

Solutions Manual for
Kinetics of
Catalytic
Reactions

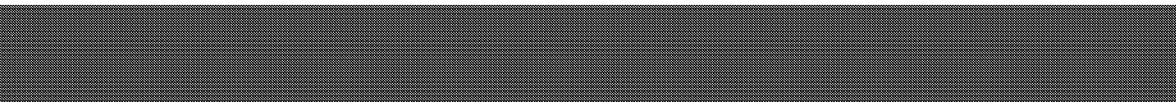
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Kinetics of Catalytic Reactions

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Solutions Manual for

Kinetics of Catalytic Reactions

 Springer

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Preface

This manual of solutions to the problems in “Kinetics of Catalytic Reactions” has been prepared to assist those who use this book in a teaching function. However, these solutions should also benefit those outside the classroom who want to apply the principles and concepts that are discussed in the book. By studying and observing the approaches used in solving these problems, it is very likely that similar applications can be envisioned in different kinetic problems that the investigator might face. Thus the availability of these solutions is a good learning tool for everyone. Additional details and insight about the solutions provided can be obtained by reading the cited references.

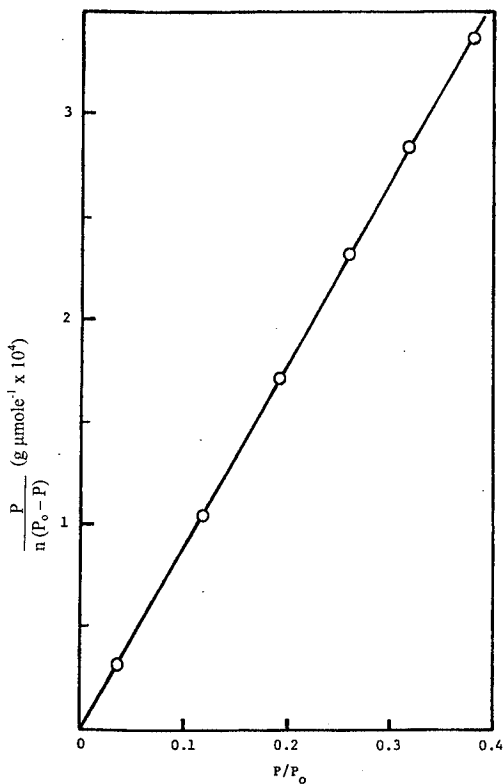
I have tried to eliminate all errors, both conceptual and typographical, in these solutions; however, the probability is high that I have not succeeded completely. Should any errors of commission (or omission) be found, I would greatly appreciate being informed. I can be reached at this email address: mavche@engr.psu.edu, or mail can be sent to me at: 107 Fenske Laboratory, Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802.

Albert Vannice

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Problem 3.1 Solution

N₂ BET Plot for BC-1

From slope and intercept:

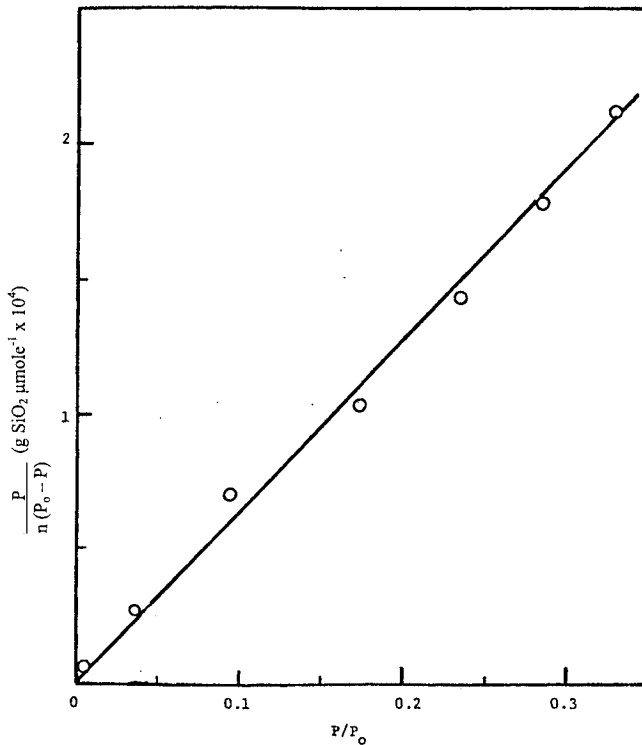
$$n_m = 1120 \mu\text{mole N}_2/\text{g}$$

$$C \cong 1000$$

$$A_m = \left(\frac{1120 \times 10^{-6} \text{ mole}}{\text{g}} \right) \left(\frac{6.023 \times 10^{23} \text{ molecule}}{\text{mole}} \right) \left(\frac{16.2 \text{ \AA}^2}{\text{molecule}} \right) \left(\frac{10^{-20} \text{ m}^2}{\text{\AA}^2} \right) = \frac{110 \text{ m}^2}{\text{g}}$$

$$\ln C = \frac{q_1 - q_L}{RT} \Rightarrow q_1 = 6.9 \left(\frac{1.987 \text{ cal}}{\text{mole} \cdot \text{K}} \right) (80 \text{ K}) + 1340 = \frac{2440 \text{ cal}}{\text{g mole}}$$

Problem 3.2(a) Solution

N₂ Bet Plot for SiO₂ (Cab-O-Sil, Grade M5)

From slope and intercept:

$$n_m = 1620 \mu\text{mole N}_2/\text{g}$$

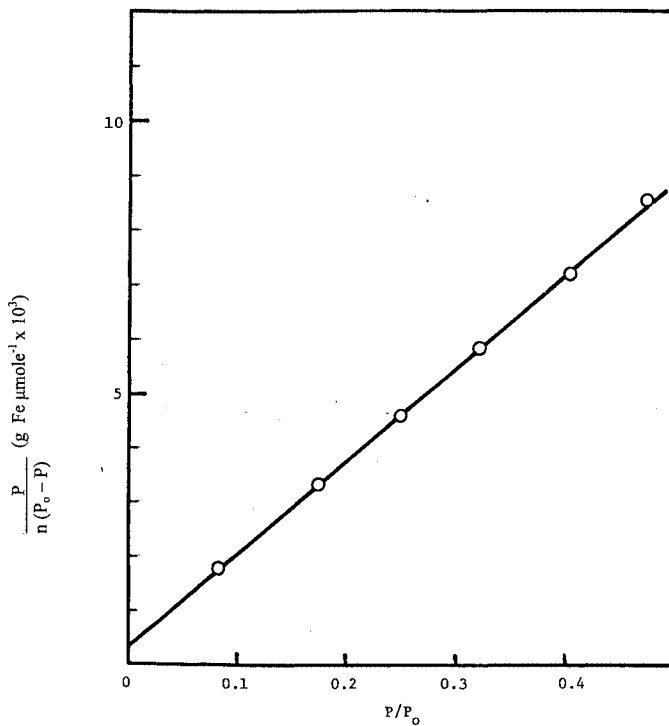
$$C = 140$$

$$A_m = \left(1620 \frac{\mu\text{mole N}_2}{\text{g}}\right) \left(\frac{6.023 \times 10^{17} \text{ molecule}}{\mu\text{mole}}\right) \left(\frac{16.2 \text{ \AA}^2}{\text{molecule}}\right) \left(\frac{10^{-20} \text{ m}^2}{\text{ \AA}^2}\right) = \frac{158 \text{ m}^2}{\text{g}}$$

$$\ln C = \frac{q_1 - q_L}{RT} = 4.94$$

$$q_1 = 4.94(1.987 \text{ cal/mole} \cdot \text{K})(77 \text{ K}) + 1340 \text{ cal/mole} = \frac{2100 \text{ cal}}{\text{mole}}$$

Problem 3.2(b) Solution

N₂ BET Plot for Fresh, Reduced Fe₂O₃

From slope and intercept:

$$n_m = 10.00 \mu\text{mole N}_2/\text{g}$$

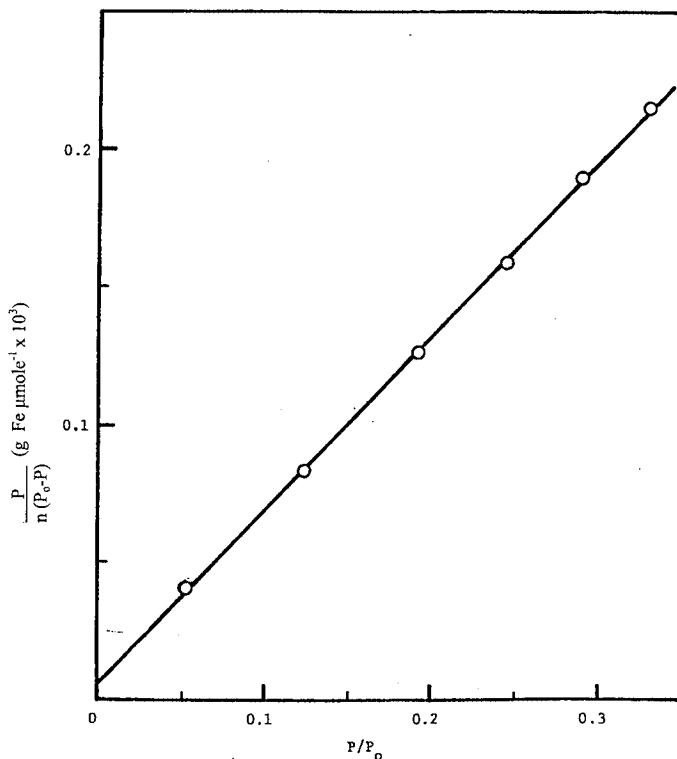
$$C = 47$$

$$A_m = \left(\frac{10.00 \times 10^6 \text{ mole N}_2}{\text{g}} \right) \left(\frac{6.023 \times 10^{23} \text{ molecule}}{\text{mole}} \right) \left(\frac{16.2 \text{ \AA}^2}{\text{molecule}} \right) \left(\frac{10^{-20} \text{ m}^2}{\text{ \AA}^2} \right) = \frac{0.98 \text{ m}^2}{\text{g}}$$

$$\ln C = \frac{q_1 - q_L}{RT} \Rightarrow q_1 = 3.85$$

$$q_1 = 3.85 (1.987 \text{ cal/mole} \cdot \text{K}) (80 \text{ K}) + 1340 \text{ cal/mole} = 1950 \text{ cal/mole}$$

Problem 3.2(c) Solution



Ar Bet Plot for Used Bulk Iron

From slope and intercept:

$$n_m = 1.60 \mu\text{mole Ar/g}$$

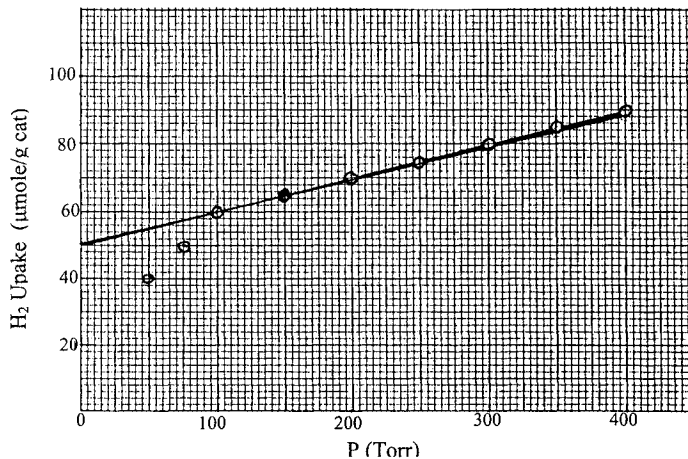
$$C = 47$$

$$A_m = \left(\frac{1.60 \times 10^{-6} \text{ mole Ar}}{\text{g}} \right) \left(\frac{6.023 \times 10^{23} \text{ molecule}}{\text{mole}} \right) \left(\frac{13.9 \text{ \AA}^2}{\text{molecule}} \right) \left(\frac{10^{-20} \text{ m}^2}{\text{\AA}^2} \right) = \frac{0.134 \text{ m}^2}{\text{g}}$$

$$\ln C = \frac{q_1 - q_L}{RT} = 3.85$$

$$q_1 = 3.85 (1.987 \text{ cal/mole} \cdot \text{K}) (77 \text{ K}) + 1550 = 2.14 \text{ kcal/mole}$$

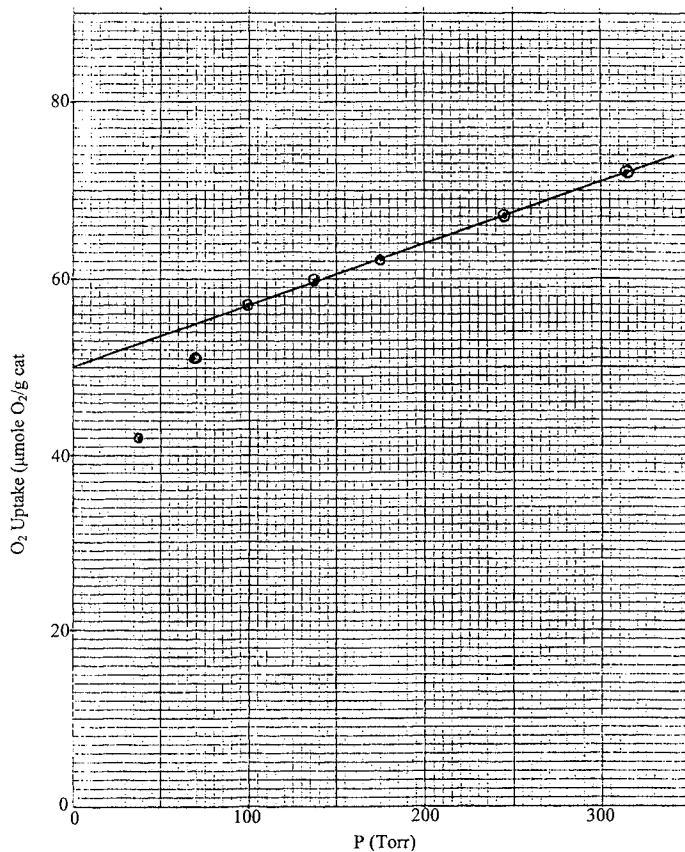
Problem 3.3 Solution



Assume $H_{ad}/Rh_s = 1$. The atomic weight of Rh is 103. The amount of hydrogen chemisorbed on the Rh is the intercept value of $50 \mu\text{mole H}_2/\text{g}$ which is determined by the high-P region where the Rh surface is essentially saturated with H atoms.

$$\frac{\left(\frac{50 \mu\text{mole H}_2}{\text{g cat}}\right) \left(\frac{2H_{ad}}{H_2}\right) \left(\frac{1 Rh_s}{1 H_{ad}}\right)}{\left(\frac{0.015 \text{ g Rh}}{\text{g cat}}\right) \left(\frac{10^6 \mu\text{mole Rh}}{103 \text{ g Rh}}\right)} = 0.69 = D_M$$

Problem 3.4 Solution



Assume no O₂ adsorption on SiO₂ and the O_{ad}/Ag_s ratio is 1
 Adsorption on Ag = 50 μmole O₂/g cat as determined by the intercept determined in the high-P region of saturation.

Dispersion = Ag_s/Ag_{total} = O_{ad}/Ag_t

$$D_M = \frac{(50 \mu\text{mole O}_2/\text{g}) (2 \text{ O}_{\text{ad}}/\text{O}_2) (1 \text{ Ag}_s/\text{O}_{\text{ad}})}{\left(\frac{0.0243 \text{ g Ag}}{\text{g cat}}\right) \left(\frac{\text{mole Ag}}{108 \text{ g Ag}}\right) \left(\frac{10^6 \mu\text{mole}}{\text{mole}}\right)} = 0.44$$

Problem 4.1 Solution

- a) For isothermal, 1st-order reaction:

$$\bar{\eta} = C_s/C_o = 1 - \bar{\eta}Da_o \quad (\text{Eq. 4.54})$$

$$\bar{\eta}Da_o = \mathfrak{R}/k_g a C_o \quad (\text{Eq. 4.50})$$

$$a = \frac{A}{V} = \frac{2\pi r^2 + 2\pi rL}{L\pi r^2} = 18.75 \text{ cm}^{-1} \text{ for cylinder}$$

$$(\text{For a sphere, } a = \frac{A}{V} = \frac{6}{2r} = 18.75 \text{ cm}^{-1})$$

$$C_{\text{SO}_2} = \frac{P}{RT} = \frac{0.06 \text{ atm}}{\left(\frac{82.06 \text{ atm} \cdot \text{cm}^3}{\text{g mole} \cdot \text{K}}\right)(763.2 \text{ K})} = 9.58 \times 10^{-7} \frac{\text{mole SO}_2}{\text{cm}^3}$$

See Table 1 for $\bar{\eta}Da_o$ and $\bar{\eta}$ values.

- b) The concentration drop can be determined from Eq. 4.52, i.e., $C_s/C_o = 1 - \bar{\eta}Da_o$
so $C_o - C_s = \mathfrak{R}/k_g a = \Delta C$

The ΔC values are given in Table 1. The concentration gradients through the film thickness, δ , will be $\Delta C/\delta$.

$$\text{From Eq. 4.44, } k_g = D/\delta \text{ so } \delta = D/k_g.$$

From Eq. 4.75, the bulk diffusivity is: $D_b = \frac{\bar{v}\lambda}{3}$. The mean-free path in the gas phase is (See Illustration 4.6):

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2(N/V)} = \frac{RT}{\sqrt{2}\pi\sigma^2 P}$$

for an ideal gas where σ = is the molecular cross-section area, so

$$\lambda = \frac{\left(\frac{82.06 \text{ atm cm}^3}{\text{g mole} \cdot \text{K}}\right)(763.2 \text{ K})\left(\frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ molecule}}\right)}{\sqrt{2}\pi\left[\frac{(4 \times 10^{-8} \text{ cm})^2}{\text{molecule}}\right](1 \text{ atm})} = 1.5 \times 10^{-5} \text{ cm}$$

$$\bar{v} = \left(\frac{8k_B T}{\pi m} \right)^{1/2} \quad (\text{Eq. 4.76})$$

$$\bar{v} = \left[\frac{8 \left(1.38 \times 10^{-16} \text{ erg/K} \right) (763.2 \text{ K})}{\pi (64 \text{ amu}) (1.66 \times 10^{-24} \text{ g/amu})} \right]^{1/2} = 5.0 \times 10^4 \text{ cm/s}$$

$$D_b = 1/3 (1.5 \times 10^{-5} \text{ cm}) (5.0 \times 10^4 \text{ cm/s}) = 0.25 \text{ cm}^2/\text{s}$$

$$\text{So, at high SV: } \delta = D/k_g = \frac{0.25 \text{ cm}^2/\text{s}}{(4.5 \times 10^4 \text{ cm/h})(1 \text{ h}/3600 \text{ s})} = 0.020 \text{ cm}$$

$$\text{and at low SV: } \delta = \frac{0.25 \text{ cm}^2/\text{s}}{(2.8 \times 10^4 \text{ cm/h})(1 \text{ h}/3600 \text{ s})} = 0.032 \text{ cm}$$

$$\text{at high SV: } \Delta C/\delta = \frac{2.6 \times 10^{-7} \text{ mole/cm}^3}{0.020 \text{ cm}} = 1.3 \times 10^{-5} \text{ mole/cm}^4$$

$$\text{at low SV: } \Delta C/\delta = \frac{2.9 \times 10^{-7} \text{ mole/cm}^3}{0.032 \text{ cm}} = 9.0 \times 10^{-6} \text{ mole/cm}^4$$

c) Nonisothermal situation, assume $C_s \cong C_o$

$$\text{From Eq. 4.51 } \bar{\eta} = \frac{k_s}{k_o} \left(\frac{C_s}{C_o} \right)^n = \frac{k_s}{k_o}$$

$$\text{and } \frac{k_s}{k_o} = e^{-E/RT(t-t_1)} \quad (\text{Eq. 4.55})$$

$$\text{also, } t = T_s/T_o = 1 + \bar{\beta} \cdot \bar{\eta} \text{Da}_o \quad (\text{Eq. 4.56})$$

$$\text{where } \bar{\beta} = \frac{-\Delta H_R^o C_o k_g}{T_o h}$$

$$\Delta H_R^o = -23.6 \text{ kcal/mole SO}_2 \quad (\text{CRC Handbook})$$

$$\bar{\beta} = - \frac{\left(\frac{-23600 \text{ cal}}{\text{mole SO}_2} \right) \left(\frac{9.58 \times 10^{-7} \text{ mole SO}_2}{\text{cm}^3} \right) \left(\frac{9 \times 10^3 \text{ cm}^3 \text{ K}}{\text{cal}} \right)}{763.2 \text{ K}} = 0.27$$

Then $\Delta T = T_s - T_o = \bar{\beta} \cdot \bar{\eta} \text{Da}_o T_o$, and the $\bar{\beta} \cdot \bar{\eta} \text{Da}_o$ values are listed in Table 1.

d) The non-isothermal effectiveness factor is

$$\bar{\eta}' = \frac{k_s}{k_o} = \frac{\mathfrak{R}_s}{\mathfrak{R}_o} = e^{-E/RT_o(t-1)} = (1 - \bar{\eta} \text{Da}_o) e^{-E/RT_o} (-\bar{\beta} \cdot \bar{\eta} \text{Da}_o) (1 + \bar{\beta} \cdot \bar{\eta} \text{Da}_o) \quad (\text{Eq. 4.57})$$

$$\text{where } E/RT_o = \frac{-30000 \text{ cal/mole}}{(1.987 \text{ cal/mole} \cdot \text{K})(763.2 \text{ K})} = -19.78$$

The $\bar{\eta}'$ values are also given in Table 1.

Table 1

\mathfrak{R} (mol/h·cm ³)	k_g (cm/h)	$\bar{\eta} \text{Da}_o$	$\bar{\eta}$ (isothermal)	ΔC (mole/cm ³)	$\bar{\beta} \cdot \bar{\eta} \text{Da}_o$	ΔT (K)	$\bar{\eta}'$ (nonisothermal)
0.215	4.5x10 ⁴	0.27	0.73	2.6x10 ⁻⁷	0.072	55	3.8
0.204	3.8x10 ⁴	0.30	0.70	2.9x10 ⁻⁷	0.080	61	4.3
0.194	3.4x10 ⁴	0.32	0.68	3.0x10 ⁻⁷	0.085	65	4.7
0.153	2.8x10 ⁴	0.30	0.70	2.9x10 ⁻⁷	0.080	61	4.3

Problem 4.2 Solution

Using the Thiele modulus:

$$\eta = \frac{\mathfrak{R}}{\mathfrak{R}_o} = k_{\text{meas}}/k_o = 3/\phi \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \text{ and } \phi = R_p k_o^{1/2} / D_{\text{eff}}^{1/2} \Rightarrow$$

$$k_o = \frac{\phi}{3} \frac{k_{\text{meas}}}{\left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right)} = \phi^2 D_{\text{eff}} / R_p^2 \Rightarrow \phi \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) = \frac{k_{\text{meas}} \mathfrak{R}^2}{3 D_{\text{eff}}}$$

$$R_p = \bar{r}_p = \frac{2 V_g}{S_g} = 2 \left(\frac{0.42 \text{ cm}^3/\text{g}}{(420 \text{ m}^2/\text{g})(100 \text{ cm/m})^2} \right) = 2.0 \times 10^{-7} \text{ cm}$$

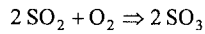
$$D_{\text{eff}} \cong D_{\text{Kn}} = 1/3 d_p \bar{v} = 1/3 (4.0 \times 10^{-7} \text{ cm}) \left[\frac{8(1.38 \times 10^{-16} \text{ erg/K})(685 \text{ K})}{\pi(120 \text{ amu})(1.66 \times 10^{-24} \text{ g/amu})} \right]^{1/2} = 4.63 \times 10^{-3} \frac{\text{cm}^2}{\text{s}}$$

$$\bar{v} = \left[\frac{8k_B T}{\pi m} \right]^{1/2} = \left[\frac{8RT}{\pi(MW)} \right]^{1/2} = 3.48 \times 10^4 \text{ cm/s} \quad (\text{Eq. 4.76})$$

$$\phi \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) = \frac{(1.49 \text{ cm}^3/\text{s} \cdot \text{g})(1.14 \text{ g/cm}^3)(0.35 \text{ cm/2})^2}{3(4.6 \times 10^{-3} \text{ cm}^2/\text{s})} = 3.75 \cong 3.8 \text{ so}$$

$$\frac{\phi}{\tanh \phi} = 4.8 \Rightarrow \phi = 4.8, \text{ and } \eta = \frac{3}{4.8} \left(1 - \frac{1}{4.8} \right) = 0.495 \cong 0.5$$

Problem 4.3 Solution



Use Weisz-Prater criterion :
$$N_{w-p} = \frac{\Re R_p^2}{C_s D_{\text{eff}}} \leq 0.3$$

Assume $C_s = C_o = \frac{n}{V} = \frac{P}{RT} = \frac{2/3 (2 \text{ atm})}{\left(\frac{82.06 \text{ atm} \cdot \text{cm}^3}{\text{mole} \cdot \text{K}} \right) (673.2 \text{ K})} = 2.4 \times 10^{-5} \frac{\text{mole}}{\text{cm}^3}$

$$D_{\text{eff}} = \frac{1}{3} \bar{v} d_p = \frac{1}{3} (3 \times 10^4 \text{ cm/s}) (1.2 \times 10^{-6} \text{ cm}) = 1.2 \times 10^{-2} \text{ cm}^2/\text{s}$$

$$R_p \leq \left[\frac{0.3 C_s D_{\text{eff}}}{\Re} \right]^{1/2} = \left[\frac{0.3 (2.4 \times 10^{-5} \text{ mol/cm}^3) (1.2 \times 10^{-2} \text{ cm}^2/\text{s})}{(2 \text{ mole SO}_2/\text{s} \cdot \ell) (1 \ell/1000 \text{ cm}^3)} \right]^{1/2} = 6.6 \times 10^{-3} \text{ cm} \Rightarrow$$

maximum particle diameter = $1.3 \times 10^{-2} \text{ cm}$

Problem 4.4 Solution

Weisz-Prater criterion: $N_{w-p} = \frac{\mathfrak{R}R_p^2}{C_s D_{\text{eff}}} < 0.3 \Rightarrow$ no significant pore diffusion effect

$$\mathfrak{R} = (0.0956 \text{ g mol SO}_2/\text{h} \cdot \text{g cat}) (1.6 \text{ g/cm}^3) (\text{h}/3600 \text{ s}) = 4.25 \times 10^{-5} \text{ mole/s} \cdot \text{cm}^3$$

$$R_p = 1.6 \text{ mm} = 0.16 \text{ cm}$$

Assume $C_s = C_o = 9.58 \times 10^{-7} \text{ mole/cm}^3$

$$D_{\text{eff}} \cong D_{Kn} = \frac{1}{3} \bar{v} d_p = \frac{1}{3} \left[\frac{8(1.38 \times 10^{-16} \text{ erg/K})(763 \text{ K})}{\pi(64 \text{ amu})(1.66 \times 10^{-24} \text{ g/amu})} \right]^{1/2} [100 \times 10^{-8} \text{ cm}] = 1.67 \times 10^{-2} \text{ cm}^2/\text{s}$$

$$N_{w-p} = \frac{(4.25 \times 10^{-5} \text{ mole/s} \cdot \text{cm}^3)(0.16 \text{ cm})^2}{(9.58 \times 10^{-7} \text{ mole/cm}^3)(1.67 \times 10^{-2} \text{ cm}^2/\text{s})} = 68 \gg 0.3$$

Mass transport limitations due to pore diffusion are definitely present.

Problem 4.5 Solution

$$N_{w-p} = \mathfrak{R} R_p^2 / C_s D_{\text{eff}} \cong \mathfrak{R} R_p^2 / CD_{K_n}$$

$$\mathfrak{R} = \left(\frac{1.99 \mu\text{mole Bz}}{\text{s g cat}} \right) \left(\frac{0.60 \text{ g cat}}{\text{cm}^3} \right) = \frac{1.2 \mu\text{ mole Bz}}{\text{s cm}^3}$$

$$C_s = C_o = P/RT = \frac{(50 \text{ Torr Bz})(1 \text{ atm}/760 \text{ Torr})}{\left(\frac{82.06 \text{ atm} \cdot \text{cm}^3}{\text{g mole K}} \right) (413 \text{ K})} = 1.9 \times 10^{-6} \frac{\text{mole}}{\text{cm}^3}$$

$D_{\text{eff}} \cong D_{K_n}$ because $\lambda \gg d_p$ (average pore diameter)

$$D_{K_n} = 1/3 \bar{v} d_p \quad \text{and let } d_p = 250 \text{ \AA} = 25 \text{ nm}$$

$$\bar{v} = (8 k_B T / \pi m)^{1/2} = \left[\frac{8 (1.38 \times 10^{-16} \text{ erg/K})(413 \text{ K})}{\pi (78 \text{ amu})(1.66 \times 10^{-24} \text{ g/amu})} \right]^{1/2} = 3.35 \times 10^4 \frac{\text{cm}}{\text{s}} \quad (\text{Eq. 4.76})$$

$$D_{K_n} = 1/3 \left(\frac{3.35 \times 10^4 \text{ cm}}{\text{s}} \right) (25 \text{ nm}) \left(\frac{1 \text{ cm}}{10^7 \text{ nm}} \right) = 2.8 \times 10^{-2} \frac{\text{cm}^2}{\text{s}} \quad (\text{Eq. 4.78})$$

(a) With Pd in mesopores = 25 nm:

$$\text{Worst case: } R_p = 500 \mu; N_{w-p} = \frac{(1.2 \times 10^{-6} \text{ mole Bz/s cm}^3) (500 \times 10^{-4} \text{ cm})^2}{(1.9 \times 10^{-6} \text{ Bz/cm}^3) (2.8 \times 10^{-2} \text{ cm}^2/\text{s})} = 0.056$$

Best case:

$$R_p = 10 \mu; N_{w-p} = \frac{(1.2 \times 10^{-6} \text{ mole Bz s} \cdot \text{cm}^3) (10 \times 10^{-4} \text{ cm})^2}{(1.9 \times 10^{-6} \text{ mole Bz/cm}^3) (2.8 \times 10^{-2} \text{ cm}^2/\text{s})} = 2.3 \times 10^{-5}$$

(b) With Pd in micropores = 0.9 nm:

$$D_{K_n} = 1/3 (3.35 \times 10^4 \text{ cm/s}) (0.9 \text{ nm}) \left(\frac{1 \text{ cm}}{10^7 \text{ nm}} \right) = 1.0 \times 10^{-3} \text{ cm}^2/\text{s}$$

$$\text{Worst case: } R_p = 500 \mu; N_{w-p} = \frac{(1.2 \times 10^{-6} \text{ mole Bz/s} \cdot \text{cm}^3) (500 \times 10^{-4} \text{ cm})^2}{(1.9 \times 10^{-6} \text{ mole Bz/cm}^3) (1.0 \times 10^{-3} \text{ cm}^2/\text{s})} = 1.6$$

$$\text{Best case: } R_p = 10 \mu; N_{w-p} = \frac{(1.2 \times 10^{-6} \text{ mole Bz/s} \cdot \text{cm}^3) (10 \times 10^{-4} \text{ cm})^2}{(1.9 \times 10^{-6} \text{ mole Bz/cm}^3) (1.0 \times 10^{-3} \text{ cm}^2/\text{s})} = 6.3 \times 10^{-4}$$

Problem 4.6 Solution

$$N_{w-p} = \mathfrak{R} R_p^2 / C_s D_{\text{eff}} \cong r_{\text{CO}_2} \rho_{\text{cat}} R_p^2 / (C_s D_{\text{Kn}}) \text{ because } D_{\text{Kn}} < D_{\text{eff}}$$

$$(1) C_{\text{CO}_2} = \frac{n}{V} = \frac{P}{RT} = \frac{(200 \text{ Torr}) \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right)}{\left(82.06 \frac{\text{atm} \cdot \text{cm}^3}{\text{g mole K}} \right) (723 \text{ K})} = 4.4 \times 10^{-6} \frac{\text{mole CO}_2}{\text{cm}^3}$$

$$(2) \bar{v} = \left(\frac{8 k_B T}{\pi m} \right)^{1/2} = \left[\frac{8 \left(1.38 \times 10^{-16} \text{ erg/K} \right) (723 \text{ K})}{\pi (44 \text{ amu}) \left(1.66 \times 10^{-24} \text{ g/amu} \right)} \right]^{1/2} = 5.9 \times 10^4 \text{ cm/s} \quad (\text{Eq. 4.76})$$

a)

$$D_{\text{Kn}} = 1/3 \bar{v} d_p = 1/3 (5.9 \times 10^4 \text{ cm/s}) (18 \text{ nm}) \left(1 \text{ cm}/10^7 \text{ nm} \right) = 3.5 \times 10^{-2} \text{ cm}^2/\text{s} \quad (\text{Eq. 4.78})$$

$$N_{w-p} = \frac{(42.6 \times 10^{-6} \text{ mole/s} \cdot \text{g}) (1 \text{ g/cm}^3) (0.01 \text{ cm})^2}{(4.4 \times 10^{-6} \text{ mole/cm}^3) (3.5 \times 10^{-2} \text{ cm}^2/\text{s})} = \underline{0.028} \quad (\text{No problem})$$

$$\text{b) } D_{\text{Kn}} = 1/3 (5.9 \times 10^4 \text{ cm/s}) (14 \text{ nm}) \left(1 \text{ cm}/10^7 \text{ nm} \right) = 2.8 \times 10^{-2} \text{ cm}^2/\text{s}$$

$$N_{w-p} = \frac{(9.6 \times 10^{-6} \text{ mole/s} \cdot \text{g}) (1 \text{ g/cm}^3) (0.01 \text{ cm})^2}{(4.4 \times 10^{-6} \text{ mole/cm}^3) (2.8 \times 10^{-2} \text{ cm}^2/\text{s})} = \underline{7.8 \times 10^{-3}} \quad (\text{No problem})$$

$$\text{c) } D_{\text{Kn}} = 1/3 (5.9 \times 10^4 \text{ cm/s}) (20 \text{ nm}) \left(1 \text{ cm}/10^7 \text{ nm} \right) = 3.9 \times 10^{-2} \text{ cm}^2/\text{s}$$

$$N_{w-p} = \frac{(118 \times 10^{-6} \text{ mole/s} \cdot \text{g}) (1 \text{ g/cm}^3) (0.01 \text{ cm})^2}{(4.4 \times 10^{-6} \text{ mole/cm}^3) (3.9 \times 10^{-2} \text{ cm}^2/\text{s})} = \underline{6.9 \times 10^{-3}} \quad (\text{No problem})$$

$$\text{d) } D_{\text{Kn}} = 1/3 (5.9 \times 10^4 \text{ cm/s}) (20 \text{ nm}) \left(1 \text{ cm}/10^7 \text{ nm} \right) = 3.9 \times 10^{-2} \text{ cm}^2/\text{s}$$

$$N_{w-p} = \frac{(237 \times 10^{-6} \text{ mole/s} \cdot \text{g}) (1 \text{ g/cm}^3) (0.01 \text{ cm})^2}{(4.4 \times 10^{-6} \text{ mole/cm}^3) (3.9 \times 10^{-2} \text{ cm}^2/\text{s})} = \underline{0.14} \quad (\text{Possible concern})$$

Problem 4.7 Solution

$$\text{Thiele modulus} \quad \phi = \frac{R_p k^{1/2} C_s^{\frac{n-1}{2}}}{D_{\text{eff}}^{1/2}}$$

$$\text{Rate} = k'P_{\text{H}_2} = kC_{\text{H}_2} = \left(\frac{1.99 \mu\text{mole Bz}}{\text{s} \cdot \text{g}} \right) (0.60 \text{ g/cm}^3) = \frac{1.19 \times 10^{-6} \text{ mole Bz}}{\text{s} \cdot \text{cm}^3}$$

$$C_{\text{H}_2} = \frac{n}{V} = \frac{P}{RT} = \frac{(710/760 \text{ atm})}{\left(\frac{82.06 \text{ cm}^3 \cdot \text{atm}}{\text{g mole} \cdot \text{K}} \right) (413\text{K})} = 2.76 \times 10^{-5} \frac{\text{mole}}{\text{cm}^3}$$

$$k = \frac{\text{Rate}}{C_{\text{H}_2}} = \frac{1.19 \times 10^{-6} \text{ mole/s} \cdot \text{cm}^3}{2.76 \times 10^{-5} \text{ mole/cm}^3} = 0.0432 \text{ s}^{-1}$$

$$D_{\text{H}_2} = 1/3 \bar{v}_{\text{H}_2} \lambda$$

$$\bar{v}_{\text{H}_2} = \left[\frac{8(1.38 \times 10^{-16} \text{ erg/K})(413\text{K})}{\pi (2 \text{ amu})(1.66 \times 10^{-24} \text{ g/amu})} \right]^{1/2} = 2.1 \times 10^5 \text{ cm/s}$$

$$\lambda = \frac{\left(\frac{82.06 \text{ cm}^3 \cdot \text{atm}}{\text{g mole} \cdot \text{K}} \right) (413\text{K}) \left(\frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ molecules}} \right)}{\sqrt{2} \pi (2.4 \times 10^{-8} \text{ cm})^2 (1 \text{ atm total P})} = 2.2 \times 10^{-5} \text{ cm}$$

$$D_{\text{H}_2} = 1/3 (2.1 \times 10^5 \text{ cm/s}) (2.2 \times 10^{-5} \text{ cm}) = 1.5 \text{ cm}^2/\text{s}$$

$$D_{\text{eff}} \cong D_{\text{Kn}} = 1/3 \bar{v} d_p \quad \text{where } d_p = \text{pore diameter}$$

Case 1: Smallest particle, all Pd in mesopores:

$$D_{Kn} = 1/3 (2.1 \times 10^5 \text{ cm/s}) (25 \times 10^{-9} \text{ m}) (10^2 \text{ cm/m}) = 0.175 \text{ cm}^2/\text{s}$$

$$\phi = \frac{(10 \times 10^{-6} \text{ m}) (10^2 \text{ cm/m}) (0.0432/\text{s})^{1/2}}{(0.175 \text{ cm}^2/\text{s})^{1/2}} = 5.0 \times 10^{-4}$$

Case 2: Largest particle, all Pd in mesopores:

$$\phi = \frac{(500 \times 10^{-6} \text{ m}) (10^2 \text{ cm/m}) (0.0432/\text{s})^{1/2}}{(0.175 \text{ cm}^2/\text{s})^{1/2}} = 0.025$$

Case 3: Largest particle, all Pd in micropores:

$$D_{Kn} = 1/3 (2.1 \times 10^5 \text{ cm/s}) (0.9 \times 10^{-9} \text{ m}) (10^2 \text{ cm/m}) = 6.3 \times 10^{-3} \text{ cm}^2/\text{s}$$

$$\phi = \frac{(500 \times 10^{-6} \text{ m}) (10^2 \text{ cm/m}) (0.0432/\text{s})^{1/2}}{(6.3 \times 10^{-3} \text{ cm}^2/\text{s})^{1/2}} = 0.13$$

No concern – in all cases η is essentially unity.

Problem 4.8 Solution

Use Weisz-Prater criterion.

$$N_{w-p} = \frac{\Re R_p^2}{C_s D_{eff}} \ll 0.6 \text{ (or } 0.3) \quad R_p = \frac{1}{2} (14.9 \times 10^{-3} \text{ cm}), \quad \lambda = d_p$$

$$D_{eff} = \frac{1}{3} \bar{v} d_p = \frac{1}{3} \left[\frac{8 \left(1.38 \times 10^{-16} \text{ erg/K} \right) (493 \text{ K})}{\pi (30 \text{ amu}) (1.66 \times 10^{-24} \text{ g/amu})} \right] (60 \times 10^{-8} \text{ cm}) = 1.18 \times 10^{-2} \text{ cm}^2/\text{s} \quad (\text{Eq. 4.78})$$

Assume 1 atm:

$$C_s = C = \frac{n}{V} = \frac{P}{RT} = \frac{(9 \text{ Torr}) (1 \text{ atm}/760 \text{ Torr})}{\left(82.06 \frac{\text{cm}^3 \cdot \text{atm}}{\text{gmol} \cdot \text{K}} \right) (493 \text{ K})} = 2.93 \times 10^{-7} \frac{\text{mole CH}_2\text{O}}{\text{cm}^3}$$

$$N_{w-p} = \frac{\left[1.4 \times 10^{-7} \text{ mole/cm}^3 \cdot \text{s} \right] \left[7.45 \times 10^{-3} \text{ cm} \right]^2}{\left[2.93 \times 10^{-7} \text{ mole/cm}^3 \right] \left[1.18 \times 10^{-2} \text{ cm}^2/\text{s} \right]} = 2.25 \times 10^{-3} \ll 0.3$$

Yes, it's free of diffusion effects.

Problem 5.1 Solution

$$K = \frac{[O-*]^2 [S-*]}{P_{SO_2} [*]^3}, \quad L = [O-*] + [S-*] + [*] \quad \text{and} \quad [O-*] = 2 [S-*]$$

$$[*] = L - [O-*] - [S-*] = L - 3 [S-*]$$

$$K = \frac{(2 [S-*])^2 [S-*]}{P_{SO_2} [*]^3} = \frac{4 [S-*]^3}{P_{SO_2} (L - 3 [S-*])^3}$$

$$K (L - 3 [S-*])^3 = 4 [S-*]^3 / P_{SO_2} \Rightarrow K^{1/3} (L - 3 [S-*]) = \sqrt[3]{4} [S-*] / P_{SO_2}^{1/3}$$

$$LK^{1/3} P_{SO_2}^{1/3} - 3 [S-*] K^{1/3} P_{SO_2}^{1/3} = \sqrt[3]{4} [S-*]$$

$$LK^{1/3} P_{SO_2}^{1/3} = [3 K^{1/3} P_{SO_2}^{1/3} + \sqrt[3]{4}] [S-*]$$

$$[S-*] = \frac{LK^{1/3} P_{SO_2}^{1/3}}{\sqrt[3]{4} + 3 K^{1/3} P_{SO_2}^{1/3}} = \frac{L (K/4)^{1/3} P_{SO_2}^{1/3}}{1 + 3 (K/4)^{1/3} P_{SO_2}^{1/3}} = \frac{L (K^{1/3} P_{SO_2}^{1/3})}{1 + 3 K^{1/3} P_{SO_2}^{1/3}}$$

$$\theta_s = \frac{[S-*]}{L} = \frac{K^{1/3} P_{SO_2}^{1/3}}{1 + 3 K^{1/3} P_{SO_2}^{1/3}}, \quad \theta_{s \max} = 1/3$$

$$\theta = 3 \theta_s = \frac{3 K^{1/3} P_{SO_2}^{1/3}}{1 + 3 K^{1/3} P_{SO_2}^{1/3}}$$

Problem 5.2 Solution

To test single-site adsorption, plot $\frac{P}{n} = \frac{1}{Kn_m} + \frac{P}{n_m}$ (Eq. 5.27), whereas to test dual (double)-site adsorption, plot $\frac{P^{1/2}}{n} = \frac{1}{K^{1/2}n_m} + \frac{P^{1/2}}{n_m}$ (Eq. 5.28). The single-site equation gives a reasonable linear fit, whereas the dual-site equation is curved with negative slopes (See Figures 1 and 2, respectively).

From the slopes and intercepts of the plots in Figure 1:

T(K)	K (atm ⁻¹)	n_m (μmole g ⁻¹)	or	V_m (cm ³ _{STP} g ⁻¹) ^a
343	181	1380		30.9
363	87	1180		26.6
383	59	772		17.1
403	28	719		16.1

Use Eq. 5.38 and plot $\ln K$ vs. $1/T$ (Figure 3)

$$\text{Slope} = 4.13 \times 10^3 = -\Delta H_{\text{ad}}^{\circ}/R, \quad \text{so } \Delta H_{\text{ad}}^{\circ} = -8.2 \frac{\text{kcal}}{\text{mole}} \text{ or } -34 \frac{\text{kJ}}{\text{mole}}$$

$$\text{Intercept} = -6.85 = \Delta S_{\text{ad}}^{\circ}/R, \quad \text{so } \Delta S_{\text{ad}}^{\circ} = -14 \frac{\text{cal}}{\text{mole} \cdot \text{K}} \text{ or } -59 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$

(a)

$$V_m = nRT/P = (n \text{ g mole}) \frac{(82.06 \text{ cm}^3 \cdot \text{atm}/\text{g mole} \cdot \text{K})(273.2 \text{ K})}{1 \text{ atm}} = n (2.242 \times 10^4 \text{ cm}^3)$$

Benzene Adsorption On Silica Gel Single Site Langmuir Isotherm

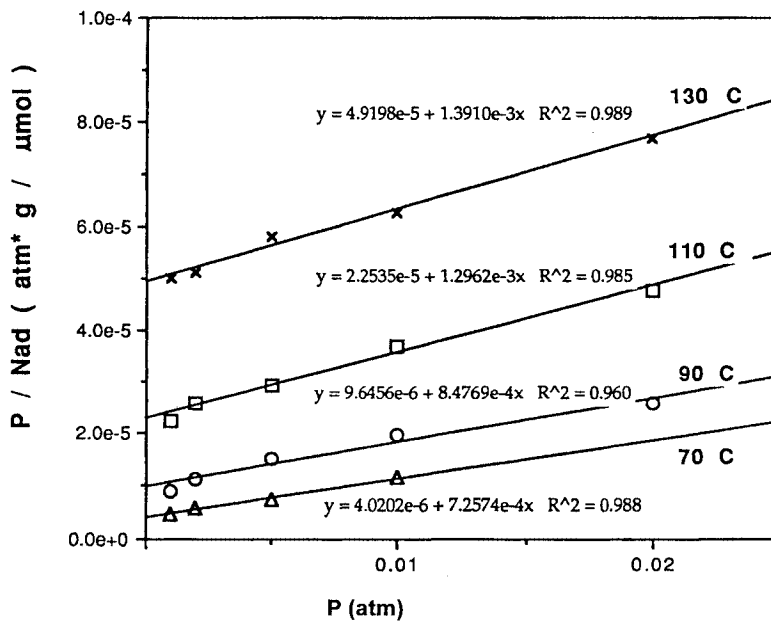


Figure 1

Benzene Adsorption On Silica Gel Double Site Langmuir Isotherm

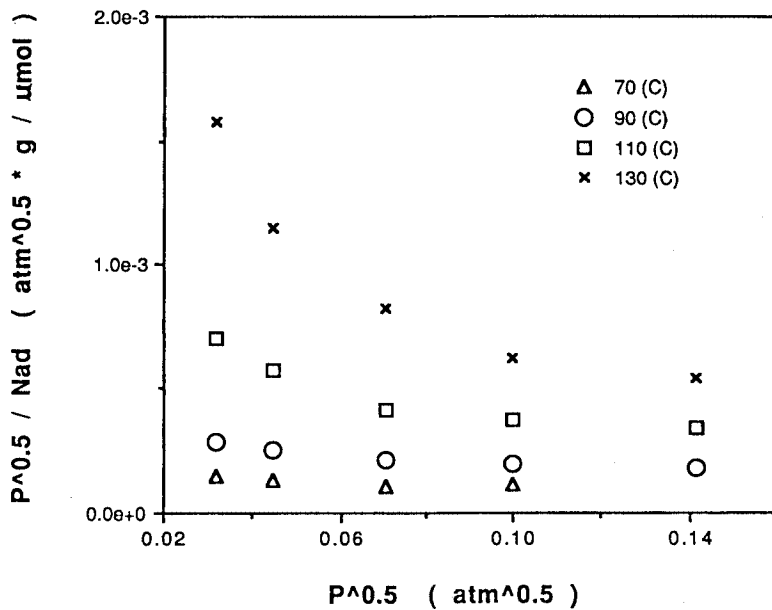
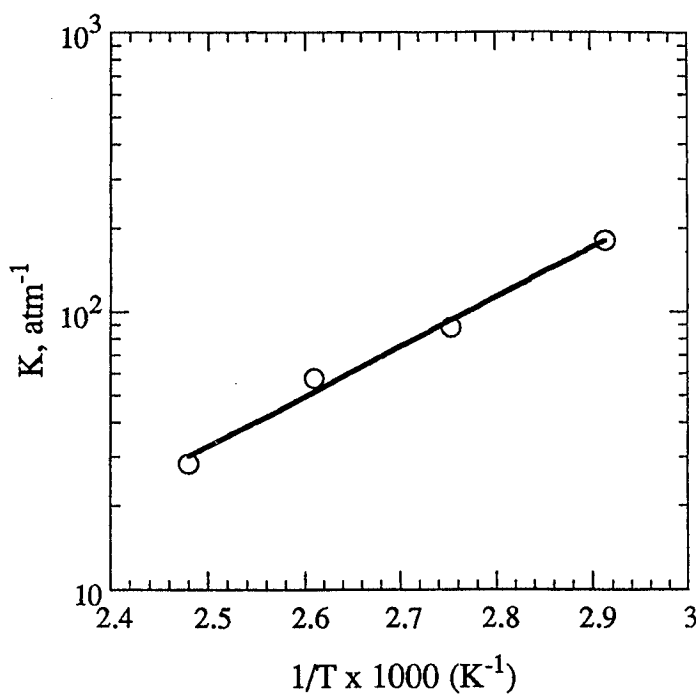


Figure 2



Plot of K vs. $1/T$ for Pure Benzene Adsorption

Figure 3

Problem 5.3 Solution

To test isotherms:

For single-site Langmuir isotherm, plot P/n vs. P (Eq. 5.71) – See Figure 4

For Freundlich isotherm, plot $\ln n$ vs. $\ln P$ (Eq. 5.73) – See Figure 5

For Temkin isotherm, plot n vs. $\ln P$ (Eq. 5.74) – See Figure 6

The Freundlich isotherm gives the most linear best fit.

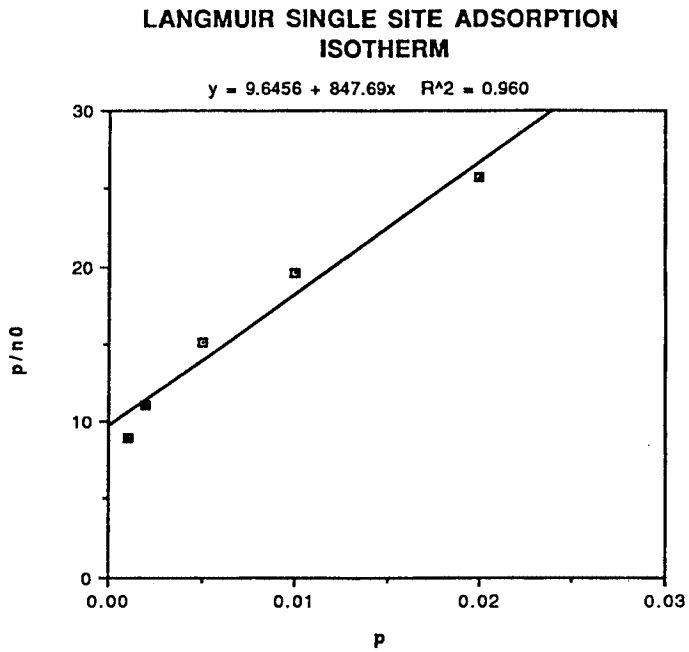


Figure 4

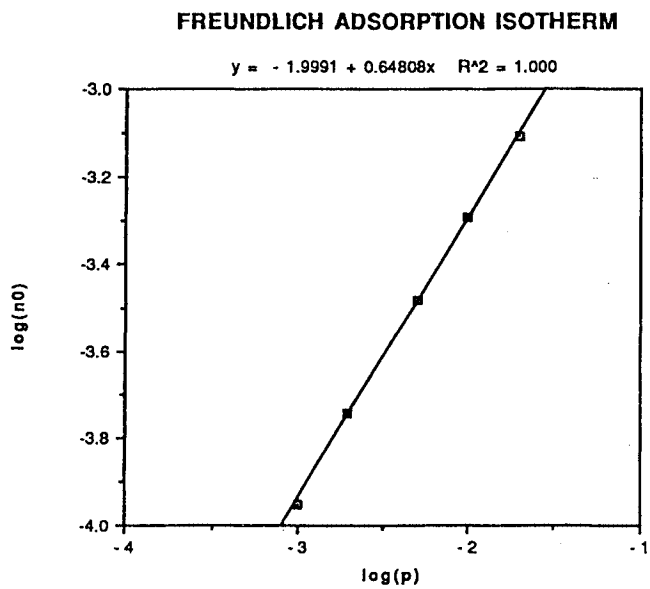


Figure 5

TEMKIN ADSORPTION ISOTHERM

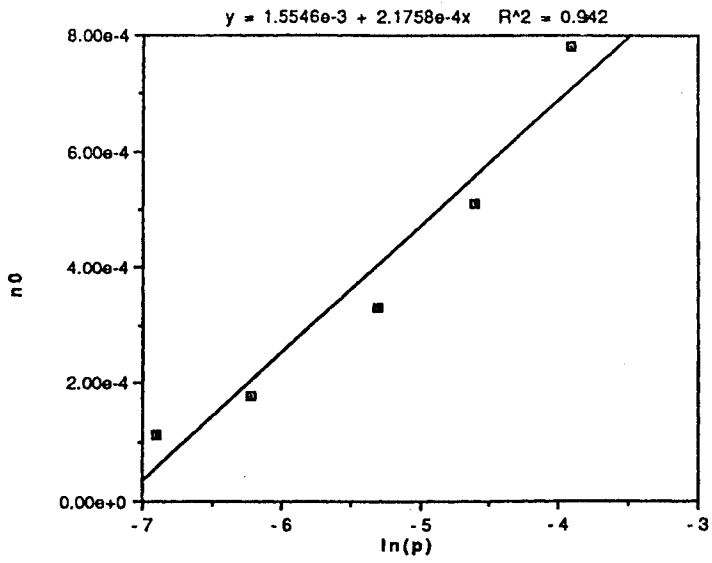


Figure 6

Problem 5.4 Solution

$$A + 2S \overset{K}{\rightleftharpoons} S-A-S$$

$$L = S + 2(SAS) \quad K = [SAS] / [A][S]^2$$

$$S = L - 2[SAS] \Rightarrow S^2 = L^2 - 4L[SAS] + 4[SAS]^2$$

$$[SAS] = [A][S]^2 K = K[A](L^2 - 4L[SAS] + 4[SAS]^2)$$

$$\underbrace{4K[A]}_a [SAS]^2 - \underbrace{(4LK[A]+1)}_b [SAS] + \underbrace{L^2K[A]}_c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \text{for } ax^2 + bx + c = 0$$

$$[SAS] = \frac{(1 + 4LK[A]) \pm \sqrt{1 + 8LK[A] + 16L^2K^2[A]^2} - 16L^2K^2[A]^2}{8K[A]}$$

$$[SAS] = \frac{(1 + 4LK[A]) - \sqrt{1 + 8LK[A]}}{8K[A]} \quad [SAS] = 0 \quad @ \quad [A] = 0$$

$$[SAS] \rightarrow L/2 \quad \text{as} \quad [A] \rightarrow \infty$$

OR, alternatively

$$2[SAS]/L = \theta_A \quad S/L = 1 - 2[SAS]/L \Rightarrow \theta = 1 - \theta_A \quad \& \quad K = \frac{L\theta_A}{L^2[A]\theta^2}$$

$$LK[A]\theta^2 = \theta_A \Rightarrow (1 - \theta_A)^2 LK[A] = \theta_A$$

$$LK[A]\theta_A^2 - (2LK[A]+1)\theta_A + LK[A] = 0$$

$$\theta_A = \frac{2LK[A]+1 \pm \sqrt{4L^2K^2[A]^2 + 4LK[A]+1 - 4L^2K^2[A]^2}}{2LK[A]} \Rightarrow$$

$$\theta_A = \frac{1 + 2LK[A] \pm \sqrt{1 + 4LK[A]}}{2LK[A]} \Rightarrow \theta_A = \frac{1 + 2LK[A] - \sqrt{1 + 4LK[A]}}{2LK[A]}$$

$$\theta_A = 0 \quad @ \quad [A] = 0 \quad \text{and} \quad \theta_A \rightarrow 1 \quad \text{as} \quad [A] \rightarrow \infty$$

Problem 6.1 Solution

$$k = Ae^{-E/RT} \quad \text{so} \quad \ln k = \ln A - E/RT$$

Plot $\ln k$ vs. $1/T$

<u>T (K)</u>	<u>k</u>
823	1.3×10^{-5}
833	2.3×10^{-5}
843	4.1×10^{-5}
853	6.2×10^{-5}
863	11.5×10^{-5}
873	17.7×10^{-5}
883	28.6×10^{-5}
893	46.2×10^{-5}
903	70.8×10^{-5}

$$\text{Slope} = -E/R = -37,200 \Rightarrow E = 73.9 \frac{\text{kcal}}{\text{mole}} = 309 \frac{\text{kJ}}{\text{mole}}$$

$$\text{Intercept} = \ln A = 33.86 \Rightarrow A = 5.1 \times 10^{14} \text{ s}^{-1}$$

Problem 6.2 Solution

$$a) \quad r = v [X^\ddagger] = k_B T/h \frac{Q_{N-N}}{Q_N^2} e^{-E/RT} [N \cdot]^2$$

pre-exponential factor $= k_o = (k_B T/h) \frac{f_{tr}^3 f_{rot}^2}{f_{tr}^6}$ because a N atom has no rotational or vibrational modes. Therefore, $k_o = (k_B T/h) \frac{(aT)^{3/2} (bT)}{(cT)^3} \Rightarrow k_o \propto T^{1/2}$

$$b) \quad Q_{CO} = f_{tr}^3 f_{rot}^2 f_{vib} \quad \text{and} \quad Q_{H_2O} = f_{tr}^3 f_{rot}^3 f_{vib}^3$$

Q_{COOH_2} has $3 \times 5 = 15$ modes, with $15 - 7 = 8$ degrees of vibrational freedom; therefore

$$k_o = (k_B T/h) \frac{f_{tr}^3 f_{rot}^3 f_{vib}^8}{f_{tr}^6 f_{rot}^5 f_{vib}^4} \cong (k_B T/h) \frac{1}{f_{tr}^3 f_{rot}^2} \quad \text{because} \quad f_{vib} \cong 1$$

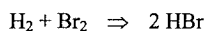
$$\text{so} \quad k_o \propto (k_B T/h) \frac{1}{(aT)^{3/2} (bT)} \quad \text{or} \quad k_o \propto T^{-3/2}$$

c) $Q_{H_2} \cong Q_{Cl_2} = f_{tr}^3 f_{rot}^2 f_{vib}$; assume non-linear activated complex, so degrees of vibrational freedom $= 3N - 7 = 5$, and $Q^\ddagger = Q_{H_2Cl_2} = f_{tr}^3 f_{rot}^3 f_{vib}^5$. Therefore,

$$k_o = (k_B T/h) \frac{f_{tr}^3 f_{rot}^3 f_{vib}^5}{f_{tr}^6 f_{rot}^4 f_{vib}^2} = (k_B T/h) \frac{1}{f_{tr}^3 f_{rot}} \quad \text{because} \quad f_{vib} \cong 1, \text{ so } k_o \propto (k_B T/h) \frac{1}{(aT)^{3/2} (bT)^{1/2}}$$

$$\text{and } k_o \propto T^{-1}$$

Problem 6.3 Solution



$$1. \quad r = \frac{d[\text{HBr}]}{dt} = k_1 [\text{Br}\cdot][\text{H}_2] + k_2 [\text{H}\cdot][\text{Br}_2] - k_{-1} [\text{H}\cdot][\text{HBr}]$$

$$(1) \quad \text{Use SSA on H}\cdot \text{ radical: } \frac{d[\text{H}\cdot]}{dt} = 0 = k_1 [\text{Br}\cdot][\text{H}_2] - k_2 [\text{H}\cdot][\text{Br}_2] - k_{-1} [\text{H}\cdot][\text{HBr}]$$

(2) Use SSA on Br \cdot radical:

$$\frac{d[\text{Br}\cdot]}{dt} = 0, \text{ but an easier way is: } r_i = r_t \Rightarrow 2k_i [\text{Br}_2] = 2k_t [\text{Br}\cdot]^2 \Rightarrow$$

$$[\text{Br}\cdot] = (k_i/k_t)^{1/2} [\text{Br}_2]^{1/2}$$

$$\text{From (1): } [\text{H}\cdot] = \frac{k_1 [\text{Br}\cdot][\text{H}_2]}{k_2 [\text{Br}_2] + k_{-1} [\text{HBr}]}, \text{ then}$$

$$[\text{H}\cdot] = \frac{k_1 (k_i/k_t)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_2 [\text{Br}_2] + k_{-1} [\text{HBr}]}$$

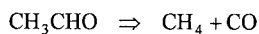
$$r = k_1 (k_i/k_t)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2] + (k_2 [\text{Br}_2] - k_{-1} [\text{HBr}]) \left(\frac{k_1 (k_i/k_t)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_2 [\text{Br}_2] + k_{-1} [\text{HBr}]} \right)$$

$$= \frac{(k_2 [\text{Br}_2] + k_{-1} [\text{HBr}]) (k_1 (k_i/k_t)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]) + (k_2 [\text{Br}_2] - k_{-1} [\text{HBr}]) (k_1 (k_i/k_t)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2])}{k_2 [\text{Br}_2] + k_{-1} [\text{HBr}]}$$

$$= \frac{2k_1 k_2 (k_i/k_t)^{1/2} [\text{Br}_2]^{3/2} [\text{H}_2]}{k_2 [\text{Br}_2] + k_{-1} [\text{HBr}]} \quad \text{or}$$

$$r = \frac{2k_1 (k_i/k_t)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{1 + \frac{k_{-1} [\text{HBr}]}{k_2 [\text{Br}_2]}}$$

Problem 6.4



$$r = -\frac{d[\text{CH}_3\text{CHO}]}{dt} = r_2 = r_3 = \frac{d[\text{CH}_4]}{dt} = \frac{d\text{CO}}{dt}$$

at constant volume

$$r_i = r_t \Rightarrow r_1 = 2 r_4 \text{ so } k_1 [\text{CH}_3\text{CHO}] = 2 k_4 [\text{CH}_3 \cdot]^2$$

$$r = k_2 [\text{CH}_3 \cdot][\text{CH}_3\text{CHO}] = k_2 (k_1/2 k_4)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}, \text{ thus}$$

$$r = k_{\text{app}} [\text{CH}_3\text{CHO}]^{3/2} \text{ so } E_{\text{app}} = E_2 + \frac{E_1}{2} - \frac{E_4}{2}$$

Problem 6.5 Solution

- a) $Q_N > Q_O$ so N end down, i.e., $\text{Fe} \begin{array}{l} \nearrow \text{N}=\text{O} \\ \searrow \end{array}$, $n = 3$.

$$\text{For } (\eta^1\mu_1): Q_{\text{ON}} = \frac{Q_N}{(2-1/n)} = \frac{140}{(5/3)} = 84 \quad \text{and} \quad Q_{\text{NO}} = \frac{Q_{\text{ON}}^2}{\frac{Q_{\text{ON}}}{n'} + D_{\text{NO}}} \quad (\text{Table 6.5})$$

$$\text{so} \quad Q_{\text{NO}} = (0.6)^2 (140)^2 / [(0.6)(140) + 151] = 30 \text{ kcal mole}^{-1}$$

$$\text{For } (\eta^1\mu_2): Q_{\text{NO}} = (0.6)^2 (140)^2 / \left[\frac{(0.6)(140)}{2} + 151 \right] = 37 \text{ kcal mole}^{-1} \Rightarrow \begin{array}{c} \text{O} \\ || \\ \text{N} \\ / \quad \backslash \\ \text{Fe} \quad \text{Fe} \end{array} \quad (\text{preferred})$$

- b) Orientation is $\eta^1\mu_1$ with O end down, $n = 4$.

$$Q_{\text{OO}} = \frac{115}{(7/4)} = 65.7 \text{ kcal mole}^{-1} \quad (\text{Table 6.5})$$

$$Q_{\text{H}_2\text{O}} = \frac{Q_{\text{OO}}^2}{Q_{\text{OO}} + D_{\text{H}_2\text{O}}} = \frac{(65.7)^2}{65.7 + 220} = 15 \text{ kcal mole} \quad (\text{Table 6.7a})$$

- c) This is a symmetric molecule with $A = \text{CH}$, i.e., $\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Pt} \quad \quad \text{Pt} \end{array}$, $n=3$.

$$\text{For } (\eta^2\mu_2): D_{\text{C}=\text{C}} = D_{\text{HC}=\text{CH}} - 2 D_{\text{CH}} = 392 - 2(81) = 230 \text{ kcal mole}^{-1} \quad (\text{Table 6.7b})$$

$$Q_{\text{OC}} = Q_{\text{C}} / (2-1/3) = (3/5)(150) = 90$$

$$D_{\text{H}-\text{C}=\text{C}} = 230 + 81 = 311 = D_{\text{C}=\text{C}} + D_{\text{C}-\text{H}}$$

$$Q_{\text{HC}=\text{CH}} = \frac{(9/2)(90)^2}{3(90) + 8(311)} = 13 \text{ kcal mole} \quad (\text{Eq. 6.46})$$

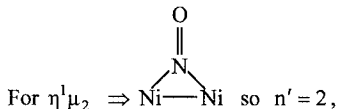
d) $Q_{\text{CH}_2} = \frac{Q_{\text{C}}^2}{Q_{\text{C}} + D_{\text{CH}_2}}$ for “strong” chemisorption (adsorbs in hollow site)

use $Q_{\text{C}} = 160 \text{ kcal mole}^{-1}$ on Pd(111) , so

$$Q_{\text{CH}_2} = \frac{(160)^2}{160 + 183} = 75 \text{ kcal mole}^{-1}$$

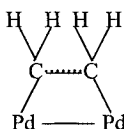
Problem 6.6 Solution

- a) $N_{ad} > O_{ad}$ regarding bond strength, so N end down. This is "weak" chemisorption, $n = 4$.



$$Q_{NO} = \frac{Q_{oA}}{\frac{Q_{oA}}{n'} + D_{AB}} = \frac{Q_{oN}}{\frac{Q_{oN}}{2} + 151} \quad (\text{Table 6.6}), \text{ so } Q_{NO} = \frac{(4/7)^2(135)^2}{\frac{(4/7)(135)}{2} + 151} = 31 \text{ kcal mole}^{-1}$$

- b) This is "weak" chemisorption, $n = 3$,



$$D_{C=C} = D_{CH_2CH_2} - 2 D_{CH_2} = 538 - 366 = 172, \text{ A equals } = CH_2, \text{ and}$$

(Table 6.7b)

$$D_{=CH_2} = D_{CH_2} + D_{C=C} = 183 + 172 = 355$$

$$Q_{A_2} = \frac{9/2 Q_{oC}^2}{3 Q_{oC} + 8 D_{A_2}} = (9/2)(0.6)^2 (160)^2 / [3(0.6)(160) + 8(355)] = 13 \text{ kcal mole}^{-1}$$

- c) This is "weak" chemisorption, $n = 3$, N end down, i.e.,



$$Q_{NH_3} = \frac{Q_{oA}^2}{Q_{oA} + D_{AB}}, \text{ from ref. 25, } D_{NH_3} = 279 \text{ kcal mole}^{-1},$$

$$\text{so } Q_{NH_3} = \frac{(0.6)^2(140)^2}{(0.60)(140) + 279} = 19 \text{ kcal mole}^{-1}$$

d) This is "strong" chemisorption

$$Q_{\text{NH}_2} = \frac{Q_{\text{N}}^2}{Q_{\text{N}} + D_{\text{NH}_2}}, \text{ from ref. 25, } D_{\text{NH}_2} = 169 \text{ kcal mole}^{-1},$$

$$\text{so } Q_{\text{NH}_2} = \frac{(140)^2}{140 + 169} = 63 \text{ kcal mole}^{-1}$$

$$Q_{\text{NH}} = \frac{Q_{\text{N}}^2}{Q_{\text{N}} + D_{\text{NH}}}, \text{ from ref. 25, } D_{\text{NH}} = 81 \text{ kcal mole}^{-1}, \text{ so } Q_{\text{NH}} = \frac{(140)^2}{140 + 81} = 89 \text{ kcal mole}^{-1}$$

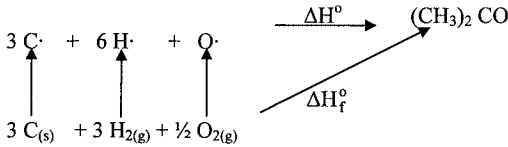
If "intermediate" chemisorption is chosen for NH_2 , then

$$Q_{\text{NH}_2} = \frac{1}{2} \left[\frac{(0.6)^2 (140)^2}{(0.6)(140) + 169} + \frac{(140)^2}{140 + 169} \right] \begin{array}{l} = 48 \text{ kcal mole}^{-1} \text{ if } n'=2 \\ = 46 \text{ kcal mole}^{-1} \text{ if } n'=1 \end{array}$$

Problem 6.7 Solution

For acetone, $(\text{CH}_3)_2\text{CO}$ $\left(\text{or } \begin{array}{c} \text{CH}_3 \\ | \\ \text{C} = \text{O} \\ | \\ \text{CH}_3 \end{array} \right)$, the enthalpy of formation is -217.3 kJ/mole or -51.9

kcal/mole [25]; therefore, $D_{\text{Total}} = D_{(\text{CH}_3)_2\text{CO}} = \sum \Delta H_{f_i}^\circ (\text{atoms}) - \Delta H_f^\circ$ so, based on:



and from reference [25]:

$$\begin{array}{rcl}
 3 (\text{C} \rightarrow \text{C}\cdot) & = & 3 (171.3 \text{ kcal/mole}) \\
 3 (\text{H}_2 \rightarrow 2 \text{H}\cdot) & = & (3) (2) (51.2 \text{ kcal/mole}) \\
 \frac{1}{2} (\text{O}_2 \rightarrow 2 \text{O}\cdot) & = & (0.5) (119.2 \text{ kcal/mole}) \\
 \hline
 \Delta H_f^\circ & = & -(-51.9 \text{ kcal/mole}) \\
 \hline
 D_{\text{Total}} & = & 938.0 \text{ kcal/mole}
 \end{array}$$

From Table 6.5, on Pt: $Q_{\text{C}} = 150 \text{ kcal/mole}$ and $Q_{\text{O}} = 85 \text{ kcal/mole}$.

- (a) For on-top adsorption ($\eta^1\mu_1$), use equation 6.35 with $n = 3$ for Pt(111). Molecule will bond O-end down; so

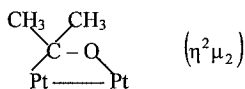
$Q_{\text{O-O}} = (3/5) (85)$ and from Table 6.7b, the bond energy associated with each C-CH₃ group is 376 kcal/mole , so

$$D_{\text{AB}} = D_{\text{C=O}} = 938.0 - 2 (376) = 186 \text{ kcal/mole.}$$

Then, for "weak" chemisorption, use equation 6.41:

$$Q_{(\text{CH}_3)_2\text{CO}} = \frac{Q_{\text{O-O}}^2}{Q_{\text{O-O}} + D_{(\text{CH}_3)_2\text{CO}}} = \frac{(0.6)^2 (85)^2}{(0.6) (85) + 186} = 11.0 \text{ kcal/mole}$$

(b) For di- σ -adsorption, i.e.,



equation 6.42 must be used, keeping in mind that atoms A and B can have other groups attached to alter the A-B bond energy, thus from part (a) $D_{AB} = D_{C=O} = 186$ kcal/mole.

From Eq. 6.43, $a = \frac{Q_{oC'}^2 (Q_{oC'} + 2 Q_{oO})}{(Q_{oC'} + Q_{oO})^2}$ where $Q_{oC'}$ represents the heat of

chemisorption of the quasi-atomic $(\text{CH}_3)_2\text{C}\cdot$ fragment. For this relatively large species, a reasonable way to calculate its heat of chemisorption is to again use eq. 6.41 where D_{AB} now represents the total bond energy of all the bonds formed by the secondary C atom, thus from Table 6.7b:

$$D_{AB} = 2 [D_{C-\text{CH}_3} - D_{\text{CH}_3}] = 2 [376 - 293] = 166 \text{ kcal/mole}$$

$$\text{so } Q_{oC'} = \frac{(0.6)^2 ((150))^2}{(0.6)(150) + 166} = 31.6 \text{ kcal/mole, then}$$

$$a = \frac{(31.6)^2 [31.6 + 2(51.0)]}{(31.6 + 51.0)^2} = \frac{1.33 \times 10^5}{6.82 \times 10^3} = 19.6 \text{ kcal/mole, and}$$

$$\text{from Eq. 6.44, } b = \frac{(51.0)^2 [51.0 + 2(31.6)]}{(51.0 + 31.6)^2} = \frac{2.97 \times 10^5}{6.82 \times 10^3} = 43.5 \text{ kcal/mole}$$

$$\text{thus } Q_{(\text{CH}_3)_2\text{CO}} = \frac{ab(a+b) + D_{AB}(a-b)^2}{ab + D_{AB}(a+b)} =$$

$$\frac{(19.6)(43.5)(19.6 + 43.5) + (186)(19.6 - 43.5)^2}{(19.6)(43.5) + (186)(19.6 + 43.5)} = \frac{1.60 \times 10^5}{1.26 \times 10^4} = 12.7 \approx 13 \text{ kcal/mole}$$

Problem 6.8 Solution

Rate constant for bimolecular surface rxn or desorption = $A_b < 10^{-4} \text{ cm}^2/\text{s}$

a. Collision theory, 2-dimensional gas $2 A_{\text{ad}} \rightarrow A_{2(\text{g})}$

$$r = P Z_{AA} [A_{\text{ad}}]^2 = A_b [A_{\text{ad}}]^2, \text{ Probability } P=1, \text{ \# collisions } = Z_{AA}$$

$$Z_{AA} = \sigma \bar{v} = \sigma \left(\frac{8 k_B T}{\pi m} \right)^{1/2} \text{ where } \sigma = \text{molecular diameter (molecule sweeps out an area)}$$

$$Z_{AA} \cong (2 \times 10^{-8} \text{ cm})(5 \times 10^4 \text{ cm/s}) \cong 10^{-3} \text{ cm}^2/\text{s} \quad (\text{given in ref. 11, p. 68})$$

b. Absolute rate theory, immobile adsorption: $\underbrace{2 A-S}_{\text{site pair}} \rightleftharpoons S-A_2-S \rightarrow A_2 + 2 S$

$$r = L_p (k_B T/h) \frac{Q^\ddagger}{Q_{A-S}^2} [A_{\text{ad}}]^2 = L_p (k_B T/h) \frac{Q^\ddagger}{Q_{SS}} [A_{\text{ad}}]^2 \quad \text{where}$$

$$L_p = \text{density of site pairs} = Z/2 L \Rightarrow (Z \cong 4), \text{ then}$$

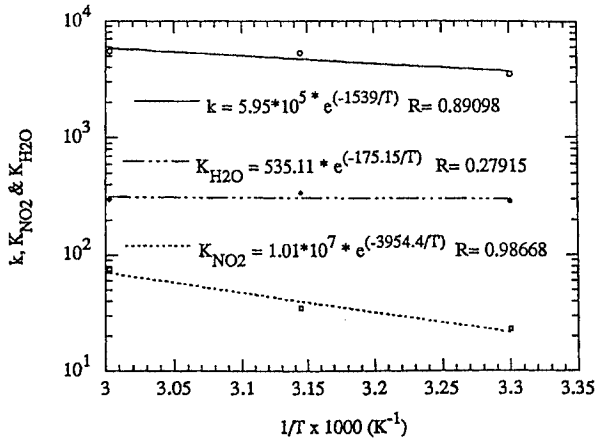
$$A_b = \frac{Z}{2 L} (k_B T/h) \frac{Q^\ddagger (\approx 1)}{Q_{A-S}^2 (\approx 1)} \cong \left(\frac{2}{10^{15}/\text{cm}^2} \right) (10^{13} \text{ s}^{-1}) \cong 2 \times 10^{-2} \text{ cm}^2/\text{s}$$

c. Absolute rate theory, 2-dimensional gas: $2 A_{\text{ad}} \rightleftharpoons A_{2 \text{ ad}} \rightarrow A_{2 \text{ g}}$

$$r = (k_B T/h) \frac{Q_{A_{2 \text{ ad}}}^\ddagger}{Q_{A_{\text{ad}}}^2} [A]^2 = (k_B T/h) \frac{q_{\text{tr}} (2-D) q_{\text{rot}}}{q_{\text{tr}} (2-D)^2} [A]^2 \Rightarrow A_b \cong (k_B T/h) \frac{(10^{17})(10)}{(10^{17})^2} \cong 10^{-3}$$

Problem 6.9 Solution

Figure a. Curves for Activation Energy, Enthalpy, Entropy Determination on activated carbon



From slope & intercept:

1) For NO₂

$$\Delta H_{ad}^{\circ} = + 7.9 \text{ kcal mole}^{-1}$$

$$\Delta S_{ad}^{\circ} = + 32.1 \text{ e.u.} \quad (1 \text{ e.u.} = 1 \text{ cal/mole} \cdot \text{K})$$

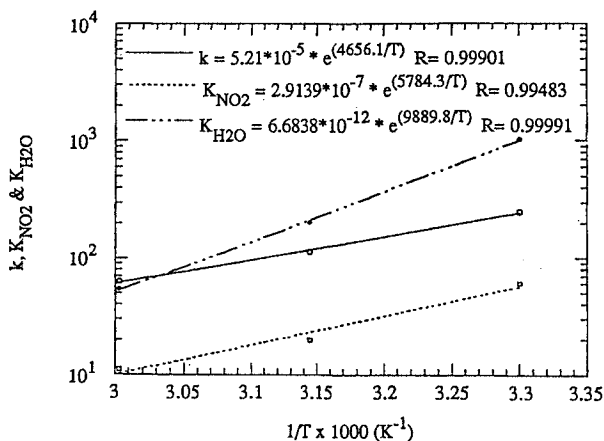
2) For H₂O

$$\Delta H_{ad}^{\circ} = + 0.4 \text{ kcal mole}^{-1}$$

$$\Delta S_{ad}^{\circ} = + 12.5 \text{ e.u.}$$

Not consistent \Rightarrow both ΔH & ΔS values are positive

Figure b. Curves for Activation Energy, Enthalpy and Entropy Determination on SiO_2



1) $E_a = -9.3 \text{ kcal mole}^{-1} \Rightarrow$ negative and inconsistent

2) For NO_2

$$\Delta H_{\text{ad}}^{\circ} = -11.5 \text{ kcal mole}^{-1}$$

$$\Delta S_{\text{ad}}^{\circ} = -29.9 \text{ e.u.}$$

$$S_{\text{g}}^{\circ} = 57 \text{ e.u.}$$

3) For H_2O

$$\Delta H_{\text{ad}}^{\circ} = -19.7 \text{ kcal mole}^{-1}$$

$$\Delta S_{\text{ad}}^{\circ} = -51.1 \text{ e.u.} \Rightarrow \text{inconsistent}$$

$$S_{\text{g}}^{\circ} = 45 \text{ e.u.} < | -51.1 \text{ e.u.} |$$

Problem 7.1 Solution

(a) SSA states that $d[O]/dt = 0 \Rightarrow r_1 = r_2 \therefore r = -d[O_3]/dt$

$$\frac{-d[O_3]}{dt} = r = 2 r_1 = 2 k_1 [O_3][M] \quad \text{or} \quad \frac{d[O_2]}{dt} = 3 k_1 [O_3][M]$$

(b) Cannot assume Quasi-Equilibrated Adsorption (No Langmuir isotherm)

$$r = \frac{d[CO_2]}{dt}; \quad @ \text{ steady state, so } r_1 = r_2, \quad \text{Site Balance: } L = [S-O] + [S]$$

$$k_1[N_2O][S] = k_2[CO][S-O] \Rightarrow [S-O] = (k_1/k_2)[N_2O][S]/[CO]$$

$$r = k_2[CO][S-O] = Lk_1k_2[CO][N_2O]/(k_1[N_2O] + k_2[CO])$$

(c) $r = d[CH_4]/dt = k_2[CH_{2ad}][H_2] \quad \& \quad K = \frac{[C_2H_{2ad}][H_2]^2}{[C_2H_6][S]}$

I. Literature solution for reaction as written

If $[C_2H_{2ad}]$ is MARI, then $L = [C_2H_{2ad}] + [S] \quad \&$

$$[C_2H_{2ad}] = K [C_2H_6][S]/[H_2]^2 = \frac{K[C_2H_6]}{[H_2]^2} (L - [C_2H_{2ad}])$$

$$[C_2H_{2ad}] \left(1 + K [C_2H_6]/[H_2]^2 \right) = \frac{LK [C_2H_6]}{[H_2]^2} \Rightarrow [C_2H_{2ad}] = \frac{LK [C_2H_6]}{[H_2]^2 \left(1 + K [C_2H_6]/[H_2]^2 \right)}$$

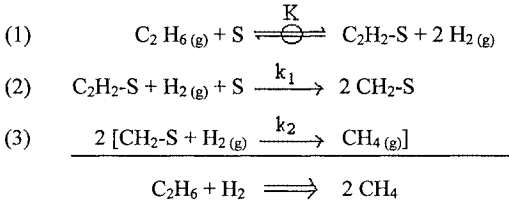
@ Steady State $\frac{d[CH_{2ad}]}{dt} = 0 \quad : \quad \frac{d\epsilon}{dt} = \frac{1}{2} \frac{d[CH_{2ad}]}{dt} = k_1 [C_2H_{2ad}][H_2]$

$$d\varepsilon/dt = -\frac{d[\text{CH}_2\text{ad}]}{dt} = k_2 [\text{CH}_2\text{ad}][\text{H}_2] \Rightarrow 2r_1 = r_2$$

$$2k_1 [\text{C}_2\text{H}_2\text{ad}][\text{H}_2] = k_2 [\text{CH}_2\text{ad}][\text{H}_2] \Rightarrow [\text{CH}_2\text{ad}] = 2(k_1/k_2)[\text{C}_2\text{H}_2\text{ad}]$$

$$d[\text{CH}_4]/dt = k_2 [\text{CH}_2\text{ad}][\text{H}_2] = \frac{2Lk_1K [\text{C}_2\text{H}_6][\text{H}_2]}{[\text{H}_2]^2 + K [\text{C}_2\text{H}_6]} = \frac{2Lk_1K [\text{C}_2\text{H}_6]}{[\text{H}_2] + K \frac{[\text{C}_2\text{H}_6]}{[\text{H}_2]}}$$

II. Alternate solution for reaction written with well defined sites, S, i.e.,



Note that a CH_2 group almost certainly requires a site for itself as shown in step 2.

$$r = \frac{d[\text{CH}_4]}{dt} = k_2 [\text{C}_2\text{H}_2\text{-S}][\text{H}_2] \quad \& \quad K = \frac{[\text{C}_2\text{H}_2\text{-S}][\text{H}_2]^2}{[\text{C}_2\text{H}_6][\text{S}]}$$

If $[\text{C}_2\text{H}_2\text{-S}]$ is the MARI, then $L = [\text{C}_2\text{H}_2\text{-S}] + [\text{S}]$ for the site balance, and

$$[\text{C}_2\text{H}_2\text{-S}] = K[\text{C}_2\text{H}_6][\text{S}]/[\text{H}_2]^2 = (K[\text{C}_2\text{H}_6]/[\text{H}_2]^2)(L - [\text{C}_2\text{H}_2\text{-S}]) \Rightarrow$$

$$[\text{C}_2\text{H}_2\text{-S}]\left(1 + K[\text{C}_2\text{H}_6]/[\text{H}_2]^2\right) = LK[\text{C}_2\text{H}_6]/[\text{H}_2]^2 \quad \&$$

$$[\text{C}_2\text{H}_2\text{-S}] = \frac{LK[\text{C}_2\text{H}_6]}{[\text{H}_2]^2\left(1 + K[\text{C}_2\text{H}_6]/[\text{H}_2]^2\right)}$$

$$\text{@ Steady state: } \frac{d[\text{CH}_2\text{-S}]}{dt} = 0 \quad \& \quad \frac{d\varepsilon}{dt} = \frac{1}{2} \frac{d[\text{CH}_2\text{-S}]}{dt} = k_1 [\text{C}_2\text{H}_2\text{-S}][\text{H}_2][\text{S}] \quad \&$$

$$\frac{d\varepsilon}{dt} = -\frac{d[\text{CH}_2\text{-S}]}{dt} = k_2 [\text{CH}_2\text{-S}][\text{H}_2] \Rightarrow 2r_1 = r_2, \text{ so}$$

$$2k_1 [C_2H_2 - S][H_2][S] = k_2 [CH_2 - S][H_2] \Rightarrow [CH_2 - S] = 2(k_1/k_2)[C_2H_2 - S][S]$$

$$[S] = L[H_2]^2 / ([H_2]^2 + K[C_2H_6]) \quad \text{so}$$

$$\begin{aligned} \frac{d[CH_4]}{dt} &= k_2 [CH_2 - S][H_2] = \left(\frac{Z}{2L}\right) 2L^2 k_1 K [C_2H_6][H_2]^3 / ([H_2]^2 + K[C_2H_6])^2 \\ &= \frac{k' [C_2H_6][H_2]^3}{([H_2]^2 + K[C_2H_6])^2} = \frac{k' [C_2H_6]}{[H_2] \left(1 + \frac{K[C_2H_6]}{[H_2]^2}\right)^2} = r \end{aligned}$$

Problem 7.2 Solution

$$r = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_3 [B-S]$$

$$K_1 = \frac{[A-S]}{[A][S]}, \quad K_2 = \frac{[B-S]}{[A-S]}$$

Site balance: $L = [S] + [A-S] + [B-S]$

(a) If $[B-S]$ is the MARI, then $L = [S] + [B-S]$ and

$$L = [S] + K_2[A-S] = [S] + K_1K_2[A][S] \Rightarrow [S] = \frac{L}{(1 + K_1K_2[A])}$$

$$r = k_3K_2[A-S] = K_1K_2k_3[A][S] = \frac{Lk_3K_1K_2[A]}{(1 + K_1K_2[A])}$$

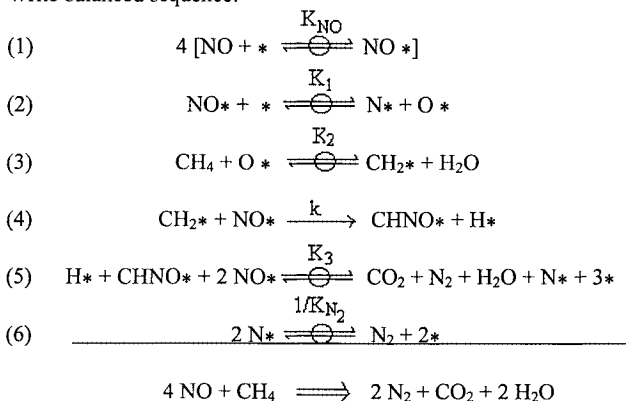
(b) If $[A-S]$ is the MARI, then $L = [S] + [A-S]$ and $L = [S] + K_1[A][S] \Rightarrow [S] = \frac{L}{(1 + K_1[A])}$

$$r = k_3K_2[A-S] = K_1K_2k_3[A][S] = \frac{Lk_3K_1K_2[A]}{(1 + K_1[A])}$$

The mathematical forms are identical.

Problem 7.3 Solution

Write balanced sequence:



Step 4 is RDS $\therefore r = k [\text{CH}_2 *][\text{NO} *]$

$$[\text{CH}_2 *] = \frac{K_2 P_{\text{CH}_4} [\text{O} *]}{P_{\text{H}_2\text{O}}}, \quad [\text{O} *] = \frac{K_1 [\text{NO} *][*]}{[\text{N} *]}, \quad [\text{NO} *] = K_{\text{NO}} P_{\text{NO}} [*]$$

$$[\text{O} *] = \frac{K_1 K_{\text{NO}} P_{\text{NO}} [*]^2}{[\text{N} *]}, \quad [\text{N} *]^2 = K_{\text{N}_2} P_{\text{N}_2} [*]^2$$

$$[\text{O} *] = \frac{K_1 K_{\text{NO}} P_{\text{NO}} [*]}{K_{\text{N}_2}^{1/2} P_{\text{N}_2}^{1/2}}, \quad [\text{CH}_2 *] = \frac{K_2 P_{\text{CH}_4} K_1 K_{\text{NO}} [*]}{K_{\text{N}_2}^{1/2} P_{\text{N}_2}^{1/2} P_{\text{H}_2\text{O}}}$$

$$r = \frac{k K_1 K_2 K_{\text{NO}}^2 P_{\text{CH}_4} P_{\text{NO}}^2 [*]^2}{K_{\text{N}_2}^{1/2} P_{\text{N}_2}^{1/2} P_{\text{H}_2\text{O}}}$$

$$L = [*] + [\text{NO} *] + [\text{CH}_2 *] = [*] + K_{\text{NO}} P_{\text{NO}} [*] + \frac{K_1 K_2 K_{\text{NO}} P_{\text{CH}_4} P_{\text{NO}} [*]}{K_{\text{N}_2}^{1/2} P_{\text{N}_2}^{1/2} P_{\text{H}_2\text{O}}}$$

$$[*] = \frac{L}{\left(1 + K_{\text{NO}} P_{\text{NO}} + \frac{K P_{\text{CH}_4} P_{\text{NO}}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2\text{O}}} \right)} \quad \text{where } K = \frac{K_1 K_2 K_{\text{NO}}}{K_{\text{N}_2}^{1/2}}$$

and

$$r = \frac{LkK_1K_2K_{\text{NO}}^2P_{\text{CH}_4}P_{\text{NO}}^2}{K_{\text{N}_2}^{1/2}P_{\text{N}_2}^{1/2}P_{\text{H}_2\text{O}} \left(1 + K_{\text{NO}}P_{\text{NO}} + \frac{KP_{\text{CH}_4}P_{\text{NO}}}{P_{\text{N}_2}^{1/2}P_{\text{H}_2\text{O}}} \right)^2}$$

Problem 7.4 Solution

$$r = \frac{-d[\text{H}_2\text{O}]}{dt} = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{CO}_2]}{dt}$$

$$r = k_3[\text{H}_2\text{O}^*] = k_4[\text{O}^*][\text{CO}^*] \quad \text{and} \quad K_1 = \frac{[\text{CO}^*]}{P_{\text{CO}}[*]}$$

$$L = [*] + [\text{CO}^*] + [\text{H}_2\text{O}^*] + [\text{O}^*] \quad (\text{Site balance})$$

Steady-state approximations:

$$\text{on } \text{H}_2\text{O}^* : k_2 P_{\text{H}_2\text{O}}[*] = k_3[\text{H}_2\text{O}^*]$$

$$\text{on } \text{O}^* : k_3[\text{H}_2\text{O}^*] = k_4[\text{O}^*][\text{CO}^*]$$

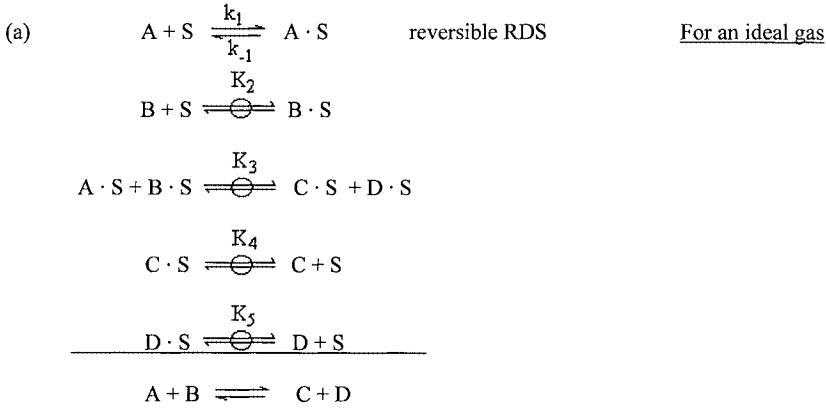
$$[\text{H}_2\text{O}^*] = \left(\frac{k_2}{k_3}\right) P_{\text{H}_2\text{O}}[*] \quad \& \quad [\text{O}^*] = \left(\frac{k_3}{k_4}\right) [\text{H}_2\text{O}^*]/[\text{CO}^*]$$

$$L = K_1 P_{\text{CO}}[*] + \left(\frac{k_2}{k_3}\right) P_{\text{H}_2\text{O}}[*] + [*] + \left(\frac{k_3}{k_4}\right) [\text{H}_2\text{O}^*]/[\text{CO}^*], \text{ the last term is negligible, so}$$

$$L = \left(K_1 P_{\text{CO}} + \left(\frac{k_2}{k_3}\right) P_{\text{H}_2\text{O}} + 1 \right) [*]$$

$$r = k_3[\text{H}_2\text{O}^*] = \frac{k_3 \cdot k_2 P_{\text{H}_2\text{O}}}{k_3} [*] = \frac{L k_2 P_{\text{H}_2\text{O}}}{(1 + K_1 P_{\text{CO}} + k' P_{\text{H}_2\text{O}})}$$

Problem 7.5 Solution



$$r = k_1 P_A [S] - k_{-1} [A \cdot S] \quad , \quad L = [S] + [A \cdot S] + [B \cdot S] + [C \cdot S] + [D \cdot S] \quad (\text{from site balance})$$

$$[B \cdot S] = K_2 P_B [S] \quad , \quad [C \cdot S] = \frac{P_C [S]}{K_4} \quad , \quad [D \cdot S] = \frac{P_D [S]}{K_5} \quad , \quad [A \cdot S] = \frac{[C \cdot S][D \cdot S]}{K_3 [B \cdot S]}$$

$$K = \frac{P_C P_D}{P_A P_B} = K_1 K_2 K_3 K_4 K_5$$

$$[A \cdot S] = \frac{P_C P_D [S]}{K_4 K_5 K_3 K_2 P_B}$$

$$L = [S] \left(1 + P_C P_D / K_2 K_3 K_4 K_5 P_B + K_2 P_B + \frac{1}{K_4 P_C} + \frac{1}{K_5 P_D} \right) \Rightarrow$$

$$r = \left[L k_1 P_A - \frac{L k_{-1} P_C P_D}{K_2 K_3 K_4 K_5 P_B} \right] [S] = \frac{L k_1 P_A - L k_{-1} P_C P_D / K_2 K_3 K_4 K_5 P_B}{\left(1 + P_C P_D / K_2 K_3 K_4 K_5 P_B + K_2 P_B + P_C / K_4 + P_D / K_5 \right)}$$

or

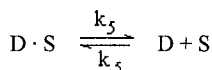
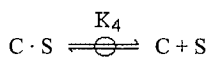
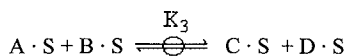
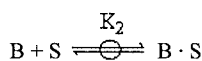
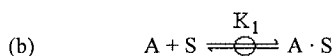
Let $k_1 = k_A$, $k_{-1} = k_{-A}$, $K_2 = K_B$, $K_4 = 1/K_C$, $K_5 = 1/K_D$, then

$$K_3 = K/K_1K_2K_4K_5 = KK_CK_D/K_AK_B \quad \text{and} \quad K_A = k_A/k_{-A} \quad \text{so,}$$

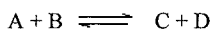
$$K_2K_3K_4K_5 = K/K_1 = K/K_A = K k_{-A}/k_A = K k_{-1}/k_1$$

substitution gives

$$r = \frac{Lk_1(P_A - P_C P_D / K P_B)}{(1 + K_A P_C P_D / K P_B + K_B P_B + K_C P_C + K_D P_D)}$$



Reversible RDS



$$r = k_5[D \cdot S] - k_{-5}P_D[S], \quad L = [A \cdot S] + [B \cdot S] + [C \cdot S] + [D \cdot S] + [S] \quad (\text{from site balance})$$

$$[A \cdot S] = K_1 P_A [S], [B \cdot S] = K_2 P_B [S], [C \cdot S] = P_C [S] / K_4, K_3 = \frac{[C \cdot S][D \cdot S]}{[A \cdot S][B \cdot S]} \quad \text{so}$$

$$[D \cdot S] = K_3 [A \cdot S][B \cdot S] / [C \cdot S] = K_1 K_2 K_3 K_4 P_A P_B [S] / P_C$$

$$L = [S] (1 + K_1 P_A + K_2 P_B + P_C / K_4 + K_1 K_2 K_3 K_4 P_A P_B / P_C) \quad \text{so}$$

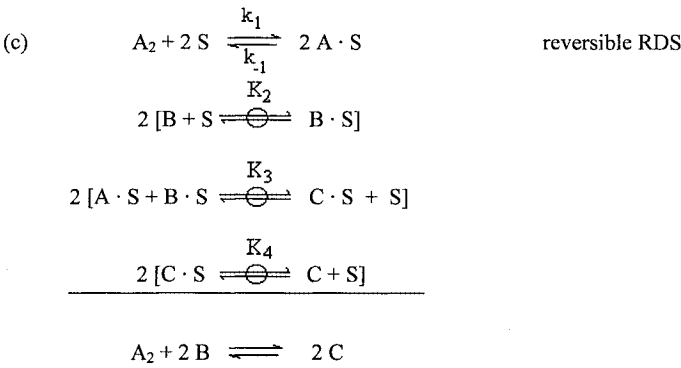
$$r = \frac{Lk_5K_1K_2K_3K_4P_A P_B/P_C - Lk_{-5}P_D}{(1 + K_1P_A + K_2P_B + P_C/K_4 + K_1K_2K_3K_4P_A P_B/P_C)}$$

Now $K = K_1K_2K_3K_4K_5$ and $K_1 = K_A, K_2 = K_B, 1/K_4 = K_C,$

$$1/K_5 = K_D = k_{-5}/k_5, K_1K_2K_3K_4 = K/K_5 = k_{-5}K/k_5$$

substitution gives

$$r = \frac{Lk_{-5}KP_A P_B/P_C - Lk_{-5}P_D}{(1 + K_A P_A + K_B P_B + K_C P_C + K_D KP_A P_B/P_C)}$$



$$r = k_1 P_{A_2} [S]^2 - k_{-1} [A \cdot S]^2, \quad L = [A \cdot S] + [B \cdot S] + [C \cdot S] + [S] \quad (\text{from site balance})$$

$$[B \cdot S] = K_2 P_B [S], \quad [C \cdot S] = \frac{P_C [S]}{K_4}, \quad K_3 = \frac{[C \cdot S][S]}{[A \cdot S][B \cdot S]}$$

$$[A \cdot S] = \frac{[C \cdot S][S]}{K_3 [B \cdot S]}, \quad K = K_1 K_2^2 K_3^2 K_4^2 \quad \text{or} \quad K^{1/2} = K_1^{1/2} K_2 K_3 K_4, \quad \text{so}$$

$$[A \cdot S] = \frac{P_C [S]}{K_2 K_3 K_4 P_B}$$

$$L = [S] \left(1 + P_C / K_2 K_3 K_4 P_B + K_2 P_B + P_C / K_4 \right) \text{ so}$$

$$r = \frac{(Z/2L)L^2 k_1 P_{A_2} - (Z/2L)L^2 k_{-1} (P_C / K_2 K_3 K_4 P_B)^2}{\left(1 + P_C / K_2 K_3 K_4 P_B + K_2 P_B + P_C / K_4 \right)^2}$$

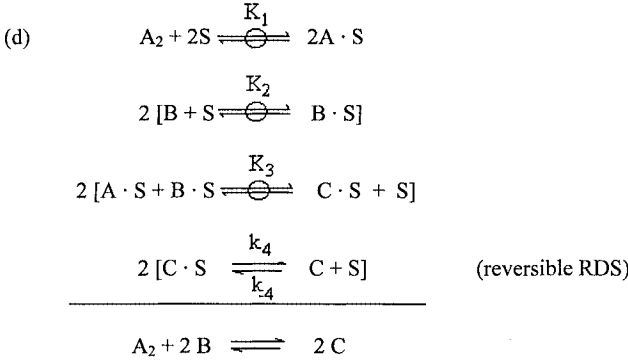
with site-pair probability of $(Z/2L)$

where $Z =$ coordination number

or, because

$$K_2 K_3 K_4 = K^{1/2} / K_1^{1/2}$$

$$r = \frac{L k_1' (P_{A_2} - P_C^2 / K P_B^2)}{\left(1 + K_1^{1/2} P_C / K^{1/2} P_B + K_2 P_B + K_3 P_C \right)^2}$$



$$r = k_4 [C \cdot S] - k_{-4} P_C [S] \quad , \quad [A \cdot S]^2 = K_1 P_{A_2} [S]^2 \quad , \quad [B \cdot S] = K_2 P_B [S] \quad ,$$

$$K_3 = \frac{[C \cdot S][S]}{[A \cdot S][B \cdot S]} \Rightarrow [C \cdot S] = \frac{K_3 [A \cdot S][B \cdot S]}{[S]} = K_1^{1/2} K_2 K_3 P_{A_2}^{1/2} P_B [S]$$

$$L = [S] + [A \cdot S] + [B \cdot S] + [C \cdot S] = [S] \left(1 + K_1^{1/2} P_{A_2}^{1/2} + K_2 P_B + K_1^{1/2} K_2 K_3 P_{A_2}^{1/2} P_B \right) \quad \text{(from site balance)}$$

$$K = K_1 K_2^2 K_3^2 K_4^2 \Rightarrow K_1^{1/2} K_2 K_3 = K^{1/2} / K_4 \quad \text{so}$$

$$r = \frac{(Z/2L)L^2 k_4 K_1^{1/2} K_2 K_3 P_{A_2}^{1/2} P_B - (Z/2L)L^2 k_{-4} P_C}{\left(1 + K_1^{1/2} P_{A_2}^{1/2} + K_2 P_B + K_1^{1/2} K_2 K_3 P_{A_2}^{1/2} P_B\right)}$$

Now with $K_1 = K_{A_2}$, $K_2 = K_B$, $1/K_4 = K_C \Rightarrow K = K_A K_B^2 K_3^2 K_4^2$ so

$$r = \frac{L(Z/2)k_{-4} \left(K^{1/2} P_{A_2}^{1/2} P_B - P_C\right)}{\left(1 + K_{A_2}^{1/2} P_{A_2}^{1/2} + K_B P_B + K K_C P_{A_2}^{1/2} P_B\right)}$$

Problem 7.6 Solution

$$(a) \quad r = \frac{-d[C_2H_6]}{dt} = Lk_3\theta_{C_2H_4}P_{H_2}$$

$$K_2 = \frac{\theta_{C_2H_4}P_{H_2}}{\theta_{C_2H_5}\theta_H}$$

Use steady-state approximation for total surface carbon atoms to get another equation for $\theta_{C_2H_5}$,

i.e., $\frac{d\theta_{C(\text{total})}}{dt} = 0$. Then, because steps 2 and 4 are very rapid:

$$\frac{d\theta_{C(\text{Total})}}{dt} = k_1P_{C_2H_6} - Lk_{-1}\theta_{C_2H_5}\theta_H - Lk_3\theta_{C_2H_4}P_{H_2} = 0 \Rightarrow$$

$$k_1P_{C_2H_6} - Lk_3\theta_{C_2H_4}P_{H_2} = Lk_{-1}\theta_{C_2H_5}\theta_H \Rightarrow \theta_{C_2H_5} = \frac{k_1P_{C_2H_6} - Lk_3\theta_{C_2H_4}P_{H_2}}{Lk_{-1}\theta_H}$$

$$\theta_{C_2H_4} = \left(\frac{K_2\theta_H}{P_{H_2}} \right) \left(\frac{k_1P_{C_2H_6} - Lk_3\theta_{C_2H_4}P_{H_2}}{Lk_{-1}\theta_H} \right) = \frac{K_2k_1P_{C_2H_6}}{Lk_{-1}P_{H_2}} - \frac{LK_2k_3\theta_{C_2H_4}}{Lk_{-1}} \Rightarrow$$

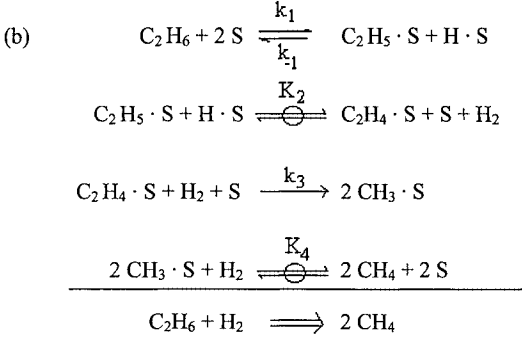
$$\theta_{C_2H_4} \left(1 + K_2k_3/k_{-1} \right) = \frac{k_1K_2P_{C_2H_6}}{Lk_{-1}P_{H_2}} \Rightarrow \theta_{C_2H_4} = \frac{(k_1K_2/Lk_{-1})P_{C_2H_6}/P_{H_2}}{(1 + K_2k_3/k_{-1})} \quad \text{and}$$

$$r = \frac{Lk_3P_{H_2}k_1K_2P_{C_2H_6}/Lk_{-1}P_{H_2}}{(1 + K_2k_3/k_{-1})} = \frac{k_1K_2k_3P_{C_2H_6}}{(1 + K_2k_3/k_{-1})} = k'P_{C_2H_6}$$

but $\theta_{C_2H_4}$ can be rewritten to give:

$$\theta_{C_2H_4} = \frac{(k_1/k_3)P_{C_2H_6}/P_{H_2}}{L(1 + k_{-1}/K_2k_3)} \quad \text{so that} \quad r = \frac{k_1P_{C_2H_6}}{1 + k_{-1}/K_2k_3}$$

which is notation consistent with reference 55.



$$r = -\frac{d[\text{C}_2\text{H}_6]}{dt} = k_3[\text{C}_2\text{H}_4 \cdot \text{S}][\text{S}]P_{\text{H}_2}$$

$$K_2 = \frac{[\text{C}_2\text{H}_4 \cdot \text{S}][\text{S}]P_{\text{H}_2}}{[\text{C}_2\text{H}_5 \cdot \text{S}][\text{H} \cdot \text{S}]}$$

Steady-state approximation on all surface C atoms gives:

$$k_1 P_{\text{C}_2\text{H}_6} [\text{S}]^2 - k_{-1} [\text{C}_2\text{H}_5 \cdot \text{S}][\text{H} \cdot \text{S}] - k_3 [\text{C}_2\text{H}_4 \cdot \text{S}][\text{S}]P_{\text{H}_2} = 0$$

$$k_1 P_{\text{C}_2\text{H}_6} [\text{S}]^2 - k_3 [\text{C}_2\text{H}_4 \cdot \text{S}][\text{S}]P_{\text{H}_2} = k_{-1} [\text{C}_2\text{H}_5 \cdot \text{S}][\text{H} \cdot \text{S}] \quad \text{and}$$

$$[\text{C}_2\text{H}_5 \cdot \text{S}] = \frac{k_1 P_{\text{C}_2\text{H}_6} [\text{S}]^2}{k_{-1} [\text{H} \cdot \text{S}]} - \frac{k_3 [\text{C}_2\text{H}_4 \cdot \text{S}][\text{S}]P_{\text{H}_2}}{k_{-1} [\text{H} \cdot \text{S}]}$$

$$[\text{C}_2\text{H}_4 \cdot \text{S}] = \left(\frac{K_2 [\text{H} \cdot \text{S}]}{[\text{S}]P_{\text{H}_2}} \right) \left(\frac{k_1 P_{\text{C}_2\text{H}_6} [\text{S}]^2 - k_3 [\text{C}_2\text{H}_4 \cdot \text{S}][\text{S}]P_{\text{H}_2}}{k_{-1} [\text{H} \cdot \text{S}]} \right)$$

$$[\text{C}_2\text{H}_4 \cdot \text{S}](1 + K_2 k_3/k_{-1}) = \frac{k_1 K_2 P_{\text{C}_2\text{H}_6}}{k_{-1} P_{\text{H}_2}} \Rightarrow [\text{C}_2\text{H}_4 \cdot \text{S}] = \frac{(k_1 K_2/k_{-1}) P_{\text{C}_2\text{H}_6}/P_{\text{H}_2}}{1 + K_2 k_3/k_{-1}}$$

Now, site balance to get [S] is:

$$L = [S] + [H \cdot S] + [C_2H_5 \cdot S] + [C_2H_4 \cdot S] + [CH_3 \cdot S]$$

Agreement with (a) is achieved only if $[S] \cong L$, i.e., the surface is essentially free of all adsorbed species, i.e.,

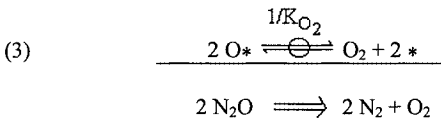
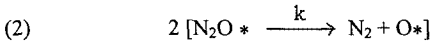
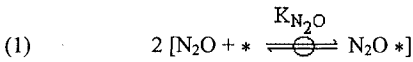
$\theta_H, \theta_{C_2H_5}, \theta_{C_2H_4}, \theta_{CH_3} \ll 1$. This a questionable assumption.

Problem 7.7 Solution

Plotting \ln rate vs. $\ln P_i$ using a power rate law gives the following reaction orders:

T(K)	Reaction Order		
	$\frac{N_2O}{O_2}$	$\frac{O_2}{N_2}$	$\frac{N_2}{O_2}$
623	0.08	-0.31	0
653	0.24	-0.12	0
673	0.31	-0.07	0

The simplest L-H model would be for unimolecular decomposition:



$$r_m = \frac{1}{m} \frac{dN_{N_2}}{dt} = \frac{1}{m} \left(-\frac{dN_{N_2O}}{dt} \right) = k [N_2O *]$$

$$\text{From (1): } K_{N_2O} = \frac{[N_2O *]}{P_{N_2O} [*]}, \quad \text{so } [N_2O *] = K_{N_2O} P_{N_2O} [*]$$

$$\text{From (3): } K_{O_2} = \frac{[O*]^2}{P_{O_2} [*]^2}, \quad \text{so } [O*] = K_{O_2}^{1/2} P_{O_2}^{1/2} [*]$$

$$\text{Site balance gives: } L = [*] + [N_2O *] + [O*] \quad \text{thus}$$

$$L = [*] + K_{N_2O} P_{N_2O} [*] + K_{O_2}^{1/2} P_{O_2}^{1/2} [*], \quad \text{and } [*] = L / (1 + K_{N_2O} P_{N_2O} + K_{O_2}^{1/2} P_{O_2}^{1/2}),$$

consequently,

$$r = k K_{N_2O} P_{N_2O} [*] = L k K_{N_2O} P_{N_2O} / (1 + K_{N_2O} P_{N_2O} + K_{O_2}^{1/2} P_{O_2}^{1/2})$$

Arrhenius plots of the fitting parameters listed in Table 2 provide the following values:

For K_{N_2O} : $\Delta H_{ad}^{\circ} = -17 \text{ kcal mole}^{-1}$ and $\Delta S_{ad}^{\circ} = -21 \text{ cal mole}^{-1} \text{ K}^{-1}$ (e.u.)

For K_{O_2} : $\Delta H_{ad}^{\circ} = -25 \text{ kcal mole}^{-1}$ and $\Delta S_{ad}^{\circ} = -35 \text{ e.u.}$

For k : $E_{RDS} = 57 \text{ kcal mole}^{-1}$

The enthalpy and entropy values for adsorption fulfill all the guidelines in Table 6.9, thus they are consistent.

From either a linear extrapolation of the high-P portions of the two isotherms in Figure 1 or using the difference between the two at 100 Torr CO pressure, the irreversible uptake is $580 \mu\text{mole CO g}_{cat}^{-1}$. The dispersion of Cu is: $D_{Cu} = Cu_s / Cu_{tot}$, and with $CO_{ad} / Cu_s = 1$,

$$D_{Cu} = \frac{580 \mu\text{mole Cu}_s \text{ g}_{cat}^{-1}}{\left(0.0456 \text{ g Cu g}_{cat}^{-1}\right)\left(\text{mole Cu}/63.55 \text{ g Cu}\right)\left(10^6 \mu\text{mole}/\text{mole}\right)} = 0.81$$

Under differential reaction conditions, $P_{O_2} \approx 0$ and can be ignored; therefore, an easy way is to choose a known differential rate and correct for temperature, for example:

$$\frac{r_{823K}}{r_{673K}} = \frac{k_{823K}}{k_{673K}} = \frac{e^{-36200 \text{ cal}/\text{mole}/(1.987 \text{ cal}/\text{mole}\cdot\text{K})(823K)}}{e^{-36200 \text{ cal}/\text{mole}/(1.987 \text{ cal}/\text{mole}\cdot\text{K})(673K)}} = 139 \quad \text{thus}$$

$$TOF_{823K} = \frac{r_{823K}}{Cu_s} = \frac{(12.6 \mu\text{mole}/\text{s} \cdot \text{g})\left(13 \text{ atm}^{-1}\right)\left(0.0666 \text{ atm}\right)(139)}{\left[1 + \left(13 \text{ atm}^{-1}\right)\left(0.0666 \text{ atm}\right)\right]\left(580 \mu\text{mole Cu}_s / \text{g}\right)} = 1.4 \text{ s}^{-1}$$

Problem 7.8 Solution

Step 2 defines the rate:

$$r_m = \frac{1}{m} \frac{dN_{N_2}}{dt} = \frac{1}{m} \left(- \frac{dN_{N_2O}}{dt} \right) = k[N_2O^*]$$

Step 1 gives: $K_{N_2O} = \frac{[N_2O^*]}{P_{N_2O}[^*]}$, so $[N_2O^*] = K_{N_2O} P_{N_2O} [^*]$

Assuming all surface species are included, a site balance gives

$$L = [^*] + [N_2O^*] + [O^*]$$

To remove the unknown $[O^*]$, the SSA must be used :

$$\frac{d[O^*]}{dt} = k[N_2O^*] + k_{-1}P_{O_2}[^*]^2 - k_1[O^*]^2 = 0$$

and

$$[O^*] = \left(\frac{k[N_2O^*] + k_{-1}P_{O_2}[^*]^2}{k_1} \right)^{1/2}$$

$$\text{Then } L = [^*] + K_{N_2O} P_{N_2O} [^*] + \left(\frac{k[N_2O^*] + k_{-1}P_{O_2}[^*]^2}{k_1} \right)^{1/2} = z[^*] + (x[^*] + y[^*]^2)^{1/2}$$

where $z = 1 + K_{N_2O} P_{N_2O}$, $x = kK_{N_2O} P_{N_2O} / k_1$, and $y = k_{-1} P_{O_2} / k_1$.

Rearranging and squaring each side gives:

$$x[^*] + y[^*]^2 = (L - z[^*])^2 = L^2 - 2Lz[^*] + z^2[^*]^2$$

and

$$(y - z^2)[^*]^2 + (x + 2Lz)[^*] - L^2 = 0$$

The solution for this quadratic expression is:

$$[*] = \frac{(x + 2Lz) \pm (x^2 + 4Lxz + 4yL^2)^{1/2}}{2(y - z^2)}$$

Substituting back and using the positive root gives:

$$[*] = \frac{kK_{N_2O} P_{N_2O}/k_1 + 2L(1 + K_{N_2O} P_{N_2O})}{-2[k_{-1} P_{O_2}/k_1 - (1 + K_{N_2O} P_{N_2O})^2]} + \frac{\left[\left(\frac{kK_{N_2O} P_{N_2O}}{k_1} \right)^2 + \frac{4LkK_{N_2O} P_{N_2O} (1 + K_{N_2O} P_{N_2O})}{k_1} + \frac{4L^2 k_{-1} P_{O_2}}{k_1} \right]^{1/2}}{-2[k_{-1} P_{O_2}/k_1 - (1 + K_{N_2O} P_{N_2O})^2]}$$

Because the rate is: $r_m = k[N_2O*] = kK_{N_2O} P_{N_2O} [*]$, the final rate expression is:

$$r_m = \frac{dP_{N_2O} \left\{ 1 + (a + c)P_{N_2O} + [aP_{N_2O} + (a^2 + ac)P_{N_2O} + bP_{O_2}]^{1/2} \right\}}{(1 + cP_{N_2O})^2 - bP_{O_2}}$$

where $a = kK_{N_2O}/k_1$, $b = k_{-1}/k_1$, $c = K_{N_2O}$ and $d = LkK_{N_2O}$. Note that these four parameters can be combined in various ways to give the values in Table 1.

An Arrhenius plot of the adsorption equilibrium constant, K_{N_2O} , gives $\Delta H_{ad}^\circ = -25.2$ kcal mole⁻¹ and $\Delta S_{ad}^\circ = -33$ e.u., which satisfy the guidelines in Table 6.9.

The rate constant Lk represents a unimolecular decomposition reaction on the surface, so guideline 2 in Table 6.10 can be applied:

$$r_a = r_m / A_{\text{cu,g}} = \left(\frac{1.1 \mu\text{mole}}{\text{s} \cdot \text{g cat}} \right) \left(\frac{1 \text{ g cat}}{2(354 \mu\text{mole Cu}_s)} \right) \left(\frac{\sim 10^{15} \text{ Cu}_s}{\text{cm}^2 \text{ Cu}} \right) \cong 2 \times 10^{12} \frac{\text{molecule}}{\text{s cm}^2}$$

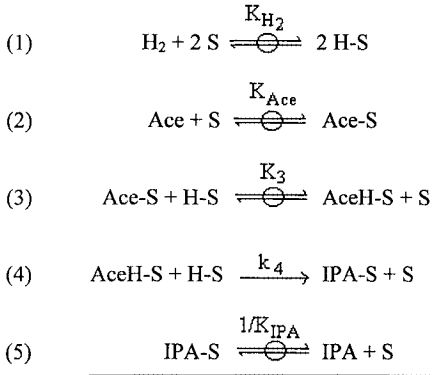
or, with correction for activation energy:

$$LA_d e^{-34400/1.987 \cdot 843} = 2 \times 10^{12} = 1.2 \times 10^{-9} LA_d \quad \text{and} \quad LA_d = 2 \times 10^{21} \text{ molecule/s cm}_s$$

Both values are below 10^{28} molecule/s cm^2 .

Problem 7.9 Solution

One has dissociative H_2 adsorption, and to get a negative dependence on a reactant (acetone), the denominator must be squared, which indicates a bimolecular surface reaction as a RDS with competitive adsorption between acetone (Ace) molecules and H atoms for active sites, so:



To get a 1st-order dependence on H_2 , step 4 and not step 3 must be the RDS.

The overall site balance appears to be simplified to:

$$L = [S] + [Ace] = [S] + K_{Ace} P_{Ace} [S] \quad (1)$$

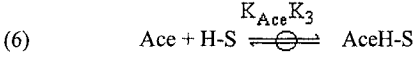
because there is no dependence on IPA at these differential conversions and the dependence on P_{H_2} must be as close to unity as possible, so $[Ace-S]$ is the MARI. Therefore,

$$r_m = \frac{1}{m} \frac{dN_{IPA}}{dt} = k_4 [AceH-S] [H-S] \quad (2)$$

and

$$[H-S] = K_{H_2}^{1/2} P_{H_2}^{1/2} [S] \quad \text{from step 1.} \quad (3)$$

Now steps 2 and 3 can be added to get



so

$$[\text{AceH-S}] = K_{\text{Ace}} K_3 P_{\text{Ace}} [H-S] = K_{H_2}^{1/2} K_{\text{Ace}} K_3 P_{H_2}^{1/2} P_{\text{Ace}} \quad (4)$$

Consequently, from equation 1:

$$[S] = L / (1 + K_{\text{Ace}} P_{\text{Ace}}) \quad (5)$$

and

$$r_m = k_4 K_{\text{Ace}} K_3 P_{\text{Ace}} [H-S]^2 = k_4 K_{\text{Ace}} K_{H_2} K_3 P_{\text{Ace}} P_{H_2} [S]^2 = \frac{L k_4' K_{\text{Ace}} K_{H_2} K_3 P_{\text{Ace}} P_{H_2}}{(1 + K_{\text{Ace}} P_{\text{Ace}})^2} \quad (6)$$

(Q_{ad} → Add later)

Problem 7.10 Solution

(a) The rate, defined by N_2 formation, is $r = \frac{d[N_2]}{dt} = \frac{-1}{2} \frac{d[NO]}{dt} = k_2 [N^*]^2$

From the 3 quasi-equilibrated steps:

$$[NO^*] = K_{NO} P_{NO} [^*], [N^*][O^*] = K_1 [NO^*][^*] \text{ and } [O^*] = K_{O_2}^{1/2} P_{O_2}^{1/2} [^*]$$

$$[N^*] = \frac{K_1 [NO^*][^*]}{[O^*]} = \frac{K_1 K_{NO} P_{NO} [^*]^2}{[O^*]} = \frac{K_1 K_{NO} P_{NO} [^*]^2}{K_{O_2}^{1/2} P_{O_2}^{1/2} [^*]}$$

Site balance gives : $L = [^*] + [NO^*] + [N^*] + [O^*] \Rightarrow$

$$L = [^*] + K_{NO} P_{NO} [^*] + \frac{K_1 K_{NO} P_{NO}}{K_{O_2}^{1/2} P_{O_2}^{1/2}} [^*]^2 + K_{O_2}^{1/2} P_{O_2}^{1/2} [^*] \quad \text{so}$$

$$[^*] = L / \left(1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2} + K_1 K_{NO} P_{NO} / K_{O_2}^{1/2} P_{O_2}^{1/2} \right),$$

for site pairs : $\frac{Z}{2L}$ is the probability factor, so

$$r = \frac{ZL}{2} k_2 K_1^2 K_{NO}^2 P_{NO}^2 [^*]^2 / K_{O_2} P_{O_2}$$

$$= L k_2' K_1^2 K_{NO}^2 P_{NO}^2 / K_{O_2} P_{O_2} \left(1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2} + K_1 K_{NO} P_{NO} / K_{O_2}^{1/2} P_{O_2}^{1/2} \right)^2$$

or $r = k P_{NO} / \left(K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{O_2}^{1/2} K_{NO} P_{O_2}^{1/2} P_{NO} + K_{O_2} P_{O_2} + K_1 K_{NO} P_{NO} \right)^2$

(b) $[NO^*] \approx O \Rightarrow r = k P_{NO}^2 / \left(K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{O_2} P_{O_2} + K_1 K_{NO} P_{NO} \right)^2$

(c) $[NO^*]$ is MARI $\Rightarrow r = k P_{NO}^2 / \left(K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{O_2}^{1/2} K_{NO} P_{O_2}^{1/2} P_{NO} \right)^2$

(d) $[O^*] \approx O \Rightarrow r = k P_{NO}^2 / \left(K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{O_2}^{1/2} K_{NO} P_{O_2}^{1/2} P_{NO} + K_1 K_{NO} P_{NO} \right)^2$

(e) $[O^*]$ is MARI $\Rightarrow r = k P_{NO}^2 / \left(K_{O_2}^{1/2} P_{O_2}^{1/2} + K_{O_2} P_{O_2} \right)^2$

$$(f) \quad [N^*] \text{ is MARI} \Rightarrow r = k P_{NO}^2 / (K_{O_2}^{1/2} P_{O_2}^{1/2} + K_1 K_{NO} P_{NO})^2$$

$$(g) \quad [N^*] \text{ near saturation } (>> [^*]) \Rightarrow [N^*] \cong L \Rightarrow r = \frac{Z}{2L} k_2 L^2 = L k_2'$$

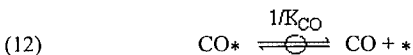
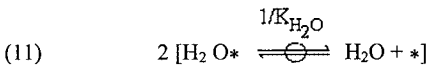
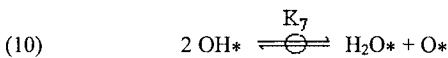
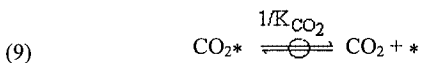
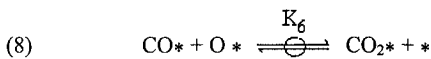
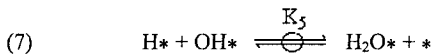
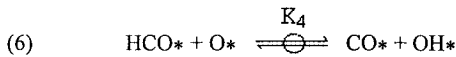
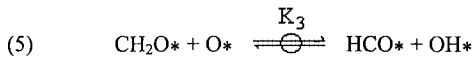
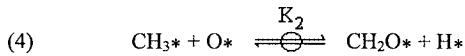
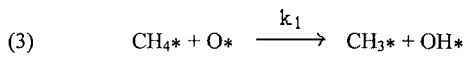
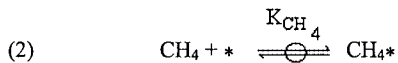
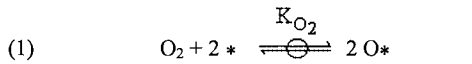
Reject: (e) – Cannot give reaction order on P_{NO} below 2

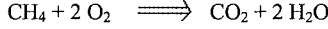
(g) – Observed reaction order is not zero order

Problem 7.11 Solution

The rate can be defined as $r_m = \frac{1}{m} \frac{dN_{N_2}}{dt} = \frac{1}{m} \left(-\frac{dN_{CH_4}}{dt} \right)$ for the reaction

$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$. With dissociative O_2 adsorption:





Step 12 allows for CO desorption as a product. The rate based on this sequence is given by step 3 (the RDS):

$$r_m = k_1 [\text{CH}_4^*] [\text{O}^*]$$

$$\text{From step 1, } K_{\text{O}_2} = [\text{O}^*]^2 / P_{\text{O}_2} [\text{O}_2] \quad \text{and} \quad [\text{O}^*] = K_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} [\text{O}_2]$$

$$\text{From step 2, } K_{\text{CH}_4} = [\text{CH}_4^*] / P_{\text{CH}_4} [\text{CH}_4] \quad \text{and} \quad [\text{CH}_4^*] = K_{\text{CH}_4} P_{\text{CH}_4} [\text{CH}_4]$$

$$\text{Thus } r_m = k_1 K_{\text{CH}_4} K_{\text{O}_2}^{1/2} P_{\text{CH}_4} P_{\text{O}_2}^{1/2} [\text{CH}_4] [\text{O}_2]$$

The site balance with only adsorbed reactants and products is:

$$L = [\text{CH}_4^*] + [\text{O}^*] + [\text{CO}_2^*] + [\text{H}_2\text{O}^*] + [\text{CO}^*] + [\text{O}^*]$$

Steps 9, 11, and 12 give, respectfully:

$$[\text{CO}_2^*] = K_{\text{CO}_2} P_{\text{CO}_2} [\text{CO}_2], [\text{H}_2\text{O}^*] = K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} [\text{H}_2\text{O}], \text{ and } [\text{CO}^*] = K_{\text{CO}} P_{\text{CO}} [\text{CO}]$$

$$\text{thus } [\text{O}^*] = L / \left(1 + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + K_{\text{CO}} P_{\text{CO}} \right)$$

and

$$r_m = L k_1 K_{\text{CH}_4} K_{\text{O}_2}^{1/2} P_{\text{CH}_4} P_{\text{O}_2}^{1/2} / \left(1 + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + K_{\text{CO}} P_{\text{CO}} \right)^2$$

From Arrhenius plots of K_{CH_4} & K_{O_2} ,

$$\text{For } \text{CH}_4 : \Delta H_{\text{ad}}^\circ = -20 \text{ kcal mole}^{-1}, \Delta S_{\text{ad}}^\circ = -13 \text{ e.u.};$$

$$\text{For } \text{O}_2 : \Delta H_{\text{ad}}^\circ = -30 \text{ kcal mole}^{-1}, \Delta S_{\text{ad}}^\circ = -25 \text{ e.u. (1 e.u. = 1 cal mole}^{-1} \text{ K}^{-1})$$

Problem 7.12 Solution

$$(a) \quad r_{mNO} = \frac{1}{m} \frac{dN_i}{v_i dt} = \frac{-1}{2m} \frac{dN_{NO}}{dt}$$

$r_{mNO} = L_* L_s k_o \theta_{NO} \theta + L_* k_1 \theta_{NO} \theta_{HNO}$ where L_* and L_s are site densities of * and S sites, respectively.

$$\text{SSA on HNO* gives: } \frac{d[\text{HNO*}]}{dt} = L_* L_s k_o \theta_{NO} \theta_H - L_* k_1 \theta_{NO} \theta_{HNO} = 0 \text{ and } r_3 = r_4,$$

$$\text{so } r_{mNO} = -\frac{dN_{NO}}{dt} = 2 L_* L_s k_o \theta_{NO} \theta_H$$

$$\text{Site balance on * sites: } L_* = [*] + [\text{NO*}] \text{ and } K_{NO} = \frac{[\text{NO*}]}{P_{NO}[*]} \text{ so}$$

$$[*] = \frac{L_*}{(1 + K_{NO} P_{NO})}, \quad [\text{NO*}] = \frac{L_* K_{NO} P_{NO}}{(1 + K_{NO} P_{NO})} \text{ and } \theta_{NO} = \frac{[\text{NO*}]}{L_*} = \frac{K_{NO} P_{NO}}{1 + K_{NO} P_{NO}}$$

$$\text{Site balance on S sites: } L_s = [S] + [H-S] \text{ and } K_{H_2} = \frac{[H-S]^2}{P_{H_2}[S]^2} \text{ so}$$

$$[S] = \frac{L_s}{(1 + K_{H_2}^{1/2} P_{H_2}^{1/2})}, \quad \theta_H = \frac{[H-S]}{L_s} = \frac{K_{H_2}^{1/2} P_{H_2}^{1/2}}{1 + K_{H_2}^{1/2} P_{H_2}^{1/2}} = K_{H_2}^{1/2} P_{H_2}^{1/2} \text{ if } \theta_H \ll 1$$

$$\text{Then } r_{mNO} = 2 L_* L_s k_o K_{NO} K_{H_2}^{1/2} P_{NO} P_{H_2}^{1/2} / (1 + K_{NO} P_{NO})$$

$$(b) \quad r_{mN_2} = \frac{1}{m} \frac{dN_{N_2}}{dt} = L_* k_2 \theta_{N_2O}$$

$$\text{SSA on } N_2O* \text{ gives: } \frac{d[N_2O]}{dt} = L_* L_s k_1 \theta_{HNO} \theta_{NO} - L_* k_2 \theta_{N_2O} - L_* k_3 \theta_{N_2O} + L_* k_{-3} P_{N_2O} \theta_* = 0$$

$$\text{so } (L_* k_2 + L_* k_3) \theta_{N_2O} = L_* L_s k_1 \theta_{HNO} \theta_{NO} + L_* k_{-3} P_{N_2O} \theta_* \text{ and}$$

$$\theta_{N_2O} = \frac{L_s k_0 \theta_{NO} \theta_H + k_{-3} P_{N_2O} \theta_*}{(k_2 + k_3)} = \frac{L_s k_0 K_{NO} K_{H_2}^{1/2} P_{NO} P_{H_2}^{1/2}}{(k_2 + k_3)(1 + K_{NO} P_{NO})} + \frac{k_{-3} P_{N_2O}}{(k_2 + k_3)(1 + K_{NO} P_{NO})}$$

$$\text{thus } r_{m_{N_2}} = \frac{L_s k_2}{k_2 + k_3} \left[\frac{L_s k_0 K_{NO} K_{H_2}^{1/2} P_{NO} P_{H_2}^{1/2} + k_{-3} P_{N_2O}}{(1 + K_{NO} P_{NO})} \right]$$

$$\begin{aligned} \text{(c) } r_{m_{N_2O}} &= \frac{1}{m} \frac{dN_{N_2O}}{dt} = L_* k_3 \theta_{N_2O} - L_* k_{-3} P_{N_2O} \theta_* \\ &= \frac{L_* k_3}{k_2 + k_3} \left[\frac{L_s k_0 K_{NO} K_{H_2}^{1/2} P_{NO} P_{H_2}^{1/2} + k_{-3} P_{N_2O}}{(1 + K_{NO} P_{NO})} \right] - \frac{L_* k_{-3} P_{N_2O}}{(1 + K_{NO} P_{NO})} \\ &= \frac{L_*}{k_2 + k_3} \left[\frac{L_s k_3 k_0 K_{NO} K_{H_2}^{1/2} P_{NO} P_{H_2}^{1/2} + k_3 k_{-3} P_{N_2O} - k_2 k_{-3} P_{N_2O} - k_3 k_{-3} P_{N_2O}}{(1 + K_{NO} P_{NO})} \right] \\ &= \frac{L_*}{k_2 + k_3} \left[\frac{L_s k_0 k_3 K_{NO} K_{H_2}^{1/2} P_{NO} P_{H_2}^{1/2} - k_2 k_{-3} P_{N_2O}}{(1 + K_{NO} P_{NO})} \right] \end{aligned}$$

Problem 7.13 Solution

$$d\xi/dt = -\frac{1}{2} \frac{d[N^*]}{dt} = k_6 [N^*]^2$$

$$r = -\frac{d[NH_3^*]}{dt} = \frac{d[N^*]}{dt} = 2k_6 [N^*]^2 = k_2 [NH_3^*][^*] - k_{-2} [NH_2^*][H^*]$$

From quasi-equilibrated steps:

$$K_1 = \frac{[NH_3^*]}{P_{NH_3}[^*]}, \quad K_5 = \frac{P_{H_2}[^*]^2}{[H^*]^2}, \quad K_3 K_4 = \frac{[N^*][H^*]^2}{[NH_2^*][^*]^2}$$

Site balance with $[N^*]$ as MARI: $L = [^*] + [N^*]$

SSA on total number of surface N atoms (atomic N_s species):

$$\frac{d[N_s]}{dt} = k_2 [NH_3^*][^*] - k_{-2} [NH_2^*][H^*] - 2k_6 [N^*]^2 = 0 \quad \Rightarrow$$

$$K_1 k_2 P_{NH_3} [^*]^2 - \frac{k_{-2} P_{H_2}^{1/2} [^*][N^*][H^*]^2}{K_3 K_4 K_5^{1/2} [^*]^2} - 2k_6 [N^*]^2 = 0 \quad \Rightarrow$$

$$K_1 k_2 P_{NH_3} [^*]^2 - \frac{k_{-2} P_{H_2}^{3/2} [N^*][^*]}{K_3 K_4 K_5^{3/2}} - 2k_6 [N^*]^2 = 0$$

$$K_1 k_2 P_{NH_3} (L - [N^*])^2 - k_{-2} P_{H_2}^{3/2} \frac{[N^*](L - [N^*])}{K_3 K_4 K_5^{3/2}} - 2k_6 [N^*]^2 = 0$$

$$K_1 k_2 P_{NH_3} (L^2 - 2L[N^*] + [N^*]^2) - \frac{Lk_{-2} P_{H_2}^{3/2} [N^*]}{K_3 K_4 K_5^{3/2}} + \frac{k_{-2} P_{H_2}^{3/2} [N^*]^2}{K_3 K_4 K_5^{3/2}} - 2k_6 [N^*]^2 = 0$$

$$\left(K_1 k_2 P_{NH_3} + \frac{k_{-2} P_{H_2}^{3/2}}{K_3 K_4 K_5^{3/2}} - 2k_6 \right) [N^*]^2 - \left(\frac{2LK_1 k_2 P_{NH_3} + Lk_{-2} P_{H_2}^{3/2}}{K_3 K_4 K_5^{3/2}} \right) [N^*] + L^2 K_1 k_2 P_{NH_3} = 0$$

Solution for quadratic equation: $ax^2 + bx + c = 0$ is $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ so

$$[N^*] = \frac{\left(\frac{2LK_1k_2P_{NH_3} + Lk_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}} \right)}{2 \left(K_1k_2P_{NH_3} + \frac{k_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}} - 2k_6 \right)} +$$

$$\frac{\left[\left(\frac{2LK_1k_2P_{NH_3} + Lk_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}} \right)^2 - 4L^2K_1k_2P_{NH_3} \left(K_1k_2P_{NH_3} + \frac{k_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}} - 2k_6 \right) \right]^{1/2}}{2 \left(K_1k_2P_{NH_3} + \frac{k_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}} - 2k_6 \right)}$$

Divide numerator and denominator by $-2k_6$ and use positive root:

$$[N^*] = - \frac{\left(\frac{2LK_1k_2P_{NH_3}}{k_6} + \frac{Lk_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}k_6} \right)}{4 \left(1 - \frac{K_1k_2P_{NH_3}}{k_6} - \frac{k_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}k_6} \right)} +$$

$$\frac{\left[\left(\frac{2LK_1k_2P_{NH_3}}{k_6} + \frac{Lk_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}k_6} \right)^2 - \frac{4L^2K_1k_2P_{NH_3}}{k_6} \left(K_1k_2P_{NH_3} + \frac{k_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}} - 2k_6 \right) \right]^{1/2}}{4 \left(1 - \frac{K_1k_2P_{NH_3}}{k_6} - \frac{k_{-2}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}k_6} \right)}$$

Inside [----]^{1/2} after factoring L out:

$$\frac{4K_1^2k_2^2P_{NH_3}^2}{k_6^2} + \frac{4K_1k_2k_{-2}P_{NH_3}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}k_6} + \frac{k_{-2}^2P_{H_2}^3}{K_3^2K_4^2K_5^3k_6^2} - \frac{4K_1^2k_2^2P_{NH_3}^2}{k_6^2} - \frac{4K_1k_2k_{-2}P_{NH_3}P_{H_2}^{3/2}}{K_3K_4K_5^{3/2}k_6} + \frac{8K_1k_2P_{NH_3}}{k_6}$$

so

$$[N^*] = \frac{\frac{L}{4} \left(\frac{-2K_1 k_2 P_{\text{NH}_3}}{k_6} - \frac{k_{-2} P_{\text{H}_2}^{3/2}}{K_3 K_4 K_5^{3/2} k_6} \right) + \left[\frac{8K_1 k_2 P_{\text{NH}_3}}{k_6} + \frac{k_{-2}^2 P_{\text{H}_2}^3}{K_3^2 K_4^2 K_5^3 k_6^2} \right]^{1/2}}{\left(1 + \frac{K_1 k_2 P_{\text{NH}_3}}{k_6} - \frac{k_{-2} P_{\text{H}_2}^{3/2}}{K_3 K_4 K_5^{3/2} k_6} \right)}$$

and, after introducing probability factor $Z/2L$ for neighbor sites:

$$r = \frac{ZLk_6}{4} \left[\frac{-2aP_{\text{NH}_3} - bP_{\text{H}_2}^{3/2} + \left(8aP_{\text{NH}_3} + b^2 P_{\text{H}_2}^3 \right)^{1/2}}{\left(1 - aP_{\text{NH}_3} - bP_{\text{H}_2}^{3/2} \right)} \right]^2 \quad \text{where}$$

$$a = \frac{K_1 k_2}{k_6} \quad \text{and} \quad b = \frac{k_{-2}}{K_3 K_4 K_5^{3/2} k_6}$$

Problem 7.14 Solution

The specific rate is: $r_m = -\frac{1}{m} \frac{dN_{N_2O}}{dt} = \frac{1}{m} \frac{dN_{N_2}}{dt} = Lk_1\theta_{N_2O}$

From steps 1 and 2: $K_{N_2O} = \frac{\theta_{N_2O}}{P_{N_2O}\theta_v}$ and $K_{CO} = \frac{\theta_{CO}}{P_{CO}\theta_v}$

SSA on O*: $\frac{d\theta_O}{dt} = Lk_1\theta_{N_2O} - Lk_2\theta_{CO}\theta_O = 0 \Rightarrow$

$$\theta_O = \frac{k_1\theta_{N_2O}}{k_2\theta_{CO}} = \frac{k_1K_{N_2O}P_{N_2O}\theta_v}{k_2K_{CO}P_{CO}\theta_v}$$

Site balance: $1 = \theta_v + K_{N_2O}P_{N_2O}\theta_v + K_{CO}P_{CO}\theta_v + \frac{k_1K_{N_2O}P_{N_2O}}{k_2K_{CO}P_{CO}}$

$$\left(1 - \frac{k_1K_{N_2O}P_{N_2O}}{k_2K_{CO}P_{CO}}\right) = \theta_v \left(1 + K_{N_2O}P_{N_2O} + K_{CO}P_{CO}\right)$$

$$r_m = Lk_1K_{N_2O}P_{N_2O}\theta_v = \frac{Lk_1K_{N_2O}P_{N_2O} \left(1 - \frac{k_1K_{N_2O}P_{N_2O}}{k_2K_{CO}P_{CO}}\right)}{\left(1 + K_{N_2O}P_{N_2O} + K_{CO}P_{CO}\right)}$$

or $r_m = (\mu\text{mole s}^{-1} \text{ g}^{-1}) = \left(\frac{cP_{N_2O} - dP_{N_2O}^2/P_{CO}}{1 + K_{N_2O}P_{N_2O} + K_{CO}P_{CO}}\right)$

where $c = Lk_1K_{N_2O}$ and $d = k_1^2 K_{N_2O}^2 / k_2 K_{CO}$

An Arrhenius plot of Lk_1 gives $E_1 = 26 \text{ kcal mole}^{-1}$ while similar plots for K_{N_2O} and

K_{CO} give:

for N_2O : $\Delta H_{ad}^{\circ} = -13 \text{ kcal mole}^{-1}$ and $\Delta S_{ad}^{\circ} = -29 \text{ cal mole}^{-1} \text{ K}^{-1}$ (e.u.)

for CO : $\Delta H_{ad}^{\circ} = -10 \text{ kcal mole}^{-1}$ and $\Delta S_{ad}^{\circ} = -23 \text{ e.u.}$

All these thermodynamic values satisfy the criteria in Table 6.9. The TOF at 573K =

$$\frac{2100 \mu\text{mole N}_2 \text{g}^{-1} \text{s}^{-1}}{(769 \mu\text{mole Cu g}^{-1})(0.91)} = 3.0 \text{ s}^{-1}. \text{ Thus the pre-exponential factor per site is: } 3.0 \text{ s}^{-1} =$$

$A_0 e^{-26000/1.987(573)}$ and $A_0 = 2.4 \times 10^{10} \text{ s}^{-1}$ which is less than 10^{13} s^{-1} and satisfies criterion 2 in Table 6.10 for a unimolecular reaction. Also, the heat of adsorption of 10 kcal mole⁻¹ for CO on Cu is consistent with values of 7-10 kcal mole⁻¹ reported in the literature.

Problem 7.15 Solution

$$r = -\frac{d[\text{CH}_4]}{dt} = k_1 P_{\text{CH}_4} [*] - k_{-1} [\text{CH}_2^*] P_{\text{H}_2} = k_7 [\text{CH}_2\text{O}^*]$$

from step (6): $[\text{CH}_2\text{O}^*] = K_6 [\text{CH}_2^*] [\text{OH}^*] / [\text{H}^*]$

from step (4): $[\text{OH}^*] = K_4 [\text{CO}_2^*] [\text{H}^*] / [\text{CO}^*]$

from step (2): $[\text{CO}_2^*] = K_2 P_{\text{CO}_2} [*]$

from step (8): $[\text{CO}^*] = K_8 P_{\text{CO}} [*]$ therefore

$$\begin{aligned} r &= k_7 K_6 [\text{CH}_2^*] [\text{OH}^*] / [\text{H}^*] = k_7 K_6 K_4 [\text{CH}_2^*] [\text{CO}_2^*] / [\text{CO}^*] \\ &= k_7 K_6 K_4 K_2 P_{\text{CO}_2} [\text{CH}_2^*] / K_8 P_{\text{CO}} \end{aligned}$$

SSA on surface CH_2^* (and CH_2O^*) species:

$$\frac{d[\text{CH}_2 \dots^*]}{dt} = k_1 P_{\text{CH}_4} [*] - k_{-1} [\text{CH}_2^*] P_{\text{H}_2} - k_7 [\text{CH}_2\text{O}^*] = 0 \quad \Rightarrow$$

$$[\text{CH}_2\text{O}^*] = \frac{(k_1 P_{\text{CH}_4} [*] - k_{-1} [\text{CH}_2^*] P_{\text{H}_2})}{k_7}$$

from step (6):
$$[\text{CH}_2^*] = \frac{[\text{CH}_2\text{O}^*][\text{H}^*]}{K_6[\text{OH}^*]} = \frac{[\text{CH}_2\text{O}^*][\text{CO}^*]}{K_6K_4[\text{CO}_2^*]} =$$

$$\frac{K_8[\text{CH}_2\text{O}^*]P_{\text{CO}}[*]}{K_2K_4K_6P_{\text{CO}_2}[*]} = \left(\frac{K_8P_{\text{CO}}}{K_2K_4K_6P_{\text{CO}_2}} \right) [\text{CH}_2\text{O}^*]$$

from SSA:
$$k_1P_{\text{CH}_4}[*] = \left(k_7 + \frac{k_{-1}K_8P_{\text{CO}}P_{\text{H}_2}}{K_2K_4K_6P_{\text{CO}_2}} \right) [\text{CH}_2\text{O}^*] \quad \text{so}$$

$$[\text{CH}_2\text{O}^*] = \frac{(k_1/k_7)P_{\text{CH}_4}[*]}{\left(1 + \frac{k_{-1}K_8P_{\text{CO}}P_{\text{H}_2}}{k_7K_2K_4K_6P_{\text{CO}_2}} \right)}$$

Site balance with $[\text{CH}_2\text{O}^*]$ as MARI: $L = [*] + [\text{CH}_2\text{O}^*] =$

$$[*] \left[1 + \frac{(k_1P_{\text{CH}_4}/k_7)}{\left(1 + k_{-1}K_8P_{\text{CO}}P_{\text{H}_2}/k_7K_2K_4K_6P_{\text{CO}_2} \right)} \right] =$$

$$[*] \left[\frac{1 + \frac{k_{-1}K_8P_{\text{CO}}P_{\text{H}_2}}{k_7K_2K_4K_6P_{\text{CO}_2}} + \frac{k_1P_{\text{CH}_4}}{k_7}}{1 + \frac{k_{-1}K_8P_{\text{CO}}P_{\text{H}_2}}{k_7K_2K_4K_6P_{\text{CO}_2}}} \right] \quad \text{so}$$

$$[*] = \frac{L \left(1 + \frac{k_{-1}K_8P_{\text{CO}}P_{\text{H}_2}}{k_7K_2K_4K_6P_{\text{CO}_2}} \right)}{\left(1 + \frac{k_1P_{\text{CH}_4}}{k_7} + \frac{k_{-1}K_8P_{\text{CO}}P_{\text{H}_2}}{k_7K_2K_4K_6P_{\text{CO}_2}} \right)}$$

$$r = k_7 [\text{CH}_2\text{O}^*] = \frac{k_7 (k_1/k_7) P_{\text{CH}_4} [^*]}{\left(1 + \frac{k_{-1} K_8 P_{\text{CO}} P_{\text{H}_2}}{k_7 K_2 K_4 K_6 P_{\text{CO}}}\right)} = \frac{L k_1 P_{\text{CH}_4}}{\left(1 + \frac{k_1 P_{\text{CH}_4}}{k_7} + \frac{k_{-1} K_8 P_{\text{CO}} P_{\text{H}_2}}{k_7 K_2 K_4 K_6 P_{\text{CO}}}\right)}$$

$$\text{or } r = \frac{L k_1 P_{\text{CH}_4} P_{\text{CO}_2}}{\left(P_{\text{CO}_2} + \frac{k_1}{k_7} P_{\text{CH}_4} P_{\text{CO}_2} + \frac{k_{-1} K_8 P_{\text{CO}} P_{\text{H}_2}}{k_7 K_2 K_4 K_6}\right)}$$

$$\text{The TOF for step 7 is: } \frac{(5.35 \mu\text{mole s}^{-1} \text{ g}^{-1})}{(2.4 \mu\text{mole H}_2 \text{ g}^{-1}) \left(\frac{2 \mu\text{mole Ni}_s}{\mu\text{mole H}_2}\right)} = 1.1 \text{ s}^{-1}$$

Rate per site: $\text{TOF} = 1.1 \text{ s}^{-1} = A e^{-E/RT} = A e^{-38000/1.987 (723)} = A (3.25 \times 10^{-12})$. Therefore $A = 1.1/3.25 \times 10^{-12} = 3.4 \times 10^{11} \text{ s}^{-1}$, which is less than 10^{13} (See Criterion 2 in Table 6.10)

Problem 7.16 Solution

$$(a) \quad r_m = \frac{1}{m} \frac{d\xi}{dt} = \frac{1}{m} \frac{dN_i}{v_i dt} = \frac{-1}{2m} \frac{dN_{NO}}{dt} = \frac{1}{m} \frac{dN_{N_2}}{dt} \Rightarrow \frac{dN_{N_2}}{dt} = \frac{-1}{2} \frac{dN_{NO}}{dt}$$

$$-\frac{dN_{NO}}{dt} = 2k_1 [NO^*]^2 \quad , \quad K_{NO} = \frac{[NO^*]}{P_{NO}[^*]} \Rightarrow [NO^*] = K_{NO} P_{NO} [^*]$$

$$L = [^*] + 2[^*(NO)_2^*] + [N_2O^*] + [O^*] + [NO^*] = [^*] + [NO^*] + [O^*]$$

$$K_{O_2} = \frac{[O^*]^2}{P_{O_2}[^*]^2} \Rightarrow [O^*] = K_{O_2}^{1/2} P_{O_2}^{1/2} [^*]$$

$$L = [^*] (1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2}) \quad \text{and} \quad [^*] = L / (1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2})$$

$$\text{So } r_{N_2} = \frac{2k_1}{2} [NO^*]^2 = k_1 K_{NO}^2 P_{NO}^2 [^*]^2 = \frac{L k_1 K_{NO}^2 P_{NO}^2}{(1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2})^2}$$

or

$$r_{N_2} = k_3 [N_2O^*] \quad \text{and} \quad \text{SSA on } N_2O^* \text{ gives } k_2 [^*(NO)_2^*] = k_3 [N_2O^*]$$

$$\text{so } r_{N_2} = k_2 [^*(NO)_2^*] \quad \text{and} \quad \text{SSA on } [^*(NO)_2^*] \text{ gives } k_1 [NO^*]^2 = k_2 [^*(NO)_2^*]$$

$$\text{so } r_{N_2} = k_1 [NO^*]^2 = L k_1 K_{NO}^2 P_{NO}^2 / (1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2})^2$$

(b) In the site balance:

$$k_3 [N_2O^*] = k_1 [NO^*]^2 \quad \text{and} \quad [N_2O^*] = (k_1/k_3) K_{NO} P_{NO} [^*]^2$$

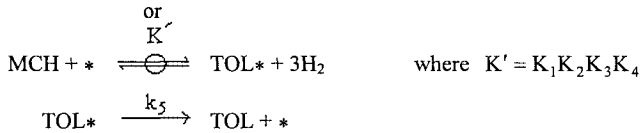
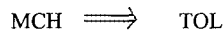
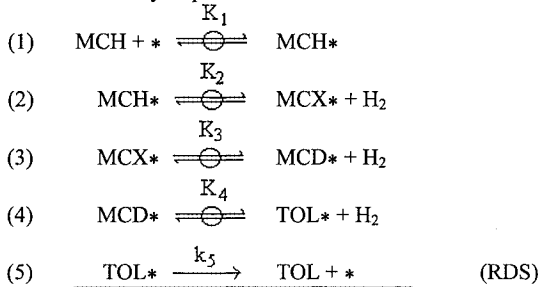
$$\text{and } k_2 [^*(NO)_2^*] = k_1 [NO^*]^2 \quad \text{and} \quad [^*(NO)_2^*] = (k_1/k_2) K_{NO} P_{NO} [^*]^2$$

$$\text{so } L = [^*] + \frac{2k_1 K_{NO} P_{NO}}{k_2} [^*]^2 + \frac{k_1 K_{NO} P_{NO}}{k_3} [^*]^2 + K_{NO} P_{NO} [^*] + K_{O_2}^{1/2} P_{O_2}^{1/2} [^*]$$

Consequently, a quadratic expression for $[^*]$ is obtained and the solution for such an equation is complicated.

Problem 7.17 Solution

The series of elementary steps is:



Step 5 is RDS, so $r = k_5 [\text{TOL}^*]$

$$K' = \frac{[\text{TOL}^*] P_{\text{H}_2}^3}{P_{\text{MCH}} [^*]} \quad \text{and} \quad [\text{TOL}^*] = \frac{K' P_{\text{MCH}} [^*]}{P_{\text{H}_2}^3}$$

$$L = [^*] + [\text{MCH}^*] + [\text{MCX}^*] + [\text{MCD}^*] + [\text{TOL}^*]$$

$$\text{If } [\text{TOL}^*] \text{ is MARI, then } L = [^*] + [\text{TOL}^*] = [^*] \left(1 + \frac{K' P_{\text{MCH}}}{P_{\text{H}_2}^3} \right) \text{ and } [^*] = \frac{L}{\left(1 + \frac{K' P_{\text{MCH}}}{P_{\text{H}_2}^3} \right)}$$

$$\text{then } r = k_5 [\text{TOL}^*] = k_5 K' P_{\text{MCH}} [^*] / P_{\text{H}_2}^3 = \frac{L k_5 K' P_{\text{MCH}}}{\left(1 + \frac{K' P_{\text{MCH}}}{P_{\text{H}_2}^3} \right) P_{\text{H}_2}^3}$$

$$\text{or } r = \frac{L k_5 K' P_{\text{MCH}}}{\left(P_{\text{H}_2}^3 + K' P_{\text{MCH}} \right)}$$

This is not consistent with the behavior because it contains a $P_{\text{H}_2}^3$ term.

Problem 7.18 Solution

$$\frac{-d[\text{O}_2(\text{g})]}{dt} = r = 2k_1 P_{\text{O}_2} [\text{S}]^2 = k_3 [\text{HCO}_2 - \text{S}] [\text{O} - \text{S}] = k P_{\text{O}_2} [\text{S}]^2 \quad L = [\text{S}] + [\text{HCO}_2 - \text{S}] + [\text{O} - \text{S}]$$

A. $[\text{HCO}_2 - \text{S}] = K_2 P_{\text{H}_2\text{CO}} [\text{O} - \text{S}]^2 / [\text{OH} - \text{S}]$

B. $[\text{OH} - \text{S}] = K_{\text{H}_2\text{O}}^{1/2} P_{\text{H}_2\text{O}}^{1/2} [\text{O} - \text{S}]^{1/2} [\text{S}]^{1/2}$

C.
$$[\text{HCO}_2 - \text{S}] = \frac{K_2 P_{\text{H}_2\text{CO}} [\text{O} - \text{S}]^2}{K_{\text{H}_2\text{O}}^{1/2} P_{\text{H}_2\text{O}}^{1/2} [\text{O} - \text{S}]^{1/2} [\text{S}]^{1/2}} =$$

$$\frac{K_2 P_{\text{H}_2\text{CO}} [\text{O} - \text{S}]^{3/2} [\text{S}]^{-1/2}}{K_{\text{H}_2\text{O}}^{1/2} P_{\text{H}_2\text{O}}^{1/2}}$$

D. At steady-state: $[\text{O} - \text{S}] = \frac{k_1 P_{\text{O}_2} [\text{S}]^2}{k_3 [\text{HCO}_2 - \text{S}]}$ (Balance on O-S species)

E. Substitute D in C: $[\text{HCO}_2 - \text{S}] = \frac{K_2 P_{\text{H}_2\text{CO}} k_1^{3/2} P_{\text{O}_2}^{3/2} [\text{S}]^{5/2}}{k_3^{3/2} [\text{HCO}_2 - \text{S}]^{3/2} K_{\text{H}_2\text{O}}^{1/2} P_{\text{H}_2\text{O}}^{1/2}} \Rightarrow$

F. $[\text{HCO}_2 - \text{S}] = \frac{K_2^{2/5} P_{\text{H}_2\text{CO}}^{2/5} k_1^{3/5} P_{\text{O}_2}^{3/5} [\text{S}]}{k_3^{3/5} K_{\text{H}_2\text{O}}^{1/5} P_{\text{H}_2\text{O}}^{1/5}}$

G. $[\text{O} - \text{S}] = \frac{k_1 P_{\text{O}_2}^{2/5} [\text{S}] K_{\text{H}_2\text{O}}^{1/5} P_{\text{H}_2\text{O}}^{1/5}}{k_3^{2/5} K_2^{2/5} k_1^{3/5} P_{\text{H}_2\text{CO}}^{2/5}}$

H. $L = [\text{S}] + \frac{K_2^{2/5} k_1^{3/5} P_{\text{H}_2\text{CO}}^{2/5} P_{\text{O}_2}^{3/5} [\text{S}]}{k_3^{3/5} K_{\text{H}_2\text{O}}^{1/5} P_{\text{H}_2\text{O}}^{1/5}} + \frac{k_1^{2/5} P_{\text{O}_2}^{2/5} K_{\text{H}_2\text{O}}^{1/5} P_{\text{H}_2\text{O}}^{1/5} [\text{S}]}{k_3^{2/5} K_2^{2/5} P_{\text{H}_2\text{CO}}^{2/5}}$

I. $[\text{S}] = L / \left(1 + K' P_{\text{H}_2\text{CO}}^{2/5} P_{\text{O}_2}^{3/5} P_{\text{H}_2\text{O}}^{-1/5} + K'' P_{\text{O}_2}^{2/5} P_{\text{H}_2\text{CO}}^{-2/5} P_{\text{H}_2\text{O}}^{1/5} \right)^2$ Assume $P_{\text{H}_2\text{O}}$ is \approx constant, plus power of 0.2 is low

Then, $r = L k_1 P_{\text{O}_2} / \left(1 + K' P_{\text{H}_2\text{CO}}^{0.4} P_{\text{O}_2}^{0.6} + K'' P_{\text{O}_2}^{0.4} P_{\text{H}_2\text{CO}}^{-0.4} \right)^2$

If $\theta_{\text{HCO}_2} \ll 1$ and $\theta_{\text{O}} \ll 1$, then $r = kP_{\text{O}_2}$

If θ_{O} is MASI, i.e., $\theta_{\text{O}} \gg \theta_{\text{HCO}_2}$ then

$$r = \frac{Lk_1 P_{\text{O}_2}}{\left(1 + K'' P_{\text{O}_2}^{0.4} / P_{\text{H}_2\text{CO}}^{0.4}\right)^2} = \frac{k' P_{\text{O}_2} P_{\text{H}_2\text{CO}}^{0.8}}{\left(P_{\text{H}_2\text{CO}}^{0.4} + K'' P_{\text{O}_2}^{0.4}\right)^2}$$

(Note typographical error in power dependence on H_2O in ref. 62)

Problem 8.1 Solution

$$r = \frac{k_1 k_2 [A_1][A_2] - k_{-1} k_{-2} [B_1][B_2]}{k_1 [A_1] + k_{-1} [B_1] + k_2 [A_2] + k_{-2} [B_2]} \quad \alpha = 2/3$$

$$k_1 = k_1^o e^{\alpha(t-t_0)} = k_1^o e^{2/3(t-t_0)}, k_{-1} = k_{-1}^o e^{-1/3(t-t_0)}, k_2 = k_2^o e^{-1/3(t-t_0)}, k_{-2} = k_{-2}^o e^{2/3(t-t_0)}$$

Substitute into r:

$$r = \frac{k_1^o k_2^o e^{2/3(t-t_0)} e^{-1/3(t-t_0)} [A_1][A_2] - k_{-1}^o k_{-2}^o e^{-1/3(t-t_0)} e^{2/3(t-t_0)} [B_1][B_2]}{k_1^o e^{2/3(t-t_0)} [A_1] + k_{-1}^o e^{-2/3(t-t_0)} [B_1] + k_2^o e^{-2/3(t-t_0)} [A_2] + k_{-2}^o e^{1/3(t-t_0)} [B_2]}$$

$$- k_{-1}^o k_{-2}^o$$

$$r = \frac{k_1^o k_2^o [A_1][A_2] - k_{-1}^o k_{-2}^o [B_1][B_2]}{[E_1 e^{1/3(t-t_0)} + E_2 e^{-2/3(t-t_0)}]} \quad \begin{array}{l} \text{where } E_1 = k_1^o [A_1] + k_{-2}^o [B_2] \\ \text{and } E_2 = k_{-1}^o [B_1] + k_2^o [A_2] \end{array}$$

Let D represent the denominator, then

$$dD/dt = 0 = 1/3 E_1 e^{-1/3(t_{\max}-t_0)} - 2/3 E_2 e^{-2/3(t_{\max}-t_0)} \quad \Rightarrow$$

$$1/3 E_1 e^{1/3(t_{\max}-t_0)} = 2/3 E_2 e^{-2/3(t_{\max}-t_0)} \quad \Rightarrow$$

$$E_2 / E_1 = 1/2 e^{(t_{\max}-t_0)} \quad ; \quad u_{\max} = u_o e^{(t_0-t_{\max})} = \frac{[S_1]}{[S_2]}$$

$$u_o = E_2 / E_1 \quad \Rightarrow \quad u_{\max} = [1/2 e^{(t_{\max}-t_0)}] e^{(t_0-t_{\max})} = 1/2$$

$$\frac{[S_1]}{[S_2]} = 1/2 \quad \Rightarrow \quad 2[S_1] = [S_2] \quad \text{and} \quad \theta = \frac{[S_2]}{[S_1] + [S_2]} = \frac{[S_2]}{1/2[S_2] + [S_2]} = \frac{2}{3}$$

Problem 8.2 Solution

Because $k_1^o P_{N_2} \ll k_{-2}^o P_{NH_3}^2$ and $k_{-1}^o \ll k_2^o P_{H_2}^3$:

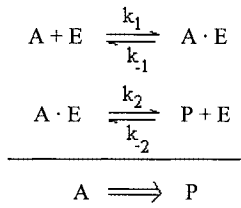
$$r = k \left[\frac{k_1^o k_2^o [N_2] [H_2]^3 - k_{-1}^o k_{-2}^o [NH_3]^2}{k_{-2}^o [NH_3]^{2m} k_2^{o(1-m)} [H_2]^{3(1-m)}} \right], \quad \text{thus}$$

$$r = k \left[\frac{k_1^o k_2^{o m} P_{N_2} P_{H_2}^{3m}}{k_{-2}^o P_{NH_3}^{2m}} - \frac{k_{-1}^o k_{-2}^{o(1-m)} P_{NH_3}^{2(1-m)}}{k_2^{o(1-m)} P_{H_2}^{3(1-m)}} \right] =$$

$$k \left[k_1^o K_2^{o m} \frac{P_{N_2} P_{H_2}^{3m}}{P_{NH_3}^{2m}} - \frac{k_{-1}^o P_{NH_3}^{2(1-m)}}{K_2^{o(1-m)} P_{H_2}^{3(1-m)}} \right], \quad m = 1/2 \quad \text{so}$$

$$r = k \left[k_1^o K_2^{o 1/2} \frac{P_{N_2} P_{H_2}^{3/2}}{P_{NH_3}} - \frac{k_{-1}^o P_{NH_3}}{K_2^{o 1/2} P_{H_2}^{3/2}} \right] = \bar{k} \frac{P_{N_2} P_{H_2}^{3/2}}{P_{NH_3}} - \bar{k} \frac{P_{NH_3}}{P_{H_2}^{3/2}}$$

Problem 9.1 Solution



$$r = \frac{d[P]}{dt} = \bar{r} - \bar{r} = k_2[A \cdot E] - k_{-2}[P][E]$$

$$\text{SSA on } A \cdot E: k_1[A][E] + k_{-2}[P][E] - k_{-1}[A \cdot E] - k_2[A \cdot E] = 0$$

$$\text{Active site balance: } L_e = [E] + [A \cdot E]$$

$$[A \cdot E](k_{-1} + k_2) = k_1[A][E] - k_{-2}[P][E] \quad \text{from SSA} \Rightarrow$$

$$[A \cdot E] = \frac{k_1[A][E] + k_{-2}[P][E]}{k_{-1} + k_2}$$

$$L_e = [E] + \frac{k_1[A][E] + k_{-2}[P][E]}{k_{-1} + k_2} = \frac{(k_{-1} + k_2)[E] + k_1[A][E] + k_{-2}[P][E]}{k_{-1} + k_2}$$

$$r = k_2 \left(\frac{k_1[A][E] + k_{-2}[P][E]}{k_{-1} + k_2} \right) - k_{-2}[P][E] = \left(\frac{k_1 k_2 [A] + k_2 k_{-2} [P] - k_{-1} k_{-2} [P] - k_2 k_{-2} [P]}{k_{-1} + k_2} \right) [E]$$

$$r = \frac{(k_{-1} + k_2)L_e}{(k_{-1} + k_2) + k_1[A] + k_{-2}[P]} \cdot \frac{(k_1 k_2 [A] - k_{-1} k_{-2} [P])}{(k_{-1} + k_2)} = \frac{L_e (k_1 k_2 [A] - k_{-1} k_{-2} [P])}{(k_{-1} + k_2) + k_1[A] + k_{-2}[P]}$$

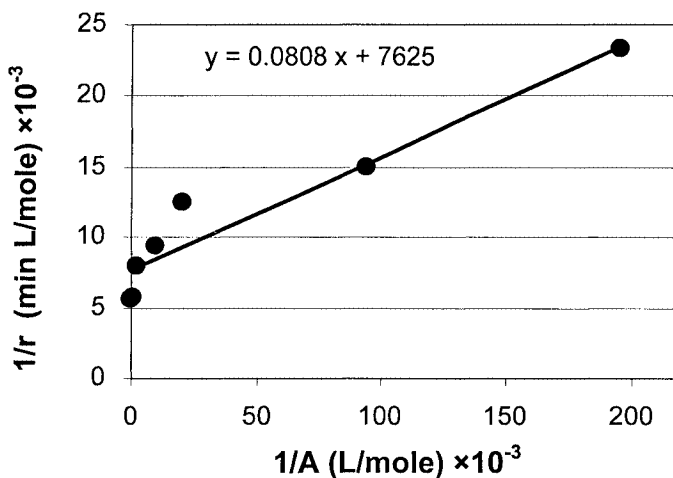
Initial forward rate, $[P] \cong 0 \Rightarrow \frac{L_e k_2 [A]}{\left(\frac{k_{-2} + k_2}{k_1}\right) + [A]} = r \Rightarrow$ same form as eq. 9.6

Initial reverse rate, $[A] \cong 0, r = -\frac{d[P]}{dt} = \frac{d[A]}{dt} = \frac{L_e k_{-1} [P]}{\left(\frac{k_{-1} + k_2}{k_{-2}}\right) + [P]} \Rightarrow$

also of Michaelis-Menten form.

Problem 9.2 Solution

Use eq. 9.9, which is: $1/r = \left(\frac{K_m}{r_{\max}}\right)\left(\frac{1}{[A]}\right) + \frac{1}{r_{\max}}$ and plot $\frac{1}{r}$ vs. $\frac{1}{[A]}$



From the slope and the intercept:

$$\text{Intercept} = \frac{1}{r_{\max}} = 7620 \text{ so } r_{\max} = 1.31 \times 10^{-4} \frac{\text{mole}}{\text{L} \cdot \text{min}}$$

$$\text{Slope} = 0.0808 \text{ min} = \frac{K_m}{r_{\max}} \Rightarrow$$

$$K_m = (0.0808 \text{ min}) \left(1.31 \times 10^{-4} \frac{\text{mole}}{\text{L} \cdot \text{min}}\right) = 1.06 \times 10^{-5} \frac{\text{mole}}{\text{L}}$$

Problem 9.3 Solution

$$r = \frac{d[P]}{dt} = k[ES]$$

Steps 1 and 2 are quasi-equilibrated, so

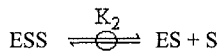
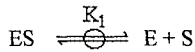
$$K_s = \frac{[ES]}{[E][S]} \quad \text{and} \quad K'_s = \frac{[ESS]}{[ES][S]}$$

Balance on enzyme: $L_e = [E] + [ES] + [ESS]$

$$L_e = \frac{[ES]}{K_s[S]} + [ES] + K'_s[ES][S], \quad \text{and} \quad [ES] = \frac{L_e}{1 + \frac{1}{K_s[S]} + K'_s[S]}$$

$$r = \frac{L_e k}{\left(1 + \frac{1}{K_s[S]} + K'_s[S]\right)} = \frac{L_e k [S]}{\left(\frac{1}{K_s} + [S] + K'_s [S]^2\right)}$$

Note: by convention, steps 1 and 2 are represented by a dissociation equilibrium constant, i.e.,

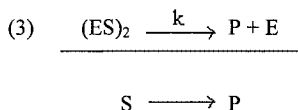
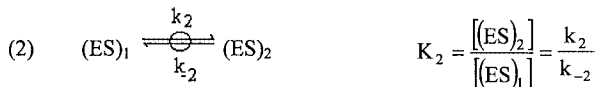
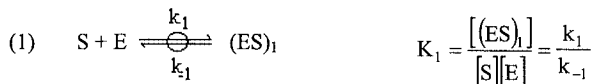


$$\text{so then } K_1 = 1/K_s \quad \text{and} \quad K_2 = 1/K'_s \quad \text{and} \quad r = \frac{L_e k [S]}{\left(K_1 + [S] + [S]^2/K_2\right)}$$

written in terms of dissociation constants. The mathematical form is identical to the above rate equation.

Problem 9.4 Solution

(a) Steps 1 and 2 are in quasi-equilibrium:



$$r = \frac{d[P]}{dt} = k[(ES)_2] = kK_2[(ES)_1] = kK_1K_2[S][E]$$

Active site balance: $L_e = E + (ES)_1 + (ES)_2$

$$L_e = [E] + K_1[S][E] + K_1K_2[S][E] = [E](1 + K_1[S] + K_1K_2[S])$$

$$r = \frac{L_e k K_1 K_2 [S]}{1 + (K_1 + K_1 K_2)[S]} = \frac{L_e k K_2 [S]}{1/K_1 + (1 + K_2)[S]} = \frac{\left(\frac{L_e k K_2}{1 + K_2}\right)[S]}{\left(\frac{1}{K_1 + K_1 K_2} + [S]\right)}$$

so r_{\max} (apparent) = $L_e k K_2 / (1 + k_2)$ and K_m (apparent) = $1 / (K_1 + K_1 K_2)$

(b) Steps 1 and 2 are reversible, so use SSA:

$$(1) \quad \frac{d[(ES)_1]}{dt} = k_1[S][E] + k_{-2}[(ES)_2] - k_{-1}[(ES)_1] - k_2[(ES)_1] = 0$$

$$(2) \quad \frac{d[(ES)_2]}{dt} = k_2[(ES)_1] - k_{-2}[(ES)_2] - k[(ES)_2] = 0$$

$$(3) \quad \text{Enzyme balance: } L_e = [E] + [(ES)_1] + [(ES)_2]$$

$$\text{From (2): } [(ES)_2](k_{-2} + k) = k_2[(ES)_1] \Rightarrow [(ES)_2] = k_2 [(ES)_1] / (k_{-2} + k)$$

$$\text{From (1): } k_1[S][E] = \frac{k_2 k_{-2} [(ES)_1]}{k_{-2} + k} - (k_{-1} + k_2) [(ES)_1] = 0 \Rightarrow$$

$$k_1[S][E] = \left(k_{-1} + k_2 - \frac{k_2 k_{-2}}{k_{-2} + k} \right) [(ES)_1] \Rightarrow$$

$$[(ES)_1] = \frac{k_1[S][E]}{k_{-1} + k_2 - \frac{k_2 k_{-2}}{k_{-2} + k}} = \frac{k_1[S][E](k_{-2} + k)}{k_{-1} k_{-2} + k_2 k_{-2} + k_{-1} k + k_2 k - k_2 k_{-2}} = \frac{k_1(k_{-2} + k)[S][E]}{k_{-1}(k_{-2} + k) + k_2 k}$$

$$L_e = [E] + \frac{k_1[S][E]}{k_{-1} + k_2 - \frac{k_2 k_{-2}}{k_{-2} + k}} + \frac{k_1 k_2 [S][E] / (k_{-2} + k)}{k_{-1} + k_2 - \frac{k_2 k_{-2}}{k_{-2} + k}} = [E] + \frac{(k_1(k_{-2} + k) + k_1 k_2)[S][E]}{k_{-1}(k_{-2} + k) + k_2 k}$$

$$L_e = [E] \left[\frac{1 + (k_1(k_{-2} + k) + k_1 k_2)[S]}{k_{-1}(k_{-2} + k) + k_2 k} \right] = [E] \left[\frac{k_{-1}(k_{-2} + k) + k_2 k + k_1(k_2 + k_{-2} + k)[S]}{k_{-1}(k_{-2} + k) + k_2 k} \right]$$

$$[E] = \frac{L_e [k_{-1}(k_{-2} + k) + k_2 k]}{k_{-1}(k_{-2} + k) + k_2 k + k_1(k_2 + k_{-2} + k)[S]}$$

$$r = k[(ES)_2] = \frac{kk_2[(ES)_1]}{(k_{-2} + k)} = \frac{kk_1k_2[S][E]}{[k_{-1}(k_{-2} + k) + k_2k]} = \frac{L_e kk_1k_2[S]}{k_{-1}(k_{-2} + k) + k_2k + k_1(k_2 + k_{-2} + k)[S]}$$

To get Michaelis-Menten form, divide numerator and denominator by

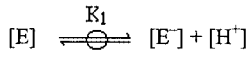
$$k_1(k_2 + k_{-2} + k) \Rightarrow$$

$$r = \frac{\left(\frac{L_e kk_2}{k_2 + k_{-2} + k} \right) [S]}{\frac{k_{-1}k_{-2} + k_{-1}k + k_2k}{k_1(k_2 + k_{-2} + k)} + [S]}$$

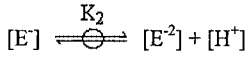
$$\text{so } r_{\max} (\text{apparent}) = \frac{L_e kk_2}{k_2 + k_{-2} + k}$$

$$\text{and } K_m (\text{apparent}) = \frac{k_{-1}k_{-2} + k_{-1}k + k_2k}{k_1k_2 + k_1k_{-2} + k_1k}$$

Problem 9.5 Solution



$$K_1 = \frac{[E^-][H^+]}{[E]}$$



$$K_2 = \frac{[E^{-2}][H^+]}{[E^-]}$$

$$L_e = [E] + [E^-] + [E^{-2}]$$

$$\text{active fraction} = y^- = \frac{[E^-]}{L_e} = \frac{[E^-]}{([E] + [E^-] + [E^{-2}])}$$

$$y^- = \frac{[E^-]}{\left(\frac{[H^+][E^-]}{K_1} + [E^-] + K_2[E^-] \right) / [H^+]} = \frac{1}{\left(1 + [H^+] / K_1 + K_2 / [H^+] \right)} \quad \text{while}$$

$$y = \frac{[E]}{L_e} = \frac{1}{\left(1 + K_1 / [H^+] + K_1 K_2 / [H^+]^2 \right)} \quad \text{and}$$

$$y^{-2} = \frac{[E^{-2}]}{L_e} = \frac{1}{\left(1 + [H^+] / K_2 + [H^+]^2 / K_1 K_2 \right)}$$

Thus the maximum rate is proportional to the active fraction and

$$r_{\max} = L_e k_2 y^- = \frac{L_e k_2}{\left(1 + [H^+] / K_1 + K_2 / [H^+] \right)}$$