \end{pmatrix} \text{ and } V = \begin{pmatrix} 0 & 0 & k_{56}-k_{57} \\ 0 & 1 & -k_{56} \\ 1 & -1 & k_{57} \end{pmatrix} \tag{63}$$

The expression for the inverse matrix of V is deduced :

$$V^{-1} = \begin{pmatrix} 1 & 1 & 1 \\ k_{56}/(k_{56}-k_{57}) & 1 & 0 \\ 1/(k_{56}-k_{57}) & 0 & 0 \end{pmatrix} \tag{64}$$

from which an expression for the variable Z is obtained :

$$Z = V^{-1}\,z = \begin{pmatrix} z_1 + z_2 + z_3 \\ k_{56}z_1/(k_{56}-k_{57}) + z_2 \\ z_1/(k_{56}-k_{57}) \end{pmatrix} \tag{65}$$

The initial differential system (58) then becomes :

$$\frac{d}{dt}\,[z_1 + z_2 + z_3] = 0$$

$$\frac{d}{dt}\left[\frac{k_{56}z_1}{(k_{56}-k_{57})} + z_2\right] = -k_{57}\left[\frac{k_{56}\,z_1}{(k_{56}-k_{57})} + z_2\right]$$

$$\frac{d}{dt}\left[\frac{z_1}{(k_{56}-k_{57})}\right] = -k_{56}\left[\frac{z_1}{(k_{56}-k_{57})}\right] \tag{66}$$

It is actually observed that the three equations are uncoupled, which allows the solution to be obtained easily :

$$z_1 + z_2 + z_3 = (z_{01} + z_{02} + z_{03}) \exp(0) \tag{67}$$

$$\frac{k_{56}z_1}{(k_{56}-k_{57}) + z_2} = \left[\frac{k_{56}z_{01}}{(k_{56}-k_{57}) + z_{02}}\right] \exp(-k_{57}\,t) \tag{68}$$

$$z_1 = z_{01} \exp(-k_{56}\,t) \tag{69}$$

- Equation (67) has an infinite characteristic time, and consequently corresponds to a constant value, i.e. to an **invariant**. This is the conservation of the global mass.
- Equation (68) has a characteristic time equal to $1/k_{57}$. Assuming that $k_{57}t >> 1$ which is the result of applying the QSSA to the intermediate C_2, results in the right-hand side of equation (68) being nearly equal to zero, which gives the following relationship between the variables z_2 and z_1 :

$$z_2 \simeq \frac{k_{56}}{k_{57} - k_{56}} z_1 \tag{70}$$

Equations (67) and (70) describe a manifold of dimension 1 of the phase space. The dynamics of the system on this manifold of lower dimension with respect to that of the original system, is given by equation (69). This means implicitly that the constant k_{56} is very much lower than k_{57}, and which is also one of the conditions of being able to use the QSSA.

The present method has a major shortcoming, as it is unknown if the level of reduction chosen a priori will give a suitable approximation. Furthermore, if the dimension of the ILDM is not very low, practical computations are cumbersome. Finally, it is not clear if it is possible to reduce it to such a level, without losing too much information.

2.3 - Other methods

The theory of singular perturbations, arising from problems of limiting layers in fluid mechanics, also applies to kinetics, where the equivalent of the limiting layer is the true induction period, i.e. the period needed to establish the quasi-stationary state. The following differential system is considered :

$$\begin{cases} \dfrac{dx}{dt} = f(x, y, \varepsilon),\ x(0) = x_o \\ \varepsilon\dfrac{dy}{dt} = g(x, y, \varepsilon),\ y(0) = y_o \end{cases} \tag{71}$$

where x and y stand for the slow and the fast variables, respectively, and ε is a small parameter close to zero.
A stretched time is defined :

$$\tau = t/\varepsilon \tag{72}$$

and a search is carried out to find the solutions to (71) which are of the following form :

$$\begin{cases} x(t) = \tilde{x}(t) + X(\tau) \\ y(t) = \tilde{y}(t) + Y(\tau) \end{cases} \tag{73}$$

The **external** solutions $\tilde{x}(t)$ and $\tilde{y}(t)$ are written as limited developments :

$$\begin{cases} \tilde{x}(t) = \tilde{x}_0(t) + \varepsilon\,\tilde{x}_1(t) + \ldots \\ \tilde{y}(t) = \tilde{y}_0(t) + \varepsilon\,\tilde{y}_1(t) + \ldots \end{cases} \tag{74}$$

The **internal** solutions $X(\tau)$ and $Y(\tau)$ are written in an analogous manner :

$$\begin{cases} X(\tau) = X_0(\tau) + \varepsilon\,X_1(\tau) + \ldots \\ Y(\tau) = Y_0(\tau) + \varepsilon\,X_2(\tau) + \ldots \end{cases} \tag{75}$$

The external solutions $\tilde{x}(t)$ and $\tilde{y}(t)$ constitute a satisfactory approximation when the following is true :

$$t >> \varepsilon, \qquad \text{that is} \qquad \tau >> 1.$$

The following asymptotic conditions result from this :

$$\lim_{\tau\to+\infty} X(\tau) = \lim_{\tau\to+\infty} Y(\tau) = 0 \tag{76}$$

The simplest external approximation of the system (71) is obtained by putting ε = 0 ; the following system is then obtained :

$$\begin{cases} \dfrac{d\tilde{x}_0}{dt} = f\left(\tilde{x}_0, \tilde{y}_0, 0\right) ; \tilde{x}_0(0) = x_0 & (77) \\ 0 = g\left(\tilde{x}_0, \tilde{y}_0, 0\right) & (78) \end{cases}$$

This is a mixed system of differential and algebraic equations which possesses exactly the same structure as the system (35)-(36) resulting from the application of the QSSA. The same conclusions can be drawn as in the corresponding paragraph 2.1.a with respect to the interest this approximation has from a numerical point of view.
The computer code S-STEP uses this approach to carry out a detailed analysis of the characteristic times and to reduce the reaction mechanisms.
A recent approach called **"repromodelling"**, which differs completely in its principle from the preceding techniques, consists in primarily carrying out numerous numerical simulations of the system (1) for a whole series of suitably chosen values of the

concentrations c_{oj} and of increments of time t, and of afterwards deducing a representation of the concentrations $c_j(t)$ as a function of the c_{oj} and of t using orthogonal polynomials. When the ulterior design of any reactor is computed, the use of these polynomial representations procures an appreciable time gain with respect to the repeated integration of the system (1).

CONCLUSION

The detailed mechanisms can be reduced firstly by methods of lumping of the species and of the reactions as seen in Chapter IX, then by the mathematical techniques described in the present Chapter XIII. However, it is clear that important advances remain indispensable in this field, with a view to the modelling of real reactors (engines, burners, industrial reactors) using CFD.

FURTHER READING

CôME G.M., *The use of computers in the analysis and simulation of complex reactions*, Comprehensive Chem. Kin., vol. 24, chap. 3 (1983).
CôME G.M., *Mechanistic modelling of homogeneous reactors: a numerical method,* Comp. & Chem. Eng., 3, 603 (1979).
GLAUDE P.A., WARTH V., FOURNET R., BATTIN-LECLERC F., CôME G.M., SCACCHI G., *Modelling of n-heptane and iso-octane oxidation at low temperature by using computer-aided designed mechanisms*, Bull. Soc. Chim. Belg., 106, 343 (1997).
TOMLIN A.S., TURANYI T., PILLING M.J., *Mathematical tools for the construction, investigation and reduction of combustion mechanisms*, Comprehensive Chem. Kin., vol. 35, chap. 4 (1997).
VARMA A., MORBIDELLI M., WU H., *Parametric Sensitivity in Chemical Systems*, Cambridge Univ. Press (1999).

COMPUTER PROGRAMS

CARM, KINALC, S-STEP, SENKIN.

CHAPTER XIV

TABLES OF THERMODYNAMIC AND KINETIC DATA AND OF MOLECULAR PARAMETERS

This chapter gives tables of numerical data which must be used when applying the methods of estimation of the thermodynamic properties, kinetic parameters and transport coefficients, described in Chapters V, VII and XI, respectively.

1 - THERMODYNAMIC TABLES

Tables 1.1 and 1.2 contain the data necessary to calculate the thermodynamic properties of molecules in the gas phase by BENSON's methods.

Table 1.3 gives the values of the R–H bond dissociation energies, which are necessary in order to be able to calculate the standard enthalpy of formation of a free radical $^\bullet R$ from that of the parent molecule RH.

Tables 1.4 to 1.10 give the data necessary to calculate the standard entropy and the heat capacity of a free radical $^\bullet R$ from those of the parent molecule RH.

Tables 1.11 to 1.13 give the thermodynamic data of elements in the standard state and of hydrocarbon and oxygenated, molecular and radical species, containing at most 2 carbon atoms.

The units used in these thermodynamic tables are the following :

$\Delta_f H^o$: kJ mol^{-1} ; S^o, C_p^o : J mol^{-1} K^{-1}

1.1 - BENSON's molecular groups

	$\Delta_f H^o$	S^o	C_p^o				
T (K)	298.15		298.15	500	800	1000	1500
C-$(H)_3$(C)	-42.26	127.32.	25.73	39.33	54.48	61.80	73.55
C-$(H)_2(C)_2$	-20.63	39.16	22.89	34.52	46.32	51.63	59.62
C-(H)$(C)_3$	-1.17	-53.60	20.08	29.97	38.95	42.05	46.74
C-$(C)_4$	19.20	-149.49	16.53	30.79	36.69	36.65	33.97
C_d-$(H)_2$	26.32	115.52	21.38	31.42	42.13	47.15	55.19

	Δ_fH^o	S^o	C_p^o				
T (K)	298.15		298.15	500	800	1000	1500
C_d-(H)(C)	36.32	33.05	18.74	24.31	32.01	35.35	40.25
C_d-$(C)_2$	44.14	-50.84	15.10	20.88	24.27	25.44	26.61
C_d-(H)(C_d)	28.28	27.74	18.54	28.24	34.94	37.61	41.76
C_d-(C)(C_d)	36.78	-61.33	17.57	24.81	27.20	27.70	28.12
C_d-(H)(C_B)C_d-	28.28	27.74	18.54	28.24	34.94	37.61	41.76
(C)(C_B)	37.95	-51.97	15.90	24.81	27.20	27.70	28.12
C_d-(H)(C_t)	28.28	27.74	18.54	28.24	34.94	37.61	41.76
C-$(H)_2$(C)(C_d)	-20.88	38.20	20.63	34.81	46.94	52.22	60.08
C-$(C)_3$(C_d)	22.13	-150.23	9.16				
C-(H)(C)$(C_d)_2$	-1.17	-53.60	20.08	29.97	38.95	42.05	46.74
C-$(H)_2$$(C_d)_2$	-18.92	42.08	24.77	35.15	47.28	52.72	60.25
C-$(H)_2$(C_d)(C_B)	-17.95	42.68	24.77	35.15	47.28	52.72	60.25
C_t-(H)	113.50	101.96	22.55	27.15	31.25	33.30	37.03
C_t-(C)	115.10	26.32	13.22	15.94	19.25	20.59	26.57
C_t-(C_d)	121.42	39.92	10.71	14.64	22.34	23.01	24.27
C_t-(C_B)	120.76	17.77	10.17	14.64	22.34	23.01	24.27
C-$(H)_2$(C)(C_t)	-19.70	42.80	20.97	33.18	45.44	51.00	59.41
C-(H)$(C)_2$(C_t)	-3.16	-45.69	17.45	28.66	38.07	41.42	46.53
C_B	142.67	26.28	15.86	19.66	22.18	23.01	23.85
C_B-(H)	13.81	48.31	13.61	22.84	31.55	35.19	40.71
C_B-(C)	23.64	-35.61	9.75	15.40	20.75	22.76	25.02
C_B-(C_d)	24.17	-33.85	14.12	18.33	22.09	23.47	24.06
C_B-(C_t)	24.17	-33.85	14.12	18.33	22.09	23.47	24.06
C_B-(C_B)	21.66	-36.57	13.12	20.46	24.10	24.89	25.31
C-$(H)_2$(C)(C_B)	-21.34	42.59	25.61	37.57	48.07	52.47	57.57
C-(H)$(C)_2$(C_B)	-4.52	-48.00	22.45	33.05	40.71	42.89	44.69
C_{BF}-(C_{BF})$(C_B)_2$	20.10	-20.9	12.6	17.6	21.8	23.0	-
C_{BF}-(C_B)$(C_{BF})_2$	16.00	-20.9	12.6	17.6	21.8	23.0	-
C_{BF}-$(C_{BF})_3$	3.59	5.9	8.4	14.6	19.7	21.3	-

1.2 - BENSON's corrections

a) Non-bonded groups (T = 298.15 K)

	Δ_fH^o	S^o	C_p^o
CH_3 tert	-2.26	0	0
CH_3 quat	-4.56	0	0
CH_3 tert-quat	-1.80	0	0
CH_3 quat-quat	-0.64	0	0
cis alkene	4.85	-8.0	5.1
t-butyl cis	17.24	0	0

	$\Delta_f H^o$	S^o	C_p^o
ortho	1.26	−2.5	6.4
meta	-0.63	0	0.7

b) Rings

	$\Delta_f H^o$	S^o	C_p^o				
T (K)	298.15		298.15	500	800	1000	1500
Cyclopropane	115.15	134.9	-12.8	-8.8	-7.4	-6.8	-6.4
Cyclobutane	110.89	126.0	-19.3	-13.1	-7.9	-5.8	-2.8
Cyclopentane	19.6	118.4	-27.2	-18.8	-11.7	-8.1	-1.5
Cyclohexane	-0.4	84.0	-24.3	-12.1	4.6	9.2	13.8
Cyclobutene	125.8	126.8	-10.6	-7.9	-6.2	-5.6	-5.1
Cyclopentene	24.3	117.1	-25.0	-20.5	-12.3	-9.5	-4.5
Cyclohexene	5.6	95.7	-17.9	-8.3	-1.2	0.3	3.4

1.3 - R-H bond dissociation energies at 298.15 K

a) Alkanes	D^o (kJ mol^{-1})	b) Alkenes	D^o (kJ mol^{-1})
H(•)	439.7	CH2//CH(•)	460.2
CH3(•)	439.7	CH2//CH/CH2(•)	361.1
CH3/CH2(•)	421.3		
CH3/CH2/CH2(•)	433.0	c) Alkynes	
CH3/CH(•)/CH3	415.5	CH///C(•)	523.0
CH3/CH2/CH2/CH2(•)	414.6	CH///C/CH2(•)	374.0
CH3/CH(•)/CH2/CH3	419.2		
CH(CH3)2/CH2(•)	419.2		
C(•)(CH3)3	398.3		
C(CH3)3/CH2(•)	418.4		

d) Cyclanes	D^o (kJ mol^{-1})
CH2(#1)/CH2/CH2/CH2/CH(•)/1	395.4
CH(#1)//CH/CH(•)/CH2/CH2/1	344.3
CH2(#1)/CH2/CH2/CH2/CH2/CH2/CH(•)/1	416.3

e) Aromatics	D^o (kJ mol^{-1})
C6H5(•)	464.0
C6H5/CH2(•)	368.2

1.4 - Free internal rotors

σ_{int} internal symmetry
I_r reduced moment of inertia in amu Å^2 of a rotor bound to an infinite mass
q_{f300} partition function of a free rotor at 300 K
S^o_{f300} standard entropy of a free rotor at 300 K in J mol^{-1} K^{-1}

Rotor	σ_{int}	I_r	q_{f300}	S^o_{f300}
$-CH_3$	3	3.0	3.7	24.3
$-{}^{\bullet}CH_2$	2	1.8	11.0	22.2
$-C_2H_5$	1	17.0	25.0	31.4
$-iC_3H_7$	1	56.0	43.0	36.0
$-tC_4H_9$	3	100.0	20.0	38.5
- phenyl	2	88.0	29.0	37.2
- benzyl	1	170.0	81.0	40.6

1.5 - Internal rotation barriers

Rotor	V (kJ mol^{-1})	Rotor	V (kJ mol^{-1})
CH_3-CH_3	12.1	CH_3-(CH=CH-CH_3)cis	3.1
CH_3-C_2H_5	11.7	CH_3-(CH=CH-CH_3)trans	8.2
CH_3-iC_3H_7	15.1	CH_3-(CH=CH_2)	8.4
CH_3-tC_4H_9	19.7	CH_3-C_6H_5	0

1.6 - Entropy corrections for the internal rotation barriers

$\delta S^o_b = S^o_f - S^o_h$. Units : J mol^{-1} K^{-1}. V : rotation barrier.
q_f : partition function of the free rotor.

V/RT		$1/q_f$	
	0.0	0.2	0.4
0	0.0	0.0	0.0
1	0.4	0.4	0.4
2	1.7	1.7	1.7
3	3.3	3.3	2.9
4	4.6	4.6	4.2
5	5.9	5.9	5.0
6	7.1	6.7	5.9
8	8.4	8.4	7.1
10	9.6	9.2	7.9
15	11.3	10.9	9.2
20	13.0	12.1	10.0

1.7 - Heat capacity C_p^o of a hindered internal rotor

V : rotation barrier. q_f : partition function of the free rotor.

V/RT	$1/q_f$		
	0.0	0.2	0.4
0	4.2	4.2	4.2
1	5.0	5.0	5.0
2	7.1	7.1	6.3
3	8.8	8.4	7.5
4	9.6	9.2	8.4
6	9.6	9.2	8.0
8	9.2	8.8	7.1
10	8.8	8.4	6.3
15	8.8	7.5	5.0
20	8.4	7.1	4.2

1.8 - Wavenumbers

Units of $\tilde{\nu}$: cm^{-1}.
Indices : t : twist ; w : wag ; r : rock ; op : out of plane ; ip : in plane.

a) Streches		b) Bends	
C=C	1 650	C—C—C	420
$C\overset{\bullet}{-}C$	1 300	C—C • C	300
C—C	1 000	C—C—O	400
C • C	675	C—O—C	400
C—H	3 100	O=C—O	420
C • H	2 200		
C—O	1 200		
C=O	1 700		
b) Bends		c) Deformations (t, w, r, op)	
H—C—H	1 450	$(H{-}C{-}C)_{t.w}$	1 150
H • C—H	1 000	$(H{-}C{-}C)_r$	700
H • C—C	800	$(H{-}C\overset{\bullet}{-}C)_r$	700
H—C=C	1 150	$(H{-}C{=}C)_{op}$	700
$H{-}C\overset{\bullet}{-}C$	1 150		
C—C=C	420		
C • C=C	290		
$C{-}C\overset{\bullet}{-}C$	420		
$C{=}C\overset{\bullet}{-}C$	635		

d) Torsions of double bonds	
$CH_2{=}CH_2$	1 000
$CH(CH_3){=}CH_2$	800
$C(CH_3)_2{=}CH_2$	700
$CH(CH_3){=}CH(CH_3)$	350
$CH(CH_3){=}C(CH_3)_2$	250
$C(CH_3)_2{=}C(CH_3)_2$	200

1.9 - Standard entropy of a harmonic oscillator

			T (K)		
Frequency (cm^{-1})	300	500	800	1 000	1 500
200	9.2	13.0	17.2	18.4	22.2
300	5.9	9.6	13.8	15.1	18.8
400	4.2	7.5	11.3	13.4	15.9
500	2.9	5.9	9.6	11.3	14.6
600	2.1	4.2	7.9	9.6	13.0
700	1.3	3.3	7.1	8.8	11.7
800	0.8	3.3	5.9	7.5	10.9
900	0.8	2.5	5.0	6.7	9.6
1 000	0.4	2.1	4.6	5.9	8.8
1 500	0.0	0.8	2.1	3.3	5.9
2 000	0.0	0.0	1.3	2.1	4.2
2 500	0.0	0.0	0.4	1.3	2.9
3 000	0.0	0.0	0.4	0.4	2.1

1.10 - Heat capacity C_p^o of a harmonic oscillator

			T (K)		
Frequency (cm^{-1})	300	500	800	1 000	1 500
200	7.7	8.1	8.2	8.2	8.3
400	6.2	7.5	8.0	8.1	8.2
600	4.4	6.5	7.5	7.8	8.1
800	2.8	5.4	7.0	7.5	7.9
1 000	1.6	4.4	6.4	7.0	7.7
1 500	0.3	2.1	4.7	5.7	7.0
2 000	0.1	0.9	3.1	4.4	5.4
3 000	0.0	0.1	1.1	2.1	4.4

1.11 - Thermodynamic data of elements in the standard state

Phases : g = gas ; l = liquid ; s = solid.

		$\Delta_f H^o$	S^o	C_p^o				
Element	Phase	298.15		298.15	500	800	1000	1500
C	s	0	5.7	8.5	14.6	19.8	21.6	23.9
H_2	g	0	130.7	28.8	29.3	29.6	30.2	32.3
0_2	g	0	205.1	29.3	31.1	33.7	34.9	36.5
N_2	g	0	191.6	29.1	29.6	31.4	32.7	34.8
F_2	g	0	202.8	31.3	34.3	39.3	37.1	38.2
Cl_2	g	0	223.1	33.9	36.1	37.1	37.4	38.0
Br_2	g^1	0	264.3^2	–	37.1	37.6	37.8	38.2
I_2	g^3	0	279.9^2	–	37.5	37.8	38.1	39.5

^{1} T > 333 K ; ^{2} T = 500 K ; ^{3} T > 458 K.

1.12 - Thermodynamic data of hydrocarbon species

	$\Delta_f H^o$	S^o	C_p^o				
T (K)	298.15		298.15	500	800	1000	1500
C	716.7	158.1	20.8	20.8	20.8	20.8	20.9
CH	594.1	183.0	29.2	29.4	31.0	32.5	36.5
CH2	386.4	193.9	34.6	37.6	42.4	45.6	51.3
CH3	145.7	194.2	38.7	45.3	54.0	59.0	68.2
CH4	-74.9	186.2	35.6	46.3	62.9	71.8	86.6
C2H	531.8	211.4	44.1	52.8	56.4	56.7	64.1
C2H2	226.7	201.0	44.1	54.9	63.7	68.2	76.6
C2H3	294.6	235.4	42.0	55.0	70.7	78.8	91.1
C2H4	52.5	219.3	42.9	62.5	83.8	93.9	110.0
C2H5	118.7	246.4	47.6	69.7	94.9	107.6	125.9
C2H6	-84.7	229.6	52.5	78.2	107.9	122.8	145.0
H	218.0	114.7	20.8	20.8	20.8	20.8	20.8
H2	0.0	130.7	28.8	29.3	29.6	30.2	32.3

1.13 - Thermodynamic data of oxygenated species

	$\Delta_f H^o$	S^o	C_p^o				
T (K)	298.15		298.15	500	800	1000	1500
CHO(•)	37.7	224.7	34.7	38.5	43.8	46.9	51.5
CH2O	-108.6	224.5	35.1	43.9	55.7	62.2	71.2
CH2(•)/OH	-25.9	247.9	42.8	54.1	67.5	74.8	84.5

	$\Delta_f H^o$	S^o	C_p^o				
T (K)	298.15		298.15	500	800	1000	1500
CH3/O(•)	17.7	227.4	36.4	51.2	68.0	76.6	87.6
CH3/O/O(•)	17.6	267.3	57.5	76.3	94.8	102.9	115.4
CH3/OH	-201.2	239.7	43.6	59.6	79.4	89.7	103.7
CH3/O/OH	-131.0	282.4	64.9	85.1	106.4	116.2	131.6
CH(•)//CO		250.4	50.6	59.5	67.2	70.1	75.7
CH2//CO	-47.7	241.8	51.9	65.5	78.9	84.6	94.5
CH2(•)/CHO	27.0	260.2	53.4	72.5	92.8	102.1	111.7
CH3/CO(•)	-166.4	264.2	55.0	76.2	101.3	113.0	132.8
CH3/CO/O/O(•)	-125.1	318.6	65.6	97.5	125.2	136.5	166.1
CH2(#1)/CH2/O/1	-52.6	242.4	48.1	75.4	103.0	115.0	134.4
CH3/CHO	-166.4	264.2	55.0	76.2	101.3	113.0	126.7
CH3/CO/O/OH	-339.7	337.4	73.1	106.3	136.8	149.7	182.3
CH3/CH2/O(•)	-16.8	269.6	58.0	86.7	115.6	128.5	148.4
CH2(•)/CH2/O/OH	33.1	331.8	82.7	111.1	136.3	147.1	168.9
CH3/CH2/O/O(•)	-23.4	304.4	75.6	107.0	136.6	149.2	172.8
CH3/CH2/OH	-234.8	282.6	65.3	95.2	127.0	141.6	164.5
CH3/CH2/O/OH	-168.1	323.3	83.0	115.7	148.2	162.3	188.9
CO	-110.6	197.6	29.1	29.9	31.8	33.2	35.2
CO2	-393.6	213.9	37.4	45.2	51.9	54.2	58.6
H/O(•)	39.3	183.7	30.1	30.1	30.1	30.6	33.1
H/O/O(•)	10.8	222.9	36.0	43.7	48.5	49.5	52.1
H2O	-241.9	188.7	33.5	35.2	38.7	41.3	46.9
H2O2	-136.1	232.9	5	52.5	60.1	62.7	68.2
O	249.2	161.1	21.9	21.3	20.9	20.9	20.9
O2	0.0	205.1	29.3	31.3	33.6	34.8	36.6
O3	143.5	238.9	39.3	47.3	53.5	55.1	57.3

BIBLIOGRAPHY

Numerical data for the application of BENSON's method

BENSON S.W., *Thermochemical kinetics*, 2nd edition, Wiley (1976).

DOMALSKI E.S., HEARING E.D., *Estimation of the thermodynamic properties of C-H-N-O-S-Halogen compounds at 298.15 K*, J. Phys. Chem. Ref. Data, vol. 22, n° 4, p. 805-1159 (1993).

Tables of thermodynamic data

BARIN I., *Thermodynamic data of pure substances*, vol. I and II, VCH (1993).

CHASE M.W., DAVIES C.A.. DOWNEY J.R., FRURIP D.J., McDONALD R.A., SYVERUD R.A., *JANAF Thermochemical tables*, vol. I et II. 3rd edition, NIST (1992).

LIDE D.R., KEHIAIAN H.V., CRC *Handbook of Thermophysical and Thermochemical Data*, CRC (1994).

PEDLEY J.B., NAYLOR R.D.. KIRBY S.P., *Thermochemical data of organic compounds*, 2nd edition, Chapman and Hall (1986).

PEDLEY J.B., *Thermochemical data and structures of organic compounds*, vol. 1, Thermodynamics Research Center. Texas A & M University (1994).

STULL D.R., WESTRUM E.G., SINKE G.C., *The chemical thermodynamics of organic compounds*, Krieger, Malabar, FL (1987).

2 - KINETIC TABLES

Tables 2.1 to 2.3 contain the data needed for the application of the collision theory to the reactions of combination and disproportionation of two free radicals.

Table 2.4 gives the values permitting the activation energy of a radical isomerization by internal transfer of an H atom, to be calculated.

Tables 2.5 to 2.8 give the kinetic parameters used for the application of the structure-reactivity correlations to initiation, radical decomposition and metathesis reactions, and to reactions of radicals with oxygen.

The indices p, s, t used for the correlations refer to the primary, secondary and tertiary H atoms, respectively.

The rate constants are written as follows $k = A\,T^b \exp(-E/RT)$. In default of a value for b, it is assumed to be equal to 0.

The units used in these tables are : mol, cm^3, s, kJ.

2.1 - Combination of free radicals : values of the steric factors

$^\bullet R_1$. $^\bullet R_2$: free radicals containing at least two carbon atoms. $^\bullet X$: free radical other than H

T (K)		300	600	1 200
$^\bullet CH_3$	$^\bullet H$	0.40	0.15	0.05
$^\bullet CH_3$	$^\bullet X$	1.00	0.50	0.25
$^\bullet CH_3$	$^\bullet CH_3$	0.80	0.40	0.20
$^\bullet R_1$	$^\bullet H$	0.20	0.08	0.03
$^\bullet R_1$	$^\bullet X$	0.50	0.25	0.10
$^\bullet R_1$	$^\bullet CH_3$	0.50	0.25	0.10
$^\bullet R_1$	$^\bullet R_1$	0.20	0.10	0.05
$^\bullet R_1$	$^\bullet R_2$	0.20	0.10	0.05

2.2 - Covalent radii (in Å)

Atom	Radius	Atom	Radius	Atom	Radius
H	0.32	0	0.74	F	0.72
C	0.77	O_d	0.62	Cl	0.99
C_d	0.67	N	0.74	Br	1.11
C_t	0.60	N_d	0.62	I	1.28
		N_t	0.65		

2.3 - Disproportionation of free radicals : values of the k_{di}/k_{co} ratio

$^\bullet R_1 + {}^\bullet R_2 \longrightarrow R_1H$ + alkene (di) ; $^\bullet R_1 + {}^\bullet R_2 \longrightarrow R_1R_2$ (co)

			$^\bullet R_1$		
$^\bullet R_2$	CH_3	C_2H_5	nC_3H_7	sC_3H_7	tC_4H_9
C_2H_5	0.05	0.1	0.1	0.2	0.3
nC_3H_7	0.05	0.1	0.1	0.2	0.3
sC_3H_7	0.2	0.3	0.3	0.6	2
tC_4H_9	0.6	0.6	0.6	0.7	2.8

2.4 - Isomerization of free radicals by internal transfer of hydrogen atoms

a) Activation energies of internal metatheses

	Transferred hydrogen		
Radical	H_p	H_s	H_t
Alkyl $^\bullet$R	56	46	38
Alkylperoxy $^\bullet$OOR	84	71	59

b) Ring strain energies

	Size of the activated complex			
Radical	4	5	6	7
Alkyl $^\bullet$R	109	26	4.2	27
Alkylperoxy $^\bullet$OOR	96	65	36	21

2.5 - Initiations

a) Unimolecular initiations

$RH \longrightarrow {}^\bullet R' + {}^\bullet R''$

Broken bond	log A	E
C_p-C_s	17.00	369
C_s-C_s	16.35	358
C_s-C_t	16.80	347
C_t-C_t	16.80	340
RO-OH	14.85	176
RO-OR'	14.85	176

b) Bimolecular initiations

$RH + O_2 \longrightarrow {}^\bullet R + {}^\bullet OOH$

Nature of H atom	log A	E
H_p	12.60	205
H_s	12.00	201
H_t	12.30	192
H_a	13.30	199
H_v	13.00	241

H_a : H allylic H_v : H vinylic

2.6 - Unimolecular decompositions of free radicals

a) Beta-scissions of hydrocarbon radicals

Products	log A	E
$^{\bullet}H$ + molecule	13.34	182
$^{\bullet}CH_3$ + molecule	13.30	130
$^{\bullet}R$ + molecule	13.30	120

b) Reactions of the hydroperoxyalkyl $^{\bullet}QOOH$ and the dihydroperoxyalkyl $^{\bullet}U(OOH)_2$ radicals

- Beta-scission

Products	log A	E
$^{\bullet}OOH$ + molecule	12.90	109
$^{\bullet}OH$ + molecule	9.00	31

- Cyclization

	log A	E
3	12.00	69
4	11.30	65
5	11.30	24

2.7 - Reactions of free radicals with molecular oxygen

a) Addition

$$\begin{cases} ^{\bullet}R+O_2 \longrightarrow {}^{\bullet}OOR \\ ^{\bullet}QOOH+O_2 \longrightarrow {}^{\bullet}OOQOOH \end{cases}$$

log A	b	E
19.34	-2.5	0

b) Oxidation

$$^{\bullet}C_nH_{2n+1}+O_2 \longrightarrow C_nH_{2n}+{}^{\bullet}OOH$$

Atom	log A	E
H_p	11.37	20.9
H_s	11.90	20.9
H_t	11.65	20.9

2.8 - Metathesis

$$^{\bullet}R + R'H \longrightarrow RH + {}^{\bullet}R'$$

The pre-exponential factors are given per H atom.

Radical	Atom	log A	b	E	Radical	Atom	log A	b	E
$^{\bullet}H$	H_p	6.98	2	32.2	:O	H_p	13.23	0	32.8
	H_s	6.65	2	20.9		H_s	13.11	0	21.7
	H_t	6.62	2	10.0		H_t	13.00	0	13.7
$^{\bullet}CH_3$	H_p	-1	4	34.3	$^{\bullet}OH$	H_p	5.95	2	1.88
	H_s	11.0	0	39.8		H_s	6.11	2	-3.20
	H_t	11.0	0	33.1		H_t	6.06	2	-7.80

Radical	Atom	log A	b	E	Radical	Atom	log A	b	E
$^{\bullet}C_2H_5$	H_p	11.00	0	56.4	$^{\bullet}OOH$	H_p	11.30	0	71.11
	H_s	11.00	0	46.0		H_s	11.30	0	64.8
	H_t	11.00	0	38.5		H_t	12.00	0	58.5
$^{\bullet}iC_3H_7$	H_p	-2.85	4.2	36.4	$^{\bullet}CHO$	H_p	4.53	2.5	77.3
	H_s	-2.85	4.2	33.4		H_s	6.73	1.9	71.1
	H_t	-2.85	4.2	25.1		H_t	4.53	2.5	56.4
$^{\bullet}R_p$	H_p	11.0	0	56.4	$^{\bullet}CH_2OH$	H_p	1.52	2.95	58.5
	H_s	11.0	0	46.8		H_s	1.48	2.95	50.2
	H_t	11.0	0	37.6		H_t	2.08	2.76	45.1
$^{\bullet}R_s$	H_p	11.0	0	60.6	$^{\bullet}OCH_3$	H_p	10.73	0	30.5
	H_s	11.0	0	51.0		H_s	10.86	0	18.8
	H_t	11.0	0	41.8		H_t	10.36	0	12.1
$^{\bullet}R_t$	H_p	11.0	0	62.7	$^{\bullet}OOR$	H_p	12.30	0	83.6
	H_s	11.0	0	53.1		H_s	12.18	0	73.2
	H_t	11.0	0	43.9		H_t	12.18	0	62.7

BIBLIOGRAPHY

ATKINSON R., BAULCH D.L., COX R.A., HAMPSON R.F. Jr, KERR J.A., ROSSI M.J., TROE J., *Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry*, J. Phys. Chem. Ref. Data, 26, 521 (1997).

BAULCH D.L., COBOS C.J., COX R.A., FRANCK P., HAYMAN G., JUST Th., KERR J.A., MURRELS T., PILLING M.J., TROE J., WALKER R.W., WARNATZ J., *Evaluated kinetic data for combustion modelling,* J. Phys. Chem. Ref. Data, 23, 847 (1994).

DE MORE W.B., SANDER S.P., GOLDEN D.M., HAMPSON R.F., KURYLO M.J., HOWARD C.J., RAVISHANKARA A.R., KOLB C.E., MOLINA M.J., *Chemical kinetics and photochemical data for use in stratospheric modeling,* Jet Propulsion Laboratory (Pasadena, Californie), Evaluation n° 12, 266 p. (1997).

GARDINER W.C. Jr., *Gas-Phase Combustion Chemistry*, Springer (2000).

TSANG W., *Chemical kinetic data base for propellant combustion,* J. Phys. Chem. Ref. Data, vol. 21, n° 4, p. 753-791 (1992) ; TSANG W., HERRON J.T., ibid., vol. 20, n° 4, p. 609-663 (1991).

TSANG W., *Chemical kinetic data base for combustion chemistry,* J. Phys. Chem. Ref. Data, vol. 20, n° 2, p. 221-273 (1991).

DATABASES

GRI, KERGAS, NIST (SRDB 17).

3 - TABLES OF MOLECULAR PARAMETERS

ε/k_B depth of the LENNARD-JONES potential well in K
σ LENNARD-JONES collision diameter in Å (1 Å = 10^{-10} m)
μ dipolar moment in Debye

	ε/k_B	σ	μ		ε/k_B	σ	μ
CH	80	2.75	0	$^\bullet CHO$	498	3.59	0
CH_2	144	3.8	0	CH_2	498	3.59	0
CH_3	144	3.8	0	$^\bullet OCH_3$	417	3.69	1.7
CH_4	141.4	3.746	0	CH_3OH	417	3.69	1.7
C_2H	209	4.1	0	CO	98	3.65	0
C_2H_2	209	4.1	0	CO_2	244	3.76	0
C_2H_3	209	4.1	0	$^\bullet OH$	80	2.75	0
C_2H_4	280.8	3.971	0	$^\bullet OOH$	107	3.46	0
C_2H_5	252.3	4.302	0	H_2O	572	2.61	1.8
C_2H_6	252.3	4.302	0	H_2O_2	107	3.46	0
H	145	2.05	0	O	80	2.75	0
H_2	38	2.92	0	O_2	107	3.46	0
				O_3	180	4.1	0

COMPUTER PROGRAMS AND DATABASES

This appendix gives a brief description of the computer programs used to estimate thermodynamic, kinetic and molecular transport data, computer programs for the generation, analysis and reduction of reaction mechanisms and computer programs for the simulation of laboratory reactors.
Most of the computer programs listed can be connected to the CHEMKIN computer program.
The descriptions are supplemented by practical information.

BAC MP4
The BAC-MP4 method allows the enthalpy of formation of a chemical species to be estimated. The calculation of electronic structures (geometry and vibration frequencies) can be carried out using the GAUSSIAN 94 computer program. The corrections are carried out using the Möller-Plasset (MP) theory of perturbations and the Bond Additivity Corrections are also carried out using the same theory.
Reference : HO P., MELIUS C.F. - J. Phys. Chem., 99, 2166 (1995).
Information : MELIUS C.F., Division 8357, Sandia National Laboratories, Livermore, California 94551-0969.

CARM
This computer program carries out the reduction of detailed mechanisms using the Quasi- Stationary-State Approximation (QSSA). When the negligible species have been eliminated and the quasi-stationary species identified, the algorithm looks for a set of independent reactions allowing the quasi-stationary concentrations to be calculated by applying the QSSA. Lumped reactions are obtained by a linear combination of elementary reactions of the detailed mechanism.
Reference : CHEN J.Y. - Comb. Sci. & Techn., 22, 63 (1997).
Information : CHEN J.Y. - Department of Mechanical Engineering, University of California, BERKELEY, CA 94720 (USA).

CEC
This computer program solves problems of complex equilibria involving both gas-phase and condensed-phase species. It also calculates the performances of rockets, shock waves and of CHAPMAN-JOUGUET detonations.

Information : GORDON S., McBRIDE B.J., NASA Lewis Research Center, WASHINGTON, DC.

CHEMACT

This computer program calculates apparent rate constants of chemically activated reactions (addition, recombination, insertion), on the basis of the RRKM theories.

Reference : DEAN A.M., BOZZELI J.W., RITTER E.R. - Comb. Sci. & Techn., 80, 63-85 (1991).

Information : DEAN A.M. - EXXON Research and Engineering Company, Clinton Township, Route 22 East, Aunandale, NEW JERSEY 08801-0998.

CHEMKIN II

This computer program accepts as input a gas-phase reaction mechanism and the associated rate constants expressed in the ARRHENIUS-KOOIJ form. It gives all the information necessary to compute laboratory reactors using the SENKIN, PSR, SHOCK, PREMIX computer programs.

Authors : KEE R.J., RUPLEY F.M., MILLER J.A.

Information : SANDIA National Laboratories, Computational Mechanics Department 8745, Livermore, CA 94551 (USA) - Email : fran@ca.sandia.gov

CHEMKIN REAL-GAS

This computer program gives equations of state of real gases, namely that of REDLICH-KWONG, which can be used in conjunction with the CHEMKIN computer programs.

Information : SCHMITT R.G., BUTTLER P.B., FRENCH N.B., The University of IOWA, IOWA City, Iowa.

CRESLAF

This computer program calculates bidimensional reactant laminar flows, either planar or asymetrical. It is used in conjunction with the other CHEMKIN computer programs.

Authors : COLTRIN M.E., MOFFAT H.K., KEE R.J., RUPLEY F.M.

Information : cf. CHEMKIN-II.

EQUIL

This computer program is an adaptation of the STANJAN code which allows the formats of the CHEMKIN data to be used.

Authors : LUTZ A.E., RUPLEY F.M.

Information : cf. CHEMKIN-II.

EXGAS

This computer program generates detailed primary mechanisms of oxidation and combustion reactions of alkanes and lumped secondary mechanisms of the primary products formed. It is interfaced with the KERGAS reaction database and the THERGAS, KINBEN and KINCOR computer programs. It produces reaction models (mechanisms, thermodynamic and kinetic data) which can be used directly in the CHEMKIN computer programs.

Reference : WARTH W., STEF N., GLAUDE P.A., BATTIN-LECLERC F., SCACCHI G., CôME G.M. - Combustion & Flame, 114, 81 (1998).

Information : CôME G.M. - DCPR, 1, rue Grandville - 54000 NANCY

FACSIMILE

FACSIMILE is a general computer program for modelling chemical processes and reaction kinetics (combustion, auto-ignition, soot formation, chemistry of the NO_x, tropospheric chemistry...).

Information : AEA Technology, 353 Harwell, Didcot, Oxfordshire OX11 0RA (GB).

FITDAT

This computer program calculates the coefficients of the NASA polynomials from thermodynamic data supplied by the user.

Authors : KEE R.J., RUPLEY F., MILLER J.A.

Information : cf. CHEMKIN-II.

GRI

The Gas Research Institute (GRI) along with several American laboratories have developed a database for reactions involved in the **combustion of natural gas**. The parameters of the mechanism have been fitted to the various experimental results of combustion ; they cannot therefore necessarily be extrapolated to other conditions.

Information : University of California, Berkley (USA).

KERGAS

KERGAS is a database of reactions of molecules and free radicals of molecular formulae $C_xH_yO_z$ with 0, 1 or 2 carbon atoms. The base contains about 850 reactions involving 42 species. KERGAS is part of the EXGAS system.

Reference : BARBE P., BATTIN-LECLERC F., CôME G.M. - J. Chim. Phys., 92, 1666 (1995).

Information : cf. EXGAS.

KINALC

This computer program carries out calculations for analysing the sensitivity, and also carries out the analysis in main components of the sensitivity matrix, the analysis of the reaction fluxes, the simplification of the mechanisms from the above information, and the determination of the quasi-stationary species. KINALC is a post-processor of the CHEMKIN computer programs.

Reference : TURANYI T. - Comput. Chem., 14, 253 (1990).

Information : TURANYI T. - Central Research Institute for Chemistry, H-1525, PO Box 17, Budapest (Hungary).

KINBEN

This computer program calculates the kinetic parameters of elementary reactions (unimolecular initiations, radical isomerizations, terminations) using BENSON's methods of thermochemical kinetics. It is part of the EXGAS system.

Reference : BLOCH-MICHEL V., Ph. D. Thesis, Nancy (1995).

Information : cf. EXGAS.

KINCOR

This computer program calculates the kinetic parameters of elementary reactions (bimolecular initiations, addition of a free radical to an unsaturated molecule, unimolecular decomposition, cyclization, oxidation of a radical, metathesis and branching) using structure-reactivity correlations. It is part of the EXGAS system.

Information : cf. EXGAS.

LUMPGAS

This computer program generates reduced primary mechanisms of oxidation and combustion reactions of alkanes from detailed primary mechanisms, by lumping of the species and of the reactions. It is part of the EXGAS system.

Reference : FOURNET R., WARTH V., GLAUDE P.A., BATTIN-LECLERC F., SCACCHI G., CÔME G.M. - Int. J. Chem. Kin., 32, 36-51 (2000).

Information : cf. EXGAS.

NIST Standard Reference Database 17

NIST Chemical Kinetics Database, version 6.0 (1994)

This database gives values for the kinetic parameters A, b, E and the associated references for reactions for which the reactant(s) is(are) represented by its(their) molecular formula(e). The base also gives recommended values. It is very easy to use on a PC.

Information : MALLARD W.G., WESTLEY F., HERRON J.T., HAMPSON R.F., NIST Standard Reference Data Program, GAITHERSBURG, MD 20899, USA.

NIST Standard Reference Database 25

NIST Structures and Properties Database and Estimation Program, version 1.1 (1991)

This computer program calculates the thermodynamic data of molecules, free radicals and positive ions in the gas phase using BENSON's methods. It also contains a database for nearly 5000 species.

Information : STEIN S.E., RUKKERS J.M., BROWN R.L. - Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, GAITHERSBURG, MD 20899.

PREMIX

This computer program calculates premixing unidimensional laminar flames. It is part of the CHEMKIN system.

Authors : KEE R.J., GRCAR J.F., SMOOKE M.D., MILLER J.A.

Information : cf. CHEMKIN-II.

PSR

This computer program calculates a well-stirred tank reactor and carries out a sensitivity analysis. It is part of the CHEMKIN system.

Authors : GLARBORG P., KEE R.J., GRCAR J.F., MILLER J.A.

Information : cf. CHEMKIN-II.

RADICALC

This computer program calculates the entropy and heat data for free radicals and transition states.

Reference : BOZELLI J.W., RITTER E.R. - Chemical and Physical Processes in Combustion, The Combustion Institute, Pittsburgh PA, p. 453 (1993).

Information : BOZELLI J. - Dept. of Chemistry and Chemical Engineering, New Jersey Institute of Technology, University Heights, NEWARK, NJ 07102-1982.

SENKIN

This computer program calculates a batch reactor working under different conditions (adiabatic, isothermal, isobaric, isochoric) and carries out a sensitivity analysis of the reaction mechanisms. It is part of the CHEMKIN system.

Authors : LUTZ A.E., KEE R.J., MILLER J.A.

Information : cf. CHEMKIN-II.

SHOCK

This computer program calculates shock tubes where the wave is incident or reflected. It is part of the CHEMKIN system.
Authors : MITCHELL R.E., KEE R.J.
Information : cf. CHEMKIN-II.

SPIN

This computer program calculates a rotating CVD disc. It is part of the CHEMKIN system.
Authors : COLTRIN M.E., KEE R.G., EVANS G.H., MEEKS E., RUPLEY F.M., GRCAR J.F.
Information : cf. CHEMKIN-II.

SPYRO

SPYRO is a computer program for calculating a steamcracking reactor with hydrocarbon loads ranging from ethane to the naphthas. The computer program contains a detailed reaction mechanism for the pyrolysis of molecules containing from 1 to 4 carbon atoms and lumped mechanisms for larger species. The approach developed by the authors has been validated industrially.
The same team has developed an analogous code for the combustion of hydrocarbons.
Reference : DENTE M.E., RANZI E. - Pyrolysis: theory and industrial practice, chap. 7, Academic Press (1983).
Information : RANZI E. - Dipartimento de Chimica Industriale e Engegneria Chimica, Politecnico di Milano, 20133, MILAN (Italy).

S-STEP

The computer program uses the CSP method (Computational Singular Perturbation). This method allows the quasi-stationary species and the quasi-equilibrated reactions to be identified, and a reduced mechanism to be generated.
The data to be supplied include the detailed mechanism, the results of a representative simulation and the requisite size of the reduced mechanism.
Reference : GOUSSIS D.A. - J. Comp. Phys., 128, 261 (1996).
Information : GOUSSIS D.A., Institute of Chemical Engineering, PO Box 1414, 26500 PATRAS (Greece).

STANJAN

This computer program calculates equilibria by the method of LAGRANGE multipliers respecting the constraints of conservation of the elements. It has been modified to be compatible with the CHEMKIN codes (cf. EQUIL).

Information : REYNOLDS W.C., Thermosciences Division, Department of Mechanical Engineering, Stanford University, STANFORD, CA.

SURFACE-CHEMKIN

The computer program accepts as input the mechanisms of gas-phase reactions and of reactions between gases and a solid surface. It gives all the information necessary to calculate reactors using the SURFACE PSR and SPIN computer programs.

Authors : COLTRIN M.E., KEE R.J., RUPLEY F.M.

Information : cf. CHEMKIN-II.

SURFACE-PSR

This computer program calculates a stirred tank reactor where gas-phase reactions and reactions between the gas and a solid surface take place.

Authors : MOFFAT H.K., GLARBORG P., KEE R.J., GRCAR J.F., MILLER J.A.

Information : cf. CHEMKIN-II.

THERGAS

This computer program calculates the thermodynamic data of molecules, of free radicals and of radical reactions in the gas phase between 300 and 5000 K by BENSON's methods. It also determines the CHETAH safety criteria.

Reference : MULLER C., MICHEL V., SCACCHI G., CôME G.M. - J. Chim. Phys., 92, 1154-1178 (1995).

Information : cf. EXGAS.

THERM

Thermodynamic Property Estimation of Radicals and Molecules

This computer program calculates thermodynamic data of free radicals and molecules in the gas phase by BENSON's methods.

Reference : RITTER E.R., BOZELLI J. - Int. J. Chem. Kin., 23, 767 (1991).

Information : cf. RADICALC.

THERMDAT

THERMDAT is a base of thermodynamic data of the CHEMKIN system, in the form of NASA polynomials.

Authors : KEE R.J., RUPLEY F.M., MILLER J.A.
Information : cf. CHEMKIN-II.

TRANDAT, TRANFIT, TRANLIB
These computer programs calculate the viscosities, the thermal conductivities and the diffusion coefficients of pure substances and gaseous mixtures. The code contains a database.
Authors : KEE R.G., DIXON-LEWIS G., WARNATZ J., COLTRIN M.E., MILLER J.A.
Information : cf. CHEMKIN-II.

UNIMOL
This computer program calculates the influence the pressure and the temperature have on the rate constants of unimolecular reactions and of association reactions.
Reference : GILBERT R.G., SMITH S.C. - Theory of Unimolecular and Recombination Reactions, BLACKWELL (1990).
Information : GILBERT R.G., Department of Theoretical Chemistry, Sydney, NSW 2006 (Australie).

XSENKPLOT
This code is a graphic post-processor of the CHEMKIN computer programs.
Information : BURGESS D. - Reacting Flows Group, Process Measurements Division, NIST, GAITHERSBURG, MD.

URLs

The appearance of Internet and in particular the World Wide Web has greatly changed the research and exchange of information. This appendix gives, with no claim to exhaustiveness and with no guarantee of non-obsolescence, the URLs of various sites where information on **thermodynamic and kinetic data, reaction mechanisms and computer programs** can be found, as well as the description of the activities of laboratories or organisms, and particularly the references of publications and reports. The sites are described by their geographical location or by the name of the organism, or those of the product.

CALTECH (USA)
http://blue.caltech.edu
TTC (ThermoChemical Calculator) : thermochemical calculations and database.

CHEMKIN™
http://www.ca.sandia.gov/chemkin
Computer programs for the simulation of gas-phase and gas-surface reaction mechanisms in laboratory reactors.

GRI-MECH™
http://www.me.berkeley.edu/gri_mech
Mechanism of combustion of methane, including thermodynamic and transport data and optimized in the range $T = 1000 - 2500$ K, $p = 10$ Torr - 10 atm, $\varphi = 0.1 - 5$.

Lawrence Livermore National Laboratory (USA)
http://www.cms.llnl.gov
See Combustion Chemistry Group :
- Combustion Modeling (Engines and Fuels)
- HCT (Computer programs for 1D-hydrodynamic transport and chemical kinetics)
- Chemical Kinetics Mechanisms (Oxidation of hydrocarbons).

LEEDS (UK) and BUDAPEST (Hungary)
http://www.chem.leeds.ac.uk
Mechanism of methane combustion, including NO_x and SO_x.
Computer programs MECHMOD (development of reaction mechanisms) and KINALC

(sensitivity and flux analysis, ILDM, repromodelling).
Numerous links : GRI-Mech, Konnov's mechanism, CALTECH and NIST, Burcat's thermodynamic data, CSP method, Chemkin, Xsenkplot, Thermo Chemical Calculator, Transport Software.

NANCY (France)
http://www.ensic.inpl-nancy.fr/ENSIC/DCPR/cinetique/Chimieinfo/Chiminfo.html
Low-temperature and flame combustion mechanisms of C_0-C_1-C_2 species, n-butane to n-decane, iso-octane, MTBE, ETBE.
Computer programs THERGAS (estimation of thermodynamical data), KINGAS (estimation of kinetic data), EXGAS (generation of combustion mechanisms).
Combustion mechanisms of alkanes, alkenes, ethers, cyclanes and mixtures thereof are available upon request.

NIST (USA)
http://kinetics.nist.gov
Chemical kinetics database for elementary thermal gas-phase reactions : 9,000 compounds, 15,000 reactions, 37,000 rate constants, 11,000 references.
http://www.cstl.nist.gov/srd/kinet.htm
Combustion mechanisms and thermochemical data for fluorinated hydrocarbons (CKMech).

FURTHER READING

GARDINER W.C.Jr (Editor), *Gas-Phase Combustion Chemistry*, 2nd edition, Springer (2000).
GLASSMAN I., *Combustion*, 3rd edition, Academic Press (1996).

NOTATIONS

1 - SYMBOLS, FUNDAMENTAL CONSTANTS , UNITS

The formulae in this book, unless stated otherwise, have been written to be used with basic SI units :

mol, m, s, J, kg, Pa, K

and not their multiples and sub-multiples.
For example, the value of the standard pressure p° has been taken to be equal to 10^5 Pa, and not 1 atm (previous value) or 1 bar (present value).

Symbol	**Quantity**	**Unit***
A_i	pre-exponential factor of the reaction i	$mol^{1-\omega}\ m^{3(\omega-1)}\ s^{-1}$
b_i	KOOIJ exponent of the reaction i	1
C_j	constituent n° j	-
C^o_{pj}	heat capacity of C_j at constant pressure	$J\ mol^{-1}\ K^{-1}$
C^o_{Vj}	heat capacity of C_j at constant volume	$J\ mol^{-1}\ K^{-1}$
c	total concentration	$mol\ m^{-3}$
c_j	concentration of C_j	$mol\ m^{-3}$
c_{pj}	specific heat of C_j at constant pressure	$J\ kg^{-1}\ K^{-1}$
c_{Vj}	specific heat of C_j at constant volume	$J\ kg^{-1}\ K^{-1}$
D^o	bond dissociation energy	$J\ mol^{-1}$
D_{AB}	binary diffusion coefficient of A in B	$m^2\ s^{-1}$
D^c_j	diffusion coefficient of C_j in a mixture of gases	$m^2\ s^{-1}$
D^p_j	barodiffusion coefficient	$mol\ m^{-1}\ s^{-1}$
D^T_j	thermal diffusion coefficient of C_j	$mol\ m^{-1}\ s^{-1}$
d	diameter	m
E_i	activation energy of the reaction i	$J\ mol^{-1}$
F	total molar flow rate	$mol\ s^{-1}$
	TROE factor	1
F_j	molar flow rate of C_j	$mol\ s^{-1}$
h	PLANCK's constant	$h=6.626076\times10^{-34}$ J s
h_j	specific enthalpy of C_j	$J\ kg^{-1}$
I	number of reactions	1
	moment of inertia	$kg\ m^2$

---

* The number 1 means that the property is adimensional.

I_r	reduced moment of inertia	$kg\ m^2$
i	index of reaction	1
J	number of constituents	1
j	index of constituent	1
K_{ci}	concentration equilibrium constant of reaction i	$(mol\ m^{-3})^{\Delta_i \nu}$
K_i^o	equilibrium constant of reaction i	1
K_{pi}	pressure equilibrium constant of reaction i	$(Pa)^{\Delta_i \nu}$
K_{xi}	mole fraction equilibrium constant of reaction i	1
k_B	BOLTZMANN's constant	$k_B=1.380658 x 10^{-23}\ J\ K^{-1}$
k_i	rate constant of reaction i	$mol^{1-\omega}\ m^{3(\omega-1)}\ s^{-1}$
M	mean molar mass	$kg\ mol^{-1}$
M_{AB}	reduced molar mass of A and B	$kg\ mol^{-1}$
M_j	molar mass of C_j	$kg\ mol^{-1}$
N_A	Avogadro's number	$N_A=6.022137 x 10^{23}\ mol^{-1}$
n	total number of moles	mol
n_j	number of moles of C_j	mol
p	pressure	Pa
p^o	standard pressure	$p^o=10^5\ Pa$
p_j	partial pressure of C_j	Pa
Q	volume flow rate	$m^3\ s^{-1}$
q_j	partition function of C_j	m^{-3}
R	gas constant	$R=8.314510\ J\ mol^{-1}\ K^{-1}$
R_j	net rate of production of C_j	$mol\ m^{-3}\ s^{-1}$
r_i	rate of reaction i	$mol\ m^{-3}\ s^{-1}$
S	surface, area	m^2
S_j^o	standard entropy of C_j	$J\ mol^{-1}\ K^{-1}$
T	temperature	K
u_j	specific internal energy of C_j	$J\ kg^{-1}$
V	volume	m^3
V_j	rate of diffusion of C_j	$m\ s^{-1}$
v	specific volume	$m^3\ kg^{-1}$
W	total mass flow rate	$kg\ s^{-1}$
W_j	mass flow rate of C_j	$kg\ s^{-1}$
w_j	mass fraction of C_j	1
x_j	molar fraction of C_j	1
Z	collision frequency	$mol\ m^{-3}\ s^{-1}$
α	thermal diffusivity	$m^2\ s^{-1}$
γ_j	fugacity coefficient of C_j	1

$\Delta_f G_j^o$	standard free enthalpy of formation of C_j	J mol^{-1}
$\Delta_f H_j^o$	standard enthalpy of formation of C_j	J mol^{-1}
$\Delta_i G^o$	standard free enthalpy of reaction i	J mol^{-1}
$\Delta_i H^o$	standard enthalpy of reaction i	J mol^{-1}
$\Delta_i S^o$	standard entropy of reaction i	J mol^{-1} K^{-1}
δ	polarity	1
ε/k_B	depth of the LENNARD-JONES potential well	K
ζ_i	extent of reaction i in a continuous flow tank reactor operating under steady-state conditions	mol s^{-1}
η	dynamic viscosity	kg m^{-1} s^{-1}
λ	thermal conductivity	J m^{-1} K^{-1} s^{-1}
μ	dipolar moment	D
μ_j	chemical potential of C_j	J mol^{-1}
μ_j^o	standard chemical potential of C_j	J mol^{-1}
ν	vibration frequency	s^{-1}
	diffusivity of momentum	m^2 s^{-1}
$\tilde{\nu}$	wavenumber	cm^{-1}
ν_{ij}	generalized stoichiometric coefficient of C_j in reaction i	1
ν'_{ij}	stoichiometric coefficient of reactant C_j of the forward reaction i	1
ν''_{ij}	stoichiometric coefficient of product C_j of the forward reaction i	1
ξ_i	extent of reaction i in a batch reactor	mol
ρ	density	kg m^{-3}
σ	total number of symmetries	1
σ_A	molecular diameter of A	m
σ_{AB}	collision diameter of A and B	m
σ_{ext}	number of external symmetries	1
σ_{int}	number of internal symmetries	1
τ	space time	s
φ	branching factor	1
	equivalence ratio	1
χ	volume expansion coefficient	1
Ω	reduced collision integral	1
ω	acentric factor	1
	order of the reaction	1

Subscripts

c	critical
el	electronic
f	formation

fa	apparent formation
i	index of reaction
j	index of constituent
o	initial instant input to the reactor
p	at constant pressure
r	end of reaction output of the reactor
rot	rotation
T	at constant temperature
tr	translation
V	at constant volume
vib	vibration
‡	activated complex

Superscripts

o	standard state
'	forward reaction
"	reverse reaction
‡	activated complex

Reference

MILLS I., CVITAS T., HOMAN K., KALLAY N., KUCHITTSV K., *Quantities, Units and Symbols in Physical Chemistry*, International Union of Pure and Applied Chemistry, 2nd edition, Blackwell (1993).
ALBERTY R.A., *Physical Chemistry*, Wiley (1987).

2 - LINEAR CHEMICAL NOTATION

The chemical notation most frequently used in this work is a **linear** or monodimensional (1D) **notation**[1]. This type of representation has been chosen as it allows the detailed chemical formulae of the molecules and of the free radicals and the equations of reaction to be conveniently entered into the computer, and also to be printed in the same format.

This linear notation is used in particular in all the computer programs for the generation of reaction mechanisms designed in Nancy and called EXGAS (EXpert System for Gas-phase reactions), described below (Chapter IX). Note that the outputs of EXGAS (reaction mechanism, kinetic parameters, thermodynamic data) are compatible with the software for the **simulation** of reactions CHEMKIN[2] of SANDIA National laboratories, in which the species are represented by a series of alphanumerical characters.

However, there is a big difference between the EXGAS notation and the CHEMKIN notation : the first is an unambiguous coding of the developed molecular formula of a chemical species, which can therefore be "understood" by the computer[3], whereas the second notation is more of a "mnemonic" easily understood by the chemist who had defined it, but not by the computer.

The essential characteristics of the EXGAS linear notation follow on from a simple principle : an EXGAS formula must be as close as possible to a classical semi-developed formula.

a) The elements

The elements whose chemical symbol consists of only one letter are represented by this letter : C for carbon, H for hydrogen. The elements whose symbol contains two letters are represented by these two letters in quotation marks : 'CL' for chlorine, 'CO' for cobalt. The formula CO represents carbon monoxide, not cobalt. The electrons of free radicals are represented by a dot.

b) Bonds and indices

Single, double and triple bonds are written as /, //, ///, respectively. Single bonds can be implicit. The formula indices are placed on the same line as the chemical symbols.

Example : ethane, ethylene and acetylene will be represented by the formulae CH3/CH3, CH2//CH2 and CH///CH, respectively. The ethyl radical will be written as follows : CH3/CH2(•).

The aromatic bond is written &. The closing of a ring is obtained by numbering an atom, the number is preceded by the symbol #.

Example : benzene is written as follows : CH(#1)&CH&CH&CH&CH&CH&1.

c) The substituents

The notation of a substituent obeys the rules given above. The substituents are placed between brackets as in the usual semi-developed formulae in chemistry.

Examples : iso-octane has the following linear formula C(CH3)3/CH2/CH(CH3)2. Paraxylene is written C(#1)(CH3)&CH&CH&C(CH3)&CH&CH&1.

d) Canonical form

The chemical notation so defined is unambiguous, as only one chemical species corresponds to a formula. On the contrary, the notation is not canonical, which signifies that a given molecule can have several representations.

Example : the formulae C(CH3)4 and CH3/C(CH3)2/CH3 both represent the neopentane molecule or in other words, that of dimethyl 2,2-propane.

To check whether two different linear formulae correspond to the same species, it is necessary to possess a canonical algorithm which establishes a unique representation of the species being considered[4].

e) Grammar

The chemical language corresponding to the rules given above is defined rigorously by a generative grammar[1]. When a chemical formula has been entered into the computer, a specific compiler[3] proceeds with its lexicographic, syntaxic and semantic analysis in order to check if it is grammatically correct. It then undergoes other analyses allowing internal representations to be established which are adapted to the purposes in question. In particular, these analyses must point out the symmetries (in the general sense of the word) of the molecules[5].

Example : the molecule of neopentane has 12 H atoms and 4 equivalent methyl groups.

The non-canonical form of the language makes the grammar very simple, which renders the learning of the reading and writing of the formulae easy.

References

[1] CôME G.M., MULLER C., CUNIN P.Y., GRIFFITHS M., *A linear chemical notation*, Comp. & Chem., 8, 233 (1984).

[2] KEE R.F., RUPLEY F.M., MILLER J.A., CHEMKIN-II : *A Fortran chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*, SANDIA Report (1993).

[3] MULLER C., SCACCHI G., CôME G.M., *A compiler for a linear chemical notation*, Comp. & Chem., 15, 337 (1991).

[4] WARTH V., BATTIN-LECLERC F., FOURNET R., GLAUDE P.A., CôME G.M., SCACCHI G., *Computer based generation of reaction mechanisms for gas-phase oxidation,* Comp. & Chem., 24, 541 (2000).

[5] MULLER C., SCACCHI G., CôME G.M., *A topological method for determining the external symmetry number of molecules.,* Comp. & Chem., 15, 17 (1991).

INDEX