SOLUTIONS

Solutions to Exercises in Chapter 2

Exercise 2.1 Reactivity and steady state

Statements (b), (d) and (e) are correct.

(a) At steady state product and reactant are <u>not</u> in equilibrum, however, the deviation from the state of equilibrium is at the minimum corresponding to the given conditions.
(c) If a reaction is at equilibrium, forward and backward rates are equal, such that the net rate of reaction is zero.
(f) A reaction system at equilibrium produces no entropy, because the entropy has a maximum value.
(g) This holds only for an elementary reaction.
(h)   A catalyst enhances both the forward and the reverse rates of a reaction to the same extent.

Exercise 2.2 Affinity and extent of reaction

First calculate all concentrations:

	$t = 0$	$t = t_1$	$t = \infty$
[A] mol L^{-1}	33.3	20	10
[B] mol L^{-1}	66.7	40	20
[C] mol L^{-1}	0	26.7	46.7
[D] mol L^{-1}	0	13.3	23.3
A kJ mol^{-1}	∞	9.4	0
ξ mol L^{-1}	0	13.3	23.3
δ mol L^{-1}	23.3	10	0

(a) The rate constant of the reverse reaction follows from that of the forward reaction once the equilibrium constant is known:

$$K = \frac{[C]^2[D]}{[A][B]^2} = \frac{(46.7)^2\ 23.3}{10\ (20)^2} = 12.7 \rightarrow k^- = k^+/K = 0.00787\ \text{mol}^3\,\text{l}^{-3}\,\text{s}^{-1}$$

(b)   The affinity equals:

$$-A = \sum_i \nu_i\, RT\ \ln \frac{c_i(t)}{c_i^{\text{eq}}}$$

answers in the Table.

(c) The extent of reaction and the deviation from equilibrium equal:

$$\xi = \frac{1}{\nu_i}(c_i - c_i^{t=0}); \quad \delta = \frac{1}{\nu_i}(c_i^{eq} - c_i)$$

answers in the Table.

Exercise 2.3 N_2O_5 Decomposition

In the proposed mechanism oxygen, O_2, is formed in the second reaction step. Hence:

$$\frac{d[O_2]}{dt} = k_1[NO_2][NO_3]$$

The concentrations of NO_2 and NO_3 are unknown but can be eliminated by using the equilibrium between N_2O_5 and $NO_2 + NO_3$:

$$K = \frac{[NO_2][NO_3]}{[N_2O_5]} \quad \text{or} \quad [NO_2][NO_3] = K[N_2O_5]$$

Substitution of $[NO_2][NO_3]$ in the rate equation yields:

$$\frac{d[O_2]}{dt} = k_1 K[N_2O_5] \quad \text{i.e.} \quad k = k_1 K$$

which represents the experimentally observed behaviour. Note that the order in the N_2O_5 concentration equals 1 and not 2, as the overall reaction suggests.

Exercise 2.4 The steady state assumption

(a) The steady state assumption is:
$$\frac{d[I_i]}{dt} = 0; \quad i = 1, ..., n$$
The steady state assumption is best applicable in a flow reactor with a constant supply of reactants and a constant rate of product formation, and also in chain reactions provided the chain length (i.e. the number of times a propagation step proceeds) is sufficiently large.

(b) A steady state process is not in equilibrium (otherwise there would be no net production of products), but is as close to the state of equilibrium as the conditions allow; the entropy is smaller than the maximum value achieved at equilibrium, and the entropy production assumes a constant, minimum value larger than zero.

(c) The rate of reaction is:
$$r = V\frac{d[C_6H_5CH_3]}{dt} = Nk_3\theta_T$$
where θ_T is the toluene coverage. Adsorbed toluene is the majority species, hence $\theta_T + \theta_* \approx 1$. Application of the steady state assumption yields:

$$\frac{d\,\theta_T}{dt} = k_2\,\theta_M \;-\; k_3\,\theta_T \;=\; 0$$

$$\frac{d\,\theta_M}{dt} = k_1[C_6H_{11}CH_3]\,\theta_* \;-\; k_2\,\theta_M \;=\; 0$$

$$\rightarrow k_3\,\theta_T = k_1\,[\,C_6H_{11}CH_3\,]\,(\,1 - \theta_T\,) \rightarrow \theta_T = \frac{k_1[C_6H_{11}CH_3]}{k_3 + k_1[C_6H_{11}CH_3]}$$

Substitution in the rate of reaction leads to the requested expression:

$$r = V\frac{d[C_6H_5CH_3]}{dt} = \frac{N\,k_1[C_6H_{11}CH_3]}{1 + \dfrac{k_1}{k_3}[C_6H_{11}CH_3]}$$

(d) If the right term in the denominator is substantially larger than unity, the order of reaction in methyl cyclohexane becomes zero. However, is this term much smaller than 1, than the reaction is first order in methyl cyclohexane. Or in the more formal manner:

$$n_M \equiv [C_6H_{11}CH_3]*\frac{\partial \ln(r)}{\partial[C_6H_{11}CH_3]} = 1 - \theta_T \text{ and } n_T = 0$$

Exercise 2.5 Steady State Assumption

The reaction rate equations of the intermediates are:

$$\frac{d[CH_3\bullet]}{dt} = k_1[CH_3CHO] \;-\; k_4[CH_3\bullet]^2 \;-\; k_2[CH_3\bullet][CH_3CHO] \;+\; k_3[CH_3CO\bullet] \;=\; 0$$

$$\frac{d[CH_3CO\bullet]}{dt} = -k_3[CH_3CO\bullet] \;+\; k_2[CH_3\bullet][CH_3CHO] = 0$$

If we add these two expressions we get:

$$k_1[CH_3CHO] \;-\; k_4[CH_3\bullet]^2 \;=\; 0 \;\rightarrow\; [CH_3\bullet] = \left(\frac{k_1}{k_4}\right)^{1/2}[CH_3CHO]^{1/2}$$

The reaction rate of CH_4 formation is:

$$\frac{d[CH_4]}{dt} = k_2[CH_3\bullet][CH_3CHO] = k_2\left(\frac{k_1}{k_4}\right)^{1/2}[CH_3CHO]^{3/2}$$

Note that the order in acetaldehyde is 3/2, whereas the overall reaction (erroneously!) suggests a first order dependence.

Exercise 2.6 The steady state assumption in the kinetics of chain reactions

The rate of HBr formation follows from:

$$\frac{d[\text{HBr}]}{dt} = k_3^f [\text{H}\bullet][\text{Br}_2] + k_2^f [\text{Br}\bullet][\text{H}_2] - k_2^b [\text{HBr}][\text{H}\bullet]$$

Equilibrium between molecular and atomic bromine leads to:

$$[\text{Br}\bullet] = \sqrt{\frac{k_1^f}{k_4^f}} \, [\text{Br}_2]$$

Application of the steady state assumption on $[\text{H}\bullet]$:

$$\frac{d[\text{H}\bullet]}{dt} = 0 = k_2^f [\text{Br}\bullet][\text{H}_2] - k_2^b [\text{HBr}][\text{H}\bullet] - k_3^f [\text{H}\bullet][\text{Br}_2]$$

$$[\text{H}\bullet] = \frac{k_2^f [\text{Br}\bullet][\text{H}_2]}{k_3^f [\text{Br}_2] + k_2^b [\text{HBr}]}$$

Substitution of $[\text{Br}\bullet]$ in $[\text{H}\bullet]$, and of $[\text{H}\bullet]$ and $[\text{Br}\bullet]$ in d[HBr]/dt leads to the requested formula with

$$k = 2k_2^f \sqrt{\frac{k_1^f}{k_4^f}} \quad \text{and} \quad k' = \frac{k_2^b}{k_3^f}$$

Exercise 2.7 Heterogeneous Catalysis

(a) Three steps occurring in every heterogeneously catalyzed reaction are:
- adsorption of the reactants on the surface of the catalyst; almost always at least one of the reactants is dissociated
- reaction between adsorbed species on the surface of the catalyst
- desorption of products into the gas phase

(b) see Fig. 1.2.

(c) Sabatier's Principle: For every catalytic reaction an optimum catalyst and optimum reaction conditions exist for which the interactions between adsorbed species and he surface of the catalyst is not too strong but not too weak either, such that the rate of reaction is maximum.

(d) In an autocatalytic reaction one of the reactants promotes its own formation, as in the schematic reaction: $X + Y \rightarrow 2X$.

(e) The reaction $\text{NO}_{ads} + \text{CO}_{ads} \rightarrow \text{CO}_2\uparrow + \frac{1}{2}\,\text{N}_2\uparrow$ proceeds via the following elementary steps:

$$NO_* + * \rightarrow N_* + O_*$$

$$CO_* + O^* \rightarrow CO_2 + 2^*$$

$$N_* + N^* \rightarrow N_2 + 2^*$$
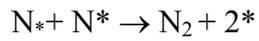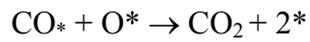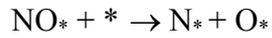
If the surface is entirely occupied, reaction (1) is inhibited, because it needs an empty site. As soon as an empty site becomes available (by desorption of a CO or an NO molecule) the sequence of three reactions creates four empty sites (three new free sites and the initial one), implying that several reaction events are enabled, which on their turn create again more free sites. The reaction thus explodes until the surface is empty. The reaction is autocatalytic with respect to the free sites.

Exercise 2.8 Potential Energy Profiles

(a)
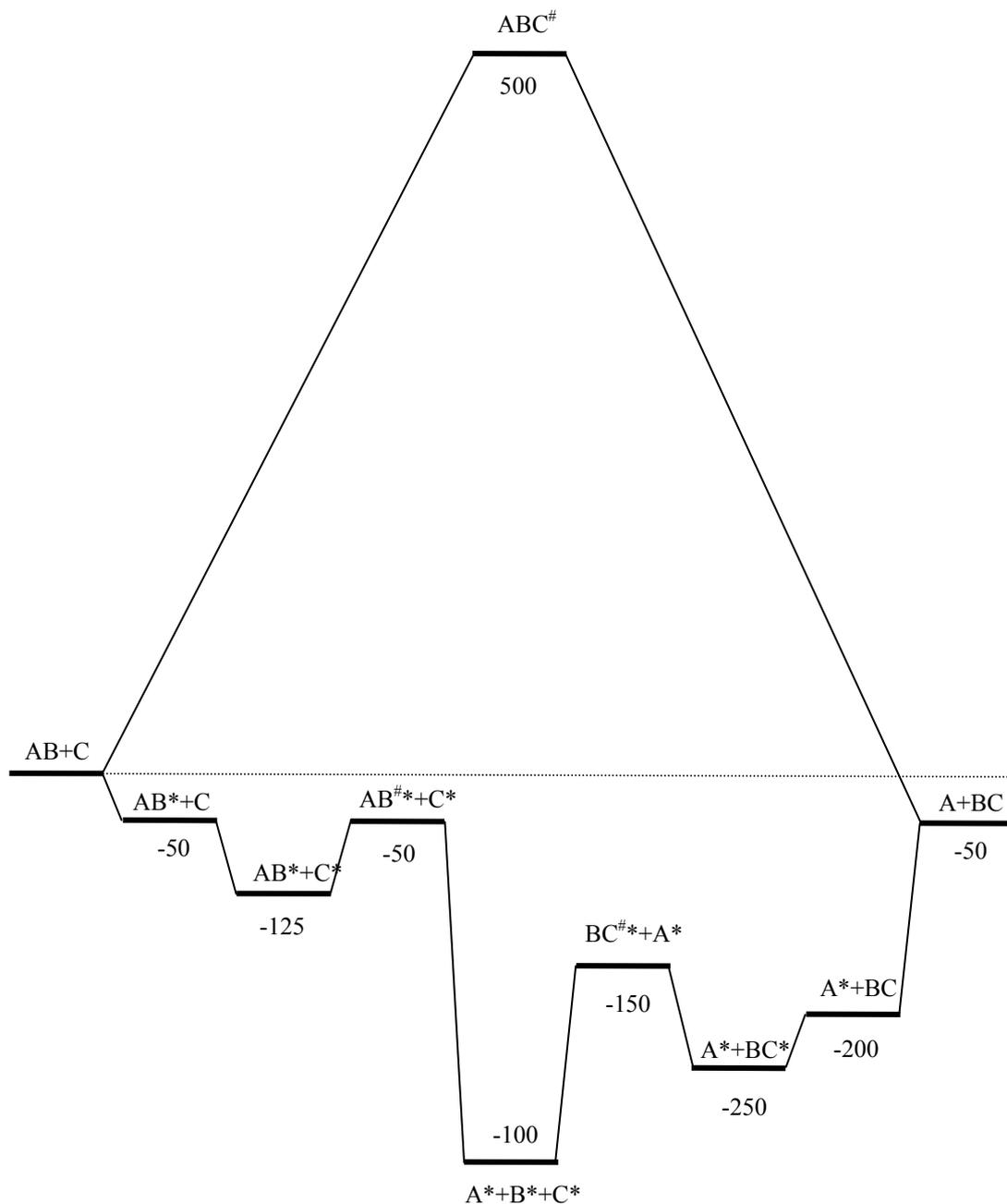
(b) A* is the most stable intermediate and the candidate for MARI

(c) The formation of BC has an activation energy of 250 kJ mol^{-1} and the most likely candiate for being the rate limiting step if we consider the energy alone. Be aware that there could also be entropy barriers in the adsorption process, but since they are considered not activated here this is not likely.

Exercise 2.9 Langmuir adsorption isotherms
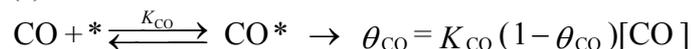
(a)
$$CO + * \xrightleftharpoons{K_{CO}} CO* \quad \rightarrow \quad \theta_{CO} = K_{CO}(1 - \theta_{CO})[CO]$$
$$\theta_{CO} = \frac{K_{CO}[CO]}{1 + K_{CO}[CO]}$$

(b)
$$CO + 2* \xleftrightarrow{K_{diss}} C* + O* \quad \rightarrow \quad \theta_C \theta_O = K_{diss}[CO](1 - \theta_C - \theta_O)^2$$

$$\theta_C = \theta_O = \theta \quad \rightarrow \quad \theta^2 = K_{diss}[CO](1 - 2\theta)^2$$

$$\theta_C = \theta_O = \frac{\sqrt{K_{diss}[CO]}}{1 + 2\sqrt{K_{diss}[CO]}}$$

(c)
$$\theta_{CO} = \frac{K_{CO}[CO]}{1 + \sqrt{K_{H_2}[H_2]} + K_{CO}[CO]} \quad ; \quad \theta_H = \frac{\sqrt{K_{H_2}[H_2]}}{1 + \sqrt{K_{H_2}[H_2]} + K_{CO}[CO]}$$

(d) $\theta_* = \dfrac{1}{1 + \sqrt{K_{H_2}[H_2]} + K_{CO}[CO]}$

(e) Mechanism:

$$CO + * \leftrightarrow CO*$$
$$H_2 + 2* \leftrightarrow 2H*$$
$$CO* + H* \xrightarrow{RLS} CHO* + *$$
$$CHO* + 3H* \leftrightarrow CH_3OH* + 3*$$
$$CH_3OH* \leftrightarrow CH_3OH + *$$
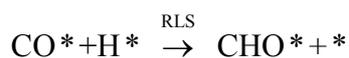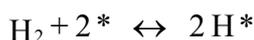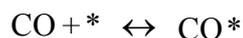
$$r = N k_3^+ \, \theta_{CO} \, \theta_H$$

$$= \frac{N k_3^+ K_{CO}\sqrt{K_{H_2}} \, [CO]\sqrt{[H_2]}}{(1 + K_{CO}[CO] + \sqrt{K_{H_2}[H_2]} + K_{CH_3OH}[CH_3OH])^2}$$

If hydrogen adsorbs weakly:

$$r = \frac{N k_3^+ \, K_{CO}\sqrt{K_{H_2}} \, [CO]\sqrt{[H_2]}}{(1 + K_{CO}[CO] + K_{CH_3OH}[CH_3OH])^2}$$

Order in hydrogen: $\quad n_{H2} = \tfrac{1}{2}$

Order in CO: $\quad -1 < n_{CO} < 1$, i.e. $n_{CO} = 1 - 2\theta_{CO}$

Order in methanol: $\quad -2 < n_{CH3OH} < 0$, i.e. $n_{CH_3OH} = -2\theta_{CH_3OH}$

Exercise 2.10 Problems in PEM fuel cells

(1) $H_2 + 2* \underset{k_1^-}{\overset{k_1^+}{\longleftrightarrow}} 2H* \quad k_H^+ = k_1^+ p_{H_2}, \ k_H^- = k_1^-$

(2) $CO + * \underset{k_2^-}{\overset{k_2^+}{\longleftrightarrow}} CO* \quad k_{CO}^+ = k_2^+ p_{CO}, \ k_{CO}^- = k_2^-$
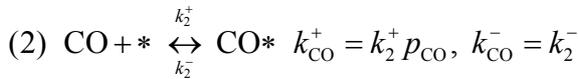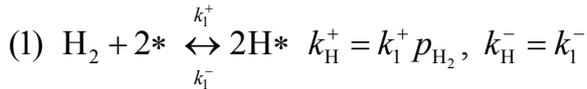
$$\frac{d\theta_H}{dt} = k_1^+ p_{H_2} \theta_*^2 - k_1^- \cdot \theta_H^2 = 0 \Rightarrow \theta_H = \sqrt{\frac{k_1^+}{k_1^-} p_{H_2}}\,\theta_* = \sqrt{K_1 p_{H_2}}\,\theta_*$$

$$k_H^+ = \frac{2 p_{H_2} S_0^{H_2}}{N_0\sqrt{2\pi m_{H_2} k_B T}}, \quad k_H^- = \nu \exp\!\left(\frac{-E_H^d}{RT}\right) \qquad k_H^+ \equiv k_1^+ P_{H_2}$$

$$\text{notice } k_H^- \equiv k_1^-$$

$$k_{CO}^+ = \frac{p_{CO} S_0^{CO}}{N_0\sqrt{2\pi m_{CO} k_B T}}, \quad k_{CO}^- = \nu \exp\!\left(\frac{-E_{CO}^d}{RT}\right) \qquad ect.$$

$$\frac{d\theta_{CO}}{dt} = k_2^+ \cdot p_{CO} \cdot \theta_* - k_2^- \cdot \theta_{CO} = 0 \Rightarrow \theta_{CO} = \frac{k_2^+}{k_2^-} \cdot p_{CO} \cdot \theta_* = K_2 p_{CO}\theta_*$$

$$\theta_* = 1 - \theta_H - \theta_{CO} = 1 - \sqrt{K_1 p_{H_2}}\,\theta_* - K_2 p_{CO}\theta_*$$

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO}} \quad K_1 = \frac{k_H^+}{k_H^- p_{H_2}}, \quad K_2 = \frac{k_{CO}^+}{k_{CO}^- p_{CO}}$$

$$\theta_H = \frac{\sqrt{K_1 p_{H_2}}}{1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO}}, \quad \theta_{CO} = \frac{K_2 p_{CO}}{1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO}}$$

(1)

P_{CO}	θ_H	θ_{CO}	θ_*
1 ppm	0.46	0.54	0
10 ppm	0.08	0.92	0
100 ppm	0.001	0.99	0

(2)   Reduce the bonding energy of CO

Exercise 2.11 Methanol synthesis

Make MeOH methanol by hydrogenation of CO_2 over the following intermediates: formate, di-oxo-methylene, methoxy, and methanol. The overall reaction reads:

$$3H_2 + CO_2 \longrightarrow CH_3OH + H_2O$$
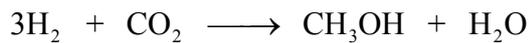
(1) Removal of adsorbed oxygen can go as:

(a) $O* + H* \rightleftarrows HO* + *$

(b) $HO* + H* \rightleftarrows H_2O* + *$ or as (bb) $2HO* \rightleftarrows H_2O* + H*$

(c) $H_2O* \rightleftarrows H_2O + *$
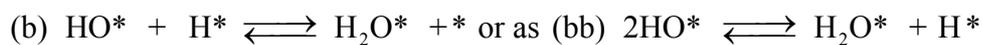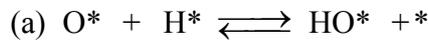
The H_2O can be disregarded, i.e. $\theta_O = 0$, and the process proceeds only forward from the rate limiting step. If the reaction order in hydrogen should be 1.5 must three hydrogenation steps be involved. Let us try the following:

(1) $H_2 + 2* \rightleftarrows 2H*$ in quasiequilibrium $\Rightarrow \theta_H = \sqrt{K_1 p_{H_2}}\ \theta_*$

(2) $CO_2 + * \rightleftarrows CO_2*$ in quasiequilibrium $\Rightarrow \theta_{CO_2} = K_2 p_{CO_2}\ \theta_*$

(3) $CO_2* + H* \rightleftarrows HCOO*$ in quasiequilibrium $\Rightarrow \theta_{HCOO} = \dfrac{K_3 \theta_{CO_2} \theta_H}{\theta_*}$

(4) $HCOO* + H* \ll \rightleftarrows H_2COO* + *$ in quasiequilibrium $\Rightarrow \theta_{H_2COO} = \dfrac{K_4 \theta_{HCOO} \theta_H}{\theta_*}$
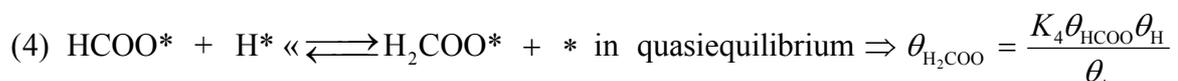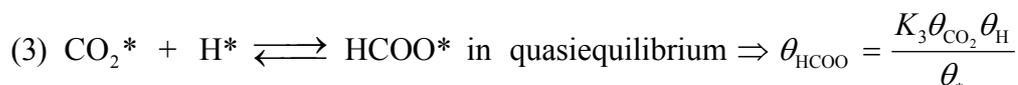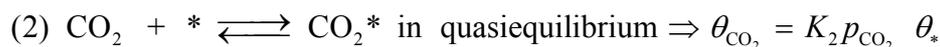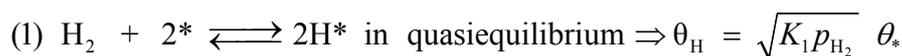
If we assume 5 to be rate limiting with no reverse rate we get:

$$(5) \quad H_2COO* + H* \longrightarrow H_3COO* \quad RLS \Rightarrow r = r_+ = k_5^+ \theta_{H_2COO} \theta_H$$

by replacing $\theta_{H_2COO} \Rightarrow r = \dfrac{k_5^+ K_4 \theta_{HCOO} \theta_H^2}{\theta_*}$

by replacing $\theta_{HCOO} \Rightarrow r = \dfrac{k_5^+ K_4 K_3 \theta_{CO_2} \theta_H^3}{\theta_*^2}$

By replacing θ_{CO_2} and θ_H we get

$$r = k_5^+ K_4 K_3 K_2 K_1^{\frac{3}{2}} p_{CO_2} p_{H_2}^{\frac{3}{2}} \theta_*^2$$

since $\theta_* \cong 1$

$$r = k_5^+ K_4 K_3 K_2 K_1^{\frac{3}{2}} p_{CO_2} p_{H_2}^{\frac{3}{2}}$$

Check reaction order

$$n_x \equiv p_x \frac{\partial \ln r_+}{\partial p_x} \Rightarrow n_{H_2} = \frac{3}{2}, \ n_{CO_2} = 1$$

Rate maximum:

$$\chi = \frac{p_{H_2}}{p_{tot}}, \Rightarrow p_{H_2} = \chi p_{tot}, \ p_{CO_2} = (1-\chi) p_{tot}$$

$$r = const \cdot \chi^{\frac{3}{2}} (1-\chi)$$

Maximum:

$$\frac{\partial r}{\partial \chi} = 0 \Rightarrow \chi = \frac{3}{5} = 0.6$$

Exercise 2.12 CO oxidation

$$(1) \quad CO + * \underset{}{\overset{K_1}{\rightleftarrows}} CO*$$

$$(2) \quad O_2 + 2* \underset{}{\overset{K_2}{\rightleftarrows}} 2O*$$

$$(3) \quad CO* + O* \underset{k_3^-}{\overset{k_3^+}{\rightleftarrows}} CO_2* + * \quad (RDS)$$

(4) $CO_2* \overset{K_4^{-1}}{\leftrightarrow} CO_2 + *$
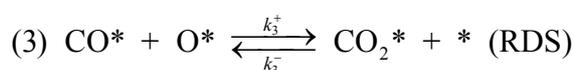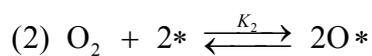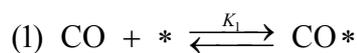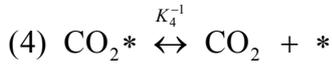
$\theta_{CO} = K_1 p_{CO} \theta_*$

$\theta_O = \sqrt{K_2 p_{O_2}} \theta_*$

$\theta_{CO_2} = K_4^{-1} p_{CO_2} \theta_*$

It is now straightforward to find an expression for the fraction of free sites from the site balance:

$$\theta_{CO} + \theta_O + \theta_{CO_2} + \theta_* = 1 \Rightarrow \theta_* = \frac{1}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + K_4^{-1} p_{CO_2}}$$

The rate is that of the rate-determining step:

$$r = k_3^+ \theta_{CO} \theta_O - k_3^- \theta_{CO_2} \theta_*$$

$$= k_3^+ K_1 \sqrt{K_2} \; p_{CO} \; \sqrt{p_{O_2}} \; \left(1 - \frac{p_{CO_2}}{p_{CO} \sqrt{p_{O_2}} K_G} \right) \theta_*^2$$

where

$$K_G = K_1 \sqrt{K_2} K_3 K_4$$

$$\ln(r_+) = \ln(k_3^+) + \tfrac{1}{2} \ln(p_{O_2}) + \ln(p_{CO}) + \ln(K_1) + \tfrac{1}{2} \ln(K_2)$$

$$-2 \ln \left(1 + \sqrt{K_2 p_{O_2}} + p_{CO} K_1 + \frac{p_{CO_2}}{K_4} \right)$$

$$n_{CO} = p_{CO} \frac{\partial \ln r_+}{\partial p_{CO}} = 1 - 2\theta_{CO}$$

$$n_{O_2} = p_{O_2} \frac{\partial \ln r_+}{\partial p_{O_2}} = 1/2 - \frac{2\theta_O}{2} = 1/2 - \theta_O$$

$$n_{CO_2} = p_{CO_2} \cdot \frac{\partial \ln r_+}{\partial p_{CO_2}} = -2\theta_{CO_2}$$

Find the overall activation energy E^{app}

$$E^{app} = RT^2 \cdot \frac{\partial \ln r_+}{\partial T} = RT^2 \left(\frac{\partial \ln k_3^+}{\partial T} + \frac{\partial \ln K_1}{\partial T} + \frac{1}{2} \frac{\partial \ln K_2}{\partial T} + \frac{2\partial \ln \theta_*}{\partial T} \right)$$

$$\frac{\partial \ln k_3^+}{\partial T} = \frac{\partial \ln k_0^3 e^{-\frac{E_3}{RT}}}{\partial T} = +\frac{E_3}{RT^2}$$

$$\frac{\partial \ln K_1}{\partial T} = \frac{\partial \ln\left(e^{-\frac{\Delta G_1}{RT}}\right)}{\partial T} = \frac{\partial \ln\left(e^{-\frac{\Delta H_1}{RT}+\frac{\Delta S_1}{R}}\right)}{\partial T} = \frac{\Delta H_1}{RT^2}$$

$$\frac{1}{2}\frac{\partial \ln K_2}{\partial T} = \frac{\Delta H_2}{2kT^2}$$

The difficult part is

$$\frac{\partial 2\ln \theta_*}{\partial T} = \frac{-2\partial \ln\left(1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + \frac{p_{CO_2}}{K_4}\right)}{\partial T} =$$

$$\frac{-2\cdot 1 \frac{\partial}{\partial T}\left(1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + \frac{p_{CO_2}}{K_4}\right)}{\left(1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + \frac{p_{CO_2}}{K_4}\right)} = -2\theta_*\left(+\frac{\Delta H_1}{RT^2}K_1 p_{CO} + \frac{\Delta H_2}{2RT^2}\sqrt{K_2 p_{O_2}} - \frac{\Delta H_4}{RT^2}\cdot\frac{p_{CO_2}}{K_4}\right) =$$

$$= -\frac{2\cdot\Delta H_1 \theta_{CO}}{RT^2} - \frac{2\Delta H_2 \theta_{O_2}}{2RT^2} + \frac{2\Delta H_4 \theta_{CO_2}}{RT^2}$$

leading to
$$E^{app} = E^3 + \Delta H_1 + \tfrac{1}{2}\Delta H_2 - 2\Delta H_1 \theta_{CO} - \Delta H_2 \theta_O + 2\Delta H_4 \cdot \theta_{CO_2}$$
$$E^{app} = E^3 + (1 - 2\theta_{CO})\Delta H_1 + \left(\frac{1}{2} - \theta_O\right)\Delta H_2 + 2\Delta H_4 \cdot \theta_{CO_2}$$

Exercise 2.13 Steam Reforming Reaction

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

High pressure will press the eq. to the left, so use moderate pressure. The process is endothermic $\Delta H > 0$ so use high temperature.

(2)

(1) $CH_4 + 2* \rightleftharpoons CH_3* + H*$ pseudoligevægt $\theta_{CH_3*} = \dfrac{K_1 P_{CH_4}\theta_*^2}{\theta_H}$

(2) $CH_3* + * \rightleftharpoons CH_2* + H*$ pseudoligevægt $\theta_{CH_2*} = \dfrac{K_2 \theta_{CH_3}\theta_*}{\theta_H}$
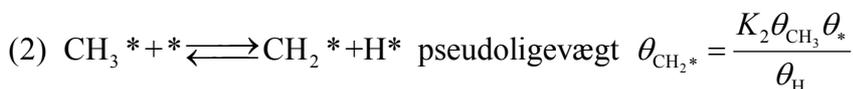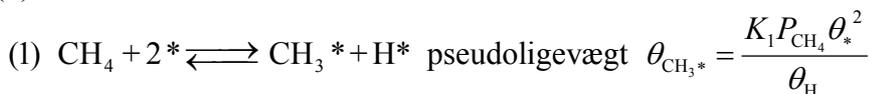
(3) $CH_2* + * \rightleftharpoons CH* + H*$ pseudoligevægt $\theta_{CH*} = \dfrac{K_3 \theta_{CH_2} \theta_*}{\theta_H}$

(4) $CH* + * \rightleftharpoons C* + H*$ pseudoligevægt $\theta_{C*} = \dfrac{K_4 \theta_{CH} \theta_*}{\theta_H}$

(5) $H_2O + * \rightleftharpoons H_2O*$ pseudoligevægt $\theta_{H_2O}* = K_5 \theta_* P_{H_2O}$

(6) $H_2O_* + * \rightleftharpoons HO* + H*$ pseudoligevægt $\theta_{OH*} = \dfrac{K_6 \theta_{H_2O} \theta_*}{\theta_H}$

(7) $HO* + * \rightleftharpoons O* + H*$ pseudoligevægt $\theta_{O*} = \dfrac{K_7 \theta_{OH} \theta_*}{\theta_H}$

(8) $2H* \rightleftharpoons H_2 + 2*$ pseudoligevægt $\theta_H = \sqrt{\dfrac{P_{H_2}}{K_8}} \theta_*$

(9) $C* + O* \rightleftharpoons CO* + *$ RLS $r = k_9^+ \theta_0 \theta_c - \dfrac{k_9^+}{K_9} \cdot \theta_{CO} \theta_*$

(10) $CO* \rightleftharpoons CO + *$ pseudoligevægt $\theta_{CO} = \dfrac{P_{CO} \theta_*}{K_{10}}$

Eliminate θ_O, θ_c and θ_{CO} utilizing $\theta_* = 1 - \sum_i \theta_i$

$\theta_{CO} = \dfrac{P_{CO} \theta_*}{K_{10}} = i\theta_*$, $\theta_H = \sqrt{\dfrac{P_{H_2}}{K_8}} \cdot \theta_* = h\theta_*$, $\theta_{H_2O} = P_{H_2O} K_5 \theta_* = g\theta_*$

$\theta_{OH} = \dfrac{K_5 K_6}{\sqrt{\dfrac{P_{H_2}}{K_8}}} \theta_* P_{H_2O} = f\theta_*$, $\theta_0 = K_5 K_6 K_7 K_8 \dfrac{P_{H_2O}}{P_{H_2}} \theta_* = e\theta_*$

$\theta_{CH_3} = \dfrac{K_1 \cdot P_{CH_4} \cdot \theta_*}{\sqrt{\dfrac{P_{H_2}}{K_8}}} = d\theta_*$, $\theta_{CH_2} = \dfrac{K_1 K_2 P_{CH_4} \theta_*}{\dfrac{P_{H_2}}{K_8}} = c\theta_*$, $\theta_{CH} = \dfrac{K_1 K_2 K_3 \cdot P_{CH_4} \cdot \theta_*}{\left(\dfrac{P_{H_2}}{K_8}\right)^{3/2}} = b\theta_*$

$\theta_c = \dfrac{K_4 \theta_{CH} \theta_*}{\theta_H} = \dfrac{K_1 K_2 K_3 K_4 P_{CH_4} \theta_*}{\left(\dfrac{P_{H_2}}{K_8}\right)^2} = a\theta_*$

$$\theta_* = 1 - \theta_C - \theta_{CH} - \theta_{CH_2} - \theta_{CH_3} - \theta_O - \theta_{OH} - \theta_{H_2O} - \theta_H - \theta_{CO}$$

$$\theta_* = 1 - a\theta_* - b\theta_* - c\theta_* - d\theta_* - e\theta_* - f\theta_* - g\theta_* - h\theta_* - i\theta_{CO}$$

$$\theta_* = \frac{1}{(1 + a + b + c + d + f + g + h)}$$

$$r = r^+ - r^- = k_9^+ \theta_O \theta_C - \frac{k_9^+}{K_9} \theta_{CO} \theta_*$$

if equilibum

$$r = 0 \Rightarrow K_9 = \frac{\theta_{CO}\theta_*}{\theta_O \theta_C} = \frac{P_{CO}P_{H_2}^3}{P_{H_2O}P_{CH_4}K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8^3 K_{10}}$$

$$K_G = \frac{P_{CO}P_{H_2}^3}{P_{H_2O}P_{CH_4}} \quad \text{at equilibrium}$$

$$K_G = K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8^3 K_9 K_{10}$$

$$r = \left(k_9^+ K_5 K_6 K_7 K_8 K_1 K_2 K_3 K_4 K_8^2 \cdot \frac{P_{H_2O} \cdot P_{CH_4}}{P_{H_2}^3} - \frac{k_9^+}{K_9} \cdot \frac{P_{CO}}{K_{10}} \right) \theta_*^2$$

$$r = k_9^- \cdot \frac{K_G}{K_{10}} \cdot \frac{P_{H_2O}P_{CH_4}}{P_{H_2}^3} \cdot \left(1 - \frac{P_{H_2}^3 P_{CO}}{K_G P_{CH_4} P_{H_2O}} \right) \theta_*^2$$

$$r_+ = k_9^- \cdot \frac{P_{H_2O}P_{CH_4}}{P_{H_2}^3} \cdot \frac{K_G}{K_{10}} \cdot \theta_*^2$$

if only oxygen on the surface (this is reasonable because O bonds strongly)

$$\theta_* \approx \frac{1}{1 + K_5 K_6 K_7 K_8 \dfrac{P_{H_2O}}{P_{H_2}}}$$

$$r_+ \approx k_9^- \cdot \frac{K_G}{K_{10}} \frac{P_{H_2O}P_{CH_4}}{P_{H_2}^3} \cdot \frac{1}{\left(1 + K_5 K_6 K_7 K_8 \dfrac{P_{H_2O}}{P_{H_2}} \right)^2}$$

(3) Find reaction order

$$n_x \equiv P_x \frac{\delta \ln r_+}{\delta P_x}$$

$n_{CH_4} = 1$, $n_{CO} = 0$, $n_{H_2O} = 1 - 2\theta_o$, $n_{H_2} = -3 + 2\theta_o$

So

$n_{CH_4} > 0$,

n_{H_2O} can be < 0 if $\theta_0 > 0.5$

$n_{H_2} < 0$

This does not fit with observations.

(4) All over again. Now let the first step be rate limiting.
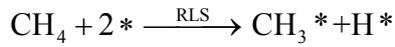
$$CH_4 + 2* \xrightarrow{\quad RLS \quad} CH_3 * + H*$$

(1) $CH_4 + 2* \xrightarrow{\quad RLS \quad} CH_3 * + H*$ RLS $r = r_+ - r_- = k_1^+ P_{CH_4} \theta_*^2 - k_1^- \theta_{CH_3} \theta_H$

(9) $C* + O* \rightleftharpoons CO* + *$ pseudoeq. $\theta_c = \frac{1}{K_9} \cdot \frac{\theta_{CO} \theta_*}{\theta_O}$

Write up expressions for all the various intermediates in terms of free sites:

$$\theta_{CO} = \frac{P_{CO} \theta_*}{K_{10}} = i\theta_* \quad , \quad \theta_H = \sqrt{\frac{P_{H_2}}{K_8}} \quad \cdot \quad \theta_* = h\theta_* \quad , \quad \theta_{H_2O} = P_{H_2O} \cdot K_5 \cdot \theta_* = g\theta_*$$

$$\theta_{OH} = \frac{K_5 K_6}{\sqrt{\dfrac{P_{H_2}}{K_8}}} \theta_* P_{H_2O} = f\theta_* , \quad \theta_O = K_5 K_6 K_7 K_8 \cdot \frac{P_{H_2O}}{P_{H_2}} \cdot \theta_* = e\theta_*$$

$$\theta_C = \frac{P_{CO} P_{H_2}}{K_9 K_{10} K_5 K_6 K_7 K_8 P_{H_2O}} \theta_*$$

$$\theta_{CH} = \frac{P_{CO} P_{H_2}^{\frac{3}{2}}}{K_9 K_{10} K_4 K_5 K_6 K_7 K_8^{\frac{3}{2}} P_{H_2O}} \theta_*$$

$$\theta_{CH_2} = \frac{P_{CO} P_{H_2}^2}{K_9 K_{10} K_3 K_4 K_5 K_6 K_7 K_8^2 P_{H_2O}} \theta_*$$

$$\theta_{CH_3} = \frac{P_{CO} P_{H_2}^{\frac{5}{2}}}{K_9 K_{10} K_2 K_3 K_4 K_5 K_6 K_7 K_8^{\frac{5}{2}} P_{H_2O}} \theta_*$$

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$$r = r_+ - r_- = k_1^+ P_{CH_4} \theta_*^2 - k_1^- \theta_{CH_3} \theta_H = \left(k_1^+ P_{CH_4} - k_1^- \frac{P_{CO} P_{H_2}^3}{K_9 K_{10} K_2 K_3 K_4 K_5 K_6 K_7 K_8^3 P_{H_2O}} \right) \theta_*^2$$

$$r = r_+ - r_- = k_1^+ P_{CH_4} \theta_*^2 - k_1^- \theta_{CH_3} \theta_H = k_1^+ P_{CH_4} \left(1 - \frac{P_{CO} P_{H_2}^3}{K_9 K_{10} K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8^3 P_{H_2O} P_{CH_4}} \right) \theta_*^2$$

$$r = k_1^+ P_{CH_4} \left(1 - \frac{P_{CO} P_{H_2}^3}{K_G P_{H_2O} P_{CH_4}} \right) \theta_*^2$$

Let us again assume that adsorbed oxygen atoms are MARI:

$$\theta_* \approx \frac{1}{1 + K_5 K_6 K_7 K_8 \dfrac{P_{H_2O}}{P_{H_2}}}$$

we get

$$r^+ = k_1^+ P_{CH_4} \left(\frac{1}{1 + K_5 K_6 K_7 K_8 \dfrac{P_{H_2O}}{P_{H_2}}} \right)^2$$

$$n_x = P_x \frac{\delta \ln r_+}{\delta P_x}$$

$$n_{CH_4} = 1$$
$$n_{H_2O} = -2\theta_O$$
$$n_{H_2} = +2\theta_O$$

All in agreement with observations.

Exercise 2.14 HDS Reaction

We are missing the reverse rate. Probably because the re-adsorption of butadiene is very weak.

(b) $\quad \theta_T = \dfrac{K_1 P_T}{1 + K_1 P_T} \qquad\qquad \theta_H = \dfrac{\sqrt{K_2 P_{H_2}}}{1 + \sqrt{K_2 P_{H_2}}}$

It is assumed that the thiophene adsorbs on $\otimes$ sites and the hydrogen on * sites. Those sites are complementary.

(1) $\text{TS} + \otimes \Leftrightarrow \text{TS}\otimes \quad \theta_{\text{TS}} = K_1 P_{\text{T}} \theta_{\otimes}$

(2) $\text{H}_2 + 2* \Leftrightarrow 2\text{H}* \quad \theta_{\text{H}} = \sqrt{K_2 P_{\text{H}_2}} \cdot \theta*$

(3) $\text{TS}\otimes + \text{H}* \Leftrightarrow \text{HTS}\otimes + * \quad \text{RLS} \quad r = k_3^+ \theta_{\text{TS}\otimes} \theta_{\text{H}*} - \dfrac{k_3}{K_3} \theta_{\text{HTS}\otimes} \theta_*$

(4) $\text{HTS}\otimes + \text{H}* \Leftrightarrow \text{H}_2\text{T}_{\text{gas}} + \text{S}\otimes + * \quad \theta_{\text{HTS}\otimes} = \dfrac{P_{\text{H}_2}T \theta_{\text{S}\otimes} \theta_*}{K_4 \theta_{\text{H}*}}$

(5) $\text{S}\otimes + \text{H}* \Leftrightarrow \text{HS}\otimes + * \quad \theta_{\text{S}\otimes} = \dfrac{\theta_{\text{HS}\otimes} \theta_*}{K_5 \theta_{\text{H}*}}$

(6) $\text{HS}\otimes + \text{H}* \Leftrightarrow \text{H}_2\text{S}\otimes + * \quad \theta_{\text{HS}\otimes} = \dfrac{\theta_{\text{H}_2\text{S}\otimes} \theta_*}{K_6 \theta_{\text{H}*}}$

(7) $\text{H}_2\text{S}\otimes \Leftrightarrow \text{H}_2\text{S}_{\text{gas}} + \otimes \quad \theta_{\text{H}_2\text{S}\otimes} = \dfrac{P_{\text{H}_2\text{S}} \theta_{\otimes}}{K_7}$

$$r = k_3^+ \cdot \theta_{\text{TS}\otimes} \cdot \theta_{\text{H}*} - \frac{k_3}{K_3} \theta_{\text{HTS}\otimes} \theta_*$$

$$r = k_3^+ \cdot K_1 \cdot P_T \cdot \theta_{\otimes} \cdot \sqrt{K_2 \cdot P_{\text{H}_2}} \cdot \theta* - \frac{k_3^+ \cdot P_{\text{H}_2\text{T}} \cdot P_{\text{H}_2\text{S}} \cdot \theta_{\otimes} \cdot \theta_*}{K_3 \cdot K_4 \cdot K_5 \cdot K_6 \cdot K_7 \cdot (K_2 P_{\text{H}_2})^{\frac{3}{2}}}$$

$$r = k_3 K_1 P_T \sqrt{K_2 P_{\text{H}_2}} \left(1 - \frac{\cdot P_{\text{H}_2\text{T}} P_{\text{H}_2\text{S}}}{P_T \sqrt{P_{\text{H}_2}} \cdot K_1 \sqrt{K_2} \cdot K_3 K_4 \cdot K_5 \cdot K_6 \cdot K_7 \cdot K_2^{\frac{3}{2}} \cdot P_{\text{H}_2}^{\frac{3}{2}}} \right) \theta_{\otimes} \theta_*$$

$$r = k_3 K_1 P_T \sqrt{K_2 P_{\text{H}_2}} \left(1 - \frac{P_{\text{H}_2\text{T}} P_{\text{H}_2\text{S}}}{P_T P_{\text{H}_2}^2 K_G} \right) \theta_{\otimes} \cdot \theta_*$$

$$K_G = K_1 K_2^{2} K_3 K_4 K_5 K_6 K_7$$

$$r = r_+ - r_- \quad r_+ = k_3 P_T K_1 \sqrt{K_2 P_{\text{H}_2}} \cdot \theta_* \theta_{\otimes}$$

This fulfills the kinetic when

$$r_+ = \frac{k_3^+ P_T K_1}{1 + P_T K_1} \cdot \frac{\sqrt{K_2 P_{\text{H}_2}}}{1 + \sqrt{K_2 P_{\text{H}_2}}} = \frac{k P_T}{1 + P_T K_1} \cdot \frac{\sqrt{K_2 P_{\text{H}_2}}}{1 + \sqrt{K_2 P_{\text{H}_2}}}$$

$$r_+ = \frac{k_3^+ P_T K_1}{1 + P_T K_1} \cdot \frac{\sqrt{K_2 P_{H_2}}}{1 + \sqrt{K_2 P_{H_2}}} = \frac{k P_T}{1 + P_T K_1} \cdot \frac{\sqrt{K_2 P_{H_2}}}{1 + \sqrt{K_2 P_{H_2}}}$$

θ_T and θ_H are MARI for the two types of sites

(3) $r = r_+$ In an excess of H_2 since there is a low tendency for forming hydrogen.

$F(5)$ $r^+ = k_3^+ K_1 P_T \sqrt{K_2 P_{H_2}} \, \theta_\otimes \cdot \theta_*$. the rate increases with P_T and P_{H2}.

Notice that the rate will not vanich even if we let P_T or P_{H2} become very large since they each use their sites. The are no competion between the two sites.

Exercise 2.15 Hydrogenation of Ethane

(1) $C_2H_6 + 2* \underset{}{\overset{Q}{\rightleftarrows}} C_2H_5* + H*$, $\dfrac{d\theta_{C_2H_5*}}{dt} = k_1^+ P_{C_2H_6} \cdot \theta_*^2 - k_1^- \theta_{C_2H_5} \theta_H = 0 \Rightarrow$

$$\theta_{C_2H_5} = \frac{K_1 P_{C_2H_6} \theta_*^2}{\theta_H}$$

(2) $C_2H_5* + H* \xrightarrow{\text{RLS}} 2CH_3* \Rightarrow r = k_2^+ \theta_{C_2H_5} \theta_H - k_2^- \theta_{CH_3}^2$

(3) $CH_3* + H* \underset{}{\overset{Q}{\rightleftarrows}} CH_4 + 2*$ $\dfrac{d\theta_{CH_3}}{dt} = -k_3^+ \theta_{CH_3} \cdot \theta_H + k_3^- P_{CH_4} \theta_*^2 = 0 \Rightarrow$

$$\theta_{CH_3} = \frac{P_{CH_4} \theta_*^2}{K_3 \theta_H}$$

(4) $H_2 + 2* \underset{}{\overset{Q}{\rightleftarrows}} 2H* \Rightarrow \dfrac{d\theta_H}{dt} = k_4^+ P_{H_2} \theta_*^2 - k_4^- \theta_H^2 = 0 \Rightarrow$

$$\theta_H = \sqrt{K_4 P_{H_2}} \cdot \theta_*$$

(a) By adding D_2 will D be incorborated through step one:

. $\Rightarrow C_2H_6 + \Leftrightarrow C_2H_5 + H*$ but $C_2H_5* + D* \longrightarrow C_2H_5D$
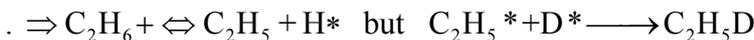
Repeat n times $C_2H_{6-n}P_n$.

(c) and (d)

RLS $r = k_2^+ \theta_{C_2H_5} * \theta_H - k_2^- \theta_{CH_3}^2$

$$\theta_{C_2H_5*} = \frac{K_1 P_{C_2H_6} \cdot \theta_*^2}{\theta_H} = \frac{K_1 P_{C_2H_6} \theta_*}{\sqrt{K_4 P_{H_2}}}, \quad \theta_{CH_3} = \frac{P_{CH_4} \theta_*^2}{K_3 \theta_H} = \frac{P_{CH_4} \cdot \theta_*}{K_3 \sqrt{K_4 P_{H_2}}} \Rightarrow$$

$$r = k_2^+ \cdot K_1 P_{C_2H_6} \theta_*^2 - k_2^- \cdot \frac{P_{CH_4}^2 \theta_*^2}{K_3^2 K_4 P_{H_2}} = k_2^+ K_1 P_{C_2H_6} \left(1 - \frac{P_{CH_4}^2}{K_1 K_2 K_3^2 K_4 P_{C_2H_6} P_{H_2}} \right) \theta_*^2$$

$$r = k_2^+ K_1 P_{C_2H_6} \left(1 - \frac{P_{CH_4}^2}{K_G P_{C_2H_6} P_{H_2}} \right) \theta_*^2 \quad \theta_* = 1 - \theta_{C_2H_5} - \theta_{CH_3} - \theta_H \Rightarrow$$

$$\theta_* = \frac{1}{1 + \dfrac{K_1 P_{C_2H_6}}{\sqrt{K_4 P_{H_2}}} + \dfrac{P_{CH_4}}{K_3 \sqrt{K_4 P_{H_2}}} + \sqrt{K_4 P_{H_2}}} \approx \frac{1}{1 + \sqrt{K_4 P_{H_2}}} \quad \text{when} \quad \theta_{C_2H_5} = \theta_{CH_3} \approx 0$$

(c)   We can not study transients $\left(\dfrac{d\theta_x}{dt} \right) = 0$ in quasequilibrium.

(d) Has been derived $r = k_2^+ K_1 P_{C_2H_6} \left(1 - \dfrac{P_{CH_4}^2}{P_{H_2} P_{C_2H_6} K_G} \right) \theta_*^2 \quad \theta_* = \dfrac{1}{1 + \sqrt{K_4 P_{H_2}}}$

Solutions to Exercises in Chapter 3

Exercise 3.1 Average molecular velocities

(a)   The expression for the average velocity of a molecule is:

$$\bar{v} = \left(\frac{8\,R\,T}{\pi\,m} \right)^{\frac{1}{2}}$$

$R = 8.314$ J K^{-1} mol^{-1}
$T = 298$ K
$m = 28 \cdot 10^{-3}$ kg mol^{-1}
1 J $= 1$ kg m^2 s^{-2}

Substitution gives: v $= 475$ m s^{-1}

(b) $\bar{v}_{He} = \left(\dfrac{8\,R\;298}{\pi\;4} \right)^{\frac{1}{2}} = \left(\dfrac{8\,R\,T}{\pi\;28} \right)^{\frac{1}{2}} = \bar{v}_{N_2}(T) \;\rightarrow\; T = 298 * \dfrac{m_{N_2}}{m_{He}} = 2090$ K

(c) The average translational energy of every ideal gas is 1.5 RT, equalling 1.247 kJ mol^{-1} at 100 K, 3.71 kJ mol^{-1} at 298 K and 12.47 kJ mol^{-1}at 1000 K.

Exercise 3.2 Collisions in the gas phase

(a) $\rho_{N_2} = \dfrac{1000\,\text{liter}}{24.7894\,\text{liter mol}^{-1}} \, 6.022 \times 10^{23} \, x \; 0.25 = 6.1 \times 10^{24}\,/\text{m}^3 \quad \rho_{H_2} = 1.82 \times 10^{25}\,/\text{m}^3$

(b) The number of collisions between molecules in a mixture is:

$$Z(A,B) = \frac{\pi\,d^2}{g_{AB}} \left(\frac{8\,k\,T}{\pi\mu} \right)^{\frac{1}{2}} \rho_A \rho_B$$

substituting the values for H$_2$ (note that $\mu = m/2$):

$$Z(H_2, H_2) = \frac{(1.82 \times 10^{25}\,\text{m}^{-3})^2 \, \pi \, (2.71 \times 10^{-10})^2}{2}\, x$$

$$\left(\frac{8\,(8.31\,\text{J/K mol})(298\,\text{K})}{\pi\,(2 \times 10^{-3}\text{kg/mol})} \right)^{\frac{1}{2}}$$
$$= 9.55 \times 10^{34}\,/\text{m}^3 \times \text{s}$$

(c) $Z(N_2,N_2) = 5.5 \cdot 10^{33}\,/\text{m}^3 \cdot \text{s}$

(d) The effective collision diameter d is ½$(d_A + d_B) = 0.322$ nm, yielding $Z(N_2,H_2) = 6.62 \times 10^{34}\,/\text{m}^3 \cdot \text{s}$

(e) The total number of collisions is:

$$Z_{total} = Z(H_2,H_2) + Z(N_2,N_2) + Z(N_2,H_2) = 1.672 \times 10^{35} \text{ /m}^3\cdot\text{s}$$

Exercise 3.3 Collision Theory of Reaction Rates

The rate of reaction of a bimolecular collision between unequal molecules is

$$r = \frac{-dC_i}{dt} = \pi d^2 \left(\frac{8RT}{\pi\mu} \right)^{\frac{1}{2}} e^{-E_a/RT} C_1 C_2 b$$

(with C_i in mol·l^{-1}, μ_i in gram per mol and d in meters).
To bring this expression in its Arrhenius form, we first calculate the activation energy:

$$E_{act} = RT^2 \frac{\partial \ln(r)}{\partial T} = E_a + \frac{1}{2}RT$$

If we rewrite the collision rate expression as follows (i.e. with the activation energy in the exponential):

$$r = \frac{-dC_i}{dt} = \pi d^2 \left(\frac{8RT}{\pi\mu} \right)^{\frac{1}{2}} e^{-(E_a + RT/2)/RT} e^{\frac{1}{2}} C_1 C_2$$

we immediately recognize the preexponential factor:

$$v_{eff} = e^{\frac{1}{2}} \pi d^2 \left(\frac{8RT}{\pi\mu} \right)^{\frac{1}{2}}$$

Substitution of values (pay attention to the units): $v_{eff} = 1.4 \times 10^{11} T^{\frac{1}{2}} \text{ L mol}^{-1} \text{ s}^{-1}$

The observed value is $10^8 T^{1/2} \text{ L mol}^{-1} \text{ s}^{-1}$. Within the collision theory, such differences are attributed to steric factors, which in this case would have to be on the order of 10^{-3}. In reality, the difference is due to the internal degrees of freedom of the reacting molecules. Transition theory provides the framework to account for these effects.
bb

Exercise 3.4 General Aspects of Partition Functions

a)
$$Q_{gas} = \frac{(q_g)^{N_g}}{N_g!} \quad N_g = N_a = \frac{PV}{kT} \quad q = q_g = \frac{V(2\pi mkT)^{\frac{3}{2}}}{h^3}$$

use Stirlings approximation $\qquad \ln(N!) \approx N \ln(N) - N$

$$\mu = -kT \cdot \frac{\partial \ln Q_{\mathrm{g}}}{\partial N_{\mathrm{g}}} = -kT \cdot \ln\left(\frac{q}{N_{\mathrm{a}}}\right) = -kT \cdot \ln\left(\frac{qkT}{PV}\right)$$

$$\mu = -kT \cdot \ln\left(\frac{qkT}{VP_{\mathrm{O}}}\right) + kT \cdot \ln\left(\frac{P}{P_{\mathrm{O}}}\right) = \mu_{\mathrm{O}} + kT \cdot \ln\left(\frac{P}{P_{\mathrm{O}}}\right)$$

where $\mu_{\mathrm{O}} = -kT \cdot \ln\left[\dfrac{(2\pi mkT)^{\frac{3}{2}} kT}{h^3 P_{\mathrm{O}}}\right]$

(b)

$$P = \frac{kT \cdot \partial \ln Q}{\partial V} = \frac{kT \cdot N_{\mathrm{a}} \cdot \partial \ln q}{\partial V} = \frac{kTN_{\mathrm{a}}}{V} \quad \text{i.e.} \quad P \cdot V = N_a kT \quad \text{ideal gas}$$

(c)

$$E = KT^2 \cdot \frac{\partial \ln Q}{\partial T} = kT^2 \cdot N_{\mathrm{a}} \cdot \frac{\partial \ln q}{\partial T} = kT^2 \cdot N_{\mathrm{a}} \frac{1}{q}\frac{\partial q}{\partial T} = kT^2 N_{\mathrm{a}} \cdot \frac{3}{2} \cdot \frac{1}{T}$$

$$E = \frac{3}{2} N_{\mathrm{a}} kT \quad N_{\mathrm{a}} \cdot k = R \Rightarrow E = \frac{3}{2} RT$$

(d)

$$S = \frac{\partial}{\partial T} \cdot (kT \ln Q) = k \ln Q + k_{\mathrm{B}} T \frac{\partial \ln Q}{\partial T}$$

$$S = kN_{\mathrm{a}} \ln q - kN_{\mathrm{a}} \cdot \ln N_{\mathrm{a}} + kN_{\mathrm{a}} + kN_{\mathrm{a}} \frac{3}{2}$$

$$S = R \cdot \ln q - R \cdot \ln N_{\mathrm{a}} + R\frac{5}{2} = R\left(\ln q - \ln N_{\mathrm{a}} + \ln e^{\frac{5}{2}}\right)$$

$$S = R \cdot \ln\left(\frac{q \cdot e^{\frac{5}{2}}}{N_{\mathrm{a}}}\right) = R \cdot \ln\left(\frac{V \cdot e^{\frac{5}{2}} (2\pi mkT)^{\frac{3}{2}}}{N_{\mathrm{a}} h^3}\right)$$

ideal gas $PV = N_a kT$

The Sackur-Tetrode equation helpful for calculating for example the standard entropy of a simple monoatomic gas like He at standard conditions.

$$S = R \cdot \ln\left[\frac{e^{\frac{5}{2}} (2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3 \cdot P}\right]$$

Exercise 3.5 Partition Functions

(a) For an ideal gas:
$$q_{trans} = \frac{(2\pi m\, k\, T)^{3/2}}{h^3} V = \frac{(2\pi m\, k\, T)^{3/2}}{h^3} \frac{nR\, T}{P}$$

Substitution gives $q_{trans} = 3.555 \times 10^{30}$

(b) q_{trans} is proportional to $T^{5/2}$, inversely proportional to P and proportional to V. The translational partition function in three dimensions is proportional to $m^{3/2}$, and thus q_{trans} (N) $= 1.258 \times 10^{30}$ and q_{trans} (N$_3$) $= 6.533 \times 10^{30}$.

(c) The vibrational partition function of vibrations with frequencies above ± 200 cm^{-1} is in practice equal to 1, if the temperature is not too high.

(d) The rotational partition function of a diatomic molecule is:
$$q_{rot} = \frac{8\pi^2 I k T}{h^2\, g_{AB}}$$
in which g_{AB} represents the symmetry number. Substitution yields $q_{rot} = 51.4$.

Hint use for example that the energy levels are separated by $\dfrac{8\pi^2 I}{h^2} = 1.9987\,\text{cm}^{-1}$ and 1 meV $=$ 8.08 cm^{-1}. As the formula indicates, q_{rot} is proportional to T and independent on either V or P.

(e) The total partition function is the product of the partition functions for translation, vibration, and rotation, and equals 1.83×10^{32} at room temperature.

Exercise 3.6 Rotational Partition Functions

In order to calculate the partition function we need to know the energy levels of the molecule. Note that the given frequencies correspond to transitions between energy levels, and not the levels themselves.

According to quantum mechanics, the rotational levels of a diatomic molecule are given by the general relation:
$$\varepsilon_j = j\,(j+1)\,\frac{h^2}{8\pi^2 I}; \quad I = \mu\, r^2$$
where in transitions the rotational quantum number changes by one unit only. Notice that for photons: The measured spectrum gives us the values of $\varepsilon_j - \varepsilon_{j-1}$ expressed in wave numbers (frequencies), and

$$E_{Photon} = h\nu = \hbar\omega = \hbar c k_{Photon} = \frac{hc}{\lambda}$$

1 meV $=$ 8.08 cm^{-1} .

Hence we can construct the energy level scheme as in the following table:

j	j(j+1)	$\varepsilon_j - \varepsilon_{j-1}$ (cm^{-1})	ε_j (cm^{-1})
0	0	-	0
1	2	20	20
2	6	40	60
3	12	60	120
4	20	80	200
5	30	100	300

The partition function equals

$$q_{\text{rot}} = \sum_{j=0}^{5} e^{-\varepsilon_j / kT} = \sum_{j=0}^{5} e^{-\frac{10}{69.5} j(j+1)}$$

$$q_{\text{rot}} = 1 + 0.75 + 0.422 + 0.178 + 0.056 + 0.013 = 2.42$$

Exercise 3.7 Vibrational Partition Functions

The expressions for the vibrational partition function with respect to the ground state, and the fraction of molecules in a certain state labeled i are:

$$q_{\text{vib}} = \frac{1}{1 - e^{-h\nu/kT}} \; ; \quad x_i = \frac{e^{-\varepsilon_i/kT}}{q_{\text{vib}}} \rightarrow x_0 = \frac{1}{q_{\text{vib}}}$$

Application of these expressions gives the following results:

molecule	ν (cm^{-1})	q_{vib} 300 K	q_{vib} 600 K	q_{vib} 1500 K	x_0 300 K	x_0 600 K	x_0 1500 K
I$_2$	213	1.563	2.500	5.411	0.640	0.400	0.185
Cl$_2$	557	1.074	1.357	2.416	0.931	0.737	0.414
O$_2$	1556	1.006	1.024	1.290	0.999	0.976	0.775
HCl	2886	1.000	1.001	1.067	1.000	0.999	0.937
H$_2$	4160	1.000	1.000	1.019	1.000	1.000	0.982

The table clearly shows the trends that the partition function increases with decreasing frequency and increasing temperature. For many molecules under typical catalytic reaction conditions, however, the vibrational partition function deviates only slightly from unity, implying that these molecules are predominantly in their vibrational ground state. This also have the interesting implication that the vibrational energy cannot contribute to the heat capacity at low temperatures. Note that upon adsorption on a surface, the bonds between the substrate and the adsorbed molecule usually give rise to low frequency modes with partition functions that are significantly larger than 1.

Exercise 3.8 Partition Function, Average Energy and Equilibrium Constant

(a)   We choose the ground state of the molecule A as the zero of energy:

$$q = \sum_i e^{-\varepsilon_i/kT} = 1 + e^{-\Delta E/kT}$$

$$T \to 0: \quad q \to 1$$
$$T \to \infty: \quad q \to 2$$

Thus, at $T = 0$ K the molecule A is entirely in the ground state, while at $T = \infty$K both levels are equally occupied.

(b) Application of the logarithmic derivative yields:

$$\overline{\varepsilon} = kT^2 \frac{\partial}{\partial T} \ln(q)$$

$$= kT^2 \frac{1}{q} \frac{\partial(q)}{\partial T}$$

$$= kT^2 \frac{1}{1 + e^{-\Delta E/kT}} \frac{\Delta E}{kT^2} e^{-\Delta E/kT}$$

$$= \frac{\Delta E}{e^{\Delta E/kT} + 1}$$

The limiting values are $\varepsilon = 0$ at low and $\varepsilon = \Delta E/2$ at high temperature (as expected!)

(c) The energy levels of B are $\Delta E/2$, $3\Delta E/4$ and ΔE with respect to the ground state of A and thus the partition function of B equals:

$$q_B = e^{-\Delta E/2kT} + e^{-3\Delta E/4kT} + e^{-\Delta E/kT}$$

Hence the equilibrium constant becomes:

$$K = \prod_i q_i{}^{v_i} = \frac{q_B}{q_A} = \frac{e^{-\Delta E/2kT} + e^{-3\Delta E/4kT} + e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}}$$

which has limiting values of 0 and 3/2 at low and high temperatures, respectively. The value $K = 0$ indicates that the equilibrium is on the side of A only, due to the ground state of A being the lowest energy state overall. At higher temperatures, entropy becomes important as well, which favours the formation of the three-level system B over the two level system A. In the limit of $T \to \infty$, all levels are equally occupied, resulting in a limiting value of $K = 3/2$.

Exercise 3.9 Equilibrium Constants from Partition Functions

The equilibrium constant for the isomerization reaction is

$$K = \frac{q_B}{q_A} = \frac{\sum_{i=0}^{\infty} e^{-\varepsilon_i^B/kT}}{\sum_{i=0}^{\infty} e^{-\varepsilon_i^A/kT}} = e^{-\frac{\Delta E}{kT}} \cdot \frac{\sum_{i=0}^{\infty} e^{-\frac{i\,\Delta E}{2\,kT}}}{\sum_{i=0}^{\infty} e^{-i\frac{\Delta E}{kT}}}$$
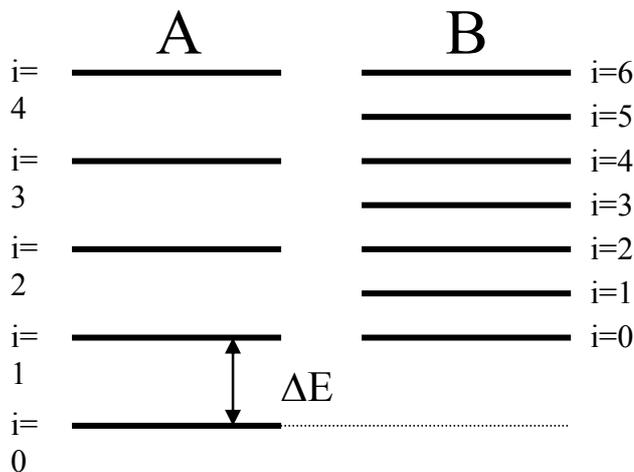
Using the expression for the sum of an infinite series $\sum_{i=0}^{\infty} e^{-ix} = \frac{1}{1-e^{-x}}$, this becomes:

$$K = e^{-x}\frac{1-e^{-x}}{1-e^{-x/2}}; \quad x = \frac{\Delta E}{kT}$$

(a) At low temperatures such as $T = 0.1\ \Delta E/k$ (or $x = 10$) the equilibrium constant is very small, in this case $K = 4.57\ 10^{-5}$. Hence the equilibrium lies mainly on the left, at A.

(b) $T = 2\ \Delta E/k$ (or $x = \frac{1}{2}$) yields $K = 1.08$, A and B are present in almost equal concentrations.

(c) $T = 10\ \Delta E/k$ (or $x = 0.1$) yields $K = 1.78$.

(d) The limiting values of the equilibrium constant are $K = 0$ at $T = 0$ and $K = 2$ for $T \to \infty$. Notice we must use le hospitals rule for finding this latter limit. The example illustrates that at low temperature the lower energy of the ground state of A dictates the equilibrium to lie at the left, while at high temperatures the higher number of levels (twice as many as in A per energy therefore $K = 2$) available for isomer B draws the equilibrium to the right. In other words, energy is dominant at low temperatures while entropy is dominant at high temperatures.

Exercise 3.10 Equilibrium Constants for Reactions on Steps

Number of step sites occupied S
Total Number of step sites M
Number of terrace sites T
Total Number of Terrace sites N

$$Q_{step} = Q_s = \frac{M!}{(M-S)!S!}q_s^S$$

$$Q_{\text{Terrace}} = Q_{\text{T}} = \frac{N!}{(N-T)! \, T!} \cdot q_{\text{T}}^{T}$$

$$\mu_S = \mu_T \Rightarrow q_s \frac{(M-S)}{S} = q_T \frac{(N-T)}{T}$$

$$\theta_s = \frac{S}{M} \qquad \theta_T = \frac{T}{N}$$

$$\frac{1-\theta_s}{\theta_s} \cdot q_s = \frac{1-\theta_T}{\theta_T} \cdot q_T$$

We choose the zero point of energy for the step $\Rightarrow$ the terrace site is ΔE higher.

$$q_{\text{step}} = q_{\text{vib } s} \quad , \quad q_T = q_{\text{vib } T} \, e^{\frac{-\Delta E}{kT}}$$

The partition function of the atoms adsorbed on the steps could be smaller as they are bonded stronger to the surface, but here we will assume:

$$q_{\text{vib } s} = q_{\text{vib } T} \Rightarrow$$

$$\frac{\dfrac{\theta_s}{1-\theta_s}}{\dfrac{\theta_T}{1-\theta_T}} = \frac{q_s}{q_T} \approx e^{\frac{-\Delta E}{kT}} \qquad g = \frac{\theta_T}{1-\theta_T} \Rightarrow$$

$$\theta_s = (1-\theta_s) \cdot g \cdot e^{\frac{-\Delta E}{kT}} \Rightarrow$$

$$\theta_s = \frac{g \cdot e^{-\Delta E/hT}}{1 + g e^{-\Delta E/hT}} = \frac{\left(\dfrac{\theta_T}{1-\theta_T}\right) e^{\frac{-\Delta E}{kT}}}{1 + \left(\dfrac{\theta_T}{1-\theta_T}\right) e^{\frac{-\Delta E}{kT}}}$$

$$\theta_T \to 0 \quad \Rightarrow \quad \theta_S \to 0$$
$$\theta_T \to 1 \quad \Rightarrow \quad \theta_S \to 1$$
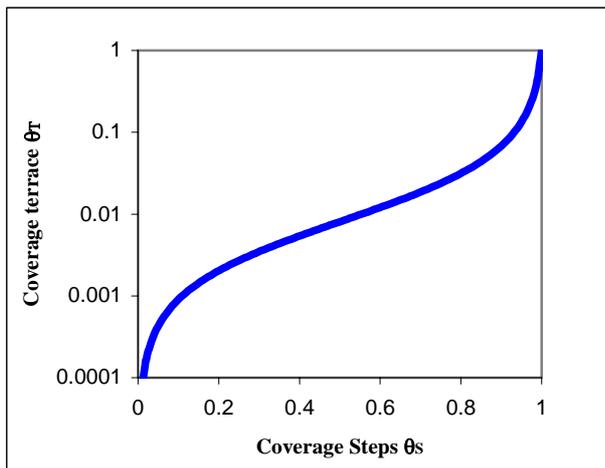
Exercise 3.11 Transition State Theory

(a) $R \xrightleftharpoons{K^{\#}} R^{\#} \xrightarrow{\frac{kT}{h}} P$
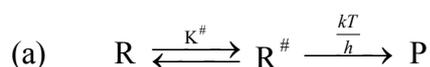
(b) $r = \dfrac{kT}{h} K^{\#}[R] = \dfrac{kT}{h} \dfrac{q'^{\#}}{q'} e^{-\frac{\Delta E}{kT}} [R]$ in which q' has been taken with respect to the energy of R, and $q'^{\#}$ with respect to that of $R^{\#}$.

(c) In collision theory all translational energy (the collision energy) is available for the overcoming the reaction barrier, whereas in transition state theory internal degrees of freedom of the reacting molecules may also exchange energy, as accounted for by the partition functions of vibration and rotation, i.e. entropy is an important quantity in transition state theory.

(d)   A sticking coefficient much smaller than unity indicates that the transition state of adsorption possesses a much smaller partition function than the molecule in the gas phase. This is the case if the transition state has no rotational freedom and/or freedom of two-dimensional translation over the surface. If the molecule can rotate and translate freely along the surface, as is the case in a so-called precursor state, the sticking coefficient will be close to unity.

(e) Dissociation proceeds usually through a rather rigid transition state in which e.g. CO binds via two atoms to the surface. In this geometry the molecule has only few degrees of freedom left (although the molecule may possess several additional low frequency vibrational modes which increase the vibrational partition function $q_{vib}^{\#}$) and the factor $q'^{\#}/q'$ in the expression under b) becomes small.

Exercise 3.12 Equilibrium Constants for Adsorption

(a)

$$A + * \Leftrightarrow A* \Rightarrow \frac{d\theta_*}{dt} = p_A k^+ \left(1 - \theta_{A*}\right) - k^- \theta_{A*} = 0 \Rightarrow \theta_{A*} = \frac{K_A p_A}{1 + K_A p_A} \quad K_A = \frac{k^+}{k^b}$$

(b) Adsorption.

$$A + * \rightleftharpoons A*^{\#}$$

$$A*^{\#} \longrightarrow A*$$
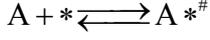
Let M be the number of sites on the surface and M^* the number of sites free

$$Q_A = \frac{q_A^{N_g}}{N_g!} \quad Q_{A*^{\#}} = \frac{M^*!}{\left(M^* - N_{\#}\right)! N_{\#}!} \cdot \left(q_{A*^{\#}}\right)^{N_{\#}}$$

$$\mu_A = \mu_{A*^{\#}} \Rightarrow \frac{q_A}{N_g} = q_{A*^{\#}} \cdot \frac{\left(M^* - N_{\#}\right)}{N_{\#}} \quad \text{since } \theta_* = \frac{M^*}{M}$$

$$\frac{d\theta_{A*^{\#}}}{dt} = \frac{k_{TST}}{N_0} = \frac{\nu N_{\#}}{A N_0} = \frac{p_A}{N_0 \sqrt{2\pi mkT}} \cdot \frac{q'_{A*^{\#}} \left(\theta_* - \theta_{A*^{\#}}\right)}{q_{A \text{ trans-unitcell}}^{2D} q_{A \text{rot}}^{gas} \cdot q_{A \text{vib}}^{gas}}$$

$$q_{A \text{rot}}^{gas} = q_{A \text{vib}}^{gas} = 1$$

$$q'_{A*^{\#}} = q'_{A*^{\#}}{}^0 e^{\frac{-\Delta E_{ads}}{kT}}$$

$$S_0(T) = \frac{q'_{A*^{\#}}}{q_{\text{tms-unitcell}}^{2D}} = \frac{q'_{A*^{\#}}{}^0}{q_{\text{tms-unitcell}}^{2D}} e^{\frac{-\Delta E_{ads}}{kT}} = S_0^A e^{\frac{-\Delta E_{ads}}{kT}}$$

$$\frac{d\theta_{A*^{\#}}}{dt} = k^+ p \left(\theta_* - \theta_{A*^{\#}}\right) \Rightarrow k^+ = \frac{\left(\theta_* - \theta_{A*^{\#}}\right)}{N_0 \sqrt{2\pi mkT}} \cdot \frac{q'_{A*^{\#}}}{q_{\text{tms-unitcell}}^{2D}} \cong \frac{\left(1 - \theta_{A*}\right)}{N_0 \sqrt{2\pi mkT}} S_0(T)$$

Since the coverage of the transition state is low and $\theta_* = \left(1 - \theta_{A*}\right)$.

$$A* \rightleftharpoons A*^{\#} \quad Q_{A*} = \frac{M^*!}{\left(M^* - N_{A*}\right)! N_{A*}!} \quad Q_{A*}{}^{\#} = \frac{\left(M^* - N_{A*}\right)!}{\left(M^* - N_{A'} - N_{A*^{\#}}\right)! N_{A*^{\#}}!}$$

$$A*^{\#} \rightarrow A + *$$
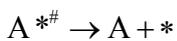
$$\mu_{A*} = \mu_{A*^{\#}} \Rightarrow \frac{q_{A*} \theta_*}{\theta_{A*}} = \frac{q_{A*^{\#}} \theta_*}{\theta_{A*^{\#}}} \quad \text{again assuming that } \theta_{A*^{\#}} \rightarrow 0$$

$$\frac{d\theta_{A*}}{dt} = \frac{-k_{TST}}{N_0} = \frac{-\nu N_{A*}^{\#}}{N_0 A} = \frac{-kT}{h} \cdot \frac{q'^{\#}}{q_{A*}} \cdot \theta_{A*}$$

$$\frac{q'^{\#}}{q_{A*}} \approx e^{\frac{-E_d}{kT}} \Rightarrow \frac{d\theta_{A*}}{dt} = \frac{-kT}{h} \cdot e^{\frac{-E_d}{kT}} \theta_{A*} \quad \frac{kT}{h} = \nu \Rightarrow k^- = \nu \cdot e^{\frac{-E_d}{kT}}$$

(c)

Now if we have equilibrium $\dfrac{d\theta_{A*}}{dt} = 0 = p_A \cdot k^+ \left(1 - \theta_{A*}\right) - k^- \cdot \theta_{A*} = 0 \Rightarrow$

$$\theta_{A*} = \frac{K_A p_A}{1 + K_A p_A} \quad K_A = \frac{k^+}{k^-} = \frac{\dfrac{S_0(T)}{N_0 \sqrt{2\pi mkT}}}{\nu \cdot e^{\frac{-E_{CO}^d}{kT}}}$$

Notice that if we had not made approximations on $q'^{\#}$ and q_{A*} we would have got a K_A

$$K_A = \frac{q'^{\#o}_{vib2DA*} e^{\frac{-\Delta E_{ads}}{kT}} e^{\frac{E_d}{kT}}}{N_0 \nu \sqrt{2\pi mhT} \cdot q^{2D}_{trans-unitcell}}$$

$$S_A^0 = \frac{q'^{\#o}_{vib2D}}{q^{2D}_{trans-unitcell}} \cong \frac{1}{\dfrac{a^2 \left(2\pi mkT\right)}{h}}$$

$$S_0^{\ A} = \frac{1}{\dfrac{9 \times 10^{-20} \times \left(6.3 \times 16 \times 1.6 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300\right) \times kg\,J\,m^2}{\left(6 \times 10^{-34}\right)^2 J^2 s^2}}$$

$$S_0^{\ A} = 6 \times 10^{-3}$$

Exercise 3.13 Dissociation in the Gas Phase

(a) $r = \dfrac{kT}{h} K^{\#}[AB] = \dfrac{kT}{h} \dfrac{q'^{\#}_{rot} \; q'^{\#}_{trans}}{q'_{vib} \; q'_{rot} \; q'_{trans}} e^{-\frac{\Delta E}{kT}}[AB]$

All partition functions have been taken with respect to the lowest occupied levels of AB and AB$^{\#}$. Note that the expression does not contain $q_{vib}'^{\#}$, as the A–B stretch mode represents the reaction coordinate of the dissociation, accounted for by the factor kT/h.

(b) A loose transition state lies close to the product (in the exit channel of the reaction), and corresponds to $r_c > r_0$. This considerably increases the moment of inertia of the transition state with respect to the ground state, causing the ratio $q_{rot}^{'\#}/q^{'rot}$ to be substantially larger than 1. A tight or rigid transition state resembles the state of the reactants, and corresponds to $r_c \approx r_0$. The preexponential factor of a dissociation reaction in the gas phase which proceeds through a tight transition state is therefore approximately equal to ekT/h, or 10^{13} s^{-1}.

(c) The molecule AB reaches the transition state by means of collisions with other molecules. Transition state theory is valid as long as the number of unreactive collisions is much larger than the number of reaction events. At low pressures, the number of collisions decreases steeply and according to Lindemann's theory we write symbolically:

$$AB + AB \rightleftharpoons AB^{\#} + AB \longrightarrow A + B + AB$$

with

$$r = \frac{kT}{h} K^{\#}[AB]^2$$

which is indeed second order in [AB].

Exercise 3.14 Transition states and preexponential factors

Reactant   Transistion state   Product

a) $q^{\#} > q$ 10^{16}-10^{17} s^{-1}

b) $q^{\#} \sim q$ 10^{13} s^{-1}

c) $q^{\#} \sim q$ 10^{13} s^{-1}

d) $q^{\#} \sim q$ 10^{13} s^{-1}

e) $q^{\#} \sim q$ 10^{13} s^{-1}
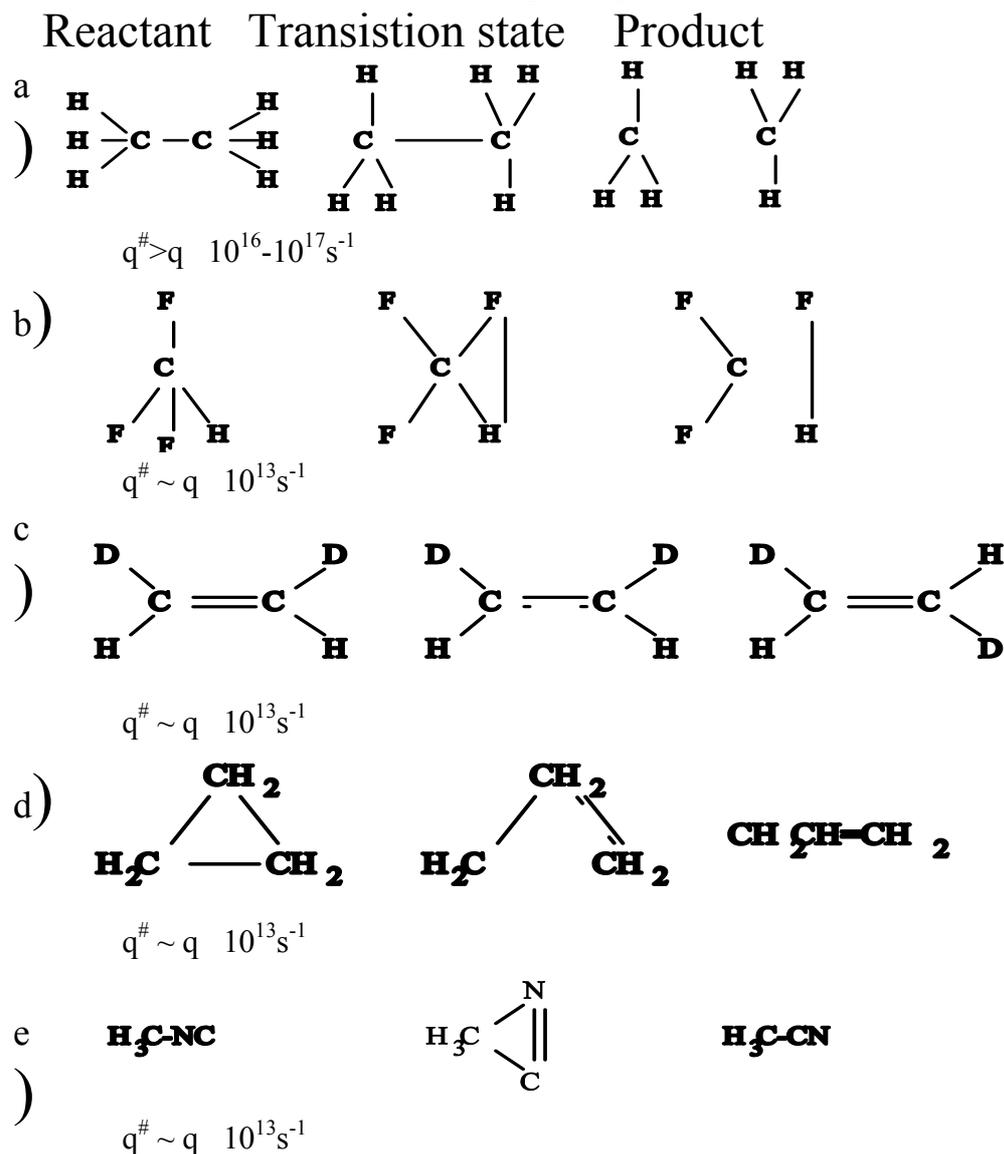
Exercise 3.15 Dissociation of Molecular Oxygen

(a) We choose the vibration between the O atoms as the reaction coordinate. The expression for the reaction rate constant becomes:

$$k_{diss} = \frac{kT}{h} K^{\#} = \frac{kT}{h} \frac{q^{/\#}}{q^{/}} e^{-\Delta E/k\,t}$$

$$= \frac{kT}{h} \frac{q^{/\#}_{trans} q^{/\#}_{rot}}{q^{/}_{trans} q^{/}_{rot}} e^{-\Delta E/kT} = \frac{kT}{h} \left(\frac{r^{\#}}{r_0}\right)^2 e^{-\Delta E/kT}$$

(b) The definition of activation energy is:

$$E_{act} = k\,T^2 \frac{\partial}{\partial T} \ln k_{diss} \quad \rightarrow \quad E_{act} = \Delta E + kT$$

If we write the preexponential factor as:

$$\nu_{eff} = e \frac{kT}{h} \left(\frac{r^{\#}}{r_0}\right)^2$$

than the expression under (a) equals:

$$k_{diss} = e \frac{kT}{h} \left(\frac{r^{\#}}{r_0}\right)^2 e^{-(\Delta E + k\,T)/k\,T} = \nu_{eff}\, e^{-E_{act}/kT}$$

Exercise 3.16 Desorption of Molecular Hydrogen

a) $\quad q_{trans}(H^*) = l^2 \frac{2\pi m\,kT}{h^2} = 10^{-19} \cdot \frac{2\pi \cdot 1.66 \times 10^{-27} \times 1.39 \cdot 10^{-23} \times 500}{\left(6.62 \times 10^{-34}\right)^2} = 16.4$

b) $\quad r_{des} = V \frac{d[H_2]}{dt} = N k_{des}\, \theta_H^2$

c) $\quad$ Transition state theory : $2H^* \underset{K^{\#}}{\overset{}{\rightleftharpoons}} H_2^{\#}** \xrightarrow{\frac{kT}{h}} H_2 + 2^*$
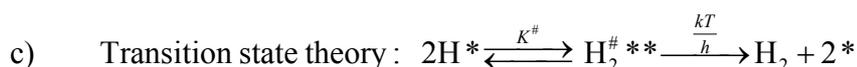
$$k_{des} = \frac{kT}{h} K^{\#} = \frac{k\,T}{h} \frac{q^{\#}}{(q_H)^2} = \frac{kT}{h} \frac{q^{/\#}_{trans} q^{/\#}_{rot}}{(q_H)^2} e^{-\Delta E/kT}$$

Rewrite k_{des} as $\nu_{eff} \cdot e^{-E_{act}/RT}$ with $\quad E_{act} = R\,T^2 \frac{\partial}{\partial T} \ln k_{diss} = \Delta E + R\,T \quad$ and

$$\nu_{\text{eff}} = e\frac{kT}{h}\frac{q^{/\#}}{(q^{/})^2} = 2.71 \times 2\times10^{10} \times 500 \times \frac{3}{(16.4)^2} = 3.2\times10^{11}\,\text{s}^{-1}$$

Exercise 3.17 Thermal Desorption of Silver from Ruthenium

(a) The rate expression for the desorption process is:

$$\text{Ag}* \xrightleftharpoons{K^\#} \text{Ag}^\# * \xrightarrow{\frac{kT}{h}} \text{Ag} + *$$
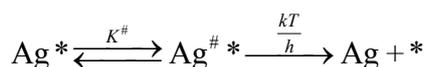
$$k_{\text{des}} = \frac{kT}{h}K^\# = \frac{kT}{h}\frac{q^{'\#}}{q^{'}}\;e^{-\frac{\Delta E}{RT}} = \frac{kT}{h}\frac{q^{'\#}_{\text{trans}}}{q^{'}_{\text{trans}}q^{'}_{\text{vib}}}\;e^{\frac{-\Delta E}{RT}}$$

Partition functions which may play a role are q_{trans}, q_{vib} and $q_{\text{trans}}{}^{\#}$ ($q_{\text{vib}}{}^{\#}$ corresponds to the reaction coordinate); q_{vib} is unknown and since $h\nu < kT$ we can expect that is is somewhat larger than unity. The translational partition functions cancel, except for the factor l^2 and $l^{\#2}$, which represents the effective area of an adsorption site and the transition site respectively:

$$k_{\text{des}} = \frac{kT}{hq^{'}_{\text{vib}}}\left(\frac{l^\#}{l}\right)^2 e^{-\frac{\Delta E}{RT}}$$

Thus:

$$E_{\text{act}} = RT^2\frac{\partial}{\partial T}\ln k_{\text{des}} = \Delta E + RT = 290\,\text{kJ / mol} \quad (\rightarrow \Delta E = 282\,\text{kJ / mol})$$

and

$$\nu_{\text{eff}} = e\frac{kT}{hq^{'}_{\text{vib}}}\left(\frac{l^\#}{l}\right)^2 \quad q^{'}_{\text{vib}} = \frac{1}{1-e^{\frac{-h\nu}{kT}}} \cong \frac{kT}{h\nu} = \frac{86.7\text{meV}}{5?\text{meV}} \approx 20$$

Because ekT/h approximately equals 5×10^{13}, and $q^{'}_{\text{vib}} > 1$ it follows that the factor $l^\# > l$ meaning that the transition state is getting somewhat lose at this high temperature.

(b) The order $n = 0$ in silver in the rate expression indicates that Ag desorbs from the edges of relatively large islands (the existence of silver islands on ruthenium has indeed been confirmed experimentally). The situation is the two-dimensional analogue of evaporation, the rate of which often also shows zero-order kinetics. This together with the above information indicates that the Ag atoms diffuses freely along the edges of the silver islands.

Exercise 3.18 Cyclopropane Isomerization

a)

Reaction coordinate
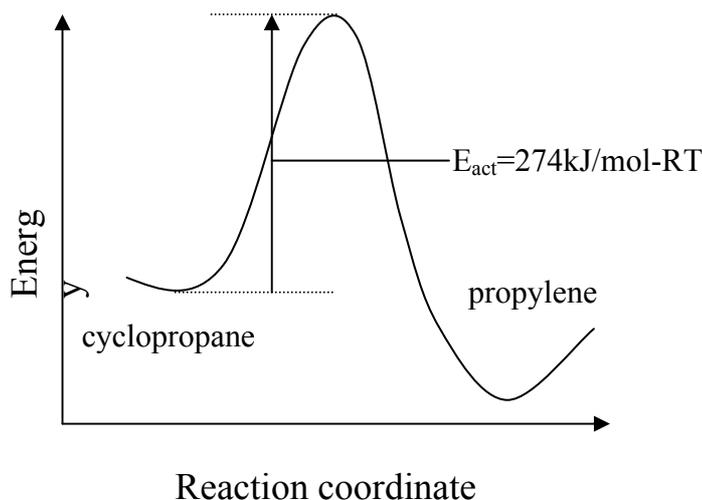
(b) The prefactor is considerably higher than $ekT/h \approx 10^{13}$, indicating that the transition state has a loose configuration.

(c) In general q_{trans} and q_{rot} provide the largest contributions to the overall partition functions. Substantial differences between $q_{trans}^{\#}$ and q_{trans}, and between $q_{rot}^{\#}$ and q_{rot} are usually the main reason that prefactors deviate from the 'standard' value, $ekT/h = 10^{13}$ s^{-1}. As for gas phase isomerizations $q_{trans}^{\#} \equiv q_{trans}$ and $q_{vib} \sim q_{vib}^{\#}$, the high prefactor implies that $q_{rot}^{\#} >> q_{rot}$. It appears that the compact cyclic form of cyclopropane is unfolded in the transition state, resulting in a substantial increase in the moment of inertia of the molecule.

(d) $r \cong \dfrac{kT}{h} \dfrac{q'^{\#}_{rot}}{q'_{rot}} e^{-\frac{\Delta E}{kT}} = \dfrac{kT}{h} \sqrt{\dfrac{I_A^{\#} I_B^{\#} I_C^{\#}}{I_A I_B I_C}} \, e^{-\frac{\Delta E}{kT}}$ where $I_B = I_C$ for cyclopropane

$E_{act} = R T^2 \dfrac{\partial}{\partial T} \ln r = \Delta E + R T; \quad \nu_{eff} = e \dfrac{kT}{h} \sqrt{\dfrac{I_A^{\#} I_B^{\#} I_C^{\#}}{I_A I_B I_C}}$ where we assume that the molecule

has three independent axis of rotation in the transition state.

Note that in the drawing the actual barrier height should be $274 - RT$ kJ mol^{-1}!

(e) The rate constant of this unimolecular reaction falls off at low pressures because the number of collisions between cyclopropane molecules decreases strongly. As a consequence only few molecules make it to the transition state.

Exercise 3.19 Molecular desorption

By definition:

$$E_{act} \equiv R T^2 \frac{\partial \ln(k_{des})}{\partial T}$$

As for taking the logarithmic derivative only the T-dependence matters, we write:

$$k_{des} = \alpha T^3 \, e^{-E_{des}/RT}$$

which yields:

$$E_{act} = R T^2 \frac{\partial}{\partial T} \left[\ln(\alpha T^3) - \frac{E_{des}}{R T} \right] = 3RT + E_{des}$$

Rewrite k_{des} as an Arrhenius equation:

$$k_{des} = \frac{kT}{h} l^2 \left(\frac{2\pi m_{cm} kT}{h^2} \right) \frac{8\pi^2 \mu r^2 kT}{h^2} \, e^3 \, e^{-\frac{E_{des} + 3RT}{RT}}$$

and thus:

$$\nu_{eff} = e^3 \, \frac{kT}{h} l^2 \left(\frac{2\pi m_{cm} kT}{h^2} \right) \frac{8\pi^2 \mu r^2 kT}{h^2}$$

and $E_{act} = E_{des} + 3kT$

Exercise 3.20 Medium effects

a)
$$CH_3NC \rightarrow CH_3CN$$
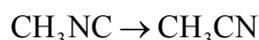
$$\text{high pressure}: \quad -\frac{d[CH_3NC]}{dt} = k_1 [CH_3NC]$$

$$\text{low pressure}: \quad -\frac{d[CH_3NC]}{dt} = k_2 [CH_3NC]^2$$

(b)   Transition state theory: $CH_3NC \leftrightarrow (CH_3NC)^{\#} \rightarrow CH_3CN$

The molecule reaches the transition state by collisions with other molecules:

$$CH_3NC + CH_3NC \underset{k_3^-}{\overset{k_3^+}{\rightleftharpoons}} CH_3NC^{\#} + CH_3NC$$
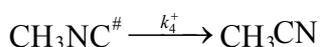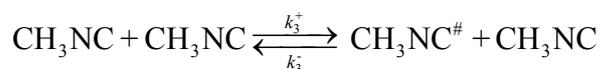
$$CH_3NC^{\#} \xrightarrow{k_4^+} CH_3CN$$

$$\frac{d[CH_3NC]^{\#}}{dt} = k_3^+[CH_3NC]^2 - k_3^-[CH_3NC^{\#}][CH_3NC] - k_4^+[CH_3NC^{\#}] = 0$$

(steady state assumption)

Thus:
$$[CH_3CN]^{\#} = \frac{k_3^+[CH_3NC]^2}{k_4^+ + k_3^-[CH_3NC]}$$

Rate of reaction:
$$-\frac{d[CH_3NC]}{dt} = k_4^+[CH_3NC^{\#}] = \frac{k_4^+ k_3^+[CH_3NC]^2}{k_4^+ + k_3^-[CH_3NC]}$$

At high pressures $k_3^-[CH_3NC] \gg k_4^+$

and
$$-\frac{d[CH_3NC]}{dt} = \frac{kT}{h}K^{\#}[CH_3NC] = k_4^+ K_3[CH_3NC]$$

Low pressure:
$$k_3^-[CH_3NC] \ll k_5$$

and
$$-\frac{d[CH_3NC]}{dt} = k_3^+[CH_3]^2$$

* Note that $k_4^+ = \dfrac{kT}{h}$

Exercise 3.21 Collision Theory

The Table indicates that reaction sets in if the collision energy equals almost 40 kJ mol^{-1}, we estimate the barrier at $E_b \approx 39$ kJ mol^{-1}.

At higher energies the reaction cross section decreases, because the colliding molecules have excess energy after the collision. As a result they separate rapidly and the time available for reaction is too short.

The activation follows by definition from:

$$E_{act} = RT^2 \frac{\partial \ln(k)}{\partial T} = E_b + \frac{1}{2}RT$$

or $E_{act} = E_b + \frac{1}{2}RT = 39 + 2 = 41$ kJ mol^{-1} at 500 K.

Solutions for Exercises in Chapter 5

Exercise 5.1 Ammonia Catalyst

(a) $-\Delta H_{Fe_3O_4} \ll -\Delta H_{Al_2O_3}$ Meaning that Al_2O_3 is basically impossible to reduce out as metallic Al. This means that the alumina stabilizes the structure and that the magnetite keeps its volume, but is becoming porous when the oxygen from the iron is removed.

(b) Consider a piece of 1 g:

$$V_i = \frac{0.97g}{\rho_{Fe_3O_4}} + \frac{0.03g}{\rho_{Al_2O_3}} = 0.187\,cm^3 + 0.0076\ cm^3 = 0.195\ cm^3$$

$$V_f = V_{pore} + \frac{m_{Fe}}{\rho_{Fe}} + \frac{0.03g}{\rho_{Al_2O_3}} \Rightarrow V_{pore} = \frac{0.97g}{\rho_{Fe_3O_4}} - \frac{m_{Fe}}{\rho_{Fe}}$$

Reducing $n_{Fe_4O_4}$ mole of Fe$_3$O$_4$ to iron result in 3 times a many moles of iron i.e.

$$n_{Fe} = 3n_{Fe_3O_4} \Rightarrow \frac{m_{Fe}}{M_{W\,Fe}} = 3\frac{m_{Fe_3O_4}}{M_{W\,Fe_3O_4}} \Rightarrow m_{Fe} = \frac{3\cdot 0.97g M_{W_{Fe}}}{M_{W_{Fe_3O_4}}} = \frac{0.97 \times 3 \times 55.85}{\left(3 \times 55.85 + 4 \times 16\right)} = 0.702\ g$$

$$V_i = V_f \Rightarrow V_{pore} = \frac{0.97g}{\rho_{Fe_3O_4}} - \frac{0.702}{\rho_{Fe}} = 0.187 - 0.089 = 0.098\,cm^3$$

Thus the pore volume constitutes $\dfrac{V_{pore}100\%}{V_i} = 50\%$. The pore volume per gram can also be given as 0.098 cm^3 g^{-1} non-reduced catalyst or 0.133 cm^3 g^{-1} active catalyst.

(c) Usually the close packed surface, i.e. the Fe(110) since Fe is BCC (at least at temperature relevant for catalysis, $T > \sim 925°C$ is it FCC), is the most stable surface since it has the lowest surface energy. This is however not the case for Fe where Fe(100) is slightly lower. The distribution of surface plane will be given by the Wulff construction.

(d) The BET area measures the total area(metal + oxide) Al$_2$O$_3$ +Fe=29m^2

1g catalyst chemisorbs 2.2 ml $N_2 = 2 * \dfrac{PV}{k_B T} = 2 * \dfrac{1 \times 10^5 \times 2,2 \times 10^{-6}}{1,38 \times 10^{-23} \times 298} = 1.1 \times 10^{20}$ N atoms

If we assume a c(2×2) overlayer on a BCC(100) surface we have that the atomic distances a is equal to the lattice distance d see figure 5.3 in C&N. Since the new unit cell in a c(2x2) is the same as a $\sqrt{2} \times \sqrt{2}$ we get that the area is for each N atom is $\sqrt{2}\,d \times \sqrt{2}d = 2d^2$. The total area covered with N atoms is then the number af atoms adsormed times the area each occupy $= 1.1 \times 10^{20} x2 \cdot \left(0.286\ nm\right)^2 = 18\ m^2 g^{-1}$

(e) Since the Iron now occupy 18m^{2}g^{-1} and the total area is 29m^{2}g^{-1} must the area of the support be 11m^{2}g^{-1}.

Exercise 5.2 BET Method

(a) First we normalize the amount adsorbed to per gram catalyst. Then we plot

$$\frac{p}{V_a(P_0 - P)} \quad vs \quad P/P_0 \text{ from this plot we find the slope } \alpha \text{ and intersection } \eta. \text{ It is then}$$

possible to estimate the volume that exactly covers the whole surface with one monolayer

$$V_0 = \frac{1}{\eta + \alpha} = 21.84 \text{ ml}. \text{ Having the volume at standard condition we can from the ideal}$$

gas low fin the number and since we know how much area each molecule takes up at the surface we can estimate the total area as

$$N = \frac{P \cdot V_0}{kT} = 5.79 \times 10^{20} N_2 \text{molecules} \Rightarrow A = NA_0 = 5.79 \times 10^{20} \cdot 0.164 \text{ nm}^2 = 95.05 = 95 \text{ m}^2 \text{ g}^{-1}$$
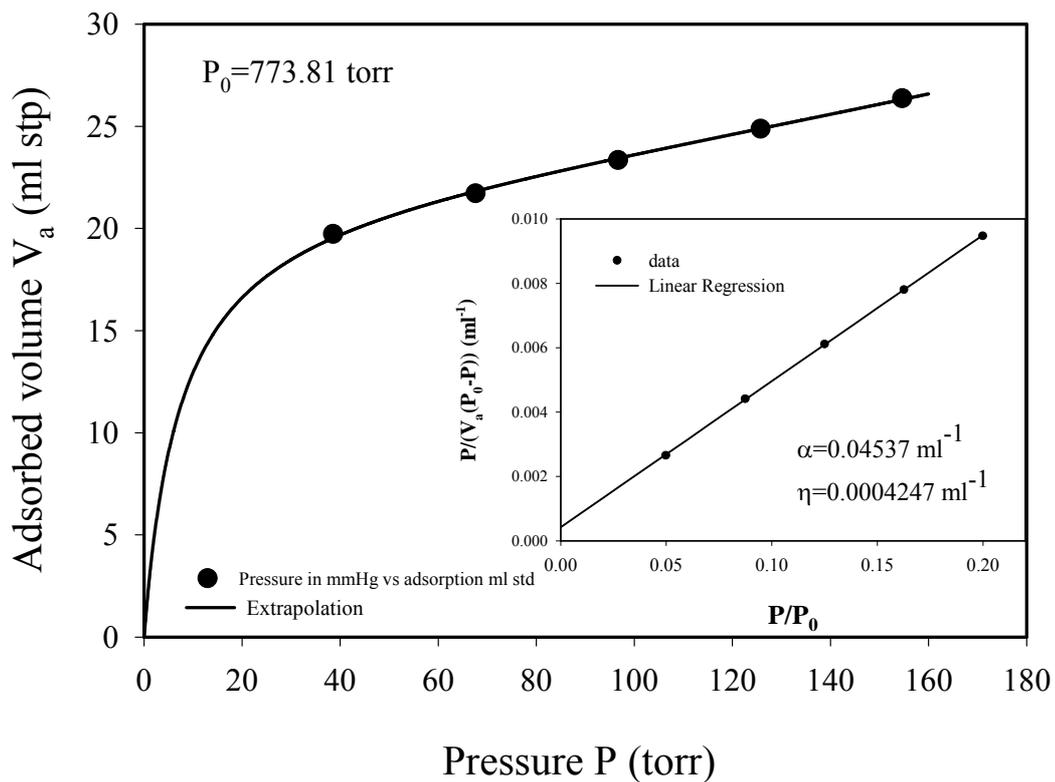
(b) $\dfrac{k_2}{k_1} = \chi = \dfrac{1}{\eta \cdot V_0} = 108 \gg 1$. Meaning that the bonding of the first layer is much stronger

than the following layers. In other words the first layer interacts stronger with the substrate than the gas layer interacts with each other.

(c) Since the BET method just measures the total area should the impregnation with Cu not change the area to much. Usually a lower area is measured.

(d) We measure 6.7 ml of water (standard gas phase conditions T=298,15 K) meaning that N_0 =1.63 10^{20} Oxygen atoms have been released from the surface. Since each oxygen atom takes up two unit cells (coverage 0.5) we just need to figure out the area of the Cu unit cells. Cu is a FCC metal where the Cu(111) is expected to be the most stable surface.

The area of a Cu(111) unit cell is $A_{unit(111)} = \dfrac{\sqrt{3}a_{lattice}^2}{4}$ where $a_{lattice}$ is the lattice distance in

Cu. This means the area per oxygen atom is: $= \dfrac{\sqrt{3}}{2} \cdot a_{lattice}^2 = 11.3 \times 10^{-20}\,\text{m}^2$.

The total Cu(111) area is then $= N_0 A_0 = 1.63 \times 10^{20}\, x11.3 \times 10^{-20}\,\text{m}^2 = 18,4\text{m}^2$

(e) The number of Cu sites is $N_{Cu} = 2N_0$

The number of water molecules formed per second is:

$$N_{H_2O/S} = \dfrac{V_{H_2O/S}P}{kT} = 2.43 \times 10^{18}\,\text{H}_2\text{O s}^{-1}$$

The Turn Over Frequency TOF is then the total number formed per second divided by the number of Cu sites which in this case is assumed to be the number of surface atoms i.e.

$$TOF = \dfrac{N_{H_2O}}{N_{Cu}} = \dfrac{2.43 \times 10^{18}}{2 \times 1.63 \times 10^{20}} = 7.5 \times 10^{-3}\,\text{s}^{-1}$$

(f) Plot TOF vs 1/T that is an Arrhenius plot and extract the slope $\alpha = -\dfrac{E_{app}}{R}$

(g) The fact that the apparent activation energy is halved should make the researcher suspicious that he/she may have made an experiment where there are transport limitations.

Exercise 5.3 Effectiveness Factor

(1) Since S is just the ratio of the pore area to the catalyst volume and since we assume that all the area of the catalyst is sitting in the pores, we get:

$$S = \dfrac{A_{cat}}{V_{cat}} = \dfrac{29\,\text{m}^2\,\text{g}^{-1}}{0.2\,\text{cm}^3\,\text{g}^{-1}} \cong 1.5 \times 10^8\,\text{m}^{-1}$$

(2) The average pore radius can be estimated assuming that all the pores have the same diameter. The pore volume is known from Exercise 5.1 to be 0.1 cm^3 g^{-1} thus

$A_{cat} \approx A_{pore} = 2\pi R_p L_p = 29\,\text{m}^2$ and $V_{pore} = \pi R_p^2 L_p = 0.1\text{cm}^3 \Rightarrow$

$$R_p = 2\dfrac{V_p}{A_p} = 2\dfrac{0.1\,\text{cm}^3}{29\,\text{m}^2} = 6.9\,\text{nm}$$

(3) The overall rate of the process is estimated from the fact that we know the TOF per iron atom and we know the active area per gram catalyst. N_N was estimated in exercise 5.1.d. and $N_{Fe} = 2*N_N$. Thus is we look at 1g catalyst then

$$\text{rate} = \frac{\text{TOF} \times N_{\text{Fe}}}{N_A} = \frac{0.05 \times 2 \times 1.1 \times 10^{20}}{6 \times 10^{23}} = 1.8 \times 10^{-5} \, \text{mol s}^{-1}$$ but the rate is also given by

$\text{rate} = V_{\text{cat}} S k C_0$. If we continue considering 1 g of cat we know the volume. S is known and C_0 can be estimated from the ideal gas law as

$$C_0 = \frac{n}{V} = \frac{P}{RT} = \frac{1 \times 10^5}{8.31 \times 600} = 20 \, \text{mol m}^{-3} \quad \text{thus} \quad k = \frac{\text{rate}}{V_{\text{cat}} S C_0} = 3 \cdot 10^{-8} \, \text{m}^3 m_{\text{surfcat}}^{-2} \, \text{s}^{-1}$$

(4) The Thiele diffusion modulus can now be calculated

$$\Phi_s = R_{\text{sphere}} \sqrt{\frac{Sk}{D_{\text{eff}}}} = 2 \times 10^{-4} \sqrt{\frac{1.5 \times 10^8 \times 3 \times 10^{-8}}{4 \times 10^{-7}}} = 0.67$$

(5) This Thiele modulus can easily be converted to an effectiveness factor since

$$\varepsilon = \frac{3}{\Phi_s} \left[\frac{1}{\tanh \Phi_s} - \frac{1}{\Phi_s} \right] = \frac{3}{\Phi_s} \left[\frac{e^{\Phi_s} + e^{-\Phi_s}}{e^{\Phi_s} - e^{-\Phi_s}} - \frac{1}{\Phi_s} \right] = 0.97 \quad \text{thus the chosen particle}$$
radius is way on the safe side.

(6) If we use a reactor with a radius of 2 mm and 1 g of catalyst we can estimate that there can be roughly 10 particles across the reactor, but what about the height. If we just consider the catalyst before it is crushed the 1 g correspond to 0.2 cm³. But if it is spherical particles will there naturally be voids in between the particles allowing for the gas transport. Ideally packing of those particles would be the FCC structure mentioned in chapter 5. That means that the volume increases roughly by a factor $\sqrt{2}$. Thus our 1g will have a volume of 0.28 cm³ and the plug will then have a height of $h = \dfrac{0.28}{\pi \cdot 0.2^2} \text{cm} \cong 2.2 \, \text{cm}$ which is just the needed factor 5 of the reactor diameter. Taking more catalyst or using smaller particles in combination with smaller reactor diameter can obtain higher ratios. The latter is god for the effectiveness factor but there are limits to how fine powders that can be kept in place and how large a pressure drop is accepted over the plug. The first is naturally easy, but as we shall see can we easily run into problems of not being in the zero conversion limit.

(7) We are only accepting a 5% conversion over the catalyst plug. We have just estimated the rate per gram catalyst to be $\text{rate} = 1.8 \cdot 10^{-5} \, \text{mol/g sec}$. That means that the flow of nitrogen must be $F_{N_2} = \dfrac{\text{rate}}{0.05} = 3.6 \times 10^{-4} \, \text{mol s}^{-1}$. Since 1mol equals 50 L under the described conditions (T=600K) and since the total amount of gas is 4 time that of Nitrogen we have that this corresponds to a total flow of
$$F = 4 \cdot F_{N_2} \cdot 0.05 \, \text{m}^3 \, \text{s}^{-1} = 7.2 \times 10^{-5} \, \text{m}^3 \, \text{s}^{-1} = 72 \, \text{ml s}^{-1} \quad \text{thus the space velocity is}$$

$$\text{Space velocity} = \frac{F}{V_{\text{catpowder}}} = \frac{72 \, \text{cm}^3 \times 3600}{0.28 \, \text{cm}^3} h^{-1} = 9.2 \times 10^5 \, \text{h}^{-1} \quad \text{This illustrates that}$$
space velocities should in general be large numbers if we want to test our catalyst in the zero conversion limit. Alternatively we would have to integrate the rate equation, since the partial pressure of N_2 is no longer constant down through the reactor.

Solutions for Exercises in Chapter 7

Exercise 7.1 Sticking of N_2 Fe(100) Continuation of Exercise 5.1

a)
Since it is saturated $\theta = 1$ and we can assume since it is symmetric that $\theta = \frac{1}{2}$ at maximum.

$$\nu = 1 \cdot 10^{13} \, s^{-1} \quad \beta = 2K/s \quad T_m = 740K \Rightarrow E_{des} = kT_m \cdot \ln\left(\frac{kT_m^{\,2}\nu}{E_{des} \cdot \beta \cdot 2 \cdot \frac{1}{2}}\right) \text{ for second-order}$$

desorption

guess $E_{des}^0 = 100 \, \text{kJ}\,\text{mol}^{-1} \Rightarrow$

$E_{des}^1 = 203.289 \, \text{J}\,\text{mol}^{-1}$ 1 iteration
$E_{des}^2 = 198.926 \, \text{J}\,\text{mol}^{-1}$ 2 iteration
$E_{des}^3 = 199.059 \, \text{J}\,\text{mol}^{-1}$ 3 iteration
$E_{des}^4 = 199.055 \, \text{J}\,\text{mol}^{-1}$ 4 iteration
$E_{des}^5 = 199.055 \, \text{J}\,\text{mol}^{-1}$ 5 iteration

$E_{des} = 199 \, \text{kJ}\,\text{mol}^{-1}$

3 iterations is sufficient.

(b)

$$S_0(T) = S_0^0 \cdot e^{-\frac{\Delta E_{act}}{kT}} \quad E_{act} = 0.03\,\text{eV} \approx 3 \, \text{kJ}\,\text{mol}^{-1}$$

$$\left(\left[S_0(500) = 2.5\times10^{-5} \Rightarrow S_0^0 = 5\times10^{-5} \right]\right)$$

$$\Delta H = E_{act} - E_{des} = -196 \, \text{kJ}\,\text{mol}^{-1}$$
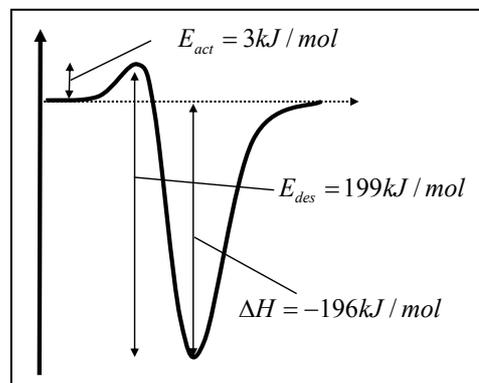
c)

$$S_0^0 = 5\times10^{-5} \quad S_0^0 \approx \frac{q^{\#0}}{q_{gas}} = e^{\frac{+\Delta S}{R}} \Rightarrow \Delta S < 0$$

$E_{act} = 3kJ/mol$

$E_{des} = 199kJ/mol$

$\Delta H = -196kJ/mol$

Adsorption results in a massive loss of entropy. The entropy of gas molecules is huge primarily due to the translational degrees of freedom. Those are lost upon adsorption where the molecule is not free to move any longer.

d)

$$\frac{d\theta_N}{dt} = \frac{2 \cdot F \cdot S_0(T)}{N_0} \cdot (1-\theta_N)^2 - \nu \cdot 1^{\frac{-E_{des}}{RT}} \cdot \theta_N^{\,2} = 0 \text{ for equilibrium.}$$

$$\theta_N = \frac{\sqrt{K \cdot p_{N_2}}}{1+\sqrt{K \cdot p_{N_2}}} \text{ where } Kp_N = \frac{2 \cdot p_{N_2} \cdot S_0^0 \cdot e^{\frac{-E_{act}+E_{des}}{RT}}}{N_0 \nu \sqrt{2\pi mkT}}$$

The number of sites per m^2 N_0 comes in here because we must normalise to per site. The numbers of sites can be estimated by utilizing the information given in exercise 5.4. If we assume that the saturation coverage is a c(2x2) structure will each Nitrogen take up two Fe(100) unit cells. As Fe is bcc will the lattice distance d be equal the inter atomic distance in the Fe(100) a, meaning each N takes up an area of $2a^2$. (we could also have performed this exercise assuming that each Fe atom was an reactive center).

for $P_{N_2} = 1\,bar = 10000\,Pa$ $T = 800\ K$ and $v = 1 \times 10^{13}$

$$N_0 = \frac{1}{2a^2} = 6.11 \times 10^{18}\,m^2 \quad \text{you get} \quad Kp_{N_2} = 1.89 \times 10^4$$

$$\theta_N = \frac{\sqrt{1.89 \times 10^4}}{1 + \sqrt{1.89 \times 10^4}} = 0.993 \quad (\text{If} \quad p_{N_2} = 1\,mbar \Rightarrow \theta_N = 0.81)$$

see Figure 7.11 where we have made a similar calculation for E_{des}=190 kJ mol^{-1} and $N_0 = 1/a^2$

(e)
Since H_2 desorbs at T= 350 K must $E_{desH_2} << E_{desN_2}$ so the surface is dominated by N or NH species

Exercise 7.2 Sticking of Methane on Ni(100)

(a) Ni is a fcc metal so the unit cell has volume d^3 contains 4 Ni atoms. We shall first find the lattice constant for Ni.

$$1\ \ m^3 = \frac{8,9 \times 10^6\,g}{58,71g}\,mol = \frac{8,9 \times 10^6}{58,71} \times 6 \times 10^{23}\ \ atoms. = \frac{8.9 \times 10^6 \times 6 \times 10^{23}}{58.71 \times 4}\ \ unitcells$$

$$1\ \ unitcell = \frac{4 \cdot M_W}{N_a \cdot \rho_{Ni}} = \frac{58.71 \times 4}{8.9 \times 10^6 \times 6 \times 10^{23}} = 4.40 \times 10^{-29}\,m^3$$

$$1\ \ unitcell = d^3 \Rightarrow d = \sqrt[3]{4 \times 4 \times 10^{-29}}\,m = 3.52 \times 10^{-10}\,m.\ \ \text{The lattice constant.}$$

The unit cell for a Ni(100) surface has length $a = \dfrac{d}{\sqrt{2}} = 2.5 \times 10^{-10}\,m$. each containing one Ni atom.

The area for each atom is therefore a^2 so the number of sites is $N_0 = \dfrac{1}{a^2} = 1.60 \times 10^{19}\,m^{-2}$.

(b)

$$\frac{d\theta_c}{dt} = \frac{P_{CH_4} \cdot S_0(T)}{N_0 \cdot \sqrt{2\pi mkT}} \cdot (1 - \theta_c)^2 \quad \text{solve} \quad \text{for} \quad \theta_c$$

$$\theta_c(t) = \dfrac{\dfrac{P_{CH_4} \cdot S_0(T) \cdot t}{N_0 \cdot \sqrt{2\pi mkT}}}{\dfrac{P_{CH_4} \cdot S_0(T) \cdot t}{N_0 \sqrt{2\pi mkT}} + 1}$$

If we only consider small doses so $t \to 0 \Rightarrow \theta_c(t) \approx \dfrac{P_{CH_4} \cdot S_0(T) \cdot t}{N_0 \sqrt{2\pi mhT}} = \alpha \cdot p_{CH_4} \cdot t = \alpha \times \text{Dosis}$

Draw a tangent to the uptake curves at zero dosis and determine, for example, at which dosis this crosses the horizontical line that corresponds to 0.8 Ml carbon. This would be the line the uptake would follow if there were no blocking as in the zero dosis limit. By repeating this procedure for each temperature we can read of the dosis that corresponds to 0.8 Ml if there was no blocking.

$$\theta(t_x \cdot P_{CH_4}) = 0.8 = \alpha \cdot \text{dosis} = \dfrac{P_{CH_4} \cdot S_0(T) \cdot t_x}{N_0 \cdot \sqrt{2\pi mhT}} \Downarrow$$

$$S_0(T) = \dfrac{0.8 \cdot N_0 \sqrt{2\pi mkT}}{P_{CH_4} \cdot t_x} = 1.9 \times 10^{-10} \cdot \dfrac{\sqrt{T(K)}}{P_{CH_4} t_x (\text{bar} \times \text{sec})} \quad \text{all} \quad \text{in} \quad \text{correct} \quad \text{units.}$$

we can now construct the following table:

T (K)	$P_{CH4} \cdot t_x$ of 0.8 ML	$S_0(T)$
550	2.4×10^{-2}	1.8×10^{-7}
500	6.6×10^{-2}	6.4×10^{-8}
475	13.4×10^{-2}	3.1×10^{-8}
450	20.0×10^{-2}	2.0×10^{-8}

c)

Make an Arrhenius plot $\text{Ln}(S_0(T))$ vs $1/T$ slope $\alpha = \dfrac{-E_a}{kT} \Rightarrow E_a \approx 46\,\text{kJ mol}^{-1}$

d)

0.2 bar s took 152 s.

$$p_{CH_4} = \dfrac{200\,\text{mbar s}}{152\;\text{s}} = 1.31\,\text{mbar} = 1.0\,\text{torr}$$

Exercise 7.3 Hydrogen Adsorption/Desorption and Equilibrium Coverage

(a)

$$H_2 + 2* \rightleftharpoons 2H*$$
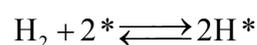
$$\frac{d\theta_H}{dt} = \frac{2F_{H_2}S(T)}{N_0}\theta_*^2 - k^-\theta_H^2 \text{ where } F_{H_2} = \frac{p_{H_2}}{\sqrt{2\pi mkT}} \text{ and } \theta_H = 1 - \theta_*$$

since $k^- \cong 0$ this differential eq is easily solved:

$$\int_0^{\theta_h} (1-\theta_H)^{-2}d\theta_H = \frac{\theta_H}{1-\theta_H} = \int_0^t \frac{2F_{H_2}S(T)}{N_0}dt = \frac{2F_{H_2}S(T)t}{N_0} \text{ leading to:}$$

$$\theta_H = \frac{\dfrac{2p_{H_2}S(T)t}{N_0\sqrt{2\pi mkT}}}{\dfrac{2p_{H_2}S(T)t}{N_0\sqrt{2\pi mkT}}+1}$$

b)

By extending the tangent at $\theta = 0$ to $\theta = 1$ and read of the dosis in bar*sec can the following table be made since $S_0(T) = \dfrac{N_0}{\dfrac{2D}{\sqrt{2\pi mkT}}}$ and $D = P_{H_2}t$

T(K)	D(bar*s)	$S_0(T)$
200	6250	9.1×10^{-14}
210	1870	3.1×10^{-13}
220	591	1.0×10^{-12}
230	212	2.9×10^{-12}
240	83	7.5×10^{-12}

c) Make an Arrhenius plot and find slope =-5299 resulting in E_a=44kJ/mol and pre-factor $S_0^0 = 0.029$.

(d) Second-order desorption.

$$E_d = RT\ln\left(\frac{\nu RT_m^2}{\beta E_d 2\theta_m}\right) \cong RT\ln\left(\frac{\nu RT_m^2}{\beta E_d}\right) \text{ solved iteratively at } T_m\text{=408 K resulting in 110 kJ mol}^{-1}$$

(e) Total area is measured by BET using N_2 = area of oxide + area of metal. Only the metal area is measured by H_2

General Exercises

Block 1

Task 1. Catalytic NO Reduction (30%, weighted as 5% for each of the questions)

(a) Surfaces with highest density has lowest surface energy therefore the low index surfaces are abundant in the order $Rh(111) > Rh(100) > Rh(110)$. Reactivity has the reverse order $Rh(111) < Rh(100) < Rh(110)$.

(b) In a BET experiment the phenomena physisorption is utilized and the total area (metal + oxide) is measured.

(c) Simple estimate for $T_M = 460$ K and $v = 10^{13}\,\text{s}^{-1}$ $\beta = 2K\,\text{min}^{-1}$:

$$E_{des} = RT_M \ln\left(\frac{RT_M^2 v}{E_{des}\beta}\right) \Rightarrow E_{des} = 100\,\text{kJ}\,\text{mol}^{-1} \Rightarrow E_{des} = 138\,\text{kJ}\,\text{mol}^{-1} \Rightarrow E_{des} = 137\ \text{kJ}\,\text{mol}^{-1}$$

(d) $A_{tot} = N_{NO} \times A_{NO} = \dfrac{PV}{k_B T} \times 2\left(\dfrac{a}{\sqrt{2}}\right)^2 = \dfrac{PVa^2}{k_B T} = \dfrac{1\times10^5 \times 1.85\times10^{-5} \times (3.81\times10^{-10})\,\text{m}^2}{1.38\times10^{-23}\times300} = 65\,\text{m}^2$

e)

$$\frac{d\theta_{NO}}{dt} = \frac{S(T)P_{NO}(1-\theta_{NO})}{N_0\sqrt{2\pi m_{NO}k_B T}} - v e^{\frac{-E_{des}}{RT}}\theta_{NO} = 0$$

$$\theta_{NO} = \frac{KP_{NO}}{1+KP_{NO}} \quad \text{where} \quad K = \frac{S(T)e^{\frac{E_{des}}{RT}}}{N_0 v\sqrt{2\pi m_{NO}k_B T}} \quad \text{and} \quad N_0 = \frac{1}{a^2}$$

$$KP_{NO} = \frac{100\times(3.81\times10^{-10})^2\,e^{\frac{140000}{8.31\times900}}}{1\times10^{13}\sqrt{6.28\times30\times1.6\times10^{-27}\times1.38\times10^{-23}\times900}} = 3.2$$

$$\theta_{NO} = \frac{3.2}{1+3.2} = 0.76 \text{ with respect to sites. (0.38 with respect to Rh atoms)}$$

(f) Use Le Sabatiers Principle: Since the reactivity decreases as we go to the right in the transition metals the metals Pd and Ag are not reactive enough to dissociate the NO while Mo and Ru are to reactive so the products O and N will not leave the surface. Thus we get an optimum in between at Rh.

Task 2. Oxidation of Hydrogen on Pt (35%, weighted as 5% for each of the questions

(a) For example

$$H_2 + * \rightleftharpoons H_2*$$

$$O_2 + * \rightleftharpoons O_2*$$

$$OH* + OH* \longrightarrow H_2O* + H*$$
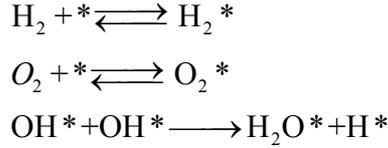
(b) (3) $r = r_+ - r_- = k_3^+ \theta_{OH} \theta_H - k_3^- \theta_{OH} \theta_*$

(c)

(1) $\dfrac{d\theta_H}{dt} = k_1^+ \theta_*^2 P_{H_2} - k_1^- \theta_H^2 = 0 \Rightarrow \theta_H = \sqrt{K_1 P_{H_2}}\, \theta_*$

(2) $\dfrac{d\theta_O}{dt} = k_2^+ \theta_*^2 P_{O_2} - k_2^- \theta_O^2 = 0 \Rightarrow \theta_O = \sqrt{K_2 P_{O_2}}\, \theta_*$

(4) $\dfrac{d\theta_{OH}}{dt} = -k_4^+ \theta_{OH} \theta_H + k_4^- \theta_{H_2O} \theta_* = 0 \Rightarrow \theta_{OH} = \dfrac{\theta_{H_2O}}{K_4 \theta_H}\theta_* = \dfrac{P_{H_2O}}{K_4 K_5 \sqrt{K_1 P_{H_2}}}\theta_*$

(5) $\dfrac{d\theta_{H_2O}}{dt} = -k_5^+ \theta_{H_2O} + k_5^- P_{H_2O} \theta_* = 0 \Rightarrow \theta_{H_2O} = \dfrac{P_{H_2O}}{K_5}\theta_*$

$\Downarrow$

(3) $r = k_3^+ \sqrt{K_1 K_2 P_{H_2} P_{O_2}}\, \theta_*^2 - \dfrac{k_3^- P_{H_2O} \theta_*^2}{K_4 K_5 \sqrt{K_1 P_{H_2}}} = k_3^+ \sqrt{K_1 K_2 P_{H_2} P_{O_2}} \left(1 - \dfrac{P_{H_2O}}{K_G P_{H_2} \sqrt{P_{O_2}}} \right) \theta_*^2$

$\Downarrow$

$K_G = K_1 \sqrt{K_2} K_3 K_4 K_5$

(d) $\theta_* = 1 - \theta_H - \theta_O - \theta_{OH} - \theta_{H_2O} \cong 1 - \theta_O = 1 - \sqrt{K_2 P_{O_2}}\, \theta_* \Rightarrow \theta_* = \dfrac{1}{1 + \sqrt{K_2 P_{O_2}}}$

(e) $n_x = P_x \dfrac{\delta \ln(r_+)}{\delta P_x} \Rightarrow n_{H_2} = \dfrac{1}{2},\ n_{O_2} = \dfrac{1}{2} - \theta_O,$ and $n_{H_2O} = 0$

(f)

$r \cong k_3^+ \sqrt{K_1 K_2} \sqrt{P_{H_2} P_{O_2}}$ and $\chi_{H_2} = \dfrac{P_{H_2}}{P_{tot}},\ \dfrac{P_{O_2}}{P_{tot}} = (1 - \chi_{H_2}) \Rightarrow$

$r = k_3^+ \sqrt{K_1 K_2}\, P_{tot} \sqrt{\chi_{H_2}(1 - \chi_{H_2})}$

Find maximum for r as a function of χ_{H_2}

$\dfrac{\delta r}{\delta \chi_H} = 0 \Rightarrow \chi_{H_2} = \dfrac{1}{2}$ i.e. max rate for $P_{H2} = P_{O2}$

(g) (1) Since oxygen is MARI can the apparent activation energy become dependent on the oxygen coverage i.e. (sufficient)

$$E_{app} = RT^2 \frac{\delta \ln(r_+)}{\delta T} = \frac{\Delta H_1}{2} + \frac{\Delta H_2}{2} + E_{3act} - \Delta H_2 \theta_O \quad \text{(this is not needed)}$$

(2) If the rate is high there will always be a danger of transport limitations at very high rates i.e. pore diffusion or normal diffusion limitations.

Task 3 N_2O_5 Decomposition (35%, weighted as 10% for each of the first three questions and 5% for the last).

a) Based on the information can the following table be constructed:

T(K)	$1/T$	k (s^{-1})	$\ln(k)$
273	0.003663	7.87×10^{-7}	-14.06
298	0.003356	3.46×10^{-5}	-10.27
308	0.003247	13.5×10^{-5}	-8.91
318	0.003145	49.8×10^{-5}	-7.60
328	0.003049	150×10^{-5}	-6.50
338	0.002959	487×10^{-5}	-5.32

By plotting $\ln(k)$ versus $1/T$ an activation energy of $E_{act} = 103$ kJ mol^{-1} and $v = 4.0\times10^{13}$ s^{-1} is found.

(b)We shall now use the steady-state approximation for the intermediates NO_3 and NO:

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_3[NO]}$$

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0$$

$$[NO] = \frac{k_2[NO_2][NO_3]}{k_3[NO_3]} = \frac{k_2}{k_3}[NO_2]$$

By inserting this we get

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_2[NO_2]}$$

The reaction rate is then given by

$$\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO] = \left(k_1 - \frac{k_{-1}k_1}{k_{-1}+2k_2}\right)[N_2O_5] \text{ i.e. a first order reaction.}$$

c)

The temperature dependence is first determined for each of the partition functions:

$$q_{trans} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \text{ contributes with } T^{3/2}.$$

$$q_{rot} = \frac{\sqrt{8\pi I k_B T}}{\sigma h} \text{ for each degree of rotational freedom i.e. } T^{1/2} \text{ for each degree.}$$

$$q_{vib} = \left[1 - \exp\left(\frac{-h\nu}{k_B T}\right)\right]^{-1} \cong \frac{k_B T}{h\nu} \text{ when } h\nu << k_B T \text{ i.e. each vibration contributes with T.}$$

Since NO_3 and the activated complex are non-linear we get the following table:

	NO	NO_3	$NOONO_2$
translation	3	3	3
rotation	2	3	3
vibration	1	6	12

The prefactor is given by

$$\nu(T) = \kappa\frac{k_B T}{h}\frac{q^\#}{q_{NO}q_{NO_3}} \propto T\frac{T^{3/2}T^{3/2}T^{11}}{\left(T^{3/2}TT\right)\left(T^{3/2}T^{3/2}T^6\right)} = T^{5/2}$$

where we remember that one of the vibrational mode in the transition state complex has been converted into the reaction coordinate resulting in the T in front of the expression.

(d) Reactions that have similar rates in gas phase and in liquid phase are characterized by being relative slow so that they are not diffusion limited and by nor involving charged particles (ions).

Block 2

Task 1. Automotive Catalyst (35%, weighted as roughly 5% for each of the questions)

(a) The net scheme is:

$$NO + CO \rightleftharpoons CO_2 + \frac{1}{2}N_2 \quad \text{and} \quad K_G = \frac{P_{CO_2}\sqrt{P_{N_2}}}{P_{NO}P_{CO}}$$
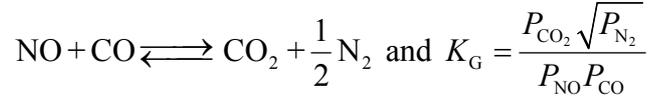
(b) Other relevant elementary steps could be:

$$O* + O* \rightleftharpoons O_2* + *$$

$$O_2* \rightleftharpoons O_2 + *$$

$$NO* + N* \rightleftharpoons N_2O* + *$$

$$N_2O* \rightleftharpoons N_2O + *$$
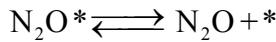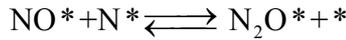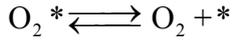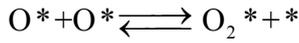
etc.

(c) (1) $\dfrac{d\theta_{NO}}{dt} = 0 = k_1^+ p_{NO}\theta_* - k_1^- \theta_{NO} \Rightarrow \theta_{NO} = K_1 p_{NO}\theta_*$

(2) $r = r_+ - r_- = k_2^+ \theta_{NO}\theta_* - k_2^- \theta_N \theta_O$

(3) $\dfrac{d\theta_{CO}}{dt} = 0 = k_3^+ p_{CO}\theta_* - k_3^- \theta_{CO} \Rightarrow \theta_{CO} = K_3 p_{CO}\theta_*$

(4) $\dfrac{d\theta_O}{dt} = 0 = k_4^+ \theta_{CO}\theta_O - k_4^- \theta_{CO_2}\theta_* \Rightarrow \theta_O = \dfrac{\theta_{CO_2}\theta_*}{K_4 \theta_{CO}}$

(5) $\dfrac{d\theta_{CO_2}}{dt} = 0 = k_5^+ \theta_{CO_2} - k_5^- p_{CO_2}\theta_* \Rightarrow \theta_{CO_2} = \dfrac{p_{CO_2}\theta_*}{K_5}$

(6) $\dfrac{d\theta_N}{dt} = 0 = k_6^+ \theta_N^2 - k_6^- \theta_{N_2}\theta_* \Rightarrow \theta_N = \sqrt{\dfrac{\theta_{N_2}\theta_*}{K_6}}$

(7) $\dfrac{d\theta_{N_2}}{dt} = 0 = k_7^+ \theta_{N_2} - k_7^- p_{N_2}\theta_* \Rightarrow \theta_{N_2} = \dfrac{p_{N_2}}{K_7}\theta_*$

By substituting (7) into (6) we get $\quad \theta_N = \sqrt{\dfrac{\theta_{N_2}\theta_*}{K_6}} = \sqrt{\dfrac{p_{N_2}}{K_6 K_7}}\theta_*$

And substituting (3) and (5) into (4) we get $\quad \theta_O = \dfrac{\theta_{CO_2}\theta_*}{K_4 \theta_{CO}} = \dfrac{\dfrac{p_{CO_2}\theta_*}{K_5}\theta_*}{K_3 K_4 p_{CO}\theta_*} = \dfrac{p_{CO_2}}{K_3 K_4 K_5 p_{CO}}\theta_*$

whereby all coverages are expressed by equilibrium constants and partial pressures. Inserting in (2) we get

$$r = k_2^+ K_1 p_{NO} \theta_*^2 - k_2^- \sqrt{\frac{p_{N_2}}{K_6 K_7}} \frac{p_{CO_2}}{K_3 K_4 K_5 p_{CO}} \theta_*^2 = k_2^+ K_1 p_{NO} \theta_*^2 \left(1 - \frac{1}{K_1 K_2 K_3 K_4 K_5 \sqrt{K_6 K_7}} \frac{\sqrt{p_{N_2}} p_{CO_2}}{p_{CO} p_{NO}} \right)$$

$$r = k_2^+ K_1 p_{NO} \theta_*^2 \left(1 - \frac{1}{K_G} \frac{\sqrt{p_{N_2}} p_{CO_2}}{p_{NO} p_{CO}} \right)$$

(d)   meaning that $K_G = K_1 K_2 K_3 K_4 K_5 \sqrt{K_6 K_7}$

(e) $\theta_* = 1 - \theta_O - \theta_N - \theta_{NO} - \theta_{CO} - \theta_{CO_2} - \theta_{N_2}$ insert the expression for each coverage and find

$$\theta_* = \frac{1}{1 + \dfrac{p_{CO_2}}{K_3 K_4 K_5 p_{CO}} + \sqrt{\dfrac{p_{N_2}}{K_6 K_7}} + K_1 p_{NO} + K_3 p_{CO} + \dfrac{p_{CO_2}}{K_5} + \dfrac{p_{N_2}}{K_7}} \cong \frac{1}{1 + \dfrac{p_{CO_2}}{K_3 K_4 K_5 p_{CO}}}$$

(f)   Find the reaction order $n_x \equiv p_x \dfrac{\delta \ln(r_+)}{\delta p_x}$ gives since $\theta_* \cong \dfrac{1}{1 + \dfrac{p_{CO_2}}{K_3 K_4 K_5 p_{CO}}}$

$n_{N_2} = 0$

$n_{NO} = 1$

$n_{CO} = 2\theta_O$

$n_{CO_2} = -2\theta_O$

(g) since $\theta_* \cong 1$ and $E_{act}^{app} \equiv RT^2 \dfrac{\delta \ln(r_+)}{\delta T}$ we get $E_{act}^{app} = E_2 + \Delta H_1$

where we have assumed that $k_2^+ = k_2^0 \exp\left(\dfrac{-E_2}{RT} \right)$ and $K_1 = \exp\left(\dfrac{-(\Delta H_1 - T\Delta S_1)}{RT} \right)$

Task 2. Capacity and Methanization Reaction (30%, weighted as roughly 5% for each of the questions)

(a) The reactivity will go up as the Ni overlayer is strained by being pseudomorfic with the larger Ru(0001) lattice. When the layer is being strained the overlap between the d-orbital will decrease and the d-band will become more narrow leading to an upward shift of the d-band. This means that the distance between the d-band and the anti-bonding orbital becomes less leading to a stronger chemical interaction.

(b) The desorption energy for a 1. order desorption can be estimated iteratively from

$$E_{des} = RT \ln\left(\frac{RT^2 \nu}{E_{des}\beta}\right)$$

Guess $E_{des}(T_m = 500 \text{ K}) = 150.000 \text{ J mol}^{-1}$ then insert and find
$E_{des}=132.414 \text{ kJ mol}^{-1}$
$E_{des}=132.933 \text{ kJ mol}^{-1}$
$E_{des}=132.916 \text{ kJ mol}^{-1}$
$E_{des}=132.917 \text{ kJ mol}^{-1}$
$E_{des}=132.917 \text{ kJ mol}^{-1}$

Guess $E_{des}(T_m = 550 \text{ K}) = 150.000 \text{ kJ mol}^{-1}$ then insert and find
$E_{des}=146.527 \text{ kJ mol}^{-1}$
$E_{des}=146.634 \text{ kJ mol}^{-1}$
$E_{des}=146.631 \text{ kJ mol}^{-1}$
$E_{des}=146.631 \text{ kJ mol}^{-1}$

Change in bonding energy $=146.6 - 132.9=13.7 \text{ kJ mol}^{-1}$

(c) The number of CO molecules adsorbed is $N_{CO} = \frac{PV_{CO}}{kT}$ and since each molecule takes up two unit cells the total metal area is:

$$A = 2N_{CO}A_{\text{Ni on Ru}} = 10.4\,\text{m}^2$$

(d) Equilibrium $\frac{d\theta_{CO}}{dt} = 0 = \frac{S_0 p_{CO}}{N_0\sqrt{2\pi m_{CO}k_B T}}\theta_* - \nu e^{\frac{-E_{des}}{RT}}\theta_{CO}$

$\Rightarrow \theta_{CO} = \frac{Kp_{CO}}{1+Kp_{CO}}$ where $K = \frac{S_0}{N_0\sqrt{2\pi m_{CO}k_B T}\nu e^{\frac{-E_{des}}{RT}}} = 9.64\times10^{-4}\,(\text{N m}^{-2})^{-1}$ where N_0

is the

total number of sites per m^2 i.e. $N_0 = \frac{1}{A_{\text{Ni on Ru}}}$

This lead to $\theta_{CO} = 0.49$

(e) The number of CH$_4$ produced per second $N_{CH_4} = \frac{p_{CH_4}F}{kT} = 4.03\times10^{18}\,\text{s}^{-1}$

The number of sites $N_{NI} = \frac{15\,\text{m}^2}{A_{\text{Ni om Ru}}} = 2.36\times10^{20}$

$\text{TOF} = \frac{N_{CH_4}}{N_{Ni}} = 1.71\times10^{-2}$

(f)   The flat Ni(111) on Ru(0001) surface is the thermodynamically most stable surface due to the lower surface energy. That, however, according to the Wulff construction does not exclude the possibility of other more open sites like for example step sites. There will be fewer of those and if they account for the reactivity the TOF for those sites must be accordingly larger.

Task 3 Pyrolysis of Ethane (35%, weighted as 5% for the first and 10% for each of the following questions).

a)
Based on the data the following table can be made:

t(s)	$[C_2H_6]$(mol m^{-3})	$Ln([C_2H_6]$(mol m^{-3}))
0.06	381	5.94
0.15	318	5.76
0.36	254	5.54
0.62	191	5.25
0.79	159	5.07
0.98	127	4.84

A plot of t vs $ln([C_2H_6])$) shows a straight line; i.e. the reaction is first order in $[C_2H_6]$). The same result can be obtained by comparing the half-lives for $[C_2H_6]$) which are roughly constant (0.60 ±0.04s) independent of starting concentration.

b)
The simplified mechanism for C_2H_6 pyrolysis at lower pressures, i.e. with reaction (R11) second order, is:

R9 $C_2H_6 \longrightarrow CH_3 + CH_3$

R10 $CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$

R11a $C_2H_5 + M \longrightarrow C_2H_4 + H + M$

R12 $C_2H_6 + H \longrightarrow H_2 + C_2H_5$

R13 $C_2H_5 + C_2H_5 \longrightarrow C_4H_{10}$

R14 $C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6$
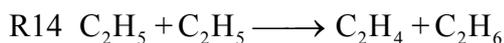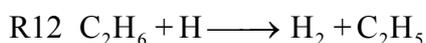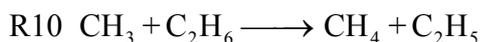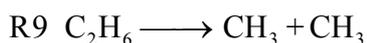
on this reaction mechanism, the following equations can be derived:

$$\frac{d[C_2H_6]}{dt} = -k_9[C_2H_6] - k_{10}[CH_3][C_2H_6] - k_{12}[C_2H_6][H] + k_{14}[C_2H_5]^2$$

$$\frac{d[CH_3]}{dt} = 2k_9[C_2H_6] - k_{10}[CH_3][C_2H_6]$$

$$\frac{d[C_2H_5]}{dt} = k_{10}[CH_3][C_2H_6] + k_{12}[C_2H_6][H] - 2(k_{13}+k_{14})[C_2H_5]^2 - k_{11a}[C_2H_5][M]$$

$$\frac{d[H]}{dt} = k_{12}[C_2H_6][H] + k_{11a}[C_2H_5][M]$$

Assuming CH_3 in steady state:

$$\frac{d[CH_3]}{dt} = 2k_9[C_2H_6] - k_{10}[CH_3][C_2H_6] = 0 \Rightarrow$$

$$[CH_3] = \frac{2k_9}{k_{10}}$$

Also C_2H_5 and H can be assumed in steady state:

$$\frac{d[C_2H_5]}{dt} = k_{10}[CH_3][C_2H_6] + k_{12}[C_2H_6][H] - 2(k_{13}+k_{14})[C_2H_5]^2 - k_{11a}[C_2H_5][M] = 0$$

$$\frac{d[H]}{dt} = k_{12}[C_2H_6][H] + k_{11a}[C_2H_5][M] = 0$$

Addition of these two equations leads to :

$$k_{10}[CH_3][C_2H_6] - 2(k_{13}+k_{14})[C_2H_5]^2 = 0 \text{ and by utilizing } [CH_3] = \frac{2k_9}{k_{10}} \text{ we get:}$$

$$[C_2H_5] = \sqrt{\frac{k_9}{k_{13}+k_{14}}}\sqrt{[C_2H_6]}$$

The steady state concentration of H is then

$$[H] = \frac{k_{11a}[C_2H_5][M]}{k_{12}[C_2H_6]} = \frac{k_{11a}}{k_{12}}\sqrt{\frac{k_9}{k_{13}+k_{14}}}\frac{[M]}{\sqrt{[C_2H_6]}}$$

Ignoring minor contributions to ethane formation and destruction in initiation and termination steps, we get

$$\frac{d[C_2H_6]}{dt} = k_{12}[C_2H_6][H] = k[C_2H_6]^{0.5}[M] \approx k[M]^{1.5}$$

Consequently, the reaction is of order 1.5 in $[C_2H_6]$.

(d)

The collision frequency factor z is given as:

$$z = \pi d^2 \bar{u}$$

d is the sum of the reactant radii: $d = r_{C_2H_5} + r_H = 6.0 \times 10^{-10}$ m

$$\bar{u} = \sqrt{\frac{8k_BT}{\pi\mu}} = 4678 \text{m/a}$$ is the relative speed.

The reduced mass is found as $\mu = \dfrac{m_{C_2H_5} m_H}{m_{C_2H_5} + m_H} = 0.967 m_H = 1.606 \times 10^{-27}$ kg

$$z = \pi \left(6.0 \times 10^{-10} \text{m}\right)^2 4678 \,\text{m s}^{-1} = 5.29 \times 10^{-10} \,\text{m}^3 \,\text{s}^{-1} = 3.2 \times 10^9 \,\text{m}^3\text{mol}^{-1}\text{s}^{-1}$$

Block 3

Task 1. Catalytic Synthesis of Hydrogen Peroxide (35%, weighted as roughly 5% for each question)

(a) Good candidates are the transition metals to the right in the periodic table as they interact most weakly with oxygen.

(b) For example

(1) $H_2 + 2* \rightleftharpoons 2H*$ QE

(2) $O_2 + 2* \rightleftharpoons 2O*$ QE

(3) $O* + H* \rightleftharpoons HO* + *$ RLS

(4) $2HO* \rightleftharpoons H_2O_2* + *$ QE

(5) $H_2O_2* \rightleftharpoons H_2O_2 + *$ QE
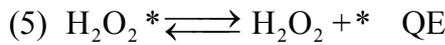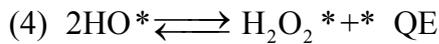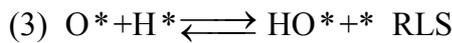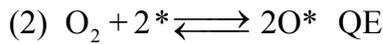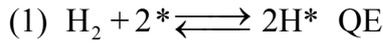
(c) Since 2 moles of reactant is reduced to one mole of product is high pressure favourable. Since the process is exothermic is low temperatures favourable, but as the process is also activated is there a limit to how low the temperature can be as a significant rate is required.

(d) From the equations the following set of relations appears

(1) $\dfrac{d\theta_H}{dt} = k_1^+ p_{H_2} \theta_*^2 - k_1^- \theta_H^2 = 0 \Rightarrow \theta_H = \sqrt{K_1 p_{H_2}}\, \theta_*$

(2) $\dfrac{d\theta_{O_2}}{dt} = k_2^+ p_{O_2} \theta_* - k_2^- \theta_{O_2} = 0 \Rightarrow \theta_{O_2} = K_2 p_{O_2} \theta_*$

(3) $r = k_3^+ \theta_{O_2} \theta_H - k_3^- \theta_{HO_2} \theta_*$

(4) $\dfrac{d\theta_{HO_2}}{dt} = k_4^+ \theta_{HO_2} \theta_H - k_4^- \theta_{H_2O_2} \theta_* = 0 \Rightarrow \theta_{HO_2} = \dfrac{\theta_{H_2O_2} \theta_*}{K_4 \theta_H}$

(5) $\dfrac{d\theta_{H_2O_2}}{dt} = k_5^+ \theta_{H_2O_2} - k_5^- p_{H_2O_2} \theta_* = 0 \Rightarrow \theta_{H_2O_2} = \dfrac{p_{H_2O_2} \theta_*}{K_5}$

$r = k_3^+ \theta_{O_2} \theta_H - k_3^- \theta_{HO_2} \theta = k_3^+ \sqrt{K_1 p_{H_2}}\, \theta_* K_2 p_{O_2} \theta_* - k_3^- \dfrac{\theta_{H_2O_2} \theta_*}{K_4 \theta_H} \theta_*$

$= k_3^+ \sqrt{K_1 p_{H_2}}\, K_2 p_{O_2} \theta_*^2 - k_3^- \dfrac{p_{H_2O_2}}{K_5 \sqrt{K_1 p_{H_2}} K_4} \theta_*^2$

$= k_3^+ \sqrt{K_1 p_{H_2}}\, K_2 p_{O_2} \theta_*^2 \left(1 - \dfrac{1}{K_1 K_2 K_3 K_4 K_5} \dfrac{p_{H_2O_2}}{p_{H_2} p_{O_2}}\right)$

$= k_3^+ \sqrt{K_1 p_{H_2}}\, K_2 p_{O_2} \theta_*^2 \left(1 - \dfrac{1}{K_G} \dfrac{p_{H_2O_2}}{p_{H_2} p_{O_2}}\right)$ for $K_G = K_1 K_2 K_3 K_4 K_5$

e)

$$\theta_* = 1 - \theta_H - \theta_{O_2} - \theta_{HO_2} - \theta_{H_2O_2} = 1 - \sqrt{K_1 p_{H_2}}\,\theta_* - K_2 p_{O_2}\theta_* - \frac{\theta_{H_2O_2}\theta_*}{K_4\theta_H} - \frac{p_{H_2O_2}\theta_*}{K_5}$$

$$= 1 - \sqrt{K_1 p_{H_2}}\,\theta_* - K_2 p_{O_2}\theta_* - \frac{\dfrac{p_{H_2O_2}\theta_*}{K_5}\theta_*}{K_4\sqrt{K_1 p_{H_2}}\,\theta_*} - \frac{p_{H_2O_2}\theta_*}{K_5}$$

$$= 1 - \left(\sqrt{K_1 p_{H_2}} + K_2 p_{O_2} + \frac{p_{H_2O_2}}{K_4 K_5 \sqrt{K_1 p_{H_2}}} + \frac{p_{H_2O_2}}{K_5} \right)\theta_* \Rightarrow$$

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{H_2}} + K_2 p_{O_2} + \dfrac{p_{H_2O_2}}{K_4 K_5 \sqrt{K_1 p_{H_2}}} + \dfrac{p_{H_2O_2}}{K_5}}$$

(f)
Oxygen is MARI $\quad \theta_* \cong 1 - \theta_{O_2} = \dfrac{1}{1 + K_2 p_{O_2}} \Rightarrow$

$$r^+ = k_3^+ \sqrt{K_1 p_{H_2}}\, K_2 p_{O_2}\theta_*^2 \cong k_3^+ \sqrt{K_1 p_{H_2}}\, K_2 p_{O_2} \left(\frac{1}{1 + K_2 p_{O_2}} \right)^2$$

$$n_x \equiv p_x \frac{\partial \ln\left(r^+\right)}{\partial p_x} \Rightarrow n_{H_2} = \frac{1}{2}, \; n_{H_2O_2} = 0, \; n_{O_2} = 1 - \frac{2 K_2 p_{O_2}}{1 + K_2 p_{O_2}} = 1 - 2\theta_{O_2}$$

g)

Now
$$\theta_* \cong 1 \Rightarrow$$

$$r^+ = k_3^+ \sqrt{K_1 p_{H_2}}\, K_2 p_{O_2} = k_3^+ \sqrt{K_1}\, K_2 p_{tot}^{3/2} \sqrt{\chi_{H_2}}\,(1 - \chi_{H_2}) \;\text{ where }\; \chi_{H_2} = \frac{p_{H_2}}{p_{H_2} + p_{O_2}} = \frac{p_{H_2}}{p_{tot}}$$

$$\frac{\partial r^+}{\partial \chi_{H_2}} = 0 \Rightarrow \frac{1}{2\sqrt{\chi_{H_2}}}\left(1 - \chi_{H_2}\right) - \sqrt{\chi_{H_2}} = 0 \Rightarrow \chi_{H_2} = \frac{1}{3}$$

R is maximal when $p_{H_2} = \dfrac{1}{2} p_{O_2}$

Task 2. Effectiveness of Pt Catalyst (30%, weighted as roughly 5% for each of the questions)

(a) How many oxygen atoms were there on the surface? $N_O = \dfrac{PV_{H_2O}}{k_B T} = 5.21 \times 10^{20}$.

Each oxygen take up on an area of $\sqrt{2} \times \sqrt{2}$ area unit cell. Pt is fcc meaning the (100) unit cell has an area of $a^2/2$. Thus

$$A_{Pt} = \frac{N_O 2a^2}{2} = \frac{PV_{H_2O}a^2}{k_B T} = \frac{10^5 \times 21.4 \times 10^{-6}(3.92 \times 10^{-10})^2}{1.38 \times 10^{-23} \cdot 298}\, m^2 = 80\, m^2/g$$

(b) Under vacuum conditions will the Pt(111) the most stable surface and the amounts of other facets would be given by the Wulff construction.

(c) The number of active sites are $N_O/2$ since each site is consisting of 4 Pt atoms. The rate of one gram of catalyst is then simply

$$\text{rate} = \frac{N_O}{2}\text{TOF} = \frac{PV_{H_2O}}{2k_BT}\text{TOF} = 4.3\times10^{-7}\frac{\text{mol}}{\text{s}} = 2.58\times10^{17}\text{s}^{-1}.$$

The amount of gas passing over the catalyst per second is

$$\text{flow} = \frac{100\times10^{-6}}{60\text{s}}\text{m}^3 = 1.66\times10^{-6}\,\text{m}^3\text{s}^{-1}\text{resulting in a product concentration of}$$

$$\frac{4.3\times10^{-7}}{1.66\times10^{-6}}\frac{\text{mol}}{\text{m}^3} = 0.26\frac{\text{mol}}{\text{m}^3}\text{ or ca. 1.1\%.}$$

(d) The volume of 1 g catalyst is 0.5 cm^3. Since S is the amount of Pt area per volume catalyst $S = \frac{80\,\text{m}^2\text{g}^{-1}}{0.5\,\text{cm}^3\text{g}^{-1}} = 1.6\times10^8\,\text{m}^{-1}$. The concentration of the reactant

oxygen is $C_o = \frac{n}{V} = \frac{p_{O_2}}{RT} = \frac{0.21\times1\times10^5}{8.31\times500} = 5.1\frac{\text{mol}}{\text{m}^3}$. Notice the concentration of oxygen must be at the catalyst condition. Meaning that

$$k = \frac{\text{rate}}{VSC_O} = \frac{4.3\times10^{-7}}{0.5\times10^{-6}\cdot1.6\times10^8\times5.1}\frac{\text{m}}{\text{s}} = 1.1\times10^{-9}\frac{\text{m}}{\text{s}}$$

(e) The rate is seen to bend of for temperatures above 660K indicating that the rate is being transport limited. The apparent activation energy is found from the Arrhenius plot for temperatures below 660K.
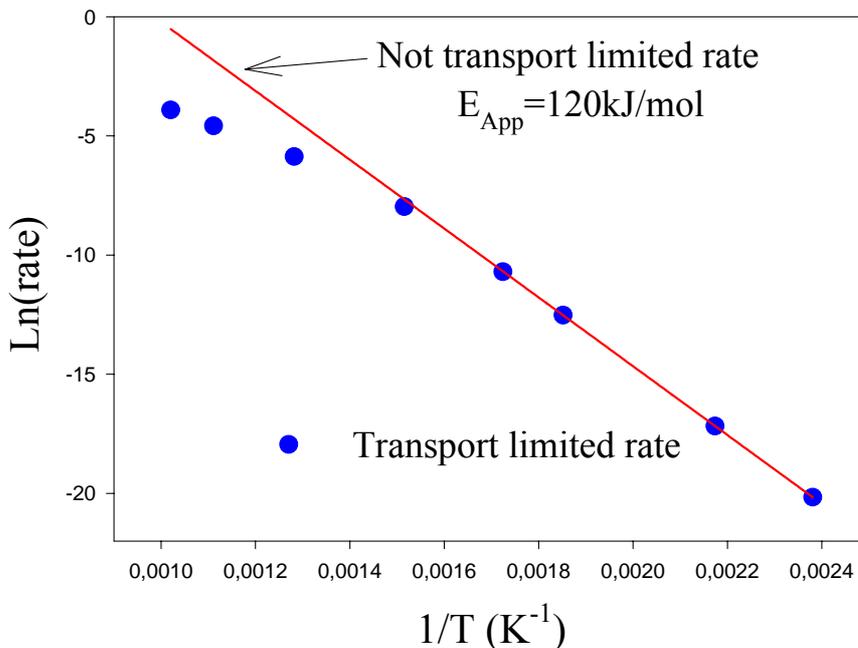
(f) The efficiency of the catalyst is estimated using the Thiele Modulus as:

$$\varepsilon = \frac{3}{\Phi_s}\left[\frac{1}{\tanh(\Phi_s)} - \frac{1}{\Phi_s}\right] \text{ where } \Phi_s = R\sqrt{\frac{kS}{D_{\text{eff}}}} .$$

k can be found at 900 K since we know the k at 500 K and the apparent activation energy i.e.. $k_0 = k(T = 500\text{K}) * e^{\frac{E_{\text{App}}}{R(T=500\text{K})}} \Rightarrow$

$$k(T = 900\,\text{K}) = 3730e^{\frac{-E_{\text{App}}}{R(T=900\text{K})}} = 4.0\times10^{-4}\,\frac{\text{m}}{\text{s}}$$

$$\Phi_s = 1\times10^{-4}\sqrt{\frac{1.6\times10^8 \times 4.0\times10^{-4}}{3\times10^{-7}}} = 46$$

$\varepsilon = 6 \times 10^{-2}$, i.e. most of the Pt inside the particle is not in contact with the reactants. We should therefore only have Pt catalyst in an outer shell of the particles. Thus a shell impregnation would do cutting down on the loading of the expensive Pt metal.

Task 3 Uncertainties in Determining Rates and Activation Energies (35%, weighted as 5% for the first and 10% for each of the following questions).

To bring the TST estimate into accordance with the experimental determination at 1000 K, we need an increase of a factor of $2.1\times10^{-12}/7.8\times10^{-13} = 2.7$ in the estimated rate constant.

(a)
A decrease of kJ mol^{-1} in the activation energy will increase k_{TST} by a factor of:

$$\frac{\exp(-(E_a - 8000\,\text{J mol}^{-1})/RT)}{\exp(-E_a / RT)} = \exp(8000/RT) = \exp(8000/R*1000) = 2.6$$

The difference between k_{exp} and k_{TST} is roughly consistent with the uncertainty in E_a.

(b)
The rotational partition function is estimated as,

$$q_R^2 = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

Only the moment of inertia depends on the bond length. An increase in the H–H bond length of 10% causes in increase in the estimated rate constant:

$$\frac{\left(q_R^2\right)_{X'}}{\left(q_R^2\right)_X} = \frac{I'}{I} = \frac{2(0.93\times10^{-10}\,\text{m}\cdot1.1)^2 \cdot m_H}{2(0.93\times10^{-10}\,\text{m})^2 \cdot m_H} = 1.1^2 = 1.21$$

A 10% increase in the H–H bond length in the activated complex leads to a minor increase in the rate constant of 21%.

(c)
There are 3×3 − 5 = 4 vibrational degrees of freedom in the activated complex: two bending modes, one stretching mode, and the dissociation mode.

The TST rate constant can be increased if the vibrational frequencies are decreased:

$$(q_V)_X = \prod_i \frac{1}{1-\exp\left(\dfrac{-h\nu_i}{k_B T}\right)}$$

$$= \left[1-\exp\left(\frac{-6.636\times10^{-34}\,J\,s\times2193\,cm^{-1}\times2.99\times10^{10}\,cm/s}{1.382\times10^{-23}\,J\,K^{-1}\times1000\,K}\right)\right]^{-2}$$

$$\cdot\left[1-\exp\left(\frac{-6.626\times10^{-34}\,J\,s\cdot978\,cm^{-1}\cdot2.99\times10^{10}\,cm/s}{1.381\times10^{-23}\,J\,K^{-1}\cdot1000\,K}\right)\right]^{-1} = 1.445$$

$$(q_V)_{X'} = \prod_i \frac{1}{1-\exp\left(\dfrac{-h\nu_i}{k_B T}\right)}$$

$$= \left[1-\exp\left(\frac{-6.636\times10^{-34}\,J\,s\times2093\,cm^{-1}\times2.99\times10^{10}\,cm/s}{1.382\times10^{-23}\,J\,K^{-1}\times1000\,K}\right)\right]^{-2}$$

$$\cdot\left[1-\exp\left(\frac{-6.626\times10^{-34}\,J\,s\times878\,cm^{-1}\times2.99\times10^{10}\,cm/s}{1.381\times10^{-23}\,J\,K^{-1}\times1000\,K}\right)\right]^{-1}$$

$$= 1.542$$

$$\frac{k'}{k} = \frac{q_V'}{q_V} = \frac{1.542}{1.442} = 1.07$$

That is only a 7% increase in the rate constant.

(d)

The collision frequency factor z is given as

$$z = \pi d^2 \bar{u}$$

d is the sum of the reactant radii:
$d = r_{H_2} + r_H$ = 0.27 nm + 0.2 nm = 0.47 nm = 4.7 × 10^{-10} m
$\bar{u}$ is the relative speed of the reactants:

$$\bar{u} = \sqrt{\frac{8k_B T}{\pi\mu}}$$

The reduced mass is found as $\mu = \dfrac{m_{H_2} m_H}{m_{H_2} + m_H} = \dfrac{2}{3} m_H = 1.108\times10^{-27}\,kg$

$$\bar{u} = \left(\sqrt{\frac{8 \times (1.38 \times 10^{-23}\,\text{J/K} \times 300\,\text{K})}{\pi \times 1.108 \times 10^{-27}\,\text{kg}}} \right) = 3085\,\text{m/s}$$

$$z = \pi \left(4.7 \times 10^{-10}\,\text{m}\right)^2 \times 3085\,\text{m/s} = 2.14 \times 10^{-15}\,\text{m}^3/s = 1.29 \times 10^{15}\,\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$$

The probability factor P is calculated as the observed A factor divided by the collision frequency factor:

$$P = \frac{2.3 \times 10^{14}\,\text{cm}^3\text{mol}^{-1}\text{s}^{-1}}{1.29 \times 10^{15}\,\text{cm}^3\text{mol}^{-1}\text{s}^{-1}} = 0.18$$