Physical Chemistry

THE FIRST
INTERNATIONAL CHEMISTRY OLYMPIAD
18–21 JULY 1968, PRAGUE, CZECHOSLOVAKIA

THEORETICAL PROBLEMS

PROBLEM 1

A mixture of hydrogen and chlorine kept in a closed flask at a constant temperature was irradiated by scattered light. After a certain time the chlorine content decreased by 20 % compared with that of the starting mixture and the resulting mixture had the composition as follows: 60 volume % of chlorine, 10 volume % of hydrogen, and 30 volume % of hydrogen chloride.

Problems:

1.1 What is the composition of the initial gaseous mixture?

1.2 How chlorine, hydrogen, and hydrogen chloride are produced?

SOLUTION

1.1 $H_2 + Cl_2 \rightarrow 2\ HCl$

30 volume parts of hydrogen chloride could only be formed by the reaction of 15 volume parts of hydrogen and 15 volume parts of chlorine. Hence, the initial composition of the mixture had to be:

Cl_2: 60 + 15 = 75 %

H_2: 10 + 15 = 25 %

1.2 Chlorine and hydrogen are produced by electrolysis of aqueous solutions of NaCl: $NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

anode: $2\ Cl^- - 2\ e \rightarrow Cl_2$

cathode: $2\ Na^+ + 2\ e \rightarrow 2\ Na$

$$2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$$

Hydrogen chloride is produced by the reaction of hydrogen with chlorine.

PROBLEM 3

The gas escaping from a blast furnace has the following composition:

12.0 volume % of CO_2 28.0 volume % of CO
3.0 volume % of H_2 0.6 volume % of CH_4
0.2 volume % of C_2H_4 56.2 volume % of N_2

Problems:

3.1 Calculate the theoretical consumption of air (in m^3) which is necessary for a total combustion of 200 m^3 of the above gas if both the gas and air are measured at the same temperature. (Oxygen content in the air is about 20 % by volume).

3.2 Determine the composition of combustion products if the gas is burned in a 20 % excess of air.

SOLUTION

3.1

	O_2
$2\,CO + O_2 \rightarrow 2\,CO_2$	14
$2\,H_2 + O_2 \rightarrow 2\,H_2O$	1.5
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	1.2
$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$	0.6
	17.3 parts x 5 = 86.5 parts of the air

200 m^3 of the gas .... 2 x 86.5 = 173.0 m^3 of the air
+ 20 % 34.6 m^3
207.6 m^3 of the air

3.2 207.6 **:** 5 = 41.52 parts of O_2 **:** 2 = 20.76 parts of O_2 for 100 m^3 of the gas
20.76 x 4 = 83.04 parts of N_2 for 100 m^3 of the gas

Balance:	CO_2	H_2O	N_2	O_2
(volume parts)	12.00	3.00	56.20	20.76
	28.00	1.20	83.04	- 17.30
	0.60	0.40		
	0.40			
	41.00	4.60	139.24	3.46

Total: 41.00 + 4.60 + 139.24 + 3.46 = 188.30 of volume parts of the gaseous components.

$$\%\,H_2O = \frac{4.60}{188.30} \times 100 = 2.44$$

$$\%\,N_2 = \frac{139.24}{188.30} \times 100 = 73.95$$

$$\%\,O_2 = \frac{3.46}{188.30} \times 100 = 1.84$$

THE THIRD

INTERNATIONAL CHEMISTRY OLYMPIAD

1–5 JULY 1970, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

An amount of 23 g of gas (density ρ = 2.05 g dm^{-3} at STP) when burned, gives 44 g of carbon dioxide and 27 g of water.

Problem:

What is the structural formula of the gas (compound)?

SOLUTION

The unknown gas : X

From the ideal gas law : $M(\text{X}) = \dfrac{\rho(\text{X})\, R\, T}{p} = 46 \text{ g mol}^{-1}$

$$n(\text{X}) = \frac{23 \text{ g}}{46 \text{ g mol}^{-1}} = 0.5 \text{ mol}$$

$$n(\text{CO}_2) = \frac{44 \text{ g}}{44 \text{ g mol}^{-1}} = 1 \text{ mol}$$

n(C) = 1 mol

m(C) = 12 g

$$n(\text{H}_2\text{O}) = \frac{27 \text{ g}}{18 \text{ g mol}^{-1}} = 1.5 \text{ mol}$$

n(H) = 3 mol

m(H) = 3 g

The compound contains also oxygen, since

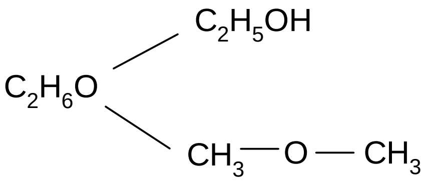
$m(C) + m(H) = 12\ g + 3\ g = 15\ g < 23\ g$

$m(O) = 23\ g - 15\ g = 8\ g$

$n(O) = 0,5\ mol$

$n(C) : n(H) : n(O) = 1 : 3 : 0,5 = 2 : 6 : 1$

The empirical formula of the compound is C_2H_6O.



C_2H_6O → C_2H_5OH ethanol

C_2H_6O → CH_3-O-CH_3 dimethyl ether

Ethanol is liquid in the given conditions and therefore, the unknown gas is dimethyl ether.

PROBLEM 4

Amount of 50 g of a 4 % sodium hydroxide solution and 50 g of a 1.825 % solution of hydrochloric acid were mixed in a heat insulated vessel at a temperature of 20 °C. The temperature of the solution obtained in this way increased to 23.4 °C. Then 70 g of a 3.5 % solution of sulphuric acid at a temperature of 20 °C were added to the above solution.

Problems:

4.1 Calculate the final temperature of the resulting solution.

4.2 Determine the amount of a dry residue that remains after evaporation of the solution.

In calculating the first problem use the heat capacity value c = 4.19 J g^{-1} K^{-1}.

Relative atomic masses:

A_r(H) = 1; A_r(O) = 16; A_r(Na)= 23; A_r(S) = 32; A_r(Cl) = 35.5.

SOLUTION

4.1 a) $NaOH + HCl \rightarrow NaCl + H_2O$

$$n(\text{NaOH}) = \frac{m(\text{solution NaOH}) \times w(\text{NaOH})}{M(\text{NaOH})} = \frac{50\text{ g} \times 0.04}{40\text{ g mol}^{-1}} = 0.05\text{ mol}$$

$$n(\text{HCl}) = \frac{50\text{ g} \times 0.01825}{36.5\text{ g mol}^{-1}} = 0.025\text{ mol}$$

unreacted: n(NaOH) = 0.025 mol

b) When 1 mol of water is formed, neutralization heat is:

$$\Delta H_{\text{neutr}} = -\frac{m\ c\ \Delta t}{n(\text{H}_2\text{O})} = \frac{100\text{ g} \times 4.19\text{ J g}^{-1}\text{ K}^{-1} \times 3.4\text{ K}}{0.025\text{ mol}} = -57\,000\text{ J mol}^{-1}$$

c) $NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$

The temperature of the resulting solution is calculated according to the equation:

$m_1\, c_1\, t_1 + m_2\, c_2\, t_2 = m\, c\, t$

$c_1 = c_2 = c$

$m_1\,t_1 + m_2\,t_2 = m\,t$

$$t = \frac{m_1\,t_1 + m_2\,t_2}{m} = \frac{(100 \times 23.4) + (70 \times 20.0)}{170} = 22\ ^\circ\text{C}$$

d) The temperature increase due to the reaction of NaOH with H_2SO_4 is as follows:

$$t = -\frac{n(\text{H}_2\text{O})\ \Delta H_{\text{neutr}}}{m\,c} = -\frac{0.025\ \text{mol}\ \times 57\,000\ \text{J mol}^{-1}}{170\ \text{g} \times 4.19\ \text{J g}^{-1}\ \text{K}^{-1}} = 2\ \text{K}$$

The final temperature of the solution: $t = 22 + 2 = 24\ ^{o}\text{C}$

4.2 e) When the solution has evaporated the following reaction is assumed to take place:

$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$

Na_2SO_4 is the dry residue.

$m(Na_2SO_4) = n\,M = 0.025\ \text{mol} \times 142\ \text{g mol}^{-1} = 3.55\ \text{g}$

THE FIFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–10 JULY 1973, SOFIA, BULGARIA

THEORETICAL PROBLEMS

PROBLEM 1

In nitrating a hydroxy derivative of benzene a compound is formed which contains 49.0 % by mass of oxygen. A charge of 4350 C is required for a total electroreduction of 0.458 g of the compound, efficiency being 80 %.

Problem:

1.1 Determine the stoichiometric as well as structural formulas of the compound if the product of the electrochemical reduction is an aromatic hydroxy amino derivative.

F (Faraday's charge) = 96 500 C mol^{-1}

SOLUTION

1.1 a) Formula of the compound: $C_6H_xO_yN_z$

The compound is a hydroxy nitroderivative of benzene:

$C_6H_{6-(y-2z)-z}(OH)_{y-2z}(NO_2)_z$

b) Equation of the reduction:

$R\text{-}NO_2 + 6\ H \rightarrow R\text{-}NH_2 + 2\ H_2O$

Combining mass of the compound:

$$E = \frac{M_r(\text{compound})}{6\ z} \qquad (1)$$

An amount of charge which is required for the electrochemical reduction:

$Q = 4350\ C \times 0.8 = 3480\ C$

Combining mass of the compound:

$$E = \frac{m}{\dfrac{3480\ \text{C}}{F}} = 0.458 \times \frac{96500\ \text{C}}{3480\ \text{C}} = 12.7$$

In relation to (1): M_r (compound) = $76.2 \times z$ (2)

c) $$\%\ \text{O} = \frac{y \times M_r(\text{O}) \times 100}{M_r(\text{compound})}$$

$$49 = \frac{y \times 16 \times 100}{M_r(\text{compound})}$$

M_r(compound) = 32.7 y

d) M_r(compound) = 6 M_r (C) + x M_r (H) + y M_r (O) + z M_r (N)

M_r (compound) = 6×12 + x + 16 y + 14 z

Taking into consideration the general formula of the unknown hydroxy derivative of benzene:

x = 6 – (y – 2 z) – z + y – 2 z

x = 6 – z (4)

Then: M_r(compound) = 72 + 6 – z + 16 y + 14 z

M_r(compound) = 78 + 16 y + 13 z (5)

By solving equations (2), (3), (4), and (5) we obtain:

$\underline{M_r\text{(compound)} = 229}$

x = 3

y = 7

z = 3

The molecular formula of the compound is: $C_6H_3O_7N_3$ or $C_6H_2(OH)(NO_2)_3$.

The compound is 2, 4, 6-trinitrophenol

PROBLEM 2

A mixture of a gaseous hydrocarbon and oxygen is in a vessel of a volume of 1 dm^3 at a temperature of 406.5 K and a pressure of 101 325 Pa. There is twice as much oxygen in the mixture as is needed for the reaction with the hydrocarbon. After combustion of the hydrocarbon the pressure in the vessel (at the same temperature) is increased by 5 %.

Problem:

2.1 What hydrocarbon was in the mixture when the mass of water formed by the combustion was 0.162 g.

SOLUTION

2.1 Amounts of substances of reactants and reaction products:

Equation: $C_xH_y + (x + \frac{y}{4})O_2 = x\,CO_2 + \frac{y}{2}\,H_2O$

$$n(H_2O) = \frac{m(H_2O)}{M(H_2O)} = \frac{0.162\text{ g}}{18\text{ g mol}^{-1}} = 0.009\text{ mol}$$

$$n(C_xH_y) = \frac{0.009\text{ mol}}{\frac{y}{2}} = \frac{0.018}{y}\text{ mol} \qquad (1)$$

$$n(O_2) = (x + \frac{y}{4}) \times \frac{0.009\text{ mol}}{\frac{y}{2}} = \frac{x + \frac{y}{4}}{y} \times 0.018\text{ mol} \qquad (2)$$

$$n(CO_2) = x\,\frac{0.009\text{ mol}}{\frac{y}{2}} = \frac{x}{y} \times 0.018\text{ mol} \qquad (3)$$

Before reaction:

$$n(\text{mixture}) = \frac{p\,V}{R\,T} = \frac{101.325\text{ kPa} \times 1\text{ dm}^3}{8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 406.5\text{ K}} = 0.03\text{ mol}$$

$$n(C_xH_y) + 2\,n(O_2) = 0.03\text{ mol} \qquad (4)$$

After reaction: p = 101. 325 kPa × 1.05 = 106.4 kPa

$$n(\text{mixture}) = \frac{p\,V}{R\,T} = \frac{106.4\ \text{kPa} \times 1\ \text{dm}^3}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 406.5\ \text{K}} = 0.0315\ \text{mol}$$

$n(CO_2) + n(O_2) + n(H_2O) = 0.0315$ mol

$n(CO_2) + n(O_2) = 0.0225$ mol (5)

When (1), (2), and (3) are substituted in (4) and (5), an equation of two unknowns is obtained which when solved yields

x = 3; y = 6

The stoichiometric formula of the unknown hydrocarbon is: C_3H_6.

PROBLEM 4

A mixture contains two organic compounds, **A** and **B**. Both of them have in their molecules oxygen and they can be mixed together in arbitrary ratios. Oxidation of this mixture on cooling yields the only substance **C** that combines with $NaHSO_3$. The ratio of the molar mass of the substance being formed in the reaction with $NaHSO_3$ to that of substance **C**, is equal to 2.7931.

The mixture of substances **A** and **B** is burned in the presence of a stoichiometric amount of air (20 % O_2 and 80 % of N_2 by volume) in an eudiometer to produce a mixture of gases with a total volume of 5.432 dm^3 at STP. After the gaseous mixture is bubbled through a $Ba(OH)_2$ solution, its volume is decreased by 15.46 %.

Problems:

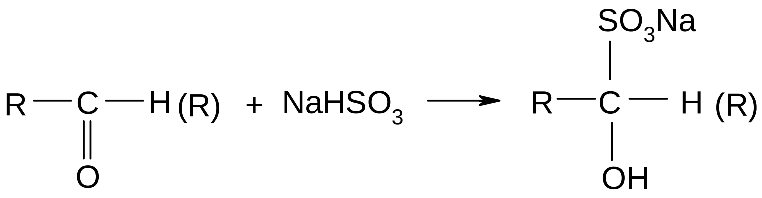
4.1 Write structural formulas of substance **A** and **B**.

4.2 Calculate the molar ratio of substances **A** and **B** in the mixture.

$A_r(C) = 12$; $A_r(O) = 16$; $A_r(S) = 32$; $A_r(Na) = 23$.

SOLUTION

4.1

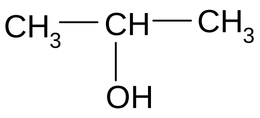


$$R-C(=O)-H\,(R) + NaHSO_3 \longrightarrow R-C(SO_3Na)(OH)-H\,(R)$$

$M_r(\mathbf{C})$ $M_r(NaHSO_3) = 104$ $M_r(\mathbf{C}) + 104$

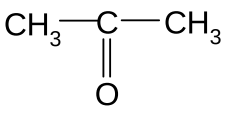
$$\frac{M_r(\mathbf{C}) + 104}{M_r(\mathbf{C})} = 2.7931 \qquad M_r(\mathbf{C}) = 58$$

A ...



$CH_3-CH(OH)-CH_3$

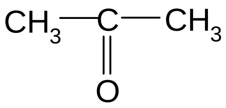
C ...



$CH_3-C(=O)-CH_3$

4.2 At STP conditions the gaseous mixture can only contain CO_2 and N_2. Carbon dioxide is absorbed in a barium hydroxide solution and therefore:

B ...



$CH_3-CO-CH_3$

(a) $V(CO_2) = 5.432\ dm^3 \times 0.1546 = 0.84\ dm^3$

(b) $V(N_2) = 5.432\ dm^3 - 0.84\ dm^3 = 4.592\ dm^3$

(c) $CH_3\text{-}CHOH\text{-}CH_3 + 9/2\ (O_2 + 4\ N_2) = 3\ CO_2 + 4\ H_2O + 18\ N_2$

(d) $CH_3\text{-}CO\text{-}CH_3 + 4\ (O_2 + 4\ N_2) = 3\ CO_2 + 3\ H_2O + 16\ N_2$

Let us mark the amounts of substances as:

$n(CH_3\text{-}CHOH\text{-}CH_3) = x$

$n(CH_3\text{-}CO\text{-}CH_3) = y$

From equations (a), (c) and (d):

(e) $(3x \times 22.4) + (3y \times 22.4) = 0.84$

From equations (b), (c) and (d):

(f) $(18x \times 22.4) + (16y \times 22.4) = 4.592$

In solving equations (e) and (f) we get:

$x = 0.0025$ mol $y = 0.01$ mol

$$\frac{x}{y} = \frac{1}{4}$$

PROBLEM 6

The equilibrium constant of the reaction $H_2 + I_2 \rightleftharpoons 2\,HI$ is at 600 ℃ equal to 70.0 .

Problems:

6.1 How much iodine (in %) is converted till the equilibrium is reached if the reactants are mixed in:

a) 1 : 1 molar ratio at 600 ℃;

b) 2 : 1 molar ratio at 600 ℃ (the amount of hydrogen is twice as great as that of iodine).

6.2 How many moles of hydrogen should be mixed with one mole of iodine when 99 % of iodine is to be converted to hydrogen iodide till the equilibrium is reached at 600 ℃?

SOLUTION

6.1a) (two alternative solutions)

i) $[H_2] = [I_2] = c - x$

$[HI] = 2\,x$

$$K = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{4\,x^2}{(c-x)^2}$$

$$\sqrt{K} = \frac{2\,x}{c-x}$$

$$x = \frac{\sqrt{70}\,.\,c}{2+\sqrt{70}} \qquad \frac{x}{c} = 0.807 \qquad 80.7\ \%$$

ii) $[H_2] = [I_2] = c - c\alpha$

$[HI] = 2\,c\alpha$

$$K = \frac{4\,\alpha^2\,c^2}{(1-\alpha)^2\,c^2} = \frac{4\,\alpha^2}{(1-\alpha^2)^2}$$

$$\sqrt{K} = \frac{2\,\alpha}{1-\alpha}$$

α = 0.807 , i. e. 80.7 %

6.1b) (two alternative solutions)

i) $[H_2] = 2\,c - x$ $[I_2] = c - x$

$[HI] = 2\,x$

$$K = \frac{4\,x^2}{(2c - x)\,(c - x)}$$

$x = 0.951\,c$ $\frac{x}{c} = 0.951$ i. e. 95.1 %

ii) $[H_2] = 2\,c - c\alpha$ $[I_2] = c - c\,\alpha$

$[HI] = 2\,c\,\alpha$

$$K = \frac{4c^2\,\alpha^2}{(2 - \alpha)\,(1 - \alpha)\,c^2}$$

$\alpha = 0.951$ i. e. 95.1 %

6.2 $[H_2] = x\,c - 0.99\,c$ $[I_2] = c - 0.99\,c$

$[HI] = 1.98\,c$

$$K = \frac{1.98^2\;c^2}{c^2\;(1 - 0.99)\,(x - 0.99)} = \frac{1.98^2}{0.01\,(x - 0.99)}$$

$x = 6.59$ mol H_2

PROBLEM 6

Temperature in a larger room should be measured by means of a gaseous thermometer. A glass tube with the internal volume of 80 cm^3 was for this purpose filled with nitrogen at a temperature of 20 °C and a pressure of 101.325 kPa. The tube was then slowly and steadily moved throughout the room. Due to the thermal expansion the gas at the higher temperature escapes from the tube and is captured above the liquid whose vapour pressure is negligible. The total volume of the gas escaped from the tube was 35 cm^3 at a temperature of 20 °C and a pressure of 101.325 kPa.

Problems:

6.1 How many moles of nitrogen were used to fill the glass tube?

6.2 How many moles of nitrogen escaped from the tube at the higher temperature?

6.3 Calculate the average temperature in the room under investigation if the thermal expansion of the glass tube is assumed to be negligible.

6.4 Does anything change if instead of pure nitrogen, a mixture containing 50 volume % of nitrogen and 50 volume % of hydrogen is used?

SOLUTION

6.1 Filling of the tube:

$$n_1(N_2) = \frac{p\,V_1}{R\,T} = \frac{101.325\text{ kPa} \times 0.080\text{ dm}^3}{8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 293.15\text{ K}} = 3.33 \times 10^{-3}\text{ mol}$$

6.2 Escaped from the tube:

$$n_2(N_2) = \frac{p\,V_2}{R\,T} = \frac{101.325\text{ kPa} \times 0.035\text{ dm}^3}{8.314\text{ J mol}^{-1}\text{ K}^{-1} \times 293.15\text{ K}} = 1.46 \times 10^{-3}\text{ mol}$$

Remained in the tube:

$n_3(N_2) = n_1 - n_2 = 1.87 \times 10^{-3}$ mol

6.3 Temperature at which the amount of substance of nitrogen (n_3) takes a volume of V_1 (the mean temperature in the room under investigation):

$$T = \frac{p\,V_1}{R\,n_3} = \frac{101.325\ \text{kPa} \times 0.080\ \text{dm}^3}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 1.87\times10^{-3}\ \text{mol}} = 521\,\text{K}$$

$\underline{t = 248\ °\text{C}}$

6.4 No change can occur in comparison with the preceding experiment.

PROBLEM 7

Photosynthesis by be summarised by the overall equation:

$$CO_2\,(g) + H_2O\,(l) \xrightarrow[\text{chlorophyll}]{\text{light}} C_6H_{12}\,(s) + 6\,O_2\,(g)$$

for which values of ΔH and ΔS at 25 ℃ are as follows:

$\Delta H = 2.816 \times 10^6$ J, $\Delta S = -182$ J K^{-1} or

$\Delta H = 2.816 \times 10^6$ J mol^{-1}, $\Delta S = -182$ J K^{-1} mol^{-1} if ΔH and ΔS values are related to one mole of reaction changes.

Imagine that there have been devised electrodes that would allow selective reduction of oxygen to water and oxidation of glucose to carbon dioxide in a galvanic cell, i. e a reverse process when compared with that of the photosynthetic reaction.

Problems:

7.1 What will be the electromotive force of the cell in which light energy would be transformed to electric energy by means of the photosynthetic reaction?

Note: In the envelope you can find the relation between the electromotive force and the change of free enthalpy of the reaction. (Attention: If you open the envelope you lose some points.)

7.2 In case we would want to quantify the symbol "light" in the equation of photosynthesis, we would ask: how many moles of photons with wavelength for example 500 nm take part in the above reaction? Calculate.

7.3 Calculate, what would be the electric power of a square swimming pool with a side of 10 m containing green algae capable of the photosynthetic reaction if under average illumination a current of 1 mA can be expected from the area of 1 cm^2.

SOLUTION

7.1 Two alternative solutions:

a) By means of quantities related to one mole of reaction changes. For the reaction taking place in the cell it would correspond: $\Delta G = -2.87 \times 10^6$ J mol^{-1}	b) By means of quantities related to the given reaction. For the reaction taking place in the cell it would correspond: $\Delta G = -2.87 \times 10^6$ J

Relation between the electromotive force and the change of free enthalpy of the reaction taking place in a cell:

$$-\Delta G = n\,F\,E$$

where n is so-called charge number	where n is the number of moles of charges which passed through the electrode during the reaction.

In our case, n has the value equal to 24 since one molecule of oxygen is reduced according to the equation:

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$

F (Faraday's constant) = 96 487 C mol^{-1}

Since one voltcoulomb is one joule, then:

$E = \dfrac{-(-2.87\times10^6)\ \text{V C mol}^{-1}}{24 \times 96\,487\ \text{C mol}^{-1}} = 1.24\ \text{V}$	$E = \dfrac{-(-2.87\times10^6)\ \text{V C}}{24\ \text{mol} \times 96\,487\ \text{C mol}^{-1}} = 1.24\ \text{V}$

7.2 Energy of absorbed photons is the only source of energy which enables the course of photosynthesis, and therefore, the number of absorbed photons x multiplied by their energy must be equal to the increase of energy in the system, i. e. to the value of 2.87×10^6 J. Thus:

$$\text{x}\ h\ \nu\ N_A = \text{x}\ h\ \frac{c}{\lambda}\ N_A = 2.87 \times 10^6\ \text{J}$$

$$\text{x} = \frac{2.87 \times 10^6\ \text{J} \times \lambda}{h\ c\ N_A} =$$

$$= \frac{2.87 \times 10^6\ \text{J} \times 500.10^{-9}\ \text{m}}{6.6256.10^{-34}\ \text{J s} \times 2.9979.10^{8}\ \text{m s}^{-1} \times 6.022.10^{23}\ \text{mol}^{-1}} =$$

$= 11.99 \approx 12$ mol of photons

7.3 The area of the swimming pool is 100 m^2. Current density at a voltage of 1.24 V is equal to 1. 10^4 mA m^{-2} = 10 A m^{-2}.

The total electric power :

$1.24\ \text{V} \times 10\ \text{A m}^{-2} \times 100\ \text{m}^2 = 1.24\ \text{kW}$

PROBLEM 8b

Among other factors, deterioration of the environment is manifested also by air pollution with carbon monoxide. Its most powerful source are combustion engines. The toxicity of carbon monoxide is caused by the fact that it forms with the blood dye - haemoglobin (Hb), the compound carbonyl haemoglobin (HbCO):

$$\text{Hb} + \text{CO} \rightarrow \text{HbCO}$$

The chemical bond in carbonyl haemoglobin is about 200 times stronger than that in oxyhaemoglobin (HbO_2) originating under common conditions. Consequently, haemoglobin cannot be used in oxygen transfer. The lack of oxygen starts to be felt from 50 ppm carbon monoxide in the air, i. e. 10 % carbonyl haemoglobin in blood.

Air oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at 1.6×10^{-6} mol dm^{-3} by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to 8×10^{-6} mol dm^{-3}

Problems:

8.1 Calculate the rate of oxyhaemoglobin formation if the rate constant is $k = 2.1 \times 10^6$ dm^3 mol^{-1} s^{-1} (at 37 °C – normal body temperature).

8.2 In some cases (carbon monoxide poisoning) an increase of the rate of oxyhaemoglobin formation up to 1.1×10^{-4} mol dm^{-3} s^{-1} is needed.

a) Calculate the required concentration of oxygen assuming that the concentration of haemoglobin in blood is constant.

b) Suggest of practical solution on the assumption that the concentration of oxygen in blood is proportional to the pressure of oxygen entering the lungs.

SOLUTION

8.1 $v = k\,[\text{Hb}][O_2]$

$k = 2.1 \times 10^6$ dm^3 mol^{-1} s^{-1}

$[\text{Hb}] = 8 \times 10^{-6}$ mol dm^{-3}

$[O_2] = 1.6 \times 10^{-6}$ mol dm^{-3}

$\underline{v = 2.688 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}$

Because 1 mole of oxygen (O_2) is needed to form 1 mole of oxyhaemoglobin, the rate of oxygen consumption is the same as the of oxyhaemoglobin formation.

8.2 $[O_2] = \dfrac{v}{k\ [\text{Hb}]}$

$v = 1.1 \times 10^{-4}$ mol dm^{-3} s^{-1}

$k = 2.1 \times 10^{6}$ dm^{3} mol^{-1} s^{-1}

[Hb] $= 8 \times 10^{-6}$ mol dm^{-3}

$\underline{[O_2] = 6.5 \times 10^{-6} \text{ mol dm}^{-3}}$

The oxygen concentration must increase up to 6.5×10^{-6} mol dm^{-3}. Oxygen concentration can be affected by elevation of air pressure only partially. The fourfold increase of oxygen concentration would demand an increase of the air pressure four times in comparison with the normal value. This pressure would be harmful for living organisms and therefore, air enriched with oxygen is breathed.

PROBLEM 3

Chromium plating is usually made by electrolysis in a solution of chromic acid. The chromium plated objects form the cathode. The anode is an alloy that is inert under given conditions, i. e. it does not react either chemically or electrochemically.

An electrolytic cell was filled with 100.0 dm^3 of an aqueous solution which contained 0.230 kg of chromium acid anhydride in 1 dm^3 of the solution.

In electrolysis a current of 1500 A passed through the electrolyte for 10.0 hours. After electrolysis an increase of the mass of the cathode was 0.679 kg.

The ratio of gas volumes

$$\frac{V_\mathrm{C}}{V_\mathrm{A}} = 1.603$$

where V_C is a volume of gases evolved at the cathode, whereas that marked as V_A is the volume of gases which are evolved at the anode. Both volumes were measured at the same conditions.

Problems

3.1 What part of the total charge (in %) was used for a deposition of 0.679 kg of chromium?

3.2 Calculate:

a) the volume ratio of both gases (at STP) which are evolved as by-products at the cathode and anode,

b) current efficiency for the corresponding reactions taking place separately at the cathode and anode when the gases are evolved.

If you find any disproportion between the data calculated and those given in the task, try to explain what process would take place in the electrolytic cell which has not been considered till now.

Write the corresponding summary equation for the reactions at electrodes and correct your previous calculations if possible.

SOLUTION

3.1 The total electric charge passed through the electrolyte:

$$Q = \frac{1500 \times 3600 \times 10}{96500} = 559.6\ \text{F}$$

Reaction at the cathode:

Cr^{VI} + 6 e^- $\rightarrow$ Cr^0 or

CrO_4^{2-} + 8 H^+ + 6 e^- $\rightarrow$ Cr + 4 H_2O

Deposited:

$$\frac{679\ \text{g}}{51.996\ \text{g mol}^{-1}} = 13.06\ \text{mol of chromium}$$

A charge of 78.36 F was required to deposit the above chromium.

Current efficiency:

$$\frac{78.36\ \text{F}}{559.6\ \text{F}} \times 100 = 14.0\ \%$$

3.2 The simplest assumption: Only hydrogen is evolved at the cathode and at the same time oxygen at the anode. On this assumption the amounts of substances of the evolved oxygen and hydrogen are as follows:

$$n(\text{H}_2) = \frac{559.6 \times 0.86}{2} = 240.63\ \text{mol}$$

$$n(\text{O}_2) = \frac{559.6}{4} = 139.9\ \text{mol}$$

The molar ratio is:

$$\frac{n(\text{H}_2)}{n(\text{O}_2)} = \frac{V(\text{H}_2)}{V(\text{O}_2)} = \frac{240.63\ \text{mol}}{139.9\ \text{mol}} = 1.720$$

This value is different from that given in the task. Thus, beyond the mentioned reactions also other processes take place at the electrodes. The current efficiency may be calculated from the volume ratio of gases evolved, without making any investigation of what kind the processes are.

Balance of the processes:

The main process: $CrO_3 \rightarrow Cr + 3/2\ O_2$

cathode anode

η_1 = 14.0 %

The by process: (electrolysis of water)

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

cathode anode

$$\eta_2 = ?$$

The amount of substance of the hydrogen evolved at the cathode is equal to:

$$n(H_2) = \frac{Q\ .\ \eta_2}{2}$$

The amount of substance of the oxygen evolved at the anode is equal to:

$$n(O_2) = \frac{Q\ .\ (\eta_1 + \eta_2)}{4}$$

According to the data given in the task:

$$\frac{V(H_2)}{V(O_2)} = \frac{n(H_2)}{n(O_2)} = \frac{\frac{Q\ .\ \eta_2}{2}}{\frac{Q\ .\ (\eta_1 + \eta_2)}{4}} = 1.603$$

In solving the equation for η_2 we get a value:

η_2 = 0.565 (56.5 %)

Volumes of the hydrogen and oxygen evolved:

$$n(H_2) = \frac{559.6 \times 0.565}{2} = 158.1\ \text{mol}$$

$V(H_2) = 22.41\ dm^3\ mol^{-1} \times 158.1\ mol = 3543\ dm^3$

$$n(O_2) = \frac{559.6 \times (0.140 + 0.565)}{4} = 98.6\ \text{mol}$$

$V(O_2) = 22.41\ dm^3\ mol^{-1} \times 98.6\ mol = 2210\ dm^3$

The current efficiency when the hydrogen is evolved at the cathode is equal to 56.5 %. The current efficiency when the oxygen is evolved at the anode is equal to 70.5 %.

Thus, 29.5 % of the electric charge is used without an apparent effect. Therefore some cyclic process is taking place in the electrolytic cell which causes that anion CrO_4^{2-} is reduced incompletely. One of the reactions which causes a decrease of the current efficiency value, is the following:

$$CrO_4^{2-} + 8\ H^+ + 3\ e^- \underset{\text{anode}}{\overset{\text{cathode}}{\rightleftarrows}} Cr^{3+} + 4\ H_2O$$

PROBLEM 4

A vessel of a volume of 5.0 dm^3 was filled with ethane at a temperature of 300 K and normal pressure and sealed. The vessel with the gas was then heated and the pressure in it was measured at distinct temperatures. The following data were found:

T (K)	Pressure p, measured (kPa)	Pressure p', calculated (kPa)
300	101.25	
500	169.20	
800	276.11	
1000	500.48	

Problems:

4.1 Calculate the pressure p' of ethane in the vessel according to the ideal gas law equation and fill in the values in a free column in the above table.
(R = 8.314 J mol^{-1} K^{-1})

4.2 Explain the differences between theoretical value p' and those (p) obtained by measurements.

4.3 Write the chemical equation for the reaction which takes place probably in the vessel at higher temperatures.

4.4 Calculate the value for the conversion degree α of ethane and that for equilibrium constant K_p of the reaction that takes place at temperatures of 800 and 1000 K.

4.5 The ratio of equilibrium constant K_p at two different temperatures is according to van't Hoff's equation equal to:

$$\ln\frac{K_1}{K_2} = \frac{\overline{\Delta H}}{R} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(ln = 2.303 log)

Calculate the mean value $\overline{\Delta H}$ for reaction heat in the temperature range of 800 – 1000 K.

4.6 What influence will have an elevation of temperature and pressure on the conversion degree of ethane?

4.7 Calculate the relative error of the calculation.

SOLUTION

4.1 The complete table contains the following data:

T (K)	Pressure p, measured (kPa)	Pressure p', calculated (kPa)
300	101.325	101.325
500	169.820	168.706
800	276.111	269.930
1000	500.748	337.412

4.2 The p values at higher temperatures are greater than those calculated (p'). Hence, the number of molecules (moles) in the system increases. Apparently, there occurs a thermal decomposition of ethane.

4.3 Alkanes are thermally decomposed to produce alkenes and hydrogen:

$C_2H_6 \rightleftharpoons C_2H_4 + H_2$

4.4 Clapeyron's equation for the substances undergoing thermal decomposition into two other gaseous substances, has the form:

$p\,V = n(1 + \alpha)\,R\,T$

where α is degree of decomposition.

From one mole of C_2H_6:

α moles of C_2H_4 and α moles of H_2 are obtained, and $(1 - \alpha)$ moles of C_2H_6 remain unreacted.

From n moles of C_2H_6:

$n\alpha$ moles of C_2H_4 and $n\alpha$ moles of H_2 are obtained, and $n(1 - \alpha)$ moles of C_2H_6 remain unreacted.

Hence, the total amounts of substances of compounds in the gaseous mixture will be:

$\Sigma n = 2n\alpha + n(1 - \alpha) = n(1 + \alpha)$

In comparing the theoretical and experimental values of pressure we obtain:

$$p'\,V = n\,R\,T \quad \Rightarrow \quad p' = \frac{n}{V}\,RT$$

$$p\,V = n(1 + \alpha)\,R\,T \Rightarrow p = \frac{n(1+\alpha)}{V}\,R\,T$$

$$\frac{p'}{p} = \frac{n}{n(1+\alpha)} \Rightarrow \alpha = \frac{p-p'}{p'}$$

$$\alpha_{800} = \frac{276.111 - 269.930}{269.930} = 0.023$$

$$\alpha_{1000} = \frac{500.748 - 337.412}{337.412} = 0.484$$

The reaction takes place in gaseous phase and thus, the equilibrium constant K_p is calculated according to the relation:

$$K_p = \frac{p_{C_2H_4}\ p_{H_2}}{p_{C_2H_6}}$$

$p_{C_2H_4} = p_{H_2} = p'\ \alpha$ $\qquad$ $p_{C_2H_6} = p'\ (1-\alpha)$

$$K_p = \frac{\alpha^2\ p'}{1-\alpha}$$

T = 800 K $\qquad K_p = \dfrac{0.023^2 \times 269.930}{0.977} = 0.146\ \text{kPa}$

T = 1000 K $\qquad K_p = \dfrac{0.484^2 \times 337.412}{0.516} = 153.18\ \text{kPa}$

4.5 According to van't Hoff's equation:

$$\overline{\Delta H} = \frac{2.303 \log \dfrac{K_1}{K_2} R}{\dfrac{1}{T_2} - \dfrac{1}{T_1}}$$

After substituting the known values:

$\overline{\Delta H}$ = 231.36 kJ mol^{-1}

4.6 The reaction is endothermic and the number of particles has increased in the course of the reaction. Thus, the equilibrium is shifted according to Le Chatelier-Bronw's principle in the sense of forward reaction when the temperature rises and on the contrary, the equilibrium is shifted in the sense of reverse reaction when the pressure is elevated.

4.7 If the correct value is ΔH_1 and ΔH_2 is a calculated one then the relative error is calculated according to the relation:

$$\frac{\Delta H_1 - \Delta H_2}{\Delta H_1} \times 100 \quad (\%)$$

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THEORETICAL PROBLEMS

PROBLEM 1

The dissociation of (molecular) chlorine is an endothermic process, ΔH = 243.6 kJ mol^{-1}. The dissociation can also be attained by the effect of light.

1.1 At what wavelength can the dissociating effect of light be expected?

1.2 Can this effect also be obtained with light whose wavelength is smaller or larger than the calculated critical wavelength?

1.3 What is the energy of the photon with the critical wavelength?

When light that can effect the chlorine dissociation is incident on a mixture of gaseous chlorine and hydrogen, hydrogen chloride is formed. The mixture is irradiated with a mercury UV-lamp (λ = 253.6 nm). The lamp has a power input of 10 W. An amount of 2 % of the energy supplied is absorbed by the gas mixture (in a 10 litre vessel). Within 2.5 seconds of irradiation 65 millimoles of HCl are formed.

1.4 How large is the quantum yield (= the number of product molecules per absorbed photons)?

1.5 How can the value obtained be (qualitatively) explained? Describe the reaction mechanism.

SOLUTION

1.1 $\lambda_1 = \dfrac{c}{\nu_1}$ from $\Delta H = N_A\, h\, \nu_1$ it follows that

$$\lambda_1 = \frac{c\, N_A\, h}{\Delta H} = \frac{3\,.\,10^8 \times 6.02\,.\,10^{23} \times 6.6\,.\,10^{-34}}{2.436\,.\,10^5} = 4.91\,.\,10^{-7}\ \text{m} = 491\,\text{nm}$$

1.2 Short-wave light is effective, as its photons have a greater energy than required whereas the photons of longer-wavelength light are too poor in energy to affect the dissociation.

1.3 $E_1 = h\,\nu_1 = \dfrac{h\,c}{\lambda_1} = \dfrac{6.6\times10^{-34}\times 3\,.\,10^{8}}{4.91\,.\,10^{-7}} = 4.03\,.\,10^{-19}$ J

1.4 The quantum yield $Ø = \dfrac{\text{the number of HCl molecules formed}}{\text{the number of absorbed photons}}$

$$Ø = \frac{n(\text{HCl})\times N_A}{\dfrac{E_{tot}}{\dfrac{h\,c}{\lambda_2}}} = \frac{6.5\times10^{-2}\times 6.02\times10^{23}}{\dfrac{0.2\times2.5}{\dfrac{6.6\times10^{-34}\times3\times10^{8}}{2.536\times10^{-7}}}} = 6.1\times10^{4}$$

The energy input = 10 × 0.02 = 0.2 W

1.5 The observed quantum yield is based on a chain mechanism.

The start of reaction chain: $Cl_2 + h\nu \rightarrow 2\,Cl\bullet$

The propagation of the chain: $2\,Cl\bullet + H_2 \rightarrow HCl + 2\,H\bullet$

$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$

The chain termination mainly by: $2\,H\bullet \rightarrow H_2$

$2\,Cl\bullet \rightarrow Cl_2$

$H\bullet + Cl\bullet \rightarrow HCl$

PROBLEM 2

Water gas equilibrium

The homogeneous gas reaction

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

is termed the water gas reaction.

Problems:

2.1 Calculate the Gibbs reaction energy, ΔG^0_{1000}, for the water gas reaction at 1000 K from the reaction enthalpy: $\Delta H^0_{1000} = 35040 \text{ J mol}^{-1}$
and the reaction entropy: $\Delta S^0_{1000} = 32.11 \text{ J mol}^{-1} K^{-1}$.

2.2 What is the value of the equilibrium constant K_p of the water gas reaction at 1000 K?

2.3 What are the values of the equilibrium constants K_x and K_c (x: mole fraction, c: concentration in mol dm^{-3} at the same temperature (1000 K)? (Note: The gas behaves ideally.)

2.4 A mixture of gases containing 35 vol. % of H_2, 45 vol. % of CO and 20 vol. % of H_2O vapours is heated to 1000 K. What is the composition of the mixture after the establishment of the water gas equilibrium?

2.5 Calculate the reaction enthalpy value, ΔH^0_{1400}, at 1400 K from the reaction enthalpy value, ΔH^0_{1000}, and the values of the molar heat, c^0_p, (valid in the temperature range 1000 K to 1400 K)

$\Delta H^0_{1000} = 35040 \text{ J mol}^{-1}$

$c^0_p(CO_2) = 42.31 + 10.09\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

$c^0_p(H_2) = 27.40 + 3.20\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

$c^0_p(CO) = 28.34 + 4.14\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

$c^0_p(H_2O) = 30.09 + 10.67\times10^{-3}\ T\ \text{ J mol}^{-1}\text{ K}^{-1}$

(It holds that $\int_a^b (c_1 + c_2 x)dx = c_1(b-a) + 0.5\,c_2(b^2 - a^2)$)

2.6 What can you say on the basis of the above findings on ΔH^0 about the shift in the water gas equilibrium with increasing temperature?

SOLUTION

2.1 ΔH^0_{1000} = 35040 J

ΔS^0_{1000} = 32.11 J mol^{-1} K^{-1}

$\Delta G^0_{1000} = \Delta H^0_{1000} - T\,\Delta S^0_{1000} = 35040 - 1000 \times 32.11 = 2930$ J

2.2 $\Delta G^0 = -RT \ln K_p$

$$\ln Kp = -\frac{\Delta G^0}{RT} = -\frac{2930}{8314} = -0.352418$$

K_p = 0.7030

2.3 As the numbers of moles do not change in the reaction, the reaction is independent on the concentration and pressure and therefore, $K_x = K_p = K_c$ (dimensionless). Volume fraction and mole fraction are identical in an ideal gas.

2.4 The original composition of the gas:

$x_{0,CO} = 0.45; \quad x_{0,H_2} = 0.35; \quad x_{0,H_2O} = 0.20; \quad x_{0,CO_2} = 0.00;$

If the mole fraction of the CO_2 formed at the equilibrium is denoted as x then the equilibrium concentrations can be obtained from:

$CO: \quad x_{0,CO} - x$
$CO_2: \quad x$
$H_2O: \quad x_{0,H_2O} - x$
$H_2: \quad x_{0,H_2} + x$

$$K_p = K_x = \frac{x_{CO}\; x_{H_2O}}{x_{CO_2}\; x_{H_2}} = \frac{(x_{0,CO} - x)(x_{0,H_2O} - x)}{x\,(x_{0,H_2} + x)} = 0.703$$

$$(x_{0,CO} - x)(x_{0,H_2O} - x) = K\,(x_{0,H_2} + x)\,x$$

$$x_{0,CO}\; x_{0,H_2O} - x(x_{0,H_2O} + x_{0,CO}) + x^2 = K\,x\,x_{0,H_2} + K\,x^2$$

where $K = K_x$

$$x^2\,(1 - K) - x\,(x_{0,H_2O} + x_{0,CO} + K\,x_{0,H_2}) + x_{0,CO}\; x_{0,H_2O} = 0$$

On substitution of the numerical values,

x^2 (1 – 0.703) – x (0.20 + 0.45 + 0.703 × 0.35) + 0.45 × 0.20 = 0

0.297 x^2 – 0.89605 x + 0.09 = 0

x^2 – 3.01703 x + 0.303030 = 0

$$x_{1,2} = 1.508515 \pm \sqrt{2.275618 - 0.303030} = 1.508515 \pm \sqrt{1.972588}$$

$x = 1.508515 \pm 1.404488 = 0.104027$

(The plus sign leads to a solution that has no physical significance, $x > 1$.)

$x = 0.104$

$x_{CO} = 0.346; \quad x_{H_2} = 0.454; \quad x_{H_2O} = 0.096; \quad x_{CO_2} = 0.104;$

2.5 $\Delta C_p^0 = C_p^0(CO) + C_p^0(H_2O) - C_p^0(CO_2) - C_p^0(H_2)$

$= - 11.28 + 1.52 \times 10^{-3}\ T\ J\ K^{-1}\ mol^{-1}$

$$\Delta H_{1400}^0 = \Delta H_{1000}^0 + \int_{1000}^{1400} C_p^0\, dT = \Delta H_{1000}^0 + \int_{1000}^{1400} (c_1 + c_2 T)\, dT$$

$$= \Delta H_{1000}^0 + c_1\,(1400 - 1000) + 0.5\,c_2\,(1.96\times10^6 - 1\times10^6) =$$

$$= \Delta H_{1000}^0 - 11.28\times400 + (1.52\times10^{-3} \times 4.8\times10^5) =$$

$$= \Delta H_{1000}^0 - 4512 + 729.6 =$$

$$= 35040 - 4512 + 729.6 = 31258\ J$$

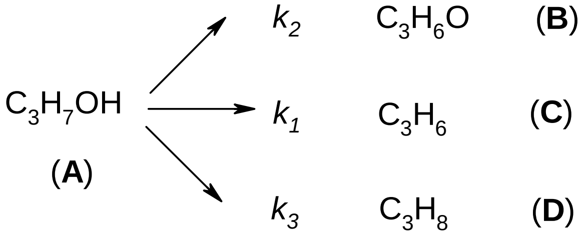
On the basis of the van't Hoff reaction isobar

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H}{RT^2}$$

2.6 $\ln K_p$ increases with increasing temperature for positive (endothermic) heat of reaction, i.e. the equilibrium shifts with increasing temperature in favour of the reaction products, CO and H_2O.

PROBLEM 6

The catalytic decomposition of isopropanol on the surface of a V_2O_5 catalyst, leading to the products in the scheme, satisfies a first order kinetic equation.



Five seconds after initiation of the reaction at 590 K, the concentrations of the components in the reaction mixture are:

c_A = 28.2 mmol dm^{-3}

c_B = 7.8 mmol dm^{-3}

c_C = 8.3 mmol dm^{-3}

c_D = 1.8 mmol dm^{-3}

6.1 What is the initial concentration c_0 of C_3H_7OH in the system?

6.2 What is the value of the rate constant k for the process:

$$C_3H_7OH \xrightarrow{k} \text{products ?}$$

6.3 What is the interval of time ($\tau_{1/2}$) in which the concentration of C_3H_7OH will reach the value $c = c_0/2$?

6.4 What are the values of rate constants k_1, k_2, and k_3?

6.5 What are the values of concentrations c_B, c_C, c_D at $t = \tau_{1/2}$?

The equation describing the concentration changes of **A** with time t for the first order reaction has the form:

$c_A = c_0 \exp(-k\,t)$

or

$\log (c_0 / c_A) = 0.4343\, k\, t$

or

$\ln (c_0 / c_A) = k\, t$

Fill in the table with the answers obtained.

1	c_0 =
2	k =
3	$\tau_{1/2}$
4	k_1 =
	k_2 =
	k_3 =
5	c_B =
	c_C =
	c_D =

SOLUTION

6.1 $c_0 = c_A + c_B + c_C + c_D = 28.2 + 7.8 + 8.3 + 1.8 = 46.1 \text{ mmol dm}^{-3}$

6.2 $$k = \frac{1}{0.4343\,t}\log\left(\frac{c_0}{c_A}\right) = \frac{1}{0.4343\times 5}\log\left(\frac{46.1}{28.2}\right) = 0.0983\,s^{-1}$$

6.3 $$t = \tau_{1/2} = \frac{1}{0.4343\,k}\log\frac{c_0}{\frac{c_0}{2}} = \frac{1}{0.4343\times 0.0983}\log 2 = 7.05 \text{ s}$$

6.4

$$v_1 = \frac{\Delta c_B}{\Delta t} = k_1\,c_A$$

$$v_2 = \frac{\Delta c_C}{\Delta t} = k_2\,c_A$$

$$v_3 = \frac{\Delta c_D}{\Delta t} = k_3\,c_A$$

$v = v_1 + v_2 + v_3 = k\,c_A$

(1) $k_1 + k_2 + k_3 = k = 0.0983 \text{ s}^{-1}$

(2) $$\frac{\Delta c_B}{\Delta c_C} = \frac{c_B - 0}{c_C - 0} = \frac{c_B}{c_C} = \frac{k_1}{k_2} = \frac{7.8}{8.3} = 0.940$$

(3) $$\frac{\Delta c_B}{\Delta c_D} = \frac{c_B - 0}{c_D - 0} = \frac{c_B}{c_D} = \frac{k_1}{k_3} = \frac{7.8}{1.8} = 4.33$$

From equations (1) – (3):

k_1 = 0.0428 s^{-1}

k_2 = 0.0455 s^{-1}

k_3 = 0.00988 s^{-1}

6.5 At t = $\tau_{1/2}$ = 7.05 s

(4) $$c_A = \frac{c_0}{2} = c_B + c_C + c_D = 23.05 \text{ mmol dm}^{-3}$$

From equations (2) – (4):

c_B = 10.0 mmol dm^{-3}

c_C = 10.7 mmol dm^{-3}

c_D = 2.32 mmol dm^{-3}

PROBLEM 4

The following data were gathered for the alkaline hydrolysis of certain chlorinated compounds:

a) A certain volume of a solution of the neutral potassium salt of chlorosuccinic acid is mixed with an equal volume of hydroxide solution. The initial concentration of each solution is 0.2 mol dm^{-3}. The potassium hydroxide concentration in the reaction mixture was determined at different time intervals at 25 °C. The following values were obtained:

t (minutes)	10	20	30	45	60	80	100
c(KOH) (mol dm^{-3})	0.085	0.074	0.065	0.056	0.049	0.042	0.036

The experiment was repeated with the same initial solutions at 35 °C. The hydroxide concentration is reduced to one half after 21 minutes.

b) In the hydrolysis of 3-chloro-3-methylhexane with potassium hydroxide, the concentration of potassium hydroxide was found to have been reduced to one half after 32 minutes at 25 °C or 11 minutes at 35 °C, regardless of the initial reactant concentrations (identical).

c) In the alkaline hydrolysis of 3-chloro-2,4-dimethyl-3-isopropylpentane an identical reaction mechanism as for reaction b was found but the reaction rate was about 100 times faster under the same reaction conditions.

Considering the above data answer the following questions:

4.1 What is the reaction order in cases a, b, and c?

4.2 What is the rate constant at 25 °C for reaction a? Indicate the units.

4.3 Calculate the activation energies for reactions a and b.

4.4 If in reaction a dipotassium salt of L-chlorosuccinic acid (which is levorotatory,) is used, what type of optical rotation will be exhibited by the corresponding salt of malic acid formed by hydrolysis?

4.5 If the levorotatory isomer is also used in reaction b, what optical rotation will be exhibited by 3-methyl-3-hexanol formed in the hydrolysis reaction?

4.6 Why is the rate of reaction c much faster than that of reaction b when both reactions are of the same type and occur under the same temperature and concentration conditions?

SOLUTION

4.1 For reaction a the reaction order is estimated as follows:

- assuming the first-order reaction:

$$k = \frac{1}{t}\ln\frac{a}{a-x}$$

t (°C)	10	20	30	45	60	80	100
k . 10^2	1.625	1.505	1.436	1.288	1.189	1.084	1.022

k is not constant, hence the reaction is not of the first-order.

- for the second-order reaction (with reactant concentrations equal at time zero):

$$k = \frac{1}{t}\left(\frac{a}{a-x} - \frac{1}{a}\right)$$

t (°C)	10	20	30	45	60	80	100
k	0.176	0.176	0.179	0.175	0.173	0.173	0.178

As *k* has almost a constant value the condition for a second-order reaction is fulfilled.

The half-life of reaction b is independent on the initial concentrations, i. e. it is a first-order reaction:

$$k = \frac{1}{t}\ln\frac{a}{a-x} = \frac{1}{t_{1/2}}\ln\frac{a}{a-\frac{a}{2}} = \frac{1}{t_{1/2}}\ln 2$$

Reaction c has the same mechanism as reaction b. Therefore, it will also be a first-order reaction.

4.2 The rate constant of reaction a is an average of the above calculated values.

k = 0.176 dm^3 mol^{-1} min^{-1}

4.3 In order to determine the activation energy, the rate constant, *k*', at 35 °C is to be calculated.

For the second-order reactions the relationship between the rate constants and half-lives is as follows:

$$k = \frac{1}{t}\left(\frac{a}{a - x} - \frac{1}{a}\right) = \frac{1}{t_{1/2}}\left(\frac{1}{a - \frac{a}{2}} - \frac{1}{a}\right) = \frac{1}{t_{1/2}}\,\frac{1}{a}$$

The half-life at 35 ℃ and the initial concentration, a = 0.1 mol dm^{-3}, are known. (By mixing equal volumes of the two solutions the concentration of each reacting species is reduced to a half.)

Calculation of the rate constant at 35 ℃:

$$k' = \frac{1}{21}\cdot\frac{1}{0.1} = 0.476\ \text{dm}^3\ \text{mol}^{-1}\ \text{min}^{-1}$$

The activation energy of reaction a will be:

$$E_a = R\ln\frac{k'}{k}\cdot\frac{T'\cdot T}{T'-T} = 8314\ \ln\frac{0.476}{0.176}\cdot\frac{308\cdot 298}{308-298} = 7.592\times10^{7}\ \text{J mol}^{-1}$$

For reaction b that is a first-order reaction, the rate constants at the two temperatures are calculated from the half-lives:

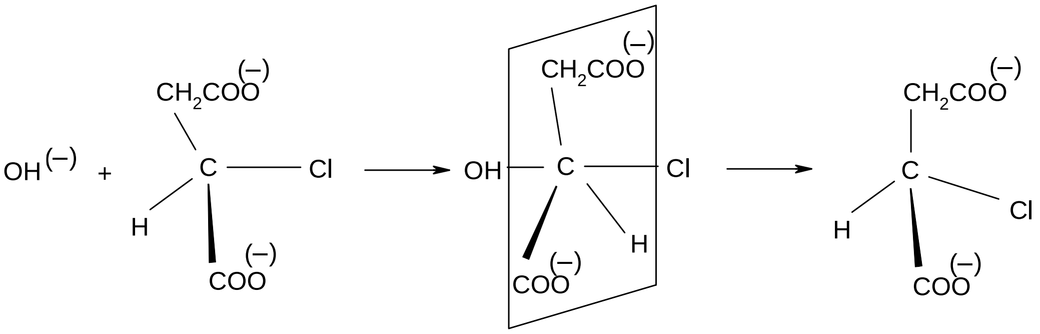
at 25 ℃: $k = \frac{\ln 2}{32} = 2.166\times10^{-2}\ \text{min}^{-1}$

at 35 ℃: $k' = \frac{\ln 2}{11} = 6.301\times10^{-2}\ \text{min}^{-1}$

Hence the activation energy is:

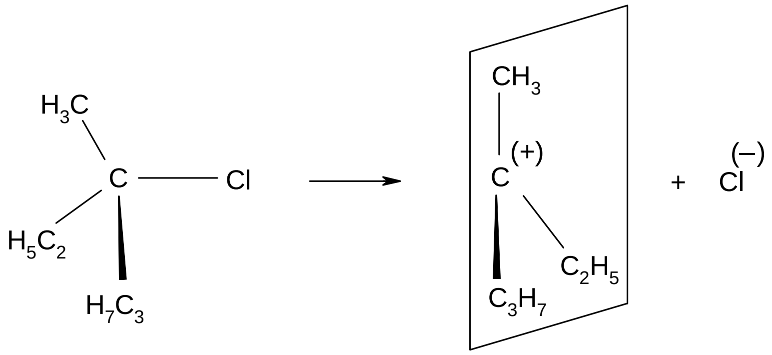
$$E_a = 8314\ \ln\frac{6.301\times10^{-2}}{2.166\times10^{-2}}\cdot\frac{308\cdot 298}{308-298} = 8.149\times10^{7}\ \text{J mol}^{-1}$$

4.4 The product of the hydrolysis reaction a will become dextrorotatory as a result of configuration inversion.



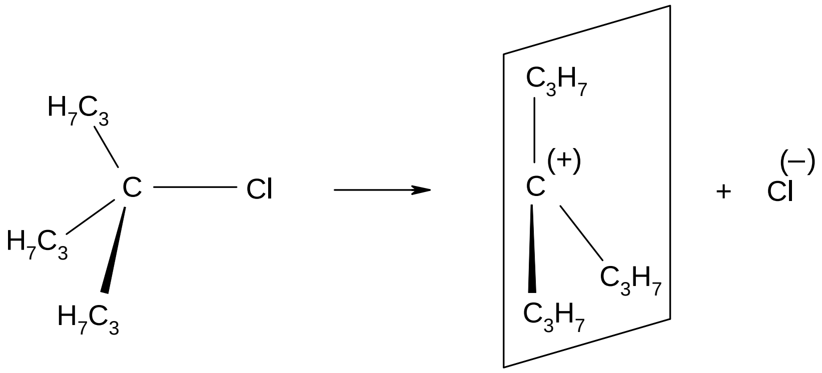
As an S_N2 type reaction, it involves a transition state in which the inversion of the configuration of the asymmetric carbon atom occurs. Thus, if the substrate is levorotatory, the product will become dextrorotatory.

4.5 The reaction b is a unimolecular S_N1 reaction and involves the transient formation of an almost stable carbonium ion in the rate-determining step.



The most probable structure of the carbonium ion is planar. The carbonium ion may be attached by the nucleophylic reagent (the OH^- ion) on both sides of the plane with the same probability. The product will result as a racemic mixture, with no optical activity, inactive by intermolecular compensation.

4.6 The same is true for the reaction c, the only difference being a more marked repulsion among bulkier substituents. The tendency towards carbonium ion formation with a planar structure and reduced repulsions is increased.



The rate of the carbonium ion formation, and therefore the overall reaction rate, is consequently increased.

PROBLEM 5

On passing ethanol over a catalyst at 400 K, a dehydration reaction occurs resulting in the formation of ethylene:

$C_2H_5OH(g) \rightarrow C_2H_4(g) + H_2O(g)$

At the above temperature and p_0 = 101.325 kPa, the conversion of ethyl alcohol is 90.6 mol %.

5.1 Calculate the equilibrium constant K_p of the reaction under given conditions.

5.2 Calculate the values of the equilibrium constants K_x and K_c at the above temperature.

5.3 Calculate the ethanol conversion at the following pressures:

$5\ p_0$, $10\ p_0$, $50\ p_0$, $100\ p_0$, and $200\ p_0$.

5.4 Plot the graph for the variation of conversion *vs*. pressure.

SOLUTION

The reaction:	C_2H_5OH	$\rightarrow$ C_2H_4	+ H_2O	
Moles:				
initial:	1	0	0	
at equilibrium:	1 – x	x	x	total: 1 + x

	Molar fraction	Partial pressure
Ethanol	$\frac{1-x}{1+x}$	$\frac{1-x}{1+x}\,p$
Ethylene	$\frac{x}{1+x}$	$\frac{x}{1+x}\,p$
Water	$\frac{x}{1+x}$	$\frac{x}{1+x}\,p$

$p = \frac{p'}{p}$ p' – total pressure, p_0 = 101.325 kPa

$$K_p = \frac{p_{C_2H_4} \cdot p_{H_2O}}{p_{C_2H_5OH}} = \frac{\left(\frac{x}{1+x}p\right)\left(\frac{x}{1+x}p\right)}{\frac{1-x}{1+x}p} = \frac{x^2}{1-x^2}p$$

5.1 $p' = 101.325$ kPa

$$K_p = \frac{x^2}{1-x^2} = \frac{0.906^2}{1-0.906^2} = 4.56$$

5.2 $K_x = K_p\, p^{-\Delta n}$; $p' = 101.325$ kPa; $\Delta n = 1$; $K_x = 4.56$

$$K_c = K_p \left(\frac{c_0 RT}{p_0}\right)^{\Delta n} \quad R = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1};\ c^0 = 1\ \text{mol dm}^{-3};\ T = 400\,K$$

$K_c = 0.139$

5.3 $\dfrac{x^2}{1-x^2} = \dfrac{K_p}{p} = \dfrac{4.56}{p}$

a) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{5} = 0.912$ x = 0.69

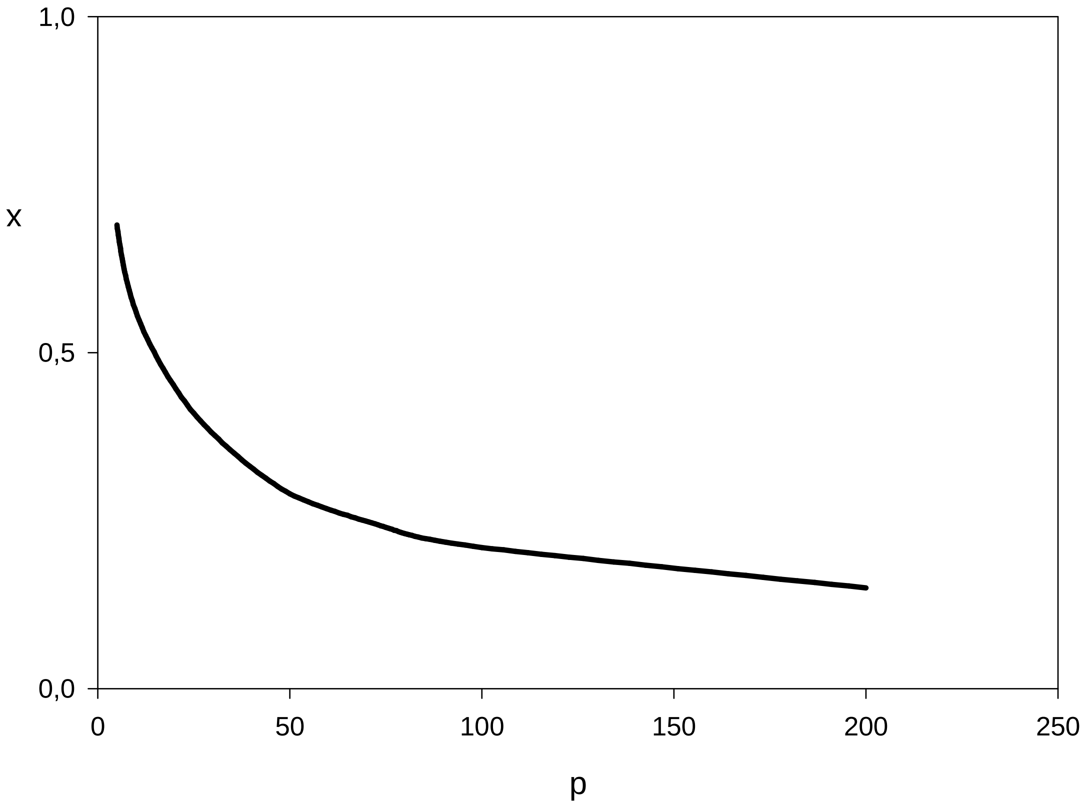
b) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{10} = 0.456$ x = 0.56

c) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{50} = 0.0912$ x = 0.29

d) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{100} = 0.0456$ x = 0.21

e) $\dfrac{x^2}{1-x^2} = \dfrac{4.56}{200} = 0.0228$ x = 0.15

5.4



THE SIXTEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
1–10 JULY 1984, FRANKFURT AM MAIN,
GERMAN FEDERAL REPUBLIC

THEORETICAL PROBLEMS

PROBLEM 1

A)

The element carbon consists of the stable isotopes ^{12}C (98.90 percent of atoms) and ^{13}C (1.10 percent of atoms). In addition, carbon contains a small fraction of the radioisotope ^{14}C ($t_{1/2}$= 5730 years), which is continuously formed in the atmosphere by cosmic rays as CO_2. ^{14}C mixes with the isotopes ^{12}C and ^{13}C via the natural CO_2 cycle.

The decay rate of ^{14}C is described by (N = number of ^{14}C atoms; t = time; λ = decay constant):

$$\text{decay rate} = -\frac{dN}{dt} = \lambda N \qquad (1)$$

Integration of (1) leads to the well-known rate law (2) for the radioactive decay:

$$N = N_0 \, e^{-\lambda t} \qquad (2)$$

N_o = number of ^{14}C atoms at t = 0

1.1 What is the mathematical relationship between the parameters α and $t_{1/2}$ (= half l life)?

1.2 The decay rate of carbon, which is a part of the natural CO_2 cycle, is found to be 13.6 disintegrations per minute and gram of carbon. When a plant (e. g. a tree) dies, it no longer takes part in the CO_2 cycle. As a consequence, the decay rate of carbon decreases.

In 1983, a decay rate of 12.0 disintegrations per minute and gram of carbon was measured for a piece of wood which belongs to a ship of the Vikings. In which year was cut the tree from which this piece of wood originated?

1.3 Assume that the error of the decay rate of 12.0 disintegrations per minute and gram of carbon is 0.2 disintegrations per minute and gram of carbon. What is the corresponding error in the age of the wood in question b)?

1.4 What is the isotope $^{12}C/^{14}C$ ratio of carbon, which takes part in the natural CO_2 cycle (1 year = 365 days)?

B)

The elements strontium and rubidium have the following isotope composition:

Strontium: 0.56 % ^{84}Sr ; 9.86 % ^{86}Sr ; 7.00 % ^{87}Sr ; 82.58 % ^{88}Sr (these isotopes are all stable).

Rubidium: 72.17 % ^{85}Rb (stable) ; 27.83 % ^{87}Rb (radioactive; $t_{1/2} = 4.7 \times 10^{10}$ years).

The radioactive decay of ^{87}Rb leads to ^{87}Sr.

In Greenland one finds a gneiss (= silicate mineral) containing both strontium and rubidium.

1.5 What is the equation rate law describing the formation of ^{87}Sr from ^{87}Rb as a function of time?

1.6 Assume that the isotope ratio ^{87}Sr/ ^{86}Sr (as determined by mass spectrometry) and the isotope ratio ^{87}Rb : ^{86}Sr are known for the gneiss. What is the mathematical relationship with which one can calculate the age of the gneiss?

SOLUTION

A)

1.1 The relationship is:

$$\alpha = \frac{\ln 2}{t_{1/2}}$$

1.2

$$t = \frac{t_{1/2}}{\ln 2} \times \ln\left(\frac{N_0}{N}\right) = \frac{5730}{0.6930} \times \ln\left(\frac{13.6}{12.0}\right) = 1035 \text{ years}$$

1.3 For N_o/N = 13.6/12.0 t = 1035 years

For N_o/N = 13.6/12.2 t = 898 years

For N_o/N = 13.6/11.8 t = 1174 years

Thus, the tree was cut 1035 (+ 139/–137) years ago.

1.4

$$N = \frac{13.6 \times t_{1/2}}{\ln 2} = 5.91 \times 10^{10} \text{ atoms}\,^{14}\text{C /g carbon}$$

1 g ≈ 0.989 g ^{12}C;   0.989 g ^{12}C ≈ (0.989/12) × 6.023 × 10^{23} atoms ^{12}C

$$^{12}\text{C} / {}^{14}\text{C} = \frac{0.989 \times 6.023 \times 10^{23}}{12 \times 5.91 \times 10^{10}} = 8.40 \times 10^{11} : 1$$

B)

1.5 Equation (2) describes the decay of the ^{87}Rb:

$^{87}\text{Rb} = {}^{87}\text{Rb}_o \,.\, \exp(-\lambda\, t)$

The symbol ^{87}Rb stands for the number of atoms of this nuclide.

Consequently, one obtains for the formation of ^{87}Sr from ^{87}Rb:

$^{87}\text{Sr} = {}^{87}\text{Rb}_o - {}^{87}\text{Rb} = {}^{87}\text{Rb} \,.\, \exp(\lambda t) - {}^{87}\text{Rb}$ (a)

1.6 The formation of the radiogenic ^{87}Sr follows equation (a).

One has to take into account that at time t = 0, when the mineral was formed, there was some non-radiogenic strontium in it already:

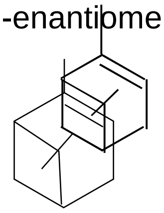
$^{87}\text{Sr} = ({}^{87}\text{Sr})_o + {}^{87}\text{Rb} \,.\, [\exp(\lambda t) - 1]$

The isotope ratio $({}^{87}\text{Sr}/{}^{86}\text{Sr})_o$ follows from the isotope composition of strontium. The time t in this equation corresponds to the age of the gneiss.

PROBLEM 4

At a temperature around 200 °C the racemisation of pinene can be followed in the gaseous phase by measuring the optical rotation.

If, for example, you take the (+)-enantiomer of α-pinene



an equilibrium is gradually established between the two enantiomers (optical isomers). The two opposing reactions are both of the first order.

In 1927 D. F. Smith obtained the following data in his study of racemisation of α-pinene:

T/K	α_1	α_2	t/min
490.9	32.75	18.01	579
490.9	29.51	15.59	587
503.9	30.64	8.74	371
505.4	12.95	8.05	120
510.1	23.22	6.15	216

α_1 and α_2 are the values for optical rotation in terms of the dimensions of the polarimeter scale; *t* is the time which has elapsed between the two measurements.

Problems:

4.1 What is the value for the equilibrium constant for the racemisation?

What is the corresponding value of $\Delta_r G^o$ (racemisation)?

What is the relationship between the forward and backward rate constants, k_1 and k_{-1}, in a state of dynamic equilibrium?

4.2 State the rate equation for the racemisation of pinene.

Derive a relationship which could be used to calculate the rate constant for the conversion of the (+)-enantiomer into the (-)-enantiomer using the data given in the table.

4.3 Calculate the rate constant for this reaction at the four temperatures given in the table.

4.4 Calculate the average value of the activation energy for this reaction. You should take the average of the values at a minimum of three temperatures or use a graphical method.

HINT:

If the loss of concentration of a substance obeys the rate equation:

$$-\frac{dc}{dt} = k(2c - constant)$$

Then the dependence of concentration on time is given by:

$$\ln\frac{2c_0 - constant}{2c - constant} = 2kt$$

where c_0 is the initial concentration at time $t = 0$.

SOLUTION

4.1 The racemisation equilibrium constant equals unity at all temperatures and $\Delta_rG^o = 0$.

4.2 If the concentration of one enantiomer is c and that of the other is c', then it holds for the rate of the loss of c that

$$-\frac{dc}{dt} = k_1c - k_{-1}c' = k(c - c') \quad \text{for} \quad k_1 = k_{-1} = k$$

If the initial concentrations are c_0 and c_0', then

$c' = c_0 - c + c_0'$

can be substituted for c' in the rate equation, obtaining

$$-\frac{dc}{dt} = k\,(2c - c_0 - c_0')$$

It then holds for concentrations c_1 and c_2 measured at times t_1 and t_2, respectively, that

$$\ln\frac{2c_1 - c_0 - c_0'}{2c_2 - c_0 - c_0'} = 2k(t_2 - t_1)$$

and since $c_0 + c_0' = c_1 + c_1' = c_2 + c_2'$

$$\ln \frac{c_1 - c_1'}{c_2 - c_2'} = 2k\,(t_2 - t_1)$$

The measured optical rotation α is proportional to c - c'; hence $\ln \frac{\alpha_1}{\alpha_2} = 2\,k\,(t_2 - t_1)$

4.3

T/K	490.9	503.9	505.4	510.1
10^4 k min^{-1}	5.3	16.9	19.8	30.7

4.4 $\ln\frac{k_2}{k_1} = \frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ $\qquad$ $E_A = \ln\frac{k_2}{k_1} \times \frac{R\,T_1\,T_2}{T_2 - T_1}$

If e.g. the value of k for 490.9 K (the average of two measurements) is combined with each of the remaining three values, three values of activation energy are obtained: 183400 J mol^{-1}, 177500 J mol^{-1}, 190500 J mol^{-1}. The average value equals 187100 J mol^{-1}.

PROBLEM 5

The equilibrium voltage of the cell,

$Zn / ZnSO_4$ (0.0125 M) || Ag_2SO_4 (0.0125 M) / Ag

was measured at several temperatures and the results of the measurements are given in the following table:

t / °C	10	20	30
E / V	1.5784	1.5675	1.5566

Problems:

5.1 Give the equation for the reaction occurring in this galvanic cell.

5.2 Determine the value of the cell voltage at the temperature T = 298 K.

5.3 Determine $\Delta_r G_{298}$ of the cell reaction.

5.4 Determine $\Delta_r H_{298}$ of the cell reaction.

SOLUTION

5.1 $Zn + Ag_2SO_4 \rightarrow ZnSO_4 + 2\ Ag$

5.2 The temperature dependence is described by the equation,

$$E_T = E_{T_0} + \frac{dE}{dT}.(T - T_0)$$

It follows from the plot for the slope,

$$\frac{dE}{dT} = -1.09 \times 10^{-3}\ \text{V K}^{-1}$$

Hence,

$E_{298} = 1.5675 - 1.09 \times 10^{-5} \times 5 = 1.562$ V

5.3 The relationship,

$\Delta_r G = - n F E$

holds for $\Delta_r G$. Then

$\Delta_r G_{298} = - 2 \times 96484.6 \times 1.563 = - 301417.9\ \text{J mol}^{-1}$

5.4 The equation,

$$\Delta G = \Delta H - T\,\Delta S,$$

is employed to calculate $\Delta_r H_{298}$, substituting

$$\Delta S = -\frac{dG}{dT}$$

Rearrangement yields the relationship

$$\Delta H = \Delta G - T\,\frac{dG}{dT}$$

As it holds that

$$\frac{dG}{dT} = -n\,F\,\frac{dE}{dT}$$

the final expression is:

$$\Delta_r H_{298} = \Delta G_{298} + n\,F\,T\,\frac{dE}{dT}$$

$$= -\,301417.9 + [2 \times 96\,484.6 \times 298 \times (-\,1.09 \times 10^{-3})] = 364098.1\ \text{J mol}^{-1}$$

PROBLEM 7

Propanal, **A**, reacts in an aqueous-ethanolic solution of sodium hydroxide to yield compound **B** that is readily dehydrated to give compound **C** ($C_6H_{10}O$).

Problems:

7.1 Give the structural formulae of substances **B** and **C**.

7.2 Give the formula of intermediate **M** that is formed from propanal **A** by the action of hydroxide ions.

7.3 Give the formulae of the two most important mesomeric structures of intermediate **M** and denote the nonbonding electron pairs and the charge distribution.

7.4 The reaction of propanal **A** with sodium hydroxide, producing substance **B**, can be described by the scheme:

$\mathbf{A} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{M} + H_2O$ the first reaction step

$\mathbf{M} + \mathbf{A} \xrightarrow{k_1} \mathbf{B}$ the second reaction step

The rate of the formation of substance **B** is given by the equation:

$$v = k_2\,[\mathbf{M}]\,[\mathbf{A}] \qquad (1)$$

The above values of k are the rate constants for the individual reaction steps.

Assume that the concentration of intermediate **M** is small and constant during the reaction and express this fact by an aquation involving terms with constants k_1, k_{-1} and k_2.

$$\frac{d[\mathbf{M}]}{dt} = 0 \qquad (2)$$

Derive an expression for the concentration of **M** from equation 2 and then substitute for [**M**] in equation 1. This gives equation 3 which is the complete rate equation for the formation of substance **B**.

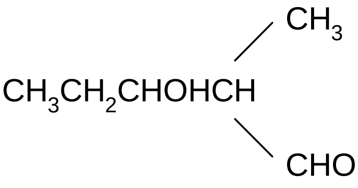
If it is assumed that the second reaction step is rate determining, then the rearrangement of equation 3 gives equation 4, the rate equation.

Give equations 2, 3, and 4.

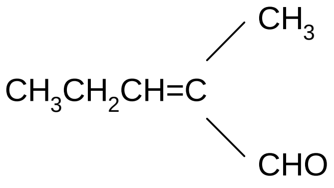
7.5 Determine the overall order of the reaction described by equation 4.

SOLUTION

7.1

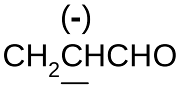


B



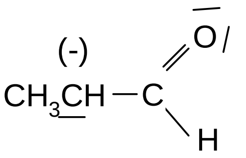
C

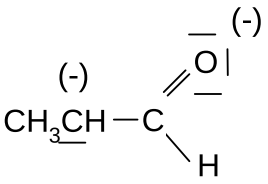
7.2



$CH_2\overset{(-)}{\underline{C}}HCHO$

7.3





7.4

$$\frac{d[\mathbf{M}]}{dt} = 0 = k_1[\mathbf{A}][OH^-] - k_{-1}[\mathbf{M}] - k_2[\mathbf{A}][\mathbf{M}] \qquad (2)$$

$$[\mathbf{M}] = \frac{k_1[\mathbf{A}][OH^-]}{k_{-1} + k_2[\mathbf{A}]} \qquad v = \frac{k_1k_2[\mathbf{A}]^2[OH^-]}{k_{-1} + k_2[\mathbf{A}]} \qquad (3)$$

for $k_2[\mathbf{A}][\mathbf{M}] << k_{-1}[\mathbf{M}]$ it holds, that

$$v = \frac{k_1 k_2[\mathbf{A}]^2[OH^-]}{k_{-1}} \qquad (4)$$

7.5 Rate equation (4) corresponds to the overall reaction order of (3).

PROBLEM 3

In order to explain why dyes are coloured, they can be considered as rod-like, one-dimensional molecules over which the electrons are distributed. The wave lengths of the electrons should fit to the available space which is the length l. When absorbing light, an electron makes a transition from a lower to a higher energy state. The energy difference is given by:

$$\Delta E = h \times coverlambda \quad where \quad \lambda = \frac{h}{p}$$

3.1 Give a general expression for possible wavelengths of the electron as a function of the length l.

In the 'particle in the box' model, only the variations in the kinetic energy of the electrons are considered.

3.2 Give an expression for the possible energies that electrons in the molecule can have (as a function of l).

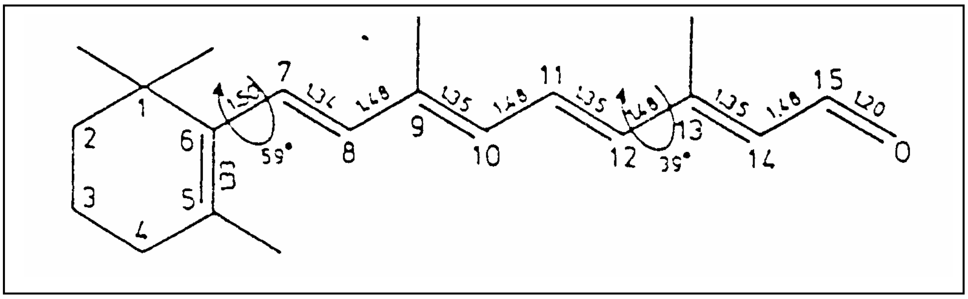
3.3 Show that for a chain of length l with k electrons, the longest wavelength absorption occurs at:

$$\lambda = \frac{8mcl^2}{h(k+1)} \quad \text{for even values of } k$$

3.4 Derive an expression for the wavelength of the first electronic transition as a function of the number of C-atoms for even values of n.

3.5 Calculate the minimum number of C-atoms (conjugated systems) to obtain a visible colour. C-C bond length is 142 pm.

The retina in the human eye contains rhodopsin, a light absorbent.



The molecule in the part of C-atoms 7 through 12 is planar. The angle between the bonds C5-C6, C7-C8, C11-C12 and C13-C14 is about 39°. According to the *'particle in the box'* theory fragment C7 through C12 should absorb at about 213 nm. In reality the absorption of retinal occurs at 308 nm.

3.6 Give a reason for the longer wavelength that is observed in practice using the above mentioned theories.

3.7 When retinal is bound to opsin to form rhodopsin, the absorption occurs around 600 nm. Which atoms must be forced into one plane by the protein? Show by calculation that it's true.

SOLUTION

3.1 $\lambda = c\nu$ = 2 l / n with n = 1, 2, 3, ...

3.2 $E = \frac{h\,c}{\lambda} = \frac{m\,v^2}{2} = \frac{p^2}{2\,m}$; $p = \frac{h}{\lambda} = \frac{h\,n}{2\,l} \Rightarrow \Delta E_n = \frac{h^2 n^2}{8\,m\,l^2} = \frac{h^2}{8\,m\,l^2} \times (n^2_{homo} n^2_{lumo})$

3.3 For k electrons and k ≡ 0 mod 2, k/2 orbitals are possible, so n_{homo}= k/2 and n_{lumo} = k/2 + 1

$$\Delta E_n = \frac{h^2}{8\,m\,l^2}[(1/2\,\mathrm{k} + 1)^2 \; 1/2\mathrm{k}^2] = \frac{h^2}{8\,m\,l^2} \times (\mathrm{k} + 1) \Rightarrow \lambda = \frac{h\,c}{\Delta E} = \frac{8\,m c\,l^2}{\mathrm{h}(\mathrm{k} + 1)}$$

3.4 If N is the number of C-atoms, N is equal to k+1 for even number of electrons k, so

$$\lambda = \frac{8\,m c\,l^2}{N\,h} = \frac{8\,m c\,l^2}{\mathrm{h}\,(\mathrm{k} + 1)}$$

for even N's, the length of the box would be a(N-1) with k = N electrons, so

$$\lambda = \frac{8\,m\,c\,(\mathrm{N1})^2\,\mathrm{a}^2}{\mathrm{h}\,(\mathrm{N}+1)}$$

3.5 For a conjugated system N has to be even. To obtain a visible colour, the wavelength should be greater than 400 nm. Therefore:

$$\frac{8mc(\mathrm{N1})^2\mathrm{a}^2}{h(\mathrm{N}+1)} \geq 4 \times 10^7 \text{ so accordingly: } \frac{(\mathrm{N1})^2}{\mathrm{N}+1} \geq 6.02$$

The equation $N^2 - 6.02\ N - 6.02 > 0$ derived from the equation above has the only positive solution N = 8.60. Since N must be even, the minimum number of C-Atoms is 10.

3.6 The angles between 5-6 and 7-8, as well as between 11-12 and 13-14 are smaller than 90° and therefore the effect of the double bonds between C5 and C6, C13, C14 and O cannot be neglected. They overlap to a small extent with the conjugated system C7 through C12 and enlarge the box significantly. A larger l leads to a larger λ, causing a shift towards a longer wavelength.

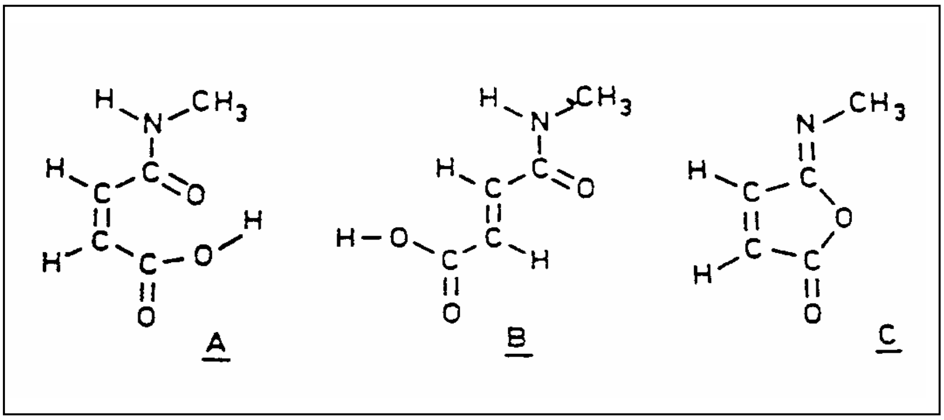
3.7 Obviously, the box must be much larger when bound to opsin. For λ = 600 nm the atoms C5 to O at the end of the chain must be forced into the plane:

$l = 0.133 + 0.150 + 4\ (0.134 + 0.148) + 0.120 = 1.54$ nm; $k = 12$;

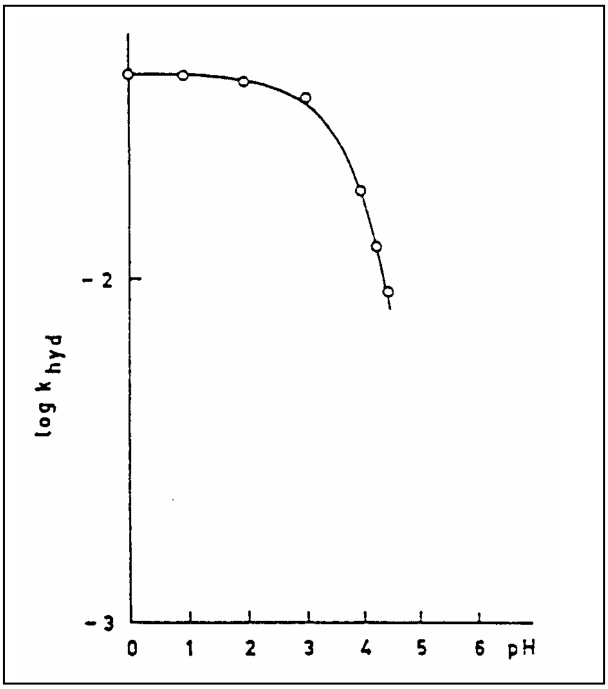
$\lambda = 3.30\times10^{12}\ l^2 / (k + 1) = \underline{602\text{ nm}}$

PROBLEM 4

The high efficiency of catalysis by enzymes is mainly due to an enzyme-reactant complex in which the reacting group is placed in a favourable position for the reaction with respect to the catalyzing groups of the enzyme. Studies are carried out with model compounds in which a catalyzing group has been introduced in the proximity of the reaction centre of the molecule. As an example we consider the hydrolysis of the amide bond in compound **A**. This reaction proceeds in water at 39 ℃ and pH = 2 more than a million times faster than the hydrolysis of compound **B**.



The relation between the rate constant k_{hyd} and pH for the hydrolysis of **A** at 39 ℃ is shown in figure below.



Further observation:

Addition of water to the iso-imide **C** gives a rapid reaction, which initially yields **A**. Subsequently, hydrolysis of **A** occurs. The amid carbonyl group in **A** is labelled with ^{13}C and the hydrolysis is allowed to take place in $H_2{}^{18}O$ at pH = 2 and 39 ℃. The diacid formed upon hydrolysis is isolated, converted into a disilver salt and completely decarboxylated with bromine in a anhydrous reaction medium. The carbon dioxide formed is a mixture of particles of masses 44, 45, 46 and 47 which are formed in equal amounts.

4.1 Why is the hydrolysis of **A** so much faster than that of **B**?

4.2 Explain why the rate of hydrolysis of **A** is independent on pH in the range between pH = 0 to pH = 2.

4.3 Why does k_{hyd} decrease so rapidly at pH values higher than 3.

4.4 Give a detailed reaction mechanism for the hydrolysis of **A**. Indicate which step in the reaction is rate determining.

4.5 Show that the observations further made are consistent with the reaction mechanism given under d.

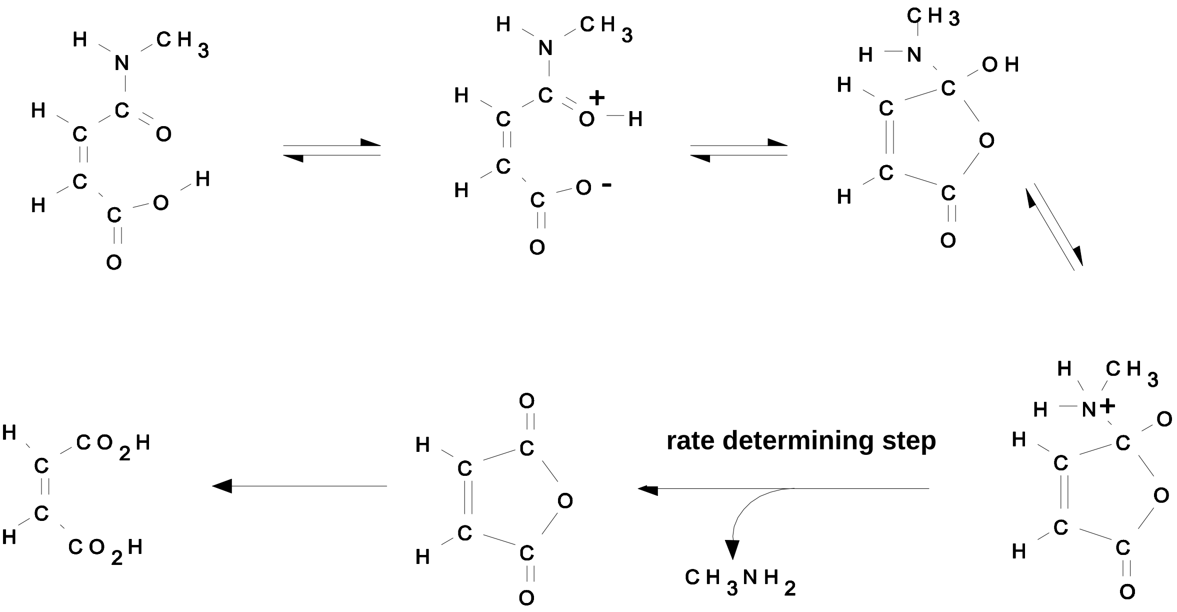
SOLUTION

4.1 The high rate of hydrolysis of **A** is caused by intramolecular catalysis of the COOH group in the cis-position. In **B** the COOH group is situated in the trans-position with respect to the amide group and therefore too far away for intramolecular catalysis.

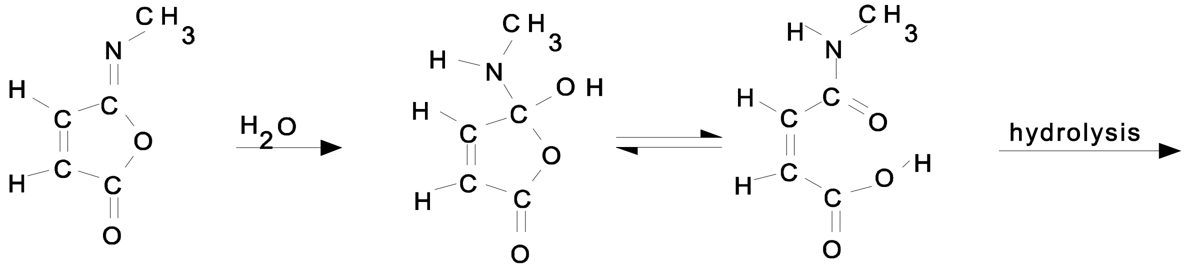
4.2 For 0 < pH < 2 the COOH group is not ionized and therefore, it can act as an intramolecular catalyser. If the hydrolysis in that pH-range is only the result of catalysis by the COOH-group and not competing with H_3O^+ the rate constant in that range is pH independent.

4.3 At pH > 3 the COOH group deprotonates giving COO^-. Intramolecular acid catalysis, in which proton transfer plays an important role, is then not possible anymore.

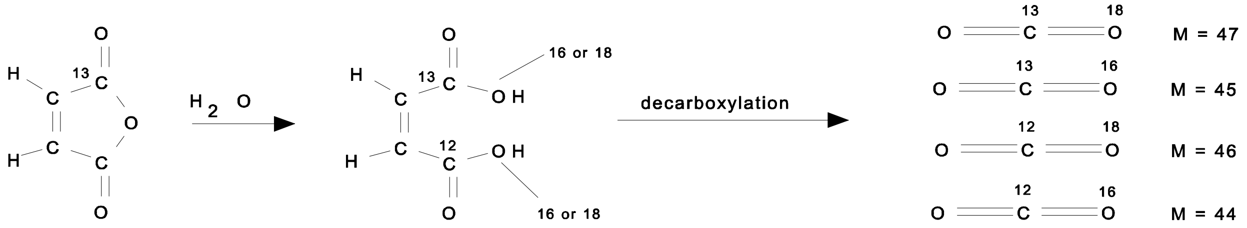
4.4 The mechanism of hydrolysis is indicated below:



4.5



With the observation given, the rate determining step can be identified.



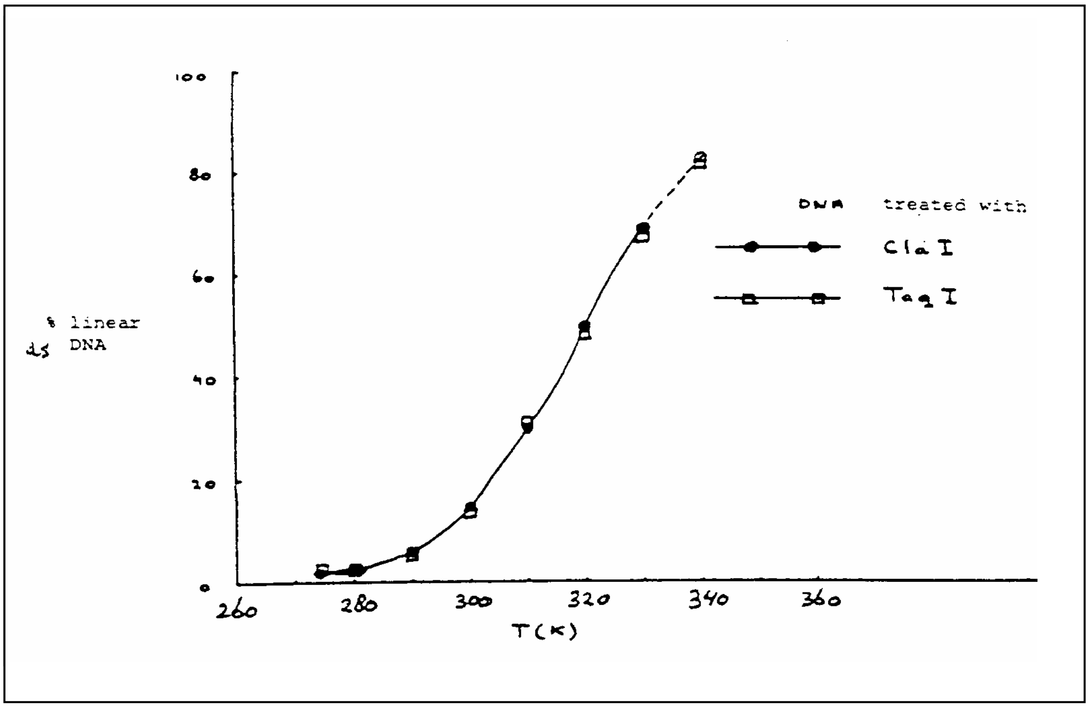
PROBLEM 6

In recombinant DNA technology specific endonucleases can recognize and hydrolyse the phosphoric ester bound in each of both strands. Cla I for example hydrolyses the bond between two nucleotides in the sequence:

5'-pApT│ pCpGpApT- 3'

6.1 Give the base sequence of the complementary strand in the 5' - 3' direction and indicate with arrows the location where the hydrolysis by Cla I would occur.

6.2 How often on average will this sequence occur in one strand of DNA molecule of 10^5 base pairs? You can assume that the four bases occur equally often and that they randomly distribute in the two chains.



Taq I hydrolyses a long double strand DNA molecule into fragments which are on average 256 base pairs long. The 3' end of these fragments treated by cleavage turns out to be a thymine(T)- and the 5' end a cytosine(C) -end.

6.3 How long is the sequence recognized by Taq I?

6.4 Give the two possible base sequences (in the direction 5' - 3') which form the recognition pattern for Taq I (must obviously have some symmetry).

The DNA of a phage which occurs as a close circle contains only 5'-pApTpCpGpApT-3' sequence in each of the two strands. After treatment with ClaI equilibrium is established: circular DNA $\rightleftharpoons$ linear DNA.

6.5 Give a schematic drawing of the circular and linear molecules. Indicate the bases adjacent to the cleaning site in both strands. Indicate also the 3' and 5' ends.

In Fig. 1 the percentage of linear DNA is given as a function of temperature, measured in a solution of 0.15 M NaCl buffered with citrate at pH = 6.5. With Taq I as cleavage enzyme, the same curve is obtained.

6.6 Is the reaction as written endothermic or exothermic? Explain your answer.

6.7 Show, considering the information given, which of the two base sequences of the answer to **6.4** is the correct one.

6.8 What would look the curve for Taq I like if the recognition pattern would have been the other possibility of d)?

A large DNA molecule is cut into fragments with the aid of Cla I. One fragment is isolated, purified and mixed in the ratio of 1:1 with phage DNA which was also cleaved with Cla I. Thereby recombinant molecules can be formed through the reaction:

phage-DNA + fragment DNA $\rightleftharpoons$ recombinant-DNA

6.9 Would the enthalpy of this reaction be positive, negative or about zero? Explain your answer.

6.10 Which combination of temperature, DNA concentration and ionic strength (high or low in each case) will give the maximum percentage of recombinant molecules?

SOLUTION

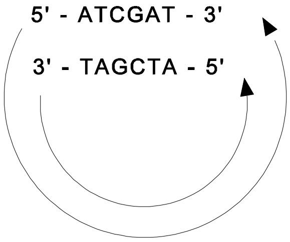
6.1 5' - pTpApGpCpT \pC

6.2 The probability of the sequence given is $(1/4)^6 = 1/4096$. Thus, this specific sequence may occur in the DNA $10^5/4096 = 24.4$ times on average

6.3 The sequence recognized by Taq I is 2 base pairs, that is 4 bases.

6.4 The sequence is 5' - pTpCpGpA - 3' or 5' - pGpApTpC - 3'

6.5



5' - CGAT_______________________ AT - 3'
3' - TA_________________________TAGC - 5'

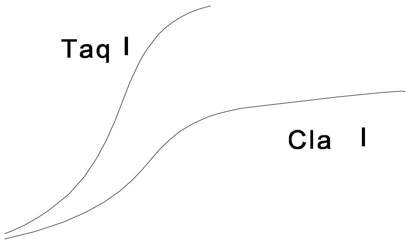
6.6 The reaction is endothermic. The reaction has a positive enthalpy, since the hydrogen bonds between the bases G and C in the complementary strands are broken.

6.7 The two relations show the same dependence on temperature. Therefore, the enthalpy of the two reactions is roughly the same. Then the interaction of the double helix must be identical and therefore we must choose TCGA for the first recognition sequence of question **6.4**. The cleavage in the two cases mentioned in d) occurs as follows:

Cla I:5' - pApT│$\underline{\text{pCpGp}}$ApT - 3'
3' - pTpApGpCp│TpA - 5'

Taq I: 5' - pT│$\underline{\text{pCpGp}}$A - 3'
3' - pApGpCp│T - 5'

6.8 The following curve would be obtained:



6.9 ΔH is negative.

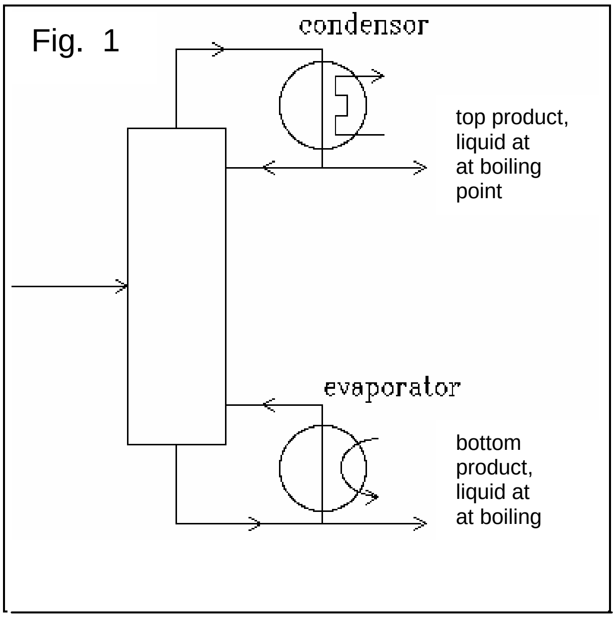
6.10 Low temperature, low DNA concentration and high ionic strength will give the maximum percentage of recombinant molecules.

PROBLEM 7

The equilibrium constant of the reaction $A_{(g)} + 2\,B_{(g)}$ _ $2\,C_{(g)}$ is $K_p = 10.0\ \text{MPa}^{-1}$. The starting materials are supplied at 25 °C and heated to 100 °C where complete equilibration takes place. Below 100 °C the reaction rate is negligibly small. The whole process is executed continuously in a stationary state. The boiling points at 0.1 MPa of **A**, **B**, and **C** are 40 °C, 80 °C, and 60 °C, respectively. The three compounds have the same heat of evaporation: q J mol^{-1}. The heat capacities of **A**, **B**, and **C** may be neglected. A schematic diagram of a distillation is shown below (Fig. 1).

The total heat used at each of the two distillations is 3q J mol^{-1} (of the top product). Apart from distillation columns (each with its own evaporator and condenser) the pieces of apparatus shown of Fig. 2 are available.

Fig. 1



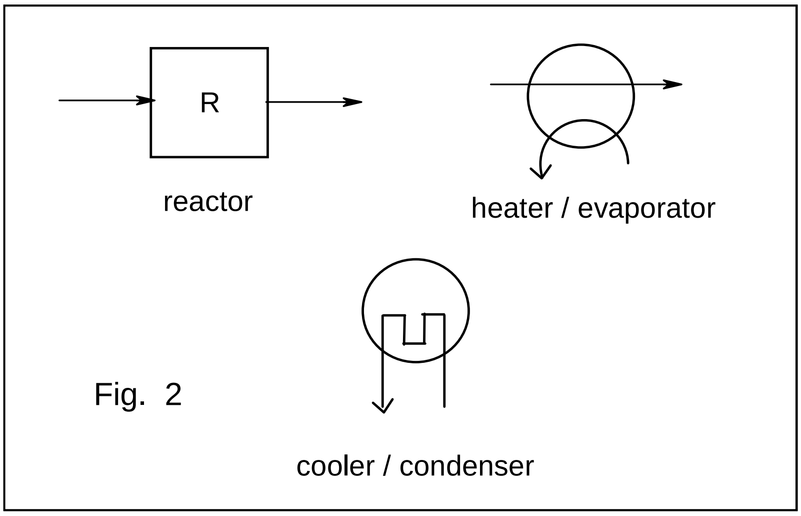


Fig. 2

7.1 Draw a flow diagram of the process in which all flows are given (flow sheet) and in which the starting materials are used as efficiently as possible using as few pieces of apparatus as possible.

7.2 Express the equilibrium constant in terms of the degree of conversion and of total pressure for the case that the feed to the reactor is stoichiometric. What is the value of the degree of conversion when total pressure is 0.100 MPa?

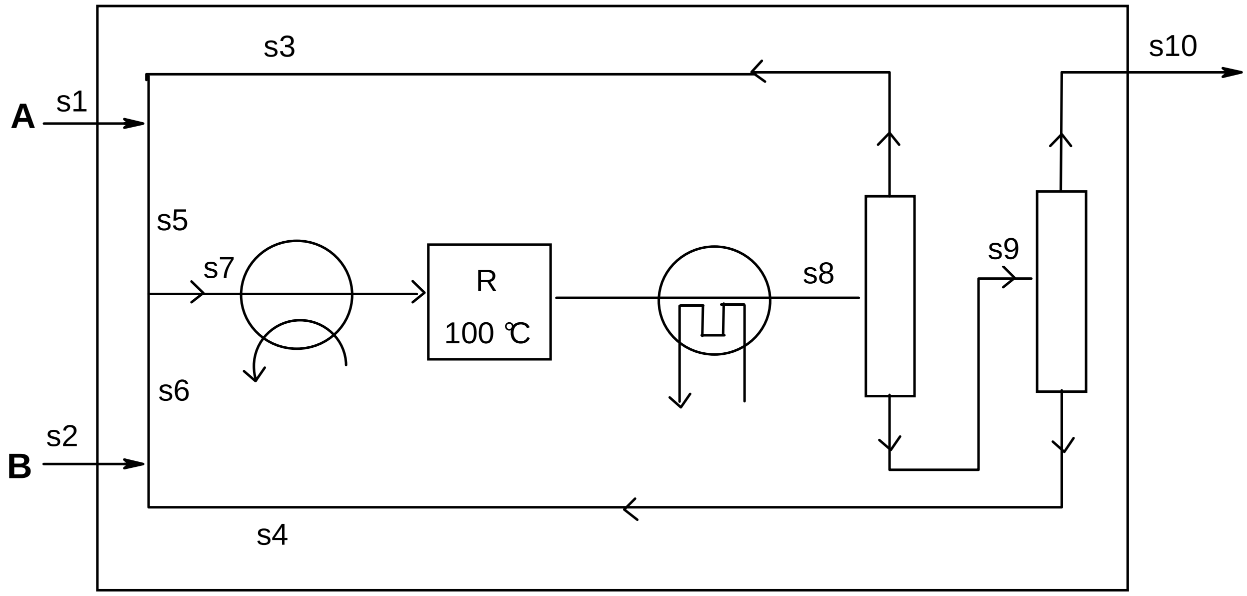
7.3 Number all flows. Calculate the composition of each flow in mol s^{-1} for a rate of production of 1 mole of **C** per second under the conditions of part b.

7.4 In what respect can the reaction conditions influence the composition of the mixture that leaves the reactor? (Refer to question b.)

7.5 The process requires energy. For the conditions of b explain where energy should be supplied in the flow diagram drawn in part a. Derive an expression for the total energy needed.

SOLUTION

7.1 In order to minimize the pieces of apparatus, the liquids A and B should evaporate together. For complete consumption of the starting materials, A and B are recirculated as feed for the reactor. The scheme of figure depicts the solution.



system boundary

7.2 $\mathbf{A} + 2\,\mathbf{B} \rightarrow 2\,\mathbf{C}$

$1-x \quad 2(1-x) \quad 2x$

In total 3-x mol gases are present after conversion. Supposing that the input of **A** is a mol (S5) and the input of B b mol (S6) we can write for the equilibrium:

$$K_p = \frac{p_C^2}{p_A \times p_B^2} = 10.0$$

If x mol of **A** are converted, S8 contains (a - x) mol of **A**, (b – 2x) mol of **B** and 2 x mol of **C**. Therefore S8 contains (a - x) + (9 b – 2x) + 2x = (a + b - x) moles and we can write for the partial pressures of A and B:

$$p_A = \frac{a - x}{a + b - x} P \qquad p_B = \frac{b - 2x}{a + b - x} P \qquad p_C = \frac{2x}{a + b - x}$$

Therefore the equilibrium can be written as

$$K_p = \frac{(2x)^2}{(a - x)(b - 2x)^2} \times \frac{a + b - x}{P} = 10$$

7.3 For P = 0.10 we obtain: $4x^2a + 4x^2b - 4x^3 = ab^2 - 4abx + 4ax^2 - xb^2 + 4x^2b - 4x^3$ and wherefrom:

$0 = ab^2 - 4abx - xb^2$ and since $b \neq 0$: $0 = ab - 4ax - bx$

With a total inflow of 0.5 mol s^{-1} **A** (S1) and 1 mol s^{-1} **B** (S2), the amount of **C** leaving the reactor (S10) is 1 mol s^{-1}. So 2x = 1 and x = 0.5. The relation between a and b can be written as: a = b / (2b - 4). Since the feed is stoichiometric a : b = 1 : 2. This leads to b = 3 and a = 1.5.

All flows (mol/s) can be calculated now:

s1 = 0.5 mol s^{-1} **A**

s2 = 1 mol s^{-1} **B**

s3 = 1.5 - 0.5 = 1 mol s^{-1} **A**

s4 = 3 - 1 = 2 mol s^{-1} **A**

s5 = a = 1.5 mol s^{-1} **A**

s6 = b = 3 mol s^{-1} **B**

s7 = 1.5 mol s^{-1} **A** + 3 mol s^{-1} **B**

s8 = 1 mol s^{-1} **A** + 2 mol s^{-1} **B** + 1 mol s^{-1} **C**

s10 = 1 mol **C**

$s9_1$ = 2 mol **B** + 1 mol **C**; $s9_2$ = 1 mol **A** + 1 mol **C**

7.4 By increasing the pressure, the equilibrium is pushed towards the side with the smallest number of molecules that means to the right side. Another possibility is changing the ratio of the feed. i. e. a : b. According to a = b / (2 b - 4), b will be larger if a decreases and vice versa. Because the net enthalpy change is 0, temperature has no effect.

7.5 Energy must be supplied for heating the evaporator and for the two distillation columns. The total energy consumed of the flow in scheme can be calculated as follows:

Q1 = q*S7 + 3q*S3 + 3q*S10 = 10.5 q

THE NINETEENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
6–15 JULY 1987, VESPZPRÉM – BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

Treating waste water in a sewage plant, 45 % of its carbohydrate $(CH_2O)_n$ is completely oxidized, 10 % undergoes anaerobic decomposition by fermentation (two components) and the rest remains in the sludge. The total gas formation is 16 m^3 per day (25 °C, 100 kPa).

1.1 What is the amount of carbohydrate remaining in the sludge measured in kg per day?

1.2 Using the heat of combustion of methane (– 882 kJ mol^{-1}), calculate the amount of energy that can be produced by combustion of the methane formed per day.

1.3 Knowing that the concentration of the carbohydrate in the waste water is 250 mg dm^{-3}, calculate the daily amount of waste water processed in the plant in m^3 of water per day.

SOLUTION

1.1 $(CH_2O)_n + n\ O_2 \rightarrow n\ CO_2(g) + n\ H_2O(l)$ (1 mol gas/ mol carbohydrate)

$(CH_2O)_n \rightarrow 0.5\ n\ CO_2(g) + 0.5\ n\ CH_4(g)$ (1 mol gas/ mol carbohydrate)

For 16 m^3 of gases: $n(\text{gas}) = \frac{pV}{RT}$ = 646 mol (55 %) with the rest (45 %) therefore being in the sludge.

The amount in the sludge is $\frac{45}{55} \times 646$ = 528 mol, that is <u>15.85 kg/day</u>.

1.2 $n(CH_4) = \frac{5}{55} \times 646 = 58.71$ mol

$\Delta H = -882 \times 58.71 = \underline{-5.178 \times 10^4 \text{ kJ/day}}$

1.3 The sum of CH_2O is $\frac{646}{0.55}$ = 1174 mol. Since 250 mg dm^{-3} = 0.25 kg m^{-3}, the daily amount of water is: $V = \frac{1174 \times 30}{0.25 \times 10^3}$ = $\underline{140.9\ \text{m}^3/\text{day}}$

PROBLEM 3

A typical family car has four cylinders with a total cylinder volume of 1600 cm^3 and a fuel consumption of 7.0 l per 100 km when driving at a speed of 90 km/h. During one second each cylinder goes through 25 burn cycles and consumes 0.4 g of fuel. Assume that fuel consists of 2,2,4-trimethylpentane, C_8H_{18}. The compression ratio of the cylinder is 1:8.

3.1 Calculate the air intake of the engine (m^3/s). The gasified fuel and air are introduced into the cylinder when its volume is largest until the pressure is 101.0 kPa. Temperature of both incoming air and fuel are 100 °C. Air contains 21.0 % (by volume) of O_2 and 79.0 % of N_2. It is assumed that 10.0 % of the carbon forms CO upon combustion and that nitrogen remains inert.

3.2 The gasified fuel and the air are compressed until the volume in the cylinder is at its smallest and then ignited. Calculate the composition (% by volume) and the temperature of the exhaust gases immediately after the combustion (exhaust gases have not yet started to expand). The following data is given:

Compound	ΔH_f (kJ/mol)	C_p (J/mol K)
O_2(g)	0.0	29.36
N_2(g)	0.0	29.13
CO(g)	-110.53	29.14
CO_2(g)	-395.51	37.11
H_2O(g)	-241.82	33.58
2,2,4-trimethylpentane	-187.82	

3.3 Calculate the final temperature of the leaving gases assuming that the piston has moved to expand the gases to the maximum volume of the cylinder and that the final gas pressure in the cylinder is 200 kPa.

3.4 To convert CO(g) into CO_2(g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\frac{n(\text{CO})}{n(\text{CO}_2)} = \frac{1}{4} k \left[\frac{n(\text{CO})}{n(\text{CO}_2)} \right]_1 v e^{-\frac{T}{T_0}}$$

where $[n(\text{CO}) / n(\text{CO}_2)]_1$ is the molar ratio before the catalyst, v is the flow rate in mol/s and T the temperature of the gases entering the catalyst (the same as the temperature of the leaving exhaust gases). T_0 is a reference temperature (373 K) and k is equal to 3.141 s/mol. Calculate the composition (% by volume) of the exhaust gases leaving the catalyst.

SOLUTION

3.1 $M_r(C_8H_{18}) = 114.0$,

Cylinder volume (V_0) = 4.00×10^{-4} m^3, p_0 = 101 000 Nm^{-2}, T_0 = 373 K

Considering one cylinder during one burn cycle one obtains (f = fuel):

$m_f = 0.400 / 25\text{ g} = 0.0160\text{g}$, $n_f = 1.4004 \times 10^{-4}$ mol

(m_f = mass of fuel, n_f = amount of substance of fuel)

$n_G = n_f + n_A = p_0V_0 / (RT_0) = 0.0130$ mol

(n_G = number of moles of gases, n_A = moles of air)

⇒ $n_A = 0.0129$ mol

⇒ Air intake of one cylinder during 25 burn cycles:

$V_A = 25\, n_A R\, T_0 / p_0 = 9.902 \times 10^{-3}$ m^3/s

⇒ The air intake of the whole engine is therefore: $V_{total} = 4\, V_A = 0.0396$ m^3/s

3.2 The composition of the exhaust gases of one cylinder during one burn cycle is considered:

before: $n_{O_2} = 0.21\, n_A = 2.709$ mmol

$n_{N_2} = 0.79\, n_A = 10.191$ mmol

$0.1 \times C_8H_{18} + 8.5\, O_2 \rightarrow 8\, CO + 9\, H_2O$ (10% C)

$0.9 \times C_8H_{18} + 12.5\, O_2 \rightarrow 8\, CO_2 + 9\, H_2O$ (90% C)

$C_8H_{18} + 12.1\, O_2 \rightarrow 0.8\, CO + 7.2\, CO_2 + 9\, H_2O$

Amounts of substances (in mol) before and after combustion:

	C_8H_{18}	O_2	CO	CO_2	H_2O
before	1.404×10^{-4}	2.709×10^{-3}	0	0	0
after	0	10.10×10^{-4}	1.123×10^{-4}	10.11×10^{-4}	12.63×10^{-4}

The composition of the gas after combustion is therefore:

Component	N_2	O_2	CO	CO_2	H_2O	Total
mol × 10^4	101.91	10.10	1.12	10.11	12.63	135.87
%	75.0	7.4	0.8	7.5	9.3	100

From thermodynamics the relation between the enthalpy and temperature change is given by

$$\Delta H = \int_{T_1}^{T_2} \sum_{i=1}^{i=k} c_{pi}\, n_i\, dT = \sum_{i=1}^{i=k} c_{pi} n_i (T_2 - T_1)$$

$\Delta H = n_f\,[0.8\,\Delta H_f(CO) + 7.2\,\Delta H_f(CO_2) + 9\,\Delta H_f(H_2O) - \Delta H_f(C_8H_{18})] = -0.6914$ kJ

This yields to: 691.4 = 0.4097 (T_2 – 373) and T_2 = 2 060 °C

3.3 The final temperature of the leaving gases from one cylinder:

$p_2 = 200\,000$ Pa, $V_0 = 4.00 \times 10^{-4}$ m^3,

n_G = moles of exhaust gases in one cylinder = 0.01359 mol

$$T_2 = \frac{p_2 V_0}{n_G R} = 708 \text{ K}$$

3.4 The flow from all four cylinders is given: v = 4 × 25 × n_G = 1.359 mol/s, so that

$$\frac{n(CO)}{n(CO)_2} = 0.25 \times 3.141 \times \frac{1.12 \times 10^4}{10.11 \times 10^4} \times 1.359 \times e^{\frac{708}{373}} = 0.01772$$

During catalysis: CO + 0.5 O_2 → CO_2

moles × 10^4 (4 cylinders):

	CO	0.5 O_2	CO_2
initial	4.48	40.40	40.44
final	4.48 - x	40.40 - 0.5 x	40.44 + x

0.01772 (40.44 + x) = 4.48 + x ⇒ x = 3.70

Thus, the composition of the gas after the catalyst is:

Component	N_2	O_2	CO	CO_2	H_2O	Total
mol × 10^4	407.64	40.40 - 0.5x	4.48 - x	40.44 + x	50.52	541.63
		38.55	0.78	44.14		
%	75.26	7.12	0.15	8.14	9.33	100

PROBLEM 2

A mixture of gases containing mainly carbon monoxide and hydrogen is produced by the reaction of alkanes with steam:

$CH_4 + ½\,O_2 \rightarrow CO + 2\,H_2$ $\Delta H = 36$ kJ mol^{-1} (1)

$CH_4 + H_2O \rightarrow CO + 3\,H_2$ $\Delta H = 216$ kJ mol^{-1} (2)

2.1 Using equations (1) and (2) write down an overall reaction (3) so that the net enthalpy change is zero.

2.2 The synthesis of methanol from carbon monoxide and hydrogen is carried out either

a) in two steps, where the starting mixture corresponding to equation (3) is compressed from 0.1×10^6 Pa to 3×10^6 Pa, and the mixture of products thereof compressed again from 3×10^6 Pa to 6×10^6 Pa

or

b) in one step, where the mixture of products corresponding to equation (3) is compressed from 0.1×10^6 Pa to 6×10^6 Pa.

Calculate the work of compression, W_a, according to the two step reaction for 100 cm^3 of starting mixture and calculate the difference in the work of compression between the reactions 1 and 2.

Assume for calculations a complete reaction at constant pressure. Temperature remains constant at 500 K, ideal gas behaviour is assumed.

To produce hydrogen for the synthesis of ammonia, a mixture of 40.0 mol CO and 40.0 mol of hydrogen, 18.0 mol of carbon dioxide and 2.0 mol of nitrogen are in contact with 200.0 mol of steam in a reactor where the conversion equilibrium is established.

$CO + H_2O \rightarrow CO_2 + H_2$

2.3 Calculate the number of moles of each gas leaving the reactor.

SOLUTION

2.1 $6\,CH_4 + 3\,O_2 \rightarrow 6\,CO + 12\,H_2$ $\Delta H = -216$ kJ mol^{-1}

$CH_4 + H_2O \rightarrow CO + 3\,H_2$ $\Delta H = 216$ kJ mol^{-1}

$7\,CH_4 + 3\,O_2 + H_2O \rightarrow 7\,CO + 15\,H_2$ $\Delta H = 0$ kJ mol^{-1}

a) For a pressure increase in two steps under the conditions given, the work of compression is:

$$W_2 = n_1\, RT \ln\frac{p_1}{p_2} + n_2\, RT \ln\frac{p_2}{p_1} = n_1\, RT (\ln\frac{p_1}{p_0} + 2 \ln\frac{p_2}{p_1})$$

$$= 100 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 500 \text{ K} \times \left(\ln \frac{3.0 \text{ MPa}}{0.1 \text{MPa}} + 2 \ln\frac{6.0 \text{ MPa}}{3.0 \text{ MPa}} \right) = 1.99 \text{ MJ}$$

b) For a pressure increase in one step the work of compression only depends on n_2, p_2 and p_0:

$$W_1 = \ n_2 RT \ln\frac{p_2}{p_0} = \ 100 \text{ mol} \times 8{,}314 \text{ J mol}^{-1} \text{ K}^{-1} \ \times 500 \text{ K} \times \ \ln\frac{6.0 \text{ MPa}}{0.1 \text{ MPa}} = 3.40 \text{ MJ}$$

It means

$\Delta W = W_1 - W_2 = \underline{1.41 \text{ MJ}}$

2.3 With K = 3.3, the following equilibrium is valid:

$$K = \frac{n_{CO_2} \times n_{H_2}}{n_{CO} \times n_{H_2O}} = \frac{(18 + x)\ (40 + x)}{(40 - x)\ (200 - x)}$$

$x_{1/2} = 184 \pm 151.6$; $x_1 = 33.2$; $x_2 = 336.4$

The composition of the leaving gas is:

6.8 mol CO, 51.2 mol CO_2, 2.0 mol CH_4 and N_2, 73.2 mol H_2 and 166.8 mol H_2O.

PROBLEM 4

CHEMICAL THERMODYNAMICS

The production of zinc from zinc sulphide proceeds in two stages: the roasting of zinc sulphide in the air and the reduction of the zinc oxide formed by carbon monoxide. In this problem we will consider the roasting of zinc sulphide.

This operation consists in burning zinc sulphide in the air. The equation of the reaction taking place is as follows:

$$ZnS(s) + 3/2\ O_2(g) \rightarrow ZnO(s) + SO_2(g) \qquad \Delta_r H^0_{1350} = -\ 448.98\ \text{kJ mol}^{-1}$$

Industrially this reaction is carried out at 1350 K.

4.1 Show that the reaction can be self-sustaining, i.e. that the heat produced is sufficient to bring the reactants from ambient temperature to the reaction temperature.

Suppose that the zinc containing mineral contains only zinc sulphide, ZnS.

4.2 Starting with a stoichiometric mixture of one mole zinc blend only and a necessary quantity of the air at 298 K, calculate the temperature to which the mixture will raise by the heat evolved during the roasting of the mineral at 1350 K under standard pressure. Is the reaction self-sustaining? Air is considered to be a mixture of oxygen and nitrogen in a volume ratio equal to 1 : 4.

In fact, zinc blend is never pure and is always mixed with a gangue that can be assumed to be entirely silica SiO_2.

4.3 Assuming that the gangue does not react during the roasting, calculate the minimum ZnS content of the mineral for which the reaction would be self-sustaining at 1350 K despite the presence of silica. Give the answer is grams of ZnS per hundred grams of zinc blend.

Data:

Standard molar heat capacities averaged over the temperature range considered (in J K^{-1} mol^{-1}):

ZnS (solid):	58.05	ZnO (solid):	51.64
SO_2 (gas):	51.10	O_2 (gas):	34.24
N_2 (gas):	30.65	SiO_2 (solid):	72.50

Molar masses (in g mol^{-1}): ZnS: 97.5 SiO_2: 60.1

SOLUTION

4.1 The heat given off heats 1 mol of ZnS, 1.5 mol of O_2 and 6 mol of N_2. Therefore:

$$\Delta_r H^0_{1350} = \int_{298}^{T} [c_p(\text{ZnS}) + 1.5\, c_p(\text{O}_2) + 6\, c_p(\text{N}_2)]\, dT = 293.3(T - 298) = 448\,980 \text{ J mol}^{-1}$$

Thus $\underline{T \approx 1830 \text{ K}}$, which indicates that the reaction is self-sustaining.

4.2 If *n* denotes the quantity (in moles) of SiO_2 per mol of ZnS, the heat given off heats 1 mol of ZnS, *n* mol of SiO_2, 1.5 mol of O_2 and 6 mol of N_2 from 298 to 1350 K:

$$\Delta_r H^o = \int_{298}^{1350} \Sigma(n_i \times c_{p(i)})\, dT = \int_{298}^{1350} (293.3 + 72.5n)\, dT$$

Wherefrom: 448 980 = (293.3 + 72.5 *n*)(1350 - 298), so $\underline{n = 1.84 \text{ mol}}$

4.3 By mass, we have 110.6 g of SiO_2 per 97.5 g of ZnS, or 46.9 g of ZnS per 100 g of mineral. Thus, the minimum tolerated ZnS content in the mineral is $\underline{46.9\ \%}$.

PROBLEM 5

CHEMICAL KINETICS

Nitramide NO_2NH_2 decomposes slowly in aqueous solution according to the reaction:

$$NO_2NH_2 \rightarrow N_2O(g) + H_2O$$

The experimental kinetic law is as follows:

$$\frac{d[N_2O]}{dt} = k\,\frac{[NO_2NH_2]}{[H_3O^+]}$$

5.1 What is the apparent order of this reaction in a buffered solution?

5.2 Which of the following mechanisms is the most appropriate for the interpretation of this kinetic law? Justify your answer.

Mechanism 1:

$$NO_2NH_2 \xrightarrow{k_1} N_2O + H_2O \qquad \text{(rate limiting step)}$$

Mechanism 2:

$$NO_2NH_2 + H_3O^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} NO_2NH_3^+ + H_2O \qquad \text{(rapid equilibrium)}$$

$$NO_2NH_3^+ \xrightarrow{k_3} N_2O + H_3O^+ \qquad \text{(rate limiting step)}$$

Mechanism 3:

$$NO_2NH_2 + H_2O \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} NO_2NH_3^- + H_3O^+$$

$$NO_2NH^- \xrightarrow{k_5} N_2O + OH^- \qquad \text{(rate limiting step)}$$

$$H_3O^+ + OH^- \xrightarrow{k_6} 2\,H_2O \qquad \text{(very fast reaction)}$$

5.3 Show the relationship between the experimentally observed rate constant and the rate constants of the selected mechanism.

5.4 Show that hydroxyl ions catalyze the decomposition of nitramide.

The decomposition is studied in a buffered solution of a constant volume *V* at a constant temperature by measuring the partial pressure of the gas N_2O, considered to be insoluble in water, in a constant volume of the same value V above the solution. The following results are obtained:

t(min)	0	5	10	15	20	25
p(Pa)	0	6800	12400	17200	20800	24000

After a sufficiently long time, the pressure stabilises at 40000 Pa.

5.5 Express the pressure *p* as a function of time and the constant *k*` such that

$$k` = \frac{k}{[H_3O^+]}\,.$$

5.6 Verify graphically that the kinetic law is confirmed by these experimental results.

5.7 Calculate *k*' giving its units.

SOLUTION

5.1 In a buffer solution $[H_3O^+]$ is constant and the reaction is of the first order:

$v = k' [NO_2NH_2]$

5.2 The rate laws of the three mechanisms proposed are:

$v_1 = k_1 [NO_2NH_2]$

$$v_2 = k_3 [NO_2NH_3^+] = \frac{k_3 k_2}{k_{-2}} [NO_2NH_2] [H_3O^+]$$

$$v_3 = k_5 [NO_2NH^-] = \frac{k_5 k_4}{k_{-4}} \frac{[NO_2NH_2]}{[H_3O^+]}$$

Thus, it is the third mechanism that is correct.

5.3 $k = \dfrac{k_5 k_4}{k_{-4}}$

5.4 Noting that $[H_3O^+] = K_e / [OH^-]$ it follows that $v = k / K_e [NO_2NH_2] [OH^-]$, which shows the catalytic role of OH^-.

5.5 $d[N_2O]$ can be expressed by the change of pressure $dp(N_2O)/RT$ (according to $pV = nRT$). We obtain:

$$v = \frac{d[N_2O]}{dt} = \frac{1}{RT}\frac{dp(N_2O)}{dt} = \frac{1}{RT}\frac{dp}{dt} = k\frac{[NO_2NH_2]}{[H_3O^+]}$$

We also know that $V\,[NO_2NH_2] = n(NO_2NH_2)_{init} - n(N_2O) = n(N_2O)_\infty - n(N_2O)$ from which

$$\frac{dp}{dt} = \frac{k}{[H_3O^+]} \times \frac{RT}{V} \times (n(N_2O)_\infty - n(N_2O))$$

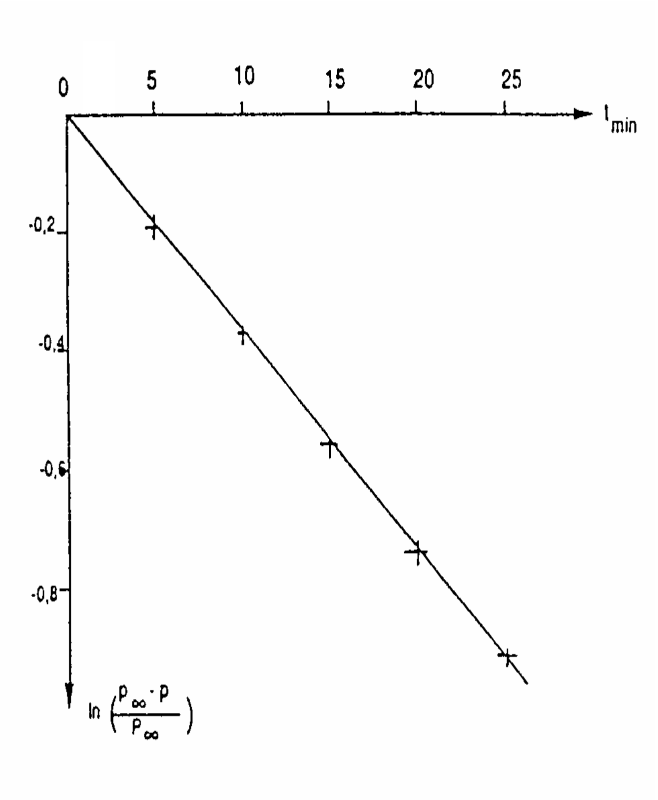
and thus

$$\frac{dp}{dt} = \frac{k}{[H_3O^+]} \times (p_\infty - p) = k'(p_\infty - p)$$

Integration gives $p = p_\infty\,(1 - e^{-k't})$

wherefrom: $e^{-k't} = 1 - p/p_\infty$

5.6



5.7 The graph of $f(x) = \ln(1 - p/p_\infty) = -k't$ is a straight line with the slope k' shown in Fig. k' was determined to be 3.7×10^{-2} min^{-1}.

PROBLEM 7

<u>In this problem tick the appropriate box in the tables of the answer sheet.</u>

Hydrogenation of benzene to cyclohexane is performed in continuous reactors. The reaction is as follows:

$C_6H_6 + 3\ H_2 \rightleftarrows C_6H_{12}$ (catalyst) ΔH^0 = 214 kJ mol^{-1} at 200 °C

Two basic types of continuous reactors are examined: a continuous plug flow reactor and a continuous stirred reactor.

The continuous plug flow reactor (Fig. 1)

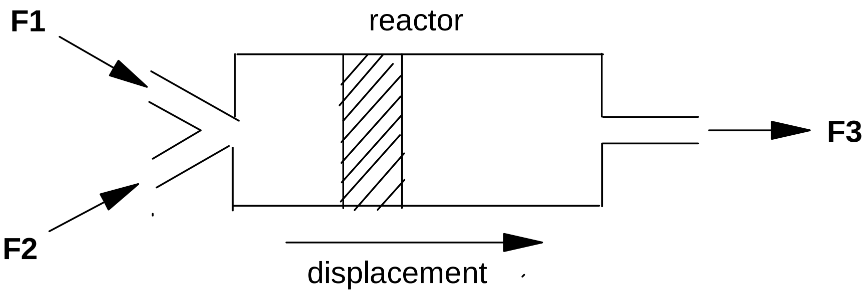


Fig. 1

The reagents are introduced and mixed at the inlet of the reactor (flow F1 and F2). Each slice of the reaction medium (marked zone in the diagram) moves along inside the plug flow reactor without mixing with the others and exits from the reactor (flow F3). When the flow has stabilized, concentrations and conditions are time-independent but dependent on the location in the reactor.

The continuous stirred reactor (Fig. 2)

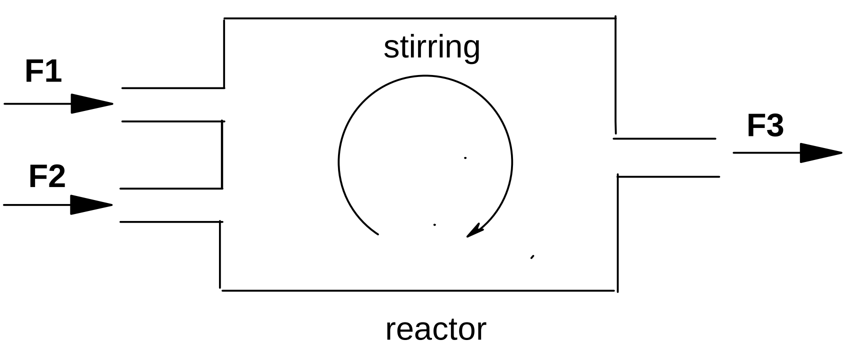


Fig. 2

The reagents are introduced into the reactor (flows F1 and F2). Inside the reactor they are stirred perfectly and instantaneously. When the flow is stabilized, concentrations and conditions are time-independent and identical at every point of the reactor.

The differential yield of hydrogenation (Y) is given by Y = $-\frac{d([C_6H_{12}])}{d([C_6H_6])}$.

The proportion of benzene already hydrogenated is given by p = $\frac{[C_6H_{12}]}{[C_6H_{12}]+[C_6H_6]}$.

The relationship between p and Y is shown in Fig. 3.

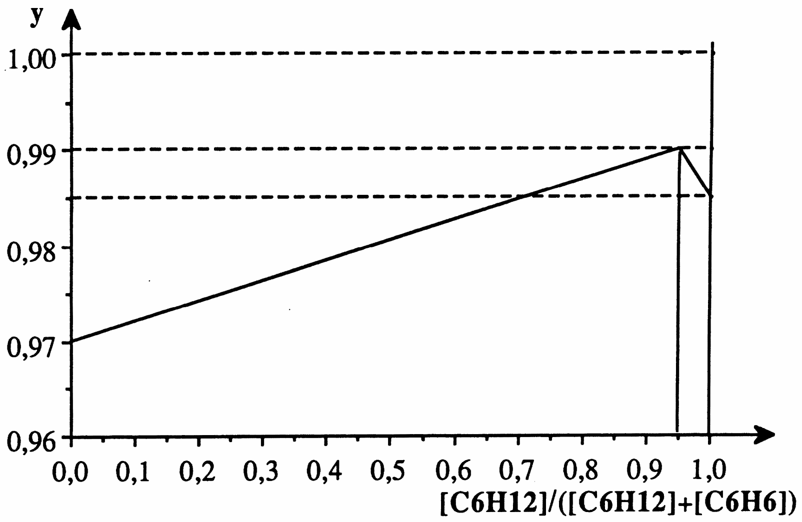


Fig. 3

The aim is to hydrogenate almost all the benzene, i.e. 0.9 ≤ p ≤ 1 with the best mean yield

Y = $-\frac{\Delta[C_6H_{12}]}{\Delta[C_6H_6]}$.

7.1 What is the value of p in a continuous stirred reactor leading to the maximal mean yield of hydrogenation? What is the maximal value of Y?

7.2 For a continuous plug flow reactor, give a rough value of Y for 0.9 ≤ p ≤ 1:

Y = 0.97, 0.98, 0.99 or 1.00 ?

7.3 Represent by grey shading in the graph (Fig. 3) the quantities of benzene lost in installation P (plug flow reactor) and installation MP (stirred reactor + plug flow reactor).

7.4 Give the amount of annual benzene lost in installation P and MP assuming an annual consumption of 100 000 tons of benzene.

SOLUTION

7.1 In the continuous stirred reactor, concentrations are time independent and identical at every point. This means that the differential yield y for a given p is identical to the mean yield Y. A maximum mean yield is therefore obtained for y_{max}. From the Fig. 1 it's seen that $y_{max} = 0.99$ with $p = 0.95$.

7.2 In a continuous plug flow reactor concentrations are time-independent but dependent upon the location in the reactor. We shall consider a thin slice dx of the reactor at the entrance and at the end of the reactor. At the entrance $[C_6H_6] = 1$ and $[C_6H_{12}] = 0$, thus $p = 0$ and $y = 0.97$. At the outlet of the reactor we have: $[C_6H_6] = 0$ and $[C_6H_{12}] = 1$. So, $p = 1$ and $y = 0.985$. The mean yield is now the average of y over all p, which is 0.98, as one can easily see from the Fig. 1.

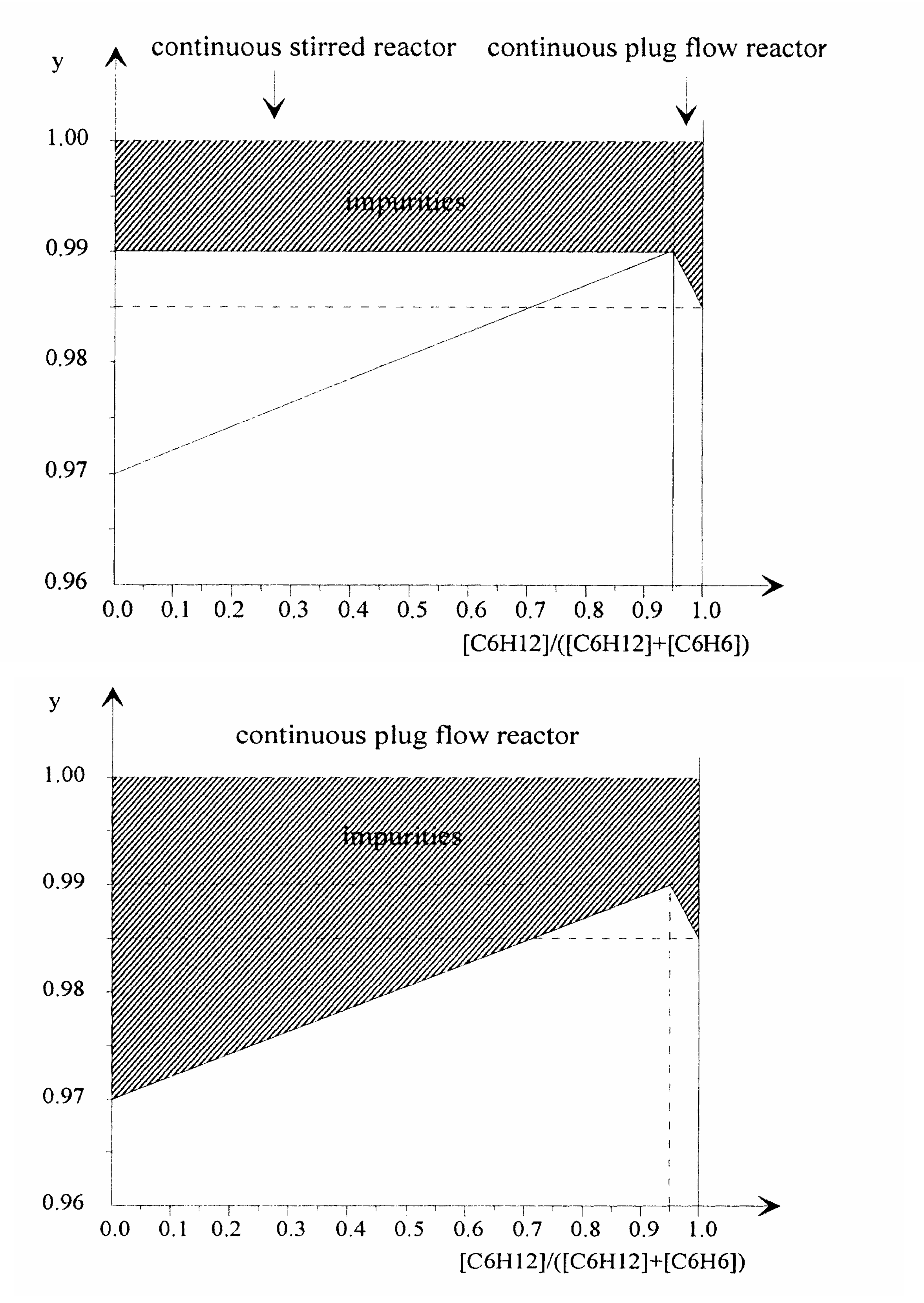
7.3 In the plug flow reactor, the quantity of benzene lost (not hydrogenated) is $1 – p$. Fig. 1 shows the area that represents the amount of benzene that is not hydrogenated and therefore lost. For the installation MP we first have the amount of benzene lost in the continuous stirred reactor which is always $1 – 0.99 = 0.01$ independent from p up to a point $p = 0.95$. At $p > 0.95$ to the continuous plug reactor has the same loss of benzene as already indicated in the Fig 1 below.

7.4 In the plug reactor the percentage of benzene lost is 2 % (the best mean yield is 0.98), therefore the amount of benzene annually lost is 2000 tons.

In a MP installation, the yield of hydrogenation is 0.99 (except for $0.95 < p < 1$ where it slightly decreases to 0.985, but this can be neglected) and therefore, the overall mean yield of hydrogenation is also 0.99.

The amount of benzene annually lost is therefore 1000 tons.

Figure 1


y
continuous stirred reactor
continuous plug flow reactor
1.00
impurities
0.99
0.98
0.97
0.96
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
[C6H12]/([C6H12]+[C6H6])
y
continuous plug flow reactor
1.00
impurities
0.99
0.98
0.97
0.96
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
[C6H12]/([C6H12]+[C6H6])

PROBLEM 5

Nitrogen dioxide NO_2 is one of a number of oxides of nitrogen found in our atmosphere. It can dimerize to give N_2O_4 (g):

$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$

5.1 With a diagram, show the bonds present in $NO_2(g)$ using the concept of resonance if necessary. Nitrogen dioxide, NO_2, is paramagnetic.

5.2 Show, with bonding diagrams, how two molecules of $NO_2(g)$ combine to give a molecule of N_2O_4 (g) which is not paramagnetic.

5.3 At 298 K, the ΔG^o of formation for $N_2O_4(g)$ is 98.28 kJ, whereas for $NO_2(g)$ is 51.84 kJ. Starting with one mole of $N_2O_4(g)$ at 1.0 atm and 298 K, calculate what fraction will be decomposed if the total pressure is kept constant at 1.0 atm and the temperature is maintained at 298 K.

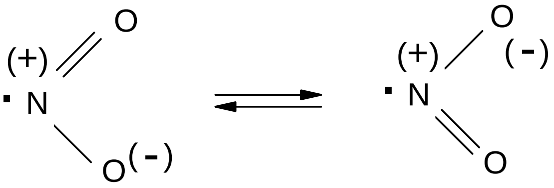
5.4 If ΔH^o for the reaction $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ is 58.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double that calculated in part 5.3?

5.5 The dissociation of $N_2O_4(g)$ to give $NO_2(g)$ is a first order process with a specific rate constant of $5.3 \times 10^4\ s^{-1}$ at 298 K. Starting with an initial concentration of 0.10 M, how many seconds would it take for 20 % of the original N_2O_4 to decompose?

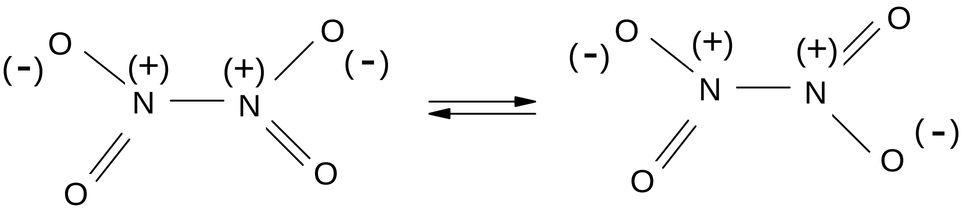
5.6 The association of $NO_2(g)$ to give $N_2O_4(g)$ is a second-order process with a specific rate constant of $9.8 \times 10^6\ dm^3mol^{-1}s^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c, at 298 K for the reaction $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$

SOLUTION

5.1 The structure of NO_2:



5.2 The structure of N_2O_4:



(At very low temperatures there is another structure of N_2O_4 possible: O=N—ONO_2 , nitrosyl nitrate)

5.3 $N_2(g) + 2\ O_2(g) \rightarrow N_2O_4(g) \qquad \Delta G^o = 98.28$ kJ

$N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g) \qquad \Delta G^o = 2 \times (51.84) = 103.68$ kJ

$N_2O_4\ (g) \rightarrow 2\ NO_2\ (g) \qquad \Delta G^o = 5.4$ kJ

If *x* denotes the fraction of decomposed N_2O_4 and P_T the partial pressure and *X* the mole fraction of the corresponding species, we obtain:

$\Delta G^0 = -RT \ln K; \qquad K = e^{(-5.4 \text{ kJ}/ 8.314\times10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})}$

$$K_p = 0.113 = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(P_T X_{NO_2})^2}{P_T X_{N_2O_4}} = \frac{\left(\frac{2x}{1+x}\right)^2}{\left(\frac{1-x}{1+x}\right)} = \frac{4x^2}{1-x^2}$$

wherefrom <u>x = 0.166</u>

5.4 If $2 \times 0.166 = 0.332$ mol N_2O_4 decomposes, 0.664 mol NO_2 are formed, thus

$$K_p = \frac{\left(\frac{0.664}{1.332}\right)^2}{\frac{1-0.332}{1.332}} = 0.496$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{0.496}{0.113}\right) = -\frac{58.03 \text{ Jmol}^{-1}}{8.314 \text{ Jmol}^{-1}\text{K}^{-1}}\left(\frac{1}{T_2} - \frac{1}{298 \text{ K}}\right)$$

T_2 = 318 K

5.5 $\ln\frac{[N_2O_4]_t}{[N_2O_4]_0} = -kt$

$$\ln 0.80 = -\,(5.3\times10^{4}\ s^{-1})\ t$$

$$t\ =\ 4.2\times10^{-6}\ \text{s}$$

5.6 $K = \dfrac{k_{\text{forward}}}{k_{\text{reverse}}} = \dfrac{9.8\times10^{6}}{5.3\times10^{4}} = 1.8\times10^{2}$

PROBLEM 3

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The student may be aware that the acceptable concentration of CO in air is ≤ 5 ppm and the maximum tolerable level is 50 ppm.

The following reactions occur in methane burner:

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ (I)

$CH_4(g) + 3/2\ O_2(g) \rightarrow CO(g) + 2\ H_2O(g)$ (II)

Compound	CH_4	O_2	CO_2	CO	H_2O
ΔH^0_f (kJ mol^{-1})	–74.9	0	–393.5	–110.5	–241.8
S^0 (J K^{-1}mol^{-1})	186.2	205.0	213.6	197.6	188.7

Questions:

3.1 Calculate the equilibrium constants for both reactions at T = 1500 K assuming that the values ΔH^o and ΔS^o are independent of the temperature.

3.2 Find the relationship between the mole numbers of oxygen and carbon monoxide at equilibrium (T = 1500 K, p = 1 atm) when air is admitted into the burner in such amount that the mole ratio $CH_4 : O_2$ is 1 : 2.

Assume the following volume composition of air: 80 % N_2 and 20 % O_2.

Make the approximation that $n(CH_4) \cong 0$ at equilibrium and justify it on the bases of the answers to the question 3.1.

3.3 Calculate the equilibrium mole fraction x of CO in the conditions given in the question 3.2. Assume that the mole fraction of CO is very small in comparison with that of CO_2 and consequently, the total number of moles does not appreciably vary during the combustion. Justify this assumption.

3.4 Repeat the calculations of items 3.2 and 3.3 assuming that twice the amount of air (compared to the conditions in question 3.2) is admitted into the burner (4 mol O_2 : 1 mol CH_4).

3.5 Calculate the concentrations of CO (expressed as ppm by volume) in the fumes after condensation of water vapour under the conditions of question 3.2 and 3.4, assuming that the composition does not change appreciably during the cooling from 1500 K to room temperature and neglecting the contribution of water vapour to the composition of the gas phase.

SOLUTION

The interest of this problem lies in its relevance to the risk of poisoning by carbon monoxide owing to faulty or ill-adjusted heating systems. Cases of poisoning due to this cause are rather common. The problem involves the calculation of equilibrium constants, consideration of simultaneous equilibria and simple stoichiometric calculations.

3.1 $\Delta_I H^0$ = 74.9 – 393.5 – (2 × 241.8) = – 802.2 kJ mol^{-1}

$\Delta_I S^0$ = –186.2 – (2 × 205.0) + 213.6 + (2 × 188.7) = – 5.2 J K^{-1} mol^{-1}

$$K_I = \exp -\frac{\Delta_I H^0 - T\Delta_I S^0}{R\,T} = \exp \frac{802.2 - 1.5 \times 5.2}{8.314 \times 1.5} = 4.62 \times 10^{27}$$

$\Delta_{II} H^0$ = 74.9 – 110.5 – (2 × 241.8) = – 519.2 kJ mol^{-1}

$\Delta_{II} S^0$ = – 186.2 – (1.5 × 205.0) + 197.6 + (2 × 188.7) = 81.3 J K^{-1} mol^{-1}

$$K_{II} = \exp \frac{519.2 - 1.5 \times 81.3}{8.314 \times 1.5} = 2.13 \times 10^{22}$$

3.2 Since K_I and K_{II} are very large, both equilibria are completely shifted to the right so that $n_{CH_4} = 0$.

At equilibrium: $n_{CH_4} = 0$; $n_{H_2O} = 2$; $n_{N_2} = 8$; $n_{CO_2} + n_{CO} = 1$;

$$n_{O_2} = 2 - (2\,n_{CO_2} + 1.5\,n_{CO}) = 0.5\,n_{CO}$$

3.3 In reaction **I** the total number of moles does not vary; in reaction **II** it changes from 8.5 to 9 (taking into account the presence of N_2), but this change affects the total number of moles only negligibly since $K_{II} << K_I$.

Before reaction: $n_{tot} = n_{CH_4} + n_{O_2} + n_{N_2} = 1 + 2 + 8 = 11$

$$\frac{K_{II}}{K_I} = \frac{p_{CO}\, p_{O_2}^{1/2}}{p_{CO_2}} = \frac{x_{CO}\,(x_{O_2}\, p)^{1/2}}{x_{CO_2}}$$

$$x_{CO_2} = \frac{n_{CO_2}}{n_{tot}} = \frac{1 - n_{CO}}{n_{tot}} = \frac{1}{11}$$ since $n_{CO} << n_{CO_2}$ as a consequence of $K_{II} << K_I$

$$x_{CO}^{3/2} = \frac{K_{II}}{K_I}\,\frac{(2/p)^{1/2}}{11} = \frac{2.13\times10^{22}\times1.414}{4.62\times10^{27}\times11} = 5.93\times10^{-7}$$

$x_{CO} = 7.06 \cdot 10^{-5}$

3.4 $n_{tot} = n_{CH_4} + n_{O_2} + n_{N_2} = 1 + 4 + 16 = 21$

At equilibrium: $n_{O_2} = 4 - (2\, n_{CO_2} + 1.5\, n_{CO}) = 2 + 0.5\, n_{CO} = 2$

$n_{CO_2} = 1 - n_{CO}$

$$\frac{K_{II}}{K_I} = \frac{x_{CO}\,(x_{O_2}\, p)^{1/2}}{x_{CO_2}} = x_{CO}\,(2/21)^{1/2}\times21 = (42)^{1/2}\, x_{CO}$$

$$x_{CO} = 42^{-1/2}\,\frac{K_{II}}{K_I} = 42^{-1/2}\times\frac{2.13\times10^{22}}{4.62\times10^{27}} = 7.11\times10^{-7}$$

3.5 As a consequence of the condensation of water vapour, the number of moles in the gaseous phase changes from 11 to 9 in case c), and from 21 to 19 in case d). Therefore the mole fraction of CO changes to:

$x_{CO} = 7.06\times10^{-5}\times\frac{11}{9} = 8.63\times10^{-5}$ and to:

$x_{CO} = 7.11\times10^{-7}\times\frac{21}{19} = 7.86\times10^{-7}$ in case 3.4

These values correspond to 86 and 0.8 ppm, respectively.

PROBLEM 7

7.1 When an ideal, monatomic gas expands reversibly from a volume V_1 to a volume V_2, a work

$$w = -\int_{V_1}^{V_2} p \, dV$$

is performed <u>on</u> the system <u>by</u> the surroundings. In this equation, w is the work and p is the pressure of the gas.

Determine the performed work when one mole ideal gas expands isothermally from V_1 = 1.00 dm^3 to V_2 = 20.0 dm^3 at the temperature T = 300.0 K.

Given: The gas constant R = 8.314 J K^{-1} mol^{-1}.

7.2 Determine how much heat must be added to the gas during the process given under 7.1.

7.3 The gas will perform less work in an adiabatic expansion than in an isothermal expansion. Is this because the adiabatic expansion is characterized by (check the square you think is most important).

1	The volume of the gas is constant
2	The expansion is always irreversible
3	No heat is supplied to the gas

7.4 The cyclic process shown schematically in Figure 1 shows the four steps in a refrigeration system with an ideal gas as working medium. Identify the isothermal and adiabatic steps in the process. Here, T_H and T_C represent high and low temperature, respectively. Specify for each step whether it is adiabatic or isothermal.

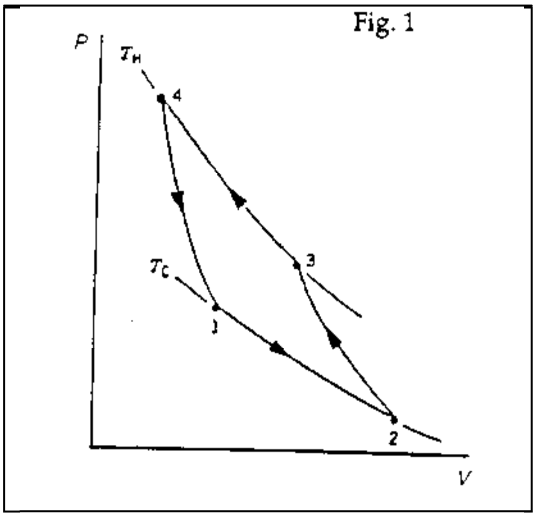


Fig. 1

SOLUTION

7.1 Work performed on the gas is

$$w = -\int_{V_1}^{V_2} p\, dV = -RT \int_{V_1}^{V_2} \frac{dV}{V} = -RT \ln \frac{V_2}{V_1}$$

$$= -8{,}314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \ln \frac{20.00}{1.00} = -7472 \text{ J mol}^{-1} = -7.47 \text{ kJ mol}^{-1}$$

7.2 Because this is an isothermal expansion of an ideal monatomic gas, there is no change in internal energy. From the first law of thermodynamics, we then have that $\Delta U = q + w = 0$

where q is the amount of supplied heat and w is performed work. This leads to $\underline{q} = -w = 7.47$ kJ mol^{-1}.

7.3 (3) No heat is supplied to the gas.

7.4

isotherm	[✓ 1-2]	2-3	[✓ 3-4]	4-1
adiabat	1-2	[✓ 2-3]	3-4	[✓ 4-1]

PROBLEM 8

Avogadro's Number: $6.022 \cdot 10^{23}$

8.1 An atom of ^{238}U disintegrates by a series of α-decays and β^--decays until it becomes ^{206}Pb, which is stable.

i) How many α-decays and how many $ß^-$-decays does an atom starting as ^{238}U undergo before it becomes stable?

ii) One of the following ten nuclides is formed from a series of disintegrations starting at ^{238}U. Which one ?

^{235}U, ^{234}U, ^{228}Ac, ^{224}Ra, ^{224}Rn, ^{220}Rn, ^{215}Po, ^{212}Po, ^{212}Pb, ^{211}Pb.

8.2 In a thermal neutron-induced fission process, ^{235}U reacts with a neutron and breaks up into energetic fragments and (normally) 2-3 new neutrons.

We consider one single fission event:

$^{235}U + n \rightarrow {}^{137}Te + X + 2\,n$

Identify the fragment X.

8.3 The half-life of ^{238}U is 4.5×10^9 years, the half-life of ^{235}U is 7.0×10^8 years. Natural uranium consists of 99.28 % ^{238}U and 0.72 % ^{235}U.

i) Calculate the ratio in natural U between the disintegration rates of these two uranium isotopes.

ii) A mineral contains 50 weight percent uranium. Calculate the disintegration rate of ^{238}U in 1.0 kg of this mineral.

8.4 We have the following radioactive sequence:

$^{97}Ru \rightarrow {}^{97}Tc \rightarrow {}^{97}Mo$ (stable).

Halflives: ^{97}Ru: 2.7 days; ^{97}Tc: 2.6×10^6 years

At $t = 0$ a radioactive source containing only ^{97}Ru has a disintegration rate of 1.0×10^9 Bq.

i) What is the total disintegration rate of the source at $t = 6.0$ days?

ii) What is the total disintegration rate of the source at $t = 6000$ years?

SOLUTION

8.1 i) 8 α's and 6 $ß^-$'s (only α's gives ^{206}Os, to come from Os to Pb requires 6 $ß^-$'s).

ii) ^{234}U, all other answers are incorrect.

8.2 ^{97}Zr

8.3 i) $D = \lambda N$, i.e. $D_1 / D_2 = \lambda_1 N_1 / \lambda_2 N_2$ = abund.(1)$T_{1/2}$·(2) / abund.(2)$T_{1/2}$(1)

= (99.28 × 7.0×10^8) / (0.72 × 4.5×10^9) = 21.4 (0.047 is also of course correct)

ii) $N = (m/\text{AW(U)}) \times \text{abundance}(238) \times N_A = (500 / 238.01) \times 0.9928 \times 6.022\times10^{23}$

$= 1.26\times10^{24}$

$D = N \ln2 / T_{1/2} = 1.26\times10^{24} \times \ln2 / (4.5\times10^9 \text{ (y)} \times 3.16\times10^7 \text{ (s/y)}) = 6.1\cdot10^6$ Bq

8.4 i) $\lambda = \ln 2 / 2.7\text{(d)} = 0.26\ \text{d}^{-1}$

$D = D_0\, e^{-\lambda t} = 1.0\times10^9 \times e^{-(0.26 \times 6.0)} = 2.1\times10^8$ Bq

ii) Number of ^{97}Ru atoms in the source:

$N = D\, T_{1/2}(^{97}\text{Ru}) / \ln 2 = 1.0\times10^9 \text{ (Bq)} \times 2.7 \text{ (d)} \times 24 \text{ (h/d)} \times 3600 \text{ (s/h)} / 0.6931 =$

$= 3.4\times10^{14}$ atoms

When all ^{97}Ru has disintegrated, these atoms have all become ^{97}Tc, and the disintegration rate of this nuclide is

$D = N \ln 2 / T_{1/2}(^{97}\text{Tc}) = (3.4\times10^{14} \times 0.6931) / (2.6\cdot10^6 \text{ y} \times 3.16\times10^7 \text{ s y}^{-1}) =$

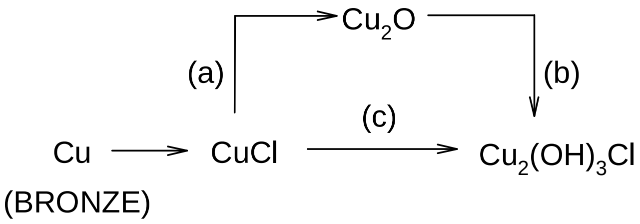
= 2.9 Bq

THE TWENTY-SEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
13–20 JULY 1995, BEIJING, CHINA

THEORETICAL PROBLEMS

PROBLEM 1

1.1 Excavated Chinese ancient bronze musical instrument, carillon, was covered entirely by rust. Chemical analysis showed that the rust contains CuCl, Cu_2O and $Cu_2(OH)_3Cl$. Simulation experiments showed that CuCl was formed first under the action of both air and Cl containing aqueous solution and then $Cu_2(OH)_3Cl$ produced through the following two different ways:



Using the molar standard formation Gibbs free energies of the species concerned answer the following questions:

Species	Cu_2O(s)	CuO(s)	CuCl(s)	**$Cu_2(OH)_3Cl$(s)**	Cl(aq)	OH(aq)	H_2O(l)
Δ_fG^0(298 K) (kJ mol^{-1})	-146	-130	-120	-1338	-131	-157	-237

i) Write balanced equations for reactions (a), (b) and (c).

ii) Calculate the molar standard Gibbs free energy Δ_fG^0(298 K) for reactions (a), (b) and (c).

iii) Decide the spontaneous direction of reaction (a) in air through calculation, when T = 298K, c(HCl) = 1.0×10^{-4} mol dm^{-3}.

1.2 Rate constants k_c for reaction (c) were measured at various temperatures in a simulation experiment in order to obtain its kinetic parameters. On the basis of the data given below answer the following questions:

t ℃	25	40
k_c / mol dm^{-3} s^{-1}	1.29×10^{-4}	2.50×10^{-4}

i) Write the equation for calculating the activation energy of reaction (c) and fínd the value.

ii) Assign the overall reaction order of reaction (c).

iii) Knowing that the rate determining step of reaction (c) is the monolayer adsorption of O_2 (g) on solid CuCl, write the overall rate equation of this heterogeneous reaction (c). Under what condition might the reaction order be the same as that you have given in ii)? Assume only O_2 can be adsorbed.

1.3 A copper plate was divided into two parts, Cu(1) and Cu(2). Cu(1) was then hammered so that Cu(1) and Cu**(2)** are different in certain thermodynamic properties.

i) An galvanic cell with Cu(1) and Cu**(2)** was designed as Cu(1)lCuSO$_4$(aq)ICu**(2)** and the electromotive force E of the above cell was expressed as $E = \Phi_R - \Phi_L$, where Φ_R and Φ_L being the right and left electrode potentials (i. e. half-cell potentials), respectively. Please choose the correct E value from the following and give the thermodynamic reason for your choice.

(A) $E < 0$ (B) $E = 0$ (C) $E > 0$ (D) It cannot be decided

ii) Write the net cell reaction for the cell.

1.4 In a Cu-Zn alloy the molar fractions of Cu and Zn are 0.750 and 0.250, respectively. The structure type of the alloy is the same as that of pure copper, except Zn atoms substitute some Cu atoms randomly and statistically, i. e. at every atomic position, the probability of the occupation of Cu and Zn is proportional to the composition of the alloy. In this sense the alloy can be considered as composed of statistical atoms Cu_xZn_{1-x}. X-ray analysis shows that the arrangement of atoms in the alloy is of the cubic face-centred close packing type. Density of the alloy d = 8.51 g cm^{-3}. Calculate the radius of the statistical atoms in the alloy.

Given: A_r (Cu) = 63.5, A_r (Zn) = 65.4.

SOLUTION

1.1 i)

a) $2\ CuCl(s) + H_2O(l) \rightarrow Cu_2O(s) + 2\ H^+(aq) + 2\ Cl^-(aq)$

b) $Cu_2O(s) + ½\ O_2(g) + H_2O(l) + H^+(aq) + Cl^-(aq) \rightarrow Cu_2(OH)_3Cl(s)$

c) $2\ CuCl(s) + ½\ O_2\ (g) + 2\ H_2O(l) \rightarrow Cu_2(OH)_3Cl\ (s) + H^+(aq) + Cl^-(aq)$

ii) a) $\Delta G^0 = 69$ kJ mol^{-1}

b) $\Delta G^0 = -824$ kJ mol^{-1}

c) $\Delta G^0 = -755$ kJ mol^{-1}

iii) Calculation (dilute HCl solution can be considered as an ideal solution)

$\Delta_r G = \Delta_r G^0 + 2\ RT \ln [H^+]\,[Cl^-] = -22.3$ kJ mol^{-1} < 0

Spontaneous: to the right

1.2 i) Formula: $\ln \frac{k_c(T_2)}{k_c(T_1)} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$E_a = 34.2$ kJ mol^{-1}

ii) overall reaction order = 0

when b $p(O_2) \gg 1$

$$r = k_c\ \theta = \frac{k_c\, b\, p(O_2)}{1 + b\, p(O_2)}; \quad r = k_c \quad \textit{zero order}$$

1.3 i) (C) $E > 0$

ii) Net cell reaction: Cu(1) = Cu(2)

Thermodynamic reason for choosing 3 (C) is $\Delta_r G < 0$, $\Delta_r G = -nFE$ and $E > 0$

1.4 $r = 1.30\times10^{-10}$

formula: $a = 2\sqrt{2r}$

$$d = \frac{4\left(63.5\times0.75\ +\ 65.4\ \times\ 0.25\right)\times10^{-3}}{a^3 N_A}\ =\ 8.51\times10^{-3}\ \text{kg m}^{-3}$$

$r^3 = 2.209\times10^{-30}$ m^3

r = 1.30×10^{-10} m

PROBLEM 3

In 1908 Rutherford together with H.Geiger measured the rate of emission of α-particles (*x*) by radium (in the nature this element is represented by a single nuclide $^{226}_{88}\mathrm{Ra}$) and found that 1.00 g of radium emits $x = 3.42\times10^{10}$ α - particles per second.

In 1911 Rutherford and American physical chemist B.Boltwood measured the rate of formation of helium from radium. This experiment permits to obtain the most accurate value of Avogadro's number available at that time, given that the value of molar volume of ideal gas was well established. To achieve this goal a sample of radium salt purified from decay products and containing m = 192 mg of Ra was put into a device and the volume of the evolved helium was measured. After 83 days (t = 83.0 days) of the experiment 6.58 mm^3 of He was collected (V_{He} = 6.58 mm^3 corrected to 0^{o} C and 1 atm).

To understand the results of this experiment we shall need the kinetic scheme of radioactive decay of Ra which is given below (half-lives are over the arrows, the type of decay is below the arrows).

$$\mathrm{Ra}\xrightarrow[\alpha]{>1500\ \text{years}}\mathrm{Rn}\xrightarrow[\alpha]{3.83\ \text{days}}\mathrm{RaA}\xrightarrow[\alpha]{3.05\ \text{min}}\mathrm{RaB}\xrightarrow[\beta]{26.8\ \text{min}}\mathrm{RaC}\xrightarrow[\beta]{19.7\ \text{min}}$$

$$\longrightarrow\mathrm{RaC'}\xrightarrow[\alpha]{1.63\times10^{-4}\text{s}}\mathrm{RaD}\xrightarrow[\beta]{27.1\ \text{years}}\mathrm{RaE}\xrightarrow[\beta]{5\ \text{days}}\mathrm{Po}\xrightarrow[\alpha]{138\ \text{days}}\mathrm{Pb}\ \text{(stable)}$$

(RaA -RaE are intermediate products of radon decay).

3.1 Write the first six radioactive decays using a modern notation showing atomic and mass numbers of all nuclei involved.

As a rough first approximation half-lives of all radium decay products, except those of RaD and Po, may be assumed to be negligible compared to the time of measurement *t*. Using this approximation perform the following calculations.

3.2 a) How many helium atoms were formed from each decayed radium atom after 83 days?

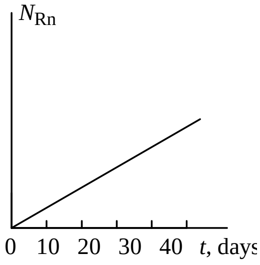
b) How many helium atoms were formed in total during the experiment?

3.3 Calculate an approximate value of Avogadro's number from the above data.

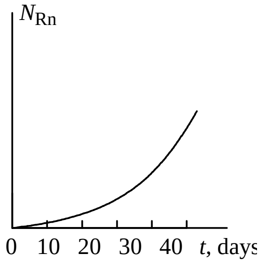
For a more accurate computation of Avogadro's number the half-life of radon $T_{1/2}$(Rn) = 3.83 days cannot be neglected as it is comparable with the duration of experiment t and not all of radon atoms decayed to the end of experiment.

3.4 Choose which of the plots given below displays the time dependence of the number N_{Rn} of radon atoms in the course of the experiment.

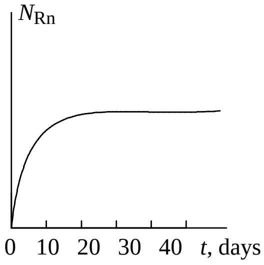
A



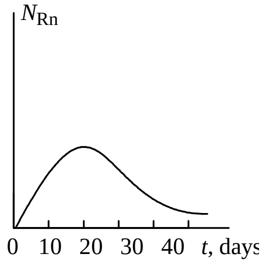
B



C

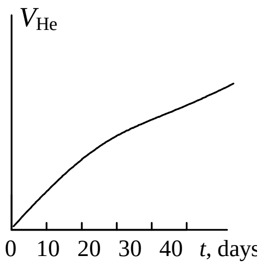


D

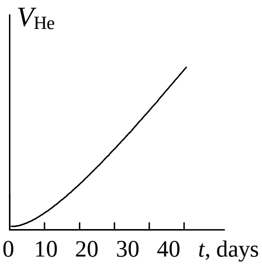


3.5 Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.

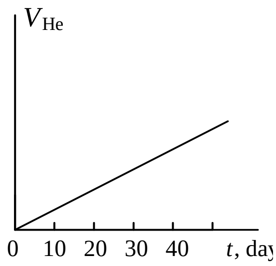
E



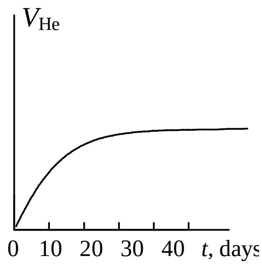
F



G



H



3.6 Choose the relation between the decay rate k of any given nuclide and its half-life $T_{1/2}$.

3.7 a) Using a short kinetic scheme

$$\text{Ra} \xrightarrow{k_1} \text{Rn} \xrightarrow{k_2} \text{RaA}$$

(where k_1 and k_2 are the rate constants of the corresponding reactions) and the plot which you have selected in question 4, write a relation between the number of radon atoms at the end of experiment N'_{Rn} and the number of radium atoms N_{Ra}.

b) Calculate N'_{Rn} using the rate of radium decay given above ($x = 3.42 \times 10^{10}$ α-particles per gram of radium per second).

3.8 How many helium atoms could be formed from radon atoms remaining at the end of experiment N'_{Rn}, if all these atoms had decayed to RaD?

3.9 Using the solutions of the above questions calculate a better approximation to:

a) the number of helium atoms formed;

b) the Avogadro's number.

SOLUTION

3.1 $^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$

$^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$

$^{218}_{84}\text{Po} \rightarrow {}^{214}_{82}\text{Pb} + {}^{4}_{2}\text{He}$

$^{214}_{82}\text{Pb} \rightarrow {}^{214}_{83}\text{Bi} + \text{e}$

$^{214}_{83}\text{Bi} \rightarrow {}^{214}_{84}\text{Po} + \text{e}$

$^{214}_{84}\text{Po} \rightarrow {}^{210}_{82}\text{Pb} + {}^{4}_{2}\text{He}$

3.2 a) The correct answer: 4

b) Number of helium atoms (rough 1.9×10^{17} estimate)

$N_{\text{He}} = 4\,x\,m\,t = 1.9\times10^{17}$

3.3 The first estimate of Avogadro's number: 6.4×10^{23} mol^{-1}

Solution: The Avogadro's number N_A is the number of particles in one mole.

$N_A = N_{\text{He}} / \nu_{\text{He}}$, where N_{He} is number of helium atoms, and ν_{He} is the number of moles of helium formed within time t. If we assume that all radon atoms formed from radium atoms decayed during the time of experiment (this assumption follows from the assumption that radon half-life can be neglected in comparison with 83 days, that introduces an error of about 5 %), then we obtain that during time t the number of helium atom emitted is $N_{\text{He}} = 4xmt$, and

$$N_A = \frac{4\,x\,m\,t}{\nu_{\text{He}}} = \frac{4\times3.42\times10^{10}\times0.192\times(83\times24\times3600)}{\dfrac{6.58\times10^{-6}}{22.4}} = 6.4\times10^{23}\ \text{mol}^{-1}.$$

3.4 Correct answer: **C.**

The number of radon atoms reaches a quasi-stationary state which is sometimes called as the radioactive equilibrium.

3.5 Correct answer: **F.**

In the beginning helium is formed only from α-particles emitted by radium, but to the end of the experiment α-particles are emitted both by radium and by decay products, the amount of which is four times that of radium.

3.6 Underline the correct answer:

$k = 1 / T_{1/2}$	$\underline{k = \ln 2 / T_{1/2}}$	$k = \ln 2 \cdot T_{1/2}$	$k = \pi / T_{1/2}$

3.7 a) Underline the correct answer:

$\underline{N'_{Rn} = k_1 \cdot N_{ra} / k_2}$	$N'_{Rn} = k_2 \cdot N_{Ra} / k_1$	$N'_{Rn} = k_1 \cdot N_{Ra} / 2k_2$	$N'_{Rn} = k_1 \cdot N_{Ra} / 3k_2$

The number of radon atoms reaches a quasi-stationary state, at which the rate of formation is equal to the rate of decay $k_2 N'_{Rn} = k_1 N_{Ra}$, whence $N'_{Rn} = k_1 \cdot N_{Ra} / k_2$

b) $N'_{Rn} = 3.14 \times 10^{15}$

The rate of radium decay is $k_1 N_{Ra} = xm$, whence

$$N'_{Rn} = \frac{xm}{\frac{\ln 2}{T_{1/2(Rn)}}} = \frac{3.42 \times 10^{10} \times 0.192}{\frac{0.693}{3.83 \times 24 \times 3600}} = 3.14 \times 10^{15}$$

3.8 Underline the correct answer:

$4N'_{Rn}$	$2N'_{Rn}$	$5N'_{Rn}$	N'_{Rn}	$\underline{3N'_{Rn}}$

3.9 a) A more accurate estimate of the number of helium atoms: 1.79×10^{17}

$$N_{He} = 4\,xmt - 3N'_{Rn} = 1.9 \times 10^{17} - 3 \times 3.14 \times 10^{15} = 1.79 \times 10^{17}$$

b) A more accurate estimate of Avogadro's number (mol^{-1}): 6.09×10^{23}

$$N_{\text{À}} = \frac{N_{He}}{n(\text{He})} = \frac{1.79 \times 10^{17}}{\frac{6.58 \times 10^{-6}}{22.4}} = 6.09 \times 10^{23}$$

PROBLEM 2

Professor Molina of the Massachusetts Institute of Technology won the 1995 Nobel Prize in Chemistry for his work on atmospheric chemistry. One reaction that he has studied in detail is the acid rain reaction which produces H_2SO_4 in the atmosphere. He has proposed two possible stoichiometric reactions:

Proposal A: $H_2O (g) + SO_3 (g) \rightarrow H_2SO_4 (g)$

Proposal B: $2 H_2O (g) + SO_3 (g) \rightarrow H_2SO_4 (g) + H_2O (g)$

2.1 Using simple collision theory, what reaction orders would be expected for Proposal A and for Proposal B?

Proposal B is thought to proceed by the following two-step process:

$$SO_3 + 2 H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3 \bullet 2 H_2O \qquad \text{(fast)}$$

$$SO_3 \bullet 2 H_2O \xrightarrow{k_2} H_2SO_4 + H_2O \qquad \text{(slow)}$$

($SO_3 \bullet 2 H_2O$ is a complex which is stabilized by hydrogen bonds and $k_2 << k_1$ or k_{-1})

2.2 By applying the principle of stationary (steady) states, derive the appropriate rate law and hence the reaction order of the two-step mechanism for Proposal B.

2.3 Recent quantum chemical calculations have shown that the overall reaction activation energies for the two proposals are:

$E_A = + 80$ kJ mol^{-1} for Proposal A $\qquad$ $E_B = – 20$ kJ mol^{-1} for Proposal B

State the relationship between the rate constant and the temperature (Arrhenius relationship) for each proposal and predict the temperature dependence of the rate constants for each proposal.

2.4 The formation of H_2SO_4 is faster in the upper atmosphere (T = 175 K) than at the earth's surface (T = 300 K). Which proposed pathway must dominate in the upper atmosphere given the activation energies in part (iii) and your understanding of the Arrhenius equation?

SOLUTION

2.1 Proposal A: $$\frac{d[\mathrm{H_2SO_4}]}{dt} = k\,[\mathrm{H_2O}]\,[\mathrm{SO_3}]$$

Summing the exponents gives a second order process

Proposal B: $$\frac{d[\mathrm{H_2SO_4}]}{dt} = k\,[\mathrm{SO_3}][\mathrm{H_2O}]^2$$

Summing the exponents gives a third order process

2.2 The steady state approximation gives:

The rate law here will be similar to that found for an enzymatic process which proceeds through a rapid reversible binding step followed by a slower reaction process.

$$\frac{d[\mathrm{SO_3 \cdot 2\,H_2O}]}{dt} = k_1[\mathrm{SO_3}][\mathrm{H_2O}]^2 - k_{-1}[\mathrm{SO_3 \cdot 2\,H_2O}] - k_2[\mathrm{SO_3 \cdot 2\,H_2O}] = 0$$

Thus: $$k_{-1}[\mathrm{SO_3 \cdot 2\,H_2O}] + k_2\,[\mathrm{SO_3 \cdot 2\,H_2O}] = k_1\,[\mathrm{SO_3}]\,[\mathrm{H_2O}]^2$$

and therefore: $$[\mathrm{SO_3 \cdot 2\,H_2O}] = \frac{k_1\,[\mathrm{SO_3}][\mathrm{H_2O}]^2}{k_{-1} + k_2}$$

Also: $\dfrac{d[\mathrm{H_2SO_4}]}{dt} = k_2\,[\mathrm{SO_3 \cdot 2\,H_2O}]$ and substituting from above yields

$$\frac{d[\mathrm{H_2SO_4}]}{dt} = k_2\,[\mathrm{SO_3 \cdot 2\,H_2O}] = \frac{k_1 k_2 [\mathrm{SO_3}]\,[\mathrm{H_2O}]^2}{k_{-1} + k_2}$$

However, since $k_2 << k_{-1}$ the above reduces to:

$$\frac{d[\mathrm{H_2SO_4}]}{dt} = \frac{k_1 k_2\,[\mathrm{SO_3}][\mathrm{H_2O}]^2}{k_{-1}} = K_{eq}\,k_2\,[\mathrm{SO_3}][\mathrm{H_2O}]^2 = k\,[\mathrm{SO_3}][\mathrm{H_2O}]^2$$

which is also third order

2.3 Knowing the Arrhenius relationship: $k = A\,\mathrm{e}^{-E/RT}$

For proposal A: $k = A\,\mathrm{e}^{-E_A/RT} = A\,\mathrm{e}^{-83.6/RT}$ which increases with increasing T.

For proposal B only the slow step is critical in determining the dependence of the rate constant on the temperature. The complexation step is very stable which explains the negative activation energy.

For proposal B: $k = A\,\mathrm{e}^{-E_B/RT} = A\,\mathrm{e}^{+83.60/RT}$ which decreases with increasing T

2.4 Assuming that the pre-exponential factors are comparable in magnitude as is usually the case, the reaction will be faster at the lower temperatures found in the upper atmosphere due to the temperature dependence deduced above, and thus Proposal B must be operating. The rational for Proposal B which involves the relative sizes of the rate constants is nonsense and was included to balance the choices. The rational for Proposal A involving collision probabilities appears plausible but is not a factor — it is the massive negative activation energy which controls the situation.

PROBLEM 5

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centred cubic (bcc) lattice known as α-iron. From 1185 K to 1667 K, the structure becomes face-centred cubic (fcc) and is called γ-iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of α-iron. The latter phase is called δ-iron.

Given that the density of pure iron metal is 7.874 g cm^{-3} at 293 K:

5.1 Calculate the atomic radius of iron (expressed in cm).

5.2 Calculate its density (expressed in g cm^{-3}) at 1250 K.

Notes: Ignore the small effects due to the thermal expansion of the metal.

Clearly define any symbols which you use, e.g. r = atomic radius of Fe.

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1 % to 4.0 %. In a blast-furnace, the melting of iron is facilitated when it contains 4.3 % of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α-iron phase. This new solid, called martensite, is extremely hard and brittle. Although is it slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of α-iron (bcc).

Assuming that the carbon atoms are evenly distributed in the iron structure:

5.3 Calculate the average number of carbon atoms per unit cell of α-iron in martensite containing 4.3 % C by mass.

5.4 Calculate the density (expressed in g cm^{-3}) of this material.

Molar masses and constants:

M(Fe) = 55.847 g mol^{-1}

M(C) = 12.011 g mol^{-1}

$N_A = 6.02214\times10^{23}$ mol^{-1}

SOLUTION

5.1 Calculation of the atomic radius of iron (expressed in cm).

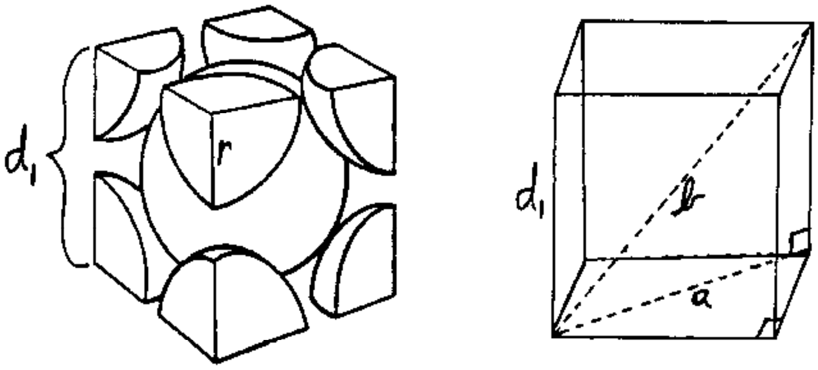
5.2 Calculation of its density (expressed in g cm^{-3}) at 1250 K.

Expected steps of the calculation:

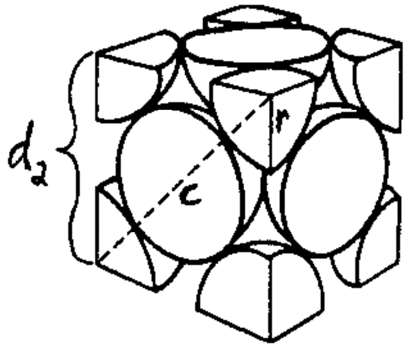
1. Define the length a, b, c, d_1, d_2, and r and volume V_1 and V_2 parameters for both bcc and fcc structures of iron (*cf.* Details below).
2. Calculate the volume V_1 of the unit cell of α-iron from its density ρ_{bcc} at 293 K, the molar weight *M*(Fe) of iron, and Avogadro's number N_A.
3. Calculate the length d_1 of the edge of the bcc unit cell from its volume V_1.
4. Calculate the atomic radius *r* of iron from the length "d_1".
5. Calculate the length d_2 of the edge of the fcc unit cell at 1250 K from the atomic radius r of iron.
6. Calculate the volume V_2 of the fcc unit cell of γ-iron from the length d_2 of its edge.
7. Calculate the mass *m* of the number of iron atoms in a unit cell of γ-iron from the molar weight *M*(Fe) of iron and Avogadro's number N_A.
8. Calculate the density ρ_{fcc} of γ-iron from the values of "*m*" and "V_2".

An alternative route to ρ_{fcc} of γ-iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

5'. Calculate the percent space filling ratio of the bcc unit cell.
6'. Calculate the percent space filling ratio of the fcc unit cell.
7'. Calculate the ρ_{fcc}/ρ_{bcc} density ratio from the fcc/bcc space filling ratios.
8'. Calculate the density ρ_{fcc} of γ-iron from the value found in step 7'.



Body centered cubic structure (bcc)



Face-centered cubic structure (fcc)

Calculations in details

At 293 K, α-iron has a bcc crystal structure.

Each unit cell possesses 2 atoms and one of them is in the center of the cell.

At 1250 K, γ-iron has a fcc crystal structure.

Each unit cell possesses 4 atoms and each side has one-half an atom at its center.

r = atomic radius of iron.

a = length of the diagonal on one side of the bcc unit cell.

b = length of the diagonal passing through the center of the bcc unit cell.

c = length of the diagonal on one side of the fcc unit cell.

d_1 = length of the edge of the bcc unit cell of α-iron.

d_2 = length of the edge of the fcc unit cell of γ-iron.

V_1 = Volume of the bcc unit cell of α-iron.

V_2 = Volume of the fcc unit cell of γ-iron.

V_a = Volume of one atom.

V_{a1} = Volume occupied by 2 atoms in one bcc unit cell.

V_{a2} = Volume occupied by 4 atoms in one fcc unit cell.

R_1 = Percent space filling ratio in a bcc unit cell.

R_2 = Percent space filling ratio in a fcc unit cell.

$V_a = (4/3)\ \pi\ r^3$ $\qquad V_{a1} = 2\ V_a$ $\qquad V_{a2} = 4\ V_a$

$b = 4\ r$; $\qquad a^2 = 2\ d_1^2$; $\qquad b^2 = d_1^2 + a^2 = 3\ d_1^2$

$d_1 = (b^2/3)^{1/2} = (16\ r^2/3)^{½}$; $\qquad V_1 = d_1^3 = [(16\ r^2/3)^{1/2}]^3$

$c = 4\ r$; $\qquad c^2 = 2\ d_2^2$

$d_2 = (c^2/2)^{1/2} = (16\ r^2/2)^{½}$; $\qquad V_2 = d_2^3 = [(16\ r^2/2)^{½}]^3$

2. 1.000 cm^3 of iron weights 7.874 g at 293 K (ρ_{bcc}).

1 mole of iron weights 55.847 g (M_{Fe}).

Thus, 0.1410 mol (7.874 g / 55.847 g mol^{-1}) of iron occupy a volume of 1.000 cm^3 or 1 mole of iron will occupy a volume of 7.093 cm^3

1 mole corresponds to 6.02214×10^{23} atoms

V_1 = (7.093 cm^3 mol^{-1}) × (2 atoms/unit cell) / (6.02214×10^{23} atoms mol^{-1})

$V_1 = 2.356\times10^{-23}$ cm^3 per unit cell

3. $d_1 = (V_1)^{1/3} = (2.356\times10^{-23}\ cm^3)^{1/3}$

   $d_1 = 2.867\times10^{-8}$ cm

4. For a bcc structure, the value of d_1 can be expressed as: $d_1 = [(16\ r^2)/3]^{1/2}$

   so the value of "r" will be: $r = (3\ d_1^2/16)^{1/2}$

   $r = [3\ (2.867\times10^{-8}\ cm)^2/16]^{1/2}$

   $r = 1.241\times10^{-8}$ cm

5. At 1250 K, in the fcc structure, the value of "d_2" is given by: $d_2 = (16\ r^2/2)^{1/2}$

   $d_2 = [16\ (1.241\times10^{-8}\ cm)^2/2]^{1/2}$

   $d_2 = 3.511\times10^{-8}$ cm

6. $V_2 = d_2^3 = (3.511\times10^{-8}\ cm)^3$

   $V_2 = 4.327\times10^{-23}\ cm^3$

7. The mass "m" of the 4 iron atoms in the fcc unit cell will be:

   m = (55.847 g mol^{-1}) × (4 atoms/unit cell) / (6.02214×10^{23} atoms mol^{-1})

   $m = 3.709\times10^{-22}$ g per unit cell

8. $\rho_{fcc} = m / V_2 = (3.709\times10^{-22}\ g) / (4.327\times10^{-23}\ cm^3)$

   $\rho_{fcc} = 8.572\ g/cm^3$

   Alternative route to ρ_{fcc} of γ-iron:

5'. $R_1 = [(V_{a1}) / (V_1)] \times 100\% = [(2\ V_a) / (V_1)] \times 100\%$

   $R_1 = ([2 \times (4/3)\ \pi\ r^3] / [(16\ r^2/3)^{1/2}]^3) \times 100\%$

   $R_1 = ([(8/3)\ \pi\ r^3] / [(16/3)^{3/2}\ r^3]) \times 100\%$

   $R_1 = ([(8/3)\ \pi] / [(16/3)^{3/2}]) \times 100\%$

   $R_1 = [(8.378) / (12.32)] \times 100\%$

   $R_1 = 68.02\ \%$

6'. $R_2 = [(V_{a2}) / (V_2)] \times 100\% = [(4\ V_a) / (V_2)] \times 100\%$

   $R_2 = ([4 \times (4/3)\ \pi\ r^3] / [(16\ r^2/2)^{1/2}]^3) \times 100\%$

   $R_2 = ([(16/3)\ \pi\ r^3] / [8^{3/2}\ r^3]) \times 100\%$

$R_2 = ([(16/3)\ \pi] / [8^{3/2}]) \times 100\%$

$R_2 = [(16.76) / (22.63)] \times 100\%$

$R_2 = 74.05\%$

7'. $\rho_{fcc} / \rho_{bcc} = (74.05\%) / (68.02\%)$

$\rho_{fcc} / \rho_{bcc} = 1.089$

8'. $\rho_{fcc} = 1.089 \times \rho_{bcc}$

$\rho_{fcc} = 1.089 \times 7.874$ g cm^{-3}

$\rho_{fcc} = 8.572$ g cm^{-3}

5.3 Calculation of the average number of carbon atoms per unit cell of α-iron in martensite containing 4.3 % C by mass.

5.4 Calculation of the density (expressed in g cm^{-3}) of this material.

Expected Steps of the Calculation:

1. From the percent composition of martensite (by mass), calculate the relative amounts of moles of carbon and iron.
2. Bring the C/Fe molar ratio to one (1) unit cell (Note: 2 Fe atoms per unit cell).
3. Find the smallest whole number of C atoms for the smallest whole number of unit cell (facultative).
4. Calculate the mass of iron per unit cell.
5. Calculate the mass of carbon per unit cell.
6. Calculate the total mass of carbon and iron in one unit cell.
7. Calculate the density of martensite [ρ(martensite at 4.3 %C)] from the total mass of C and Fe and volume (V_1) of α-iron bcc unit cell.

Details:

1. In 100.0 g of martensite at 4.3 % C: (4.3 g C) / (12.011 g mol^{-1}) = 0.36 mol C
   (95.7 g Fe) / (55.847 g mol^{-1}) = 1.71 mol Fe
   So we have 1 carbon atom for 4.8 iron atoms or
   0.21 carbon atoms per iron atom.
2. Martensite has a "bcc" crystal structure (2 iron atoms per unit cell).
   [(1 C atom) / (4.8 Fe atoms)] × (2 Fe atoms / unit cell)
   or: 0.42 carbon atoms per unit cell

3. 5 carbon atoms [(0.42 C atom / 0.42) × 5] in 12 unit cells [(1 unit cell/0.42) × 5].

   5 carbon atoms dispersed in 12 unit cells

4. [(55.847 g/mol) / (6.02214×10^{23} atoms/mol)] × (2 atoms/unit cell of α-iron)

   1.8547×10^{-22} g Fe per unit cell of α-iron

5. (12.011 g/mol) / (6.02214×10^{23} atoms/mol)

   1.9945×10^{-23} g C per atom

6. [1.8547×10^{-22} g Fe + (0.42 C at. × 1.9945×10^{-23} g / C at.)] per unit cell

   1.938×10^{-22} g C and Fe per unit cell

7. Each unit cell of α-iron occupies a volume, $V_1 = 2.356\times10^{-23}$ cm^3

   (*cf.* Question i)

   ρ(martensite at 4.3 % C) = (1.938×10^{-22} g C and Fe) / (2.356×10^{-23} cm^3)

   ρ(martensite at 4.3 % C) = 8.228 g cm^{-3}

PROBLEM 7

7.1 One mole of Cl_2 (g), which may be assumed to obey the ideal gas law, initially at 300 K and 1.01325×10^7 Pa, is expanded against a constant external pressure of 1.01325×10^5 Pa to a final pressure of 1.01325×10^5 Pa. As a result of the expansion, the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl_2), and 0.100 mol of Cl_2 condensed.

The enthalpy of vaporization of Cl_2 (l) is 20.42 kJ mol^{-1} at the normal boiling point, the molar heat capacity of Cl_2 (g) at constant volume is C_v = 28.66 J K^{-1} mol^{-1} and the density of Cl_2 (l) is 1.56 g cm^{-3} (at 239 K). Assume that the molar heat capacity at constant pressure for Cl_2 (g) is $C_p = C_v + R$.

(1 atm = 1.01325×10^5 Pa, R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

i) Either draw a complete molecular orbital energy diagram or write the complete electronic configuration of Cl_2. Predict the bond order of Cl_2 and thus whether this molecule will be diamagnetic, ferromagnetic, or paramagnetic.

ii) For the changes described above, calculate the change in the internal energy (ΔE) and the change in the entropy (ΔS_{sys}) of the system.

7.2 For the following reactions occurring in dilute aqueous solution at 298 K:

$[Ni(H_2O)_6]^{2+} + 2\ NH_3 \rightleftarrows [Ni(NH_3)_2(H_2O)_4]^{2+} + 2\ H_2O$ (1)

$\ln K_c = 11.60$ and $\Delta H^0 = -33.5$ kJ mol^{-1}

$[Ni(H_2O)_6]^{2+} + en \rightleftarrows [Ni(en)(H_2O)_4]^{2+} + 2\ H_2O$ (2)

$\ln K_c = 17.78$ and $\Delta H^0 = -37.2$ kJ mol^{-1}

Note: *en* is ethylenediamine (a neutral bidentate ligand)

(R = 8.314510 J K^{-1} mol^{-1} = 0.0820584 L atm K^{-1} mol^{-1})

Calculate ΔG^0, ΔS^0, and K_c at 298 K for reaction [3] occurring in a dilute aqueous solution:

$[Ni(NH_3)_2(H_2O)_4]^{2+} + en \rightleftarrows [Ni(en)(H_2O)_4]^{2+} + 2\ NH_3$ (3)

SOLUTION

7.1

i) Electronic configuration of a Cl atom:

$1s^2 2s^2 2p_x^{\ 2} 2p_y^{\ 2} 2p_z^{\ 2} 3s^2 3p_x^{\ 2} 3p_y^{\ 2} 3p_z^{\ 1}$

Significant atomic orbitals (AO) = 1(K) + 4(L) + 4(M) = 9 AO

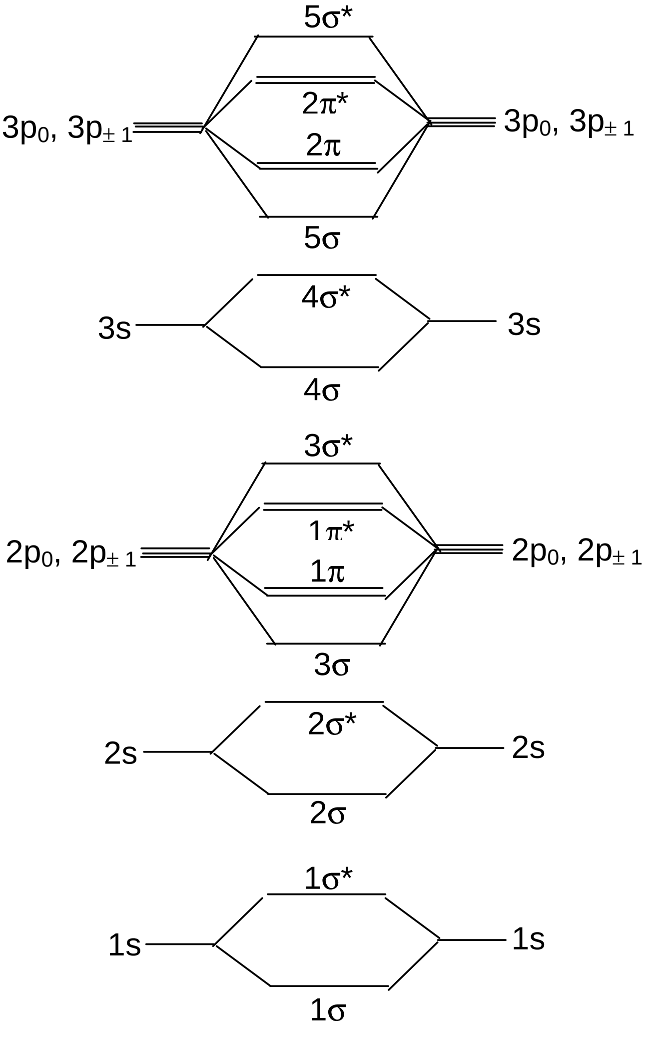
Number of electrons in these AOs: 17

Number of molecular orbitals (MO) equals number of AOs:

Thus 2 x [1(K) + 4(L) + 4(M)] = 18 MOs are present in a Cl_2 molecule

In the formation of Cl_2: 2 x 17 = 34 electrons to go into the 18 MOs.

MO description of Cl_2:



$1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 1\pi^{*4} 3\sigma^{*2} 4\sigma^2 4\sigma^{*2} 5\sigma^2 2\pi^4 2\pi^{*4}$

or

$(KK)(LL)(\sigma 3s)^2(\sigma^* 3s)^2(\sigma 3p)^2(\pi 3p)^4\ (\pi^* 3p)^4$

or

$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2(\sigma^* 2p_z)^2$

$(\sigma 3s)^2(\sigma^* 3s)^2(\sigma 3p_z)^2(\pi 3p_x)^2(\pi 3p_y)^2(\pi^* 3p_x)^2(\pi^* 3p_y)^2(\sigma^* 2p_z)^0$

or

$(KK)(LL)\ (\sigma 3s)^2(\sigma^* 3s)^2(\sigma 3p_z)^2(\pi 3p_x)^2(\pi 3p_y)^2(\pi^* 3p_x)^2(\pi^* 3p_y)^2(\sigma^* 2p_z)^0$

*assumption: - bond formation is along the z-axis

(equivalent formulae for x or y axes are accepted)

Bond order is given by (n-n*)/2:

n = 18; n* = 16

(18 – 16) / 2 = 1

(1 σ bond, no π bond)

The Cl_2 molecule has a bond order of 1.

The Cl_2 molecule is diamagnetic since there are no unpaired electrons.

ii) Summary of the changes involved:

$$\begin{array}{c} Cl_2\ (g) \\ 1\ \text{mol} \\ 300\ \text{K} \end{array} \xrightarrow[\substack{\text{cooled} \\ 1.013\times10^7\ \text{Pa} \\ (100\ \text{atm})}]{\Delta E_1} \begin{array}{c} Cl_2\ (g) \\ 1\ \text{mol} \\ 239\ \text{K} \end{array} \xrightarrow[\substack{1.013\times10^5\ \text{Pa} \\ (1\ \text{atm})}]{\Delta E_2} \begin{array}{c} Cl_2\ (l) \\ 0.1\ \text{mol} \\ 239\ \text{K} \end{array}$$

The total process is an expansion plus an isobaric change of phase (gas to liquid) and since the internal energy (E) is a function of state, the total change in the internal energy is $\Delta E = \Delta E_1 + \Delta E_2$.

Process 1:

$$\Delta E_1 = \int n\, C_v dT = 1 \times 28.66 \times 239 - 300 = -1748.3\ \text{J}$$

Note: a) ΔE for a perfect gas is a function only of T

b) C_v is constant

c) "–" sign means a loss of energy due to the work needed for expansion of 1 mole of gas

Process 2: For convenience, the data were manipulated in atm; equivalent procedure in Pa will require the appropriate conversion factor

From an energetic point of view, the liquid formation Process 2 can be split into two separate steps :

- the vaporization heat loss (decreased internal energy, -) from the system into surroundings (since the process takes place at constant pressure, the heat is equal to the change in the enthalpy)
- the work done by the surroundings in compressing the system to a smaller volume (increased internal energy, +).

Volume of gas which condensed is

$V = n\,R\,T\,/\,P$ = (0.1 × 0.0820584 × 239) / 1 = 1.96 dm^3

Volume of liquid Cl_2: (0.1 × 2 × 35.454) / 1.56 = 4.54 cm^3

$$\Delta E_2 \;=\; \Delta H_2 - \int P_{\text{ext}} \Delta V(\text{phase change}) \;=\; \Delta H_2 - P_{\text{ext}}(V_{\text{l}} - V_{\text{g}})$$

but V_l is approximately 0 and can be neglected

(ca. 4.5 cm^3 liquid volume vs. ca. 17.6 dm^3; ca. 0.03 % error)

$\Delta E_2 = (0.1)\,(-\Delta H_{vap}) + P_{\text{ext}}V\text{g}$

= 0.1 × (– 20420) + (1 × 1.96 L) × 101.325 J dm^{-3} atm^{-1} = –2042.0 + 198.5 = –1843.5

$\Delta E = \Delta E_1 + \Delta E_2$ = –1748.3 + (–1843.5) = –3591.8

Entropy S is a function of two variables of state. Since in Process 1 the known variables are T and P, expression of S is chosen as $S(T,P)$.

$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2$ and

$$\overline{C}_p \;=\; \overline{C}_v + R \;=\; 28.66 + 8.314 \;=\; 36.97\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta S_1 = n\,C_p \ln\frac{T_2}{T_1} - n\,R\ln\frac{P_2}{P_1} = 1.0 \times 36.97 \ln\frac{239}{300} - 8.314\ln\frac{1}{100} == \;-8.40\;+\;38.29\;=$$

$= 29.89\ \text{J K}^{-1}$

For the phase transition (constant temperature), by definition $\Delta S_2 = Q\,/\,T$

Since the pressure is constant in this case, $Q\,/\,T = Q_{\text{p}}\,/\,T = \Delta H\,/\,T$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{0.1 \times (-20420)}{239} = -8.54\ \text{J K}^{-1}$$

ΔS_{sys} = 29.89 – 8.54 = 21.35 J K^{-1}

7.2 Beware of round-off errors in the variations to the solution to this problem: One can get small differences due to conversion into and out of the *ln* relationships. It is the approach which matters.

One reverses the signs of $\ln K_c$ and ΔH^0 for Reaction 1 when it is reversed.
Equilibrium constants are multiplied when equations are added, thus ln*K*'s will add.

Reaction 3 = Reaction 2 - Reaction 1
Thus $\Delta S_3 = \Delta S_2 - \Delta S_1$ and $\Delta G_3 = \Delta G_2 - \Delta G_1$
$\Delta G^0_1 = - R\ T \ln K_{c1} = - 8.314 \times 298 \times 11.60 = - 28740$ J mol^{-1} = –28.74 kJ mol^{-1}
$\Delta H^0_1 = - 33.5$ kJ mol^{-1}
$\Delta S^0_1 = (\Delta H^0_1 - \Delta G^0_1) / T$
= (– 33.5) – (– 28.74)) / 298 = – 0.0161 kJ K^{-1} mol^{-1} = –16.1 J K^{-1} mol^{-1}
Similarly:
$\Delta G^0_2 = - 44.05$ kJ mol^{-1}
$\Delta H^0_2 = - 37.2$ kJ mol^{-1}
$\Delta S^0_2 = - 22.98$ J K^{-1} mol^{-1}
Reaction 3 = Reaction 2 – Reaction 1, thus
$\Delta H^0_3 = \Delta H^0_2 - \Delta H^0_1 = - 3.7$ kJ
$\Delta S^0_3 = \Delta S^0_2 - \Delta S^0_1 = 39.08$ J K^{-1}
$\Delta G^0_3 = \Delta H^0_3 - \mathrm{T}\ \Delta S^0_3 = -15.35$ kJ mol^{-1}

Thus $K_{c3} = \mathrm{e}^{\frac{15.35}{RT}} = 4.90 \times 10^2$

Alternatively:
$\Delta G^0_3 = \Delta G^0_2 - \Delta G^0_1 = - 44.05 - (-28.74) = -15.31$ kJ mol^{-1} thus $K = 4.82 \times 10^2$)
$\Delta S^0 = (\Delta H^0 - \Delta G^0) / \mathrm{T} = (- 3700 - (-15311)) / 298 = 38.96$ J K-1

PROBLEM 2

Part A: Dating Historical Events Using Pb-210

Nathan Thompson, one of the first inhabitants of Lord Howe Island, decided to plant some European deciduous trees in his garden. Unfortunately the exact timing of the planting of the seeds is not known. Over the years, pollen produced by the European oak and elm accumulated at the bottom of the lake near Nathan's house. Very small quantities of radioactive Pb-210 (half-life = 22.0 years) were deposited at the same time. Note that the European oak and elm trees pollinate in their first year of growth.

In 1995, a team of researchers sampled a sediment core from the bottom of the lake. The sediment core was cut into 1 cm slices and examined for pollen and radioactive Pb-210.

The examination of the sediment core found that:

- Pollen of European oak and elm first occur at a depth of 50 cm.
- The activity of Pb-210 at the top of the sediment core is 356 Bq/kg and at 50 cm depth 1.40 Bq/kg.

2.1 In what year did Nathan Thompson plant the seeds?

Radioactive Pb-210 is one of the daughters of U-238. U-238 is present in the earth's crust and for some reason a certain amount of Pb-210 rains out of the atmosphere and attaches itself to sediment particles that accumulate at the bottom of lakes.

- The U-238 decay chain is:
- U-238 – U-234 – Th-230 – Ra-226 – Rn-222 – (Po-218 – Bi-214)* – Pb-210 – Pb-206 (stable)

  * Very short half-lives: minutes and days

2.2 Which step in the decay scheme explains how Pb-210 ends up in rainwater while its parent U-238 is only present in the earth's crust?

Part B: Separation of Radionuclides for Nuclear Medicine Applications.

The Ga-67 is used to image lymphoma. It is preferentially produced by bombarding a target enriched in Zn-68 (> 98%) with high energy protons for 11 hrs. Zn-68 has a natural abundance of 18.8%. Due to the target design other radionuclides may be produced (see Table 1). Twelve hours after the end of bombardment, Ga-67 is bound on a cation exchange. Then the other radionuclides and the Zn-68 are eluted in the wash solution leaving Ga-67 bound to the column.

Table 1

Radionuclide	Half-life
Co-55	18.2 hr
Ni-57	36.0 hr
Co-57(daughter of Ni-57)	270 days
Cu-64	12.7 hr
Cu-67	61.7 hr
Zn-65	244 days
Ga-67	78.35 hr
Ga-66	9.4 hr

Cu-64 and Co-55 have ideal half-lives for use in nuclear medicine applications and it would be useful to isolate them from the wash solution.

The distribution coefficient *D* is a measure of the partition of a metal ion between the ion-exchange resin and the eluant.

For a given ion-exchange resin and eluant, *D* is given by

$$D = \frac{\text{radioactivity per mg of resin}}{\text{radioactivity per cm}^3\text{ of eluant}}$$

For a reasonable separation of two metal ions their *D* values should differ by at least 10 units.

2.3 The wash solution is evaporated to dryness and the residue resuspended in a small amount of 0.2 M HCl 96 % methanol and loaded onto an anion exchange column. Use the distribution coefficients *D* given in Figures 1 and 2 and rank the best solvent systems (from given alternatives) for eluting Cu-64 and Co-55.

2.4 Having isolated relevant radionuclides, the presence of some long-lived radionuclides could interfere with medical use of Cu-64 or Co-55 or Ga-67. Indicate which of the following statements is either true or false (one or more may be true).

a) Ni-57 may be present as a contaminant of Co-55.
b) Co-57 will interfere with the medical use of Co-55.
c) Cu-67 will interfere with the medical use of Cu-64.
d) Ga-66 will interfere with the use of Ga-67.
e) Ga-67 will interfere with the medical use of Cu-64.

2.5 If radionuclide contamination of Cu-64 or Co-55 or Ga-67 occurred, which method would reduce the amount of radionuclide contaminant/s? Indicate which of the following statements is either true or false. (one or more may be true).

a) Remove Ni-57 before isolating Co-55.
b) Separate the Ni-57 from the bombarded target material before isolating the Ga-67.
c) Separate the radionuclides closer to the end of bombardment.
d) Allow the Ni-57 to decay before isolation of Co-55.

2.6 If zinc of natural isotopic abundance, instead of enriched Zn-68, was bombarded with high energy protons, indicate which of the following statements is either true or false. (one or more may be true).

a) Ga-67 would be produced at 5 fold higher yields.
b) Ga-67 would be produced at 5 fold lower yields.
c) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would increase.
d) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would remain the same.

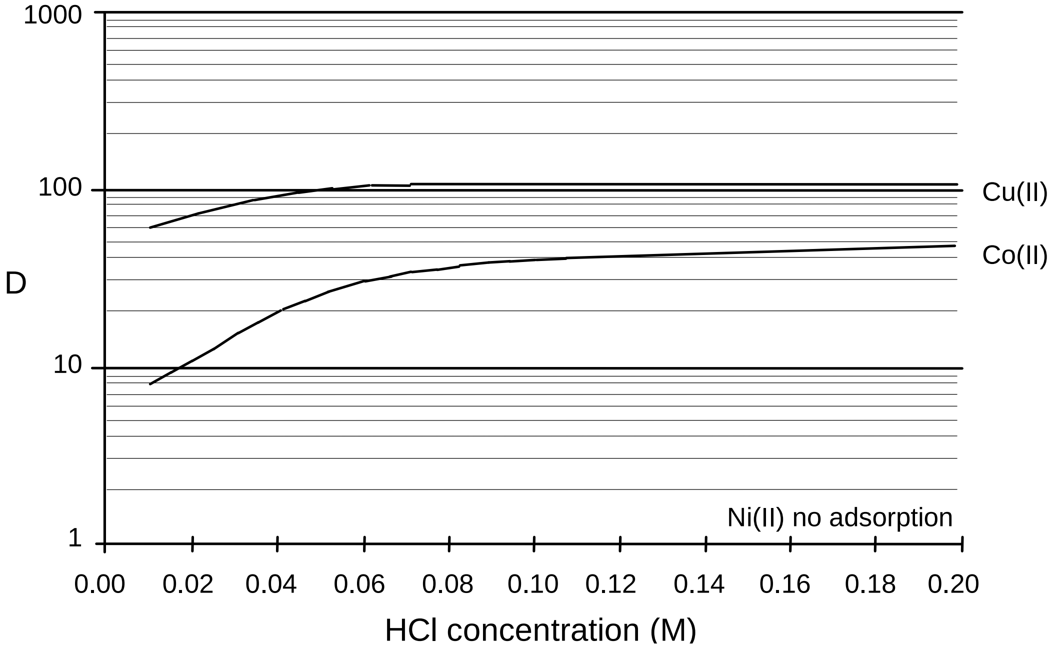


Figure 1. Distribution coefficients, *D* of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note *D* value for Zn > 1000)

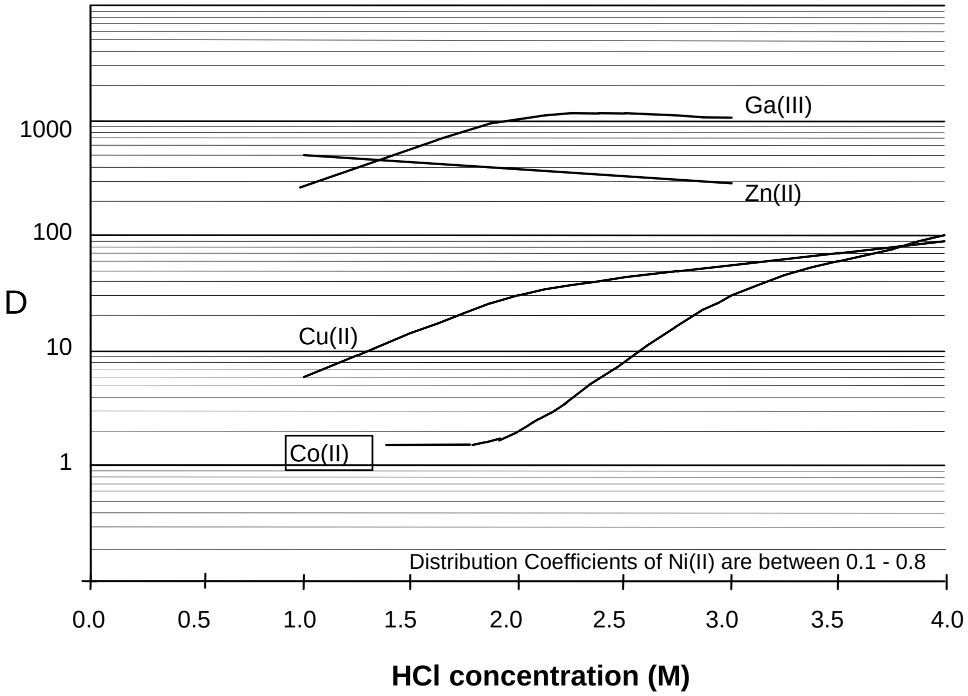


Figure 2. Distribution coefficients, *D* of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

SOLUTION

2.1 In what year did Nathan Thompson plant the seeds?

Calculations:

Over a depth of 50 cm the apparent decay of Pb-210 was equal to 356 – 178 – 89 – 44.5 – 22.5 – 11.25 – 5.63 – 2.81 – 1.39 = 8 half-lives = 8 × 22 years = 176 years

If 1995 was the year of coring then the year of arrival was 1995 – 176 = 1819 (±2)

2.2 Correct answer: Ra-226 - Rn-222

2.3 Use the distribution coefficients *D* given in Figures 1 and 2 and rank the following solvent systems for isolating Cu-64 and Co-55 by writing the numbers 1 to 4 in the boxes (1 is best).

A 0.2 M HCl 96% methanol to remove Ni-57 followed by
2.0 M HCl 55% isopropyl alcohol to remove Cu-64 followed by
1.0 M HCl 55% isopropyl alcohol to remove Co-55

B 0.2 M HCl 96% methanol to remove Ni-57 followed by
2.0 M HCl 55% isopropyl alcohol to remove Co-55 followed by
1.0 M HCl 55% isopropyl alcohol to remove Cu-64

C 2.0 M HC1 55% isopropyl alcohol to remove Co-55 followed by
1.0 M HC1 55% isopropyl alcohol to remove Cu-64

D 0.2 M HC1 96% methanol to remove Ni-57 followed by
3.0 M HC1 55% isopropyl alcohol to remove Co-55 followed by
4.0 M HC1 55% isopropyl alcohol to remove Cu-64

The best sequence: B, C, D, A

The other sequences: B, C, A, D or C, B, D, A or C, B, A, D were also accepted but evaluated by less points.

2.4 a) False;
b) True;
c) True
d) False
e) False

2.5 a) True

b) True

c) True

d) False

2.6 a) False

b) True

c) False

d) True

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THEORETICAL PROBLEMS

PROBLEM 1

A compound **Q** (molar mass 122.0 g mol^{-1}) consists of carbon, hydrogen and oxygen.

PART A

The standard enthalpy of formation of CO_2(g) and H_2O(l) at 25.00 °C are –393.51 and –285.83 kJ mol^{-1}, respectively. The gas constant, R = 8.314 J K^{-1} mol^{-1}.
(Relative atomic masses : H = 1.0; C = 12.0; O = 16.0)

A sample of solid **Q** that weighs 0.6000 g, is combusted in an excess of oxygen in a bomb calorimeter, which initially contains 710.0 g of water at 25.000 °C. After the reaction is completed, the temperature is observed to be 27.250 °C, and 1.5144 g of CO_2 (g) and 0.2656 g of H_2O(l) are produced.

1.1 Determine the molecular formula and write a balanced equation with correct state of matters for the combustion of **Q**.

If the specific heat of water is 4.184 J g^{-1} K^{-1} and the internal energy change of the reaction (ΔU^0) –3079 kJ mol^{-1}.

1.2 Calculate the heat capacity of the calorimeter (excluding the water).

1.3 Calculate the standard enthalpy of formation ($\Delta H_f^{\,0}$) of **Q**.

PART B

The following data refer to the distribution of **Q** between benzene and water at 6 °C, C_B and C_W being equilibrium concentrations of the species of **Q** in the benzene and water layers, respectively:

Assume that there is only one species of **Q** in benzene independent of concentration and temperature.

Concentration (mol dm^{-3})	
c_B	c_W
0.0118	0.00281
0.0478	0.00566
0.0981	0.00812
0.156	0.0102

1.4 Show by calculation whether **Q** is monomer or dimer in benzene. Assume that **Q** is a monomer in water.

The freezing point depression, for an ideal dilute solution, is given by

$$T_f^0 - T_f = \frac{R(T_f^0)^2\ X_s}{\Delta H_f}$$

where T_f is the freezing point of the solution, T_f^0 the freezing point of solvent, ΔH_f the heat of fusion of the solvent, and X_s the mole fraction of solute. The molar mass of benzene is 78.0 g mol^{-1}. At 1 atm pure benzene freezes at 5.40 ℃. The heat of fusion of benzene is 9.89 kJ mol^{-1}.

1.5 Calculate the freezing point (T_f) of a solution containing 0.244 g of **Q** in 5.85 g of benzene at 1 atm.

SOLUTION

PART A

1.1 Mole C : H : O = $\dfrac{\dfrac{15144 \times 12.0}{44.0}}{12.0} : \dfrac{\dfrac{0.2656 \times 2.0}{18.0}}{1.0} : \dfrac{0.1575}{16.0}$

$= 0.0344 : 0.0295 : 0.00984 = 7 : 6 : 2$

The formula mass of $C_7H_6O_2$ = 122 which is the same as the molar mass given.

$C_7H_6O_2(s) + 15/2\ O_2(g) \rightarrow 7\ CO_2(g) + 3\ H_2O(l)$ or

$2\ C_7H_6O_2(s) + 15\ O_2(g) \rightarrow 14\ CO_2(g) + 6\ H_2O(l)$

1.2 $n(\text{Q}) = \dfrac{0.6000}{122.0} = 4.919\times10^{-3}$ mol

$$q_v = n\,\Delta U^0 = \frac{0.6000}{122.0} \times (-3079) = -15.14 \text{ kJ}$$

$$\text{Total heat capacity} = \frac{-q_v}{\Delta T} = \frac{15.14}{2.250} = 6.730 \text{ kJ K}^{-1}$$

Heat capacity of water = 710.0 × 4.184 = 2971 J K^{-1}

Heat capacity of calorimeter = 6730 – 2971 = 3759 J K^{-1}

1.3 $\Delta n_\text{g} = 7 - 15/2 = -0.5$ mol

$\Delta H° = \Delta U° + \text{RT}\,\Delta n_\text{g} = -3079 + (8.314\times10^{-3}) \times (298) \times (-0.5) = -3079 - 1 = -3080$

$\Delta H° = (7\,\Delta_\text{f}H°, \text{CO}_2(\text{g}) + 3\,\Delta_\text{f}H°, \text{H}_2\text{O(l)}) - (\Delta_\text{f}H°, \text{Q})$

$\Delta_\text{f}H°$ of Q = $7 \times (-393.51) + 3 \times (-285.83) - (-3080)$ $\underline{= -532 \text{ kJ mol}^{-1}}$

PART B

1.4

c_B (mol dm^{-3})	0.0118	0.0478	0.0981	0.156
c_W (mol dm^{-3})	0.00281	0.00566	0.00812	0.0102
either c_B/c_W	4.20	8.44	12.1	15.3
or c_B/c_W^2	1.49×10^3	1.49×10^3	1.49×10^3	1.50×10^3
(or $\sqrt{c_B}\,/\,c_W$	38.6	38.6	38.6	38.7)

From the results show that the ratio c_B/c_W varies considerably, whereas the ratio c_B/c_W^2 or $\sqrt{c_B}\,/\,c_W$ is almost constant, showing that in benzene, Q is associated into double molecule. Q in benzene is dimer.

1.5 If Q is completely dimerized in benzene, the apparent molecular mass should be 244.

$$\text{Mole fraction of Q}_2 = \frac{\dfrac{0.244}{244}}{\dfrac{0.244}{244} + \dfrac{5.85}{78.0}} = 1.32\times10^{-2} \quad (0.01316)$$

$$\Delta T_\text{f} = \frac{8.314 \times 278.55^2}{9.89\times10^3} \times 1.32\times10^{-2} = 0.861$$

$T_\text{f} = 5.40 - 0.861 = 4.54$ ℃

PROBLEM 2

Bridge between Denmark and Sweden

On July 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial island, and a bridge from the island to Malmö in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production a small amount of gypsum, $CaSO_4 \cdot 2\ H_2O$, is added to improve subsequent hardening of the concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $CaSO_4 \cdot ½\ H_2O$. Consider the following reaction:

$$CaSO_4 \cdot 2\ H_2O(s) \rightarrow CaSO_4 \cdot ½\ H_2O(s) + 1½\ H_2O(g)$$

The following thermodynamic data apply at 25 °C, standard pressure: 1.00 bar:

Compound	$\Delta_f H$ (kJ mol^{-1})	S (J K^{-1} mol^{-1})
$CaSO_4 \cdot 2\,H_2O(s)$	–2021.0	194.0
$CaSO_4 \cdot \frac{1}{2}\,H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

Gas constant: R = 8.314 J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

0 °C = 273.15 K.

2.1 Calculate ΔH (in kJ) for transformation of 1.00 kg of $CaSO_4 \cdot 2\,H_2O(s)$ to hemihydrate $CaSO_4 . \frac{1}{2}\,H_2O(s)$. Is this reaction endothermic or is it exothermic?

2.2 Calculate the equilibrium pressure (in bar) of water vapour in a closed vessel containing $CaSO_4 \cdot 2\,H_2O(s)$, $CaSO_4 \cdot \frac{1}{2}\,H_2O(s)$ and $H_2O(g)$ at 25 °C.

2.3 Calculate the temperature at which the equilibrium water vapour pressure is 1.00 bar in the system described in problem 2-2. Assume that ΔH and ΔS are temperature independent.

Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:

(1) $Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-$

(2) $O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$

An electrochemical cell in which these electrode reactions take place is constructed. The temperature is 25 °C. The cell is represented by the following cell diagram:

$Fe(s)\,|\,Fe^{2+}(aq)\,||\,OH^-(aq), O_2(g)\,|\,Pt(s)$

Standard electrode potentials (at 25 °C):

$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$ E = – 0.44 V

$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$ E = 0.40 V

Nernst factor: $RT \ln 10 / F$ = 0.05916 volt (at 25 °C)

Faraday constant: F = 96485 C mol^{-1}

2.4 Calculate the standard electromotive force (the standard cell voltage), E, at 25 °C.

2.5 Write down the overall reaction which takes place during discharge of the cell under standard conditions.

2.6 Calculate the equilibrium constant at 25 °C for the overall cell reaction.

2.7 The overall reaction referred to above is allowed to proceed for 24 hours under standard conditions and at a constant current of 0.12 A. Calculate the mass of Fe converted to Fe^{2+} after 24 hours. Oxygen and water may be assumed to be present in excess.

2.8 Calculate E for the cell at 25 °C for the following conditions:

$[Fe^{2+}]$ = 0.015 M, $pH_{\text{right-hand half-cell}}$ = 9.00, $p(O_2)$ = 0.700 bar.

SOLUTION

2.1 ΔH^0 = –1575.0 kJ mol^{-1} + 1.5× (–241.8) kJ mol^{-1} – (–2021.0 kJ mol^{-1}) = 83.3 kJ mol^{-1}

$n = m / M$ = 1000g / 172.18 g mol^{-1} = 5.808 mol

ΔH^0 = 484 kJ

The reaction is endothermic.

2.2 ΔS^0 = 130.5 J K^{-1} mol^{-1} + 3/2 × 188.6 J K^{-1} mol^{-1} – 194.0 J K^{-1} mol^{-1}

= 219.4 J K^{-1} mol^{-1}

$\Delta G^0 = \Delta H^0 - T\Delta S^0$ = 17886 J mol^{-1}

$\Delta G^0 = - RT \ln K$

$K = (p(H_2O))^{3/2} = 7.35 \times 10^{-4}$ (pressure in bar)

$p(H_2O) = 8.15 \times 10^{-3}$ bar

2.3 $p(H_2O)$ = 1.00 bar implies K = 1.00 and $\Delta G^0 = - RT \ln K = 0$

$\Delta G = \Delta H - T\Delta S$

0 = 83300 J K^{-1} – T 219.4 J K^{-1} mol^{-1}

T = 380 K or 107 °C

2.4 E^0(cell) = E^0(right) – E^0(left) = 0.40 V – (– 0.44 V) = 0.84 V

2.5 Oxidation takes place at the negative, left half-cell.

Left half: $2\ Fe \rightarrow 2\ Fe^{2+} + 4\ e^-$ (multiplied by 2)

Right half: $O_2 + 2\ H_2O + 4\ e^- \rightarrow\ 4\ OH^-$

Overall: $2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ OH^-$

2.6 $K = [Fe^{2+}]^2\ [OH^-]^4\ /\ p(O_2)$ (conc. in M and pressure in bar)

$\Delta G = -\ n\ F\ E\ (\text{cell}) = -\ RT\ \ln K$

$K = 6.2\times10^{56}$

2.7 $Q = I\ t = 0.12\ \text{A} \times 24 \times 60 \times 60\ \text{s} = 10\ 368\ \text{C}$

$n(e^-) = Q\ /\ F = 10\ 368\ \text{C}\ /\ 96485\ \text{C mol}^{-1} = 0.1075\ \text{mol}$

$m(\text{Fe}) = n(\text{Fe})\ M(\text{Fe}) = 1/2 \times 0.1075\ \text{mol} \times 55.85\ \text{g mol}^{-1} = 3.0\ \text{g}$

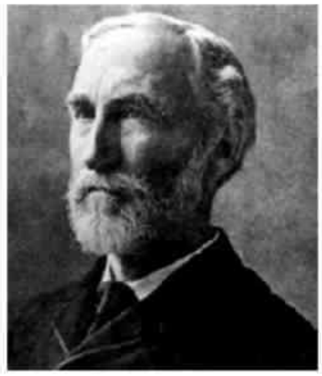
2.8 $$E(\text{cell}) = E^0(\text{cell}) - \frac{0.05916\ \text{V}}{n} \log \frac{[Fe^{2+}]^2\ [OH^-]^4}{p(O_2)}$$

$pH = 9.00$ implies $[H^+] = 1\times10^{-9}$ and $[OH^-] = 1\times10^{-5}$

$$E(\text{cell}) = 0.84\ \text{V} - \frac{0.05916\ \text{V}}{4} \log \frac{0.015^2\ [1\times10^{-5}]^4}{0.700} = 1.19\ \text{V}$$

PROBLEM 3

Second Law of Thermodynamics



J.W.Gibbs (1839 –1903)

The second law of thermodynamics is a fundamental law of science. In this problem we consider the thermodynamics of an ideal gas, phase transitions and chemical equilibrium.

3.00 mol of CO_2 gas expands isothermically (in thermal contact with the surroundings; temperature = 15 °C) against a fixed external pressure of 1.00 bar. The initial and final volumes of the gas are 10.0 dm^3 and 30.0 dm^3, respectively.

3.1 Choose the correct option for change in the entropy of the system (ΔS_{sys}) and of the surroundings (ΔS_{sur}):

(a) $\Delta S_{sys} > 0$ $\Delta S_{sur} = 0$ ☐

(b) $\Delta S_{sys} < 0$ $\Delta S_{sur} > 0$ ☐

(c) $\Delta S_{sys} > 0$ $\Delta S_{sur} < 0$ ☐

d) $\Delta S_{sys} = 0$ $\Delta S_{sur} = 0$ ☐

(Mark X in the correct box.)

3.2 Calculate ΔS_{sys} assuming CO_2 to be an ideal gas.

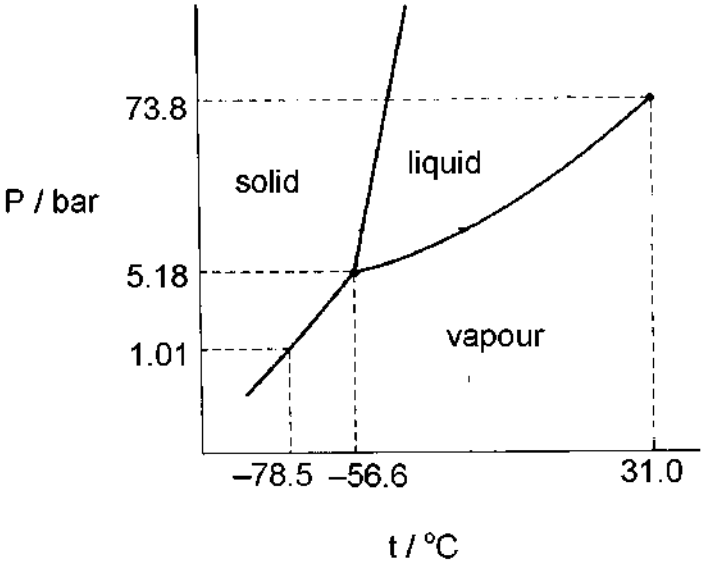
3.3 Calculate ΔS_{sur}.

3.4 Calculate the change in entropy of the universe.

Does your answer agree with the Second Law of Thermodynamics? ☐ Yes ☐ No

(Mark X in the correct box.)

The pressure – temperature phase diagram of CO_2 is given below schematically. The diagram is not to scale.



Phase diagram of CO_2

3.5 CO_2 gas, initially at a pressure of 4.0 bar and temperature of 10.0 °C is cooled at constant pressure. In this process,

(a) it goes first to the liquid phase and then to the solid phase. ☐

(b) it goes to the solid phase without going through the liquid phase. ☐

3.6 Starting with the same pressure and temperature as above (in 3.5), CO_2 is compressed isothermatically. In this process,

(a) it goes first to the liquid phase and then to the solid phase. ☐

(b) it goes to the solid phase without going through the liquid phase. ☐

3.7 From the data given in the phase diagram, calculate the molar enthalpy change of sublimation of CO_2. Write down the formula used.

3.8 CO gas, used extensively in organic synthesis, can be obtained by reacting CO_2 gas with graphite. Use the data given below to show that the equilibrium constant at 298.15 K is less than unity.

At 298.15 K

CO_2(g): ΔH_f^0 = –393.51 kJ mol^{-1}; S^0 = 213.79 J K^{-1} mol^{-1}

CO(g): ΔH_f^0 = –110.53 kJ mol^{-1}; S^0 = 197.66 J K^{-1} mol^{-1}

C(graphite) S^0 = 5.74 J K^{-1} mol^{-1}

3.9 Estimate the temperature at which the reaction would have an equilibrium constant equal to 1. Ignore slight variations in the thermodynamic data with temperature.

3.10 The reaction above (in 3.8) is carried out between CO_2 and excess hot graphite in a reactor maintained at about 800 °C and a total pressure of 5.0 bar. The equilibrium constant K_p under these conditions is 10.0. Calculate the partial pressure of CO at equilibrium.

SOLUTION

3.1 Correct solution: (c) $\Delta S_{sys} > 0$ $\Delta S_{sur} < 0$

3.2 Since ΔS_{sys} is independent of path, it is the same as for isothermal reversible expansion of an ideal gas.

$$\Delta S_{sys} = nR \ln\frac{V_f}{V_i} = 27.4 \text{ J K}^{-1}$$

3.3 $q = p_{ext}\,\Delta V$

$$\Delta S_{sur} = -\frac{q}{T} = -6.94 \text{ J K}^{-1}$$

3.4 $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur} = 20.5 \text{ J K}^{-1}$

The answer agrees with the second law of thermidynamics (correct is YES)

3.5 Correct answer:

(b) it goes to the solid phase without going through the liquid phase.

3.6 Correct answer:

(a) it goes first to the liquid phase and then to the solid phase.

3.7 $$\ln\frac{p_2}{p_1} = -\frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta H_{sub} = 26.1 \text{ kJ mol}^{-1}$

3.8 $\Delta H^0 = 172.45 \text{ kJ mol}^{-1}$

$\Delta S^0 = 176 \text{ J K}^{-1}\text{mol}^{-1}$

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 120 \text{ kJ mol}^{-1}$

$\Delta G^0 > O$ implies $K < 1$

3.9 $\Delta G^0 = 0$ when $\Delta H^0 = T\Delta S^0$

$T = 980 \text{ K}$

3.10

$$CO_2\,(g) + C(s) \rightleftharpoons 2\,CO\,(g)$$

$$1 - \alpha \qquad\qquad 2\,\alpha$$

Partial pressure: $\frac{1-\alpha}{1-\alpha}\times 5$ $\qquad$ $\frac{2\,\alpha}{1-\alpha}\times 5$

$$K_p = \frac{p^2(\text{CO})}{\text{p}(\text{CO}_2)}$$

$p(\text{CO}) = 3.7 \text{ bar}$

THE THIRTY-FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD
5–14 JULY 2002, GRONINGEN, THE NETHERLANDS

THEORETICAL PROBLEMS

Theme 1 - Chemistry of Life

Life runs on chemistry. Understanding and monitoring life processes receive much attention in chemistry.

PROBLEM 1

OXYGEN IN YOUR LIFE

Oxygen is of vital importance for all of us. Oxygen enters the body via the lungs and is transported to the tissues in our body by blood. There it can deliver energy by the oxidation of sugars:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$$

This reaction releases 400 kJ of energy per mol of oxygen. O_2 uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).

Free Hm consists of an Fe^{2+} ion attached to four N atoms of a porphyrin^{2-} ligand. Oxygen can bind at the coordination site of Fe^{2+} giving a $Hm{\cdot}O_2$ complex. Carbon monoxide can be complexed similarly, giving a Hm·CO complex. CO is a poison as it binds more strongly to Hm than O_2 does. The equilibrium constant K_1 for the reaction:

$$Hm + CO \rightleftharpoons Hm{\cdot}CO \qquad (1)$$

is 10 000 times larger than the equilibrium constant K_2 for the reaction:

$$Hm + O_2 \rightleftharpoons Hm{\cdot}O_2 \qquad (2)$$

Each Hb molecule can take up four molecules of O_2. Blood in contact with O_2 absorbs a fraction of this amount, depending on the oxygen pressure, as shown in Figure 1 (curve 1). Also shown are the curves (2) and (3) for blood with two kinds of deficient Hb. These occur in patients with certain hereditary diseases.

Relevant data: O_2 pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum flow of blood through heart and lungs is 4×10^{-4} m^3 s^{-1}. The red cells in blood occupy 40 % of the blood volume; inside the cells the concentration of Hb is 340 kg m^{-3}; Hb has a molar mass of 64 kg mol^{-1}. R = 8.314 J mol^{-1} K^{-1}. T = 298 K.

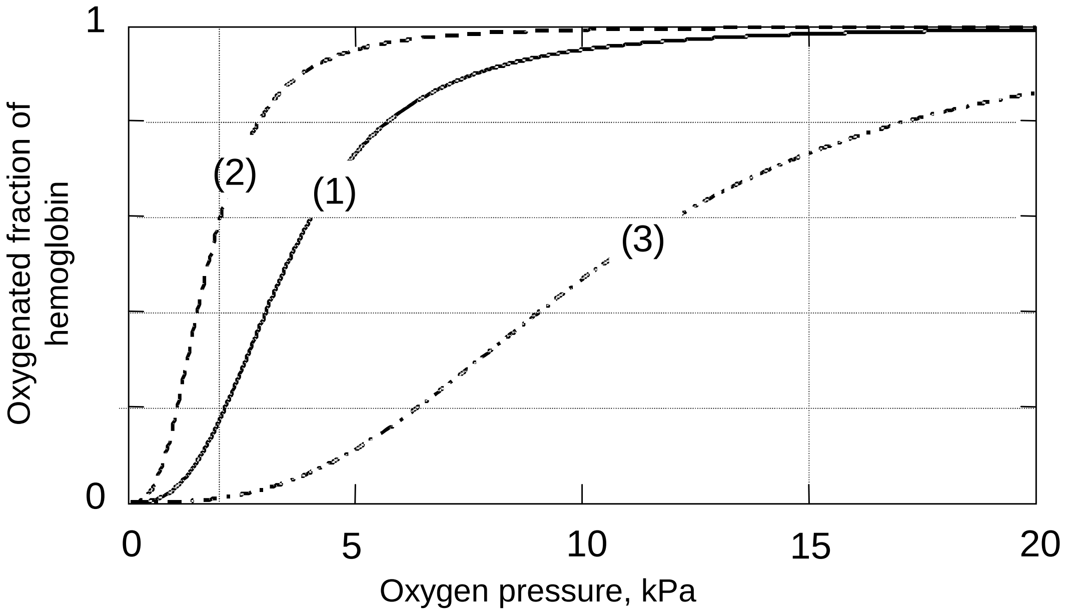


Figure 1

1.1 Using the relation between K and the standard Gibbs energy ΔG^0 for a reaction, calculate the difference between the ΔG^0 values for the heme reactions (1) and (2).

1.2 Estimate from Figure 1 (to 2 significant figures) how many moles of O_2 are deposited in muscle tissue when one mole of Hb travels from the lungs to the muscles and back again for the three different types of Hb.

1.3 The special S-shaped uptake curve 1 is the result of subtle structural features of Hb. The deficient Hb shown in curve 2 is not optimal because:

☐ The binding with O_2 is too weak.

☐ The binding with O_2 is too strong.

☐ The maximum oxygen capacity is too low.

☐ The deficiency is caused by carbon monoxide poisoning.

1.4 Calculate how much oxygen (in mol s^{-1}) can be deposited in tissue by blood with normal Hb (1).

1.5 Calculate the maximum power that the body can produce (assuming it is limited by oxygen transfer).

SOLUTION

1.1 $\Delta G_1^0 = – RT \ln K_1 \qquad \Delta G_2^0 = – RT \ln K_2$

$$\Delta G_2^0 - \Delta G_1^0 = RT \ln \frac{K_1}{K_2}$$

$$\Delta G_2^0 - \Delta G_1^0 = (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln 10\,000) \text{ J} = 23 \text{ kJ mol}^{-1}$$

1.2 Hb-Typ 1: (0.98 – 0.17) mol × 4 = 3.2 mol

Hb-Typ 2: (1.00 – 0.60) mol × 4 = 1.6 mol

Hb-Typ 3: (0.73 – 0.01) mol × 4 = 2.9 mol

1.3 Correct answer: The binding with O_2 is too strong.

1.4 $(4\times10^{-4} \text{ m}^3 \text{ s}^{-1}) \times 0.4 \times (340 \text{ kg m}^{-3}) \times (3.2 \text{ mol } O_2 \text{ / mol Hb}) / (64 \text{ kg mol}^{-1}) =$

$= 2.72\times10^{-3} \text{ mol s}^{-1}$

1.5 $(2.72\times10^{-3} \text{ mol s}^{-1}) \times (400 \text{ kJ mol}^{-1}) = 1088 \text{ W}$

PROBLEM 4

Production of Methanol

Methanol (CH_3OH) is a chemical that is used for the production of additives in gasoline and many common plastics. A factory, producing methanol, is based on the reaction:

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

Hydrogen and CO are obtained by the reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$$

The three units of the factory, namely, the "reformer" for the hydrogen / carbon monoxide production, the "methanol reactor" and a "separator" to separate methanol from CO and H_2, are schematically shown in Figure 1. Four positions are indicated by α, β, γ and δ.

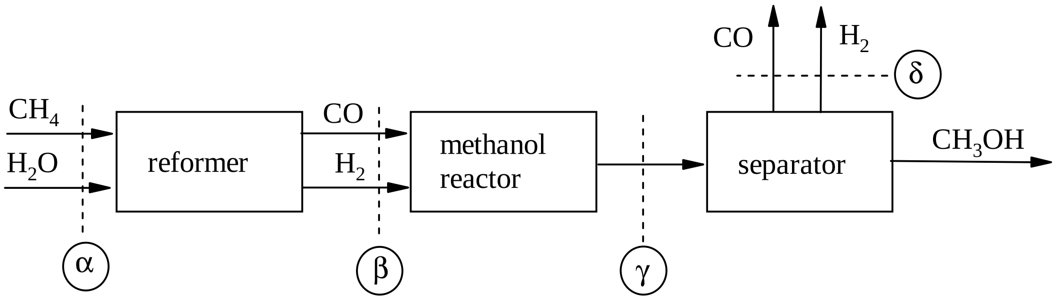


Figure 1

The flow of methanol at position **γ** is $n[CH_3OH, \gamma] = 1000$ mol s^{-1}. The factory is so designed that 2/3 of the CO is converted to methanol. Excess CO and H_2 at position **δ** are used to heat the first reactor. Assume that the reformer reaction goes to completion.

4.1 Calculate the flow of CO and H_2 at position **β**.

4.2 Calculate the flow of CO and H_2 at position **γ**.

4.3 Calculate the flows of CH_4 and H_2O needed at position **α**.

4.4 At point **γ** all species are gases. Calculate the partial pressures in MPa for CO, H_2 and CH_3OH at position γ using the equation:

$$p_i = p\,\frac{n_i}{n_{tot}}$$

wherein n_i is the flow and p_i the partial pressure of the compound i, n_{tot} is the total flow at the position considered, and p the total pressure in the system. (p = 10 MPa)

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures at point γ obey the equation:

$$K_p = \frac{p_{CH_3OH}\, p_0^2}{p_{CO}\, p_{H_2}^2}$$

wherein p_0 is a constant (0.1 MPa) and K_p is a function of temperature as is shown in Figure 2 (the vertical scale is logarithmic).

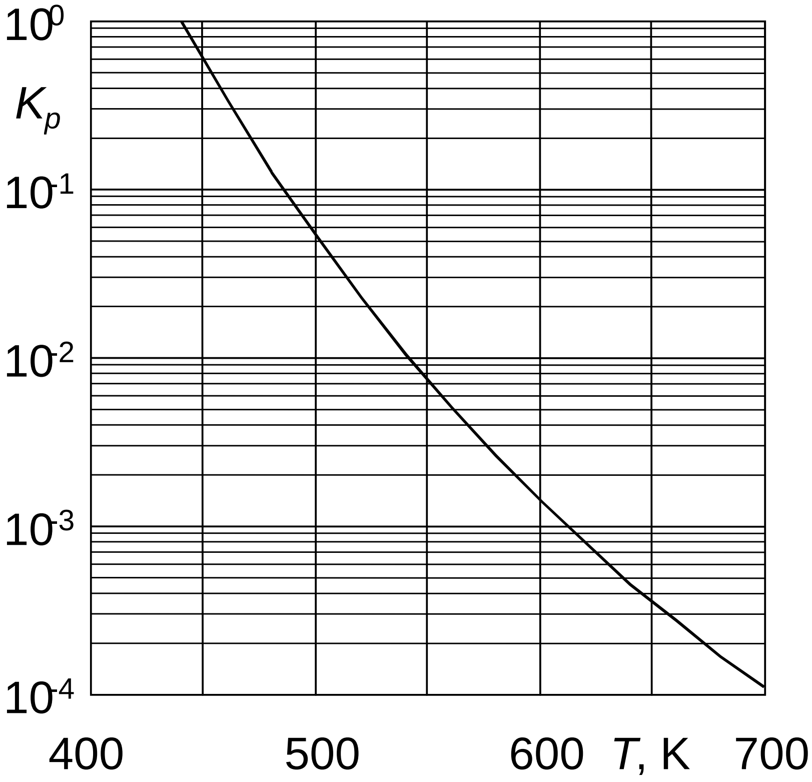


Figure 2

4.5 Calculate K_p and indicate at which temperature T the reaction must be operated to achieve this equilibrium.

SOLUTION

4.1 $n(CO, \beta) = 3/2 \times n(CH_3OH, \gamma) = 1500 \text{ mol s}^{-1}$

$n(H_2, \beta) = 3 \times n(CO, \beta) = 4500 \text{ mol s}^{-1}$

4.2 $n(CO, \gamma) = n(CO, \beta) - n(CH_3OH, \gamma) = (1500 - 1000) \text{ mol s}^{-1} = 500 \text{ mol s}^{-1}$

$n(H_2, \gamma) = n(H_2, \beta) - 2 \times n(CH_3OH, \gamma) = (4500 - 2 \times 1000) \text{ mol s}^{-1} = 2500 \text{ mol s}^{-1}$

4.3 $n(CH_4, \alpha) = n(CO, \beta) = 1500 \text{ mol s}^{-1}$

$n(H_2O, \alpha) = n(CO, \beta) = 1500 \text{ mol s}^{-1}$

4.4 $n_{tot} = (1000 + 500 + 2500) \text{ mol s}^{-1} = 4000 \text{ mol s}^{-1}$

$p_i = p_{tot} \cdot (n_i/n_{tot})$

$p(CO, \gamma) = 10 \text{ MPa} \times (500/4000) = 1{,}25 \text{ MPa}$

$p(H_2, \gamma) = 10 \text{ MPa} \times (2500/4000) = 6{,}25 \text{ MPa}$

$p(CH_3OH, \gamma) = 10 \text{ MPa} \times (1000/4000) = 2{,}50 \text{ MPa}$

4.5 Calculation of K_p: $K_p = (2.5 \times 0.1^2) / (1.25 \times 6.25^2) = 5.12\times10^{-4}$.

The temperature corresponding to this value (see Fig. 2) is ≈ 630 K.

Theme IV - Chemistry Related to Light and Energy

Chemistry plays a major role in meeting our needs of light and energy. Our life is unthinkable without artificial light and energy for mobility.

PROBLEM 8

LIGHTING LAMPS

Since 1891 lighting lamps have been manufactured in The Netherlands. The improvement today in comparison to the first lamp is enormous, especially with the introduction of the gas discharge lamps. The life-time has increased by orders of magnitude. The colour is also an important aspect. Rare earth metal compounds like $CeBr_3$ are now included to reach a colour temperature of 6000 K in the lamp. These compounds are ionic solids at room temperature, and upon heating they sublime partially to give a vapour of neutral metal halide molecules. To achieve a high vapour pressure, the sublimation enthalpy should be as low as possible.

8.1 Give a thermochemical cycle (Law of Hess) for sublimation of $CeBr_3$, via a vapour of mononuclear ions. ($H_l = H_{\text{lattice}}$; $H_e = H_{\text{electrostatic}}$; $H_s = H_{\text{sublimation}}$;H is not absolute, H means ΔH)

$\xrightarrow{-H_l}$ +

\+ $\xrightarrow{+H_e}$

\+

$\xrightarrow{+H_s}$; $H_s = -H_l + H_e$

The lattice energy of the solid can be calculated using the Born–Landé formula:

$$H_l = f\,\frac{Z_+Z_-Ae^2}{r_+ + r_-}\left(1-\frac{1}{n}\right)$$

The factor fe^2 (necessary in order to calculate the lattice energy in kJ mol^{-1}) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant A for the lattice is

2.985. The Born exponent *n* is 11. The charges of the ions Z_+ and Z_- are integer numbers (Z_- is negative). For the calculation of the energy of gaseous $CeBr_3$ (when formed from ions) the same Born-Landé formula can be used without A. The structure of $CeBr_3$ in the gas phase is planar triangular. The radius of Ce^{3+} is 0.115 nm and of Br^- is 0.182 nm.

8. 2 Calculate the enthalpy of sublimation of $CeBr_3$ (in integers; be aware of the signs!)

Attempts to make a better lamp have been undertaken by adding a stoichiometric amount of CsBr to the $CeBr_3$ in the lamp leading at room temperature to solid $CsCeBr_4$. When the sublimation temperature decreases the life time of the lamp will increase likewise. The $CsCeBr_4$ lattice has a NaCl structure with Cs^+ as cations and tetrahedral $CeBr_4^-$ as complex anions. Sublimation of $CsCeBr_4$ leads to a vapour of CsBr and $CeBr_3$ molecules.

8.3 Give the reaction equations of the thermochemical cycle (Law of Hess) for this process in which some steps involve $CeBr_4^-$ ions, mononuclear ions and/or neutral molecules in the gas phase.

Step 1: $\xrightarrow{+H_1}$ +

Step 2: + $\xrightarrow{+H_2}$

Step 3: + $\xrightarrow{+H_3}$

Step 4: + $\xrightarrow{+H_4}$

Total: $(CsCeBr_4)_{lattice} \xrightarrow{+H_{total}} (CeBr_3)_{molecule} + (CsBr)_{molecule}$

8.4 Calculate the enthalpy of sublimation of $CsCeBr_4$ (in integers).

Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The

Cs–Ce distance in the lattice is 0.617 nm. The $CeBr_4^-$ anion is a tetrahedron in which the ratio between the edge and the distance between a corner of the tetrahedron and the centre of gravity (body-radius) amounts to (2√6)/3 = 1.633. The Born exponent of CsBr is 11. The radius of Cs^+ is 0.181 nm.

8.5 Conclusion in relation to the previous answers: Was adding CsBr a good idea? Mark the correct answer.

☐ Adding CsBr is counterproductive.
☐ Adding CsBr has no influence.
☐ Adding CsBr is advantageous.
☐ From these data no clear answer can be given.

SOLUTION

8.1 $(CeBr_3)_{latitce} \xrightarrow{-H_l} Ce^{3+} + 3\ Br^-$

$Ce^{3+} + 3\ Br^- \xrightarrow{-H_e} (CeBr_3)_{molecule}$

$(CeBr_3)_{lattice} \xrightarrow{+H_S} (CeBr_3)_{molecule} \qquad H_s = -H_l + H_e$

8.2 $H_l = -\dfrac{139\times 3\times 1\times 2.985}{0.297}\times\dfrac{10}{11}$ kJ mol^{-1} = – 3810 kJ mol^{-1}

$$H_e = \left(-3\times\frac{139\times 3\times 1}{0.297}\times\frac{10}{11}\right)+\left(3\times\frac{139\times 1\times 1}{0.297\sqrt{3}}\times\frac{10}{11}\right) \text{ kJ mol}^{-1} = -3092 \text{ kJ mol}^{-1}$$

H_s = 718 kJ mol^{-1}

8.3 Step 1: $(CsCeBr_4)_{lattice} \xrightarrow{+H_1} Cs^+ + CeBr_4^-$

Step 2: $CeBr_4^- \xrightarrow{+H_2} Ce^{3+} + 4\ Br^-$

Step 3: $Ce^{3+} + 3\ Br^- \xrightarrow{+H_3} (CeBr_3)_{molecule}$

Step 4: $Cs^+ + Br^- \xrightarrow{+H_4} (CsBr)_{molecule}$

Total $(CsCeBr_4)_{lattice} \xrightarrow{+H_{total}} (CeBr_3)_{molecule} + (CsBr)_{molecule}$

8.4 Step 1: The lattice energy of $CsCeBr_4$ with opposite sign is:

$$H_1 = \frac{139 \times 1 \times 1 \times 1.75}{0.617} \times \frac{10}{11} \text{ kJ mol}^{-1} = 358 \text{ kJ mol}^{-1}$$

Step 2:

$$H_2 = 4 \times \frac{139 \cdot 3 \cdot 1}{0,297} \cdot \frac{10}{11} - 6 \times \frac{139 \times 1 \times 1}{0.297 \times \frac{2}{3} \times \sqrt{6}} \times \frac{10}{11} \text{ kJ mol}^{-1} = 3543 \text{ kJ mol}^{-1}$$

Step 3: The electronic energy in the gas phase of $CeBr_3$ is (see answer 8.2):

$$H_3 = -3 \times \frac{139 \times 3 \times 1}{0.297} \times \frac{10}{11} + 3 \times \frac{139 \times 1 \times 1}{0.297 \times \sqrt{3}} \times \frac{10}{11} \text{ kJ mol}^{-1} = -3092 \text{ kJ mol}^{-1}$$

Step 4: The electrostatic energy in the gas phase of CsBr is

$$H_4 = -\frac{139 \times 1 \times 1}{0.363} \times \frac{10}{11} \text{ kJ mol}^{-1} = -348 \text{ kJ mol}^{-1}$$

Total sum:

$$H_{total} = H_1 + H_2 + H_3 + H_4 = 461 \text{ kJ mol}^{-1}$$

8.5 The third answer is correct: Adding CsBr is advantageous.

PROBLEM 10

Vehicle Traction Batteries

Battery-powered electric vehicles (EV's) are likely to become increasingly common in the next 50 years because of growing concern over pollution caused by vehicles using combustion engines. The reason for the current meagre commercial success of EV's is that the battery specifications must have a performance and cost profile comparable to conventionally powered vehicles.

Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

In the current evolution of EV batteries, the most promising long-term solution is the rechargeable light weight lithium-ion battery. Such batteries are under intensive investigation worldwide and hold also promise for the storage of electricity from solar cells. Their weight is 1/3 of a lead-acid battery. Lithium is used as a negative electrode. It has a high specific capacity and electrode potential. A common positive electrode material is the environmentally benign spinel-type $LiMn_2O_4$. The spinel structure comprises a matrix of cubic close-packed oxide ions, stabilised by lithium ions in tetrahedral sites and manganese ions in octahedral sites. In $LiMn_2O_4$ half of the manganese ions has an oxidation state +3 and half the oxidation state +4.

A lead-acid battery is represented by:

$$Pb(s) \mid PbSO_4(s) \mid H_2SO_4(aq) \mid PbSO_4(s) \mid PbO_2(s) \mid (Pb(s))$$

A lithium battery is represented by:

$$Li(s) \mid Li^+\text{-conducting (solid) electrolyte(s)} \mid LiMn_2O_4(s)$$

Upon discharge the insertion product $Li_2Mn_2O_4$ is formed. Charging the battery leads to the products Li(s) and $LiMn_2O_4$.

10.1 Give the electrochemical reactions at the electrodes of the lead-acid battery during discharge.

10.2 Give the electrochemical reactions at the electrodes of the lithium-ion battery upon discharge.

10.3 Give the coordination numbers of the lithium ions and of the manganese ions in the spinel structure of $LiMn_2O_4$.

A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 litres or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is 10 km L^{-1}.

10.4 Calculate the extra weight of the car if the petrol tank is replaced by an equivalent battery in an EV based on (**a**) lead-acid battery and (**b**) lithium battery. Assume that in all cases the engine efficiency is the same. Calculate:

(**a**) Extra weight of a lead-acid battery car.

(**b**) Extra weight of a lithium battery car.

SOLUTION

10.1 Reaction at the negative electrode:

$$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\ e^-$$

Reaction at the positive electrode:

$$PbO_2(s) + 3\ H^+(aq) + HSO_4^-(aq) + 2\ e^- \longrightarrow PbSO_4(s) + 2\ H_2O(l)$$

10.2 Reaction at the negative electrode:

$$Li(s) \longrightarrow Li^+ + e^-$$

Reaction at the positive electrode:

$$Li^+ + e^- + LiMn_2O_4(s) \longrightarrow Li_2Mn_2O_4(s)$$

10.3 Li – ions: coordination number = 4 Mn – ions: cordination number = 6

10.4 Distance of the petrol car = 500 km $\Rightarrow$ 50 kWh

Mass of petrol tank = 10 kg + 50 $\times$ (3.78 / 5) = 47.8 kg

(a) Mass of a lead-acid battery = 50000 Wh / 45 Wh kg^{-1} = 1111.1 kg

Extra weight of a lead-acid battery car = 1111.1 kg – 47.8 kg = 1063.3 kg

(b) Mass of the lithium battery = 1/3 of the mass of a lead-acid battery

Extra weight of a lithium battery car = 1111.1 kg / 3 – 47.8 kg = 322.6 kg.

SECTION B: PHYSICAL CHEMISTRY

PROBLEM 25 Muon

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

a) The most common spontaneous disintegration reaction for the muon is:

$\mu \rightarrow e + \bar{\nu}_e + v_\mu$,

where $\bar{\nu}_e$ is the electron antineutrino, and v_μ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + v_\mu$, carried away a total energy of 2.000×10^{-12} J, while the electron was moving with a kinetic energy of 1.4846×10^{-11} J. Determine the mass of the muon.

b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a ^{1}H nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

SOLUTION

a) Energy of a stationary muon:

$E_\mu = m_\mu c^2 = E_e + E_{v,v}$

$m_\mu c^2 = m_e c^2 + (T_e + E_{v,v})$

$$m_\mu = \frac{m_e + (T_e + E_{v,v})}{c^2} = \frac{9.109\times10^{-31} + (1.4846\times10^{-11} + 2.000\times10^{-12})}{(2.998\times10^8)^2} =$$

$$= 1.883\times10^{-28} \text{ kg}$$

b) From Bohr theory:

$$E_n = -\frac{m e^4}{2 n^2 h^2} = -109700 \text{ cm}^{-1} \times \frac{1}{n^2} \times \left(\frac{m}{m_e}\right),$$

where

$$m = \frac{m_\mu \, m_H}{m_\mu + m_H}$$

$$\lambda = \frac{1}{E_4 - E_2} = \frac{1}{109700\left(\dfrac{m}{m_e}\right)\left(\dfrac{1}{4} - \dfrac{1}{16}\right)} = 2.615\times10^{-7} \text{ cm}$$

$$\frac{m}{m_e} = 185.9$$

$$m = 185.9 \times 9.109\times10^{-31} = 1.693\times10^{-28} \text{ kg}$$

The mass of a proton from Tables attached :

m_H = 1.673×10^{-27} kg

$$m_\mu = \frac{m \, m_H}{m_H - m} = \frac{1.693\times10^{-28} \times 1.673\times10^{-27}}{1.673\times10^{-27} - 1.693\times10^{-28}} = 1.884\times10^{-28} \text{ kg}$$

PROBLEM 26 Spectrum of CO

Rotational energy levels of diatomic molecules are well described by the formula $E_J = B\ J(J+1)$, where J is the rotational quantum number of the molecule and B its rotational constant. Constant B is related to the reduced mass μ and the bond length R of the molecule through the equation

$$B = \frac{h^2}{8\pi^2 \mu R^2}\ .$$

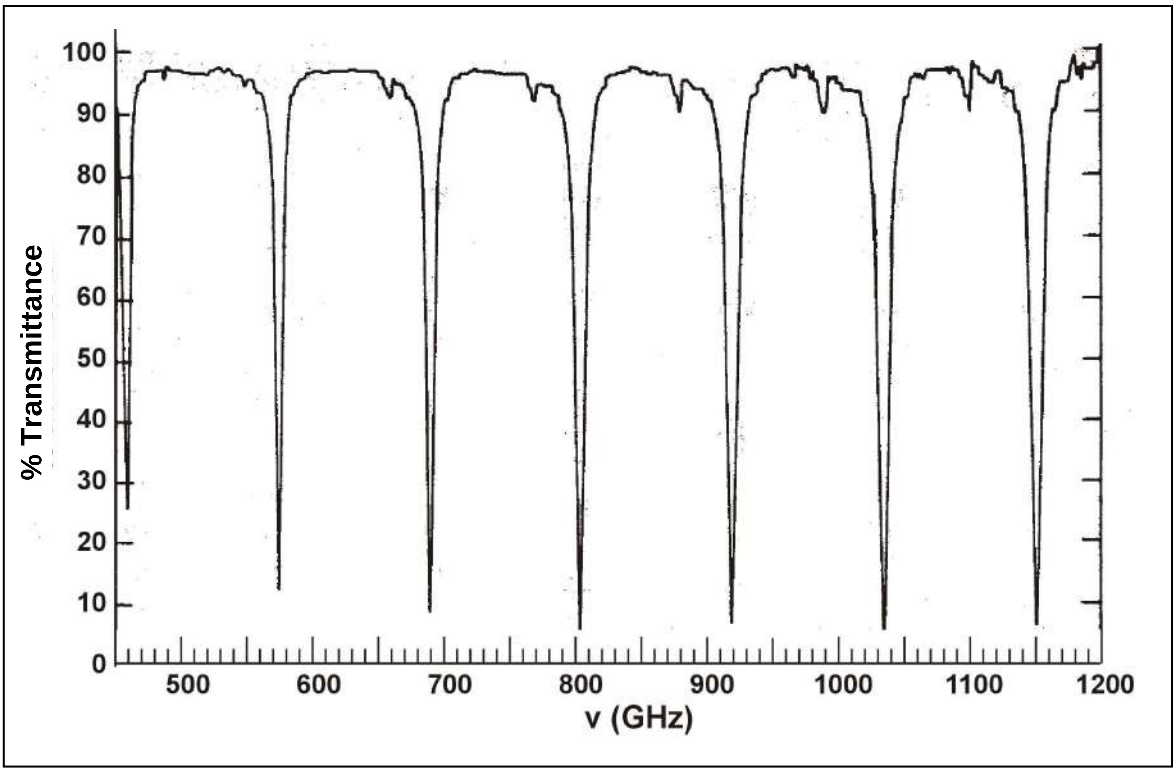
In general, spectroscopic transitions appear at photon energies which are equal to the energy difference between appropriate states of a molecule ($h\ \nu = \Delta E$). The observed rotational transitions occur between adjacent rotational levels, hence $\Delta E = E_{J+1} - E_J = 2\ B\ (J+1)$. Consequently, successive rotational transitions that appear on the spectrum (such as the one shown here) follow the equation $h\ (\Delta v) = 2\ B$.

By inspecting the spectrum provided, determine the following quantities for $^{12}C^{16}O$ with appropriate units:

a) Δv

b) B

c) R



SOLUTION

a) For example: Δv = 1150 – 1035 = 115 GHz

b) $$B = \frac{h\ \Delta\nu}{2} = \frac{6.63\times10^{-34}\times115\times10^{9}}{2} = 3.81\times10^{-23}\ \text{J}$$

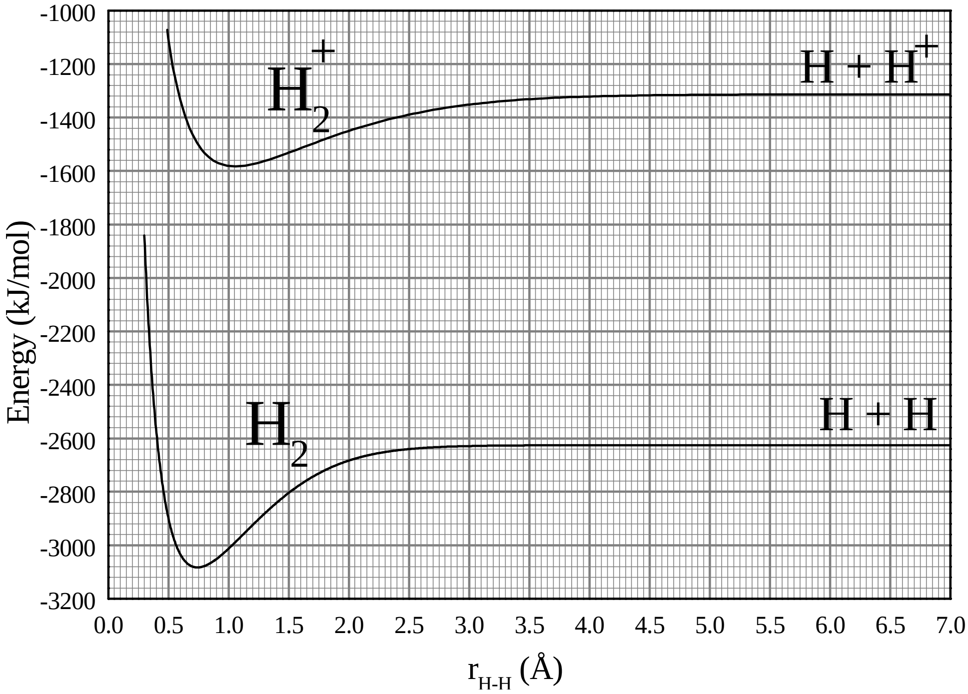
c) $$\mu = \frac{m(\text{C})\times m(\text{O})}{m(\text{CO})} = \frac{12\times16}{28} = 6.86\ \text{a.u.} = 1{,}14\times10^{-26}\ \text{kg}$$

For interatomic distance R:

$$R = \frac{h}{2\pi\sqrt{2\mu B}} = \frac{6.63\times10^{-34}}{2\times3.14\sqrt{2\times1.14\times10^{-26}\times3.81\times10^{-23}}} = 1.13\times10^{-10}\ \text{m} = 1.13\ \text{Å}$$

PROBLEM 27 Hydrogen molecule

Using the information provided on this graph, give numerical answers with appropriate units to the following questions:



1. What are the equilibrium bond lengths of H_2 and H_2^+?
2. What are the binding energies of H_2 and H_2^+?
3. What is the ionisation energy of the H_2 molecule?
4. What is the ionisation energy of the H atom?
5. If we use electromagnetic radiation of frequency 3.9×10^{15} Hz in order to ionise H_2, what will be the velocity of the extracted electrons? (Ignore molecular vibrational energy.)

SOLUTION

1. The equilibrium bond lengths of H_2 and H_2^+ can be read from the minimum of the curves: $r(H_2) = 0.75$ Å; $r(H_2^+) = 1.05$ Å

2. The binding energies of H_2 and H_2^+ can be calculated as the differences in the values for infinitive bond lengths and those for minima of the particular curves:

$E_{bond}(H_2) = -2620 - (-3080) = 460 \text{ kJ mol}^{-1}$

$E_{bond}(H_2^+) = -1310 - (-1580) = 270 \text{ kJ mol}^{-1}$

3. The ionization energy $E_{ion}(H_2)$:

$E_{ion}(H_2)$ = – 1580 – (– 3080) = 1500 kJ mol^{-1}

4. $E_{ion}(H)$ = – 1310 – (– 2620) = 1310 kJ mol^{-1}

5. $H_2 + h\nu \rightarrow H_2^+ + e^-$

$$E(H_2) + h\nu \rightarrow E(H_2^+) + \frac{m_e v_e^2}{2}$$

$$v_e = \sqrt{\frac{2\,(E(H_2) - E(H_2^+) + h\nu}{m_e}} =$$

$$= \sqrt{\frac{2\left(\dfrac{-3080\times10^3 - (-1510\times10^3)}{6.02\times10^{23}}\right) + 6.63\times10^{-34} \times 4.1\times10^{15}}{9.11\times10^{-31}}} = 492\times10^3\ \text{m s}^{-1}$$

PROBLEM 28 Cryoscopy

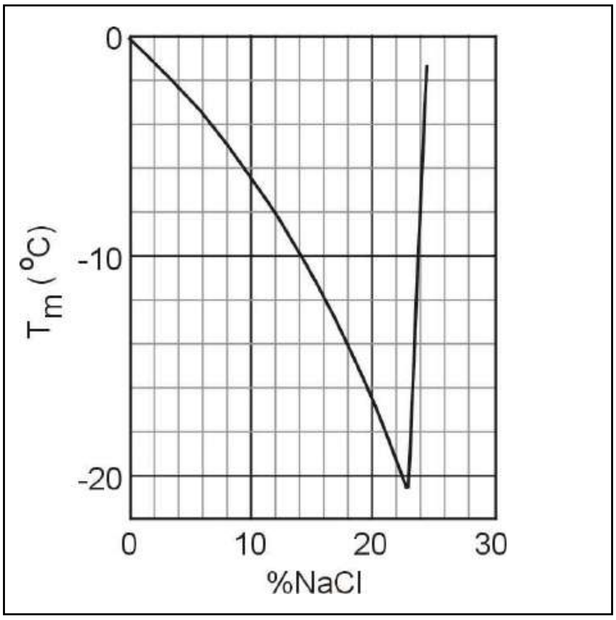
Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point (0 ℃) and well above the CO_2 sublimation point (–78 ℃) this case they mix water ice prepared at its melting point and NaCl. Depending on the quantities used temperatures as low as –20 ℃ can be reached.

We prepare a cold bath mixing 1 kg of ice at 0 ℃ with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

a) The mixing process is spontaneous. (Y) (N)

b) The change of entropy during the mixing process is negative. (Y) (N)

c) The following diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is is the freezing point of the bath based on the diagram?



d) If an equal mass of $MgCl_2$ were used instead of NaCl, would the freezing point be higher? (Y) (N)

SOLUTION

The correct answers are as follows:

a) Y (Yes)

b) N (No)

c) The freezing point of the bath is –9 ℃.

d) Y (Yes)

PROBLEM 29 Pool

A very large swimming pool filled with water of temperature equal to 20 °C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine:

a) The heat delivered to the water.

b) Is the change of entropy of the resistor positive, negative, or zero?

(i) $\Delta S_{res} > 0$ ( )

(ii) $\Delta S_{res} = 0$ ( )

(iii) $\Delta S_{res} < 0$ ( )

c) Is the change of entropy of the water positive, negative, or zero?

i) $\Delta S_{pool} > 0$ ( )

(ii) $\Delta S_{pool} = 0$ ( )

(iii) $\Delta S_{pool} < 0$ ( )

d) Is the change of entropy of the system positive, negative, or zero?

(i) $\Delta S_{total} > 0$ ( )

(ii) $\Delta S_{total} = 0$ ( )

(iii) $\Delta S_{total} < 0$ ( )

e) Is the process reversible? (Y) (N)

SOLUTION

a) Q = 500 W× 20 min × 60 = 600 kJ

b) $\Delta S_{res} = 0$

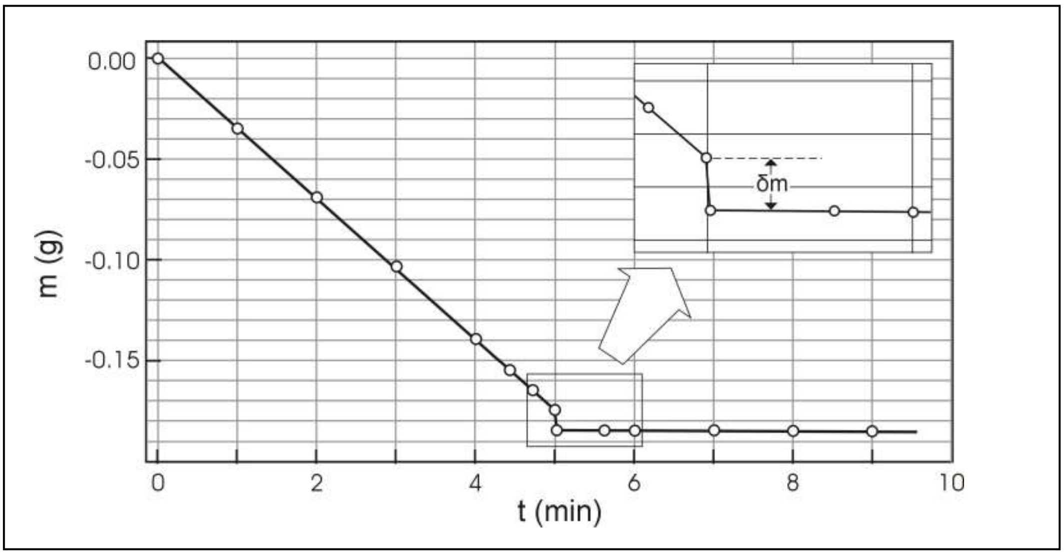
c) $\Delta S_{pool} > 0$

d) $\Delta S_{total} > 0$

e) The answer is No (N).

PROBLEM 30 Gas velocity

The experiment described here gives a simple way to determine the mean velocity *u* of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time *t* = 0. Balance readings are recorded as shown on the diagram.



At *t* = 5 min the lid is placed over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δ*m*. Therefore, the force exerted on the lid is *f* = δ*m g*. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., *f* = ½ *u* dm/dt. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume *g* = 9.8 m s^{-2}.

SOLUTION

$$\frac{dm}{dt} = \frac{\Delta m}{\Delta t} = \frac{0.14\text{ g}}{4\text{ min}} = 0.035\text{ g min}^{-1} = 5.8\times 10^{-4}\text{ g s}^{-1}$$

$$\delta m\ g = \frac{1}{2} u \frac{dm}{dt}$$

$$u = \frac{0.01\times 9.81\times 2}{5.8\times 10^{-4}} = 338\text{ m s}^{-1}$$

PROBLEM 35 Kinetics

The acid-catalyzed reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ was found to be of first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by 0.010 mol dm^{-3} was measured under various concentrations of the reactants.

Based on the information provided in the table, answer fulfil the following tasks:

$[CH_3COCH_3]$	$[I_2]$	Time
(mol dm^{-3})	(mol dm^{-3})	(min)
0.25	0.050	7.2
0.50	0.050	3.6
1.00	0.050	1.8
0.50	0.100	3.6
0.25	0.100	…
1.50	…	…
…	…	0.36

a) Derive the rate law for the reaction and calculate the rate constant.

b) Calculate the time needed for 75 % of CH_3COCH_3 to react in excess I_2.

c) Show graphically the dependence of the rate on $[CH_3COCH_3]$ and on $[I_2]$, for fixed initial concentration of the other reagents.

d) If the rate is doubled by raising the temperature by 10 °C from 298 K, calculate the activation energy for this reaction.

SOLUTION

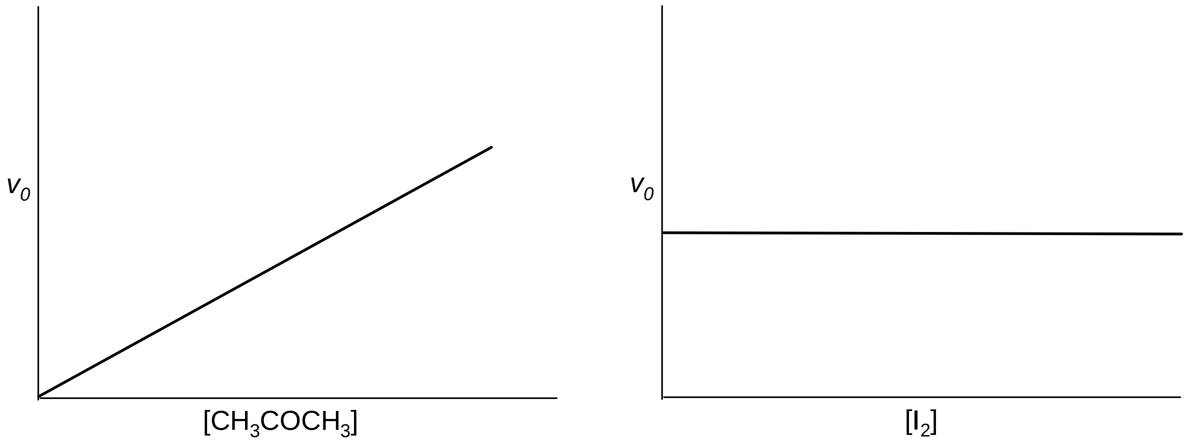
a) $v = k\,[CH_3COCH_3]$

$$k = \frac{v}{[CH_3COCH_3]} = \frac{\frac{0.010}{7.2}}{0.25} = 5.56\times10^{-3}\ \text{min}^{-1} = 9.26\times10^{-5}\ \text{s}^{-1}$$

b) $\tau = \ln 2\,/\,k = 125$ min

$t = 2\,\tau = 250$ min

c)



d)

$$k = A\exp\left(-\frac{E_A}{RT}\right)$$

$$\frac{v_2}{v_1} = \frac{k_2}{k_1} = \frac{\exp\left(-\frac{E_A}{RT_2}\right)}{\exp\left(-\frac{E_A}{RT_1}\right)} = \exp\left(-\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\ln\frac{v_2}{v_1} = -\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_A = -R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1}\ln\frac{v_2}{v_1}$$

$$E_A = -8.314\left(\frac{1}{308} - \frac{1}{298}\right)^{-1}\ln\frac{2}{1} = 52.9\ \text{kJ mol}^{-1}$$

THE THIRTY-SIXTH
INTERNATIONAL CHEMISTRY OLYMPIAD
18–27 JULY 2004, KIEL, GERMANY

THEORETICAL PROBLEMS

PROBLEM 1

Thermodynamics

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.

Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0 °C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.

The thermodynamic properties and the composition of natural gas can be found in Table 1.

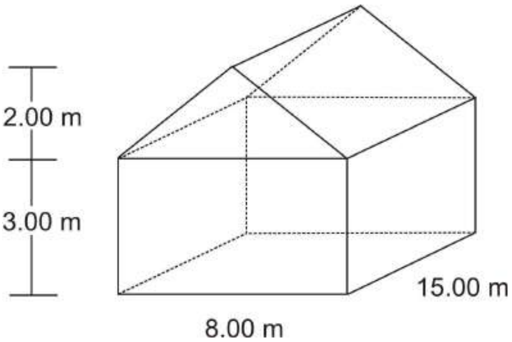
1.2 The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C) specified by PUC, the public utility company.

a) Calculate the amount of methane and ethane (in moles) in 1.00 m^3 of natural gas (natural gas, methane, and ethane are not ideal gases!).

b) Calculate the combustion energy which is released as thermal energy during the burning of 1.00 m^3 of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 m^3 natural gas corresponds to 40.00 mol natural gas.)

According to the PUC the combustion energy will be 9.981 kWh per m^3 of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00 °C and the air temperature in the house (dimensions given in the figure below) is 10.0 °C. Assume a water density of ρ = 1.00 kg dm^{-3} and air behaving like an ideal gas.



1.3 Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0 °C and the energy which is required to heat the initial amount of air (21.0 % of O_2, 79.0 % of N_2) to 30.0 °C at a pressure of 1.013×10^5 Pa.

In February, the outside temperature is about 5 °C in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is 1.00 W K^{-1} m^{-1}.

1.4 Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at 30.0 °C during the party (12 hours).

1.00 m^3 of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

1.5 What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0 %? What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100 % efficiency for the electric heater.

Table 1: Composition of natural gas

Chemical Substance	mol fraction x	$\Delta_f H^0$ (kJ mol^{-1})$^{-1}$	S^0 (J mol^{-1} K^{-1})$^{-1}$	C_p^0 (J mol^{-1} K^{-1})$^{-1}$
CO_2 (g)	0.0024	-393.5	213.8	37.1
N_2 (g)	0.0134	0.0	191.6	29.1
CH_4 (g)	0.9732	-74.6	186.3	35.7
C_2H_6 (g)	0.0110	-84.0	229.2	52.5
H_2O (l)	-	-285.8	70.0	75.3
H_2O (g)	-	-241.8	188.8	33.6
O_2 (g)	-	0.0	205.2	29.4

Equation:

$J = E \times (A \times \Delta t)^{-1} = \lambda_{wall} \times \Delta T \times d^{-1}$

J	energy flow E along a temperature gradient (wall direction z) per area A and time Δt
d	wall thickness
λ_{wall}	heat conductivity
ΔT	difference in temperature between the inside and the outside of the house

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SOLUTION

1.1 Chemical equations:

a) methane: $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

b) ethane: $2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$

Thermodynamic data for the equations:

$\Delta H^0 = [2 \times (-241.8) - 393.5 - (-74.6)]$ kJ mol^{-1} = -802.5 kJ mol^{-1}

$\Delta S^0 = [2 \times (188.8) + 213.8 - 186.3 - 2 \times 205.2]$ J mol^{-1} K^{-1} = -5.3 J mol^{-1} K^{-1}

$\Delta G^0 = -802.5\ \text{kJ mol}^{-1} - 298.15\ \text{K} \times (-5.3\ \text{J mol}^{-1}\ \text{K}^{-1}) = -800.9\ \text{kJ mol}^{-1}$

Methane: $\Delta H^0 = -802.5\ \text{kJ mol}^{-1}$; $\Delta S^0 = -5.3\ \text{J mol}^{-1}\ \text{K}^{-1}$; $\Delta G^0 = -800.9\ \text{kJ mol}^{-1}$

$\Delta H^0 = [6 \times (-241.8) - 4 \times 393.5 - 2 \times (-84.0)]\ \text{kJ mol}^{-1} = -2856.8\ \text{kJ mol}^{-1}$

$\Delta S^0 = [6\times188.8 + 4\times213.8 - 2\times229.2 - 7\times205.2]\ \text{J mol}^{-1}\ \text{K}^{-1} = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta G^0 = -2856.8\ \text{kJ mol}^{-1} - 298.15\ \text{K} \times (93.2\ \text{J mol}^{-1}\ \text{K}^{-1}) = -2884.6\ \text{kJ mol}^{-1}$

Ethane: $\Delta H^0 = -2856.8\ \text{kJ mol}^{-1}$; $\Delta S^0 = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$; $\Delta G^0 = -2884.6\ \text{kJ mol}^{-1}$

1.2 a) Amount of methane and ethane in 1 m^3 natural gas:

$m = \rho \times V = 0.740\ \text{g dm}^{-3} \times 1000\ \text{dm}^3 = 740\ \text{g}$

$M_{av} = \sum_i x(i)M(i) = (0.0024 \times 44.01\ \text{g mol}^{-1}) + (0.0134 \times 28.02\ \text{g mol}^{-1})$

$+ (0.9732 \times 16.05\ \text{g mol}^{-1}) + (0.011 \times 30.08\ \text{g mol}^{-1}) = 16.43\ \text{g mol}^{-1}$

$n_{tot} = m\ (M_{av})^{-1} = 740\ \text{g} \times (16.43\ \text{g/mol})^{-1} = 45.04\ \text{mol}$

$n(i) = x(i) \cdot n_{tot}$

$n(CH_4) = x(CH_4) \times n_{tot} = 0.9732 \times 45.04\ \text{mol} = 43.83\ \text{mol}$

$n(C_2H_6) = x(C_2H_6) \times n_{tot} = 0.0110 \times 45.04\ \text{mol} = 0.495\ \text{mol}$

b) Energy of combustion, deviation:

$E_{comb.}(H_2O(g)) = \sum_i n(i)\Delta_c H°(i) =$

$= 43.83\ \text{mol} \times (-802.5\ \text{kJ mol}^{-1}) + 0.495\ \text{mol} \times 0.5 \times (-2856.8\ \text{kJ mol}^{-1})$

$= -35881\ \text{kJ}$

$E_{comb.}(H_2O(g)) = -35881\ \text{kJ}$

Deviation from PUC

$E_{PUC}(H_2O(g)) = 9.981\ \text{kWh m}^{-3} \times 1\ \text{m}^3 \times 3600\ \text{kJ (kWh)}^{-1} = 35932\ \text{kJ}$

Deviation: $\Delta E = (E_{comb.}(H_2O(g)) - E_{PUC}(H_2O(g)) \times 100\ \% \times [E_{comb.}(H_2O(g))]^{-1}$

$= (35881\ \text{kJ} - 35932\ \text{kJ}) \times 100\ \% \times (35881\ \text{kJ})^{-1} = -0.14\%$

1.3 Energy for heating the water:

Volume of water: $V_{water} = 22.5\ \text{m}^3$

$n_{\text{water}} = V_{\text{water}}\ \rho_{\text{water}}\ (M_{\text{water}})^{-1}$ = 22.5 m^3 × 10^6 g m^{-3} × (18.02 g mol^{-1})$^{-1}$ = 1.249×10^6 mol

$E_{\text{water}} = n_{\text{water}} \times C_p \times \Delta T$ = 1.249×10^6 mol × 75.30 J K^{-1} mol^{-1} × 14 K = 1316 MJ

Energy for heating the air:

Volume of the house is:

V_{air} = (15 m × 8 m × 3 m) + 0.5 × (15 m × 8 m × 2 m) = 480 m^3

$n_{\text{air}} = pV\ (RT)^{-1}$ = 1.013×10^5 Pa × 480 m^3 × (8.314 J (K mol)$^{-1}$ × 283.15 K)$^{-1}$ =

= 2.065×10^4 mol

C_p(air) = 0.21 × 29.4 J (K mol)$^{-1}$ + 0.79 × 29.1 J (K mol)$^{-1}$ = 29.16 J (K mol)$^{-1}$

$E_{\text{air}} = n_{\text{air}} \times C_p(\text{air}) \times \Delta T$ = 2.065×10^4 mol × 29.17 J (K mol)$^{-1}$ × 20 K = 12.05 MJ

1.4 Energy for maintaining the temperature:

Surface area of the house:

A_{house} = 3 m × 46 m + 8 m × 2 m + ((2 m)^2 + (4 m)^2)$^{1/2}$ × 2 × 15 m = 288.16 m^2

Heat conductivity: λ_{wall} = 1 J (s K m)$^{-1}$

Energy flux along a temperature gradient (wall thickness d = 0.2 m)

$J = E_{\text{loss}}\ (A \times \Delta t)^{-1} = \lambda_{\text{wall}}\ \ \Delta T\ \ d^{-1}$

E_{loss} = 288.16 m^2 × (12·60·60 s) × 1 J (s K m)$^{-1}$ × 25 K × (0.2 m)$^{-1}$ = 1556 MJ

E_{loss} = 1556 MJ

1.5 Total energy and costs:

Total energy: $E_{\text{tot}} = E_{\text{water}} + E_{\text{air}} + E_{\text{loss}}$ = 1316 MJ + 12 MJ + 1556 MJ = 2884 MJ

2884 MJ corresponds to 2.884×10^6 kJ × (3600 s h^{-1} × 9.981 kJ s^{-1} m^{-3} × 0.9)$^{-1}$ = 89.18 m^3

Volume of gas: V = 89.18 m^3

2884 MJ correspond to a cost of:

0.40 € m^{-3} × 89.18 m^3 = 35.67 €

Rent for equipment: 150.00 €

Total cost of gas heating = 185.67 €

2884 MJ correspond to a cost of

$2.884 \cdot 10^6$ kJ × 0.137 € × $(3600\ \text{s h}^{-1} \times 1\ \text{kJ s}^{-1}\ \text{h})^{-1}$ = 109.75 €

Rent for equipment: 100.00 €

Total cost of electric heating: 209.75 €

PROBLEM 2

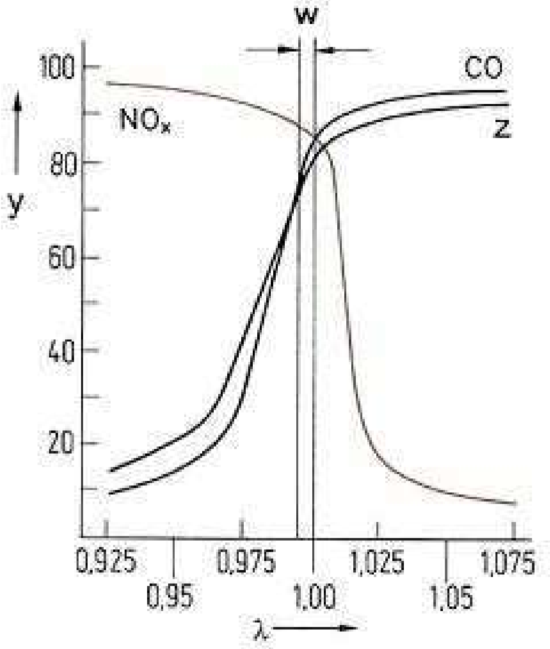
Kinetics at catalyst surfaces

Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the λ-value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.

The lambda value is defined as $\lambda = \dfrac{\text{amount of air at the inlet}}{\text{amount of air necessary for complete combustion}}$.



w: λ-window

y: conversion efficiency (%)

z: Hydrocarbons

2.2 Decide the questions on the answer sheet concerning the λ probe.

The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \times p}{1 + K \times p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.

The adsorption of a gas at 25 °C may be described by using the Langmuir isotherm with $K = 0.85$ kPa^{-1}.

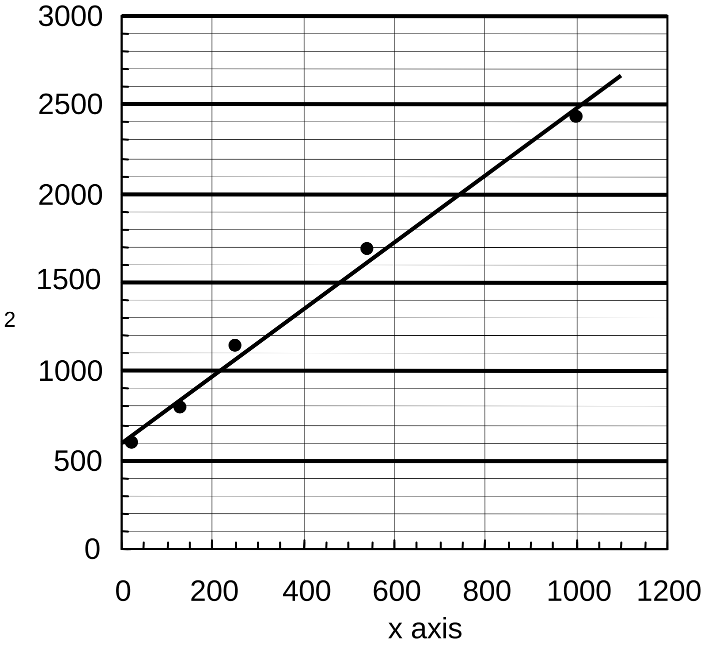
2.3 a) Determine the surface coverage θ at a pressure of 0.65 kPa.

b) Determine the pressure p at which 15 % of the surface is covered.

c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k\,\theta$

Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).

d) Data for the adsorption of another gas on a metal surface (at 25 °C)



x axis: $p \cdot (\text{Pa})^{-1}$

y axis: $p \cdot V_a^{-1} \cdot (\text{Pa cm}^{-3})^{-1}$

V_a is the gas volume that has been adsorbed.

If the Langmuir isotherm can be applied, determine the gas volume $V_{a,max}$ needed for a complete coverage of the metal surface and the product $K\,V_{a,max}$.

Hint: Set $\theta = V_a / V_{a,max}$.

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:

In a first step adsorbed CO and adsorbed O_2 form adsorbed CO_2 in a fast equilibrium,

$$\text{CO (ads.)} + 0.5\ \text{O}_2\ \text{(ads.)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{CO}_{5000}\ \text{(ads.)}$$

In a slow second step, CO_2 is then desorbed from the surface:

$$\text{CO}_2\ \text{(ads.)} \xrightarrow{k_2} \text{CO}_2\ \text{(g)}$$

2.4 Derive the formula for the reaction rate of the CO_2(g) - formation as a function of the partial pressures of the reaction components.

Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta_i = \frac{K_i \times p_i}{1 + \sum_j K_j \times p_j} \qquad \text{j: relevant gas components}$$

SOLUTION

2.1 Reaction equations:

$2\ CO + O_2 \rightarrow 2\ CO_2$

$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$

$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$

2.2 Questions concerning the λ probe:

	true	false	no decision possible
If the λ-value is in the range of the λ-window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	☒	☐	☐
With λ > 1, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	☒	☐	☐
With λ < 0.975, nitrogen oxides can be reduced poorly.	☐	☒	☐

2.3 a) Surface coverage:

$$\theta = \frac{0.85\ \text{kPa}^{-1} \times 0.65\ \text{kPa}}{1 + 0.85 \times 0.65}$$

θ = 0.356 or 35.6 %

b) Pressure at which 15 % of the surface is covered:

$$\theta = \frac{K \times p}{1 + K \times p} \quad \Leftrightarrow \quad K \times p = \theta + \theta \times K \times p \quad \Leftrightarrow \quad p \cdot (K - \theta \times K) = \theta \quad \Leftrightarrow$$

$$p = \frac{\theta}{K - \theta \times K}$$

θ = 0.15

p = 0.21 kPa

c) Orders of decomposition:

Order of the decomposition reaction at low gas pressures 1

Order of the decomposition reaction at high gas pressures 0

Notes:

$$r = k \times \theta = k \, \frac{K \times p}{1 + K \times p},$$

$$p \text{ low} \Rightarrow \quad p << \frac{1}{K} \Rightarrow r = k \; K \; p \qquad \text{reaction order 1.}$$

$$p \text{ high} \Rightarrow \quad p >> \frac{1}{K} \Rightarrow r = k \qquad \text{reaction order 0.}$$

d) Gas volume $V_{\text{a,max}}$ and product $K \cdot V_{\text{a,max}}$:

$$\frac{1}{\theta} = \frac{1}{K \; p} + 1 = \frac{V_{\text{a,max}}}{V_{\text{a}}} \quad \Rightarrow \quad \frac{1}{K \, V_{\text{a,max}}} + \frac{p}{V_{\text{a,max}}} = \frac{p}{V_{\text{a}}}$$

Slope: $\frac{1}{V_{\text{a,max}}} = 1.9 \text{ cm}^{-3} \Rightarrow V_{\text{a,max}} = 0.53 \text{ cm}^3$

Intercept: $\frac{1}{K \; V_{\text{a,max}}} = 6 \times 10^2 \text{ Pa cm}^{-3} \Rightarrow K \, V_{\text{a,max}} = 1.7 \times 10^{-3} \text{ Pa}^{-1} \text{ cm}^3$

2.4 Equation for reaction rate:

The information given in the text leads directly to $r = k_2 \; \theta_{\text{CO}_2}$

The law of mass action for the first step of the mechanism is given by

$$\theta_{\text{CO}_2} = \frac{k_1}{k_{-1}} \cdot \theta_{\text{co}} \; \theta_{\text{o}_2}^{\frac{1}{2}}, \; \Rightarrow \qquad r = k_2 \, \frac{k_1}{k_{-1}} \, \theta_{\text{co}} \; \theta_{\text{o}_2}^{\frac{1}{2}}.$$

The Langmuir isotherm gives:

$$\theta_{CO} = \frac{K_{CO}\ p_{CO}}{1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}} \text{ and } \theta_{O_2} = \frac{K_{O_2}\ p_{O_2}}{1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}}$$

$$r = k_2\ \frac{k_1}{k_{-1}}\ \frac{K_{CO}\ p_{CO}\left(K_{O_2}\ p_{O_2}\right)^{\frac{1}{2}}}{\left(1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}\right)^{\frac{3}{2}}}$$

PROBLEM 3

Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these “compounds” was not known but they are still of great interest to solid state chemists.

Attempts to reduce $CaCl_2$ to CaCl have been made with

(a) Calcium (b) Hydrogen (c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl.

After an attempt to reduce $CaCl_2$ with the stoichiometric 1 : 1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colourless crystals.

3.2 What substance are the metallic particles and the colourless crystals?

When $CaCl_2$ is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 % (by mass) of calcium and 46.32 mass % of chlorine.

3.3 Determine the empirical formula of the compound formed.

When $CaCl_2$ is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3.

3.4 a) Show the two acyclic constitutional isomers of the gas that are formed by hydrolysis.

b) What compound is formed by the reaction of $CaCl_2$ with carbon?
(Provided that monovalent calcium does not exist.)

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl. One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(M^{m+})$ and anion $r(X^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio r_M/r_X	Structure type	estimated $\Delta_L H^0$ for CaCl
3	Triangular	0.155 – 0.225	BN	–663.8 kJ mol^{-1}
4	Tetrahedral	0.225 – 0.414	ZnS	–704.8 kJ mol^{-1}
6	Octahedral	0.414 – 0.732	NaCl	–751.9 kJ mol^{-1}
8	Cubic	0.732 – 1.000	CsCl	–758.4 kJ mol^{-1}

$\Delta_L H^0$(CaCl) is defined for the reaction $Ca^+(g) + Cl^-(g) \rightarrow CaCl(s)$

3.5 a) What type of structure is CaCl likely to have?

[$r(Ca^+) \approx 120$ pm (estimated), $r(Cl^-) \approx 167$ pm)]

Not only the lattice energy $\Delta_L H^0$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_f H^0$ of CaCl has to be known.

b) Calculate the value of $\Delta_f H^0$ (CaCl) with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{fusion} H^0$(Ca)		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1.\,IE} H$(Ca)	$Ca \rightarrow Ca^+$	589.7 kJ mol^{-1}
ionization enthalpy	$\Delta_{2.\,IE} H$(Ca)	$Ca^+ \rightarrow Ca^{2+}$	1145.0 kJ mol^{-1}
heat of vaporization	$\Delta_{vap} H^0$(Ca)		150.0 kJ mol^{-1}
dissociation energy	$\Delta_{diss} H(Cl_2)$	$Cl_2 \rightarrow 2\ Cl$	240.0 kJ mol^{-1}

enthalpy of formation	$\Delta_f H^0(CaCl_2)$		–796.0 kJ mol^{-1}
electron affinity	$\Delta_{EA}H(Cl)$	$Cl + e^- \rightarrow Cl^-$	–349.0 kJ mol^{-1}

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and $CaCl_2$ the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

SOLUTION

3.1 Chemical equations:

(a) $CaCl_2 + Ca \rightarrow 2\ CaCl$

(b) $2\ CaCl_2 + H_2 \rightarrow 2\ CaCl + 2\ HCl$

(c) $4\ CaCl_2 + C \rightarrow 4\ CaCl + CCl_4$

3.2

Silvery metallic particles:	Ca
Colourless crystals:	$CaCl_2$

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and $CaCl_2$

3.3 Empirical formula:

100 % –(mass % Ca + mass % Cl) = mass % X

100 % –(52.36 % + 46.32 %) = 1.32 % X

mol % of Ca = 52.36 mass % / M(Ca)

= 52.36 mass % / 40.08 g mol^{-1} = 1.31 mol %

mol % of Cl = 46.32 mass % / M (Cl)

= 46.32 mass % / 35.45 g mol^{-1} = 1.31 mol %

mol % of X = 1.32 % X / M (H)

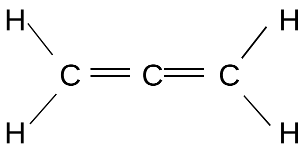
= 1.32 % X / 1.01 g mol^{-1} = 1.31 mol %

$n(Ca) : n(Cl) : n(H) = 1 : 1 : 1$

Empirical formula: CaClH

Notes: The reaction of $CaCl_2$ with hydrogen does not lead to CaCl. The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.

3.4 a) Structures only:



$H-C\equiv C-CH_3$

b) Empirical formula of the compound formed:

$Ca_3C_3Cl_2$

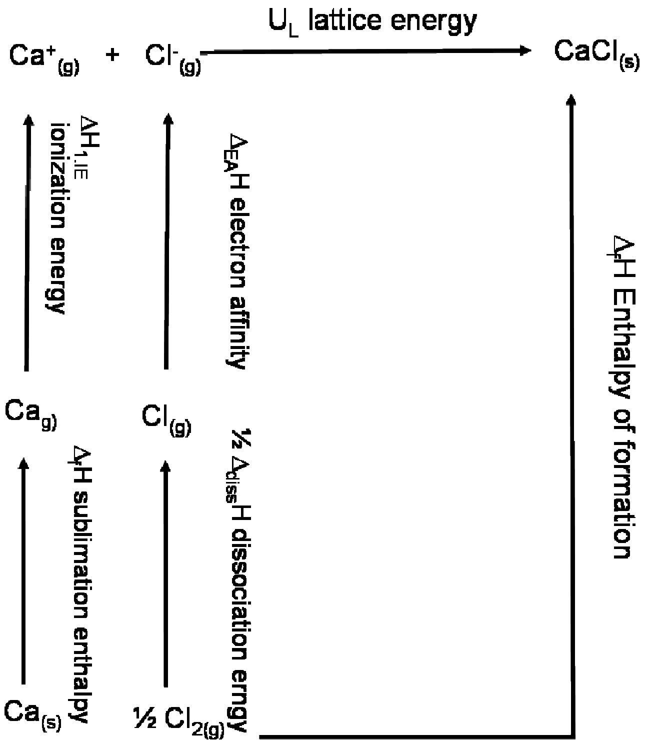
Notes: If the ratio of n(Ca) : n(Cl) = 1.5 : 1 [or better = 3 : 2 which can be rewritten as $CaCl_2 \cdot 2\,Ca^{2+} = Ca_3Cl_2^{4+}$] is given and the reduction product must contain a C_3^{4-} anion which needs two Ca^{2+} cations for electroneutrality, the composition $Ca_3C_3Cl_2$ will follow.

3.5 a) Structure type CaCl likely to have:

$r(Ca^+)/r(Cl^-) = 120\text{ pm} / 167\text{ pm} = 0.719$

NaCl	CsCl	ZnS	BN	no decision possible
☒	☐	☐	☐	☐

b) $\Delta_f H^0$(CaCl) with a Born-Haber-cycle:



Summing up of all the single steps of the Born-Haber-cycle:

$\Delta_f H^0$ (CaCl) = $\Delta_{subl}H^0$(Ca) + $\Delta_{1.\ IE}H$(Ca) + ½ $\Delta_{diss}H$(Cl$_2$) + $\Delta_{EA}H$(Cl) + $\Delta_L H$(CaCl)

= (159.3 + 589.7 + 120 – 349.0 – 751.9) kJ mol^{-1}

= –231.9 kJ mol^{-1}

3.6 Stability to disproportionation:

2 CaCl → CaCl$_2$ + Ca

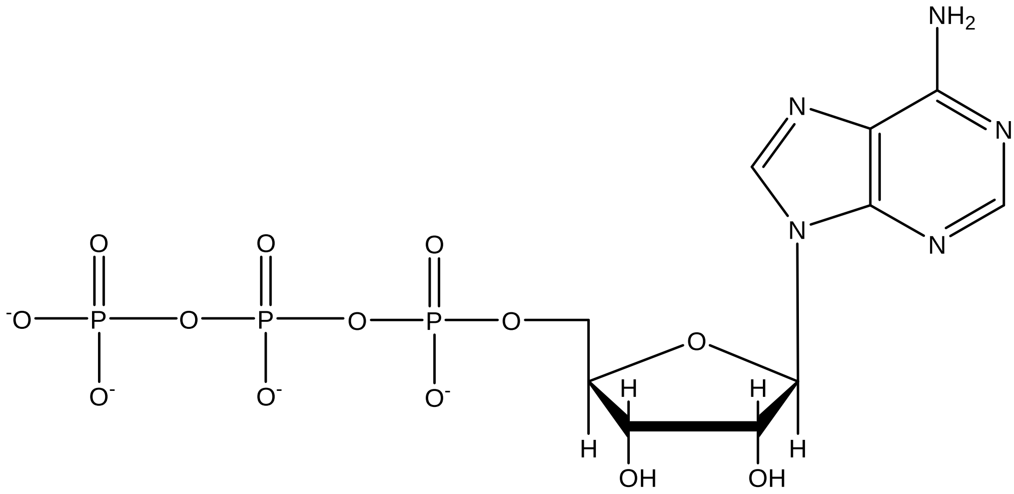
$\Delta H = \Delta_f H^0$(CaCl$_2$) – 2 $\Delta_f H^0$(CaCl) = –796.0 kJ mol^{-1}+ 463.8 kJ mol^{-1} = –332.2 kJ mol^{-1}

Disproportionation:	yes	no	no decision possible, more information needed
	☐	☒	☐

PROBLEM 5

Biochemistry with Thermodynamics

Structure of ATP^{4-}



Shifting chemical equilibria with ATP:

Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

$$c(ATP^{4-}) = 2.25\ \text{mmol dm}^{-3}$$
$$c(ADP^{3-}) = 0.25\ \text{mmol dm}^{-3}$$
$$c(HPO_4^{2-}) = 1.65\ \text{mmol dm}^{-3}$$

Free energy stored in ATP can be released according to the following reaction:

$$ATP^{4-} + H_2O \rightleftarrows ADP^{3-} + HPO_4^{2-} + H^+ \qquad \Delta G^{\circ\prime} = -30.5\ \text{kJ mol}^{-1} \qquad (1)$$

As the pH is close to 7 in most living cells, biochemists use $\Delta G^{\circ\prime}$ instead of ΔG°. The standard state of $\Delta G^{\circ\prime}$ is defined as having a constant pH of 7. In equations with $\Delta G^{\circ\prime}$ and K' for reactions at $pH = 7$ the concentration of H^+ is therefore omitted. Standard concentration is 1 mol dm^{-3}.

5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25 ℃ and *pH* = 7.

In living cells many so-called “anabolic” reactions take place, which are at first sight thermodynamically unfavourable because of a positive ΔG. The phosphorylation of glucose is an example:

glucose + $HPO_4^{2-} \rightleftharpoons$ glucose 6-phosphate^{2-} + H_2O $\Delta G°' = +13.8$ kJ mol^{-1} (2)

5.2 Calculate first the equilibrium constant K' of reaction (2) and then the ratio *c*(glucose 6-phosphate) / *c*(glucose) in the red blood cell in chemical equilibrium at 25 ℃ and *pH* = 7.

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with hydrolysis of ATP:

$$\text{glucose} + \text{ATP}^{4-} \overset{\text{hexokinase}}{\rightleftharpoons} \text{glucose 6-phosphate}^{2-} + \text{ADP}^{3-} + \text{H}^+ \qquad (3)$$

5.3 Calculate $\Delta G°$ and K' of reaction (3).

What is now the ratio c(glucose 6-phosphate) / c(glucose) in the red blood cell in chemical equilibrium at 25 ℃ and *pH* = 7?

ATP synthesis:

An adult person ingests about 8000 kJ of energy ($\Delta G'$) per day with the food.

5.4 a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a $\Delta G'$ of –52 kJ mol^{-1} for reaction (1), and a molecular weight of 503 g mol^{-1} for ATP.

b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?

c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.

In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

5.5 a) How many protons (H^+) are in a spherical mitochondrium with a diameter of 1 μm at $pH = 7$?

b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.

SOLUTION

5.1 Actual $\Delta G'$ of reaction (1):

$$\Delta G' = \Delta G^{o\prime} + R\ T\ \ln \frac{[\mathrm{ADP}^{3-}]\,[\mathrm{HPO}_4^{2-}]}{[\mathrm{ATP}^{4-}]}$$

$$= -30500 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1}\,\text{K}^{-1} \times 298.15 \text{ K} \times \ln \frac{0.00025 \times 0.00165}{0.00225}$$

$$= -30.5 \text{ kJ mol}^{-1} - 21.3 \text{ kJ mol}^{-1} = -51.8 \text{ kJ mol}^{-1}$$

5.2 Equilibrium constant K' of reaction (2), ratio c(glucose 6-phosphate) / c(glucose):

$$\Delta G^{o\prime} = -R\ T \ln K'$$

$$K' = e^{-\Delta G^{o\prime}/RT} = e^{-13800 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 0.0038$$

$$K' = \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]\,[\mathrm{HPO}_4^{2-}]}$$

$$\frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]} = K' \cdot [\mathrm{HPO}_4^{2-}]$$

$$= 0.0038 \cdot 0.00165$$

$$= 6.3 \cdot 10^{-6}$$

5.3 $\Delta G^{o\prime}$ and K' of reaction (3), ratio c(glucose 6-phosphate) / c(glucose):

$$\Delta G^{o\prime}(3) = \Delta G^{o\prime}(1) + \Delta G^{o\prime}(2) = -30.5 \text{ kJ mol}^{-1} + 13.8 \text{ kJ mol}^{-1} = -16.7 \text{ kJ mol}^{-1}$$

$$\Delta G^{o\prime} = -R\ T \ln K'$$

$$K' = e^{-\Delta G^{o\prime}/RT} = e^{16700 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 843$$

$$K' = \frac{c(\text{glucose 6-phosphate}) \times c(\text{ADP}^{3-})}{c(\text{glucose}) \times c(\text{ATP}^{4-})}$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \, \frac{c(\text{ATP}^{4-})}{c(\text{ADP}^{3-})}$$

$$= 843 \times (2.25 \text{ mmol dm}^{-3} / 0.25 \text{ mmol dm}^{-3}) = 7587$$

5.4 a) Mass of ATP produced per day:

Energy available for ATP synthesis: 8000 kJ day^{-1} × 0.5 = 4000 kJ day^{-1}

Energy required for synthesis of ATP: 52 kJ mol^{-1}

Amount of ATP produced: 4000 kJ day^{-1} / 52 kJ mol^{-1} = 76.9 mol day^{-1}

Mass of ATP produced: 76.9 mol day^{-1} × 503 g mol^{-1} = 38700 g day^{-1}

$\underline{m_{\textbf{day-1}} = 38.7 \text{ kg day}^{-1}}$

b) Mass of ATP in the human body:

Average lifetime: 1 day = 1440 min 1 min = 1440^{-1} day

Mass of ATP in the body: 38.7 kg day^{-1} / (1440 min day^{-1}) · 1 min = 26.9 g

m_{body} **=** 26.9 g

c) What happens to the rest of the free energy? Mark one correct answer:

- It is used to reduce the entropy of the body. ☐
- It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule. ☐
- It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP. ☐
- It heats the body of the person. ☒

5.5 a) How many protons are in a spherical mitochondrium with a diameter of 1 m at *pH* = 7?

$V = 4/3\,\pi\,r^3 = 4/3\,\pi\,(0.5\times10^{-6}\text{ m})^3 = 5.2\times10^{-19}\text{ m}^3 = 5.2\times10^{-16}\text{ dm}^3$

$c = 1\times10^{-7}\text{ mol dm}^{-3}$

$n = V\,c\cdot N_A = 5.2\times10^{-16}\text{ dm}^3 \times 1\times10^{-7}\text{ mol dm}^{-3} \times 6.022\times10^{23}\text{ mol}^{-1} = 31$

b) How many protons have to enter a mitochondrium?

Number of ATP molecules:

$$n(ATP) \quad = \quad \frac{m(\text{ATP})\, N_A}{M(\text{ATP})} \quad = \quad \frac{0.2\times10^{-15} g \times 6.022\times10^{23} \text{mol}^{-1}}{503 \text{ g mol}^{-1}} \quad = \quad 239400$$

Number of H$^+$ per cell: $n(\text{H}^+_{\text{per cell}}) = n(\text{ATP}) \times 3 = 718300$

Number of H$^+$ per mitochondrium: $n(\text{H}^+_{\text{mit}}) = n(\text{H}^+_{\text{per cell}}) / 1000 = 718$

PROBLEM 7

Kinetic Behaviour of Ozone

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,

$$2\ O_3 \rightarrow 3\ O_2.$$

One of the proposed mechanisms is expressed as

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O + O_2 \qquad (1)$$

$$O_3 + O \xrightarrow{k_2} 2\ O_2 \qquad (2)$$

where k_1, k_{-1}, and k_2 are the rate constants.

7.1 According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3, O_2, and O at time *t*, assuming step 2 is irreversible.

7.2 Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.

7.3 Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is d[O]/dt = 0, show that the rate equation is:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ($2O_3 \rightarrow 3O_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:

$$CCl_2F_2 \xrightarrow{h\nu} CF_2Cl + Cl \qquad (3)$$

7.4 Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:

$$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)} \qquad (4)$$

Assuming a two-step mechanism, propose the second step in the mechanism.

7.5 The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ mol^{-1}, while the activation energy for the reaction without the presence of catalyst is 14.0 kJ mol^{-1}. Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25 ^{o}C. Assume the frequency factor is the same for each reaction.

SOLUTION

7.1 $$-\frac{d[O_3]}{dt} = k_1[O_3] - k_{-1}[O][O_2] + k_2[O_3][O]$$

$$-\frac{d[O_2]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] - 2k_2[O_3][O]$$

$$-\frac{d[O]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O]$$

7.2 Equilibrium constant K is expressed as

$$K = \frac{[O][O_2]}{[O_3]} = \frac{k_1}{k_{-1}}$$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$-\frac{d[O_3]}{dt} = k_2[O_3][O] = \frac{k_1\,k_2\,[O_3]^2}{k_{-1}\,[O_2]}$$

7.3 $$-\frac{d[O]}{dt} = 0$$

$$-k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O] = 0$$

Thus $$-\frac{d[O_3]}{dt} = 2k_2[O_3][O] = \frac{2k_1 k_2 [O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$$

7.4 $ClO(g) + O_3(g) \rightarrow Cl(g) + 2\,O_2(g)$

7.5 According to equation $k = A \exp(-E_a / RT)$,

the ratio of rate constants yields

Ratio = $\exp[(14.0 - 2.1) \times 1000 / (8.314 \times 298)] = 122$.

PROBLEM 8

Protein Folding

Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:

$$\mathbf{N} \xrightleftharpoons{K(T)} \mathbf{U}$$

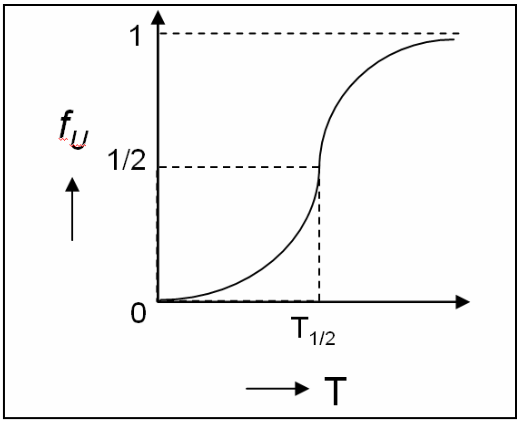
where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. K(*T*) is the equilibrium constant for the process at absolute temperature *T*.

8.1 What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?

8.2 What is the standard free energy change of the process ($\Delta G°(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.

8.3 If $(C_N)_{eq}$ and $(C_U)_{eq}$ denote the equilibrium concentrations of *N* and *U* in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{eq}/C$. Deduce an expression for f_U in terms of the equilibrium constant *K*. Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by f_U = ½ and $T = T_{½}$. The latter is often referred to as the denaturation temperature. At temperatures higher than $T_{½}$, f_U increases above ½, but at temperatures lower than $T_{½}$, f_U decreases below ½.

8.4 What is the sign of $\Delta G°(T)$ at temperatures below and above $T_{½}$? Select your answer from the following choices.

a) Negative both below and above $T_{½}$.

b) Positive both below and above $T_{½}$.

c) Positive below $T_{½}$, but negative above $T_{½}$.

d) Negative below $T_{½}$, but positive above $T_{½}$..

8.5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{½}$ and (ii) decreases below $T_{½}$? Select your answer from the following choices.

a) Decrease in both cases.

b) Increase in both cases.

c) Increases above $\mathrm{T}_{½}$, but decreases below $\mathrm{T}_{½}$.

d) Decreases above $\mathrm{T}_{½}$, but increases below $\mathrm{T}_{½}$.

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:

$$\mathbf{N} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{U}$$

where k_f and k_b denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8.6 For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b?

8.7 Derive a rate law for the overall process, that is $\mathrm{d}C_U/dt$ in terms of only rate constants, C_U and $(C_U)_{eq}$.

SOLUTION

8.1 Answer: 1

8.2 Answer: 0 kJ mol^{-1}

8.3 $$f_U = \frac{C_U^{eq}}{C_N^{eq} + C_U^{eq}} = \frac{\dfrac{C_U^{eq}}{C_N^{eq}}}{1 + \dfrac{C_U^{eq}}{C_N^{eq}}} = \frac{K}{1+K}$$

8.4 Correct answer is (c). Positive below $T_{1/2}$, but negatíve above $T_{1/2}$

8.5 Correct answer is (d). Decreases above $T_{1/2}$, but increases below $T_{1/2}$.

8.6 Answer: $K = k_f / k_b$

8.7 $dC_U/dt = k_fC_N - k_bC_U$

$= k_f(C - C_U) - k_bC_U = k_fC - k_fC_U - k_bC_U = k_fC - (k_f + k_b)\, C_U$ (1)

$K = k_f / k_b = (C_U)_{eq} / (C_N)_{eq}$

$1 / K = k_b / k_f = (C_N)_{eq} / (C_U)_{eq}$

$\Rightarrow \quad k_b / k_f + 1 = (C_N)_{eq} / (C_U)_{eq} + 1$

$\Rightarrow \quad (k_b + k_f) / k_f = [(C_N)_{eq} + (C_U)_{eq}] / (C_U)_{eq}$

$\Rightarrow \quad (k_b + k_f) / k_f = C/(C_U)_{eq}$

$C = [(k_b + k_f)\, (C_U)_{eq}\,] / k_f$ (2)

Now substitute C obtained from eq (2) to eq (1).

We get $k_f\{ [(k_b + k_f)\, (C_U)_{eq}] / k_f\} - (k_f + k_b)\, C_U$

$\Rightarrow \quad [(k_b + k_f)\, (C_U)_{eq}] - (k_f + k_b)\, C_U$

$\Rightarrow \quad - (k_f + k_b)\, [C_U - (C_U)_{eq}]$

So we get

$dC_U/dt = - (k_f + k_b)\, [C_U - (C_U)_{eq}]$

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THEORETICAL PROBLEMS

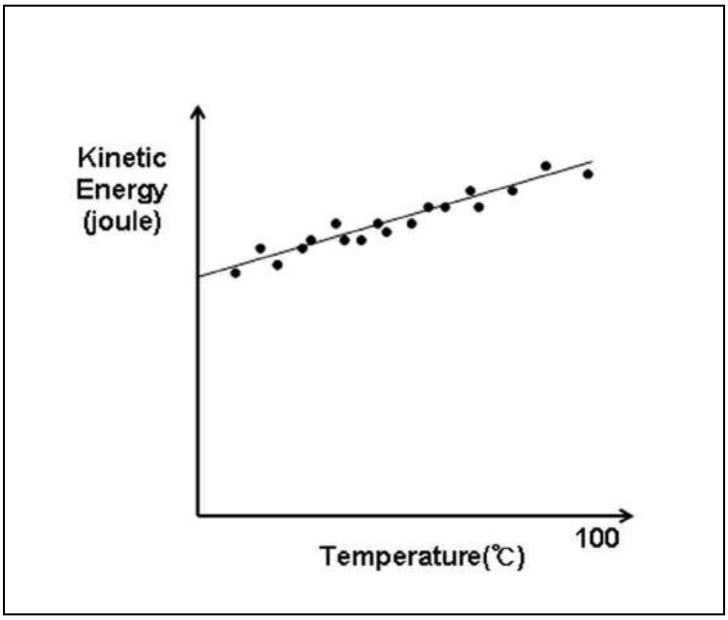
PROBLEM 1

Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27 °C, each droplet is 1.0 micrometer in diameter and undergoes collisions with argon. Assume that inter-droplet collisions do not occur. The root-mean-square speed of these droplets was determined to be 0.50 cm s^{-1} at 27 °C. The density of a water droplet is 1.0 g cm^{-3}.

1.1 Calculate the average kinetic energy ($mv^2/2$) of this droplet at 27 °C. The volume of a sphere is given by (4/3) π r^3 where r is the radius.

If the temperature is changed, then droplet size and speed of the droplet will also change. The average kinetic energy of a droplet between 0 °C and 100 °C as a function of temperature is found to be linear. Assume that it remains linear below 0 °C.



At thermal equlibrium, the average kinetic energy is the same irrespective of particle masses (equipartition theorem).

The specific heat capacity, at constant volume, of argon (atomic weight, 40) gas is 0.31 J g^{-1} K^{-1}.

1.2. Calculate Avogadro's number without using the ideal gas law, the gas constant, Boltzmann's constant).

SOLUTION

1.1 The mass of a water droplet:

$$m = V\rho = [(4/3)\,\pi\, r^3]\,\rho = (4/3)\,\pi\,(0.5\times10^{-6}\text{ m})^3\,(1.0\text{ g cm}^{-3}) = 5.2\times10^{-16}\text{ kg}$$

Average kinetic energy at 27°C:

$$E_k = \frac{m\,v^2}{2} = \frac{(5.2\times10^{-16}\text{ kg})\times(0.51\times10^{-2}\text{ m/s})^2}{2} = 6.9\times10^{-21}\text{ kg m}^2/\text{s}^2 = \underline{6.9\times10^{-21}\text{ J}}$$

1.2 The average kinetic energy of an argon atom is the same as that of a water droplet. E_k becomes zero at –273 °C.

From the linear relationship in the figure, $E_k = a\,T$ (absolute temperature) where a is the increase in kinetic energy of an argon atom per degree.

$$a = \frac{E_k}{T} = \frac{6.9\times10^{-21}\text{ J}}{(27+273)\text{ K}} = 2.3\times10^{-23}\text{ J K}^{-1}$$

S: specific heat of argon N: number of atoms in 1g of argon

$$S = 0.31\text{ J g}^{-1}\text{ K}^{-1} = a\times N$$

$$N = \frac{S}{a} = \frac{0.31\text{ J g}^{-1}\text{ K}^{-1}}{2.3\times10^{-23}\text{ J K}^{-1}} = 1.4\times10^{22}\text{ g}^{-1}$$

Avogadro's number (N_A) : Number of argon atoms in 40 g of argon

$$N_A = 40\text{ g mol}^{-1}\times1.4\times10^{22}\text{ g}^{-1} = \underline{5.6\times10^{23}\text{ mol}^{-1}}$$

PROBLEM 2

Detection of hydrogen

Hydrogen is prevalent in the universe. Life in the universe is ultimately based on hydrogen.

2.1 There are about 1×10^{23} stars in the universe. Assume that they are like our sun (radius, 700,000 km; density, 1.4 g cm^{-3}; 3/4 hydrogen and 1/4 helium by mass). Estimate the number of stellar protons in the universe to one significant figure.

In the 1920s Cecilia Payne discovered by spectral analysis of starlight that hydrogen is the most abundant element in most stars.

2.2 The electronic transition of a hydrogen atom is governed by $\Delta E(n_i\rightarrow n_f) = - C(1/n_f^2 - 1/n_i^2)$, where n is principle quantum number, and C is a constant. For detection of the $\Delta E(3\rightarrow2)$ transition (656.3 nm in the Balmer series), the electron in the ground state of the hydrogen atom needs to be excited first to the $n = 2$ state. Calculate the wavelength (in nm) of the absorption line in the starlight corresponding to the $\Delta E(1\rightarrow2)$ transition.

2.3 According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature T is given by $\lambda T = 2.9\times10^{-3}$ m K. Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the $n = 1 \rightarrow n = 2$ excitation of hydrogen.

The ground state of hydrogen is split into two hyperfine levels due to the interaction between the magnetic moment of the proton and that of the electron. In 1951, Purcell discovered a spectral line at 1420 MHz due to the hyperfine transition of hydrogen in interstellar space.

2.4 Hydrogen in interstellar space cannot be excited electronically by starlight. However, the cosmic background radiation, equivalent to 2.7 K, can cause the hyperfine transition. Calculate the temperature of a blackbody whose peak intensity corresponds to the 1420 MHz transition.

2.5 Wien generated hydrogen ions by discharge of hydrogen gas at a very low pressure and determined the e/m value, which turned out to be the highest among different gases tested. In 1919, Rutherford bombarded nitrogen with alpha-particles and observed emission of a positively charged particle which turned out to be the hydrogen ion observed by Wien. Rutherford named this particle the "proton". Fill in the blank.

____

SOLUTION

2.1 Mass of a typical star = $(4/3) \times (3.1) \times (7\times10^8 \text{ m})^3 \times (1.4\times10^6 \text{ g m}^{-3}) = 2\times10^{33}$ g

Mass of protons of a typical star = $(2\times10^{33} \text{ g}) \times (3/4 + 1/8) = 1.8\times10^{33}$ g

Number of protons of a typical star = $(1.8\times10^{33} \text{ g}) \times (6\times10^{23} \text{ g}^{-1}) = 1\times10^{57}$

Number of stellar protons in the universe = $(1\times10^{57}) \times (10^{23}) = \underline{1\times10^{80}}$

2.2 $\Delta E(2\rightarrow3) = C(1/4 - 1/9) = 0.1389\ C$ $\qquad \lambda(2\rightarrow3) = 656.3$ nm

$\Delta E(1\rightarrow2) = C(1/1 - 1/4) = 0.75\ C$

$\lambda(1\rightarrow2) = (656.3) \times (0.1389 / 0.75) = 121.5$ nm

2.3 $T = 2.9\times10^{-3}$ m K / 1.215×10^{-7} m = 2.4×10^4 K

2.4 $\lambda = 3\times10^8$ m / 1.42×10^9 = 0.21 m

$T = 2.9\times10^{-3}$ m K / 0.21 m = 0.014 K

2.5 $^{14}N + {}^{4}He \rightarrow {}^{17}O + {}^{1}H$

PROBLEM 3

Interstellar chemistry

Early interstellar chemistry is thought to have been a prelude to life on Earth. Molecules can be formed in space via heterogeneous reactions at the surface of dust particles, often called the interstellar ice grains (IIGs). Imagine the reaction between H and C atoms on the IIG surface that forms CH. The CH product can either be desorbed from the surface or further react through surface migration with adsorbed H atoms to form CH_2, CH_3, etc.

Depending on how energetically a molecule "jumps" from its anchored site, it either leaves the surface permanently (desorption) or returns to a new position at the surface (migration). The rates of desorption and migratory jump follow the Arrhenius formula, $k = A \exp(-E/RT)$, where k is the rate constant for desorption or migratory jump, A the jumping frequency, and E the activation energy for the respective event.

3.1 Desorption of CH from the IIG surface follows first-order kinetics. Calculate the average residence time of CH on the surface at 20 K. Assume that $A = 1\times10^{12}$ s^{-1} and E_{des} = 12 kJ mol^{-1}.

3.2 Consider the shortest time it would take for one CH unit to move from its initial position to the opposite side of an IIG by successive migratory jumps. Assume that the activation energy for migration (E_{mig}) is 6 kJ mol^{-1}, and the IIG is a sphere with a 0.1 µm radius. Each migratory jump laterally advances the molecule by 0.3 nm. Show work and choose your answer from (a) – (e) below.

(a) $t \le 1$ day (b) 10 days $\le t \le 10^2$ yr c) 10^3 yr $\le t \le 10^6$ yr

(d) 10^7 yr $\le t \le 10^{10}$ yr (e) $t \ge 10^{11}$ yr

3.3 Consider the reaction of CO with H_2 to form H_2CO. The activation energy on a metal catalyst is 20 kJ mol^{-1} that is produced by formaldehyde at a rate of 1 molecule/s per site at 300 K. Estimate the rate of formaldehyde formation per site if the reaction takes place at 20 K.

3.4 Which is a set of all true statements? Circle one.

(a) Most CH species are desorbed from the IIG surface before encountering other reactants by surface migration.

(b) IIGs can assist transformation of simple molecules to more complex ones in interstellar space.

(c) For a reaction on the IIG to occur at an appreciable speed during the age of the Universe (1×10^{10} yr), the reaction energy barrier must be absent or negligible.

☐ (a) ☐ (b) ☐ (c) ☐ (a, b) ☐ (a, c) ☐ (b, c) ☐ (a, b, c)

SOLUTION

3.1 $k_{des} = A \exp(-E_{des}/RT) = (1\times10^{12}\ s^{-1}) \times (5\times10^{-32}) = 5\times10^{-20}\ s^{-1}$ at $T = 20$ K

surface residence time, $T_{residence} = 1 / k_{des} = 2\times10^{19}$ s = $\underline{6\times10^{11}\ yr}$

(full credit for $T_{half\text{-}life} = \ln 2 / k_{des} = 1\times10^{19}$ s = 4×10^{11} yr)

residence time = 2×10^{19} s

3.2 The distance to be traveled by a molecule: $x = \pi r = 300$ nm.

$k_{mig} = A \exp(-E_{mig} / RT) = (1\times10^{12}\ s^{-1}) \times (2\times10^{-16}) = 2\times10^{-4}\ s^{-1}$ at $T = 20$ K

Average time between migratory jumps, $T = 1 / k_{mig} = 5\times10^{3}$ s

Time needed to move 300 nm = (300 nm / 0.3 nm) jumps × (5×10^{3} s/jump) =

= 5×10^{6} s = 50 days

The correct answer is (b).

(Full credit for the calculation using a random-walk model. In this case:

$t = T\,(x/d)^{2} = 5\times10^{9}$ s = 160 yr. The answer is still (b).)

3.3 $k(20\ K) / k(300\ K) = \exp[(E/R)\ (1/T_1 - 1/T_2)] = e^{-112} = \sim 1\times10^{-49}$ for the given reaction

The rate of formaldehyde production at 20 K = = ~ 1×10^{-49} molecule/site/s =

= ~ 1×10^{-42} molecule/site/ yr

(The reaction will not occur at all during the age of the universe (1×10^{10} yr).)

3.4 The correct answer is (b, c).

PROBLEM 7

Hydrogen Economy

Hydrogen is more energy-dense than carbon, by mass. Thus, historically there has been a move toward fuel with higher hydrogen content: coal → oil → natural gas → hydrogen. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

7.1 Consider hydrogen in a cylinder of 80 MPa at 25 °C. Using the ideal gas law, estimate the density of hydrogen in the cylinder in kg m^{-3}.

7.2 Calculate the ratio between heat generated when hydrogen is burned and heat generated when the same weight of carbon is burned. The difference comes to a large extent from the fact that the most abundant isotope of hydrogen has no neutron and hydrogen has no inner electron shell. ΔH_f^o [$H_2O(l)$] = -286 kJ/mol, ΔH_f^o [$CO_2(g)$] = -394 kJ/mol.

7.3 Calculate the theoretical maximum work produced by the combustion of 1 kg hydrogen (a) from the electric motor using hydrogen fuel cell and (b) from the heat engine working between 25 °C and 300 °C. The efficiency (work done/heat absorbed) of an ideal heat engine working between T_{cold} and T_{hot} is given by [$1 - T_{cold}/T_{hot}$].

$S^o_{298}[H_2(g)] = 131\ \text{J mol}^{-1}\ \text{K}^{-1}$

$S^o_{298}[O_2(g)] = 205\ \text{J mol}^{-1}\ \text{K}^{-1}$

$S^o_{298}[H_2O(l)] = 70\ \text{J mol}^{-1}\ \text{K}^{-1}$

If the fuel cell is working at 1 W and the standard potential difference, how long will the electric motor run at what current?

SOLUTION

7.1 $$\frac{n}{V} = \frac{p}{RT} = \frac{80\times10^6\ \text{Pa}}{8{,}314\ \text{J mol}^{-1}\ \text{K}^{-1}\times 298\ \text{K}} = 32\ \text{kmol m}^{-3}$$

$$\rho = \frac{m}{V} = 32\ \text{kmol m}^{-3} \times 2\ \text{kg kmol}^{-1} = 64\ \text{kg m}^{-3}$$

7-2. $Hg_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta H_{\text{rexn-1}} = \Delta H_f\,[H_2O(l)] = -286\ \text{kJ mol}^{-1} = -143\ \text{kJ g}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H_{\text{rexn-2}} = \Delta H_f\,[CO_2(g)] = -394\ \text{kJ mol}^{-1} = -33\ \text{kJ g}^{-1}$

$$\frac{(-\Delta H_{\text{rexn}-1})}{(-\Delta H_{\text{rexn}-2})} = 4.3 \quad \text{or} \quad \frac{(-\Delta H_{\text{rexn}-2})}{(-\Delta H_{\text{rexn}-1})} = 0.23$$

7.3 $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$\Delta H_c = -286\ \text{kJ mol}^{-1} = -143\ \text{kJ g}^{-1} = -143\times10^3\ \text{kJ kg}^{-1}$

$\Delta G = \Delta H - T\Delta S$

$\Delta S_c = 70 - 131 - 205/2 = -163.5\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta G_c = -286\ \text{kJ mol}^{-1} + 298\ \text{K} \times 163.5\ \text{J mol}^{-1}\,\text{K}^{-1} = -237\ \text{kJ mol}^{-1} = -1.2\times10^5\ \text{kJ kg}^{-1}$

(a) electric motor: $W_{\max} = \Delta G_c \times 1\ \text{kg} = -1.2\times10^5\ \text{kJ}$

(b) heat engine: $W_{\max} = \text{efficiency} \times \Delta H_c$

$= (1 - 298 / 573) \times (-143\times10^3\ \text{kJ}) = -6.9\times10^4\ \text{kJ}$

$119\times10^3\ \text{kJ} = 1\ \text{W} \times \text{t(sec)}$

$t = 1.2\times10^8\ \text{s} = 3.3\times10^4\ \text{h} = 1.4\times10^3\ \text{days} = 46\ \text{month} = 3.8\ \text{yr}$

$\Delta G = -n\,F\,E$ n = number of electrons involved in the reaction

$F = 96.5\ \text{kC mol}^{-1}$

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ n = 2

$$E = \frac{-\Delta G}{n\,F} = \frac{237\ \text{kJ mol}^{-1}}{2\times 96.5\ \text{kC mol}^{-1}} = 123\ \text{V}$$

$$I = \frac{W}{E} = 0.81\ \text{A}$$

PROBLEM 8

Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0 = –393.51$ kJ(/mol) (1)

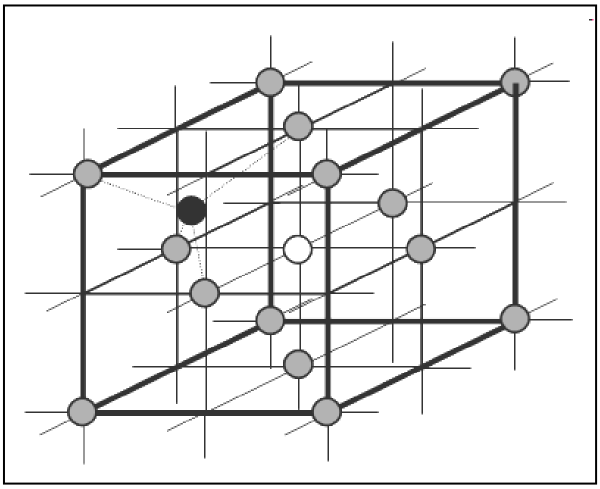
$CO_2(g) + C(s) \rightarrow 2\ CO(g)$ $\Delta H^0 = 172.46$ kJ(/mol) (2)

$Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$ $\Delta H^0 =$? (3)

8.1 Indicate the reducing agent in each reaction.

8.2 Balance reaction (3) and calculate the equilibrium constant of reaction (3) at 1200 °C. $\Delta H_f^\circ(Fe_2O_3(s)) = –824.2$ kJ mol^{-1},
S°(J mol^{-1} K^{-1}): Fe(s) = 27.28, Fe_2O_3(s) = 87.40, C(s) = 5.74, CO(g) = 197.674, CO_2(g) = 213.74

In the manufacture of celadon pottery, Fe_2O_3 is partially reduced in a charcoal kiln to mixed oxides of Fe_3O_4 and FeO. The amount of the different oxides seems to be related to the "mystic" color of celadon ceramics. Fe_3O_4 (magnetite) itself is a mixed oxide containing Fe^{2+} and Fe^{3+} ions and belongs to a group of compounds with a general formula of AB_2O_4. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.



8.3 How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighbouring units.

AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

8.4 What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4?

8.5 Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.

SOLUTION

8.1 (1): C (2): C (3): CO

8.2 Balanced equation (3): $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0_{(1)} = -393.51\ kJ = \Delta H_f^0\ (CO_2(g))$

(2) $CO_2(g) + C(s) \rightarrow 2\ CO(g)$ $\Delta H^0_{(2)} = 172.46\ kJ$

From (1) and (2):

$\Delta H_f^0(CO(g)) = (1/2)\ \{172.46 + (-393.51)\} = -110.525\ kJ$

$\Delta H_f^0(Fe_2O_3) = –824.2$ kJ

$\Delta H^0_{(3)} = 3 \times \Delta H_f^0(CO_2(g)) – \Delta H_f^0(Fe_2O_3) – 3 \times \Delta H_f^0(CO(g))$

$= [3 \times (–393.51)] – (–824.2) – [3 \times (–110.525)] = –24.8$ kJ

$\Delta S°_{(3)} = (2 \times 27.28) + (3 \times 213.74) – 87.4 – (3 \times 197.674) = 15.36$ J K^{-1}

$\Delta G^0_{(3)} = \Delta H^0 – T\Delta S^0 = –24.8$ kJ – (15.36 J K^{-1} $\times$ 1 kJ /1000 J x 1473.15 K) =

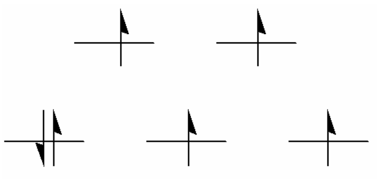
= – 47.43 kJ

$$K = e^{(-\Delta G°/RT)} = e^{(47430\,J\ /\ (8.314\ J\ K^{-1} \times 1473.15\,K))} = 48$$

8.3 One AB_2O_4 unit has available 4 (= 1 + (1/4 $\times$ 12) octahedral sites.

8.4 Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives (1/8) x 100 % = 12.5 % occupancy in available tetrahedral sites.

8.5



PROBLEM 2

Nanochemistry

Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)

$$CO + 3\ H_2 \xrightarrow{Fe,Co} CH_4 + H_2O$$

Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:

$$Co(s) + H_2O(g) \rightleftarrows CoO(s) + H_2(g) \qquad (1)$$

Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

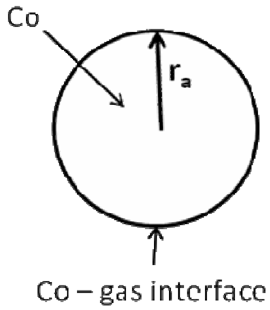


Fig. 1

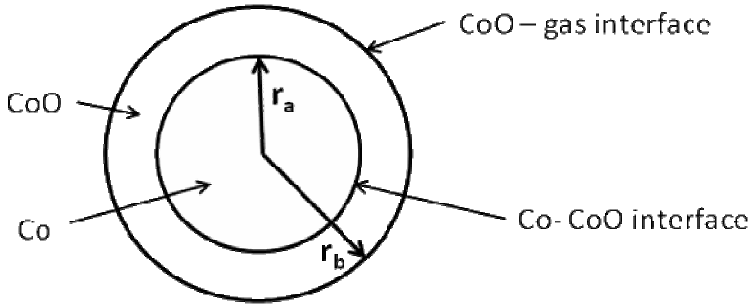


Fig. 2

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^0(r) = G^0(\text{bulk}) + \frac{2\sigma}{r}V$$

2.1 Calculate the standard Gibbs energy $\Delta_r G^0(1)$ and the equilibrium constant for the reaction (1) at T = 500 K.

2.2 Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig. 1) of radius:

(a) 10^{-8} m,·

(b) 10^{-9} m.

The surface tension at the Co-gas interface is 0.16 J m^{-2}. CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO, CH_4, H_2, H_2O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is p = 1 bar, temperature is T = 500 K. The mole fraction of hydrogen (%) in the mixture is 0.15 %.

2.3 At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of

(a) a bulk phase

(b) spherical nanoparticles with r_a = 1 nm (Fig. 1).

2.4 What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p(H_2O)/p(H_2)$ and a constant temperature:

(a) to increase r_a;

(b) to decrease r_a;

(c) change of r_a has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (Fig. 2).

In the following problems denote surface tensions as $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, radii as r_a, r_b, molar volumes as V(Co); V(CoO).

2.5 Write down the expression for the standard molar Gibbs function of CoO.

2.6 Write down the expression for the standard molar Gibbs function of Co.

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{in} - P_{ex} = \Delta P = \Delta P_1 + \Delta P_2 = 2\frac{\sigma_1}{r_1} + 2\frac{\sigma_2}{r_2}$$

r_i, σ_i are radius and surface tension at the spherical interface i, respectively.

2.7 Express the standard Gibbs energy of the reaction (1) $\Delta_r G^0(1,r_a,r_b)$ in terms of $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, r_a, r_b, V(Co); V(CoO) and $\Delta_r G^0(1)$.

2.8 When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, r_a = r_b = r_0, and $\Delta_r G^0(1,r_a,r_b) = \Delta_r G^0(1,r_0)$. Assume that

$\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_r G^0(1,r_0)$ on r_0?

2.9 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p(H_2O)/p(H_2)$ and a constant temperature:

a) increase r_0

b) decrease r_0

c) change of r_0 has no effect.

.

Reference data:

Substance	ρ, g cm^{-3}	$\Delta_f G^o_{500}$, kJ mol^{-1}
Co (s)	8.90	
CoO (s)	5.68	–198.4
H_2O (gas)		–219.1

SOLUTION

2.1 The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G^0_{500}(1) = \Delta G^0_{f,500}(\text{CoO,s}) - \Delta G^0_{f,500}(\text{H}_2\text{O,g}) = -198.4 + 219.1 = 20.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\frac{\Delta_r G^0_{500}(1)}{RT}} = e^{-\frac{20700}{8.314 \times 500}} = 6.88\times10^{-3}$$

2.2 The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\Delta_r G^o_{500}(1,r_a) = G^0_{\text{bulk},500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,g}) - G^0_{\text{sph}}(\text{Co}) =$$

$$= G^0_{500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,gas}) - \left(G^0_{500}(\text{Co,s}) + \frac{2\,\sigma_{\text{Co-gas}}\text{V(Co)}}{r_a}\right) =$$

$$= \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}V(\text{Co})}{r_a};$$

$$V(\text{Co}) = \frac{M_{\text{Co}}}{\rho(\text{Co})} = \frac{1\times10^{-6}\times59.0}{8.90} = 6.6\times10^{-6}\ \text{m}^3\ \text{mol}^{-1}$$

for spherical particles with r_a = 10^{-8}, 10^{-9} m one gets, respectively

$$\frac{2\,\sigma_{\text{Co-gas}}\,V(\text{Co})}{r_a} = 210 \text{ and } 2100 \text{ J mol}^{-1}$$

$\Delta_r G^o_{500}(1,r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ mol^{-1}, respectively.

The equilibrium constant is calculated from the equation

$$K(1,r_a) = \exp\left(-\frac{\Delta_r G^o_{500}(1,r_a)}{RT}\right)$$

$$K(1,\text{r}_a) = 7.22\times10^{-3}; \quad r_a = 10^{-8}\text{ m} \qquad K(1,r_a) = 11.4\times10^{-3}; \quad r_a = 10^{-9}\text{ m}$$

2.3 The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G^o_{500}(1,r_a) = \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a}V(\text{Co})$$

$\Delta_r G^o_{500}(1)$ is 20.7 kJ mol^{-1}. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^o_{500}(1,r_a)$ is 18.6 kJ mol^{-1}.

Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$\Delta_r G(1) = \Delta_r G^o_{500}(1) + RT\ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G^o_{500}(1) - \text{RT}\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and for spherical cobalt nanoparticles with r_a = 1 nm:

$$\Delta_r G(1,r_a) = \Delta_r G^o_{500}(1,r_a) + \text{RT}\ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) =$$

$$= \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a}V(\text{Co}) - \text{RT}\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

$\Delta_r G^o_{500}(1)$ is equal to 20.7 kJ mol^{-1}. For spherical cobalt particles with r_a = 1 nm equals to 18.6 kJ mol^{-1}

2.4 For the spontaneous oxidation

$$\Delta_r G(1,r_a) = \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and

$$\Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \le RT\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right)$$

The left hand side of the last inequality becomes more positive with the increase of *r_a*. At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius *r_a*. The answer (a) is correct.

2.5 The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G^0_{\text{sph}}(\text{CoO},r_b) = G_{\text{bulk}}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) = G^o(\text{CoO,s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO})$$

2.6 The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$G^0_{\text{sph}}(\text{Co},r_a,r_b) = G_{\text{bulk}}(\text{Co}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= G^o(\text{Co,s}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right)$$

The expression in brackets gives the additional pressure in the internal layer
(see the Hint).

2.7 The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\Delta_r G^0(1,r_a,r_b) = G^0_{\text{sph}}(\text{CoO},\text{r}_b) + G^o(\text{H}_2,\text{gas}) - G^o(\text{H}_2\text{O},\text{gas}) - G^0_{\text{sph}}(\text{Co},r_a,r_b) =$$

$$= G^o(\text{CoO,s}) + G^o(\text{H}_2,\text{gas}) - G^o(\text{H}_2\text{O},\text{gas}) - G^o(\text{Co,s}) +$$

$$+ \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) - 2V(\text{Co})\left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= \Delta_r G^o(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\text{CoO}) - V(\text{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co})$$

2.8 Under the assumptions made

$$\Delta_r G^{\circ}(1,r_a,r_b) = \Delta_r G^0(1,r_0) =$$

$$= \Delta_r G^{\circ}(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\text{CoO}) - V(\text{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a}\text{V(Co)} =$$

$$= \Delta_r G^{\circ}(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right)$$

The term in brackets in the right-hand side is positive

$$\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) = 6.56\times10^{-6}\ \text{m}^3$$

$\Delta_r G^0(1,r_0)$ is directly proportional to $\left(\frac{1}{r_0}\right)$. The plot (a) is correct.

2.9 The spontaneous forward reaction (1) is possible, when $\Delta_r G(1,r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) \leq RT\ \ln\frac{p_{H_2O}}{p_{H_2}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0. At certain point the inequality will be violated and the spontaneous oxidation will not take place.

In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0.

The answer (b) is correct.

PROBLEM 3

Unstable chemical reactions

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:

$$\mathrm{B + 2\,X \xrightarrow{k_1} 3\,X}$$

$$\mathrm{X + D \xrightarrow{k_2} P}$$

(B and D are reagents, X is an intermediate and P is a product).

3.1 Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.

3.2 Deduce a rate equation using steady-state approximation. Find the orders:

(i) a partial reaction order with respect to B;

(ii) a partial reaction order with respect to D;

(iii) the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: [B] = [D] = const.

3.3 Without solving the kinetic equation draw the kinetic curve [X](t) for the cases:

1) $[X]_0 > \dfrac{k_2}{k_1}$; 2) $[X]_0 < \dfrac{k_2}{k_1}$.

3.4 Without solving the kinetic equation draw the kinetic curve [X](t) for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[B]_0 = [D]_0$, $[X]_0 > \dfrac{k_2}{k_1}$.

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:

$$C_2H_6 + X + ... \xrightarrow{k_1} 2\,X$$

$$X + Y \xrightarrow{k_2} 2\,Y + ...$$

$$C_2H_6 + Y + ... \xrightarrow{k_3} 2\,P$$

Under specific conditions this reaction displays oscillatory behavior: Intermediates are peroxide $C_2H_6O_2$ and aldehyde C_2H_4O, P is a stable product.

3.5 Identify X, Y, and P. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	A, cm^3 mol^{-1}s^{-1}	E_A, kJ mol^{-1}
1	1.0×10^{11}	90
2	3.0×10^{12}	100

3.6 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

SOLUTION

3.1 The overall reaction equation

B + D → P

The kinetic equation for X

$$\frac{d[X]}{dt} = k_1[B][X]^2 - k_2[D][X]$$

3.2 Under the steady-state conditions

$$\frac{d[P]}{dt} = k_2[D][X] = k_1[B][X]^2,$$

whence

$$[\mathrm{X}] = \frac{k_2[\mathrm{D}]}{k_1[\mathrm{B}]}$$

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = \frac{k_2^2[\mathrm{D}]^2}{k_1[\mathrm{B}]}$$

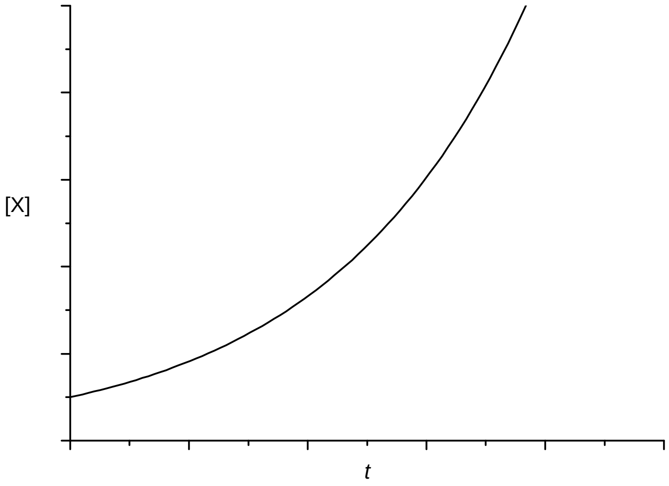
The reaction order is 2 with respect to D, and –1 with respect to B.

The overall order is 1.

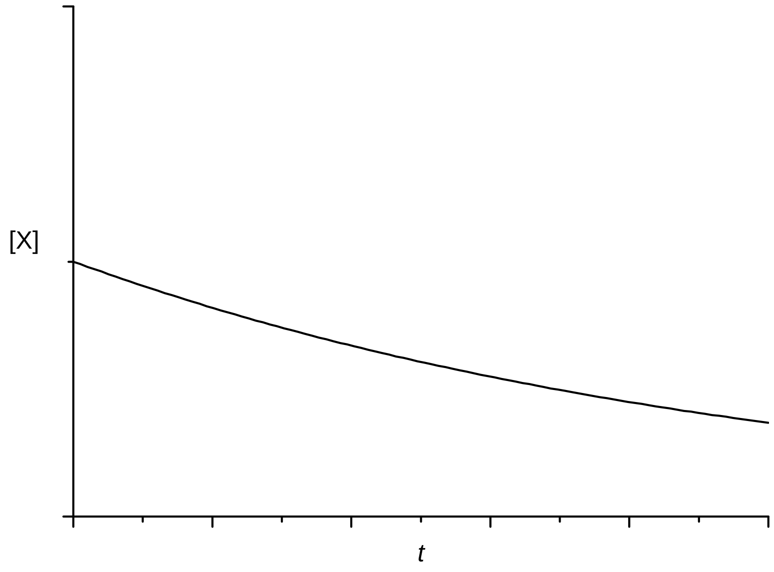
3.3 In an open system the initial reaction rate is:

$$\frac{\mathrm{d[X]}}{\mathrm{d}t} = [\mathrm{B}][\mathrm{X}]\left(k_1[\mathrm{X}] - k_2\right)$$

1) If $[X]_0 > k_2/k_1$, then d[X]/dt > 0 at any time, and the concentration of X monotonically increases:



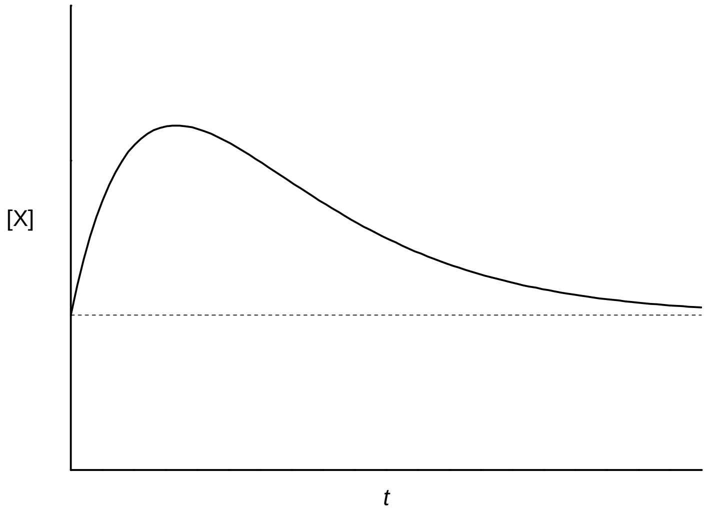
2) If $[X]_0 < \frac{k_2}{k_1}1$, then $\frac{\mathrm{d[X]}}{\mathrm{d}t} < 0$ at any time, and the concentration of X monotonically decreases:



3.4 In a closed system the initial reaction rate is:

$$\left.\frac{d[X]}{dt}\right|_{t=0} = k_1[B]_0[X]_0^2 - k_2[D]_0[X]_0 = [B]_0[X]_0\left(k_1[X]_0 - k_2\right) > 0$$

Hence, at the beginning of the reaction [X] increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



3.5 X – $C_2H_6O_2$, Y – C_2H_4O, P – C_2H_6O. Dots denote O_2 and H_2O.

$$C_2H_6 + C_2H_6O_2 + O_2 \rightarrow 2\,C_2H_6O_2$$

$$C_2H_6O_2 + C_2H_4O \rightarrow 2\,C_2H_4O + H_2O$$

$$C_2H_6 + C_2H_4O + H_2O \rightarrow 2\,C_2H_6O$$

3.6 At the highest possible temperature the rate constants are equal:

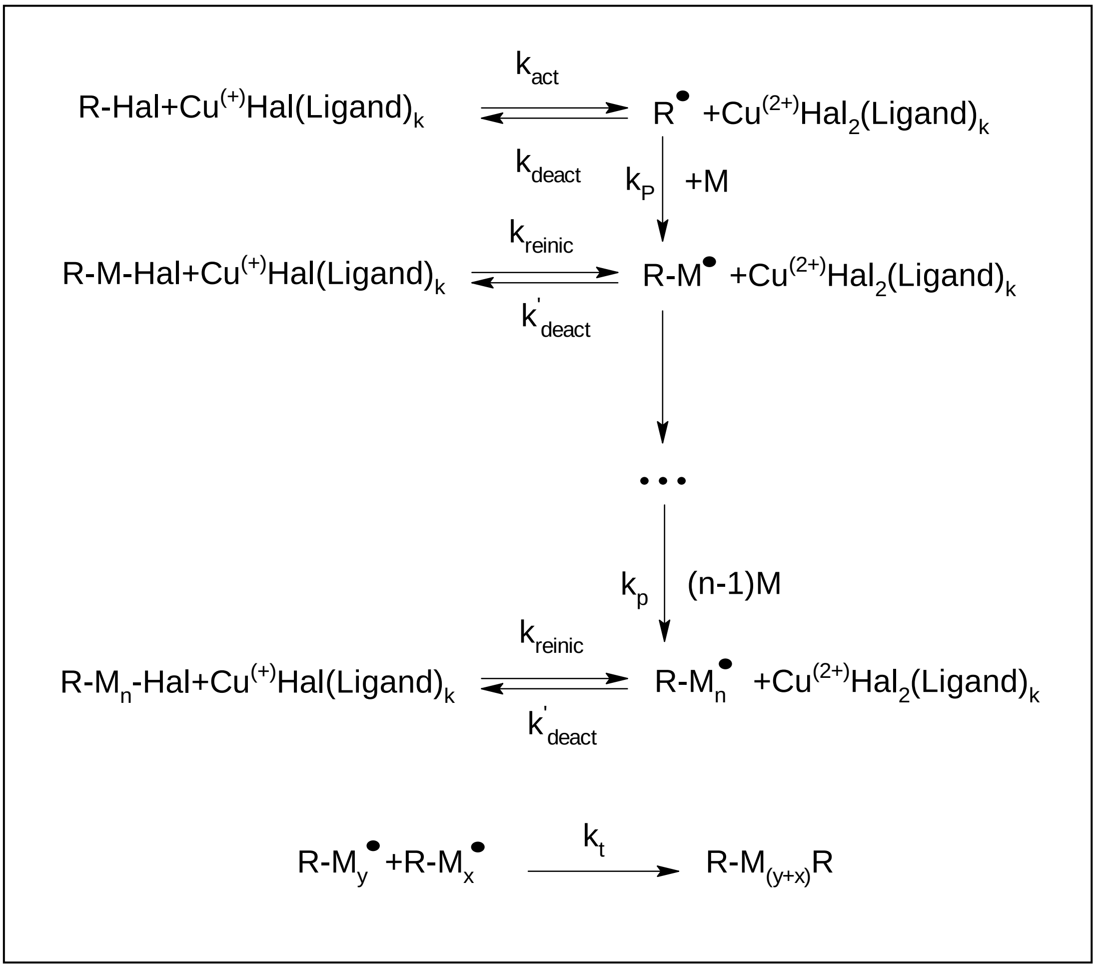
$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R \ln \dfrac{A_2}{A_1}} = 354\ \text{K}$$

PROBLEM 8

ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen):



The reaction rate constants are:

k_{act} - all activation reactions, k_{deact} – all reversible deactivation reactions, k_p - chain propagation, and k_t - irreversible termination.

8.1 Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species R'X.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

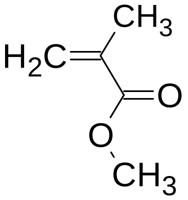
8.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

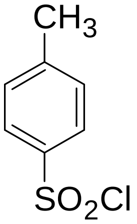
Dependence of monomer concentration ([M]) on reaction time (t) for ATRP is:

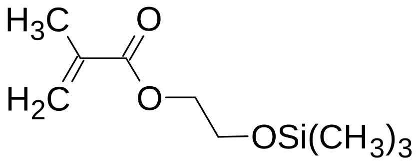
$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = -k_p\,[\mathrm{R}\bullet]\,t\,,$$

$[M]_0$ - initial monomer concentration, k_p – rate constant of propagation, [R•] – concentration of active radicals.

To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is 1616 L mol^{-1}s^{-1}, and the steady state concentration of radicals is 1.76×10^{-7} mol dm^{-3}.


MMA


TsCl


HEMA-TMS

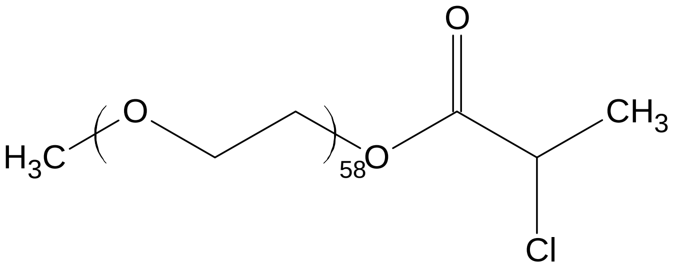
8.3 Calculate mass (*m*) of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.4 Calculate degree of polymerization (DP) of the obtained polymer.

8.5 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, (A_{65}-graft-C_{100})-stat-B_{34} means that chains of polymer C are grafted on units A in the statistic copolymer of A and B.

ATRP was applied to synthesize two block copolymers, P_1 and P_2. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P_1 consisted of styrene (C), and in P_2 of p-chloromethylstyrene (D) units.

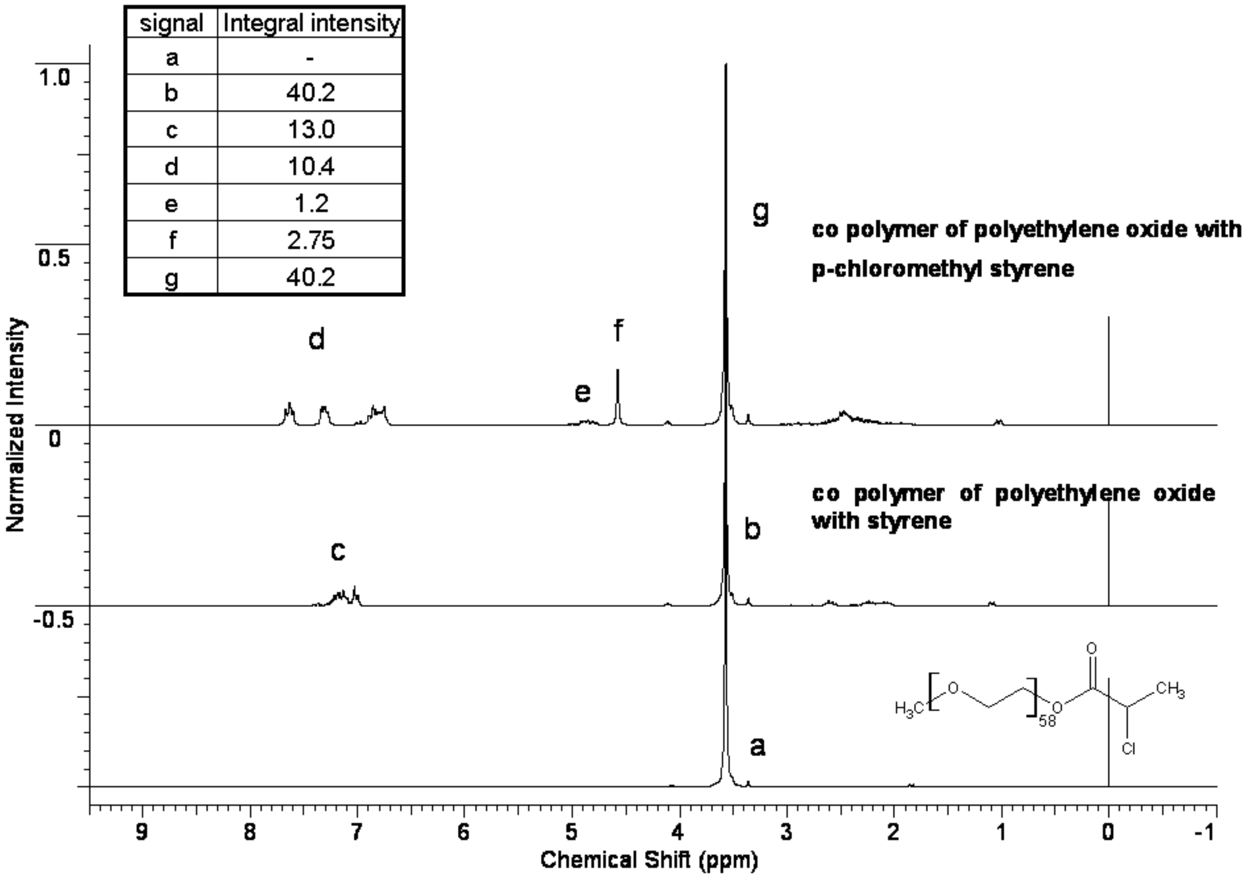
^{1}H NMR spectra of the macroinitiator, P_1 and P_2 are given below. Integral intensities of characteristic signals can be found in the table.

8.6 Assign ^{1}H NMR signals to substructures given in the Answer Sheet.

8.7 Determine molar fractions of units C and D and molecular weights of P_1 and P_2.

8.8 Write down all possible reactions of activation occurring during the synthesis of P_1 and P_2. You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.

8.9 Draw the structure of P_1 and one of possible structures of P_2 representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.



signal	Integral intensity
a	-
b	40.2
c	13.0
d	10.4
e	1.2
f	2.75
g	40.2

SOLUTION

8.1 Expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t)

$v_{act} = k_{act}$ [R-Hal] [CuHal(Ligand)$_k$]

$v_{deact} = k_{deact}$ [R•] [CuHal$_2$(Ligand)$_k$]

$v_p = k_p$ [R•] [M]

$v_t = 2\, k_t$ [R•]^2

8.2 Comparison of rates of ATRP elementary stages

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination.

Thus:

$$v_{\text{deact}} >> v_{\text{act}}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$v_{\text{deact}} >> v_{\text{p}}$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$v_{\text{deact}} >> v_{\text{t}}$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

$$v_{\text{deact}} >> v_{\text{act}}$$

$$v_{\text{deact}} >> v_{\text{p}}$$

$$v_{\text{deact}} >> v_{\text{t}}$$

8.3 Calculation of mass (m) of the obtained polymer.

1st variant

$[\text{M}] = [\text{M}]_0 \exp(-k_\text{P}[\text{R}\bullet]\,t)$ or $n(\text{MMA}) = n_0(\text{MMA})\exp(-k_\text{P}[\text{R}\bullet]\,t)$

Quantity of MMA monomer remaining after polymerization during 1400 s is

$31.0\times\exp(-1616\times1.76\times10^{-7}\times1400) = 20.8$ mmol.

Quantity of monomer consumed during polymerization: 31 – 20.8 = 10.2 mmol

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA})\times M(\text{MMA}) = \frac{10.2}{1000}\times100.1 = 1.03\ \text{g}$$

2nd variant

$[\text{M}] = [\text{M}]_0 \exp(-\,k_P[\text{R}\bullet]\,t)$ or $n(\text{MMA}) = n_0(\text{MMA})\exp(-k_P[\text{R}\bullet]\,t)$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

$$\Delta n(\text{MMA}) = n_0(\text{MMA})\,(1-\exp(-k_p\times[\text{R}\bullet]\times t)) = 31.0\times(1-1616\times1.76\times10^{-7}\times1400) =$$

$$= 10.2\ \text{mmol}$$

Mass of the obtained polymer is:

$$m = \Delta n(\text{MMA})\times M(\text{MMA}) = (10.2\,/\,1000)\times100.1 = 1.03\,\text{g}$$

3rd variant

$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_P[R\bullet]\,t = -1616 \times 1.76 \times 10^{-7} \times 1400 = -0.398$$

$$\frac{[M]}{[M]_0} = e^{-0.398} = 0.672$$

$$\frac{[M]}{[M]_0} = \frac{n(MMA)}{n_0(MMA)}$$

$$n(MMA) = 0.672 \times n_0(MMA) = 20.8 \text{ mmol}$$

Quantity of monomer consumed during polymerization is 31 – 20.8 = 10.2 mmol.

Mass of the obtained polymer is

$$m = \Delta n(MMA) \times M(MMA) = (10.2 / 1000) \times 100.1 = 1.03 \text{ g}$$

8.4 Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol)

At the first stage, 7.3 mmol of MMA was consumed (0.73 / 100.1).

The total quantity of monomers at the beginning of the 2nd stage is 23.7 + 23.7 = 47.4 mmol.

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$$\Delta n = n_0(1 - \exp(-k_P[R\cdot]\,t)) = 47.4\,(1 - \exp(-1616 \times 1.76 \times 10^{-7} \times 1295)) = 14.6 \text{ mmol.}$$

Totally 7.3 + 14.6 = 21.9 mmol of monomers was polymerized during two stages.

DP = 21.9 / 0.12 = 182.5

DP = 182 – 183 (all answers within this range are credited)

8.5 Structure of the obtained polymer.

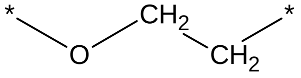
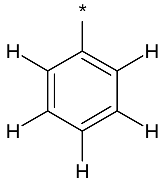
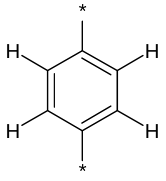
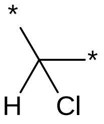
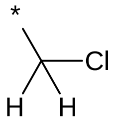
The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is 7.3 / 0.12 = 60.8 ≈ 61 monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning of the 2nd stage were equal. The DP of the 2nd block is 183 – 61 = 122 monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A_{61}-block-(A-stat-B)$_{61}$-Cl or Ts-A_{61}-block-(A_{61}-stat-B_{61})-Cl

8.6 Assignment of NMR signals to substructures given in the Answer Sheet.

	a, b, g
	c
	d
	e
	f

8.7 Determination of molar fractions of units C and D and molecular weights of P_1 and P_2.

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is 40.2 / 4 / 58 = 0.173 for both copolymer spectra

Intensity of multiplet c is 13.0, which is equivalent to 13.0 / 0.173 = 75 protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is 75 / 5 = 15.

Molar fraction of styrene units in P1 is 15 / (15 + 58) = 20.5 %

Intensity of multiplet d is 10.4, which is equivalent to 10.4 / 0.173 = 60 protons. Since each monomer unit of p-chloromethylstyrene has 4 protons, DP of PCS is 60 / 4 =15.

Molar fraction of D is 15 / (15 + 58) = 20.5%

$M(P_1) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 104.15 + 35.45 = \mathbf{4240}$

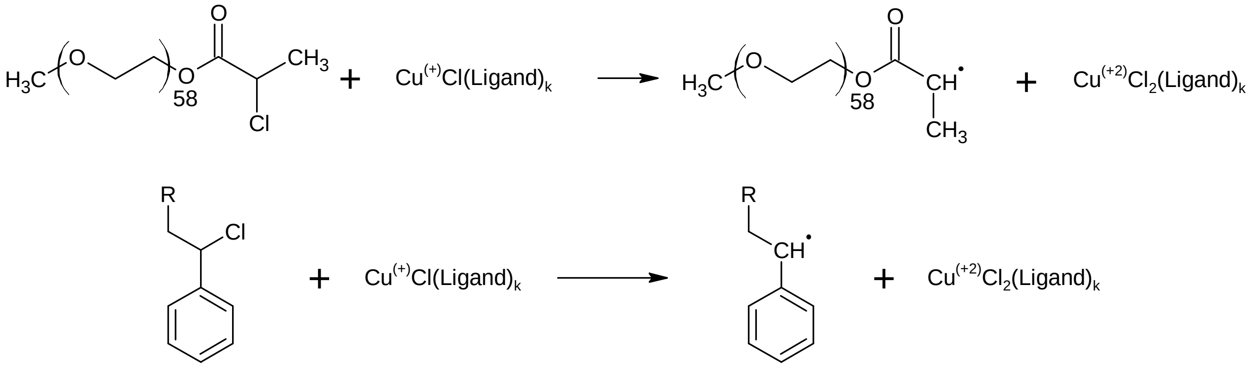
$M(P_2) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 152.62 + 35.45 = \mathbf{4967}$

$M(P_1) = 4240$; $M(P_2) = 4967$

$n(C) = 20.5$ %; $n(D) = 20.5$ %

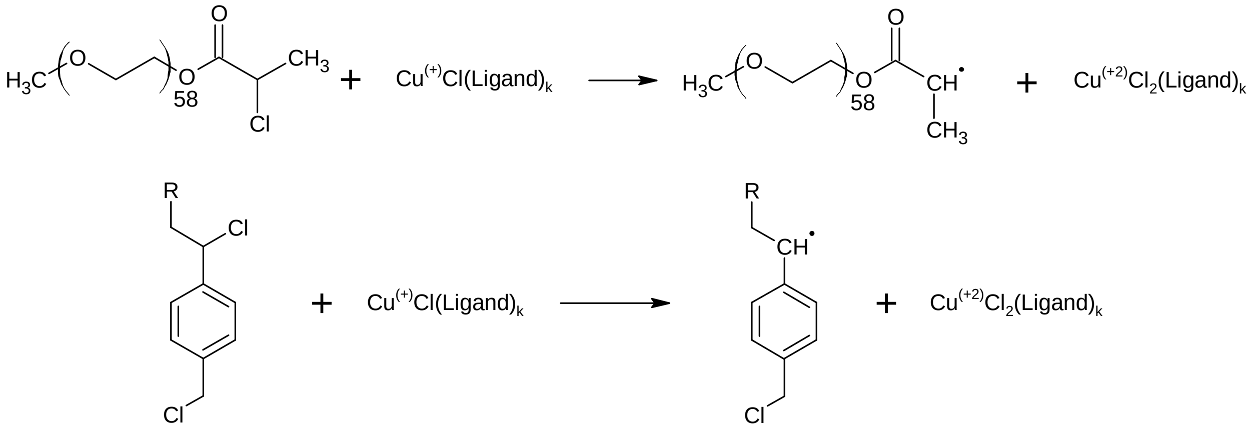
8.8 All possible reactions of activation occurring during the synthesis of P_1 and P_2.

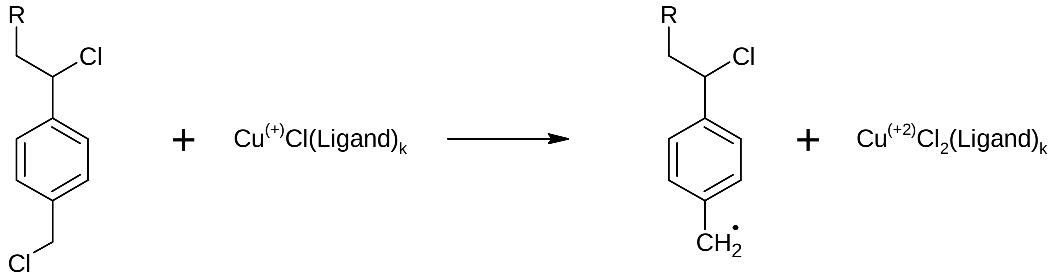
P1:



Here R is used for the macroinitiator fragment with one or several styrene units attached.

P$_2$:





Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

8.9 The structure of P_1 and one of possible structures of P_2

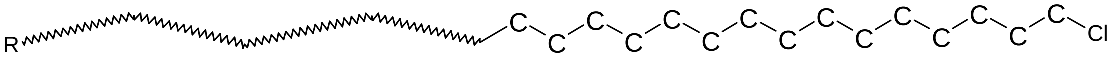
P_1 is a block copolymer of PEO and PS. The PS block contains 15 units.

P_2 is a block copolymer composed of PEO block and branched styrene block.

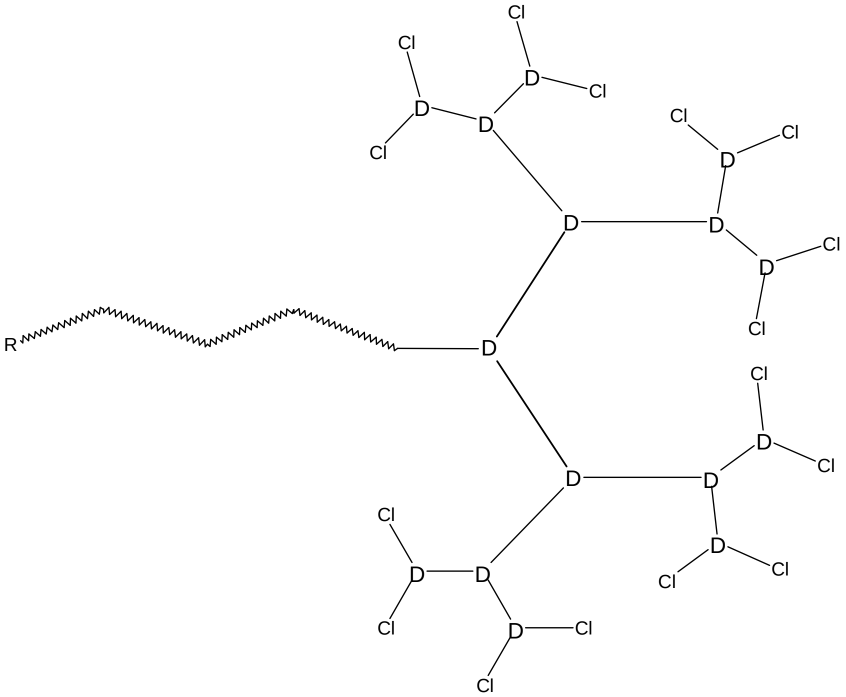
The integral intensity of multiplet f is 2.75, so 2.75/0.173=15.9, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P_2, it would contain 15 choromethyl groups. Each branching reduces the number of such groups by 1. Thus P_2 has 15 – 8 = 7 branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units

P_1



P_2



PROBLEM 6

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates. The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm.

There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

6.1 How many type **A** cavities can be found in a unit cell?

6.2 How many water molecules are there in a unit cell?

6.3 If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?

6.4 Methane hydrate is formed with the structure in **c)** at temperatures between 0-10 ℃. What is the density of the clathrate?

6.5 The density of chlorine hydrate is 1.26 g/cm^3. What is the ratio of the number of water and guest molecules in the crystal?

Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

☐ Some **A** ☐ Some **B** ☐ All **A** ☐ All **B**

Covalent radii reflect atomic distances when the atoms are covalently bonded. Non-bonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modelled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

6.6 Based on the covalent and non-bonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Let us consider the following processes

$H_2O(l) \rightarrow H_2O(s)$ (1)

$x\ CH_4(g) + H_2O\ (l) \rightarrow\ x\ CH_4.1H_2O(clathrate)$ (2)

6.7 What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? Mark with a –, 0 or +.

	sign
$\Delta G_m(1)$	
$\Delta G_m(2)$	
$\Delta H_m(1)$	
$\Delta H_m(2)$	
$\Delta S_m(1)$	
$\Delta S_m(2)$	
$\Delta S_m(2) - \Delta S_m(1)$	
$\Delta H_m(2) - \Delta H_m(1)$	

SOLUTION

6.1 The number of **A** cavities in a unit cell: $\boxed{2}$

6.2 The number of water molecules in a unit cell?

46 = 20 x 2 (dodecahedra) + 6 x 2 /2 (faces)

6.3 The number of water to the number of guest molecules?

46 : 8 = 5.75

6.4 A unit cell has a volume of 1.182^3 nm^3 = 1.651 nm^3.

It contains 8 methane and 46 water molecules with a mass of 957 g mol^{-1}/ N_A = 1.589×10^{-21} g.

The density is 1.589 / 1.651 = 0.962 g/cm^3.

6.5 The mass of a unit cell with this density is: 1.651 nm^3 × 1.26 g cm^{-3} = 2.081×10^{-21} g, meaning 1253 g/mol for the contents.

Substracting the waters, this means 424.3 g mol^{-1} for the chlorine atoms, giving 11.97 chlorine atoms in a unit cell.

The ratio is then 6 (5.98) chlorine molecules for the 46 waters, or a ratio of 7.68.

It is expected that only the 6 larger B type cavities contain chlorine. Thus:

☐ Some **A** ☐ Some **B** ☐ All **A** ☑ All **B**

6.6 Methane fits in both cavities, its radius is approximately 37 + 77 + 120 pm = 234 pm.

The chlorine molecule, with a radius of 180 + 99 pm = 279 pm, fits only in **B**.

Thus 234 pm < r(**A**) < 279 pm and 279 pm < r(**B**)

6.7

	sign
$\Delta G_m(1)$	+
$\Delta G_m(2)$	–
$\Delta H_m(1)$	–
$\Delta H_m(2)$	–
$\Delta S_m(1)$	–
$\Delta S_m(2)$	–
$\Delta S_m(2) - \Delta S_m(1)$	–
$\Delta H_m(2) - \Delta H_m(1)$	–

Under these conditions, methane clathrate forms, while ice melts to water, so the Gibbs energy changes are of opposite signs.

Freezing is an exothermic process with an entropy decrease in both cases.

The entropy decrease of the clathrate formation is larger in magnitude, as it involves a gas-solid transition.

The relation of the reaction enthalpies can be inferred from these facts:

$\Delta G_m(1) > \Delta G_m(2)$

$\Delta H_m(1) - T\,\Delta S_m(1) > \Delta H_m(2) - T\,\Delta S_m(2)$

$T\,(\Delta S_m(2) - \Delta S_m(1)\,) > \Delta H_m(2) - \Delta H_m(1)$

a negative quantity $> \Delta H_m(2) - \Delta H_m(1)$

PROBLEM 7

The dithionate ion ($S_2O_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continuously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

7.1 Write the balanced chemical equations for the two reactions.

After the reaction is complete, $Ba(OH)_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3.

7.2 Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3.

Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with $BaCl_2$ solution. When the solid is heated and maintained at 130 °C, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with $BaCl_2$ solution. When another sample of the original crystals is kept at 300 °C for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with $BaCl_2$ solution.

7.3 Give the composition of the prepared crystals and write balanced equations for the two processes that occur during heating.

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At 75 °C, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

7.4 Write the balanced chemical equation for the reaction between bromine and dithionate ion.

The initial rates (v_0) of the reaction were determined in a number of experiments at 75 °C.

$[Br_2]_0$ (mmol dm^{-3})	$[Na_2S_2O_6]_0$ (mol dm^{-3})	$[H^+]_0$ (mol dm^{-3})	v_0 (nmol dm^{-3}s^{-1})
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

7.5 Determine the order of the reaction with respect to Br_2, H^+ and $S_2O_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75 °C. The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are 2.53×10^{-5} (Cl_2), 2.60×10^{-5} (BrO_3^-), 2.56×10^{-5} (H_2O_2), and 2.54×10^{-5} ($Cr_2O_7^{2-}$).

Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

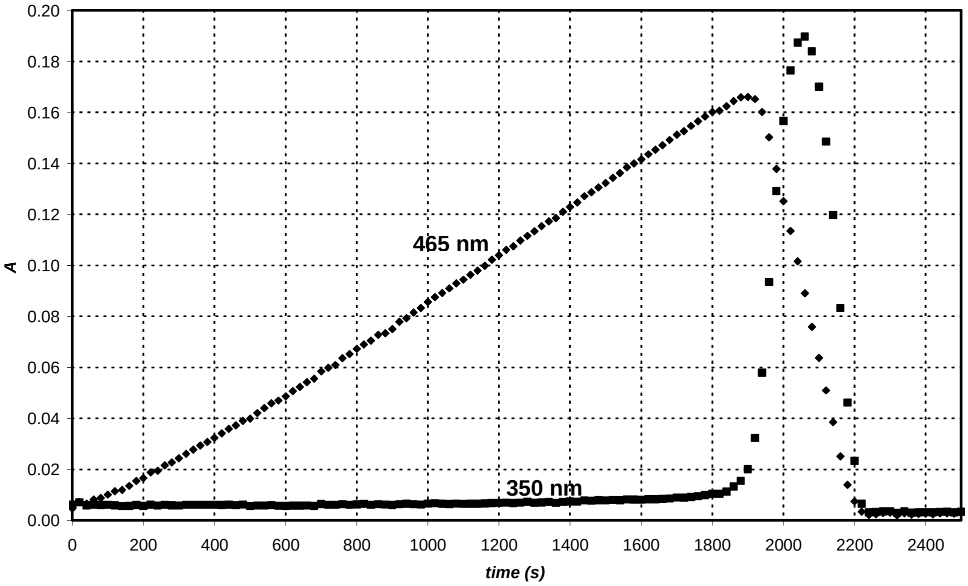
7.6 Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: [$Na_2S_2O_6$] = 0.0022 mol dm^{-3}, [$HClO_4$] = 0.70 mol dm^{-3}, and the temperature was 75 ℃. A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

7.7 Calculate the rate constant of the reaction.

Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

When periodate ion (which is present as $H_4IO_6^-$ in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75 ℃ in the same experiment at two different wavelengths. The initial concentrations were [$H_4IO_6^-$] = 5.3·10^{-4} mol dm^{-3}, [$Na_2S_2O_6$] = 0.0519 mol dm^{-3}, [$HClO_4$] = 0.728 mol dm^{-3}. At 465 nm, only I_2 absorbs and its molar absorption coefficient is 715 dm^3 mol^{-1} cm^{-1}. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is 11000 dm^3 mol^{-1} cm^{-1}. The optical path length was 0.874 cm.



7.8 Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm.

SOLUTION

7.1 $MnO_2 + 2\ SO_2 \rightarrow Mn^{2+} + S_2O_6^{2-}$

$MnO_2 + SO_2 \rightarrow Mn^{2+} + SO_4^{2-}$

7.2 $MnS_2O_6 + Na_2CO_3 \rightarrow Na_2S_2O_6 + \underline{MnCO_3}$

7.3 Formula: $Na_2S_2O_6 \cdot 2\ H_2O$

Equation (130 °C): $Na_2S_2O_6 \cdot 2\ H_2O \rightarrow Na_2S_2O_6 + 2\ H_2O$

Equation (300 °C): $Na_2S_2O_6 \rightarrow Na_2SO_4 + SO_2$ or with H_2O

7.4 $S_2O_6^{2-} + Br_2 + 2\ H_2O \rightarrow 2\ SO_4^{2-} + 2\ Br^- + 4\ H^+$

7.5 Reaction order for Br_2: 0 for H^+: 1 for $S_2O_6^{2-}$: 1

Experimental rate equation: $v = k\ [HSO_4^-]\ [H^+]$

$k = 2.56 \cdot 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$

7.6 Species: SO_2 (or H_2SO_3)

Reaction: $S_2O_6^{2-} + H^+ \rightarrow HSO_4^- + SO_2$

7.7 $t_{½}$ = 10 h 45 min = $3.87 \cdot 10^4$ s

$k_{obs} = \ln 2\ /\ t_{½} = 1.79 \times 10^{-5}\ s^{-1}$

$k = k_{obs}\ /\ [H^+] = 2.56 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$

Rate determining step: $S_2O_6^{2-} + H^+ \rightarrow HSO_4^- + SO_2$

7.8 Increase: $2\ H_4IO_6^- + 7\ S_2O_6^{2-} + 2\ H_2O + 2\ H^+ \rightarrow 14\ HSO_4^- + I_2$

Decrease: $I_2 + S_2O_6^{2-} + 2\ H_2O \rightarrow 2\ HSO_4^- + 2\ I^- + 2\ H^+$

The expected time for the maximum absorbance of the kinetic curve measured at 465 nm:

$$t_{\max} = \frac{7}{2}\frac{[H_4IO_6^-]_0}{k[S_2O_6^{2-}]_0[H^+]_0} = \frac{7\times 5.3\times 10^{-4}\ M}{2\times 2.56\times 10^{-5}\ M^{-1}s^{-1}\times 0.0519\ M\times 0.728\ M} = 1900\ s$$

The expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm: 1; –7 (it reflects the stoichiometry).

PROBLEM 8

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One day she monitored the UV-VIS absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified $CeCl_3$ solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

c_{NaCl} (mol/dm^3)	E (mV)
0.1000	26.9
1.000	–32.2

8.1 Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (E).

Ms. Z also determined the molar absorption coefficient for Ce^{3+} (ε = 35.2 dm^3 mol^{-1}cm^{-1}) at 295 nm, and, as a precaution, also for Ce^{4+} (ε = 3967 dm^{3}mol^{-1}cm^{-1}).

8.2 Give a formula to calculate the Ce^{3+} concentration from an absorbance reading at 295 nm (A) measured in a solution containing $CeCl_3$ (cuvette path length: 1.000 cm).

Ms. Z prepared a solution which contained 0.0100 mol/dm^3 $CeCl_3$ and 0.1050 mol/dm^3 HCl, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

8.3 What were the expected initial absorbance (A_{295nm}) and voltage (E) readings?

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

8.4 Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectophotometric measurements is ±0.002 and the accuracy of the voltage measurements is ±0.3 mV.

time (min)	0	120	240	360	480
$A_{295\text{ nm}}$	0.3496	0.3488	0.3504	0.3489	0.3499
E (mV)	19.0	18.8	18.8	19.1	19.2

8.5 Estimate the average rate of change in the concentrations of Ce^{3+}, Cl^{-}, and H^{+}.
$d[Ce^{3+}]/dt = d[Cl^{-}]/dt = d[H^{+}]/dt = ?$

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic $CeCl_3$ solution she had used before. She measured the molar absorption coefficient for Ce^{3+} (ε = 2400 dm^3 mol^{-1} cm^{-1}) at 254 nm.

8.6 What percentage of the light is absorbed in this experimental setup?

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm^3. The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was 22.0 °C.

8.7 Estimate the amount of substance of the gas collected in the chamber.

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

8.8 Suggest the formula(s) of the gas(es) formed and collected, and give the balanced equation for the original chemical reaction taking place under illumination.

8.9 What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?

8.10 Estimate the quantum yield of product formation in the Ce(III) solution.

SOLUTION

8.1 $[\mathrm{Cl^-}] = 10^{-(E+32.2 mV)/59.1 mV}$

8.2 $[\mathrm{Ce^{3+}}] = \dfrac{A_{295nm}}{35.2\,\mathrm{dm^3 mol^{-1}}}$

8.3 $[\mathrm{Ce^{3+}}]$ = 0.0100 mol/dm^3 $\Rightarrow$ $A_{295\mathrm{nm}}$= 0.352

$[\mathrm{Cl^-}]$ = 3·0.0100 mol/dm^3 + 0.1050 mol/dm^3 = 0.1350 mol/dm^3 $\Rightarrow$ E = 19.2 mV

8.4 HCl, Cl_2, (O_3, ClO_2) (no oxidation of indicator)

8.5 d$[\mathrm{Ce^{3+}}]$/dt = ?   d$[\mathrm{Cl^-}]$/dt = ?   d$[\mathrm{H^+}]$/dt = ?

No significant change in either $\mathrm{Cl^-}$ or $\mathrm{Ce^{3+}}$ concentrations.

$[\mathrm{H^+}] = [\mathrm{Cl^-}] - 3\,[\mathrm{Ce^{3+}}]$, no significant change.

All three values are zero.

8.6 What percentage of the light is absorbed in this experimental setup?

A = 2400 dm^3 mol^{-1} cm^{-1} × 5 cm × 0.0100 M = 120 $\Rightarrow$ (100 – 10^{-118}) % ≈ 100 %

8.7 $p_{\mathrm{partial}} = p_{\mathrm{final}} - p_{\mathrm{initial}}$ = 114075 Pa – 102165 Pa = 11910 Pa

$n = p_{\mathrm{partial}}V/(RT)$ = 11910 Pa·0.000068 m^3 / (8.314 J mol^{-1} K × 295.15 K) =

= 3.3×10^{-4} mol

identity of gases: H_2, O_2

8.8 reaction: $2\ H_2O \xrightarrow{h\nu} 2\ H_2 + O_2$

8.9 Final pressure: 104740 Pa (saturated water vapour)

8.10 Quantum yield:

3.3×10^{-4} mol gas formed altogether: 2.2×10^{-4} mol H_2 and 1.1×10^{-4} mol O_2.

Light beam intensity 0.0500 J s^{-1} $\Rightarrow \dfrac{0.0500\ \text{Js}^{-1}\lambda}{h\,c\,N_A} = 1.06\times10^{-7}\text{mol s}^{-1}\text{photon}$

Total time 18.00 h = 64800 s

Total number of absorbed photons: 64800 s × 1.06×10^{-7} mol s^{-1} = 6.87×10^{-3} mol

Quantum yield for H_2 production: Φ = 2.2×10^{-4} mol / 6.87×10^{-3} mol = 0.032

Quantum yield for O_2 production: Φ = 1.1×10^{-4} mol / 6.87×10^{-3} mol = 0.016

Either value or the quantum yield of the gas production (0.048) is acceptable when demonstrated in a calculation.

PROBLEM 9

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+}. Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aqueous solutions,

The standard redox potentials for some relevant reactions are:

$Tl^+(aq) + e^- \rightarrow Tl(s)$ $E^o_1 = -0.336$ V

$Tl^{3+}(aq) + 3e^- \rightarrow Tl(s)$ $E^o_2 = +0.728$ V

$I_2(s) + 2e^- \rightleftharpoons 2\ I^-(aq)$ $E^o_3 = +0.540$ V

The equilibrium constant for the reaction $I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$: $K_1 = 0.459$.

Use T=25 °C throughout this problem.

9.1 Calculate the redox potentials E^o_4 and E^o_5 for the following reactions:

$Tl^{3+}(aq) + 2\ e^- \rightarrow Tl^+(aq)$ E^o_4

$I_3^-(aq) + 2\ e^- \rightarrow 3\ I^-(aq)$ E^o_5

9.2 Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).

There is an empirical formula that could belong to two different compounds. Which one? Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $Tl^{3+} + 4I^- \rightarrow TlI_4^-$ is $\beta_4 = 10^{35.7}$

9.3 Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant K_2 for this reaction.

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

9.4 What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

SOLUTION

9.1 $E_4^0 = \dfrac{3\,E_2^0 - E_1^0}{2} = 1.26\text{ V}$

$E_5^0 = E_3^0 + 0.059 / 2 \log(1 / K_1) = 0.550$ V

9.2 Tl I, Tl I_3, Tl I_5, Tl I_7, Tl I_9

Tl I_3 can be either $Tl^{3+}(I^-)_3$ or $Tl^+(I_3^-)$

More stable: $Tl^+(I_3^-)$

as $E_4^0 > E_5^0$ or E_3^0,

Isomerisation: $Tl^{3+} + 3\ I^- = Tl^+ + I_3^-$

9.3 Reaction: $Tl^+ + I_3^- + I^- \rightarrow Tl\,I_4^-$

This reaction could be regarded as sum of three reactions:

$Tl^+(aq) \rightarrow Tl^{3+}(aq) + 2e^-$ $E_4^0 = -1.26$ V, thus $\Delta_r G_4^o = n\,F\,E_4^0 = 243.1$ kJ mol^{-1}

$I_3^-(aq) + 2\,e^- \rightarrow 3\,I^-(aq)$ $E^o_5 = 0.550$ V, thus $\Delta_r G_5^o = -n\,F\,E_5^o = -106.1$ kJ mol^{-1}

$Tl^{3+} + 4I^- \rightarrow Tl\,I_4^-$ $\beta_4 = 10^{35.7}$ thus $\Delta_r G_6^o = -R\,T \ln\beta_4 = -203.8$ kJ mol^{-1}

The net free enthalpy change is $\Delta_r G_7^o = \Delta_r G_4^o + \Delta_r G_5^o + \Delta_r G_6^o = -66.8$ kJ mol^{-1}

Thus $K_2 = \exp\left(-\dfrac{\Delta_r G_7}{RT}\right) = 4.96 \cdot 10^{11}$

9.4 Supposing that the substance contains Tl and an anion, the formula of the compound is Tl_aX_b and the following equation holds:

$$\frac{a \cdot 204.4}{a \cdot 204.4 + bM_X} = 0.895$$

From the values b = 1, 3 and a = 1, 2, 3 only b = 3, a = 2 gives a realistic:

M_X = 16.0 g mol^{-1}.

X is oxygen.

Formula: Tl_2O_3.

Equation: $2\ Tl\,I_3 + 6\ OH^- \rightarrow Tl_2O_3 + 6\ I^- + 3\ H_2O$

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THEORETICAL PROBLEMS

PROBLEM 1

Estimating the Avogadro constant

Many different methods have been used to determine the Avogadro constant. Three different methods are given below.

Method A – from X-ray diffraction data (modern)

The unit cell is the smallest repeating unit in a crystal structure. The unit cell of a gold crystal is found by X-ray diffraction to have the face-centred cubic unit structure (i.e. where the centre of an atom is located at each corner of a cube and in the middle of each face). The side of the unit cell is found to be 0.408 nm.

1.1 Sketch the unit cell and calculate how many Au atoms the cell contains.

1.2 The density of Au is $1.93 \cdot 10^4$ kg m^{-3}. Calculate the volume and mass of the cubic unit cell.

1.3 Hence calculate the mass of a gold atom and the Avogadro constant, given that the relative atomic mass of Au is 196.97.

Method B – from radioactive decay (Rutherford, 1911)

The radioactive decay series of ^{226}Ra is as follows:

$$^{226}\text{Ra} \xrightarrow{t} {}^{222}\text{Rn} \xrightarrow{3.825\text{ d}} {}^{218}\text{Po} \xrightarrow{3.10\text{ m}} {}^{214}\text{Pb} \xrightarrow{26.8\text{ m}} {}^{214}\text{Bi} \xrightarrow{19.9\text{ m}}$$

$$^{214}\text{Po} \xrightarrow{164.3\ \mu\text{s}} {}^{210}\text{Pb} \xrightarrow{22.3\text{ y}} {}^{210}\text{Bi} \xrightarrow{5.013\text{ d}} {}^{210}\text{Po} \xrightarrow{138.4\text{ d}} {}^{206}\text{Pb}$$

The times indicated are half-lives, the units are y = years, d = days, m = minutes. The first decay, marked *t* above, has a much longer half-life than the others.

1.4 In the table below, identify which transformations are α-decays and which are β-decays.

	α-decay	β-decay
$^{226}Ra \longrightarrow {}^{222}Rn$		
$^{222}Rn \longrightarrow {}^{218}Po$		
$^{218}Po \longrightarrow {}^{214}Pb$		
$^{214}Pb \longrightarrow {}^{214}Bi$		
$^{214}Bi \longrightarrow {}^{214}Po$		
$^{214}Po \longrightarrow {}^{210}Pb$		
$^{210}Pb \longrightarrow {}^{210}Bi$		
$^{210}Bi \longrightarrow {}^{210}Po$		
$^{210}Po \longrightarrow {}^{206}Pb$		

1.5 A sample containing 192 mg of ^{226}Ra was purified and allowed to stand for 40 days. Identify the first isotope in the series (excluding Ra) that has not reached a steady state.

1.6 The total rate of α-decay from the sample was then determined by scintillation to be 27.7 GBq (where 1 Bq = 1 count s^{-1}). The sample was then sealed for 163 days. Calculate the number of α particles produced.

1.7 At the end of the 163 days the sample was found to contain 10.4 mm^3 of He, measured at 101325 Pa and 273 K. Calculate the Avogadro constant from these data.

1.8 Given that thee relative isotopic mass of ^{226}Ra measured by mass spectrometry is 226.25, use the textbook value of the Avogadro constant ($6.022 \cdot 10^{23}$ mol^{-1}) to calculate the number of ^{226}Ra atoms in the original sample, n_{Ra}, the decay rate constant, λ, and the half-life, t, of ^{226}Ra (in years). You need only consider the decays up to but not including the isotope identified in 1.5.

Method C – dispersion of particles (Perrin, 1909)

One of the first accurate determinations of the Avogadro constant was carried out by studying the vertical distribution under gravity of colloidal particles suspended in water. In one such experiment, particles with radius $2.12 \cdot 10^{-7}$ m and density $1.206 \cdot 10^{3}$ kg m^{-3} were suspended in a tube of water at 15 °C. After allowing sufficient time to equilibrate, the mean numbers of particles per unit volume observed at four heights from the bottom of the tube were:

height / 10^{-6} m	5	35	65	95
mean number per unit volume	4.00	1.88	0.90	0.48

1.9 Assuming the particles to be spherical, calculate:

i) the mass, m, of a particle;

ii) the mass, m_{H_2O}, of the water it displaces;

iii) the effective mass, m*, of the particle in water accounting for buoyancy (i.e. taking account of the upthrust due to the displaced volume of water).

Take the density of water to be 999 kg m^{-3}.

At equilibrium, the number of particles per unit volume at different heights may be modelled according to a Boltzmann distribution:

$$\frac{n_h}{n_{h_0}} = \exp\left[-\frac{E_h - E_{h_0}}{RT}\right]$$

where

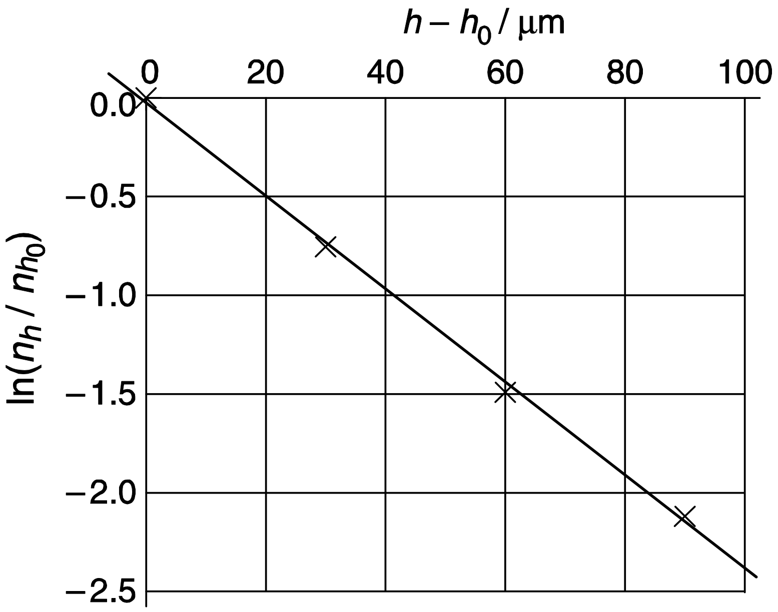
n_h is the number of particles per unit volume at height h,

n_{h0} is the number of particles per unit volume at the reference height h_0,

E_h is the gravitational potential energy per mole of particles at height h relative to the particles at the bottom of the tube,

R is the gas constant, 8.3145 J K^{-1} mol^{-1}.

A graph of $\ln(n_h / n_{h0})$ against $(h - h_0)$, based on the data in the table above, is shown below. The reference height is taken to be 5 μm from the bottom of the tube.

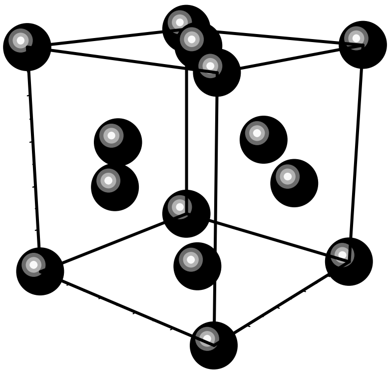


1.10 Derive an expression for the gradient (slope) of the graph.

1.11 Determine the Avogadro constant from these data.

SOLUTION

1.1 Unit cell:



Number of Au atoms in the unit cell:

8 × 1/8 from each corner = 1

6 × ½ from each face = 3

Total = 4 atoms

1.2 Volume:

$V = (0.408\ \text{nm})^3 = 6.79 \cdot 10^{-29}\ \text{m}^3$

Mass:

$m = \rho V = 1.93 \cdot 10^4\ \text{kg m}^{-3} \times 6.79 \cdot 10^{-29}\ \text{m}^3 = 1.31 \cdot 10^{-24}\ \text{kg}$

1.3 Mass of Au atom:

$$m = \frac{1.31 \cdot 10^{-24}\ \text{kg}}{4} = 3.28 \cdot 10^{-25}\ \text{kg}$$

Avogadro constant:

$$N_A = \frac{196.97\ \text{g mol}^{-1}}{3.28 \cdot 10^{-22}\ \text{g}} = 6.01 \cdot 10^{23}\ \text{mol}^{-1}$$

1.4

	α-decay	β-decay
$^{226}Ra \longrightarrow {}^{222}Rn$	✓	
$^{222}Rn \longrightarrow {}^{218}Po$	✓	
$^{218}Po \longrightarrow {}^{214}Pb$	✓	
$^{214}Pb \longrightarrow {}^{214}Bi$		✓
$^{214}Bi \longrightarrow {}^{214}Po$		✓
$^{214}Po \longrightarrow {}^{210}Pb$	✓	
$^{210}Pb \longrightarrow {}^{210}Bi$		✓
$^{210}Bi \longrightarrow {}^{210}Po$		✓
$^{210}Po \longrightarrow {}^{206}Pb$	✓	

1.5 Answer: ^{210}Pb

1.6 $2.77 \cdot 10^{10}\ s^{-1} \times 163 \times 24 \times 60 \times 60\ s = 3.90 \cdot 10^{17}$

1.7 Answer:

$$n = \frac{pV}{RT} = 4.64 \cdot 10^{-7}\ \text{mol}$$

$$N_A = \frac{3.90 \cdot 10^{17}}{4.64 \cdot 10^{-7}\ \text{mol}} = 8.4 \cdot 10^{23}\ \text{mol}^{-1}$$

1.8 $$n_{Ra} = \frac{0.192\ \text{g} \times 6.022 \cdot 10^{23}\ \text{mol}^{-1}}{226.25\ \text{g mol}^{-1}} = 5.11 \cdot 10^{20}\ \text{atoms}$$

$$\lambda = \frac{2.77 \cdot 10^{10}\ s^{-1}}{5.11 \cdot 10^{20} \times 4} = 1.36 \cdot 10^{-11}\ s^{-1}$$

(only ¼ of the decays are from ^{226}Ra)

$$t = \frac{\ln 2}{\lambda} = 5.12 \cdot 10^{10}\ s = 1620\ \text{years}$$

1.9 $V = 3.99 \cdot 10^{-20}\ \text{m}^3$

$m = 4.81 \cdot 10^{-17}\ \text{kg}$

$m_{H_2O} = 3.99 \cdot 10^{-17}\ \text{kg}$

$m^* = 8.3 \cdot 10^{-18}\ \text{kg}$

1.10 gradient = $\dfrac{-m^* N_A g}{RT}$

1.11 Acceptable range of slopes is 0.0235 ± 0.002 μm

Hence $N_A = (6.9 \pm 0.8) \cdot 10^{23}\ \text{mol}^{-1}$ (error range needs widening here).

PROBLEM 2

Interstellar production of H_2

If two atoms collide in interstellar space the energy of the resulting molecule is so great that it rapidly dissociates. Hydrogen atoms only react to give stable H_2 molecules on the surface of dust particles. The dust particles absorb most of the excess energy and the newly formed H_2 rapidly desorbs. This question examines two kinetic models for H_2 formation on the surface of a dust particle.

In both models, the rate constant for adsorption of H atoms onto the surface of dust particles is $k_a = 1.4 \cdot 10^{-5}$ cm^3 s^{-1}. The typical number density of H atoms (number of H atoms per unit volume) in interstellar space is [H] = 10 cm^{-3}.

[Note: In the following, you may treat numbers of surface-adsorbed atoms and number densities of gas-phase atoms in the same way as you would normally use concentrations in the rate equations. As a result, the units of the rate constants may be unfamiliar to you. Reaction rates have units of numbers of atoms or molecules per unit time.]

2.1 Calculate the rate at which H atoms adsorb onto a dust particle. You may assume that this rate is constant throughout.

Desorption of H atoms is first order with respect to the number of adsorbed atoms. The rate constant for the desorption step is $k_d = 1.9 \cdot 10^{-3}$ s^{-1}.

2.2 Assuming that only adsorption and desorption take place, calculate the steady-state number, N, of H atoms on the surface of a dust particle.

The H atoms are mobile on the surface. When they meet they react to form H_2, which then desorbs. The two kinetic models under consideration differ in the way the reaction is modelled, but share the same rate constants k_a, k_d, and k_r, for adsorption, desorption, and bimolecular reaction, as given below.

$k_a = 1.4 \cdot 10^{-5}$ cm^3 s^{-1}

$k_d = 1.9 \cdot 10^{-3}$ s^{-1}

$k_r = 5.1 \cdot 10^{4}$ s^{-1}

Model A

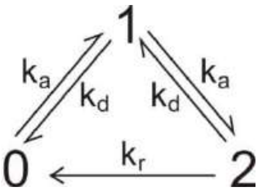
Reaction to form H_2 is assumed to be second order. On a dust particle the rate of removal of H atoms by reaction is $k_r N^2$.

2.3 Write down an equation for the rate of change of *N,* including adsorption, desorption and reaction. Assuming steady state conditions, determine the value of *N*.

2.4 Calculate the rate of production of H_2 per dust particle in this model.

Model B

Model B attempts to analyse the probability that the dust particles carry 0, 1 or 2 H atoms. The three states are linked by the following reaction scheme. The assumption is made that no more than 2 atoms may be adsorbed simultaneously.



x_0, x_1 and x_2 are the fractions of dust particles existing in state 0, 1 or 2, respectively. These fractions may be treated in the same way as concentrations in the following kinetic analysis. For a system in state *m* with fraction x_m, the rates of the three possible processes are

Adsorption ($m \rightarrow m + 1$) : rate = $k_a\,[H]\,x_m$

Desorption ($m \rightarrow m - 1$) : rate = $k_d\,m\,x_m$

Reaction ($m \rightarrow m - 2$) : rate = $\frac{1}{2}\,k_r\,m(m-1)\,x_m$

2.5 Write down equations for the rates of change, dx_m / dt, of the fractions x_0, x_1 and x_2.

2.6 Assuming steady-state conditions, use the above rate equations to find expressions for the ratios x_2/x_1 and x_1/x_0 , and evaluate these ratios.

2.7 Evaluate the steady state fractions x_0, x_1 and x_2.

[If you were unable to determine the ratios in 2.6, use $x_2/x_1 = a$ and $x_1/x_0 = b$ and give the result algebraically.]

2.8 Evaluate the rate of production of H_2 per dust particle in this model.

2.9 It is currently not possible to measure the rate of this reaction experimentally, but the most recent computer simulations of the rate give a value of $9.4 \cdot 10^{-6}$ s^{-1}. Which of the following statements apply to each model under these conditions? Mark any box you consider to be appropriate.

Statement	**Model A**	**Model B**	**Neither model**
The rate determining step is adsorption of H atoms.			
The rate-determining step is desorption of H_2 molecules.			
The rate determining step is the bimolecular reaction of H atoms on the surface.			
The rate determining step is adsorption of the second H atom.			
The implicit assumption that reaction can take place regardless of the number of atoms adsorbed leads to substantial error (at least a factor of two).			
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at least a factor of two).			

SOLUTION

2.1 Answer: $1.4 \cdot 10^{-4}\ s^{-1}$

2.2 Answer: $1.4 \cdot 10^{-4}\ s^{-1} = 1.9 \cdot 10^{-3}\ s^{-1}\ N \Rightarrow N = 7.4 \cdot 10^{-2}$

2.3 $\frac{dN}{dt} = 0 = k_a[H] - k_d N - k_r N^2$

$$N = \frac{-k_d + \sqrt{k_d^2 + 4\,k_r k_a[H]}}{2\,k_r}$$

$N = 5.2 \cdot 10^{-5}$

2.4 Answer: $\frac{1}{2}\,k_r\,N^2 = 7.0 \cdot 10^{-5}\ s^{-1}$

2.5

$$\frac{dP_0}{dt} = -k_a[H]P_0 + k_d P_1 + k_r P_2$$

$$\frac{dP_1}{dt} = k_a[H]P_0 - (k_a[H] + k_d)P_1 + 2\,k_d P_2$$

$$\frac{dP_2}{dt} = k_a[H]P_1 - (2\,k_d + k_r)P_2$$

(remember P is changed to x)

2.6

$$\frac{P_2}{P_1} = \frac{k_a[H]}{(2\,k_d + k_r)} \approx \frac{k_a[H]}{k_r} = 2.7 \cdot 10^{-9}$$

$$\frac{P_1}{P_0} = \frac{k_a[H]\,(2\,k_d + k_r)}{k_d\,(2\,k_d + k_r) + k_r k_a[H]} \approx \frac{k_a[H]}{k_d + k_a[H]} = 6.9 \cdot 10^{-2}$$

2.7

$P_0 = 0.94,$

$P_1 = 0.064,$

$P_2 = 1.8 \cdot 10^{-10}$

2.8 $k_r\,x_2 = 9.0 \cdot 10^{-6}\ s^{-1}$

2.9

Statement	**Model A**	**Model B**	**Neither model**
The rate determining step is adsorption of H atoms.	✓	(✓)	
The rate-determining step is desorption of H_2 molecules.			✓
The rate determining step is the bimolecular reaction of H atoms on the surface.			✓
The rate determining step is adsorption of the second H atom.		✓	
The implicit assumption that reaction can take place regardless of the number of atoms adsorbed leads to substantial error (at least a factor of two).	✓		
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at least a factor of two).			✓

PROBLEM 3

Protein Folding

The unfolding reaction for many small proteins can be represented by the equilibrium:

$$\text{Folded} \rightleftharpoons \text{Unfolded}$$

You may assume that the protein folding reaction takes place in a single step. The position of this equilibrium changes with temperature; the melting temperature T_m is defined as the temperature at which half of the molecules are unfolded and half are folded.

The intensity of the fluorescence signal at a wavelength of 356 nm of a 1.0 μM (M = mol dm^{-3}) sample of the protein Chymotrypsin Inhibitor 2 (CI2) was measured as a function of temperature over the range 58 to 66 °C:

Temperature / °C	58	60	62	64	66
Fluorescence intensity (arbitrary units)	27	30	34	37	40

A 1.0 μM sample in which all of the protein molecules are folded gives a fluorescence signal of 21 units at 356 nm. A 1.0 μM sample in which all of the protein molecules are unfolded gives a fluorescence signal of 43 units.

3.1 Assuming that the fluorescence intensity from each species is directly proportional to its concentration, calculate the fraction, x, of unfolded molecules present at each temperature.

3.2 Give an expression for the equilibrium constant, K, in terms of x, and hence calculate the value of K at each temperature.

3.3 Estimate the value of T_m for this protein (to the nearest 1 °C).

Assuming that the values of ΔH^o and ΔS^o for the protein unfolding reaction are constant with temperature then:

$$\ln K = -\frac{\Delta H^o}{RT} + C$$

where C is a constant.

3.4 Plot a suitable graph and hence determine the values of ΔH^o and ΔS^o for the protein unfolding reaction.

[If you have been unable to calculate values for ΔH^o and ΔS^o, you should use the following incorrect values for the subsequent parts of the problem:
$\Delta H^o = 130$ kJ mol^{-1}; $\Delta S^o = 250$ J K^{-1} mol^{-1}.]

3.5 Calculate the equilibrium constant for the unfolding reaction at 25 °C.
[If you have been unable to calculate a value for K, you should use the following incorrect value for the subsequent parts of the problem: $K = 3.6 \cdot 10^{-6}$]

The first order rate constant for the CI2 protein folding reaction can be determined by following the fluorescence intensity when a sample of unfolded protein is allowed to refold (typically the pH of the solution is changed). The concentration of protein when a 1.0 μM sample of unfolded CI2 was allowed to refold was measured at a temperature of 25 °C:

time / ms	0	10	20	30	40
concentration / μM	1	0.64	0.36	0.23	0.14

3.6 Plot a suitable graph and hence determine the value of the rate constant for the protein folding reaction, k_f, at 25 °C.
[If you have been unable to calculate the value for k_f, you should use the following incorrect value for the subsequent parts of the question: $k_f = 60$ s^{-1}.]

3.7 Determine the value of the rate constant for the protein *unfolding* reaction, k_u, at 25 °C.

3.8 At 20 °C the rate constant for the protein folding reaction is 33 s^{-1}. Calculate the activation energy for the protein folding reaction.

SOLUTION

3.1

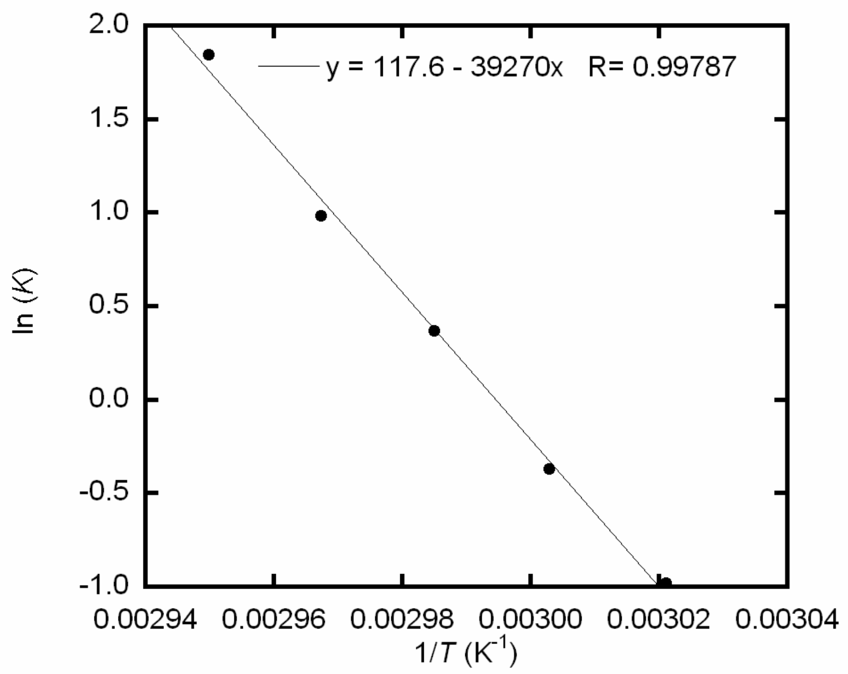
Temp / ℃	58	60	62	64	66
x	0.27	0.41	0.59	0.73	0.86

3.2

Temp / ℃	58	60	62	64	66
K	0.38	0.69	1.4	2.7	6.3

3.3 Answer: T_m = 61 ℃

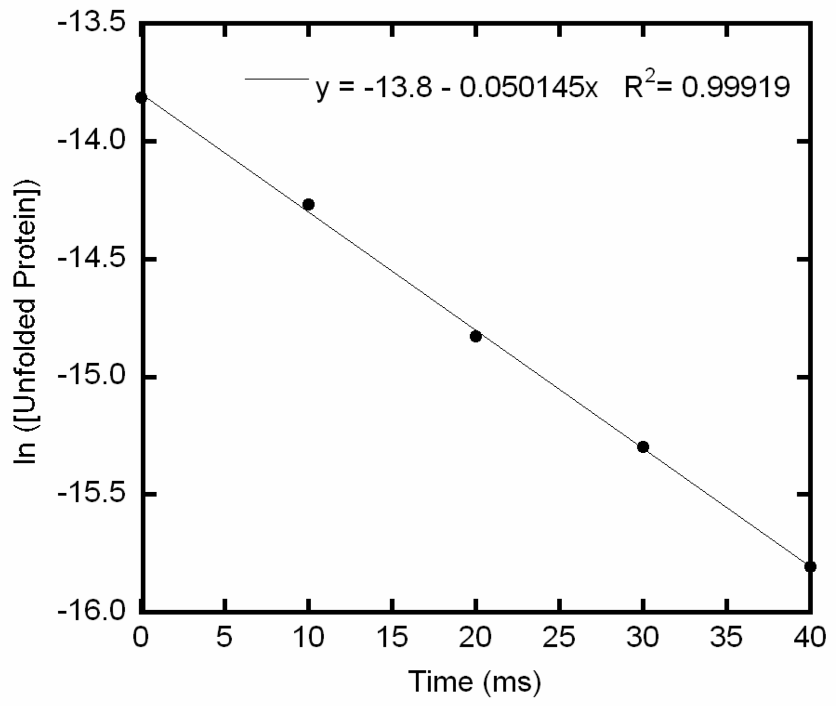
3.4



Answers: ΔH^o = 330 kJ mol^{-1} ; ΔS^o = 980 J mol^{-1} K^{-1}

3.5 ΔH^o = 330000 J mol^{-1} and ΔS^o= 980 J mol^{-1} K^{-1} then ΔG^o = 35000 J mol^{-1} at 25 °C, hence $K = 6.9 \cdot 10^{-7}$.

3.6



Answer: Rate constant for the protein folding reaction, k_f = 50 s^{-1}.

3.7 Answer: Rate constant for the protein *unfolding* reaction, k_u = 3.5 · 10^{-5} s^{-1}.

3.8 Answer: Activation energy = 61 kJ mol^{-1}.

THE FORTY-SECOND
INTERNATIONAL CHEMISTRY OLYMPIAD
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THEORETICAL PROBLEMS

PROBLEM 1

In 1894, Lord Rayleigh reported that the mass of chemically prepared nitrogen was different from that of nitrogen extracted from the atmosphere, as shown in Tables 1 and 2. Later, this difference was attributed to the presence of argon in *atmospheric nitrogen*. The masses of gases were measured by using a glass vessel with a known volume under atmospheric pressure ($1.013 \cdot 10^5$ Pa).

Table 1. Mass of *Chemical Nitrogen* in the Vessel

From nitric oxide	2.3001 g
From nitrous oxide	2.2990 g
From ammonium nitrite purified at a red heat	2.2987 g
From urea	2.2985 g
From ammonium nitrite purified in the cold	2.2987 g
Mean	**2.2990 g**

Table 2. Mass of *Atmospheric Nitrogen* in the Vessel

O_2 was removed by hot copper (1892)	2.3103 g
O_2 was removed by hot iron (1893)	2.3100 g
O_2 was removed by ferrous hydrate (1894)	2.3102 g
Mean	**2.3102 g**

1.1 Calculate the volume V [m^3] of the vessel used by Rayleigh from the mean mass of *chemical nitrogen*, which must have been pure nitrogen. Assume that the measurements were carried out at a temperature of 15.0 °C.

1.2 Estimate the mole fraction x of argon in Rayleigh's *atmospheric nitrogen*, by assuming that argon and nitrogen were the only constituents. Use the mean masses of the *atmospheric* and *chemical nitrogen* for the calculation.

Ramsay and Clève discovered helium in cleveite (a mineral consisting of uranium oxide and oxides of lead, thorium, and rare earths; an impure variety of uraninite) independently and virtually simultaneously in 1895. The gas extracted from the rock showed a unique spectroscopic line at around 588 nm (indicated by D_3 in Figure 1), which was first observed in the spectrum of solar prominence during a total eclipse in 1868, near the well-known D_1 and D_2 lines of sodium.

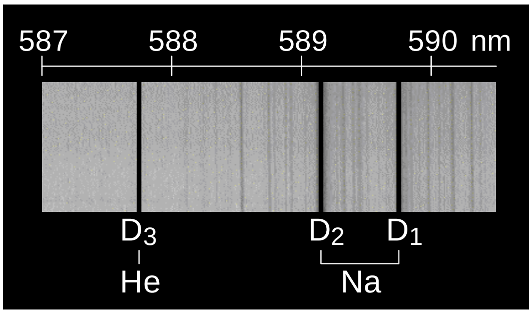


Figure 1. Spectral lines around 588 nm

1.3 Calculate the energy E [J] of a photon with the wavelength of the D_3 line of helium shown in Figure 1.

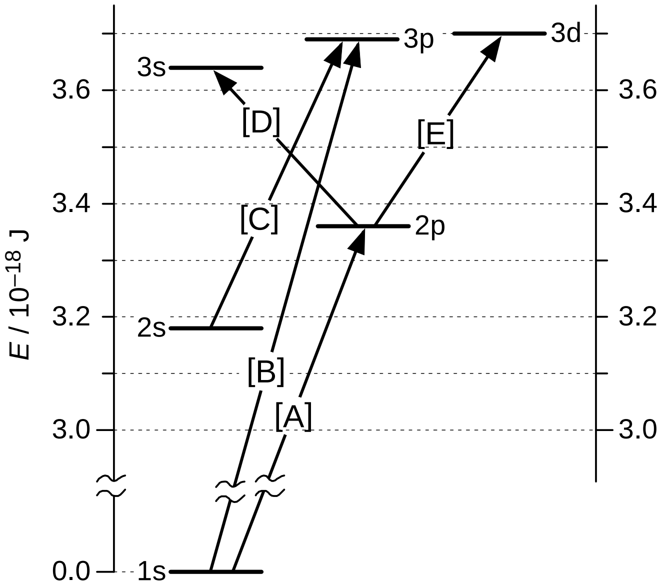


Figure 2.
Energy diagram of atomic orbitals of helium when an electron resides in the 1s orbital.

Figure 2 shows an energy diagram of the atomic orbitals of helium. The arrows indicate the "allowed" transitions according to the spectroscopic principle.

1.4 Identify the transition relevant to the D_3 line of helium among the transitions [A] to [E] indicated in Figure 2. Mark one of the following:

☐ [A] ☐ [B] ☐ [C] ☐ [D] ☐ [E]

1.5 Which equation explains the occurrence of helium in cleveite among [A] to [D] below? Mark one.

☐ [A] $^{238}U \rightarrow {}^{234}Th + \alpha$

☐ [B] $UHe_2 \rightarrow U + 2\ He$

☐ [C] $^{240}U \rightarrow {}^{240}Np + \beta^-$

☐ [D] $^{235}U + n \rightarrow {}^{95}Y + {}^{139}I + 2\ n$

Argon is also found in minerals such as *malacon*.

1.6 Which equation explains the occurrence of argon in rocks among [A] to [D] below? Mark one.

☐ [A] $ArF_2 \rightarrow Ar + F_2$

☐ [B] $ArXe \rightarrow Ar + Xe$

☐ [C] $^{40}K \rightarrow {}^{40}Ar + \varepsilon/\beta^+$ (electron capture / positron emission)

☐ [D] $^{126}I \rightarrow {}^{126}Ar + \beta^-$

One of the strongest evidences for the monoatomicity of argon and helium is the ratio of the heat capacity under constant pressure to that at constant volume, $\gamma = C_p / C_V$, which is exactly 5/3 (1.67 ± 0.01) for a monoatomic gas. The ratio was derived from the measurement of speed of sound v_s by using the following equation, where f and λ are the frequency and wavelength of the sound, and R, T, and M denote the molar gas constant, absolute temperature, and molar mass, respectively.

$$v_s = f\lambda = \sqrt{\frac{\gamma RT}{M}}$$

For an unknown gas sample, the wavelength of the sound was measured to be λ = 0.116 m at a frequency of f = 3520 Hz (Hz = s^{-1}) and temperature of 15.0 °C and under atmospheric pressure ($1.013 \cdot 10^5$ Pa). The density ρ of the gas for these conditions was measured to be 0.850 ± 0.005 kg m^{-3}.

1.7 Calculate the molar mass M [kg mol^{-1}] of this gas.

1.8 Calculate the heat capacity ratio γ for this gas sample.

1.9 Which is this gas? Choose and mark among [A] to [D] .

☐ [A] HCl

☐ [B] HF

☐ [C] Ne

☐ [D] Ar

SOLUTION

1.1 The amount of the pure nitrogen (*chemical nitrogen*), M = 28.02 g mol^{-1}, is

$$n(N_2) = \frac{m(N_2)}{M(N_2)} = \frac{2.2990 \text{ g}}{28.02 \text{ g mol}^{-1}} = 8.205 \cdot 10^{-2} \text{ mol}$$

$$V(N_2) = \frac{nRT}{p} = \frac{8.205 \cdot 10^{-2} \times 8.314 \times 288.15}{1.013 \cdot 10^{5}} = 1.940 \cdot 10^{-3} \text{ m}^3$$

1.2 The equation for the ratio of the mass of *atmospheric nitrogen* to the mass of *chemical nitrogen* is

$$\frac{28.02\,(1-x) + 39.95\,x}{28.02} = \frac{2.3102}{2.2990}$$

Transformation gives

$$x = \frac{\dfrac{2.3102 - 2.2990}{2.2990}}{39.95 - 28.02} \times 28.02 = 1.14 \cdot 10^{-2} \text{ (or } 1.14\text{ \%)}$$

1.3 According to Figure 1, the wavelength of the D_3 line is approximately 587.7 nm.

The corresponding photon energy is

$$E = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34} \times 2.998 \cdot 10^{8}}{587.7 \cdot 10^{9}} = 3.380 \cdot 10^{-19} \text{ J}$$

1.4 The correct answer is [E].

The energy 3.380 · 10^{-19} J matches with the energy of the transition between 2p and 3d orbitals.

1.5 Considering that the α particle is the nucleus of helium, α decay [A] is the relevant source of helium in such rocks. No compounds of He such as UHe_2 in [B] is known to be stable at ambient temperature. [C] is a radioactive decay of ^{240}U in the thorium series. [D] is a nuclear fission reaction of ^{235}U occurring in nuclear reactors. Thus, the correct answer is [A].

1.6 [C] is a well known radioactive decay reaction occurring with a half life of the order of the earth age. No stable compound of Ar, such as ArF_2 or ArXe, can be expected. Products of [D] should be $^{126}Xe + \beta^-$. The correct answer is [C].

1.7 The density ρ is given by $\rho = \frac{nM}{V}$

By combining with the ideal gas law gives:

$$M = \frac{\rho RT}{p} = \frac{0.850 \times 8.314 \times 288.15}{1.013 \cdot 10^5} = 2.01 \cdot 10^{-2} \text{ kg mol}^{-1} \quad (20.1 \text{ g mol}^{-1})$$

1.8 From the equation for the sonic velocity, $f\lambda = \sqrt{\frac{\gamma RT}{M}}$,

$$\gamma = \frac{M}{RT}(f\lambda)^2 = \frac{2.01 \cdot 10^{-2}}{8.314 \times 288.15}(3520 \times 0.116)^2 = 1.40$$

(or using $\frac{M}{RT} = \frac{\rho}{p}$, $\gamma = \frac{\rho}{p}(f\lambda)^2 = \frac{0.850}{1.013 \cdot 10^5}(3520 \times 0.116)^2 = 1.40$)

1.9 From M = 20.1 g mol^{-1}, this gas must be HF or Ne.

From γ = 1.4 (≠ 5/3 ≈ 1.67), this is NOT a monoatomic gas. Thus, the gas must be HF. The correct answer is [B].

Note: It is not possible to distinguish between HF (M = 20.01 g mol^{-1}) and Ne (M = 20.18 g mol^{-1}) from the molar mass only which is 20.10 ± 0.12 g mol^{-1} by taking into account uncertainty of γ (± 0.005/0.850 = ± 0.6 %). However, the precision of γ = 1.40 is enough to exclude the possibility of monoatomic gas (γ = 5/3 ≈ 1.67).

PROBLEM 2

Crystal structure of alkali metal halide

In crystals of ionic compounds, cations are generally arranged in the interstices of the closest packed lattice of anions. The structure of an ionic crystal such as sodium chloride becomes stable when the cations are in contact with the nearest anions.

2.1 In the crystal of sodium chloride, both Na^+ and $Cl^–$ ions form a face-centred cubic lattice. Give the numbers of Na^+ and $Cl^–$ ions in a unit cell and the coordination numbers of Na^+ and $Cl^–$ ions in sodium chloride crystal.

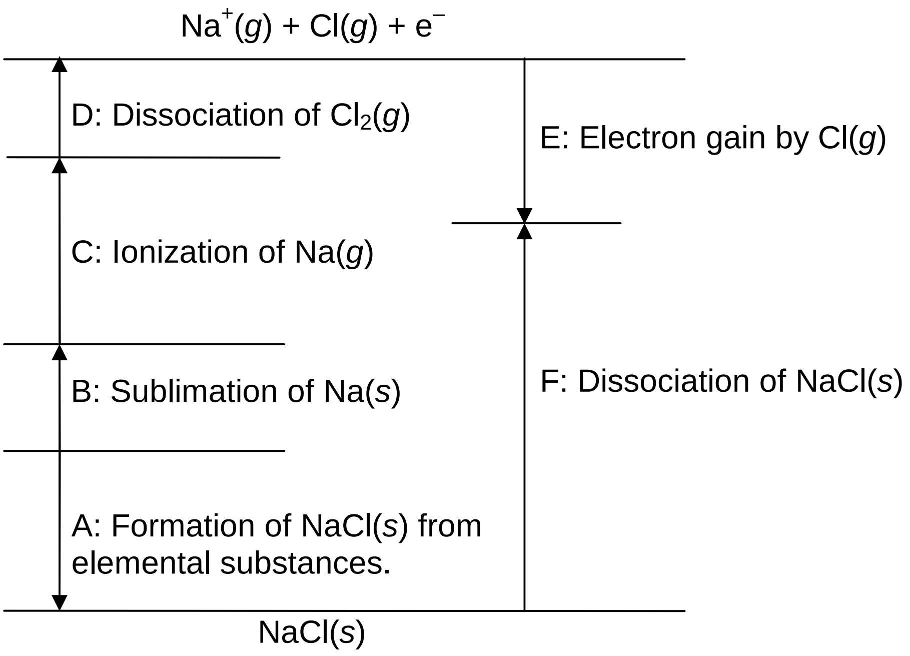
2.2 The ionic radii of Na^+ and $Cl^–$ ions in the crystal of sodium chloride are 0.102 nm and 0.181 nm, respectively.

Calculate the density [kg m^{-3}] of the sodium chloride crystal.

Born-Haber cycle and lattice enthalpy

In ionic inorganic compounds such as sodium chloride, the heat of lattice formation from gaseous ions is very high, and the contribution of the change in entropy is small. Therefore, the lattice formation enthalpy is estimated from enthalpy data by using a Born-Haber cycle.

2.3 The figure below shows the Born-Haber cycle of NaCl. The labels "*g*" and "*s*" represent "gas" and "solid" states, respectively. Show chemical equations in the A and F steps.



2.4 Calculate the enthalpy of the lattice formation of NaCl [kJ mol^{-1}] by using the following enthalpy data of the respective steps in the above Born-Haber cycle.

Formation of NaCl(*s*)	Sublimation of Na(*s*)	Ionization of Na(*g*)	Dissociation of Cl_2(*g*)	Electron gain by Cl(*g*)
–411 kJ mol^{-1}	109 kJ mol^{-1}	496 kJ mol^{-1}	242 kJ mol^{-1}	–349 kJ mol^{-1}

Synthesis of sodium carbonate by the ammonia-soda process (Solvay process)

Sodium carbonate (anhydrous soda ash) is a raw material in the manufacture of glass, medicaments, alkaline detergents, etc.

2.5 The total chemical reaction in the ammonia-soda process is represented as follows:

$2\ NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$

This reaction between sodium chloride and calcium carbonate does not proceed directly. The process comprises the following five reactions involving ammonia:

$CaCO_3 \xrightarrow{\Delta} [\ A\ ] + [\ B\ ]$

$NaCl + NH_3 + [\ B\ ] + H_2O \rightarrow [\ C\ ] + [\ D\ ]$

$2\ [\ C\ ] \xrightarrow{\Delta} Na_2CO_3 + H_2O + [\ B\ ]$

$[\ A\ ] + H_2O \rightarrow [\ E\ ]$

$[\ E\ ] + 2\ [\ D\ ] \rightarrow CaCl_2 + 2\ H_2O + 2\ NH_3$

where Δ represents applying heat treatment. Insert the chemical formulas of the appropriate compounds instead of [A] – [E] in the above reactions.

SOLUTION

2.1

Number of ions	$Na^+ = 4$	$Cl^- = 4$
Coordination number of ions	$Na^+ = 6$	$Cl^- = 6$

2.2 Length of lattice *l*: $l = 0.102 \times 2 + 0.181 \times 2 = 0.566$ nm

Density ρ :

$$\rho = \frac{(22.99 + 35.45) \times 4}{(0.566 \cdot 10^{-9})^3 \times 6.022 \cdot 10^{23}} = 2.1408 \cdot 10^6 \text{ g m}^{-3} = 2.14 \cdot 10^3 \text{ kg m}^{-3}$$

2.3 **A**: $Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$

F: $NaCl(s) \rightarrow Na(g) + Cl^-(g)$

2.4 Enthalpy conservation condition: – **A** + **B** + **C** + **D**/2 = **F** – **E**

From the above equation: – (–411) + 109 + 496 + (242 / 2) = F + 349

Thus: F = 788

Lattice formation enthalpy of NaCl is –**F**, thus –788 kJ mol^{-1}.

2.5 **A**: CaO

B: CO_2

C: $NaHCO_3$

D: NH_4Cl

E: $Ca(OH)_2$

PROBLEM 4

The rechargeable lithium ion battery has been developed in Japan.

The standard electromotive force of the battery is 3.70 V. Assume that the half-reaction at the cathode is

$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the half-reaction at the anode is

$$LiC_6 \rightarrow 6\ C + Li^+ + e^-.$$

4.1 Write the total reaction equation of the battery and calculate the value of the standard Gibbs energy of the reaction [kJ mol^{-1}].

The battery cell is constructed using $LiCoO_2$ and graphite (C) as the electrode materials.

4.2 Calculate the mass of the anode in the completely charged state and that in completely discharged state if 10.00 g of $LiCoO_2$ and 10.00 g of graphite (C) are present initially.

4.3 Calculate the maximum energy generated per mass of the lithium ion battery cell [kJ kg^{-1}]. Assume that the correct ratio for complete reaction between the cathode and anode materials is used and the sum of the mass of electrodes is 50.0 % of the total mass of the battery cell. In comparison, the energy density of lead-acid batteries used for vehicles is about 200 kJ kg^{-1}.

Because an aqueous solution cannot be used as an electrolyte, an organic solution is used in the lithium ion battery cell.

4.4 Give the chemical formula of the gas generated if water is present in the electrolyte.

SOLUTION

4.1 Total reaction equation:

$CoO_2 + LiC_6 \rightarrow LiCoO_2 + 6\,C$

The standard Gibbs energy of the reaction:

$\Delta G^o = -nFE^o = -1 \times 96485\ \text{C mol}^{-1} \times 3.70\ \text{V} = -357\ \text{kJ mol}^{-1}$

4.2 <u>In the completely charged state</u>: 10.71 g

$$n(LiCoO_2) = \frac{10.00\ \text{g}}{97.87\ \text{g mol}^{-1}} = 0.1022\ \text{mol}$$

$$n(C) = \frac{10.00\ \text{g}}{12.01\ \text{g mol}^{-1}} = 0.8326\ \text{mol}$$, which is larger than 0.1022 mol × 6 = 0.6132 mol

Thus, the mass in the completely charged state of the anode is

$10.00 + (0.1022 \times 6.94) = 10.71$ g

<u>In the completely discharged state</u>: 10.00 g

4.3 The mass of 1 mol $LiCoO_2$ is 97.87 g

The mass of 6 mol C is 12.01 g × 6 = 72.06 g

The total mass of the electrode is (97.87 + 72.06) g = 169.93 g

The mass of the cell is 169.93 / 0.500 = 340 g

The maximum energy generated is 357 kJ

Thus, the maximum energy per unit mass of the cell is 1050 kJ kg^{-1}

4.4 <u>H_2</u> or <u>H_2 and O_2</u>

PROBLEM 5

When an atom X absorbs radiation with a photon energy greater than the ionization energy of the atom, the atom is ionized to generate an ion X^+ and the electron (called a photoelectron) is ejected at the same time. In this event, the energy is conserved as shown in Figure 1, that is,

Photon energy ($h\nu$) = ionization energy (IE) of X + kinetic energy of photoelectron.

When a molecule, for example, H_2, absorbs short-wavelength light, the photoelectron is ejected and an H_2^+ ion with a variety of vibrational states is produced. A photoelectron spectrum is a plot of the number of photoelectrons as a function of the kinetic energy of the photoelectrons. Figure 2 shows a typical photoelectron spectrum when H_2 in the lowest vibrational level is irradiated by monochromatic light of 21.2 eV. No photoelectrons are detected above 6.0 eV. (eV is a unit of energy and 1.0 eV is equal to $1.6 \cdot 10^{-19}$ J.)

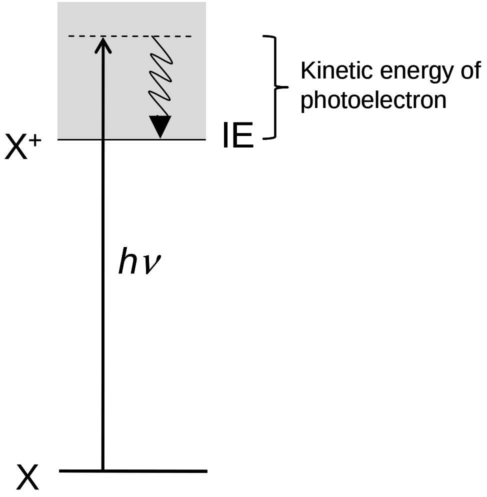


Figure 1.
Schematic diagram of photoelectron spectroscopy.

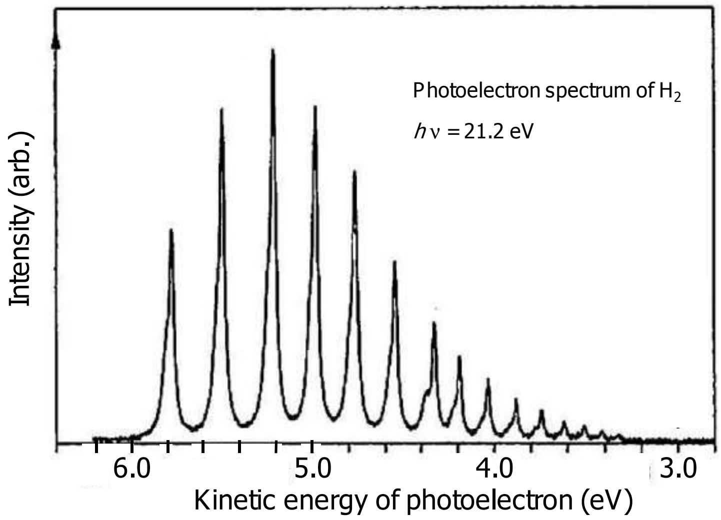


Figure 2.
Photoelectron spectrum of H_2.
The energy of the incident light is 21.2 eV.

5.1 a) Determine the energy difference ΔE_{A1} (eV) between H_2 (v = 0) and H_2^+ (v_{ion} = 0) to the first decimal place. v and v_{ion} denote the vibrational quantum numbers of H_2 and H_2^+, respectively.

b) Determine the energy difference ΔE_{A2} (eV) between H_2^+ (v_{ion} = 0) and H_2^+ (v_{ion} = 3) to the first decimal place.

The electronic energy levels E_n^H of a hydrogen atom are given by the equation

$$E_n^H = -\frac{Ry}{n^2} \qquad \mathbf{(}n = 1, 2, 3\cdots\mathbf{)}$$

Here n is a principal quantum number, and Ry is a constant with dimensions of energy. The energy from n = 1 to n = 2 of the hydrogen atom is 10.2 eV.

5.2 Calculate the ionization energy E_B (eV) of the hydrogen atom to the first decimal place.

The energy threshold for the generation of two electronically excited hydrogen atoms H* (n = 2) from H_2 (v = 0) has been derived to be 24.9 eV by an experiment.

5.3 Determine the bond energy E_C (eV) of H_2 to the first decimal place.

5.4 Considering an energy cycle, determine the bond energy E_D (eV) of H_2^+ to the first decimal place. If you were unable to determine the values for E_B and E_C, then use 15.0 eV and 5.0 eV for E_B and E_C, respectively.

5.5 Calculate the threshold energy E_E (eV) of the following dissociative ionization reaction to the first decimal place:

$$H_2 \rightarrow H^*(n = 2) + H^+ + e^-.$$

If you were unable to determine the values for E_B and E_C, then use 15.0 eV and 5.0 eV for E_B and E_C, respectively.

When H_2 absorbs monochromatic light of 21.2 eV, the following dissociation process occurs at the same time.

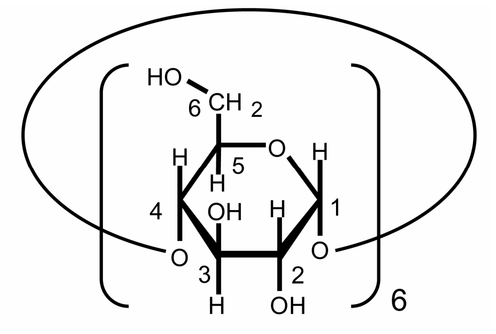
$$H_2 \xrightarrow{\text{21.2 eV}} H\,(n = 1) + H\,(n = 1)$$

Two hydrogen atoms move in opposite directions with the same speed.

5.6 Calculate the speed *u* (m s^{-1}) of the hydrogen atoms generated in the above reaction. H_2 is assumed to be at rest. If you were unable to determine the value for E_C, then use 5.0 eV for E_C.

PROBLEM 9

α-Cyclodextrin (αCyD), which is a cyclic oligosaccharide of six α(1→4) linked α-D-glucopyranoside units, can be topologically represented as toroids (Figure 1). α-D-glucopyranoside units in αCyD are usually in the most stable chair conformation.



αCyDe

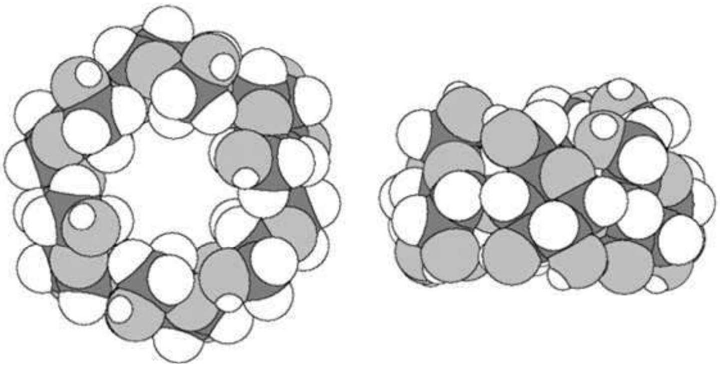
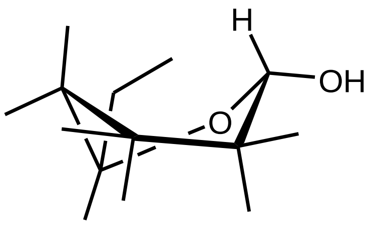
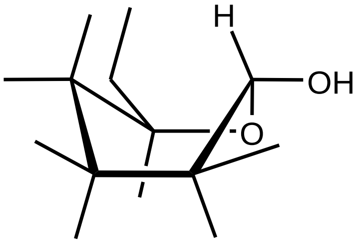


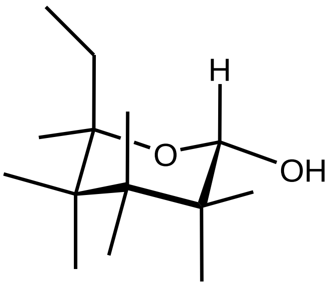
Figure 1. Space filling model of αCyD.
Left: view through the hole.
Right: side view.

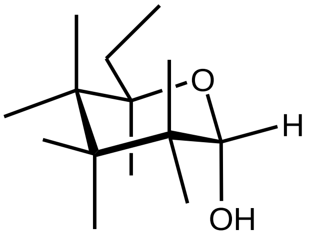
9.1 Give the absolute configuration (*R* or *S*) at stereogenic carbons C-2 and C-5 of D-glucose. Also, draw a stereostructure of the open chain form of D-glucose.

9.2 Choose the most stable conformation from the following four incomplete α-D-glucopyranose formulas. Also, add four OH groups and four H atoms to complete the α-D-glucopyranose formula.



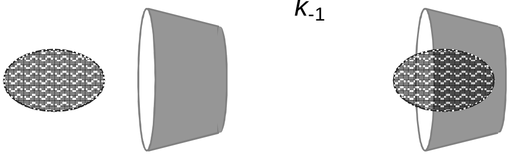






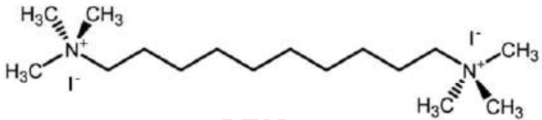
αCyD in water is able to host hydrophobic molecules. When the host : guest (H : G) stoichiometry is 1 : 1, the inclusion complexation can be given by the following equilibrium.

$$G + H \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HG \qquad (1)$$



where k_1 and k_{-1} are the rate constant for the forward and backward reaction, respectively. The complexation of a guest to αCyD causes a chemical shift change in ^{1}H NMR spectra.

Figure 2 shows a part of ^{1}H NMR spectra (signals from H–1 of αCyD) showing the chemical shift change in the presence of varying amounts of BTAD (1,10-bis(trimethylammonium)decane diiodide). The doublet peak at 5.06 ppm is from H–1 of free αCyD, while the doublet at 5.14 ppm is from H–1 of αCyD complexed with BTAD. (Note that the spectra given in Figure 2 were measured in the complexation equilibrium state.)



BTAD

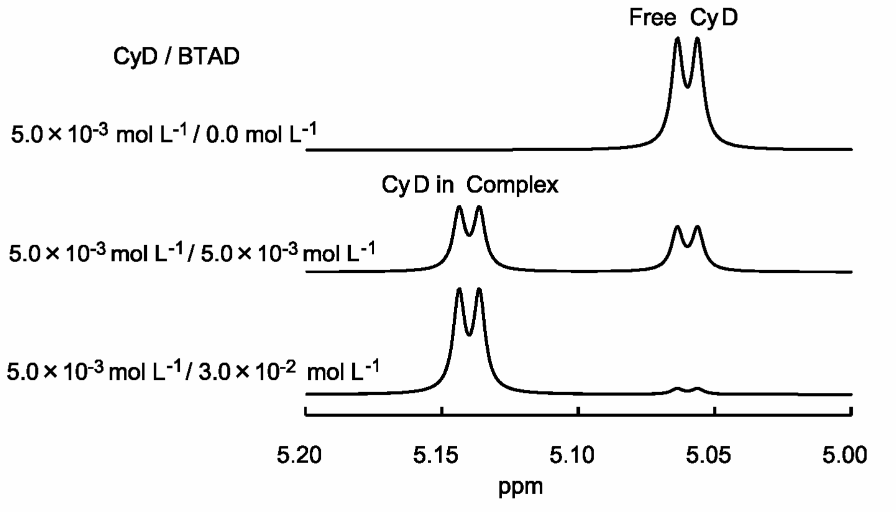
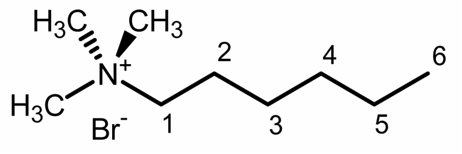


Figure 2.

Expanded ^{1}H NMR spectra (signals from H–1 of αCyD) of solutions with concentration of αCyD equal to $5.0 \cdot 10^{-3}$ mol dm^{-3} and that of BTAD equal from 0 to $3.0 \cdot 10^{-2}$ mol dm^{-3}.

9.3 Consider a solution in which concentrations of αCyD as well as BTAD are equal to $5.0 \cdot 10^{-3}$ mol dm^{-3} and the relative peak areas of the doublets at 5.06 and 5.14 ppm are 0.41 and 0.59, respectively. Calculate (to 2 significant figures) the concentration equilibrium constant, *K,* for the inclusion complexation of αCyD / BTAD.

Complexation of αCyD with hexyltrimethylammonium bromide (HTAB) appears in NMR spectra in a way different from the αCyD/BTAD complexation. Figure 3 shows a part of ^{1}H NMR spectra (H-6 signal of HTAB) in αCyD/HTAB solutions. The signal appears as one triplet (not two triplets), which shifts depending on the concentration of αCyD from the position of free HTAB to the position of αCyD/HTAB in proportion to the fraction of the complex in the solution. The H-6 signals from free HTAB and HTAB complexed with αCyD are triplets at 0.740 ppm and 0.860 ppm, respectively.



HTAB

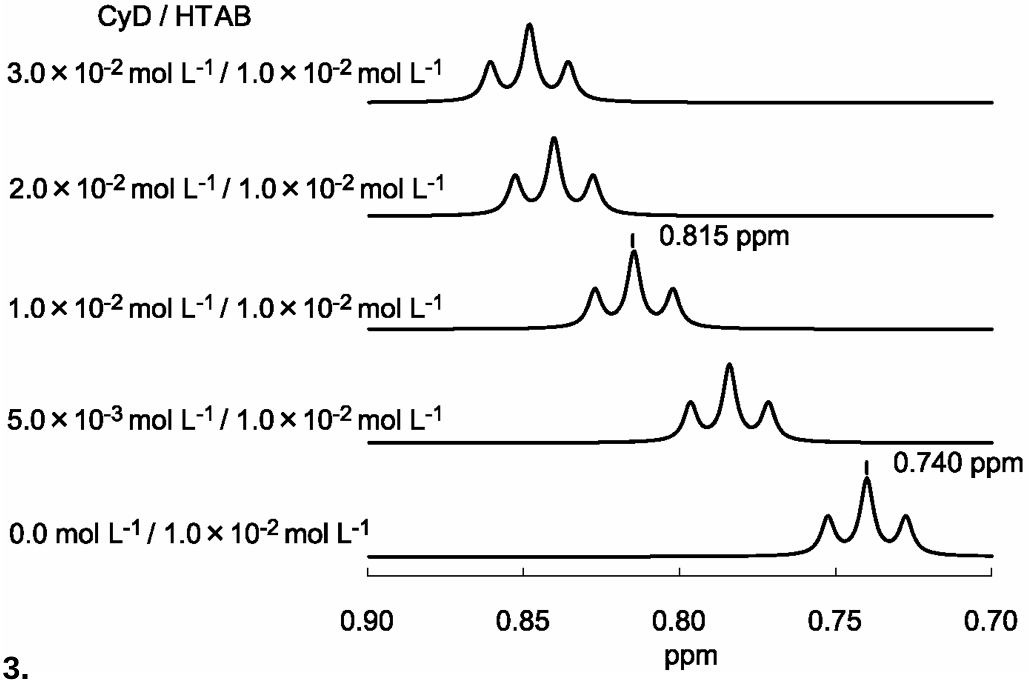


Figure 3.

Expanded ^{1}H NMR spectra (H-6 signal of HTAB) of solutions with concentration of HTAB equal to $1.0 \cdot 10^{-2}$ mol dm^{-3} and that of αCyD equal from 0 to $3.0 \cdot 10^{-2}$ mol dm^{-3}.

9.4 The signal of HTAB in αCyD/HTAB_solutions appears as one triplet that shifts depending on the concentration of αCyD. Choose the rational interpretation(s) just from these spectra.

Hint: When a guest molecule move in and out of αCyD rapidly and repeatedly, only one signal of the guest is observed at the weighted average of the chemical shifts of the free guest and the shift of the guest included in αCyD.

a) k_1 of αCyD/HTAB > k_1 of αCyD/BTAD

b) k_1 of αCyD/HTAB < k_1 of αCyD/BTAD

c) K of αCyD/HTAB > K of αCyD/BTAD

d) K of αCyD/HTAB < K of αCyD/BTAD

9.5 The signals of HTAB in the solution with concentrations of αCyD as well as HTAB equal to $1.0 \cdot 10^{-2}$ mol dm^{-3} are positioned at 0.815 ppm. Calculate (to 2 significant figures) the value of K for the complexation of αCyD/HTAB.

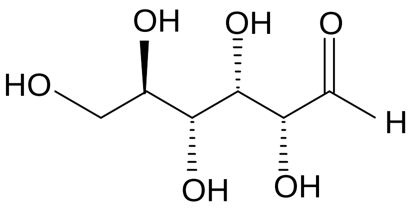
9.6 At 40.0 °C and 60.0 °C, K for the complexation of αCyD / HTAB are $3.12 \cdot 10^2$ and $2.09 \cdot 10^2$ respectively. Calculate (to 2 significant figures) the enthalpy change, ΔH^o [kJ mol^{-1}] and the entropy change, ΔS^o [J K^{-1} mol^{-1}]. (Ignore the temperature dependence of ΔH^o and ΔS^o.)

SOLUTION

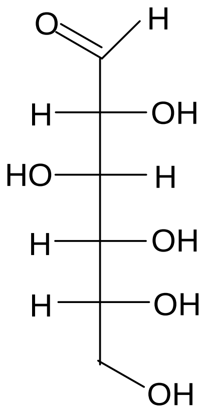
9.1 Absolute configuration at C-2: *R*

Absolute configuration at C-5: *R*

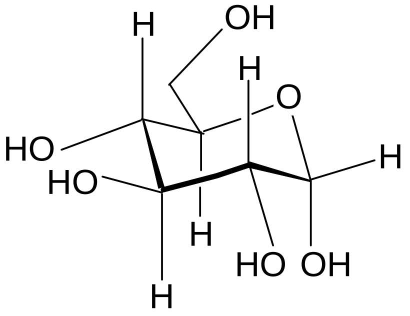
Chain form:



or



9.2



9.3 $$K = \frac{[HG]}{[H][G]} = \frac{[\alpha\text{CyD}]_0 \times a_{5.14}}{\{[\alpha\text{CyD}]_0 \times a_{5.06} \times \{[\text{BTAD}]_0 - [\alpha\text{CyD}]_0 \times a_{5.14}\}} =$$

$$= \frac{5.0 \cdot 10^{-3} \times 0.59}{(5.0 \cdot 10^{-3} \times 0.41)^2} = 7.0 \cdot 10^2$$

$a_{5.06}$: relative area of the peak at 5.06 ppm = mole fraction of free αCyD

$a_{5.14}$: relative area of the peak at 5.14 ppm = mole fraction of αCyD complexed with BTAD

9.4 The correct answer: **a**

9.5 (M = mol dm^{-3})

In $1.0 \cdot 10^{-2}$ M / $1.0 \cdot 10^{-2}$ M αCyD/HTAB

$$f_{10/10} = \frac{s_{10/10} - s_{\text{free}}}{s_{\text{complex}} - s_{\text{free}}} = \frac{0.815 - 0.740}{0.860 - 0.740} = 0.625$$

s_{free} : chemical shift of HTAB in free, and complexed state

s_{complex}: chemical shift of HTAB in a complexed state

$s_{10/10}$: chemical shift of HTAB in 10.0 mM / 10.0 mM αCyD/HTAB

$f_{10/10}$: mole fraction of complexed HTAB in 10.0 mM / 10.0 mM αCyD/HTAB

$$K = \frac{[HG]}{[H][G]} =$$

$$= \frac{[\text{HTAB}]_0 \times f_{10/10}}{\{[\alpha\text{CyD}]_0 - f_{10/10}\,[\text{HTAB}]_0\}\,[\text{HTAB}]_0(1 - f_{10/10})} =$$

$$= \frac{1.0 \cdot 10^{-2} \times 0.625}{[1.0 \cdot 10^{-2} \times (1 - 0.625)]^2} = 4.4 \cdot 10^2$$

$K = 4.4 \cdot 10^2$

9.6 From $\Delta G^o = -RT \ln K$

$\Delta G^o(40.0\ °C) = -8.314 \times 313.2 \times \ln(3.12 \cdot 10^2) = -14.94 \cdot 10^3\ \text{J mol}^{-1}$

$\Delta G^o(60.0\ °C) = -8.314 \times 333.2 \times \ln(2.09 \cdot 10^2) = -14.79 \cdot 10^3\ \text{J mol}^{-1}$

From $\Delta G^o = \Delta H^o - T\Delta S^o$

$-14.94 \cdot 10^3 = \Delta H^o - 313.2 \times \Delta S^o$

$-14.79 \cdot 10^3 = \Delta H^o - 333.2 \times \Delta S^o$

$\Delta S^o = -7.5\ \text{J K}^{-1}\text{mol}^{-1}$; $\Delta H^o = -17\ \text{kJ mol}^{-1}$

THE FORTY-THIRD
INTERNATIONAL CHEMISTRY OLYMPIAD
9–18 JULY 2011, ANKARA, TURKEY

THEORETICAL PROBLEMS

PROBLEM 1

Nitrogen oxides, common pollutants in the ambient air, are primarily nitric oxide, NO, and nitrogen dioxide, NO_2. Atmospheric nitric oxide is produced mainly during thunderstorms and in the internal combustion engines. At high temperatures NO reacts with H_2 to produce nitrous oxide, N_2O, a greenhouse gas.

$$2\ NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

To study the kinetics of this reaction at 820 °C, initial rates for the formation of N_2O were measured using various initial partial pressures of NO and H_2.

Exp.	Initial pressure, torr		Initial rate of production of N_2O, torr s^{-1}
	p_{NO}	p_{H_2}	
1	120.0	60.0	$8.66 \cdot 10^{-2}$
2	60.0	60.0	$2.17 \cdot 10^{-2}$
3	60.0	180.0	$6.62 \cdot 10^{-2}$

Throughout this problem do not use concentrations. Use units of pressure (torr) and time in seconds.

1.1 Determine the experimental rate law and calculate the rate constant.

1.2 Calculate the initial rate of disappearance of NO, if NO with a pressure of $2.00 \cdot 10^2$ torr and H_2 with $1.00 \cdot 10^2$ torr are mixed at 820 °C.

(If you have been unable to calculate the value for the rate constant, you can use the value of $2 \cdot 10^{-7}$ in appropriate unit.)

1.3 Calculate the time elapsed to reduce the partial pressure of H_2 to the half of its initial value, if NO with a pressure of $8.00 \cdot 10^2$ torr and H_2 with 1.0 torr are mixed at 820 °C.

(If you have been unable to calculate the value for the rate constant, you can use the value of $2 \cdot 10^{-7}$ in appropriate unit.)

A proposed mechanism for the reaction between NO and H_2 is given below:

$$2\,NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$$

1.4 Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

1.5 Under what condition does this rate law reduce to the experimentally determined rate law found in Part 1.1? Tick the relevant answer.

☐ If $k_{-1} << k_2\, p_{H2}$

☐ If $k_{-1} >> k_2\, p_{H2}$

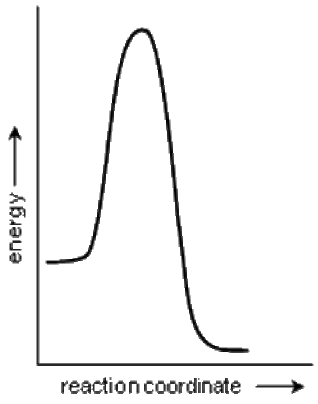
☐ If $k_{-1} > k_2$

☐ If $k_1 > k_{-1}$

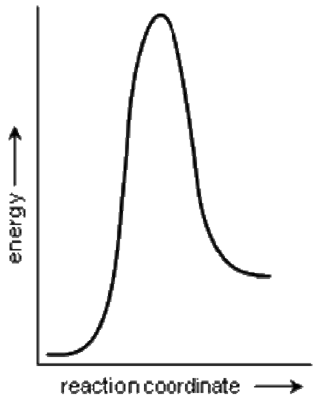
1.6 Express the experimentally determined rate constant k in terms of k_1, k_{-1} and k_2.

1.7 Select the schematic energy diagram that is consistent with the proposed reaction mechanism and experimental rate law.

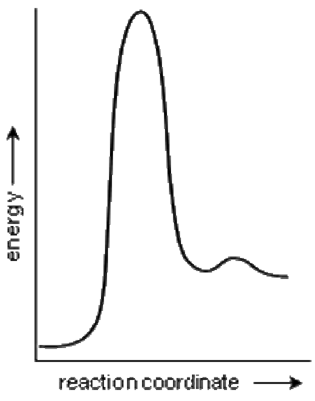
a.



b.



c.



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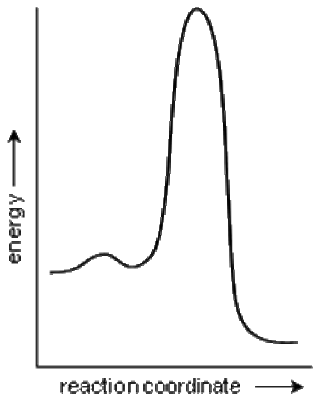
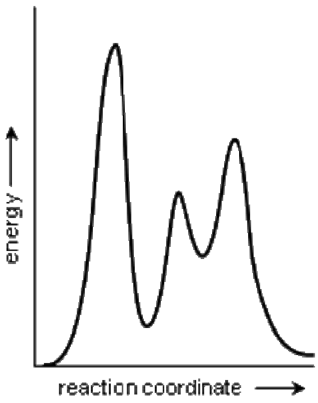
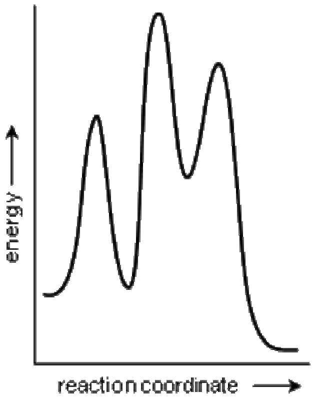

energy
reaction coordinate

e.


energy
reaction coordinate

f.


energy
reaction coordinate

SOLUTION

1.1 Rate = $R = k\,(p_{NO})^a\,(p_{H_2})^b$

$$\frac{R_1}{R_2} = \frac{8.66 \cdot 10^{-2}}{2.17 \cdot 10^{-2}} = 3.99 = \frac{k \times 120^a \times 60^b}{k \times 60^a \times 60^b} \qquad 2^a = 3.99 \;\Rightarrow\; a = 2$$

$$\frac{R_3}{R_2} = \frac{6.62 \cdot 10^{-2}}{2.17 \cdot 10^{-2}} = 3.05 = \frac{k \times 60^a \times 180^b}{k \times 60^a \times 60^b} \qquad 3^b = 3.05 \;\Rightarrow\; b = 1$$

Rate = $R = k\,(p_{NO})^2\,p_{H_2}$

$$k = \frac{8.66 \cdot 10^{-2}}{120^2 \times 60} = 1.00 \cdot 10^{-7}\ \text{torr}^{-2}\,\text{s}^{-1}$$

1.2 $\text{Rate} = \dfrac{\Delta p_{N_2O}}{\Delta t} = -\dfrac{1}{2}\dfrac{\Delta p_{NO}}{\Delta t} = 1.0 \cdot 10^{-7} \times 200^2 \times 100 = 0.40\ \text{torr s}^{-1}$

$$-\frac{\Delta p_{NO}}{\Delta t} = 0.80\ \text{torr s}^{-1}$$

1.3 Rate = $R = k\,(p_{NO})^2\,p_{H_2}$

Since $p_{NO} \gg p_{H_2}$

$\text{Rate} = k'\,p_{H_2} \;\Rightarrow\; k' = k\,(p_{NO})^2$

$k' = 1.0 \cdot 10^{-7} \times (8.00 \cdot 10^2)^2 = 0.064\ \text{s}^{-1}$

$$t_{1/2} = \frac{\ln 2}{k'} = 10.8\ \text{s}$$

1.4 $\dfrac{\Delta p_{N_2O}}{\Delta t} = k_2\,p_{N_2O_2}\,p_{H_2}$

Steady state approximation for N_2O_2:

$$\frac{\Delta p_{N_2O_2}}{\Delta t} = 0 = k_1\,(p_{NO})^2 - k_{-1}\,p_{N_2O_2} - k_2\,p_{N_2O_2}\,p_{H_2} = 0$$

$$p_{N_2O_2} = \frac{k_1\,(p_{NO})^2}{k_{-1} + k_2\,p_{H_2}}$$

$$\frac{\Delta p_{N_2O}}{\Delta t} = k_2\,p_{H_2}\,\frac{k_1\,(p_{NO})^2}{k_{-1} + k_2\,p_{H_2}}$$

$$\text{Rate} = \frac{\Delta p_{N_2O}}{\Delta t} = k_1 k_2\,\frac{(p_{NO})^2\,p_{H_2}}{k_{-1} + k_2\,p_{H_2}}$$

1.5 The correct answer: If $k_{-1} >> k_2\, p_{H_2}$

1.6 $k = \dfrac{k_1 k_2}{k_{-1}}$

1.7 Energy diagram **d** is correct.

PROBLEM 4

For sustainable energy, hydrogen appears to be the best energy carrier. The most efficient way of using hydrogen is generation of electrical energy in a fuel cell. However, storing hydrogen in large quantities is a challenge in fuel cell applications. Among the chemical hydrides considered as solid hydrogen storage materials, sodium borohydride ($NaBH_4$), being non-toxic, stable and environmentally benign, appears to be the most promising one. The hydrolysis of sodium borohydride that releases H_2 gas is a slow reaction at ambient temperature and, therefore, needs to be catalyzed.

$$NaBH_4(aq) + 2\,H_2O(l) \xrightarrow{\text{catalyst}} Na^+(aq) + BO_2^-(aq) + 4\,H_2(g)$$

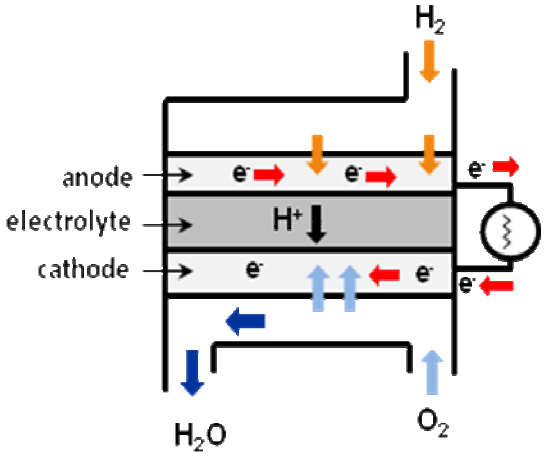
Colloidal ruthenium(0) nanoclusters are the most active catalysts in this hydrolysis even at room temperature and lead to a complete H_2 release from sodium borohydride. Kinetic studies show that the catalytic hydrolysis of $NaBH_4$ is a first order reaction with respect to the catalyst, but a zero order with respect to the substrate. The rate of hydrogen production per mole of ruthenium is 92 mol $H_2\cdot(\text{mol Ru})^{-1}\cdot\text{min}^{-1}$ at 25 °C.

4.1 Calculate the amount of ruthenium catalyst (in mg) which must be added to 0.100 dm^3 of $NaBH_4$ solution with a concentration of 1.0 mol dm^{-3} to supply the hydrogen gas at a rate of 0.100 $dm^3\cdot min^{-1}$ at 25 °C and 1.0 atm, that is required for a portable fuel cell.

4.2 For how many minutes will this system supply hydrogen gas at this rate?

4.3 The Arrhenius activation energy for this catalytic hydrolysis of sodium borohydride is E_a = 42.0 kJ mol^{-1}. Calculate the temperature required to achieve the same rate of hydrogen evolution by using a half of the amount of ruthenium catalyst used at 25.0 °C.

4.4 A fuel cell (see figure) is made up of three segments sandwiched together: the anode, the electrolyte, and the cathode. Hydrogen is used as fuel and oxygen as oxidant. Two chemical reactions occur at the interfaces of the three different segments:



$$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$$

$H_2(g) + 2\ OH^-(aq) \rightarrow 2\ H_2O(l) + 2\ e^-$

The net result of the two reactions is

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

The hydrogen for the fuel cell is supplied from the hydrolysis of sodium borohydride. Calculate the standard potential for the cathode half reaction if the standard reduction potential for the anode half reaction is –0.83 V and $\Delta_f G^o(H_2O(l))$ is –237 kJ mol^{-1}.

4.5 Calculate the volume of air at a temperature of 25 °C and a pressure of 1.0 atm needed to generate a constant current of 2.5 A for 3.0 hours in this fuel cell. Assume that air contains 20 % by volume O_2(g).

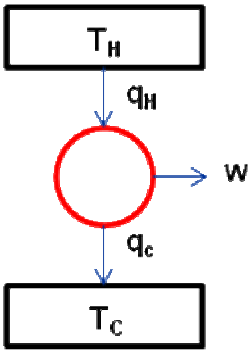
4.6 The efficiency of a fuel cell is given by the ratio of the work produced to the heat dissipated by the cell reaction. Thus, the maximum efficiency for a fuel cell is given by:

$$\eta_{\text{fuel cell}} = \frac{\text{work}}{\text{heat}}$$

Calculate the maximum efficiency for the fuel cell using the data given below at 25 °C and a standard pressure.

	$S°$ (J mol^{-1} K^{-1})
$H_2(g)$	130.7
$O_2(g)$	205.2
$H_2O(l)$	70.0

The second law of thermodynamics states that it is impossible to convert all of the heat, q_H, from a high-temperature reservoir at T_H into work. At least, some of the energy, q_C, must be transferred to a low-temperature reservoir at T_C. Thus, a heat engine with 100% efficiency is thermodynamically impossible. When the heat engine is working reversibly, as in a Carnot cycle, the efficiency will be a maximum.



For a heat engine working reversibly between two reservoirs the following relations are applied:

$$q_H = w + q_C$$

and

$$\frac{q_H}{T_H} = \frac{q_C}{T_C}$$

4.7 What should be the temperature of the hot reservoir, T_H, of a Carnot heat engine to maintain the efficiency of the fuel cell calculated in part 4.6, if the temperature of cold reservoir T_C is 40 °C?

(If you have been unable to calculate the value for the efficiency then use the value 0.80 for the calculation.)

SOLUTION

4.1 $n(H_2) = \dfrac{0.100\ \text{dm}^3\ \text{min}^{-1} \times 101.325\ \text{kPa}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times\ 298\ \text{K}} = 4.1 \cdot 10^{-3}\ \text{mol min}^{-1}$

$$n(\text{Ru}) = \dfrac{4.1 \cdot 10^{-3}\ \text{mol H}_2\ \text{min}^{-1}}{\dfrac{92\ \text{mol H}_2\ \text{min}^{-1}}{1\ \text{mol Ru}}} = 4.5 \cdot 10^{-5}\ \text{mol}$$

$m(\text{Ru}) = 4.5 \cdot 10^{-5}\ \text{mol} \times 101.07\ \text{g mol}^{-1} = 4.5 \cdot 10^{-3}\ \text{g} = 4.5\ \text{mg}$

4.2 $n(NaBH_4) = 1.0\ \text{mol dm}^{-3} \times 0.100\ \text{dm}^3 = 0.10\ \text{mol}$

0.04 mol of H_2 are released from 0.10 mol $NaBH_4$.

Thus:

$$t = \dfrac{0.40\ \text{mol H}_2}{4.1 \cdot 10^{-3}\ \text{mol H}_2\ \text{min}^{-1}} = 98\ \text{min}$$

4.3 Rate = k [Ru] = $A\, e^{-E_a/RT}$ [Ru]

$$\dfrac{e^{-E_a/R \times 298}}{e^{-E_a/RT}} = \dfrac{1}{2}$$

$$-\dfrac{E_a}{R}\left(\dfrac{1}{298} - \dfrac{1}{T}\right) = \ln\dfrac{1}{2}$$

$$\dfrac{4.20 \cdot 10^4\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\text{K}^{-1}}\left(\dfrac{1}{298} - \dfrac{1}{T}\right) = \ln 2$$

T = 311 K or 38 °C

4.4 Since $\Delta G^o = -\, n\, F\, E^o$

$2\,(-2.37 \cdot 10^5) = -\,4 \times 96485 \times E^0_{\text{cell}}$ $\qquad E^0_{\text{cell}} = 1.23\ \text{V}$

$1.23\ \text{V} = E^0_{\text{cathode}} - (-0.83\ \text{V})$

$E^0_{\text{cathode}} = 0.40\ \text{V}$

4.5 2.5 A × 3 × 3600 s = 27000 C

$n(O_2) = 27000\ \text{C} \times \dfrac{1\ \text{mol}}{4 \times 96485\ \text{C}} = 0.070\ \text{mol}$

$V(O_2) = \dfrac{0.070\ \text{mol} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{101.325\ \text{kPa}} = 1.7\ \text{dm}^3$ $\qquad V(\text{air}) = 8.6\ \text{dm}^3$

4.6 $\Delta_{rxn}G^o = \Delta_{rxn}H^o - T\,\Delta_{rxn}S^o$

$\Delta_{rxn}S^o = 2\,S^o\,(H_2O_{(l)}) - [\,2S^o\,(H_2(g)) + S^o(O_2\,(g))\,] = 2 \times 70.0 - (2 \times 130.7 + 205.2)$

$= -326.6\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta_{rxn}H^o = \Delta_{rxn}G^o + T\,\Delta_{rxn}S^o = -\,474 + 298.15 \times (-326.6 \cdot 10^{-3}) = -571.4\ \text{kJ}$

maximum w = $\Delta_{rxn}G^o = -\,474$ kJ

$$\eta = \frac{-\,474000\ \text{J}}{-\,571400\ \text{J}} = 0.83$$

4.7 $\eta_{\text{engine}} = \dfrac{w}{q_H} = \dfrac{q_H - q_C}{q_H} = 1 - \dfrac{q_C}{q_H}$

Since $\dfrac{q_H}{T_H} = \dfrac{q_C}{T_C} \qquad \dfrac{q_C}{q_H} = \dfrac{T_C}{T_H}$

Thus: $\eta_{\text{engine}} = 1 - \dfrac{T_C}{T_H}$

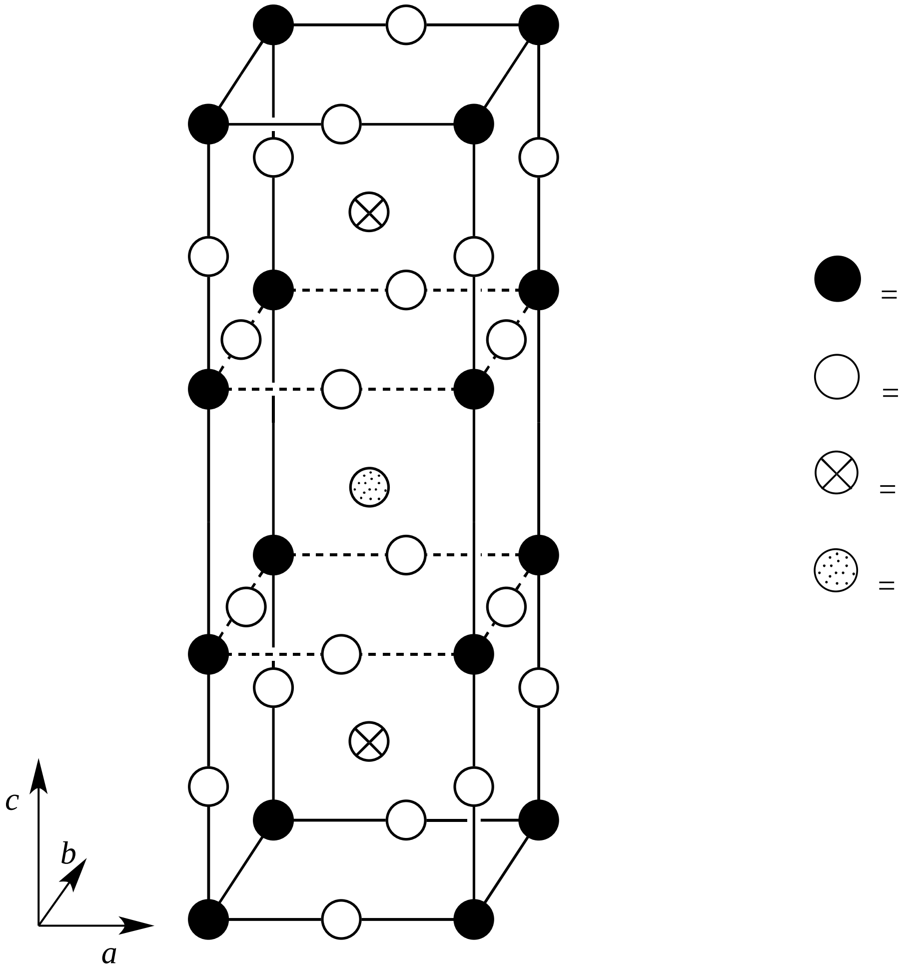
$0.83 = 1 - \dfrac{313}{T_H}$

$T_H = 1.8 \cdot 10^3$ K or $T_H \approx 1.5 \cdot 10^3$ °C

PROBLEM 4

In the 1980's a class of ceramic materials was discovered that exhibits superconductivity at the unusually high temperature of 90 K. One such material contains yttrium, barium, copper and oxygen and is called "YBCO". It has a nominal composition of $YBa_2Cu_3O_7$, but its actual composition is variable according to the formula $YBa_2Cu_3O_{7-\delta}$ $(0 < \delta < 0.5)$.

4.1 One unit cell of the idealized crystal structure of YBCO is shown below. Identify which circles correspond to which elements in the structure.



The true structure is actually orthorhombic ($a \neq b \neq c$), but it is approximately tetragonal, with $a \approx b \approx (c/3)$.

4.2 A sample of YBCO with δ = 0.25 was subjected to X-ray diffraction using CuKα radiation (λ = 154.2 pm). The lowest-angle diffraction peak was observed at $2\,\theta$ = 7.450º. Assuming that $a = b = (c/3)$, <u>calculate</u> the values of *a* and *c*.

4.3 <u>Estimate</u> the density of this sample of YBCO (with δ = 0.25) in g cm^{-3}. If you were unable to calculate the values for *a* and *c* from part 4.2, then use *a* = 500 pm and *c* = 1500 pm.

When YBCO is dissolved in aqueous HCl (*c* = 1.0 mol dm^{-3}) bubbles of gas are observed (identified as O_2 by gas chromatography). After boiling for 10 min to expel the dissolved gases, the solution reacts with excess KI solution, turning yellow-brown. This solution can be titrated with thiosulfate solution to a starch endpoint. If YBCO is added under Ar directly to a solution in which concentrations of both KI and HCl are equal to 1.0 mol dm^{-3}, the solution turns yellow-brown but no gas evolution is observed.

4.4 <u>Write</u> a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl with evolution of O_2.

4.5 <u>Write</u> a balanced net ionic equation for the reaction when the solution from 4.4 reacts with excess KI in acidic solution after the dissolved oxygen is expelled.

4.6 <u>Write</u> a balanced net ionic equation for the reaction when the solution from 4.5 is titrated with thiosulfate ($S_2O_3^{2-}$).

4.7 <u>Write</u> a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl containing excess KI in an Ar atmosphere.

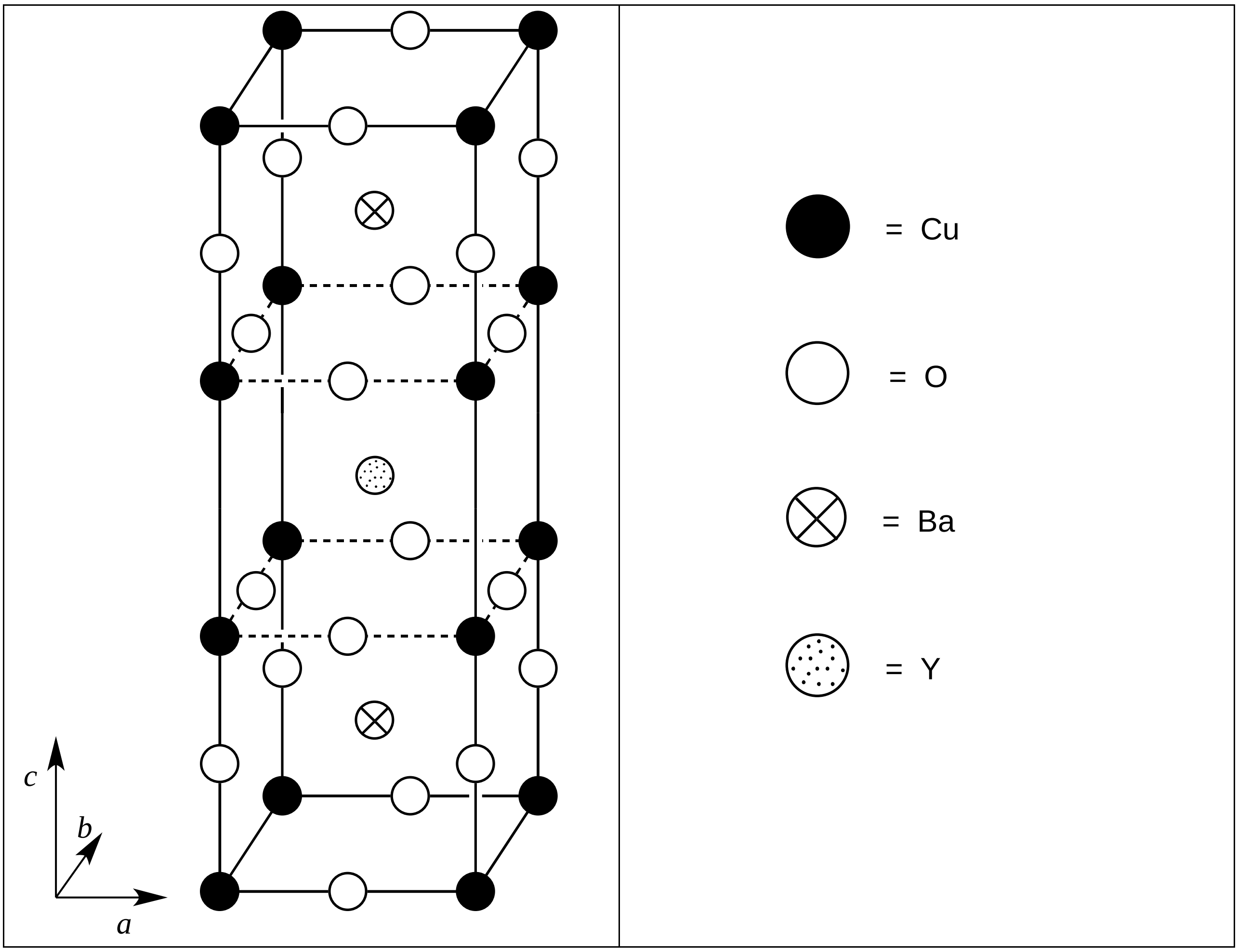
Two identical samples of YBCO with an unknown value of δ were prepared. The first sample was dissolved in 5 cm^3 of aqueous HCl (*c* = 1.0 mol dm^{-3}), evolving O_2. After boiling to expel gases, cooling, and addition of 10 cm^3 of KI solution (*c* = 0.7 mol dm^{-3}) under Ar, titration with thiosulfate to the starch endpoint required $1.542 \cdot 10^{-4}$ mol thiosulfate. The second sample of YBCO was added under Ar directly to 7 cm^3 of a solution in which *c*(KI) = 1.0 mol dm^{-3} and c(HCl) = 0.7 mol dm^{-3}. Titration of this solution required $1.696 \cdot 10^{-4}$ mol thiosulfate to reach the endpoint.

4.8 <u>Calculate</u> the amount of substance of Cu (in mol) in each of these samples of YBCO.

4.9 <u>Calculate</u> the value of δ for these samples of YBCO.

SOLUTION

4.1



4.2 $\sin\theta = n\lambda / 2d$

$d = (1)(154.2\text{ pm}) / 2\sin(3.725°)$

$d = 1187\text{ pm}$

lowest-angle = > d = longest axis = c

$c = 1187\text{ pm}$

$a = c / 3 = 396\text{ pm}$

$a = 396\text{ pm}$

4.3 $V_{\text{unit cell}} = a \times b \times c = 3a^3 = 3\,(396\text{ pm})^3 = 1.863 \cdot 10^{-22}\text{ cm}^3$

$$m_{\text{unit cell}} = \frac{88.91 + 2\times 137.33 + 3\times 63.55 + 6.75\times 16.00}{N_A}$$

$$m_{\text{unit cell}} = \frac{662.22\ \text{g mol}^{-1}}{6.0221 \cdot 10^{23}\ \text{mol}^{-1}} = 1.100 \cdot 10^{-21}\ \text{g}$$

$$\text{density} = \frac{1.100 \cdot 10^{-21}\,\text{g}}{1.863 \cdot 10^{-22}\,\text{cm}^3} = 5.90\ \text{g cm}^{-3}$$

4.4 $YBa_2Cu_3O_{7-\delta}(s) + 13\ H^+(aq) \rightarrow$

$\rightarrow Y^{3+}(aq) + 2\ Ba^{2+}(aq) + 3\ Cu^{2+}(aq) + (0.25\ [1 - 2\delta])\ O_2(g) + 6.5\ H_2O(l)$

4.5 $2\ Cu^{2+}(aq) + 5\ I^-(aq) \rightarrow 2\ CuI(s) + I_3^-(aq)$

or

$2\ Cu^{2+}(aq) + 4\ I^-(aq) \rightarrow 2\ CuI(s) + I_2(aq)$

4.6 $I_3^-(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 3\ I^-(aq) + S_4O_6^{2-}(aq)$

or

$I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 2\ I^-(aq) + S_4O_6^{2-}(aq)$

4.7 $YBa_2Cu_3O_{7-\delta}(s) + (14 - 2\ \delta)\ H^+(aq) + (9 - 3\ \delta)\ I^-(aq) \rightarrow$

$\rightarrow Y^{3+}(aq) + 2\ Ba^{2+}(aq) + 3\ CuI(s) + (7 - \delta)\ H_2O(l) + (2 - \delta)\ I_3^-(aq)$

or

$YBa_2Cu_3O_{7-\delta}(s) + (14 - 2\ \delta)\ H^+(aq) + (7 - 2\ \delta)\ I^-(aq) \rightarrow$

$\rightarrow Y^{3+}(aq) + 2\ Ba^{2+}(aq) + 3\ CuI(s) + (7 - \delta)\ H_2O(l) + (2 - \delta)\ I_2(aq)$

4.8 n(Cu) = n(thiosulfate) in the first titration

$n(\text{Cu}) = 1.542 \cdot 10^{-4}$ mol

4.9 Total $n(\text{Cu}) = 1.542 \cdot 10^{-4}$ mol

$n(\text{Cu}^{\text{III}}) = (1.696 \cdot 10^{-4}\ \text{mol}) - (1.542 \cdot 10^{-4}\ \text{mol}) = 1.54 \cdot 10^{-5}$ mol

Thus: 90 % of Cu is present as Cu(II) and 10 % as Cu(III).

From charge balance:

$2(7 - \delta) = 3 + (2 \times 2) + 3 \times [(0.90 \times 2) + (0.10 \times 3)] = 13.30$

$\delta = 0.35$

Alternatively, using the balanced equations in (d):

In the 1st titration, each mol YBCO corresponds 1.5 mol I_3^- and 3 mol $S_2O_3^{2-}$

In the 2nd titration, each mol YBCO corresponds (2 – δ) mol I_3^- and (4 – 2 δ) mol $S_2O_3^{2-}$

Thus,

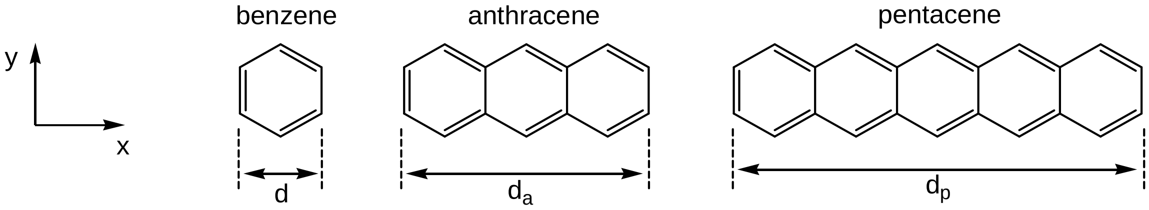
$$\frac{1.542\times10^{-4}\text{ mol}}{1.696\times10^{-4}\text{ mol}} = \frac{3}{4-2\,\delta} = \frac{1.5}{2-\delta}$$

$2 - \delta = 1.650$

$\delta = 0.35$

PROBLEM 8

Polycyclic aromatic hydrocarbons (PAHs) are atmospheric pollutants, components of organic light emitting diodes and components of the interstellar medium. This problem deals with so-called linear PAHs, i.e., those being just one benzene ring wide whereas the length is varied. Specific examples are benzene, anthracene and pentacene whose structures are shown below. Their physical and chemical properties depend on the extent to which the π electron cloud is delocalized over the molecule.



8.1 The distance across the benzene ring is d = 240 pm. Use this information to estimate the distances along the horizontal (x) axis for anthracene and pentacene, d_a and d_p, respectively.

Assume for simplicity that the π electrons of benzene can be modelled as being confined to a square. Within this model, the conjugated π electrons of PAHs may be considered as free particles in a two dimensional rectangular box in the x-y plane.

For electrons in a two-dimensional box along the x- and y-axes, the quantized energy states of the electrons are given by

$$E = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \frac{h^2}{8m_e}$$

In this equation, n_x and n_y are the quantum numbers for the energy state and are integers between 1 and ∞, h is Planck's constant, m_e is the mass of the electron and L_x and L_y are the dimensions of the box.

For this problem, treat the π electrons of the PAHs as particles in a two dimensional box. In this case, the quantum numbers n_x and n_y are independent.

8.2 Assume that the benzene unit has x and y dimensions that are each of length d. Derive a general formula for the quantized energies of linear PAHs as a function of quantum numbers n_x and n_y, the length d, the number of fused rings w, and the fundamental constants h and m_e.

The energy level diagram below for pentacene shows qualitatively the energies and quantum numbers n_x, n_y, for all levels occupied by π electrons and the lowest unoccupied energy level, with the electrons of opposite spins represented as the arrows pointing up or down. The levels are labelled with quantum numbers (n_x; n_y).

Pentacene:

__ (3; 2)
↑↓ (9; 1)
↑↓ (2; 2)
↑↓ (1; 2)
↑↓ (8; 1)
↑↓ (7; 1)
↑↓ (6; 1)
↑↓ (5; 1)
↑↓ (4; 1)
↑↓ (3; 1)
↑↓ (2; 1)
↑↓ (1; 1)

8.3 The energy level diagram for anthracene is shown below. Note that some energy levels may have the same energy. Draw the correct number of up and down arrows to represent the π electrons in this diagram. Also, the blanks in parentheses within this diagram are the quantum numbers n_x, n_y, which you need to determine. Fill these blanks with the pertinent values of n_x, n_y for each filled and the lowest unfilled energy level(s).

Anthracene:

__ (__; __)

__ (__; __)   __ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

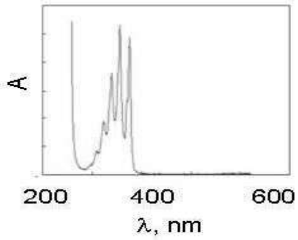
8.4 Use this model to create an energy level diagram for benzene and fill the pertinent energy levels with electrons. Include energy levels up to an including the lowest unoccupied energy level. Label each energy level in your diagrams with the corresponding n_x, n_y. Do not assume that the particle-in-a-square-box model used here gives the same energy levels as other models.

Often the reactivity of PAHs correlates inversely with the energy gap ΔE between the highest energy level occupied by π electrons and the lowest unoccupied energy level.

8.5 Calculate the energy gap ΔE (in joules) between the highest occupied and lowest unoccupied energy levels for benzene, anthracene and pentacene. Use your result from parts 8.3 and 8.4 for anthracene or benzene, respectively, or use (2, 2) for the highest occupied energy level and (3, 2) for the lowest unoccupied energy level for these two molecules (these may not be the true values).

8.6 Rank benzene (**B**), anthracene (**A**), and pentacene (**P**) in order of increasing reactivity by placing the corresponding letters from left to right in the box below.

8.7 The electronic absorption spectra (molar absorptivity vs. wavelength) for anthracene (**A**), benzene (**B**), and pentacene (**P**) are shown below. Based on a qualitative understanding of the particle in the box model, indicate which molecule corresponds to which spectrum by writing the appropriate letter in the box to its right.



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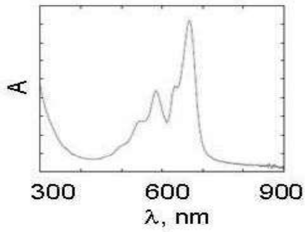

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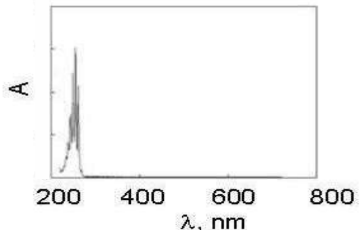
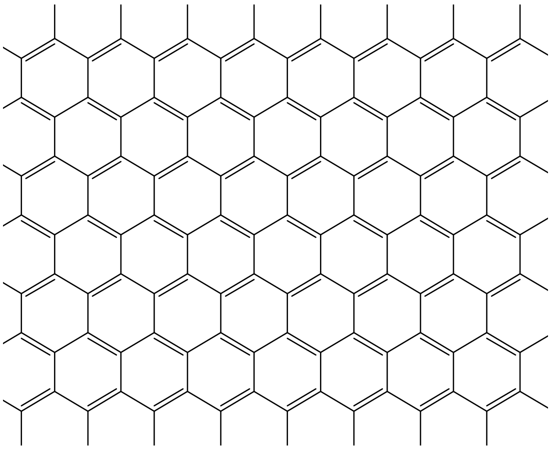


☐

Graphene is a sheet of carbon atoms arranged in a two-dimensional honeycomb pattern. It can be considered as an extreme case of a polyaromatic hydrocarbon with essentially infinite length in the two dimensions. The Nobel Prize for Physics was awarded in 2010 to Andrei Geim and Konstantin Novoselov for groundbreaking experiments on graphene.

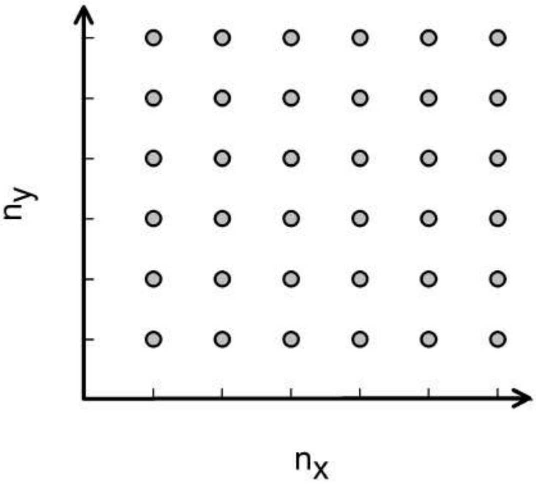
Consider a sheet of graphene with planar dimensions of $L_x = 25$ nm by $L_y = 25$ nm. A section of this sheet is shown below. The area of one hexagonal 6-carbon unit is ~52 400 pm^2.

8.8 Calculate the number of π electrons in a (25 nm $\times$ 25 nm) sheet of graphene. For this problem you can ignore edge electrons (i. e. those outside the full hexagons in the picture).



We can think about the π electrons in graphene as being free electrons in a 2-dimensional box. In systems containing large numbers of electrons, there is no single highest occupied energy level. Instead, there are many states of nearly the same energy above which the remaining are empty. These highest occupied states determine the so-called Fermi level. The Fermi level in graphene consists of multiple combinations of n_x and n_y quantum numbers.

8.9 Determine the energy of the Fermi level for the 25 nm $\times$ 25 nm square of graphene relative to the lowest filled level. The lowest filled level has a non-zero energy; however, it is negligible, and can be assumed to be zero. To solve this problem it might be helpful to represent the (n_x, n_y) quantum states as points on a 2-D grid (as shown below) and consider how the energy levels are filled with pairs of electrons. For the number of electrons use your result from part 8.8 or use a value of 1000 (this may not be the true value).



8.10 The conductivity of graphene-like materials correlates inversely with the energy gap between the lowest unoccupied and highest occupied energy levels. Use your analysis and understanding of π electrons in PAHs and graphene to predict whether the conductivity of a 25 nm × 25 nm square of graphene, at a given temperature, is less than, equal to or greater than the conductivity of a 1 m × 1 m square of graphene (which is the largest obtained to date). Circle the correct answer:

less	equal	greater

SOLUTION

8.1 For anthracene: $d_a = 3 \times 240$ pm = 720 pm

For pentacene: $d_p = 5 \times 240$ pm = 1200 pm

8.2

$$E = \left(\frac{n_y^{\ 2}}{d^2} + \frac{n_x^{\ 2}}{w^2 d^2} \right) \frac{h^2}{8\, m_e} = \left(n_y^{\ 2} + \frac{n_x^{\ 2}}{w^2} \right) \frac{h^2}{8\, m_e d^2}$$

8.3 Anthracene:

__ (__; __)

__ (_6_; _1_)   __ (_3_; _2_)

↑↓ (_2_; _2_)

↑↓ (_1_; _2_)

↑↓ (_5_; _1_)

↑↓ (_4_; _1_)

↑↓ (_3_; _1_)

↑↓ (_2_; _1_)

↑↓ (_1_; _1_)

8.4 Benzene:

__ (_2_; _2_)

↑↓ (_2_; _1_)   ↑↓ (_1_; _2_)

↑↓ (_1_; _1_)

8.5

ΔE for benzene: $\Delta E = E\left(2;2\right) - E\left(1;2\right) = 3\,\dfrac{h^2}{8\; m_e d^2} = 3.14 \cdot 10^{-18}\,\text{J}$

Alternate solution:

$$\Delta E = E\left(3;2\right) - E\left(2;2\right) = 5\,\frac{h^2}{8\; m_e d^2} = 5.23 \cdot 10^{-18}\,\text{J}$$

ΔE for anthracene: $\Delta E = E(6;1) - E(2;2) = \frac{5}{9}\left(\frac{h^2}{8\, m_e d^2}\right) = 5.81 \cdot 10^{-19}$ J

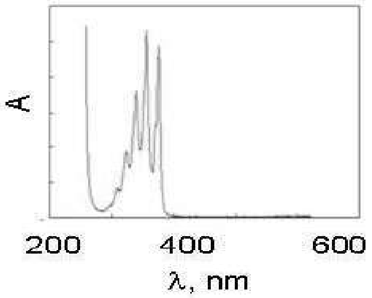
Alternate solution:

$$\Delta E = E(3;2) - E(2;2) = \frac{5}{9}\left(\frac{h^2}{8\, m_e d^2}\right) = 5.81 \cdot 10^{-19}\text{ J}$$

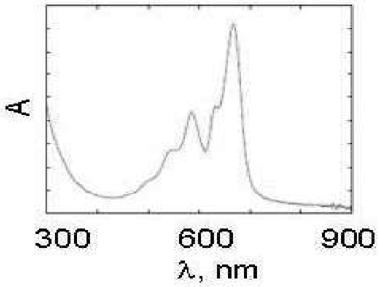
ΔE for pentacene: $\Delta E = E(3;2) - E(9;1) = \frac{3}{25}\left(\frac{h^2}{8\, m_e d^2}\right) = 1.26 \cdot 10^{-19}$ J

8.6 (least reactive) **B** < **A** < **P** (most reactive)

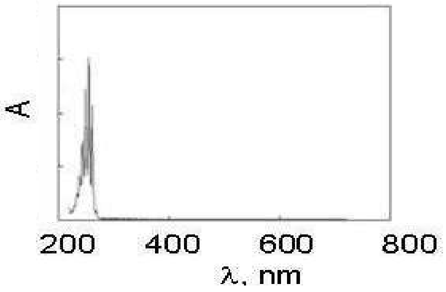
8.7



A



P



B

8.8 The number of hexagonal units in the graphene sheet:

$$N_{units} = \frac{\text{Area}_{\text{graphene}}}{\text{Area}_{\text{unit}}} = \frac{(25000\ \text{pm})^2}{52400\ \text{pm}^2} = 12\,000\ \text{units}$$

Since each carbon atom in a graphene sheet is shared by three hexagonal units, each unit of the area 52 400 pm^2 contains 6/3 = 2 carbon atoms contributing 2 π electrons total.

Therefore, 12 000 units contribute 12 000 pairs of π electrons.

<u>Correct answer:</u> 24 000 π electrons.

8.9 Two electrons fill each state, so the Fermi level has 12 000 filled levels. This corresponds to the number of (n_x, n_y) pairs that are occupied.

Since $L_x = L_y$ and the lowest energy level's energy is approximated as zero,

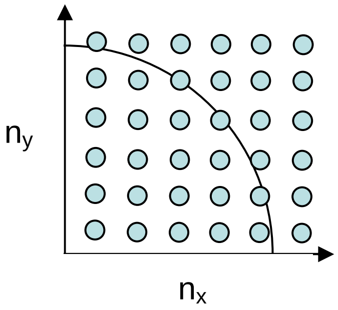
$$\Delta E = E_{\text{highest occupied}} = (n_x^2 + n_y^2)\frac{h^2}{8\, m_e L^2}$$

This is rearranged to the equation of a circle.

$$R^2 = (n_x^2 + n_y^2) = \frac{E\, 8 m_e L^2}{h^2} = \text{constant}$$

The area of the populated grid is

$$\text{Area}_{\text{grid}} = \frac{\pi R^2}{4}$$



The area of each quantum number pair is 1.

Therefore, the number of points is given as

$$N_{\text{points}} = \frac{\text{Area}_{\text{grid}}}{\text{Area}_{\text{pair}}} = \frac{\pi R^2}{4} = N_{\text{states}} = 12\,000\,.$$

Rearranging and solving for energy yields the Fermi energy.

$$N_{\text{states}} = \frac{\pi R^2}{4} = \frac{\pi 8 m_e L^2 E}{4 h^2} = 12\,000$$

$$E = \frac{4h^2 \times 12\,000}{\pi 8 m_e L^2} = 1.48 \cdot 10^{-18}\ \text{J}$$

Alternate solution:

$$N_{\text{states}} = \frac{\pi R^2}{4} = \frac{\pi 8 m_e L^2 E}{4 h^2} = 1000$$

$$E = \frac{4h^2 \times 1000}{\pi 8 m_e L^2} = 1.23 \cdot 10^{-19}\ \text{J}$$

8.10 Less is correct.

The energy gaps decrease with the graphene sample size increase and the conductivity increases as the energy gap decreases.

THE FORTY-FIFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
15–24 JULY 2013, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

Clathrate gun

The only gun that is able to kill all living people in one shot

On the floors of oceans and seas there are vast reserves of methane in the form of clathrate compounds called methane hydrates. These reserves can be mined and serve as a source of energy or raw materials for organic synthesis. However, scientists are seriously worried about the possibility of spontaneous decomposition of hydrates caused by the raising ocean temperature. It is believed that if a sufficient amount of methane is released into the atmosphere, the oceans will warm up quicker due to the greenhouse effect, further accelerating the decomposition of clathrates. Due to the explosion of the resulting methane-air mixture and/or changes in the composition of the atmosphere, all living creatures may become extinct. This apocalyptic scenario is called a clathrate gun.

Upon decomposition of 1.00 g of a methane hydrate with a fixed composition at 25 ℃ and atmospheric (101.3 kPa) pressure, 205 cm ^{3} of methane is released.

1.1 Determine *n* (not necessarily integer) in the formula of methane hydrate, $CH_4 \cdot n\ H_2O$.

Real methane hydrate has a non-stoichiometric composition close to $CH_4 \cdot 6\ H_2O$. At atmospheric pressure, methane hydrate decomposes at –81 ℃. However, under high pressures (e.g. on the ocean floor) it is stable at much higher temperatures.

Decomposition of methane hydrate produces gaseous methane and solid or liquid water depending on temperature.

1.2 Write down the equation of decomposition of 1 mol of $CH_4 \cdot 6\ H_2O$ producing solid water (ice) $H_2O(s)$.

The enthalpy of this process equals 17.47 kJ mol^{-1}. Assume that the enthalpies do not depend on temperature and pressure, the volume change upon decomposition of hydrate is equal to the volume of released methane, and methane is an ideal gas.

1.3 At what external pressure does decomposition of methane hydrate into methane and ice take place at –5 °C?

1.4 What is the minimum possible depth of pure liquid water at which methane hydrates can be stable?

To answer this question, you should first deduce at which minimum temperature methane hydrate can coexist with liquid water. Choose the correct answer.

☐ 272.9 K ☐ 273.15 K ☐ 273.4 K

Large methane hydrate stocks on the floor of Baikal lake, the largest freshwater lake in Russia and in the world, have been discovered in July 2009 by the crew of a deep-submergence vehicle «Mir-2». During the ascent from the depth of 1400 m methane hydrate samples started to decompose at the depth of 372 m.

1.5 Determine the temperature in Baikal lake at the depth of 372 m. The enthalpy of fusion of ice is equal to 6.01 kJ mol^{-1}.

Total amount of methane in hydrates on the Earth is no less than $5 \cdot 10^{11}$ tons.

1.6 By how many degrees would the Earth atmosphere heat up, if such amount of methane is burned by reacting with atmospheric oxygen?

The enthalpy of combustion of methane is –889 kJ mol^{-1}, the total heat capacity of the Earth's atmosphere is about $4 \cdot 10^{21}$ J K^{-1}.

SOLUTION

1.1 By the ideal gas law, the amount of methane ν is equal:

$$\nu = \frac{pV}{RT} = \frac{101300 \times 205 \cdot 10^{-6}}{8.314 \times 298.15} = 8.38 \cdot 10^{-3}\,\text{mol},$$

Then the amount of water in hydrate $\nu = \dfrac{1 - 8.38 \cdot 10^{-3} \times 16}{18} = 4.81 \cdot 10^{-2}$ mol.

The ratio of amounts of water and methane is $\dfrac{4.81 \cdot 10^{-2}}{8.38 \cdot 10^{-3}} \approx 5.75$, i. e. the composition of methane hydrate is $CH_4 \cdot 5.75\ H_2O$ or $x\ CH_4 \cdot 5.75x\ H_2O$, where x is any natural number.

1.2 $CH_4 \cdot 6\ H_2O = CH_4 + 6\ H_2O$

1.3 Decomposition of methane hydrate can be viewed as a phase transition that obeys the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}.$$

$$\Delta V = \frac{RT}{p} + \frac{6\,M(H_2O_{(s)})}{\rho(H_2O_{(s)})} - \frac{M(CH_4 \cdot 6\,H_2O)}{\rho(CH_4 \cdot 6\,H_2O)}.$$

The difference between two last terms is negligibly small in comparison with the first term. Thus, we can write the following equation:

$$\frac{1}{p} dp = \frac{\Delta H}{RT^2} dT$$

The dependence of the pressure on temperature is thus given by

$$p = p_0 \exp\left(\frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right).$$

Substituting T_0 = 192.15 K, T = 268.15 K, p_0 = 1 atm, we find that p = 22 atm or 2.2 MPa.

The correct answer: p = 2.2 MPa

1.4 The correct answer is: ☑ 272.9 K.

At the minimum possible depth, the sum of pressures of atmosphere and water column is equal to the dissociation pressure of methane hydrate. The temperature should be as low as possible, but it cannot be less than the melting point of water at the corresponding pressure. Thus, the temperature and pressure should correspond to the point of coexistence of water, ice, methane hydrate and gaseous methane. Since the melting point of water decreases with increasing pressure, the correct answer is 272.9 K.

Substituting T = 272.9 K into the equation from the previous question, we obtain p = 2.58 MPa. The height of the water column can be calculated using the formula $h = \dfrac{p - p_{atm}}{g\,\rho(H_2O)}$, where g = 9.8 m s^{-2}. From here $h \approx 250$ m.

1.5 From the Hess's law, the enthalpy of the process

$CH_4 \cdot 6\,H_2O = CH_4 + 6\,H_2O(l)$

is equal to 17.47 + (6 × 6.01) = 53.53 kJ mol^{-1}.

From the previous question we know that an equilibrium between methane, water and methane hydrate is established at T_o = 272.9 K and p_o = 2.58 MPa.

Thus, we can calculate the temperature of decomposition T at a pressure *of* $p = 9.8 \times 1000 \times 372 + 101000 = 3746600$ Pa using the equation:

$$\frac{1}{T} = \frac{1}{T_o} + \frac{R}{\Delta H} ln \frac{p_o}{p} \ .$$

The temperature obtained is T = 277.3 K or about 4 °C (which is in agreement with the measured temperature of Baikal water at such depth).

1.6 Upon burning of methane,

$$\frac{500 \times 10^9 \times 10^3}{0.016} \times 889 \cdot 10^3 = 2.78 \cdot 10^{22}\ \text{J}$$

of heat is released. The Earth atmosphere will heat up by

$$\frac{2.78 \cdot 10^{22}}{4 \cdot 10^{21}} \approx 7\,\text{K}$$

ΔT = 7 K

PROBLEM 2

Break down photosynthesis – the Hill reaction

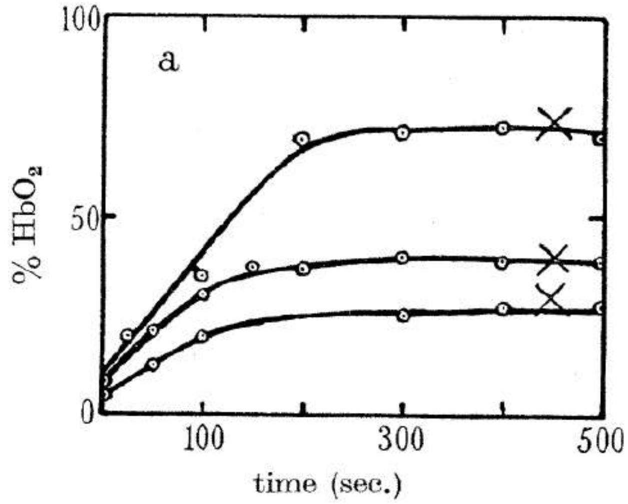
In the history of photosynthesis research, there were some breakthrough experiments which added much to our knowledge of this very complex process. One of such experiments was performed in 1930s by an English biochemist Robert Hill. In this problem, we consider some of his data together with the data of more recent experiments.

2.1 In plants, under illumination, carbon dioxide is reduced to carbohydrates (denote as $\{CH_2O\}$) and oxygen is produced. Write the overall equation of photosynthesis in plants.

Much of the photosynthesis takes place in chloroplasts – organelles found in plant cells and containing chlorophyll – the light-absorbing substance. Hill isolated chloroplasts from the cells by grinding the leaves in the sucrose solutions. The cell-free chloroplasts did not produce oxygen under illumination even in the presence of CO_2. However, upon adding potassium ferrioxalate $K_3[Fe(C_2O_4)_3]$ (with the excess of potassium oxalate) to the chloroplast suspension Hill observed oxygen liberation under illumination even without CO_2.

2.2 Hill's experiment enabled to determine the source of oxygen during photosynthesis. Write the formulas of the oxidant and the reducing agent in the photosynthesis inside the plant cells and in the cell-free chloroplasts (the Hill reaction).

Hill measured the amount of evolved oxygen using muscle haemoglobin (Hill denoted it Hb) which binds all molecular oxygen in a 1 : 1 ratio to form HbO_2. The initial concentration of Hb was $0.6 \cdot 10^{-4}$ mol dm^{-3}. Kinetic curves corresponding to different ferrioxalate concentrations are shown in the figure (the upper curve corresponds to $2.0 \cdot 10^{-4}$ mol dm^{-3}).



The fraction of bound haemoglobin HbO_2 (with respect to the initial amount of Hb) as a function of time. Crosses denote the end of the reaction

(Figure 2a from the original Hill's paper: *R. Hill. Oxygen produced by isolated chloroplasts. – Proc. R. Soc. B, 1939, v. 127, pp. 192-210.*)

2.3 **a.** From the figure, estimate the Fe / O_2 mole ratio at the end of the reaction. Do not take into account the iron from Hb.

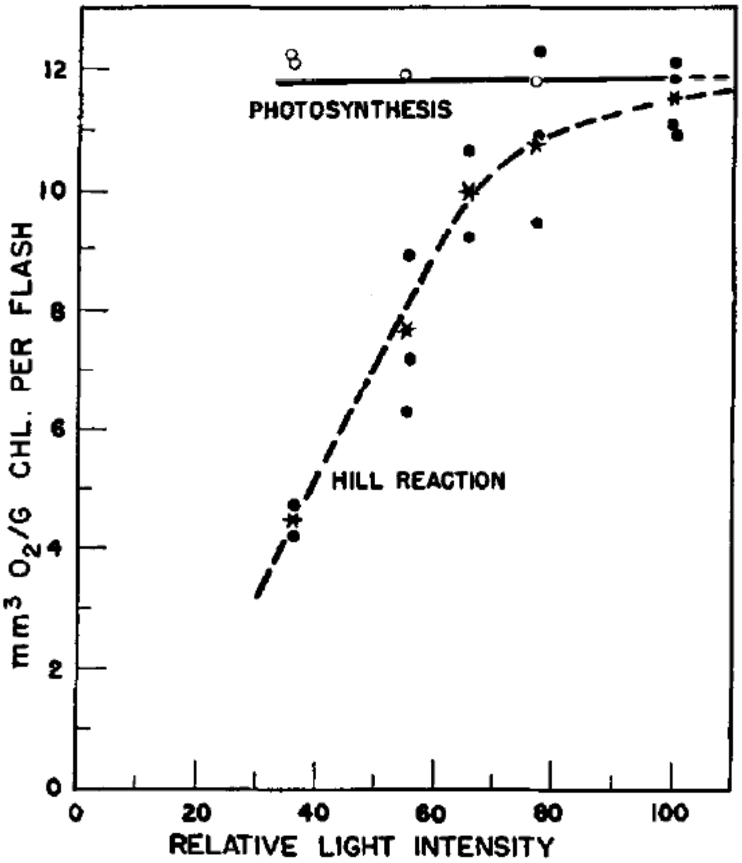
b. Write the equation of Hill reaction assuming that it proceeds with a high yield.

c. Using the table of standard electrode potentials, determine the Gibbs energy of the Hill reaction at T = 298 K, oxygen pressure 1 mm Hg, pH = 8 and standard concentrations of other species. Is this reaction spontaneous at such conditions?

Half-reaction	E°, V
$O_2 + 4 H^+ + 4 e \rightarrow 2 H_2O$	+1.23
$CO_2 + 4 H^+ + 8 e \rightarrow \{CH_2O\} + H_2O$	–0.01
$Fe^{3+} + e \rightarrow Fe^{2+}$	+0.77
$Fe^{3+} + 3 e \rightarrow Fe^0$	–0.04
$[Fe(C_2O_4)_3]^{3-} + e \rightarrow [Fe(C_2O_4)_3]^{4-}$	+0.05
$[Fe(C_2O_4)_3]^{4-} + 2 e \rightarrow Fe + 3 C_2O_4^{2-}$	–0.59

Now, the name "Hill reaction" denotes photochemical oxidation of water by any oxidant other than carbon dioxide which is sensitized by plant cells or isolated chloroplasts.

In another experiment (1952), quinone in an acid solution was used as an oxidant in the Hill reaction initiated by light flashes in the *Chlorella* algae. Experimental data are shown in the figure. The volume of oxygen (in mm^3, at temperature 10 ^oC and pressure 740 mm Hg) per one gram of chlorophyll per one flash was determined as a function of light intensity for natural photosynthesis and for isolated chloroplasts. It was found that the maximum yield of oxygen is the same for natural photosynthesis and the Hill reaction.



(Figure 1 from: *H. Ehrmantraut, E. Rabinovitch. Kinetics of Hill reaction. – Archives of Biochemistry and Biophysics, 1952, v. 38, pp. 67-84*)

2.4 **a.** Determine the reaction order of a photochemical Hill reaction with respect to light intensity at low and high intensity. For each case choose one of the following three values: 0, 1 or 2.

b. How many chlorophyll molecules participate in the formation of one oxygen molecule in the saturation limit of the Hill reaction? (The molecular mass of chlorophyll is about 900 Da).

The quantum requirement of the light redox reactions is defined as the average number of light photons (not necessarily integer) needed for the transfer of one electron from a reducing agent to an oxidant. The isolated chloroplasts were irradiated during 2 hours by a monochromatic light (wavelength 672 nm) with the energy input 0.503 mJ s^{-1}, and the total volume of oxygen formed was 47.6 mm^3 (under the same conditions as in question 4).

2.5 Calculate the quantum requirement for the Hill reaction.

2.6 Try to make conclusions from the above experiments (questions 2.2 – 2.5). Tick the relevant boxes.

	Yes	**No**
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.		
In chloroplasts, O_2 is produced from CO_2.		
Oxidation of water in chloroplasts requires light illumination.		
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		

SOLUTION

2.1 $H_2O + CO_2 = \{CH_2O\} + O_2$

2.2

Natural photosynthesis		Hill reaction	
Oxidant	Reducing agent	Oxidant	Reducing agent
CO_2	H_2O	$K_3[Fe(C_2O_4)_3]$	H_2O

2.3

a. The upper curve in the saturation limit gives ~ 75 % of HbO_2

$$\frac{n(\text{Fe})}{n(\text{O}_2)} = \frac{c(\text{Fe})}{c(\text{HbO}_2)} = \frac{2.0 \cdot 10^{-4}}{(0.75 \times 0.6 \cdot 10^{-4})} = \frac{4.4}{1}$$

b. Ratio ~ 4 : 1 shows that Fe(III) is reduced to Fe(II), which in the presence of excess oxalate exists as a complex:

$2\ H_2O + 4\ [Fe(C_2O_4)_3]^{3-} \rightarrow O_2 + 4\ [Fe(C_2O_4)_3]^{4-} + 4\ H^+$

c. Calculations:

$[Fe(C_2O_4)_3]^{3-} + e \rightarrow [Fe(C_2O_4)_3]^{4-}$ $\quad E_1° = 0.05\ V$

$O_2 + 4\ H^+ + 4\ e \rightarrow 2\ H_2O$ $\quad E_2° = 1.23\ V$

emf: $E° = E_1° - E_2° = -1.18\ V$

$$\Delta G = \Delta G^o + RT\ln(p_{O_2}[H^+]^4) =$$

$$= -4 \times 96\,500 \times (-1.18) + 8.314 \times 298 \times \ln\left(\frac{1}{750}(1 \cdot 10^{-8})^4\right) =$$

$$= 2.57 \cdot 10^5\ \text{J mol}^{-1} = 257\ \text{kJ mol}^{-1}$$

The reaction is highly endoergic and, hence, not spontaneous.
Light is necessary.

2.4 **a.** Reaction order:

– at low intensity: 1

– at high intensity: 0.

b. $n(\text{Chl})/n(\text{O}_2) = 1/900 / [(12 \cdot 10^{-6} \times (740/760) \times 101.3) / (8.314 \times 283)] =$

$= 2200$

2.5 Total energy absorbed: $E = 0.503 \cdot 10^{-3} \times 3600 \times 2 = 3.62$ J

Energy of one mole of photons:

$$E_\text{m} = \frac{h\,c\,N_A}{\lambda} =$$

$$= \frac{6.63 \cdot 10^{-34} \times 3.00 \cdot 10^{8} \times 6.02 \cdot 10^{23}}{672 \cdot 10^{-9}} = 1.78 \cdot 10^{5}\ \text{J mol}^{-1}$$

$n(\text{phot}) = E / E_\text{m} = 2.03 \cdot 10^{-5}$ mol

$$n(\text{O}_2) = \frac{pV}{RT} = \frac{\frac{740}{760} \times 101.3 \times 47.6 \cdot 10^{-6}}{8.314 \times 283} = 2.00 \cdot 10^{-6}\ \text{mol.}$$

Formation of one mole of O_2 requires the transfer of 4 electrons:

$n(e) = 8.00 \cdot 10^{-6}$ mol

Quantum requirement: $\dfrac{n(\text{phot})}{n(\text{e})} = 2.5$

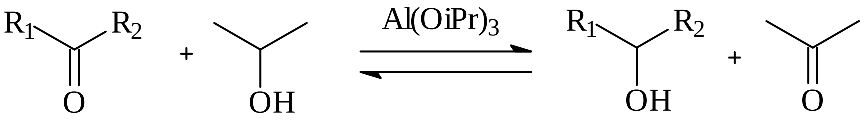
2.6

	Yes	No
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.	✓	
In chloroplasts, O_2 is produced from CO_2.		✓
Oxidation of water in chloroplasts requires light illumination.	✓	
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		✓
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		✓

PROBLEM 3

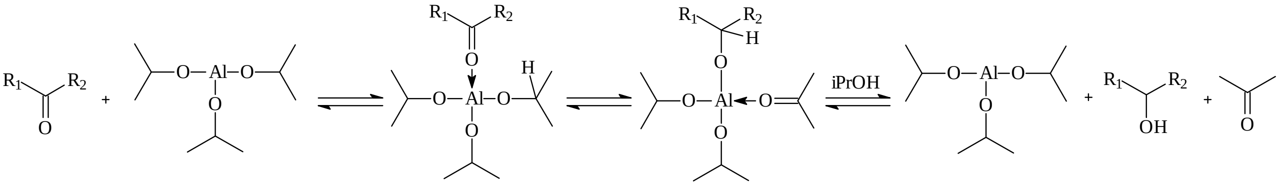
Meerwein-Schmidt-Ponndorf-Verley reaction

Meerwein-Schmidt-Ponndorf-Verley (MSPV) reaction is a useful tool for reduction of carbonyl compounds to alcohols. The reaction is the reduction of carbonyl compounds by low molecular weight alcohols in the presence of alkoxides of aluminium or other metals:



(1)

The mechanism of the reaction includes coordination of carbonyl compound by aluminium alkoxide, hydride transfer in the inner sphere of the complex and subsequent transalkoxylation. It can be schematically represented as follows (transalkoxylation is shown as a one-step process for brevity):



(2)

The reaction is reversible and shifting the equilibrium to the desired product requires some excess of the reductant. In some cases (e. g. in the case of reduction of aromatic aldehydes and ketones) the equilibrium constant is so large that the reverse reaction can be neglected.

The table below contains standard entropies and standard enthalpies of formation of liquid substances at 298 K. The boiling points of the substances at 1 bar are also given.

Substance	$\Delta_f H^o_{298}$, kJ mol^{-1}	S^o_{298}, J mol^{-1} K^{-1}	t_{vap}, °C
Acetone	–248.4	200.4	56
Isopropanol	–318.1	180.6	82
Cyclohexanone	–271.2	229.0	156
Cyclohexanol	–348.2	203.4	161

3.1 a Calculate the minimum isopropanol to cyclohexanone mass ratio which is required to reach a 99 % yield of reaction at 298 K. Assume that:

i) the reaction mixture eventually gets at equilibrium,

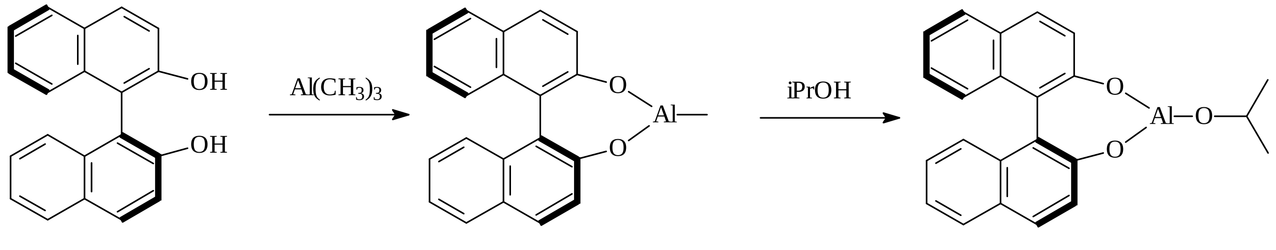
ii) no products are initially present.

3.1 b Choose the appropriate way(s) to increase the cyclohexanol yield. Tick the relevant boxes.

Increase the temperature up to 50 °C using a reflux	
Increase the temperature up to 60 °C, evaporating (distilling) the acetone	
Add some ethanol to the reaction mixture	
Add some ethanal to the reaction mixture	

3.2 Often the rate-limiting step in the MSPV reaction is the hydride transfer or the alcoholysis of the alkoxide after hydride transfer. For these two cases, using the above mechanism (2), derive an expression for the rate of reaction as a function of current concentrations of a carbonyl compound, isopropanol and a catalyst. In both cases determine the rate orders in the reactants and the catalyst. Assume that all reaction steps before the limiting step are fast and reversible. Use equilibrium approximation, if necessary. For brevity use the following notation: **A** for carbonyl compound, **B** for isopropanol, **C** for catalyst. Denote intermediates as you wish.

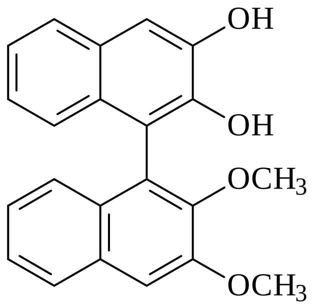
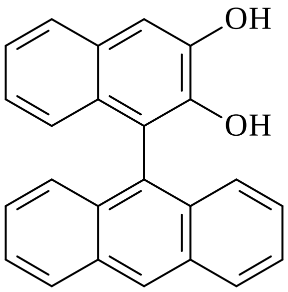
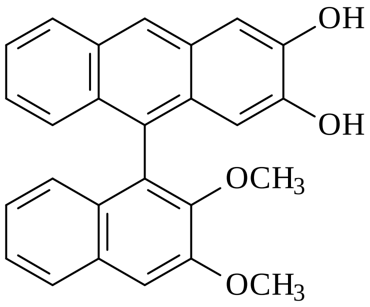
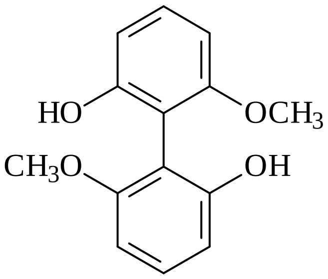
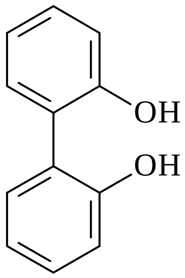
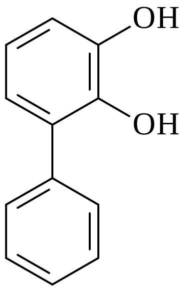
MSPV reaction can be used to obtain chiral alcohols, if the chiral catalyst is employed. For instance, Campbell et al. used the catalyst based on the chiral 2,2'-dihydroxy-1,1'-binaphtyl (BINOL), which is synthesized *in situ* from binaphtol and trimethylaluminium:



(BINOL)Al(OiPr) (3)

The chirality of BINOL is due to the sterically hindered rotation around the C-C bond. Though perfectly stable at room temperature, BINOL may racemize when heated.

3.3 Which of the phenols below can form stable (at room temperature) enantiomers so that they can be used in the same fashion to produce a chiral catalyst? Tick the relevant boxes.

Substance	Can be used	Substance	Can be used
			
			
			

Enantiomeric excess, *ee*, is used to characterize the enantiomeric purity of the substance. This quantity equals to the ratio of the difference of concentrations of enantiomers *R* and *S* to their sum:

$$ee = \frac{[\mathrm{R}] - [\mathrm{S}]}{[\mathrm{R}] + [\mathrm{S}]}$$

Enantiomeric excess of the pure *R* isomer is unity, *ee* of the racemic mixture is zero.

3.4 When using the enantiomerically pure (BINOL)Al(OiPr) as a catalyst for reduction of α-bromoacetophenone, the *ee* of the product equals 81 %. What is the *ee* of the product if the catalyst *ee* equals 50 %? Provide your calculation with an illustration or derivation of the final formula.

SOLUTION

3.1 a

The reaction enthalpy is:

$\Delta_r H^o_{298} = \Delta_f H^o_{298}(C_3H_6O) + \Delta_f H^o_{298}(C_6H_{12}O) - \Delta_f H^o_{298}(C_3H_8O) - \Delta_f H^o_{298}(C_6H_{10}O) =$

$= (-248.4) + (-348.2) - (-318.1) - (-271.2) = -\ 7.3$ kJ mol^{-1}

The reaction entropy is:

$\Delta_r S^o_{298} = S^o_{298}(C_3H_6O) + S^o_{298}(C_6H_{12}O) - S^o_{298}(C_3H_8O) - S^o_{298}(C_6H_{10}O) =$

$= 200.4 + 203.4 - 180.6 - 229.0 = -5.8$ J mol^{-1} K^{-1}

The reaction Gibbs energy is:

$\Delta_r G^o_{298} = \Delta_r H^o_{298} - T\,\Delta_r S^o_{298} = -5.6$ kJ mol^{-1}

The equilibrium constant equals

$K = \exp(-\Delta_r G^o_{298}/RT) = 9.6$

The expression for equilibrium constant is as follows:

$$K = \frac{x(C_3H_6O)\ x(C_6H_{12}O)}{x(C_3H_8O)\ x(C_6H_{10}O)} = \frac{\nu(C_3H_6O)\ \nu(C_6H_{12}O)}{\nu(C_3H_8O)\ \nu(C_6H_{10}O)},$$

where x is the molar fraction of a substance in the equilibrium mixture, ν is an amount of a substance in the mixture. Denote the initial amount of cyclohexanone as y. The yield of the reaction is 99 %, i. e. 99 % of cyclohexanone must react. Hence, in equilibrium the amounts of $C_6H_{10}O$ and $C_6H_{12}O$ are $0.01y$ and $0.99y$, respectively. Denote the initial amount of isopropanol z. Due to the reaction stoichiometry the amounts of C_3H_6O and C_3H_8O in equilibrium are $0.99y$ and $(z - 0.99y)$, respectively. Substituting these amounts in the expression for equilibrium constant one gets:

$$K = \frac{0.99y \times 0.99y}{0.01y \times (z - 0.99y)} = \frac{98.01}{\left(\frac{z}{y} - 0.99\right)} = 9.6$$

The solution is:

$$\frac{z}{y} = 11.2$$

Hence, the mole ratio $\nu(C_3H_8O) : \nu(C_6H_{10}O)$ is 11.2. The mass ratio can be calculated as follows:

$$\frac{m(C_3H_8O)}{m(C_6H_{10}O)} = \frac{\nu(C_3H_8O)\ M(C_3H_8O)}{\nu(C_6H_{10}O)\ M(C_6H_{10}O)} = \frac{11.2 \times 60}{98} = 6.9$$

3.1 b

Increase the temperature up to 50 °C using a reflux	
Increase the temperature up to 60 °C, evaporating (distilling) the acetone	✓
Add some ethanol to the reaction mixture	✓
Add some ethanal to the reaction mixture	

3.2 *i) Rate-limiting step is the hydride transfer*

Kinetic scheme:

$A + C \rightleftarrows A{\cdot}C$ fast, K

$A{\cdot}C \rightarrow A'{\cdot}C'$ rate-determining, k

Expression for equilibrium constant:

$$K = \frac{[A \cdot C]}{[A][C]}$$

The rate of the rate determining step is:

$$r = k[A \cdot C]$$

Final expression:

$$r = k[A \cdot C] = kK[A][C]$$

Answer:

Order in carbonyl compound: 1

Order in isopropanol: 0

Order in the catalyst: 1

ii) Rate-limiting step is the transalkoxylation of the alcoholate by isopropanol

Kinetic scheme:

$A + C \rightleftarrows A{\cdot}C$ fast, K_1

$A{\cdot}C \rightleftarrows A'{\cdot}C'$ fast, K_2

$A'{\cdot}C' + B \rightarrow P$ rate-determining, k

Expression for equilibrium constants:

$$K_1 = \frac{[A \cdot C]}{[A][C]}$$

$$K_2 = \frac{[A' \cdot C']}{[A \cdot C]}$$

The rate of reaction is:

$$r = k[A' \cdot C'][B]$$

Final expression:

$$r = k[A' \cdot C'][B] = k K_1 K_2 [A][B][C]$$

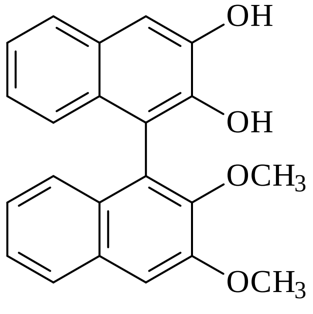
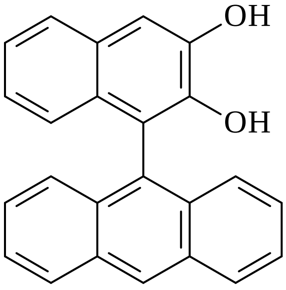
Answer:

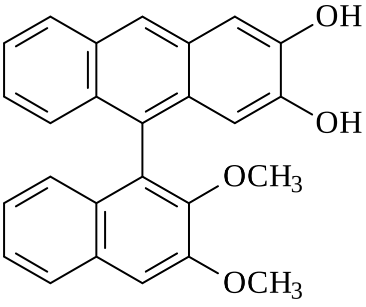
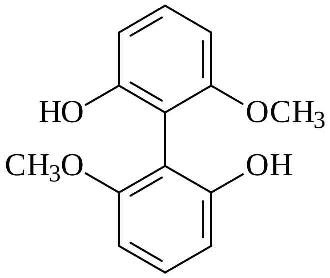
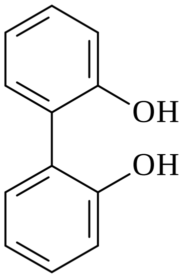
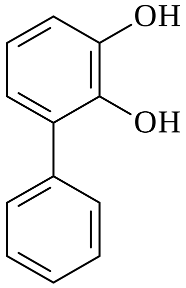
Order in carbonyl compound: 1

Order in isopropanol: 1

Order in the catalyst: 1

3.3

Substance	Can be used	Substance	Can be used
	✓		

	✓		✓
			

3.4

Solution 1

The total kinetic scheme is:

$$\begin{tikzcd}
(\mathit{S})\text{ catalyst} \arrow[r, "k"] \arrow[dr, "k'" near start] & (\mathit{S})\text{ product} \\
(\mathit{R})\text{ catalyst} \arrow[r, "k"'] \arrow[ur, "k'"' near end] & (\mathit{R})\text{ product}
\end{tikzcd}$$

According to the scheme, the *R* : *S* ratio is

$$\frac{[\text{(R)product}]}{[\text{(S)product}]} = \frac{k[\text{(R)catalyst}] + k'[\text{(S)catalyst}]}{k[\text{(S)catalyst}] + k'[\text{(R)catalyst}]}$$

After inserting this expression into *ee* definition one gets:

$$ee_{\text{product}} = \frac{[\text{(R)product}] - [\text{(S)product}]}{[\text{(R)product}] + [\text{(S)product}]} = \frac{\dfrac{[\text{(R)product}]}{[\text{(S)product}]} - 1}{\dfrac{[\text{(R)product}]}{[\text{(S)product}]} + 1} =$$

$$= \frac{\left(k[\text{(R)catalyst}] + k'[\text{(S)catalyst}]\right) - \left(k[\text{(S)catalyst}] + k'[\text{(R)catalyst}]\right)}{\left(k[\text{(R)catalyst}] + k'[\text{(S)catalyst}]\right) + \left(k[\text{(S)catalyst}] + k'[\text{(R)catalyst}]\right)} =$$

$$= \frac{[\text{(R)catalyst}] - [\text{(S)catalyst}]}{[\text{(R)catalyst}] + [\text{(S)catalyst}]} \times \frac{k - k'}{k + k'} = ee_{\text{catalyst}} \frac{k - k'}{k + k'}$$

That is, the *ee* of the product is proportional to the *ee* of the catalyst:

$$ee_{\text{product}} = ee_{\text{catalyst}} \frac{k - k'}{k + k'}$$

Applying numbers one gets:

$$ee_{\text{product}} = 0.50 \times 0.81 = 0.41$$

Solution 2

$$50\,\%\,ee \equiv \begin{cases} 50\,\%\,\text{rac.} \\ 50\,\%\,\text{R} \end{cases}$$

$$\text{R cat.} \rightarrow 90.5\,\%\,\text{R} + 9.5\,\%\,\text{S}$$

$$\text{rac. cat.} \rightarrow 50\,\%\,\text{R} + 50\,\%\,\text{S}$$

$$\%\text{ of R prod.} = 0.5 \times 0.905 + 0.5 \times 0.5 = 0.7025$$

$$\%\text{ of S prod.} = 0.5 \times 0.095 + 0.5 \times 0.5 = 0.2975$$

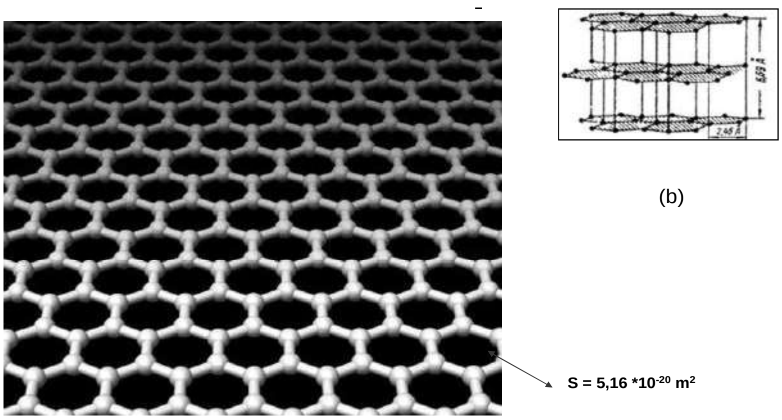
$$ee\text{ prod.} = 0.7025 - 0.2975 = 0.405$$

Answer: 41 %

PROBLEM 5

Simple estimates of graphene properties

Graphene is a two-dimensional, one atom thick carbon material (Fig. 1 a). Many layers of graphene stack together to form graphite (Fig. 1 b).



(b)

(a)

Fig. 1. (a) The structure of graphene. Spheres are carbon atoms. They are arranged in hexagons. The area of one carbon hexagon is $5.16 \cdot 10^{-20}$ m^2.
(b) Crystal lattice of graphite. Three graphene layers are shown.

Such atomic structure was long considered to be unstable. However, in 2004 Andrey Geim and Konstantin Novoselov have reported production of the first samples of this unusual material. This groundbreaking invention was awarded by Nobel prize in 2010.

Experimental studies of graphene are still restricted. Production of massive portions of the new substance still is a challenging synthetic problem. Many properties of graphene were estimated. Usually, there is not enough information for rigorous calculations, so we have to make assumptions and neglect unimportant factors. In this problem, you will estimate the adsorption properties of graphene.

5.1 Estimate the specific surface of graphene open for adsorption in units m^2 g^{-1}. Consider that graphene plane is separated from any other solid or liquid substance.

The single layer of nitrogen molecules adsorbed on the outer surface of graphite is shown in Fig. 2. Assume that the same arrangement of nitrogen molecules is formed on a graphene surface.

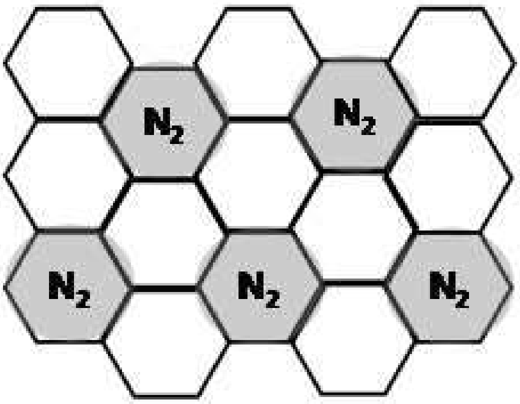


Fig. 2. Nitrogen molecules N_2 (grey circles) on the outer surface of graphite

5.2 How many grams of nitrogen can be adsorbed on 1 gram of graphene assuming that the graphene layer is placed onto the surface of a solid support? Estimate the volume occupied by these nitrogen molecules after the complete desorption from 1 g of graphene (pressure 1 bar, temperature 298 K).

Let us consider adsorption as a common chemical equilibrium

$$A_{gas} \rightleftarrows A_{ads}\,, \qquad (1)$$

(A_{gas} are molecules A in the gaseous state, A_{ads} are the same molecules on the surface) with the equilibrium constant K:

$$K = \frac{n_{A_{ads}}(\text{mol m}^{-2})}{p_{A_{gas}}(\text{bar})}$$

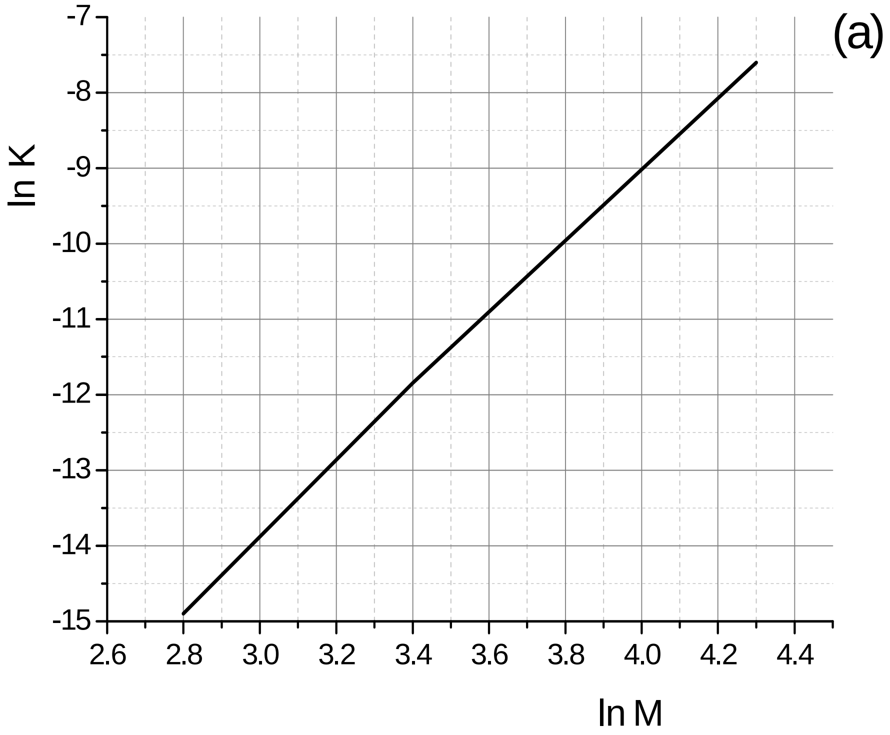
(Such an assumption holds if a small number of molecules is adsorbed on the surface.)

Adsorption properties of graphene can be estimated from the data for adsorption on a regular three-dimensional graphite. The enthalpy of adsorption (ΔH^o of reaction (1)) of any molecule A on graphene is on average by 10 % less negative compared to that on graphite. On graphite, the adsorbed molecule is bound more strongly due to the interaction with the lower graphene layers in the lattice (Fig. 1b) and hence the enthalpy of adsorption is more negative. The standard entropies of adsorption on graphene and graphite are assumed to be the same.

5.3 How many moles, *n*, of CCl_4 are adsorbed on 1 g of graphene at $p(CCl_4) = 10^{-4}$ bar if $2.0 \cdot 10^{-7}$ mol of CCl_4 are adsorbed on 1 m^2 of graphite at $p(CCl_4) = 6.6 \cdot 10^{-5}$ bar? Assume that graphene is placed onto the surface of a solid support and the interaction of CCl_4 with the support does not change the enthalpy of adsorption of CCl_4 on graphene.The temperature in both cases is 293 K. ΔH^0 of adsorption of CCl_4 on graphite is –35.1 kJ/mol.

The graphene films are expected to be sensitive gas detectors. If 10^9 particles of a gas are adsorbed on 1 cm^2 of a graphene surface this is enough to measure an electrical resistivity change of the graphene layer and to detect the presence of a gas in the environment.

5.4 Determine the minimal content of ethane, C_2H_6, in the air (in mol. %) at atmospheric pressure (T = 293 K) at which a graphene sensor will detect this gas. The known data for the adsorption of alkanes on graphite are shown in Fig 3. Assume that air doesn't affect the adsorption properties of ethane.



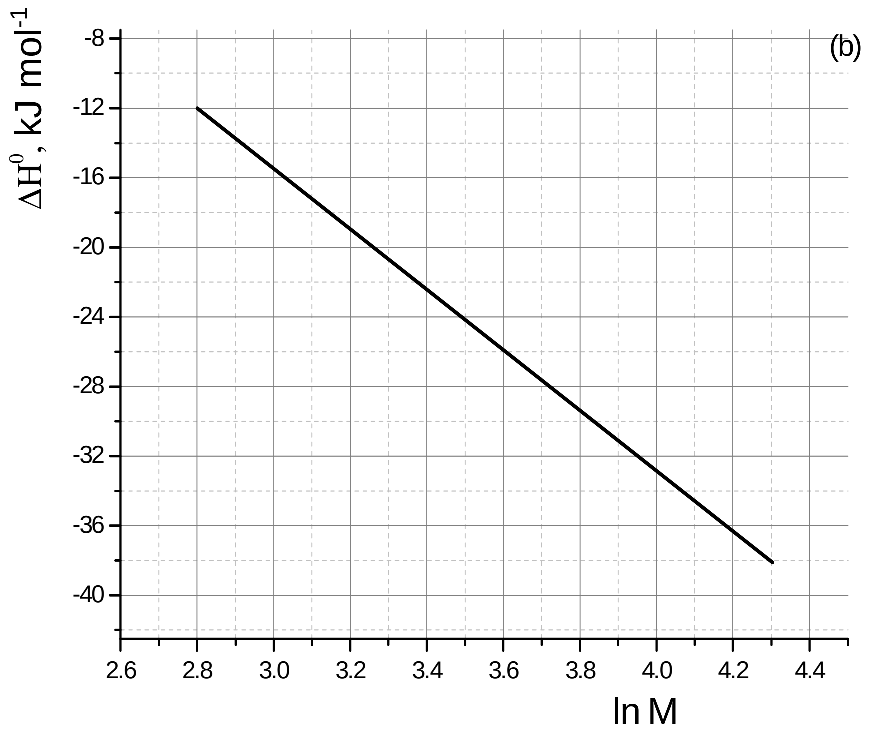


Fig. 3
Thermodynamic properties for adsorption of alkanes on a graphite surface.
(a) ln K [mol m^{-2} bar^{-1}] as a function of ln M (M - molar mass of alkane in g mol^{-1});
(b) ΔH^o of adsorption as a function of ln M.
Linear dependences are assumed in both cases

SOLUTION

5.1 The area of a hexagon is $S = 5.16 \cdot 10^{-20}$ m^2.

Calculations:

The number of hexagons per gram of carbon, *n*, is

$$n = N_A \times \frac{3}{6} \times \frac{1}{12} = 6.022 \cdot 10^{23} \times 0.5 \times \frac{1}{12} = 2.51 \cdot 10^{22}$$

The area per gram is

$$S_{\text{total}} = S \times n \times 2 = 5.16 \cdot 10^{-20} \times 2.51 \cdot 10^{22} \times 2 = 2590 \text{ m}^2 \text{ g}^{-1}$$

In the case of two-dimensional material both sides of the layer are open for adsorption and have to be taken into consideration. The total area of hexagons should be multiplied by two!

5.2 Graphene is on the solid support and only one side of the plane works. One molecule of nitrogen falls on six atoms of carbon (three hexagons) (see Fig. 2).

Mass of nitrogen adsorbed per gram of graphene:

$$\frac{m_{N_2}}{m_C} = \frac{1 \times 28}{6 \times 12} = 0.39; \quad m_{N_2} = 0.39 \text{ g}$$

The volume of nitrogen isw

$$V_{N_2} = \frac{\frac{m}{M} RT}{p} = \frac{\frac{0.39}{28} \times 8.314 \times 298}{100} = 0.34 \text{ dm}^3.$$

5.3 The equilibrium constant for the adsorption on graphite surface is

$$K(\text{graphite}) = \frac{n(\text{CCl}_4 \text{ on graphite})}{p(\text{CCl}_4)} = \frac{2.0 \cdot 10^{-7}}{6.6 \cdot 10^{-5}} = 3.0 \cdot 10^{-3} \text{ mol m}^{-2} \text{ bar}^{-1}$$

The equilibrium constant need to be re-calculated for the graphene surface. There is a 10 % difference in enthalpies of adsorption on graphene and on graphite, respectively, while the entropies are the same. Thus:

$$\frac{K(\text{graphene})}{K(\text{graphite})} = e^{\frac{-(\Delta H_{\text{graphene}} - \Delta H_{\text{graphite}})}{RT}} = e^{\frac{-3510}{8.314 \times 293}} = 0.24$$

$$K(\text{graphene}) = 0.24\, K(\text{graphite}) = 7.2 \cdot 10^{-4} \text{ mol m}^{-2} \text{ bar}^{-1}$$

The adsorption of CCl_4 on graphene is calculated based on the equilibrium constant for graphene surface and the area of graphene surface in $m^2\ g^{-1}$. One side of the graphene layer works in this case,

$$S_{\text{total}} = 2590 / 2 = 1295\ \text{m}^2\ \text{g}^{-1}$$

$$n\,[\text{mol g}^{-1}] = K(\text{graphene})\,[\text{mol m}^{-2}\,\text{bar}^{-1}] \times p(\text{CCl}_4)\,[\text{bar}] \times S(\text{graphene})\,[\text{m}^2\,\text{g}^{-1}] =$$
$$= (7.2 \cdot 10^{-4}) \times 1 \cdot 10^{-4} \times 1295 = 9.3 \cdot 10^{-5}\ \text{mol g}^{-1}$$

The area of the graphene surface (the number!) determined in question 5.1 is used here.

5.4 The lower limit of detectable concentration of a substance on the graphene surface is

$$n\,[\text{mol m}^{-2}] = \frac{\dfrac{1 \cdot 10^9}{6.02 \cdot 10^{23}}}{1 \cdot 10^{-4}} = 1.7 \cdot 10^{-11}$$

The equilibrium constant and the enthalpy of adsorption of ethane on graphite are given in Fig. 3:

$M = 30$; $\ln M = 3.4$; $\ln K = -11.8$; $\Delta H^o = -22.5$ kJ mol^{-1}

$$K_{C_2H_6} = 7.5 \cdot 10^{-6}\ \text{mol m}^{-2}\,\text{bar}^{-1}$$

This equilibrium constant needs to be re-calculated to the graphene surface (as in question 5.2).

$$K_{C_2H_6}(\text{graphene}) = K_{C_2H_6}(\text{graphite}) \times e^{-2250/(8.314\times293)} =$$
$$= 7.5 \cdot 10^{-6} \times 0.4 = 3.0 \cdot 10^{-6}\ \text{mol m}^{-2}\ \text{bar}^{-1}$$

The partial pressure of ethane is

$$p(C_2H_6) = \frac{n(C_2H_6\ \text{on graphene})}{K_{C_2H_6}(\text{graphene})} = \frac{1.7 \cdot 10^{-11}}{3.0 \cdot 10^{-6}} = 5.7 \cdot 10^{-6}\ \text{bar}$$

Content of C_2H_6: $\dfrac{5.7 \cdot 10^{-6}}{1.013} \times 100\,\% = 5.6 \cdot 10^{-4}\,\%$

Student name **Student code**

Theoretical **Problem 1** **5.0 %** of the total	**Code:**		Question	1	2	3	4	5	Total
	Examiner		Mark	3	7	6	4	7	**27**
			Grade						

Problem 1. Particles in a box: polyenes

In quantum mechanics, the movement of π electrons along a neutral chain of conjugated carbon atoms may be modeled using the 'particle in a box' method. The energy of the π electrons is given by the following equation:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where n is the quantum number (n = 1, 2, 3, …), h is Planck's constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2)\times 1.40$ Å (k being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength λ may promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength λ, to the number of double bonds k and constant B is as follows:

$$\lambda\ (\text{nm}) = B \times \frac{(k+2)^2}{(2k+1)} \qquad \text{Equation 1}$$

1. Using this semi-empirical formula with $B = 65.01$ nm **calculate** the value of the wavelength λ (nm) for octatetraene ($CH_2 = CH - CH = CH - CH = CH - CH = CH_2$).

Student name **Student code**

2. <u>Derive</u> Equation 1 (an expression for the wavelength λ (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of k and the fundamental constants, and hence **<u>calculate</u>** theoretical value of the constant $B_{\text{calc.}}$.

3. We wish to synthesize a linear polyene for which the excitation of a π electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part 2, **<u>determine</u>** the <u>number of conjugated double bonds</u> (k) in this polyene and **<u>give</u>** its structure. [*If you did not solve Part 2, use the semi-empirical Equation 1 with B = 65.01 nm to complete Part 3.*]

Student name **Student code**

4. For the polyene molecule found in Part 3, **calculate** the difference in energy between the HOMO and the LUMO, ΔE, (kJ·mol^{-1}).

In case Part 3 was not solved, take k = 5 to solve this problem.

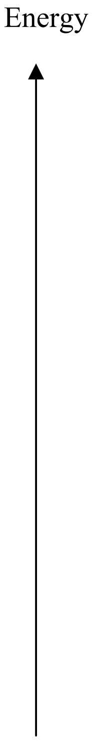
5. The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions L_x, L_y, and L_z, yielding the following expression for the allowed energy levels:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

The three quantum numbers n_x, n_y, and n_z must be integer values and are independent of each other.

5.1 Give the expressions for the three **different** lowest energies, assuming that the box is cubic with a length of L.

5.2 Levels with the same energy are said to be degenerate. **Draw** a sketch showing all the energy levels, including any degenerate levels, that correspond to quantum numbers having values of 1 or 2 for a cubic box.



Theoretical **Problem 1** **5.0 %** of the total	**Code:**		Question	1	2	3	4	5	Total
	Examiner		Mark	3	7	6	4	7	**27**
			Grade						

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$$E_n = \frac{n^2h^2}{8mL^2}$$

where n is the quantum number (n = 1, 2, 3, …), h is Planck's constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2)\times 1.40$ Å (k being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength λ may promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength λ, to the number of double bonds k and constant B is as follows:

$$\lambda\ (\text{nm}) = B \times \frac{(k+2)^2}{(2k+1)} \qquad \text{Equation 1}$$

1. Using this semi-empirical formula with $B = 65.01$ nm **calculate** the value of the wavelength λ (nm) for octatetraene ($CH_2 = CH - CH = CH - CH = CH - CH = CH_2$).

1. From the given semi-empirical formula, the wavelength λ (nm) is calculated as follows: $\lambda\ (nm) = 65.01\times\frac{(k+2)^2}{(2k+1)}$ For octatetraene molecule, with k = 4; **λ = 260.0 nm**	3 points

2. <u>Derive</u> Equation 1 (an expression for the wavelength λ (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of k and the fundamental constants, and hence **<u>calculate</u>** theoretical value of the constant $B_{\text{calc.}}$.

2. The formula: $E = \frac{n^2h^2}{8mL^2}$ (1) ΔE is calculated as: $\Delta E = E_{LUMO} - E_{HOMO} = h\nu = \frac{hc}{\lambda}$ (2) In which, λ and ν are wavelength and frequency for the corresponding photon respectively, k is the quantum number for the HOMO, which is equal to the number of double bonds. So, we have: $\Delta E = \frac{h^2}{8mL^2}[(k+1)^2 - k^2] = \frac{hc}{\lambda} = \frac{h^2}{8mL^2}[2k+1]$ (3) Replace $L = (k+2) \times 1.40$ Å into (3): $\frac{hc}{\lambda} = \frac{h^2(2k+1)}{8m[(k+2)\times 1.40\times 10^{-10}]^2} \Rightarrow \lambda = \frac{8mc[(k+2)\times 1.40\times 10^{-10}]^2}{h(2k+1)}$ $\Rightarrow \lambda = \frac{8\times 9.1094\times 10^{-31}\times 2.9979\times 10^{8}\times (1.40\times 10^{-10})^2}{6.6261\times 10^{-34}}\times\frac{(k+2)^2}{(2k+1)}$ $\Rightarrow \lambda\,(m) = 6.462\times 10^{-8}\times\frac{(k+2)^2}{(2k+1)}$; $\Rightarrow \lambda\,(nm) = 64.62\times\frac{(k+2)^2}{(2k+1)}$ (4) $B_{\text{calc.}}$ = 64.6 nm	5 points 2 points

3. We wish to synthesize a linear polyene for which the excitation of a π electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part 2, **<u>determine</u>** the <u>number of conjugated double bonds</u> (k) in this polyene and **<u>give</u>** its structure. [*If you did not solve Part 2, use the semi-empirical Equation 1 with B = 65.01 nm to complete Part 3.*]

3. With λ = 600 nm, we have $\frac{600}{64.62} = \frac{(k+2)^2}{(2k+1)} = 9.285 \Rightarrow k^2 - 14.57k - 5.285 = 0$ Solve the equation to obtain: $\mathbf{k_1 = 14.92}$, k_2 = - 0.355 (Eliminated).	4 points

Thus, $k = 15$. So, the formula of polyene is: **$CH_2 = CH – (CH = CH)_{13} – CH = CH_2$**	2 points

4. For the polyene molecule found in Part 3, **calculate** the difference in energy between the HOMO and the LUMO, ΔE, ($kJ \cdot mol^{-1}$).

In case Part 3 was not solved, take $k = 5$ to solve this problem.

$\Delta E = E_{LUMO} - E_{HOMO} = \frac{h^2}{8mL^2}\left[(k+1)^2 - k^2\right]$ $\Delta E = \frac{(6.6261\times10^{-34})^2\times10^{-3}\times6.022\times10^{23}}{8\times9.1094\times10^{-31}\times(1.40\times10^{-10})^2}\times\left[\frac{2k+1}{(k+2)^2}\right]$ ($kJ \cdot mol^{-1}$) $\Delta E = 1851\times\left[\frac{2k+1}{(k+2)^2}\right]$ (kJ/mol) For polyene **with** $k = 15$; $\Delta E =$ **199** $kJ \cdot mol^{-1}$. Taking the value of $k = 5$; $\Delta E =$ **415** $kJ \cdot mol^{-1}$	4 points

5. The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions L_x, L_y and L_z, yielding the following expression for the allowed energy levels:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

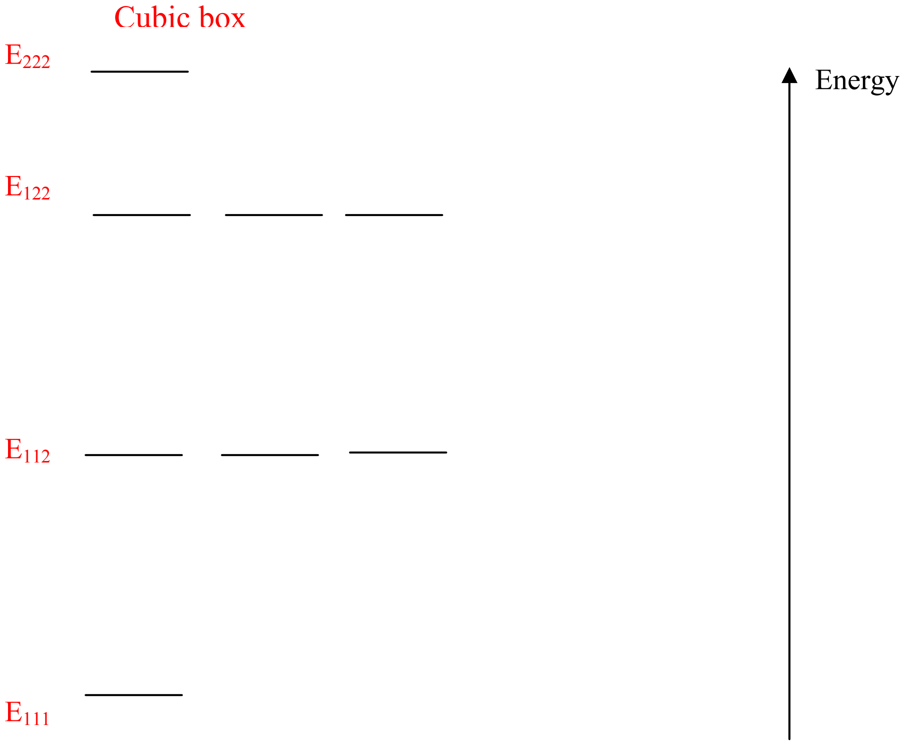
The three quantum numbers n_x, n_y, and n_z must be integer values and are independent of each other.

5.1 **Give** the expressions for the three **different** lowest energies, assuming that the box is cubic with a length of L.

$L_x = L_y = L_z; E_{xyz} = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2}$	1 point
$E_{111} = \frac{h^2(1^2 + 1^2 + 1^2)}{8mL^2} = \frac{3h^2}{8mL^2}$	1 point

$E_{112} = \frac{h^2(1^2+1^2+2^2)}{8mL^2} = \frac{6h^2}{8mL^2} = E_{121} = E_{211}$ $E_{122} = \frac{h^2(1^2+2^2+2^2)}{8mL^2} = \frac{9h^2}{8mL^2} = E_{212} = E_{221}$	1 point

5.2 Levels with the same energy are said to be degenerate. **Draw** a sketch showing all the energy levels, including any degenerate levels, that correspond to quantum numbers having values of 1 or 2 for a cubic box.

E_{111}: only a single state. E_{112}: triple degenerate, either n_x, n_y or n_z can equal to 2. E_{122}: triple degenerate, either n_x, n_y or n_z can equal to 1. E_{222}: single state. Energy diagram: 	4 pts

Student name **Student code**

Theoretical **Problem 2** **5.0 %** of the total	**Code:**		Question	1a	1b	2	3	Total
	Examiner		Mark	12	8	3	10	**33**
			Grade					

Problem 2. Dissociating Gas Cycle

Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide:

$$\mathbf{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

1.00 mole of N_2O_4 was put into an empty vessel with a fixed volume of 24.44 dm^3. The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

1a. **Calculate** ΔG^0 of the reaction at 298K, assuming the gases are ideal.

1b. **Calculate** ΔH^0 and ΔS^0 of the reaction, assuming that they do not change significantly with temperature.

Student name **Student code**

ΔG^0 (298 K) = ________________________________

ΔH^0 = ________________________________

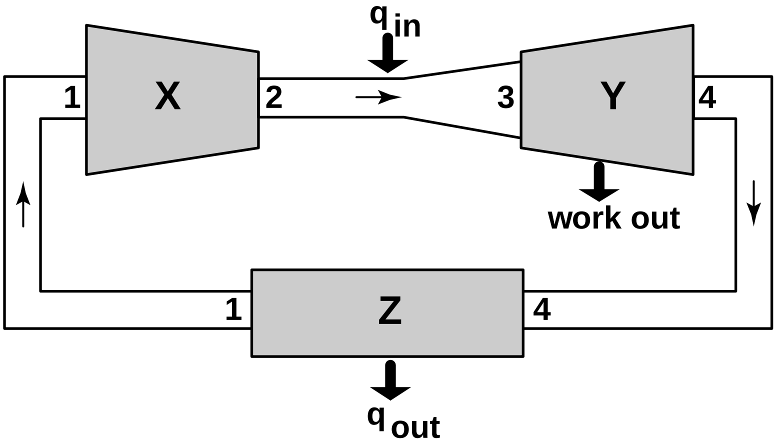
ΔS^0 = ________________________________

If you cannot calculate ΔH^0, use $\Delta H^0 = 30.0$ kJ·mol^{-1} for further calculations.

Student name **Student code**

The tendency of N_2O_4 to dissociate reversibly into NO_2 enables its potential use in advanced power generation systems. A simplified scheme for one such system is shown below in Figure (a). Initially, "cool" N_2O_4 is compressed (1→2) in a compressor (**X**), and heated (2→3). Some N_2O_4 dissociates into NO_2. The hot mixture is expanded (3→4) through a turbine (**Y**), resulting in a decrease in both temperature and pressure. The mixture is then cooled further (4→1) in a heat sink (**Z**), to promote the reformation of N_2O_4. This recombination reduces the pressure, thus facilitates the compression of N_2O_4 to start a new cycle. All these processes are assumed to take place reversibly.

(a)



To understand the benefits of using reversible dissociating gases such as N_2O_4, we will focus on step 3 → 4 and consider an ideal gas turbine working with 1 mol of air (which we assume to be an inert, non-dissociating gas). During the reversible adiabatic expansion in the turbine, **no heat is exchanged**.

2. **Give the equation** to calculate the work done by the system w(air) during the **reversible adiabatic** expansion for 1 mol of air during stage 3 → 4. Assume that $C_{v,m}$(air) (the isochoric molar heat capacity of air) is constant, and the temperature changes from T_3 to T_4.

3. **Estimate** the ratio $w_{(N2O4)}/w_{(air)}$, in which $w_{(N2O4)}$ is the work done by the gas during the reversible adiabatic expansion process 3 → 4 with the cycle working with 1 mol of N_2O_4. T_3 and T_4 are the same as in Part 2. Take the conditions at stage 3 to be $T_3 = 440$ K and $P_3 = 12.156$ bar and assume that:

(i) the gas is at its equilibrium composition at stage 3;

(ii) $C_{v,m}$ for the gas is the same as for air;

(iii) the adiabatic expansion in the turbine takes place in a way that the composition of the gas mixture (N_2O_4 + NO_2) is unchanged until the expansion is completed.

Student name **Student code**

Theoretical	**Code:**		Question	1a	1b	2	3	Total
Problem 2	**Examiner**		Mark	12	8	3	10	**33**
5.0 % of the total			Grade					

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$$\mathbf{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

1.00 mole of N_2O_4 was put into an empty vessel with a fixed volume of 24.44 dm^3. The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

1a. Calculate ΔG^0 of the reaction at 298K, assuming the gases are ideal.

1b. Calculate ΔH^0 and ΔS^0 of the reaction, assuming that they do not change significantly with temperature.

1a.	N_2O_4	$\rightleftharpoons$	$2\ NO_2$
Initial molar number	1		0
At equilibrium	1 - x		2x

$n_{total,equi.} = 1 - x + 2x = 1 + x$ (mol)

$P_{total,equi} = P_{ini}(1 + x)$

(P_{ini} - initial pressure; $n_{total,equi.}$ – total molar number of gases at equilibrium; $P_{total,equi}$ - total pressure of gases at equilibrium; x – number of moles N_2O_4 dissociated).

$$n_{total,equi} = \frac{PV}{RT} = \frac{(1.190\ \text{bar})\left(\frac{10^5\ \text{Pa}}{1\ \text{bar}}\right)(24.44\ \text{dm}^3)\left(\frac{1\ \text{m}^3}{1000\ \text{dm}^3}\right)}{(8.3145\ \text{J}\cdot\text{K}^{-1}\cdot mol^{-1})(298\ \text{K})} = 1.174\ \text{(mol)}$$

1.174 = 1 + x

4pts

x = 0.174 (mol)

ΔG^0 at 298 K 4pts

At equilibrium:

$$P_{N_2O_4} = \frac{1-x}{1+x} \times P_{total} = \frac{1-0.174}{1+0.174} \times (1.190 \text{ bar}) = 0.837 \text{ bar}$$

$$P_{NO_2} = \frac{2x}{1+x} \times P_{total} = \frac{2 \times 0.174}{1+0.174} \times (1.190 \text{ bar}) = 0.353 \text{ bar}$$

$$K_{298} = \frac{\left(\frac{P_{NO_2}}{P^0}\right)^2}{\left(\frac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\frac{0.353}{1}\right)^2}{\left(\frac{0.837}{1}\right)} = 0.1489$$

At 298 K, 4pts

$$\Delta G^0 = -RT \ln K_{298} = -8.3145 \times 298 \times \ln(0.1489) = 4719\,(J \cdot mol^{-1}) = 4.72\,(\text{kJ} \cdot \text{mol}^{-1})$$

1b. ΔG^0 at 348 K

$$n_{total,equi} = \frac{PV}{RT} = \frac{(1.886 \text{ bar})\left(\frac{10^5 \text{ Pa}}{1 \text{ bar}}\right)(24.44 \text{ dm}^3)\left(\frac{1 \text{ m}^3}{1000 \text{ dm}^3}\right)}{(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot mol^{-1})(348 \text{ K})} = 1.593\,(\text{mol})$$

1.593 = 1 + x

x = 0.593 (mol)

At equilibrium:

$$P_{N_2O_4} = \frac{1-x}{1+x} \times P_{total} = \frac{1-0.593}{1+0.593} \times (1.886 \text{ bar}) = 0.482 \text{ bar}$$

$$P_{NO_2} = \frac{2x}{1+x} \times P_{total} = \frac{2 \times 0.593}{1+0.593} \times (1.886 \text{ bar}) = 1.404 \text{ bar}$$

$$\Rightarrow K_{348} = \frac{\left(\frac{P_{NO_2}}{P^0}\right)^2}{\left(\frac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\frac{1.404}{1}\right)^2}{\left(\frac{0.482}{1}\right)} = 4.0897$$

At 348 K,

$$\Delta G^0 = -RT \ln K_{348} = -8.3145 \times 348 \times \ln(4.0897) = -4075\ \ (J \cdot mol^{-1}) = -4.07\,(\text{kJ} \cdot \text{mol}^{-1})$$

ΔS^0	4pts
ΔG^0_{348} = - 4.07 kJ = $\Delta H - 348\Delta S$ (1)	
ΔG^0_{298} = 4.72 kJ = $\Delta H - 298\Delta S$ (2)	
(2) - (1) → ΔS = **0.176 kJ·mol^{-1}·K^{-1}**	
ΔH^0	
$\Delta H^0 = 4.720 + 298 \times 0.176 = 57.2$ (kJ·mol^{-1})	4pts

If you cannot calculate ΔH^0, use $\Delta H^0 = 30.0$ kJ·mol^{-1} for further calculations.

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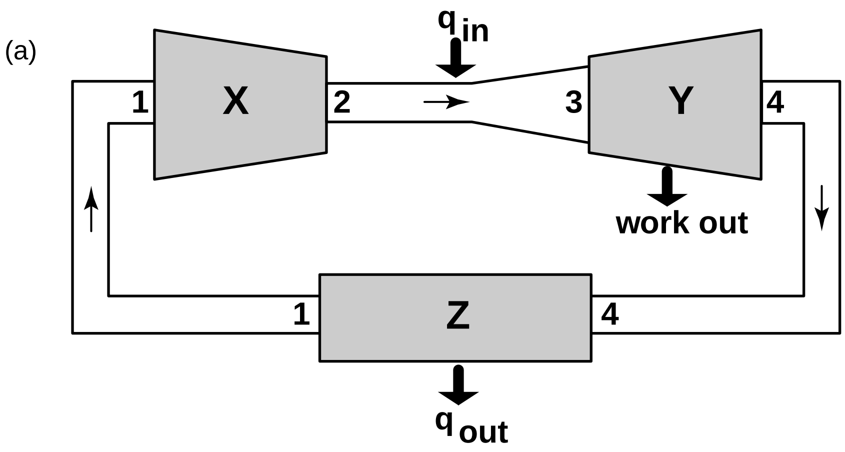

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2. **Give the equation** to calculate the work done by the system w(air) during the **reversible adiabatic** expansion for 1 mol of air during stage 3 → 4. Assume that $C_{v,m}$(air) (the isochoric molar heat capacity of air) is constant, and the temperature changes from T_3 to T_4.

$\Delta U = q + w$; work done by turbine w(air)=-w	1 pt	
$q = 0$, thus $w(\text{air}) = \Delta U = C_{v,m}(\text{air})[T_3 - T_4]$	2 pts	

3. **Estimate** the ratio $w_{(N2O4)}/w_{(air)}$, in which $w_{(N2O4)}$ is the work done by the gas during the reversible adiabatic expansion process 3 → 4 with the cycle working with 1 mol of N_2O_4, T_3 and T_4 are the same as in Part 2. Take the conditions at stage 3 to be T_3 = 440 K and P_3 = 12.156 bar and assume that:

(i) the gas is at its equilibrium composition at stage 3;

(ii) $C_{v,m}$ for the gas is the same as for air;

(iii) the adiabatic expansion in the turbine takes place in a way that the composition of the gas mixture (N_2O_4 + NO_2) is unchanged until the expansion is completed.

$$\ln\frac{K_{440}}{K_{348}} = \frac{\Delta H^0}{R}\left(\frac{1}{348}-\frac{1}{440}\right) = \frac{57200}{8.3145}\left(\frac{1}{348}-\frac{1}{440}\right)$$

$$\ln K_{440} = \ln K_{348} + \frac{57200}{8.3145}\times\left(\frac{1}{348}-\frac{1}{440}\right) = \ln 4.0897 + \frac{57200}{8.314}\times\left(\frac{1}{348}-\frac{1}{440}\right) = 5.542$$

3 pts

→ $\mathbf{K_{440} = 255.2}$

$$N_2O_4 \rightleftharpoons 2\,NO_2 \qquad (1)$$

	N_2O_4	NO_2
Initial molar number	1	0
At equilibrium	1 - x	2x

n_{total} = 1 - x + 2x = 1 + x (mol); P_{total} = 12.156 bar

At equilibrium: $P_{N_2O_4} = \dfrac{1-x}{1+x}\times 12.156\,(\text{bar})$; $P_{NO_2} = \dfrac{2x}{1+x}\times 12.156\,(\text{bar})$

$$\Rightarrow K_{440} = \frac{\left(\frac{P_{NO_2}}{P^0}\right)^2}{\left(\frac{P_{N_2O_4}}{P^0}\right)} = \frac{\left(\frac{\frac{2x}{1+x}\times 12.156}{1}\right)^2}{\left(\frac{\frac{1-x}{1+x}\times 12.156}{1}\right)} = 255.2$$

$(P^0 = 1\ \text{bar})$ → $\frac{\left(\frac{2x}{1+x}\right)^2}{\left(\frac{1-x}{1+x}\right)} = 20.99 \Rightarrow \frac{4x^2}{1-x^2} = 20.99 \Rightarrow$ $4x^2 = 20.99 - 20.99\,x^2$

→ $24.99\,x^2 = 20.99$ → $x = 0.92$; $n_{total} = 1 + x = 1.92$

3pt

→ $w_{N_2O_4} = 1.92 \times C_{v,air} \times (T_3 - T_4)$; → $\frac{w_{N_2O_4}}{w_{air}} = 1.92$

4 pt

Student name **Student code**

Theoretical **Problem 6** **7.0 %** of the total	**Code:**		Question	6a	6b	6c	6d	6e	Total
	Examiner		Marks	6	8	4	12	2	**32**
			Grade						

Problem 6. Chemical Kinetics

The transition-metal-catalyzed amination of aryl halides has become one of the most powerful methods to synthesize arylamines. The overall reaction for the nickel-catalyzed amination of aryl chloride in basic conditions is:

$$\mathbf{ArCl} + \mathbf{RNH_2} \xrightarrow[\text{NaO}^t\text{Bu, } \textit{Solvent}]{\text{NiLL'}} \mathbf{Ar\text{-}NHR} + \mathbf{HCl}$$

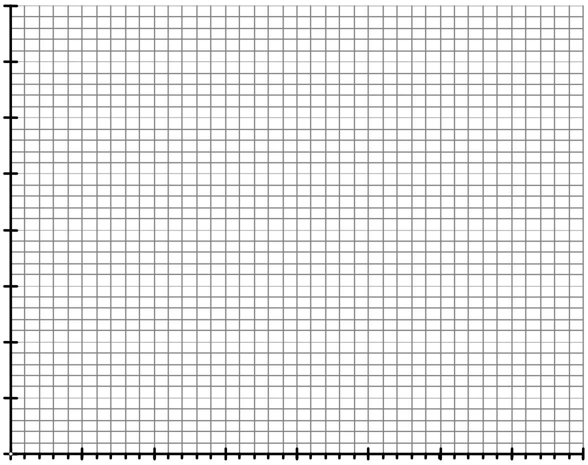
in which NiLL’ is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

6a. To determine the reaction order with respect to each reactant, the dependence of the initial rate of the reaction on the concentrations of each reagent was carried out with all other reagents present in large excess. Some kinetic data at 298 K are shown in the tables below. **(Use the grids if you like)**

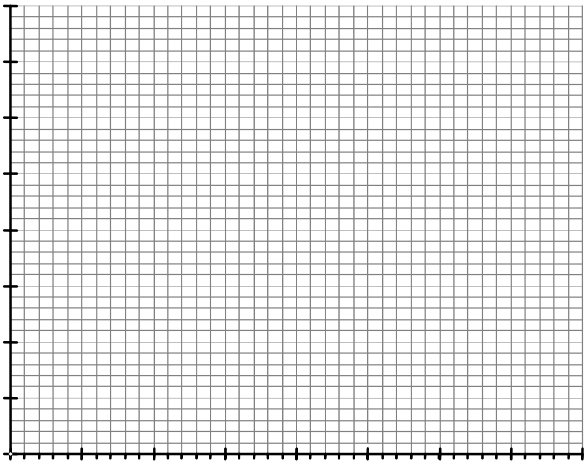
[**ArCl**] (M)	Initial rate ($M\ s^{-1}$)
0.1	1.88×10^{-5}
0.2	4.13×10^{-5}
0.4	9.42×10^{-5}
0.6	1.50×10^{-4}

Student name **Student code**

[**NiLL’**] (M)	Initial rate (M s^{-1})
6×10^{-3}	4.12×10^{-5}
9×10^{-3}	6.01×10^{-5}
1.2×10^{-2}	7.80×10^{-5}
1.5×10^{-2}	1.10×10^{-4}



[**L’**] (M)	Initial rate (M s^{-1})
0.06	5.8×10^{-5}
0.09	4.3×10^{-5}
0.12	3.4×10^{-5}
0.15	2.8×10^{-5}



Determine the order with respect to the reagents assuming they are integers.

- Order with respect to [**ArCl**] =
- Order with respect to **[NiLL'**] =
- Order with respect to **[L'**] =

6b. To study the mechanism for this reaction, ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopy have been used to identify the major transition metal complexes in solution, and the initial rates were measured using reaction calorimetry. An intermediate, NiL(Ar)Cl, may be isolated at room temperature. The first two steps of the overall reaction involve the dissociation of a ligand from NiLL' (step 1) at 50 °C, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

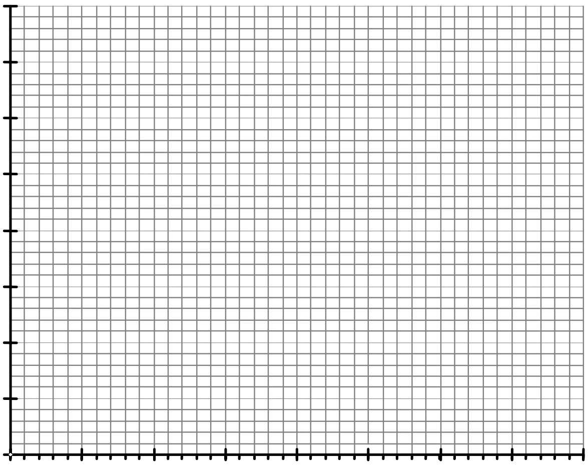
$$\mathbf{NiLL'} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{NiL} + \mathbf{L'} \qquad \mathbf{(1)}$$

$$\mathbf{NiL} + \mathbf{ArCl} \xrightarrow{k_2} \mathbf{NiL(Ar)Cl} \qquad \mathbf{(2)}$$

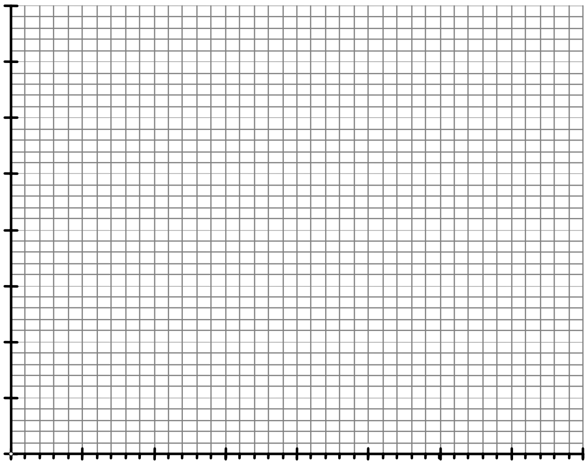
Using the steady state approximation, **derive** an expression for the rate equation for the formation of [NiL(Ar)Cl].

The next steps in the overall reaction involve the amine (RNH_2) and ^{t}BuONa. To determine the order with respect to RNH_2 and ^{t}BuONa, the dependence of the initial rates of the reaction on the concentrations of these two reagents was carried with the other reagents present in large excess. Some results are shown in the tables below.

[**NaO^{t}Bu**], (M)	Initial rate ($M \cdot s^{-1}$)
0.2	4.16×10^{-5}
0.6	4.12×10^{-5}
0.9	4.24×10^{-5}
1.2	4.20×10^{-5}



[**RNH_2**] (M)	Initial rate ($M\ s^{-1}$)
0.3	4.12×10^{-5}
0.6	4.26×10^{-5}
0.9	4.21×10^{-5}
1.2	4.23×10^{-5}



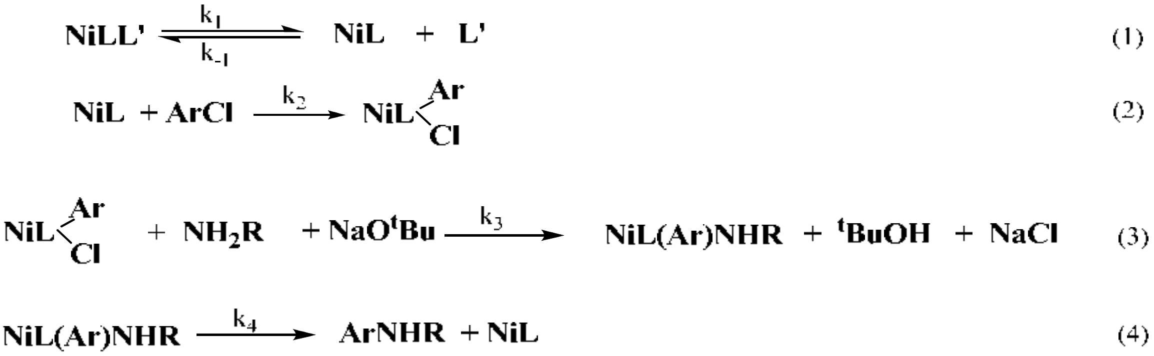
6c. **Determine** the order with respect to each of these reagents, assuming each is an integer. **(Use the grids if you like.)**

- Order with respect to [NaO^{t}Bu] =

- Order with respect to [RNH$_2$] =

During a catalytic cycle, a number of different structures may be involved which include the catalyst. One step in the cycle will be rate-determining.

A proposed cycle for the nickel-catalyzed coupling of aryl halides with amines is as follows:



$$\mathrm{NiLL'} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NiL} + \mathrm{L'} \qquad (1)$$

$$\mathrm{NiL} + \mathrm{ArCl} \xrightarrow{k_2} \mathrm{NiL}{<}^{\mathrm{Ar}}_{\mathrm{Cl}} \qquad (2)$$

$$\mathrm{NiL}{<}^{\mathrm{Ar}}_{\mathrm{Cl}} + \mathrm{NH_2R} + \mathrm{NaO^tBu} \xrightarrow{k_3} \mathrm{NiL(Ar)NHR} + \mathrm{^tBuOH} + \mathrm{NaCl} \qquad (3)$$

$$\mathrm{NiL(Ar)NHR} \xrightarrow{k_4} \mathrm{ArNHR} + \mathrm{NiL} \qquad (4)$$

6d. **Use** the steady-state approximation and material balance equation to **derive** the rate law for d[ArNHR]/dt for the above mechanism in terms of the initial concentration of the catalyst [NiLL']$_0$ and concentrations of [ArCl], [NH$_2$R], [NaO^{t}Bu], and [L'].

Student name **Student code**

Student name **Student code**

6e. <u>Give</u> the simplified form of the rate equation in **6d** assuming that k_1 is very small.

d[ArNHR]/dt = - d[ArCl]/dt =

Theoretical **Problem 6** **7.0 %** of the total	**Code:**		Question	6a	6b	6c	6d	6e	Total
	Examiner		Marks	6	8	4	12	2	**32**
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in which NiLL’ is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

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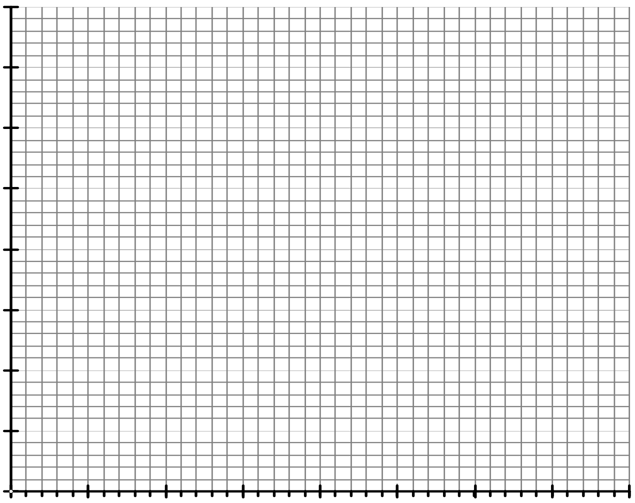
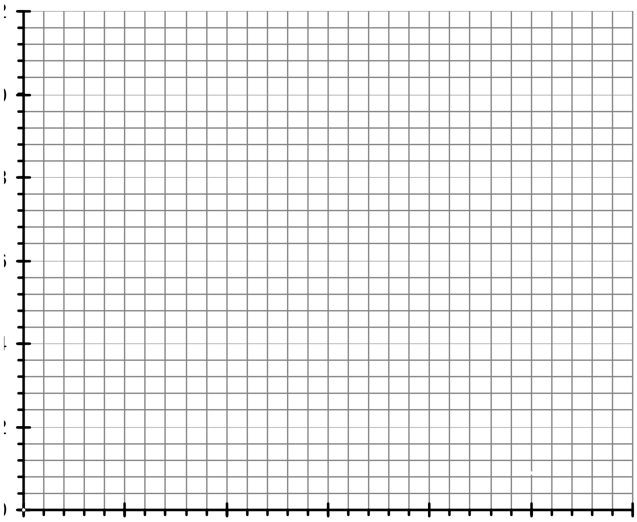
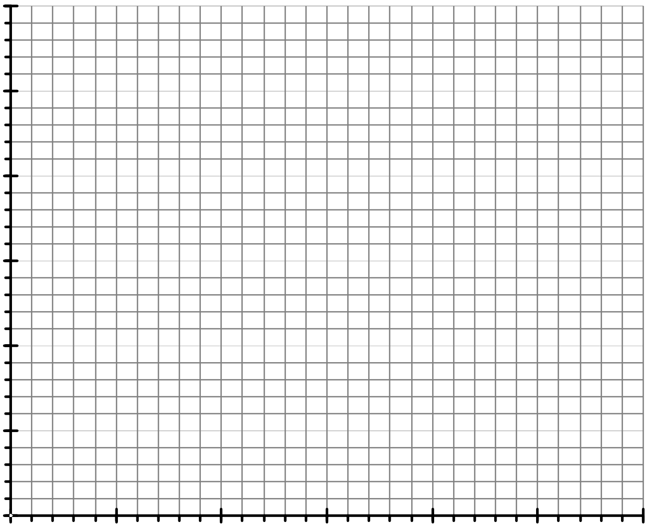
0.6	1.50×10^{-4}



[**NiLL'**] (M)	Initial rate (M s^{-1})	
6 × 10^{-3}	4.12 × 10^{-5}	
9 × 10^{-3}	6.01 × 10^{-5}	
1.2 × 10^{-2}	7.80 × 10^{-5}	
1.5 × 10^{-2}	1.10 × 10^{-4}	

[**L'**] (M)	Initial rate (M s^{-1})	
0.06	5.8 × 10^{-5}	
0.09	4.3 × 10^{-5}	
0.12	3.4 × 10^{-5}	
0.15	2.8 × 10^{-5}	

Determine the order with respect to the reagents assuming they are integers.

- Order with respect to [**ArCl**] = = 1
- Order with respect to [**NiLL'**] = = 1
- Order with respect to [**L'**] = = **-1** 6 pts

6b. To study the mechanism for this reaction, ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopy have been used to identify the major transition metal complexes in solution, and the initial rates were measured using reaction calorimetry. An intermediate, NiL(Ar)Cl, may be isolated at room temperature. The first two steps of the overall reaction involve the dissociation of a ligand from NiLL' (step 1) at 50 °C, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

$$\mathbf{NiLL'} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{NiL} + \mathbf{L'} \qquad \mathbf{(1)}$$

$$\mathbf{NiL} + \mathbf{ArCl} \xrightarrow{k_2} \mathbf{NiL(Ar)Cl} \qquad \mathbf{(2)}$$

Using the steady state approximation, **derive** an expression for the rate equation for the formation of [NiL(Ar)Cl].

The rate law expression for the formation of NiLAr(Cl)

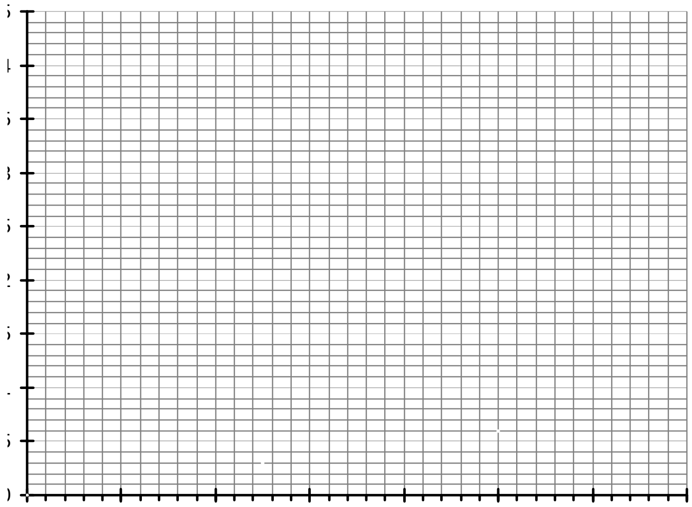
$$\text{rate} = \frac{k_1 k_2 [NiLL'] \, [ArCl]}{k_{-1}[L'] + k_2[ArCl]} = \frac{k_1 (k_2 / k_{-1})[NiLL'] \, [ArCl]}{[L'] + (k_2 / k_{-1})[ArCl]}$$

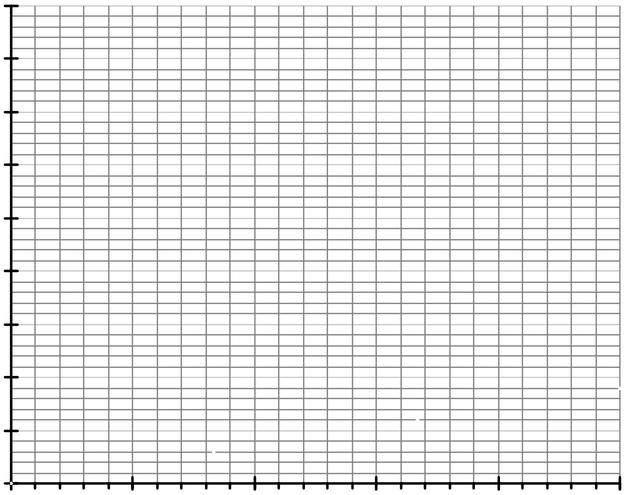
8 pts

(4pts for [NiL] calculation)

(4 pts for rate calculation)

The next steps in the overall reaction involve the amine (RNH_2) and ^tBuONa. To determine the order with respect to RNH_2 and ^tBuONa, the dependence of the initial rates of the reaction on the concentrations of these two reagents was carried with the other reagents present in large excess. Some results are shown in the tables below.

[NaO^{t}Bu], (M)	Initial rate ($M\cdot s^{-1}$)	
0.2	4.16×10^{-5}	
0.6	4.12×10^{-5}	
0.9	4.24×10^{-5}	
1.2	4.20×10^{-5}	

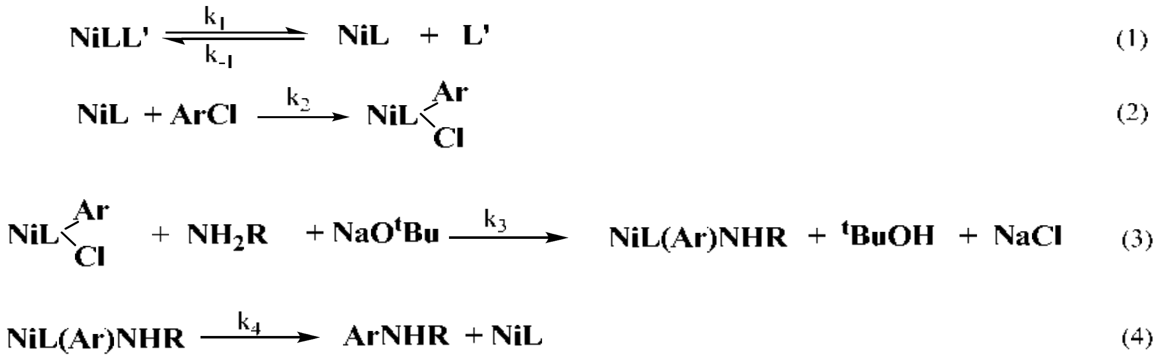
[RNH_2] (M)	Initial rate ($M\ s^{-1}$)	
0.3	4.12×10^{-5}	
0.6	4.26×10^{-5}	
0.9	4.21×10^{-5}	
1.2	4.23×10^{-5}	

6c. **Determine** the order with each of these reagents, assuming each is an integer. **(Use the grids if you like)**

- Order with respect to [NaO^{t}Bu] = 0 2 pts
- Order with respect to [RNH_2] = 0 2 pts

During a catalytic cycle, a number of different structures may be involved which include the catalyst. One step in the cycle will be rate-determining.

A proposed cycle for the nickel-catalyzed coupling of aryl halides with amines is as follows:



6d. **Use** the steady-state approximation and material balance equation to **derive** the rate law for d[ArNHR]/dt for the above mechanism in terms of the initial concentration of the catalyst [NiLL']$_0$ and concentrations of [ArCl], [NH_2R], [NaO^{t}Bu], and [L'].

Using the mechanism depicted by Reaction (1) through (4), the rate equation:

$$\frac{d[NiLL']}{dt} = -k_1[NiLL'] + k_{-1}[NiL][L']$$

$$\frac{d[NiL]}{dt} = k_1[NiLL'] - k_{-1}[NiL][L'] - k_2[NiL][ArCl] + k_4[NiL(Ar)NHR]$$

Apply the steady-state approximation to the concentrations for the intermediates:

$$\frac{d[NiL]}{dt} = 0$$

k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] – k_4[NiL(Ar)HNR] (Equation 1) 1pt

$$\frac{d[NiL(Ar)Cl]}{dt} = k_2[NiL][ArCl] - k_3[RNH_2][NaOBu][NiL(Ar)Cl] = 0$$

$$[NiL(Ar)Cl] = \frac{k_2}{k_3}\frac{[ArCl][NiL]}{[NH_2R][NaOBu]}$$ (Equation 2) 1pt

$$\frac{d[NiL(Ar)NHR]}{dt} = k_3[NiL(Ar)Cl][NH_2R][NaOBu] - k_4[NiL(Ar)NHR] = 0$$

$$[NiL(Ar)NHR] = \frac{k_3}{k_4}\frac{[NiL(Ar)Cl][NH_2R][NaOBu]}{} \qquad \text{(Equation 3)}$$

Substitute Equation 2 into Equation 3:

$$[NiL(Ar)NHR] = \frac{k_3}{k_4}\frac{[NH_2R][NaOBu]}{} \times \frac{k_2}{k_3}\frac{[ArCl][NiL]}{[NH_2R][NaOBu]} = \frac{k_2}{k_4}[ArCl][NiL] \qquad \text{(Eq. 4)} \quad \text{1pt}$$

Substitute Equation 4 into Equation 1:

$$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4[NiL(Ar)NHR]$$

$$k_1[NiLL'] = k_{-1}[NiL][L'] + k_2[NiL][ArCl] - k_4 \times \frac{k_2}{k_4}[ArCl][NiL] = k_{-1}[NiL][L'] \qquad \text{(Eq.5)}$$

The material balance equation with respect to the catalyst is

$[NiLL']_0 = [NiLL'] + [NiL] + [NiLAr(Cl)] + [NiLAr(Cl)NHR]$ 2 pts

$$[NiLL']_0 = \frac{k_{-1}}{k_1}[NiL][L'] + [NiL] + \frac{k_2}{k_3}\frac{[NiL][ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[NiL][ArCl]$$

$$[NiLL']_0 = [NiL]\left[\frac{k_{-1}}{k_1}[L'] + 1 + \frac{k_2}{k_3}\frac{[ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[ArCl]\right] \qquad \text{3 pts}$$

$$[NiL] = [NiLL']_0 \times \frac{k_1k_3k_4[NH_2R][NaOBu]}{k_{-1}k_3k_4[L'][NH_2R][NaOBu] + k_1k_3k_4[NH_2R][NaOBu] + k_1k_2k_4[ArCl] + k_1k_2k_3[ArCl][NH_2R][NaOBu]}$$

Equation 6

Substituting Equation 6 into the differential rate for [ArCl]:

$-\frac{d[ArCl]}{dt} = k_2[ArCl][NiL]$, results in the following predicted rate law expression for the reaction mechanism:

d[ArNHR]/dt = - d[ArCl]/dt =

$k_2[ArCl]\ [NiL] = k_1k_2k_3k_4\ [ArCl][NiLL']_0[NaO^tBu][NH_2R]$

$/\{k_{-1}k_3k_4[NH_2R][NaOBu][L'] + k_1k_3k_4[NaOBu][NH_2R] + k_1k_2k_4[ArCl] + k_1k_2k_3$

$[ArCl][NH_2R][NaOBu]\}$ 4 pts

6e. **Give** the simplified form of the rate equation in 6d assuming that k_1 is very small.

d[ArNHR]/dt = - d[ArCl]/dt = $k_2[ArCl]\ [NiL] = k_1k_2\ [ArCl][NiLL']_0\ /\ k_{-1}[L']$

(i.e. consistent with all the orders of reaction as found in the beginning) 2 pts

Problem 1. New and well-forgotten old refrigerants
(8 points)

Question	1			2			3	4				**Total**
	1.1	1.2	1.3	2.1	2.2	2.3		4.1	4.2	4.3	4.4	
Marks	4	2	2	1	1	1	3	10	2	6	1	**33**

The problem of choosing a refrigerant for refrigeration and air conditioning systems attracted the attention of scientists and technologists throughout the last century. It has been suggested that during this time refrigerants progressed through four generations. Ammonia, which was ascribed to the first generation, had been used in most of the oldest refrigeration units. It was later replaced by chlorofluorocarbons (CFCs) – derivatives of methane and ethane with the hydrogen atoms replaced by fluorine and chlorine.

In Baku, at "Bakkonditsioner" factory, production of the first Soviet serial household air conditioners BK-1500 had been launched. A second-generation refrigerant chlorodifluoromethane CHF_2Cl was used in them. In this problem, we compare various refrigerants in terms of thermodynamics.

First air conditioner of Baku factory in a souvenir shop in the Old City ("Icheri Sheher")

Thermodynamic properties of various refrigerants

Refrigerant	"Generation"	ΔH_{vap} / kJ·mol^{-1} (at 280 K)	$C_{V(gas)}$ / J·K^{-1}·mol^{-1}
NH_3	1	21.3	26.7
CHF_2Cl	2	20.0	48.8
CF_3CH_2F	3	22.1	79
$CF_3CF{=}CH_2$	4	19.1	120

Consider a model refrigeration cycle consisting of 4 steps schematically shown below in the pressure (p) – internal energy (U) coordinates.

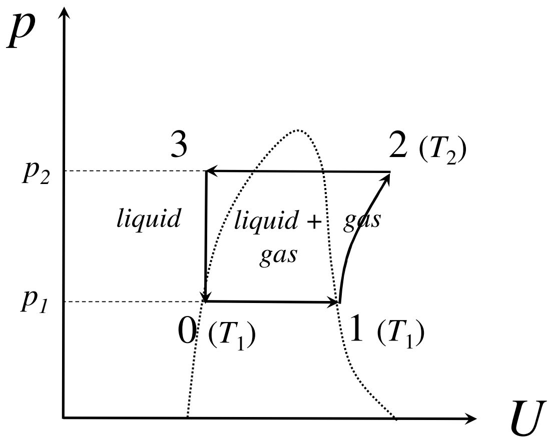


Diagram 1
(dashed line indicates the phase boundaries)

During the first step of the cycle (line 0-1 in diagram 1), a liquid refrigerant is boiling at constant pressure p_1 and temperature T_1 (boiling temperature) until it completely evaporates. At this step, the refrigeration unit absorbs heat from surrounding objects. At the second step, the refrigerant undergoes reversible adiabatic compression and heats up to temperature T_2 (line 1-2). After that the compressed refrigerant is cooled in a condenser at constant pressure p_2 (line 2-3) and then returns to the initial state (line 3-0).

Let the cycle involve 1 mole of refrigerant, which is initially (point 0) completely liquid, T_1 = 280 K, T_2 = 380 K, assume that the vapor of any refrigerant behaves like an ideal gas. The thermodynamic characteristics of refrigerants are listed in the table above.

1.1. For each of refrigerants, ammonia and chlorodifluoromethane, calculate the amount of heat Q absorbed by refrigeration unit during heat exchange (line 0-1) and the work W required to compress its vapor adiabatically (line 1-2).

Calculations

Ammonia

Q =

W =

Chlorodifluoromethane

$Q =$	$W =$

1.2. Which quantity(ies) remain(s) constant during the adiabatic compression step? Indicate by the circle(s).

U H S G V

To compare the energy efficiency of refrigeration cycles with different parameters and refrigerants, the coefficient of performance (*COP*) is used, which is defined as a ratio of heat removed from a cooled system to the work of compressor: $COP = Q/W$.

1.3. Calculate the values of *COP* in a considered cycle for ammonia and chlorodifluoromethane.

Calculations

Ammonia

$COP =$

Chlorodifluoromethane

$COP =$

2.1. Why was ammonia replaced by CFCs in household refrigeration units? (Choose only one option)

a) to increase the energy efficiency of refrigeration cycles
b) because the density of ammonia is less than that of air under the same conditions
c) for user safety reasons

A search for replacement of CFCs as refrigerants started when it was shown that their use can cause irreparable damage to the protective ozone layer of the atmosphere. The third, ozone-friendly generation of refrigerants came on the scene. Its typical representatives are fluoroalkanes.

2.2. What is the cause of the damage made by CFCs to the ozone layer? (Choose only one option)

a) ozone molecule easily adds to C–F bond
b) C–F bond is easily broken by radiation, which leads to the formation of free radicals
c) ozone molecule easily adds to C–Cl bond
d) C–Cl bond is easily broken by radiation, which leads to the formation of free radicals

However, under the 1997 Kyoto Protocol, fluoroalkanes also had to be replaced because they accumulate in the atmosphere and rapidly absorb infrared radiation, causing a rise in temperature of the atmosphere (the greenhouse effect). The refrigerants of the fourth generation such as 2,3,3,3-tetrafluoropropene $CF_3CF{=}CH_2$ have been suggested and are coming into use.

2.3. Why does this compound enhance the greenhouse effect less than fluoroalkanes? (Choose only one option)

a) it is more reactive and easier to decompose
b) it easily reacts with ozone
c) it is better soluble in water

3. Calculate the values of the *COP* in the refrigeration cycle considered above for two refrigerants of the third and fourth generations – CF_3CH_2F and $CF_3CF{=}CH_2$. Did the energy efficiency improve in comparison with CHF_2Cl? Choose "Yes" or "No".

Calculations

CF_3CH_2F

COP =

Yes **No**

$CF_3CF{=}CH_2$

COP =

Yes	**No**

Unlike household appliances, industrial refrigeration systems are often still using ammonia. It does not contribute to the greenhouse effect nor does it destroy the ozone layer. Industrial units can have a huge size and a large cost. Prior to their construction, they should be carefully modeled taking into account many different factors. In real systems, some part of the refrigerant at the start of the heat exchange with the environment is in the vapor phase (point 0 in the diagram below), and at the end (point 1) it is always overheated above the boiling point.

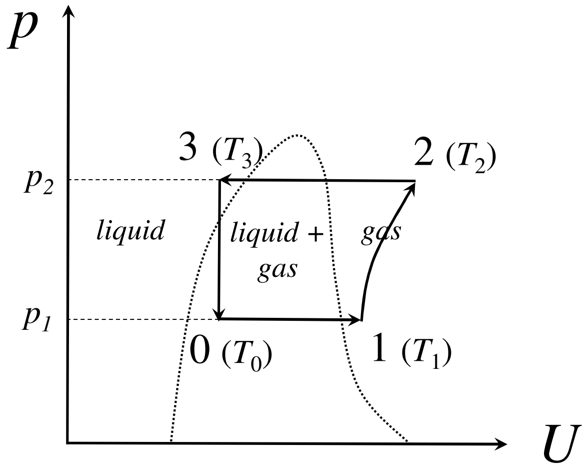


Diagram 2
(dashed line indicates the phase boundaries)

Consider a cycle with 1 mole of ammonia. Its thermodynamic properties are the following: enthalpy of vaporization $\Delta H_{vap} = 23.35$ kJ·mol^{-1} at $T_{vap} = 239.8$ K (boiling temperature at 1 bar pressure). Heat capacity of the liquid phase $C_{V(liq)} = 77$ J·K^{-1}·mol^{-1}, of the gas phase $C_{V(gas)} = 26.7$ J·K^{-1}·mol^{-1}. Assume that the heat capacities are temperature-independent and the vapor behaves like an ideal gas. The temperature dependence of the saturated vapor pressure of ammonia can be described by the empirical equation:

$$\log (p/\text{bar}) = 4.87 - 1114 / (T/\text{K} - 10.4).$$

During the first step of the cycle (line 0-1 in diagram 2), the equilibrium mixture of liquid refrigerant and its vapor receives heat from the environment at constant pressure $p_1 = 3.0$ bar. The refrigerant completely evaporates and overheats up to the temperature $T_1 = 275$ K. In the beginning of the process (point 0), the molar fraction of gaseous ammonia is $x = 0.13$.

4.1. Calculate the initial temperature of refrigerant T_0, its volume change ΔV and the amount of heat Q absorbed by refrigeration unit during this step. Take into account that the dependence of ΔH_{vap} from the temperature **cannot** be neglected.

Calculations:

$T_0 =$

$\Delta V =$

$Q =$

Then the refrigerant is reversibly and adiabatically compressed. It heats up to the temperature T_2 = 393 K (line 1-2).

4.2. Find the work W required for compression and the COP of the system. If you were not able to find Q in 4.1, use Q = 20.15 kJ.

Calculations:

$W =$

$COP =$

At the next step corresponding to the line 2-3 in diagram, the compressed refrigerant is cooled in a condenser at constant pressure. Then it returns to the initial state through adiabatic expansion with zero work (line 3-0).

4.3. Determine the temperature T_3 at point 3 to which the refrigerant is cooled in a condenser.

Calculations:

T_3 =

In the production of refrigeration units it is necessary to consider climatic factors. If a condenser is cooled by atmospheric air, the temperature T_3 increases as the air temperature increases.

4.4. How will the *COP* change if T_3 increases while T_0, T_1, T_2 remain the same?

a) Increase

b) Remain the same

c) Decrease

Problem 1. New and well-forgotten old refrigerants
(8 points)

Question	1			2			3	4				Total
	1.1	1.2	1.3	2.1	2.2	2.3		4.1	4.2	4.3	4.4	
Marks	4	2	2	1	1	1	3	10	2	6	1	**33**

The problem of choosing a refrigerant for refrigeration and air conditioning systems attracted the attention of scientists and technologists throughout the last century. It has been suggested that during this time refrigerants progressed through four generations. Ammonia, which was ascribed to the first generation, had been used in most of the oldest refrigeration units. It was later replaced by chlorofluorocarbons (CFCs) – derivatives of methane and ethane with the hydrogen atoms replaced by fluorine and chlorine.

In Baku, at "Bakkonditsioner" factory, production of the first Soviet serial household air conditioners BK-1500 had been launched. A second-generation refrigerant chlorodifluoromethane CHF_2Cl was used in them. In this problem, we compare various refrigerants in terms of thermodynamics.

First air conditioner of Baku factory in a souvenir shop in the Old City ("Icheri Sheher")

Thermodynamic properties of various refrigerants

Refrigerant	"Generation"	ΔH_{vap} / kJ·mol^{-1} (at 280 K)	$C_{V(gas)}$ / J·K^{-1}·mol^{-1}
NH_3	1	21.3	26.7
CHF_2Cl	2	20.0	48.8
CF_3CH_2F	3	22.1	79
$CF_3CF{=}CH_2$	4	19.1	120

Consider a model refrigeration cycle consisting of 4 steps schematically shown below in the pressure (p) – internal energy (U) coordinates.

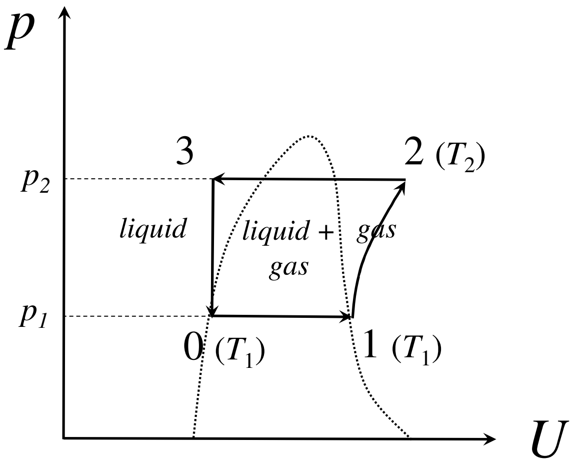


Diagram 1. Dashed line indicates the phase boundaries

During the first step of the cycle (line 0-1 in diagram 1), a liquid refrigerant is boiling at constant pressure p_1 and temperature T_1 (boiling temperature) until it completely evaporates. At this step, the refrigeration unit absorbs heat from surrounding objects. At the second step, the refrigerant undergoes reversible adiabatic compression and heats up to temperature T_2 (line 1-2). After that the compressed refrigerant is cooled in a condenser at constant pressure p_2 (line 2-3) and then returns to the initial state (line 3-0).

Let the cycle involve 1 mole of refrigerant, which is initially (point 0) completely liquid, T_1 = 280 K, T_2 = 380 K, assume that the vapor of any refrigerant behaves like an ideal gas. The thermodynamic characteristics of refrigerants are listed in the table above.

1.1. For each of refrigerants, ammonia and chlorodifluoromethane, calculate the amount of heat Q absorbed by refrigeration unit during heat exchange (line 0-1) and the work W required to compress its vapor adiabatically (line 1-2).

Calculations

Note: here and below in this problem, only correct VALUES are marked except 4.1, 4.3

Ammonia

$Q = \nu\Delta H_{vap} = 21.3$ kJ; **1p**

$W = \nu C_{V(gas)}(T_2 - T_1) = 2.67$ kJ. **1p**

Q = 21.3 kJ

W = 2.67 kJ

Chlorodifluoromethane

$Q = \nu\Delta H_{vap} = 20.0$ kJ; **1p**

$W = \nu C_{V(gas)}\cdot(T_2 - T_1) = 4.88$ kJ. **1p**

Q = 20.0 kJ

W = 4.88 kJ

1.2. Which quantity(ies) remain(s) constant during the adiabatic compression step? Indicate by the circle(s).

U H [✓ S] G V

2p for the correct answer

Minus 1p for every incorrect option, total – no less than 0.

To compare the energy efficiency of refrigeration cycles with different parameters and refrigerants, the coefficient of performance (*COP*) is used, which is defined as a ratio of heat removed from a cooled system to the work of compressor: $COP = Q/W$.

1.3. Calculate the values of *COP* in a considered cycle for ammonia and chlorodifluoromethane.

Calculations

Ammonia

$COP = Q/W = 7.98$ **1p**

COP = 7.98

Chlorodifluoromethane

$COP = Q/W = 4.10$ **1p**

COP = 4.10

2.1. Why was ammonia replaced by CFCs in household refrigeration units? (Choose only one option)

a) to increase the energy efficiency of refrigeration cycles
b) because the density of ammonia is less than that of air under the same conditions
c) for user safety reasons

c

1p

A search for replacement of CFCs as refrigerants started when it was shown that their use can cause irreparable damage to the protective ozone layer of the atmosphere. The third, ozone-friendly generation of refrigerants came on the scene. Its typical representatives are fluoroalkanes.

2.2. What is the cause of the damage made by CFCs to the ozone layer? (Choose only one option)

a) ozone molecule easily adds to C–F bond
b) C–F bond is easily broken by radiation, which leads to the formation of free radicals
c) ozone molecule easily adds to C–Cl bond
d) C–Cl bond is easily broken by radiation, which leads to the formation of free radicals

d

1p

However, under the 1997 Kyoto Protocol, fluoroalkanes also had to be replaced because they accumulate in the atmosphere and rapidly absorb infrared radiation, causing a rise in temperature of the atmosphere (the greenhouse effect). The refrigerants of the fourth generation such as 2,3,3,3-tetrafluoropropene $CF_3CF{=}CH_2$ have been suggested and are coming into use.

2.3. Why does this compound enhance the greenhouse effect less than fluoroalkanes? (Choose only one option)

a) it is more reactive and easier to decompose
b) it easily reacts with ozone
c) it is better soluble in water

a

1p

3. Calculate the values of the *COP* in the refrigeration cycle considered above for two refrigerants of the third and fourth generations – CF_3CH_2F and $CF_3CF{=}CH_2$. Did the energy efficiency improve in comparison with CHF_2Cl? Choose “Yes” or “No”.

Calculations

CF_3CH_2F

$COP = \Delta H_{vap} / (C_{V(gas)}(T_2 - T_1)) = 2.80$ **1p**

$COP = 2.80$

Yes [✓ **No**] **0.5p**

$CF_3CF{=}CH_2$

$COP = \Delta H_{vap} / (C_{V(gas)}(T_2 - T_1)) = 1.59$ **1p**

$COP = 1.59$

Yes [✓ **No**] **0.5p**

Unlike household appliances, industrial refrigeration systems are often still using ammonia. It does not contribute to the greenhouse effect nor does it destroy the ozone layer. Industrial units can have a huge size and a large cost. Prior to their construction, they should be carefully modeled taking into account many different factors. In real systems, some part of the refrigerant at the start of the heat exchange with the environment is in the vapor phase (point 0 in the diagram below), and at the end (point 1) it is always overheated above the boiling point.

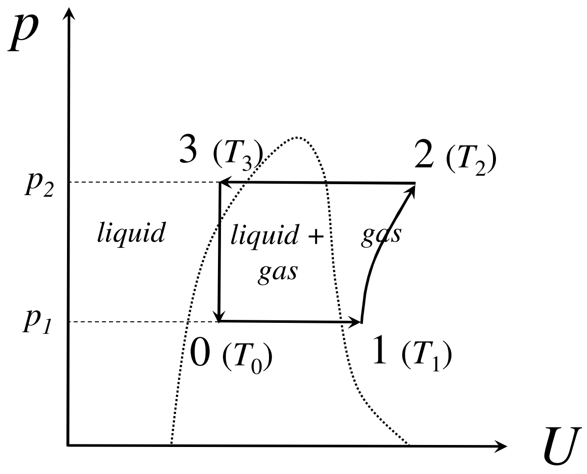


Diagram 2. Dashed line indicates the phase boundaries

Consider a cycle with 1 mole of ammonia. Its thermodynamic properties are the following: enthalpy of vaporization $\Delta H_{vap} = 23.35$ kJ·mol^{-1} at $T_{vap} = 239.8$ K (boiling temperature at 1 bar pressure). Heat capacity of the liquid phase $C_{V(liq)} = 77$ J·K^{-1}·mol^{-1}, of the gas phase $C_{V(gas)} = 26.7$ J·K^{-1}·mol^{-1}. Assume that the heat capacities are temperature-independent and the vapor behaves like an ideal gas. The temperature dependence of the saturated vapor pressure of ammonia can be described by the empirical equation:

$$\log (p/\text{bar}) = 4.87 - 1114 / (T/\text{K} - 10.4).$$

During the first step of the cycle (line 0-1 in diagram 2), the equilibrium mixture of liquid refrigerant and its vapor receives heat from the environment at constant pressure $p_1 = 3.0$ bar. The refrigerant completely evaporates and overheats up to the temperature $T_1 = 275$ K. In the beginning of the process (point 0), the molar fraction of gaseous ammonia is $x = 0.13$.

4.1. Calculate the initial temperature of refrigerant T_0, its volume change ΔV and the amount of heat Q absorbed by refrigeration unit during this step. Take into account that the dependence of ΔH_{vap} from the temperature **cannot** be neglected.

Calculations:

$T_0 = 10.4 + 1114 / (4.87 - \log p_1) = 264$ K **2p**

$T_0 = 264$ K

$\Delta V = (\nu R T_1 / p_1) - (x\nu R T_0 / p_1) = 6.7$ L **3p**

$\Delta V = 6.7$ L

$Q = \Delta H = \Delta U + p_1\Delta V = \Delta U(\text{liquid fraction}) + \Delta U(\text{gas fraction}) + p_1\Delta V =$

$= \Delta U(\text{vaporization of liquid fraction at } T_0) + \Delta U(\text{heating evaporated liquid fraction up to } T_1) +$

$+ \Delta U(\text{gas fraction}) + p_1\Delta V =$

$= \nu\,(1-x)(\Delta H_{\text{vap}} - RT_{\text{vap}} + (C_{V(\text{gas})} - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + \nu C_{V(\text{gas})}\,(T_1 - T_0) + p_1\Delta V = 19.8$ kJ

or

$Q = \nu\,(1-x)(\Delta H_{\text{vap}} + (C_{V(\text{gas})} + R - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + \nu(C_{V(\text{gas})} + R)(T_1 - T_0) = 19.8$ kJ

5p

(3p for a correct equation for calculation and 2p for correct value)

$Q = 19.8$ kJ

Then the refrigerant is reversibly and adiabatically compressed. It heats up to the temperature $T_2 = 393$ K (line 1-2).

4.2. Find the work W required for compression and the COP of the system. If you were not able to find Q in 4.1, use $Q = 20.15$ kJ.

Calculations:

$W = \nu C_{V(\text{gas})}\,(T_2 - T_1) = 3.15$ kJ **1p**

$W = 3.15$ kJ

$COP = Q/W = 6.3$ **1p**

$COP = 6.3$

At the next step corresponding to the line 2-3 in diagram, the compressed refrigerant is cooled in a condenser at constant pressure. Then it returns to the initial state through adiabatic expansion with zero work (line 3-0).

4.3. Determine the temperature T_3 at point 3 to which the refrigerant is cooled in a condenser.

Calculations:

The internal energies of the refrigerant are equal in points 0 and 3. Thus,

$x\cdot(\Delta H_{\text{vap}} - RT_{\text{vap}} + (C_{V(\text{gas})} - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + C_{V(\text{liq})}(T_0 - T_3) = 0$,

$T_3 = 298$ K.

6p

(3p for a correct equation and 3p for correct value)

$T_3 = 298$ K

In the production of refrigeration units it is necessary to consider climatic factors. If a condenser is cooled by atmospheric air, the temperature T_3 increases as the air temperature increases.

4.4. How will the *COP* change if T_3 increases while T_0, T_1, T_2 remain the same?

a) Increase

b) Remain the same

c) Decrease

c

1p

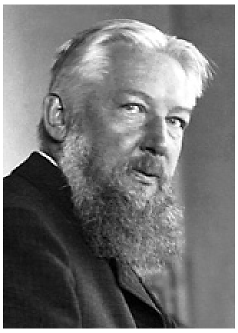
Comment: It will decrease because the length of 0-1 line decreases or because x (see 4.3) increases and less liquid is in the equilibrium mixture at T_0, so less heat Q is necessary to evaporate it!

Problem 2. Coupling of chemical reactions
(7 points)

Question	1			2		3	**Total**
	1.1	1.2	1.3	2.1	2.2		
Marks	4	6	4	3	6	2	**25**


I.Prigogine (left)


N. Shilov


W. Ostwald

When in the system one reaction allows another one to proceed they say that these two reactions are coupled. Ilya Prigogine, Nobel prize winner in chemistry (1977) in his books widely used the concept of “coupled reactions”. Coupling of reactions is an essential feature of living systems, including human body.

How one reaction makes another one to occur? In this problem we are going to discuss several possible mechanisms of coupling.

(I) “Chemical coupling”

“On Chemical coupling” was the title of the dissertation defended by Russian chemist N.Shilov in 1905. N. Shilov was the graduate student of famous professor W. Ostwald. Dr. Shilov described the following set of reactions.
The substance ***A*** does not react with ***Ac***. In the presence of the third reagent (called inductor), ***In***, however, the reaction of ***A*** with ***Ac*** takes place:

$$A + Ac \xrightarrow{\text{In the absence of In}} \text{no reaction!} \qquad (1)$$
$$A + Ac \xrightarrow{\text{In the presence of In}} P_1 \qquad (2)$$

In is not a catalyst! Its concentration decreases in the course of the reactions.

According to the scheme proposed by Shilov, ***Ac*** reacts not with ***A*** itself, but with the intermediate product ***R*** of the reaction of ***A*** with ***In***. There is another, competing reaction of ***R*** that forms P_2.

$$\begin{aligned} &(a) \quad \alpha \boldsymbol{A} + \beta \boldsymbol{In} \xrightarrow{k(3a)} \boldsymbol{R} \\ &(b) \quad \boldsymbol{R} \xrightarrow{k(3b)} \boldsymbol{P}_2 \qquad\qquad (3) \\ &(c) \quad \boldsymbol{R} + \boldsymbol{Ac} \xrightarrow{k(3c)} \boldsymbol{P}_1 \end{aligned}$$

α and β are stoichiometric coefficients. Other stoichiometric coefficients and **reaction order with respect to all reactants in all three reactions are unity.**

In the Shilov's experiments the ratio of the consumed amounts of ***Ac*** and ***In***, $I = \frac{\Delta n_{Ac}}{\Delta n_{In}}$ increased up to the constant value with the increasing initial concentration $[\boldsymbol{Ac}]_0$ at $[\boldsymbol{In}]_0$ = const.

1.1. What was this limiting constant value of I at $[\boldsymbol{Ac}]_0 \to \infty$, $[\boldsymbol{In}]_0$ = const?

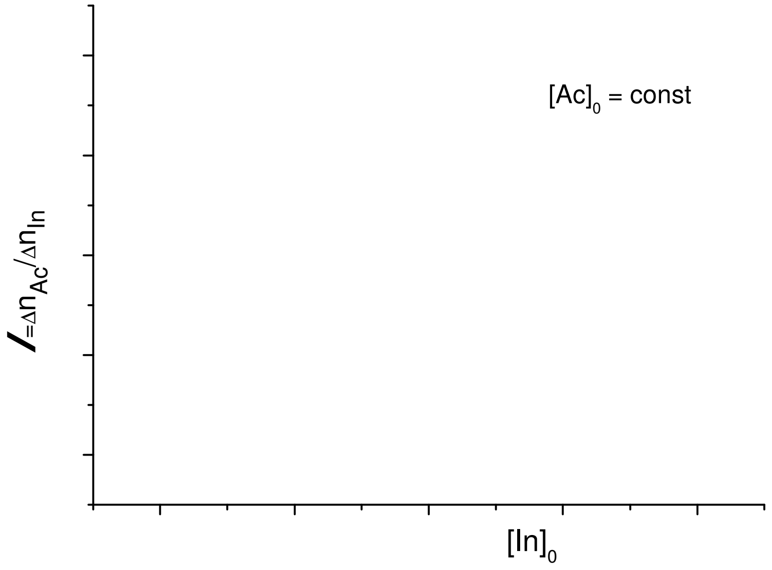
Brief explanation

$I_\infty =$

1.2. Derive an expression for I using the steady-state approximation if necessary. Plot the graph of I vs $[\boldsymbol{In}]_0$ at $[\boldsymbol{Ac}]_0$ = const. Assume that ***In*** was completely consumed and ***Ac*** was in excess..

Calculations

Graph



What if Shilov's mechanism is not valid and ***In*** is a conventional catalyst of the reaction (2)? Simultaneously ***In*** reacts with ***A*** and its concentration decreases. The reaction scheme in this case is

$$\begin{aligned} &(a) \quad \alpha \boldsymbol{A} + \beta \boldsymbol{In} \longrightarrow \boldsymbol{P}_2 \\ &(b) \quad \boldsymbol{A} + \boldsymbol{Ac} \xrightarrow{\boldsymbol{In},\ \text{catalysis}} \boldsymbol{P}_1 \end{aligned} \qquad (4)$$

1.3. What is the limiting value of *I* for the reaction scheme (4) at $[\boldsymbol{Ac}]_0 \rightarrow \infty$, $[\boldsymbol{In}]_0$ = const?

Brief explanation

$I_\infty =$

(II) «Kinetic coupling»

The standard Gibbs energy of the gas-phase reaction

$$\mathrm{Br} + \mathrm{H}_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \mathrm{HBr} + \mathrm{H} \qquad (5)$$

is positive, $\Delta G°(5) = 66$ kJ·mol^{-1} at $T = 600$ K.

2.1. What is the ratio of the rates of forward and reverse reactions, $\frac{r_5}{r_{-5}}$, at this temperature, standard pressures of H_2 and HBr and equal pressures of H and Br?

Calculations

$\frac{r_5}{r_{-5}} =$

If you could not answer this question, for further calculations use the reference value $r_5/r_{-5} = 3.14 \cdot 10^{-7}$.

Reaction (5) proceeds in the forward direction due to the reaction (6) which simultaneously occurs in the system:

$$Br + H_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} HBr + H \qquad (5)$$

$$H + Br_2 \xrightarrow{k_6} HBr + Br \qquad (6)$$

k_5, k_{-5}, k_6 are rate constants of forward and reverse reaction (5) and forward reaction (6), respectively.

This is the *kinetic coupling* of two reactions.

Let pressures of neutral molecules keep standard values $p(H_2) = p(Br_2) = p(HBr) = 1$ bar, and pressures of radicals $p(H)$, $p(Br)$ reach steady-state values. Rate constant k_6 is 10 times larger than k_{-5}.

2.2. Calculate $\Delta G(5)$ and $\frac{r_5}{r_{-5}}$ under such conditions.

Calculations

$\Delta G(5) =$

$\frac{r_5}{r_{-5}} =$

(III) "Second law of thermodynamics restricts coupling"

According to the Second Law of thermodynamics, two simultaneously occurring chemical reactions should decrease the system's Gibbs energy G_{syst}, $\frac{\Delta G_{\text{Syst}}}{\Delta t} < 0$.

One of these reactions may have positive Gibbs energy and still proceed in the forward direction due to the coupling with the second reaction. This second reaction must have negative Gibbs energy and the requirements of the Second law must be fulfilled! Consider the example.

The synthesis of urea under specific conditions

$$2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O \qquad (7)$$

$\Delta G(7) = 46.0$ kJ·mol^{-1}

is supposed to be coupled with the complete oxidation of glucose (under the same conditions)

$$1/6\ C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O \qquad (8)$$

$\Delta G(8) = -481.2$ kJ·mol^{-1},

$r(8) = 6.0 \cdot 10^{-8}$ M·min^{-1}.

Both reactions are presented schematically. No other reactions are considered.

3. What is the maximum rate of the reaction (7) permitted by the Second Law if this reaction is coupled to reaction (8)?

Calculations $r_7(\text{max})$ =

Problem 2. Coupling of chemical reactions
(7 points)

Question	1			2		3	Total
	1.1	1.2	1.3	2.1	2.2		
Marks	4	6	4	3	6	2	**25**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$$\boldsymbol{A} + \boldsymbol{Ac} \xrightarrow{\text{In the absence of In}} \text{no reaction!} \qquad (1)$$

$$\boldsymbol{A} + \boldsymbol{Ac} \xrightarrow{\text{In the presence of In}} \boldsymbol{P}_1 \qquad (2)$$

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According to the scheme proposed by Shilov, ***Ac*** reacts not with ***A*** itself, but with the intermediate product ***R*** of the reaction of ***A*** with ***In***. There is another, competing reaction of ***R*** that forms $\boldsymbol{P}_2$.

$$
\begin{aligned}
&(a) \quad \alpha A + \beta \boldsymbol{In} \xrightarrow{k(3a)} \boldsymbol{R} \\
&(b) \quad \boldsymbol{R} \xrightarrow{k(3b)} \boldsymbol{P}_2 \qquad\qquad\qquad (3) \\
&(c) \quad \boldsymbol{R} + \boldsymbol{Ac} \xrightarrow{k(3c)} \boldsymbol{P}_1
\end{aligned}
$$

α and β are stoichiometric coefficients. Other stoichiometric coefficients and **reaction order with respect to all reactants in all three reactions are unity.**

In the Shilov's experiments the ratio of the consumed amounts of ***Ac*** and ***In***, $I = \frac{\Delta n_{Ac}}{\Delta n_{In}}$ increased up to the constant value with the increasing initial concentration $[\boldsymbol{Ac}]_0$ at $[\boldsymbol{In}]_0$ = const.

1.1. What was this limiting constant value of I at $[\boldsymbol{Ac}]_0 \to \infty$, $[\boldsymbol{In}]_0$ = const?

Brief explanation

The value of I should increase with the increase of $[\boldsymbol{Ac}]_0$ at $[\boldsymbol{In}]_0$ = const, because the larger fraction of the intermediate product ***R*** will enter the reaction (3c). The maximum value of I will be achieved if all ***R*** reacts in (3c), therefore $I_\infty = 1/\beta$.

$I_\infty = 1/\beta$ **4 points** (**2 points** if only $I_\infty = 1/\beta$ is given!)

1.2. Derive an expression for I using the steady-state approximation if necessary. Plot the graph of I vs $[\boldsymbol{In}]_0$ at $[\boldsymbol{Ac}]_0$ = const. Assume that ***In*** was completely consumed and ***Ac*** was in excess..

Calculations

Shilov's mechanism includes the initial reaction

$\alpha A + \beta \boldsymbol{In} \to \boldsymbol{R}$ (3a)

and two competitive reactions

$\boldsymbol{R} + \boldsymbol{Ac} \to \boldsymbol{P}_1$ (3c)

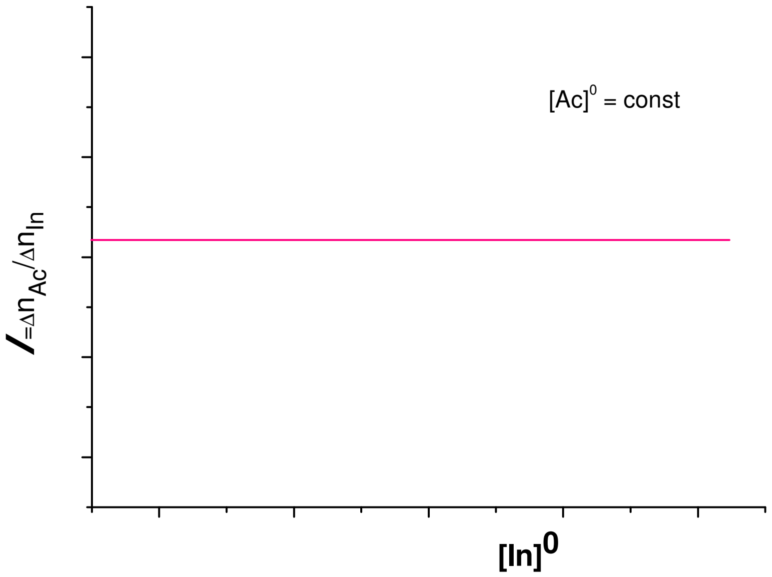
$\boldsymbol{R} \to \boldsymbol{P}_2$ (3b)

The rates of conversion of ***In*** and ***Ac*** are determined by the rates of the reactions (3a) and (3c), respectively:

$$\frac{r(3c)}{r(3a)}=\frac{k(3c)[R][Ac]}{k(3a)[A][In]}=\frac{k(3c)[Ac]\times\frac{k(3a)[A][In]}{k(3c)[Ac]+k(3b)}}{k(3a)[A][In]}=\frac{k(3c)[Ac]}{k(3c)[Ac]+k(3b)}$$

in steady-state approximation for [***R***]. We see that the ratio of two rates does not depend on the initial concentration $[\boldsymbol{In}]_0$ and *I* will also not depend on it. This gives the straight line parallel to the $[\boldsymbol{In}]_0$ axis on the graph.

Graph



6 points (**2 points** for the graph + **4 points** for the steady-state equations)

What if Shilov's mechanism is not valid and ***In*** is a conventional catalyst of the reaction (2)? Simultaneously ***In*** reacts with ***A*** and its concentration decreases. The reaction scheme in this case is

$$\begin{aligned}&(a)\quad \alpha \boldsymbol{A}+\beta \boldsymbol{In}\longrightarrow \boldsymbol{P}_2\\&(b)\quad \boldsymbol{A}+\boldsymbol{Ac}\xrightarrow{\boldsymbol{In},\ \text{catalysis}}\boldsymbol{P}_1\end{aligned}\qquad(4)$$

1.3. What is the limiting value of *I* for the reaction scheme (4) at $[\boldsymbol{Ac}]_0 \to \infty$, $[\boldsymbol{In}]_0 = \text{const}$?

Brief explanation

In this case *I* will permanently increase with the increase of $[\boldsymbol{Ac}]_0 \to \infty$ at $[\boldsymbol{In}]_0 = \text{const}$. The rate of the reaction (4b) may be so high that conversion of ***In*** in reaction (4a) will be negligible. Hence $I \to \infty$ if $[\boldsymbol{Ac}]_0 \to \infty$ at $[\boldsymbol{In}]_0 = \text{const}$.

$I_\infty = \infty$ (infinity) **4 points** (**2 points** if only $I_\infty = \infty$ (infinity) is given).

(II) «Kinetic coupling»

The standard Gibbs energy of the gas-phase reaction

$$\mathrm{Br} + \mathrm{H_2} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \mathrm{HBr} + \mathrm{H} \qquad (5)$$

is positive, $\Delta G^\circ(5) = 66\ \mathrm{kJ{\cdot}mol^{-1}}$ at $T = 600$ K.

2.1. What is the ratio of the rates of forward and reverse reactions, $\frac{r_5}{r_{-5}}$, at this temperature, standard pressures of H_2 and HBr and equal pressures of H and Br?

Calculations

The standard Gibbs energy of reaction (5) at 600K is 66 kJ/mol. The equilibrium constant is

$$K = e^{-66000/8.314/600} = 1.8\cdot10^{-6} = k_5 / k_{-5}.$$ **1 point**

Reaction is considered at standard pressures of all the reactants and products. The ratio of the rates of forward and reverse reactions is

$$\frac{r_5}{r_{-5}} = \frac{k_5[\mathrm{Br}][\mathrm{H_2}]}{k_{-5}[\mathrm{HBr}][\mathrm{H}]} = \frac{k_5}{k_{-5}} = 1.8\cdot10^{-6}$$

$$\frac{r_5}{r_{-5}} = 1.8\cdot10^{-6}$$ **2 points**

Total – **3 points**

If you could not answer this question, for further calculations use reference value $r_5/r_{-5} = 3.14\cdot10^{-7}$.

Reaction (5) proceeds in the forward direction due to the reaction (6) which simultaneously occurs in the system:

$$\mathrm{Br} + \mathrm{H_2} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \mathrm{HBr} + \mathrm{H} \qquad (5)$$

$$\mathrm{H} + \mathrm{Br_2} \xrightarrow{k_6} \mathrm{HBr} + \mathrm{Br} \qquad (6)$$

k_5, k_{-5}, k_6 are rate constants of forward and reverse reaction (5) and forward reaction (6), respectively.

This is the *kinetic coupling* of two reactions.

Let pressures of neutral molecules keep standard values $p(H_2)$ = $p(Br_2)$ = p(HBr) = 1 bar, and pressures of radicals p(H), p(Br) reach steady-state values. Rate constant k_6 is 10 times larger than k_{-5}.

2.2. Calculate ΔG(5) and $\frac{r_5}{r_{-5}}$ under such conditions.

Calculations

The steady-state condition is the same for both radicals, e.g. for radical H

$$\frac{d[\mathrm{H}]}{dt} = k_5[\mathrm{Br}][\mathrm{H_2}] - k_{-5}[\mathrm{HBr}][\mathrm{H}] - k_6[\mathrm{H}][\mathrm{Br_2}] = 0$$

$$\frac{[\mathrm{H}]}{[\mathrm{Br}]} = \frac{k_5[\mathrm{H_2}]}{k_{-5}[\mathrm{HBr}] + k_6[\mathrm{Br_2}]}$$

The concentrations of all the neutral molecules are the same (they correspond to the pressure of 1 bar), therefore

$$\frac{[\mathrm{H}]}{[\mathrm{Br}]} = \frac{k_5}{k_{-5} + k_6} = \frac{k_5 / k_{-5}}{1 + k_6 / k_{-5}} = \frac{1.8 \cdot 10^{-6}}{1 + 10} = 1.6 \cdot 10^{-7}$$ **2 points**

The Gibbs energy of reaction (5) under such conditions is:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\mathrm{H}][\mathrm{HBr}]}{[\mathrm{Br}][\mathrm{H_2}]} = 66 + 8.314 \cdot 10^{-3} \cdot 600 \cdot \ln\left(1.6 \cdot 10^{-7}\right) = -12\,\mathrm{kJ \cdot mol^{-1}}$$

2 points

The ratio of rates is:

$$\frac{r_5}{r_{-5}} = \frac{k_5[\mathrm{Br}][\mathrm{H_2}]}{k_{-5}[\mathrm{HBr}][\mathrm{H}]} = \frac{k_5}{k_{-5}}\frac{[\mathrm{Br}]}{[\mathrm{H}]} = \frac{k_5}{k_{-5}}\frac{1 + k_6 / k_{-5}}{k_5 / k_{-5}} = 1 + \frac{k_6}{k_{-5}} = 11$$ **2 points**

ΔG(5) = –12 kJ·mol^{-1}

$\frac{r_5}{r_{-5}}$ = 11

Total – **6 points**

(III) "Second law of thermodynamics restricts coupling"

According to the Second Law of thermodynamics, two simultaneously occurring chemical reactions should decrease the system's Gibbs energy G_{Syst}, $\frac{\Delta G_{\text{Syst}}}{\Delta t} < 0$.

One of these reactions may have positive Gibbs energy and still proceed in the forward direction due to the coupling with the second reaction. This second reaction must have negative Gibbs energy and the requirements of the Second law must be fulfilled! Consider the example.

The synthesis of urea under specific conditions

$$2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O \qquad (7)$$

$\Delta G(7) = 46.0\ \text{kJ}\cdot\text{mol}^{-1}$

is supposed to be coupled with the complete oxidation of glucose (under the same conditions)

$$1/6\ C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O \qquad (8)$$

$\Delta G(8) = -481.2\ \text{kJ}\cdot\text{mol}^{-1}$,
$r(8) = 6.0\cdot10^{-8}\ \text{M}\cdot\text{min}^{-1}$.

Both reactions are presented schematically. No other reactions are considered.

3. What is the maximum rate of the reaction (7) permitted by the Second Law if this reaction is coupled to reaction (8)?

Calculations

According to the Second law the following condition has to be met:

$$\frac{\Delta G_{\text{Syst}}}{\Delta t} = \Delta G(7)\times r_7 + \Delta G(8)\times r_8 \le 0$$

therefore

$$r_7 \le \frac{-\Delta G(8)}{\Delta G(7)} r_8 = \frac{481.2}{46.0}\cdot 6.0\cdot 10^{-8} = 6.3\cdot 10^{-7}\ \text{M}\cdot\text{min}^{-1}$$

This is the maximum possible rate of the coupled reaction.

$r_7(\text{max}) = 6.3\cdot10^{-7}\ \text{M}\cdot\text{min}^{-1}$ **2 points**

2. Diagnosis of diseases

The derivative of glucose, 2-deoxy-2-(^{18}F)fluoro-D-glucose (FDG), is the most common radiopharmaceuticals for diagnosis of cancer using positron emission tomography. The first step of FDG preparation is to produce a radionuclide fluoro-18 by nuclear reaction in a cyclotron. The next step is the radiochemical synthesis. Fluorine-18 is introduced into D-glucose molecule by nucleophilic substitution. 2-deoxy-2-(^{18}F)fluoro-D-glucose once injected into the patient actively accumulates in cells of malignant tumors; this process is accompanied by decomposition of fluorine-18. This radionuclide is a β^+ emitter – nucleus emits a positron (anti-electron). Positron interacts with an electron and after that annihilation occurs, which can be detected. This allows determining precisely the tumor sizes and type.

2.1. Complete the nuclear reactions leading to various fluorine isotopes.

a) $^{18}O + {}^{1}_{1}H \rightarrow \ldots + {}^{18}F$

b) $\ldots + {}^{2}_{1}D \rightarrow {}^{18}F + \alpha$

c) $^{19}F + {}^{2}_{1}D \rightarrow {}^{20}F + \ldots$

d) $^{16}O + \ldots \rightarrow {}^{18}F + {}^{1}_{1}H + n$

2.2. The decay mode of unstable light nuclei depends on the ratio between the number of neutrons and protons in them. If this ratio is greater than that for a stable isotope then the nucleus decays in a β^--mode, if it is smaller – in a β^+-mode.

Determine the type of decay for the nuclei in the table:

Nucleus	^{11}C	^{20}F	^{17}F	^{14}C
Decay mode				

When nuclear reaction (a) is used for fluorine-18 preparation, the target material is presented as water enriched with $H_2{}^{18}O$. The presence of usual water $H_2{}^{16}O$ leads to a side nuclear reaction with ^{16}O, leading to the formation of isotope ^{17}F.

2.3. It is known that within five minutes after completion of irradiation of the target the ratio of radioactivities of ^{18}F and ^{17}F is 10^5. Assuming that irradiation time is short and the radioactivity of each isotope is proportional to the nuclear reaction yield and the mole fraction of a component in the irradiated target, **calculate** the mass fraction of $H_2{}^{18}O$ in the target. $t_{1/2}(^{18}F)$ = 109.7 minutes, $t_{1/2}(^{17}F)$ = 65 seconds. The ratio between nuclear reactions yields is $\eta_{^{18}O-^{18}F} / \eta_{^{16}O-^{17}F}$ = 144.7.

2.4. Calculate the yield of labeling D-glucose with fluorine-18, if initial radioactivity of a fluorine-18 sample was 600.0 MBq and radioactivity of the obtained 2-deoxy-2-(^{18}F)fluoro-D-glucose is 528.2 MBq. Synthesis time is 3.5 minutes.

η =

2.5. Biological half-life (through the excretory organs) of 2-deoxy-2-(^{18}F)fluoro-D-glucose is 120.0 minutes. How much radioactivity (in MBq) will remain in the patient ten hours after injection of FDG with the initial radioactivity of 450.0 MBq.

nucleophilic substitution. 2-deoxy-2-(^{18}F)fluoro-D-glucose once injected into the patient actively accumulates in cells of malignant tumors; this process is accompanied by decomposition of fluorine-18. This radionuclide is a β^+ emitter – nucleus emits a positron (anti-electron). Positron interacts with an electron and after that annihilation occurs, which can be detected. This allows determining precisely the tumor sizes and type.

2.1. Complete the nuclear reactions leading to various fluorine isotopes.

a)	$^{18}O + {}^{1}_{1}H \rightarrow \ldots + {}^{18}F$	n	**0.5 points**
b)	$\ldots + {}^{2}_{1}D \rightarrow {}^{18}F + \alpha$	^{20}Ne	**0.5 points**
c)	$^{19}F + {}^{2}_{1}D \rightarrow {}^{20}F + \ldots$	${}^{1}_{1}H$	**0.5 points**
d)	$^{16}O + \ldots \rightarrow {}^{18}F + {}^{1}_{1}H + n$	α or ${}^{4}_{2}He$	**0.5 points**

2.2. The decay mode of unstable light nuclei depends on the ratio between the number of neutrons and protons in them. If this ratio is greater than that for a stable isotope then the nucleus decays in a β^--mode, if it is smaller – in a β^+-mode.

Determine the type of decay for the nuclei in the table:

Nucleus	^{11}C	^{20}F	^{17}F	^{14}C
Decay mode	β^+	β^-	β^+	β^-
	0.5 points	**0.5 points**	**0.5 points**	**0.5 points**

When nuclear reaction (a) is used for fluorine-18 preparation, the target material is presented as water enriched with $H_2{}^{18}O$. The presence of usual water $H_2{}^{16}O$ leads to a side nuclear reaction with ^{16}O, leading to the formation of isotope ^{17}F.

2.3. It is known that within five minutes after completion of irradiation of the target the ratio of radioactivities of ^{18}F and ^{17}F is 10^5. Assuming that irradiation time is short, the radioactivity of each isotope is proportional to the nuclear reaction yield and the mole fraction of a component in the irradiated target, **calculate** the mass fraction of $H_2{}^{18}O$ in the target. $t_{1/2}(^{18}F)$ = 109.7 minutes, $t_{1/2}(^{17}F)$ = 65 seconds. The ratio between nuclear reactions yields is $\eta_{^{18}O-^{18}F}/\eta_{^{16}O-^{17}F} = 144.7$.

Radioactivity is:

$A = \lambda N$, where N is the number of atoms, $\lambda = \ln 2 / t_{1/2}$ **1 point**

The initial ratio of radioactivities:

$$\frac{A_0(^{18}\mathrm{F})}{A_0(^{17}\mathrm{F})} = \frac{\lambda\left(^{18}\mathrm{F}\right)}{\lambda\left(^{17}\mathrm{F}\right)}\cdot\frac{\eta(^{18}\mathrm{O}\to{}^{18}\mathrm{F})}{\eta(^{16}\mathrm{O}\to{}^{17}\mathrm{F})}\cdot\frac{\chi(\mathrm{H_2}^{18}\mathrm{O})}{\chi(\mathrm{H_2}^{16}\mathrm{O})} = \frac{65/60}{109.7}\cdot 144.7\cdot\frac{\chi(\mathrm{H_2}^{18}\mathrm{O})}{\chi(\mathrm{H_2}^{16}\mathrm{O})} = 1.43\frac{\chi(\mathrm{H_2}^{18}\mathrm{O})}{\chi(\mathrm{H_2}^{16}\mathrm{O})}$$

After 5 minutes the ratio changed due to radioactive decay of fluorine:

$$\frac{A_{300}(^{18}\mathrm{F})}{A_{300}(^{17}\mathrm{F})} = \frac{A_0(^{18}\mathrm{F})\cdot\exp\left(-\frac{\ln 2}{109.7}\cdot 5\right)}{A_0(^{17}\mathrm{F})\cdot\exp\left(-\frac{\ln 2}{65}\cdot 300\right)} = 23.75\cdot\frac{A_0(^{18}\mathrm{F})}{A_0(^{17}\mathrm{F})} = 33.94\cdot\frac{\chi(\mathrm{H_2}^{18}\mathrm{O})}{\chi(\mathrm{H_2}^{16}\mathrm{O})} = 10^5$$

1 point

$$\frac{\chi(\mathrm{H_2}^{18}\mathrm{O})}{\chi(\mathrm{H_2}^{16}\mathrm{O})} = 2947$$

1 point

Mass fraction of $\mathrm{H_2}^{18}\mathrm{O}$ is:

$$\omega(\mathrm{H_2}^{18}\mathrm{O}) = \frac{2947\cdot 20}{2947\cdot 20+18} = 0.9997$$

1 point

$\omega(\mathrm{H_2}^{18}\mathrm{O}) = 0.9997 = 99.97\%$.

Total – **4 points**

2.4. Calculate the yield of labeling D-glucose with fluorine-18, if initial radioactivity of a fluorine-18 sample was 600.0 MBq and radioactivity of the obtained 2-deoxy-2-(^{18}F)fluoro-D-glucose is 528.2 MBq. Synthesis time is 3.5 minutes.

During the synthesis, the radioactivity will decrease:

$$A_{3.5} = A_0\cdot\exp\left(-\frac{\ln 2}{109.7}\cdot 3.5\right) = 586.9\ \mathrm{MBq}$$

1 point

$\eta = 528.2 / 586.9 = 0.900 = 90.0\%$

1 point

2.5. Biological half-life (through the excretory organs) of 2-deoxy-2-(^{18}F)fluoro-D-glucose is 120.0 minutes. How much radioactivity (in MBq) will remain in the patient ten hours after injection of FDG with the initial radioactivity of 450.0 MBq.

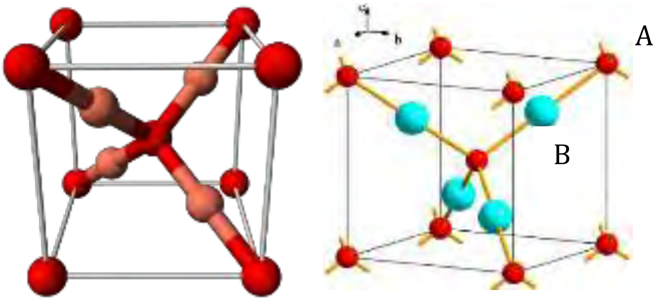
Radioactivity is excreted by radioactive decay and through the excretory organs (e.g. kidneys). The excretion process may be considered as two competitive first-order reactions. Activity after one hour is:

$$A_{60} = A_0\exp\left(-(\lambda_1+\lambda_2)t\right) = 450\cdot\exp\left(-\left(\frac{\ln 2}{109.7}+\frac{\ln 2}{120}\right)\cdot 600\right) = 0.32\ \mathrm{MBq}$$

2 points.

Problem 2 8% of the total

One of the first materials used in solid state electronics was red copper(I) oxide. Interest is renewed nowadays because it could be a non-toxic and cheap component of solar cells.



The two figures above depict the cubic unit cell of the Cu_2O crystal. The lattice constant of the structure is 427.0 pm.

2.1.1. Which of the atoms (A or B) is copper?
Which basic structure (primitive cubic, face centered cubic, body centered cubic, diamond) is formed by the A atoms and which structure is formed by the B atoms?
What are the coordination numbers of the atoms?

2.1.2. Calculate the smallest O-O, Cu-O and Cu-Cu distances in the structure.

2.1.3. What is the density of pure copper(I) oxide?

A common defect in this crystal is some copper atoms missing with the oxygen lattice unchanged. The composition of one such crystal sample was studied, and 0.2% of all copper atoms were found to be in oxidation state +2.

2.2. What percentage of normal copper sites are empty in the crystal sample? What is x in the empirical formula $Cu_{2-x}O$ of the crystal?

Copper(I) oxide is insoluble in water. It is stable in dry air, but humidity in the air catalyzes a transformation (Reaction 1).

When copper(I) oxide is dissolved in dilute sulfuric acid, a blue solution containing a precipitate is formed without evolution of a gas (Reaction 2). When hot, concentrated sulfuric acid is used, no precipitate remains, but an odorous gas forms (Reaction 3). The same gas forms when the precipitate from reaction 2 is dissolved in hot concentrated sulfuric acid.

2.3. Write balanced chemical equations for reactions (1-3).

Copper(I) oxide can be produced in a number of ways. Heating copper in air is a common method in the synthesis of semiconductor Cu_2O. In a pure oxygen atmosphere, the three species containing copper (Cu(s), Cu_2O(s) or CuO(s)) can potentially interconvert.

Suppose that the $\Delta_f H^o$ and S^o data given for 10^5 Pa are independent of temperature:

	$\Delta_f H^o$ / kJ mol^{-1}	S^o/ J mol^{-1} K^{-1}
Cu(s)	0	65
O_2(g)	0	244
CuO(s)	−156	103
Cu_2O(s)	−170	180

2.4. Determine the temperature ranges, if any, of thermodynamic stability of copper and its oxides between 500 and 1500 K in a 10^5 Pa oxygen atmosphere.

Important data are given for 298 K. Use this temperature in the following calculations:

$K_{sp}(Cu(OH)_2)=2\cdot 10^{-19}$

$Cu_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Cu(s) + 2OH^-(aq)$ $E^o= -0.360$ V

$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$ $E^o= +0.159$ V

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ $E^o= +0.337$ V

One possibility for producing Cu_2O is the anodic oxidation of copper. Electrolysis of an aqueous basic solution (e.g. NaOH) with a copper anode and platinum cathode can lead to formation of copper(I) oxide on the anode.

2.5. Write the half reaction equations for the electrode processes during the anodic production of Cu_2O in NaOH solution with a platinum cathode and copper anode.

Electrolytic reduction of copper(II) ions in solution is another possibility.

2.6.1. Write the half reaction equation of the cathode process giving Cu_2O in acidic medium.

Let us use 0.100 mol dm^{-3} Cu^{2+} solution and carry out electrolysis with platinum electrodes.

2.6.2. What is the maximum pH at which the concentration of copper(II) can be maintained at 0.100 mol dm^{-3}?

If the pH is too low, reduction to metallic copper is preferred to the formation of copper(I) oxide.

2.6.3. What is the minimum pH at which the cathodic production of Cu_2O in a 0.100 mol dm^{-3} Cu^{2+} solution is still possible?

Problem 2 8% of the total

2.1.1	2.1.2	2.1.3	2.2	2.3	2.4	2.5	2.6.1	2.6.2	2.6.3	Sum
5	3	2	2	3	6	2	1	3	6	33

2.1.1. Which of the atoms (A or B) is copper?

Cu: There are 2 A atoms and 4 B atoms in the cell. Cu: B

Which basic structure (primitive cubic, face centered cubic, body centered cubic, diamond) is formed by the A atoms and which structure is formed by the B atoms?

	pr. cubic	fcc	bcc	diamond
A				
B				

B: fcc A: bcc

What are the coordination numbers of the atoms?

A: B: B: 2 A: 4

2.1.2. Calculate the smallest O-O, Cu-O and Cu-Cu distances in the structure.

Your work:

O-O:

Cu-O:

Cu-Cu:

O-O: half of the cell body diagonal $1/2\cdot 427.0\ \text{pm}\cdot\sqrt{3} = 369.8$ pm.

Cu-O: 1/4th of the cell body diagonal $1/4\cdot 427.0\ \text{pm}\cdot\sqrt{3} = 184.9$ pm.

Cu-Cu: half of the face diagonal: $1/2\cdot 427.0\ \text{pm}\cdot\sqrt{2} = 301.9$ pm.

1p each, no penalty for Cu and O switched.

2.1.3. What is the density of pure copper(I) oxide?

Your work:

The volume of the unit cell is $(427.0\ \text{pm})^3$.
The mass of a unit cell is $(4M_{Cu} + 2\,M_O)/\,N_A$. The density is 6.106 g/cm^3.

2p

density:

2.2. What percentage of normal copper sites are empty in the crystal sample?

Your work:

From 1000 coppers 998 atoms are Cu(I) and 2 are Cu(II). To balance the charge of the anions, there has to be 2 vacant Cu sites.
The percentage of empty sites is: 2/1002 ≈ 0.2%

1 p

percentage:

What is x in the empirical formula $Cu_{2\text{-}x}O$ of the crystal?

Your work:

0.2% of 2 coppers is missing. That is 0.004.

1 p

x:

2.3. Write balanced chemical equations for reactions (1-3).

Reaction 1:

(1) $2\ Cu_2O + O_2 \longrightarrow 4\ CuO$ (copper(II)-hydroxides and carbonates accepted)

Reactio

(2) $Cu_2O + 2\ H^+ \longrightarrow Cu + Cu^{2+} + H_2O$

(3) $Cu_2O + H_2SO_4 + 4\ H^+ \longrightarrow 2\ Cu^{2+} + SO_2 + 3\ H_2O$

Reactio

3p (non-ionic equations also accepted)

2.4. Determine the temperature ranges, if any, of thermodynamic stability of copper and its oxides between 500 and 1500 K in a 10^5 Pa oxygen atmosphere.

Your work:

$\Delta_f G(\text{CuO}) = -156000\ \text{J mol}^{-1} + 84\ \text{J mol}^{-1}\ \text{K}^{-1}\ T$
$\Delta_f G(\text{Cu}_2\text{O}) = -170000\ \text{J mol}^{-1} + 72\ \text{J mol}^{-1}\ \text{K}^{-1}\ T$

Both Gibbs energies of formation are negative in the range 500-1500 K, so the oxides are more stable than the elements. Cu is not stable.

Looking at the conversion process: $2\ CuO = Cu_2O + 0.5\ O_2$
$\Delta_r G = 142000\ \text{J mol}^{-1} - 96\ \text{J mol}^{-1}\ \text{K}^{-1}\ T$
The Gibbs energy of the reaction is negative above 1480 K.
CuO is stable below 1480 K, Cu_2O above 1480 K.

6 p (1 for each ΔG or equivalent calculation, 1 for each conclusion)

Temperature range between 500-1500K	The most stable form (Cu, Cu_2O or CuO)

2.5. Write the half reaction equations for the electrode processes during the anodic production of Cu_2O in NaOH solution with a platinum cathode and copper anode.

Cathode

C: $2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$

A: $2\ Cu + 2\ OH^- \longrightarrow Cu_2O + H_2O + 2e^-$

Anode:

2p

2.6.1. Write the half reaction equation of the cathode process giving Cu_2O in acidic medium.

$2\ Cu^{2+} + H_2O + 2\ e^- \longrightarrow Cu_2O + 2\ H^+$

1p

2.6.2. What is the maximum pH at which the concentration of copper(II) can be maintained at 0.100 mol dm^{-3}?

Your work:

If the pH is too high, $Cu(OH)_2$ precipitates.

$K_{sp} \geq 0.1[OH^-]^2 \quad \Rightarrow \quad pH \leq 5.15$

3 p (1p realizing that precipitation occurs, 1p equation, 1p result)

maximum pH:

2.6.3. What is the minimum pH at which the cathodic production of Cu_2O in a 0.100 mol dm^{-3} Cu^{2+} solution is still possible?

Your work:

The potential of the cathodic process ($2\ Cu^{2+} + H_2O + 2\ e^- = Cu_2O + 2\ H^+$) depends on the pH.

The standard potential of the cathodic process can be calculated from:

$Cu_2O(s) + H_2O(l) + 2e^- \longrightarrow 2\ Cu(s) + 2\ OH^-(aq)$ $\quad \Delta G^o_1 = -2F(-0.36\ V)$

$Cu^{2+}(aq) + 2\ e^- \longrightarrow Cu(s)$ $\quad \Delta G^o_2 = -2F(+0.337\ V)$

$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$ $\quad \Delta G^o_3 = -RT \ln K_w$

For $2\ Cu^{2+}(aq) + H_2O(l) + 2\ e^- \longrightarrow Cu_2O(s) + 2\ H^+(aq)$:

$\Delta G^o = -\Delta G^o_1 + 2\Delta G^o_2 + 2\Delta G^o_3$

$E^o = -\Delta G^o / 2F = 0.36\ V + 2 \cdot 0.337\ V - (RT/F) \cdot \ln K_w = 0.208\ V$

The concentration dependence of the cathodic Cu_2O production potential:

$E = 0.208\ V + 0.059/2 \log ([Cu^{2+}]^2/[H^+]^2)$

This potential has to be higher than the potential of the reduction of Cu^{2+}.

$0.337 + 0.059/2 \log [Cu^{2+}] = 0.208 + 0.059/2 \log ([Cu^{2+}]^2/[H^+]^2)$

$[H^+]^2 = [Cu^{2+}]/23600$

pH = 2.69

6 p (3p for standard potential, 3p for calculation)

Many other routes possible – all correct ones accepted.

minimum pH:

Problem 4 8% of the total

Application of kinetic studies in water treatment

Industrial waste is a major cause of water pollution and kinetic studies are carried out in a laboratory to design effluent treatment. 1,4-dioxane, more commonly known as dioxane ($C_4H_8O_2$), an industrial solvent and by-product, is a significant water contaminant. It can be oxidised to hazard free chemicals using oxidants such as peroxodisulfate, ozone or hydrogen peroxide.

The data obtained in the kinetic study of oxidation of dioxane with potassium peroxodisulfate ($K_2S_2O_8$) as oxidant and $AgNO_3$ as catalyst at T = 303.15 K are given below. The reaction was monitored by the estimation of unreacted peroxodisulfate. The concentration of $AgNO_3$ used in this study was $1.00 \cdot 10^{-3}$ mmol·dm^{-3}.

Trial	Dioxane mmol·dm^{-3}	$K_2S_2O_8$ mmol·dm^{-3}	Initial rate mmol·dm^{-3}·min^{-1}
1	0.0100	2.50	$1.661 \cdot 10^{-2}$
2	0.0100	5.10	$3.380 \cdot 10^{-2}$
3	0.00500	13.8	$9.200 \cdot 10^{-2}$
4	0.0110	13.8	$9.201 \cdot 10^{-2}$

In many countries the accepted maximum level of dioxane in drinking water is specified as 0.35 μg dm^{-3}.

A water sample contains an initial dioxane concentration of 40.00 μg dm^{-3}. Assume that 1 mol dioxane requires 1 mol of peroxodisulfate for oxidation. The concentration of $AgNO_3$ used in this study was $1.00 \cdot 10^{-3}$ mmol·dm^{-3}.

4.1.1. Calculate the time in minutes the oxidation process has to continue in order to reach the accepted level of dioxane at 303.15 K if the initial concentration of $K_2S_2O_8$ is $5.0 \cdot 10^{-6}$ mol dm^{-3}. Assume that the rate law obtained from the data above is valid under these conditions.

Various mechanisms have been proposed for the peroxodisulfate oxidation of dioxane. Misra and Ghosh (1963) proposed the following mechanism:

$$S_2O_8^{2-} + Ag^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ag^{3+} + 2SO_4^{2-}$$

$$Ag^{3+} + \text{D (dioxane)} \xrightarrow{k_3} \text{D' (dioxane oxidised)} + 2H^+ + Ag^+$$

4.1.2. Assuming Ag(III) to be in steady state, deduce the rate equation for the oxidation of dioxane.

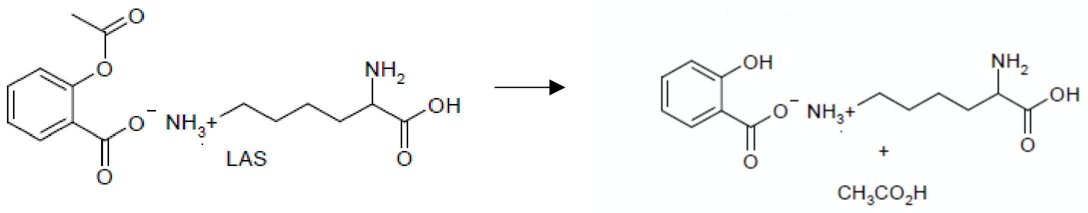
4.1.3. Which of the following is/are correct?

A) The rate equation based on the mechanism given in **4.1.2**, at very high concentrations of dioxane, is consistent with the experimental data in **4.1.1.**
B) The rate equation based on the mechanism given in **4.1.2**, at very low concentrations of dioxane, is consistent with the experimental data in **4.1.1.**
C) The units of the observed rate constant are $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at very high concentrations of dioxane.
D) The units of the observed rate constant are $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at very low concentrations of dioxane.

Degradation of pharmaceutical products – a kinetic overview

Kinetic studies are important in deciding the shelf life of a pharmaceutical product. Several chemical reactions can affect the shelf life of pharmaceutical products and the rates of these reactions depend on conditions such as pH, temperature, humidity.

Lysine acetylsalicylate (LAS) is prescribed as a pain killer and anti-inflammatory drug under the brand name Aspegic. LAS on hydrolysis forms lysine salicylate and acetic acid.



Hydrolysis of LAS can proceed via three different pathways (a) acid catalysed, (b) uncatalysed and (c) base catalysed.

If [LAS] denotes the concentration of LAS at time '*t*', the overall rate of the hydrolysis reaction can be written as

$$-\frac{d[\mathrm{LAS}]}{dt} = \mathrm{k_H[LAS][H^+]} + \mathrm{k_0[LAS]} + \mathrm{k_{OH}[LAS][OH^-]}$$

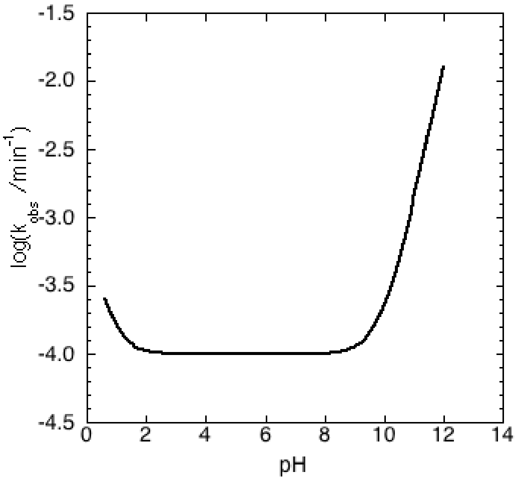
where k_H, k_0 and k_{OH} are the rate constants of the acid catalysed, uncatalysed and base catalysed pathways of hydrolysis, respectively. The observed rate constant is defined by:

$$-\frac{d[\mathrm{LAS}]}{dt} = \mathrm{k_{obs}[LAS]}$$

4.2.1. Write an expression for k_{obs} in terms of k_H, k_0, k_{OH} and $[H^+]$.

Hydrolysis of LAS was carried out at 298.15 K at various pH values (0.50 to 13.0). A very low initial concentration of LAS ensured that the pH did not change during the course of the reaction.

The following graph shows the pH dependence of the hydrolysis of LAS.



4.2.2. Which of the following is/are correct?

A) $k_{obs} \cong k_0$ at pH = 12

B) $k_{obs} \cong k_0$ at pH = 5.0

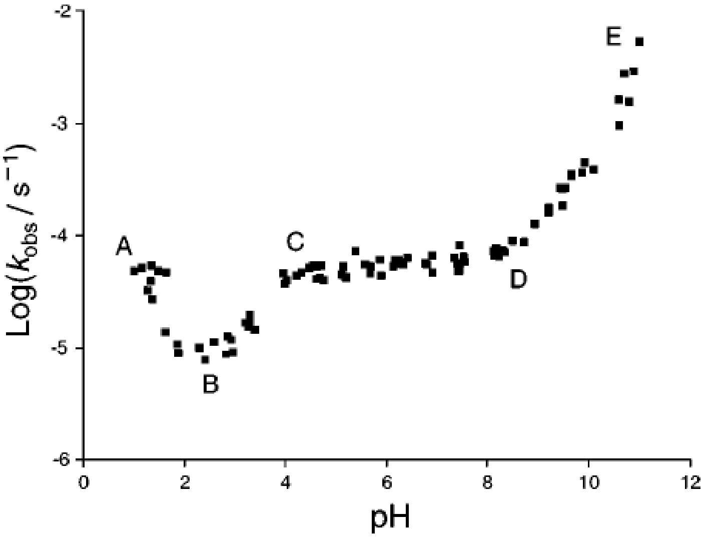
C) The rate of the reaction increases when the pH is changed from 0.50 to 1.0.

D) The rate of the reaction increases when the pH is changed from 10 to 12.

4.2.3. Using the diagram and the data given below, calculate k_H, k_0 and k_{OH}. Make sure to specify the units.

pH	1.300	5.300	12.180
log (k_{obs}/min^{-1})	−3.886	−4.000	−1.726

Acetylsalicylic acid, more commonly known as aspirin, is a medicine often used for reducing fever, pain and inflammation. Like LAS, the hydrolysis of aspirin can also take different pathways depending on the pH. The pH rate profile of aspirin hydrolysis at **333.15 K** is given below:



The following are possible reactions for the hydrolysis of aspirin. Depending on the pH, one or more of these reactions will predominate.

I. $CH_3COOC_6H_4COOH + H_3O^+ \longrightarrow HOC_6H_4COOH + CH_3COOH + H^+$
II. $CH_3COOC_6H_4COOH + H_2O \longrightarrow HOC_6H_4COOH + CH_3COOH$
III. $CH_3COOC_6H_4COOH + OH^- \longrightarrow HOC_6H_4COO^- + CH_3COOH$
IV. $CH_3COOC_6H_4COO^- + H_3O^+ \longrightarrow HOC_6H_4COOH + CH_3COOH$
V. $CH_3COOC_6H_4COO^- + H_2O \longrightarrow HOC_6H_4COO^- + CH_3COOH$
VI. $CH_3COOC_6H_4COO^- + OH^- \longrightarrow HOC_6H_4COO^- + CH_3COO^-$

4.3.1. Using the pH-rate profile diagram and the reactions given above, state which of the following statements is/are correct. (pK_a of aspirin = 3.57 at 333.15 K)

a) In the region C-D, reaction IV is predominant
b) In the region C-D, reaction V is predominant
c) In the region D-E reaction VI is predominant
d) In the region A-B, reaction II is predominant

A separate plot of k_{obs} vs pH for the hydrolysis of aspirin has been confirmed to show a minimum at a particular pH. At **290.15 K** the following rate constants for reactions I, II and III were determined:

k_H (reaction I)	k_0 (reaction II)	k_{OH} (reaction III)
1.99 dm^3·mol^{-1}·day^{-1}	2.29·10^{-4} day^{-1}	3.18·10^9 dm^3·mol^{-1}·day^{-1}

The ionic product of water at 290.15 K can be taken as 1.0·10^{-14}.

4.3.2. Assuming that only reactions I, II and III occur, calculate the value of the pH at the minimum of k_{obs}.

Problem 4 8% of the total

4.1.1	**4.1.2**	**4.1.3**	**4.2.1**	**4.2.2**	**4.2.3**	**4.3.1**	**4.3.2**	Sum
5	3	2	1	2	6	2	4	25

4.1.1. Calculate the time in minutes the oxidation process has to continue in order to reach the accepted level of dioxane at 303.15 K if the initial concentration of $K_2S_2O_8$ is $5.0 \cdot 10^{-6}$ mol/dm^3. Assume that the rate law obtained from the data above is valid under these conditions.

Your work:

Trial1 and 2 ⇒the rate doubles when concentration of $K_2S_2O_8$ is doubled. Order w.r.t. $K_2S_2O_8$ =1.

Trial3 and 4 ⇒the rate does not change with concentration of dioxane. Order w.r.t. dioxane =0.

Initial rate = $k[K_2S_2O_8]$ Average $k = 6.65 \cdot 10^{-3}$ min^{-1}

Change in dioxane concentration: $(40.00 - 0.35)$ μg·dm^{-3} / 88.1 g·mol^{-1} = 0.450 μmol·dm^{-3}

$[K_2S_2O_8]_0$ = 5.00 μmol dm^{-3}; $[K_2S_2O_8]_t$ = 4.55 μmol dm^{-3}

$4.55 = 5.00 \exp(-6.65 \cdot 10^{-3}\, t)$

t = 14.2 minutes

5p (1p for each order, 1 p for k, 2p for final answer)

Oxidation time:

4.1.2. Assuming Ag(III) to be in steady state, deduce the rate equation for the oxidation of dioxane.

Your work:

$$k_1[\mathrm{S_2O_8^{-2}}][\mathrm{Ag^+}] - k_2[\mathrm{SO_4^{-2}}]^2[\mathrm{Ag^{+3}}] - k_3[\mathrm{Ag^{+3}}][\mathrm{D}] = 0$$

$$[\mathrm{Ag^{+3}}] = \frac{k_1[\mathrm{S_2O_8^{-2}}][\mathrm{Ag^+}]}{k_2[\mathrm{SO_4^{-2}}] + k_3[\mathrm{D}]}$$

$$rate\ of\ oxidation = \frac{k_1 k_3[\mathrm{S_2O_8^{-2}}][\mathrm{D}][\mathrm{Ag^+}]}{k_2[\mathrm{SO_4^{-2}}]^2 + k_3[\mathrm{D}]}$$

3p (1p for each step)

4.1.3. A,C

2p, (1p penalty for every mistake)

4.2.1. Write an expression for k_{obs} in terms of k_{H}, k_0, k_{OH} and $[\mathrm{H^+}]$.

Your work:

$$k_{\mathrm{obs}} = k_{\mathrm{H}}[\mathrm{H^+}] + k_0 + k_{\mathrm{OH}}\frac{K_{\mathrm{w}}}{[\mathrm{H^+}]}$$

1p, (0.5p if $[\mathrm{OH^-}]$ is included in the expression)

4.2.2. B, D

2p, (1p penalty for every mistake)

4.2.3. Using the diagram and the data in the table, calculate k_{H}, k_0 and k_{OH}. Make sure to specify the units.

Your work:

At pH = 5.30, k_0 is dominant
$\log(k_{\mathrm{obs}}/\mathrm{min^{-1}}) = -4.000 \Rightarrow k_{\mathrm{obs}} = k_0 = 1.00\cdot10^{-4}\ \mathrm{min^{-1}}$

At pH = 12.18, $[\mathrm{OH^-}] = 0.01514\ \mathrm{mol\ dm^{-3}}$
$\log(k_{\mathrm{obs}}/\mathrm{min^{-1}}) = -1.726 \Rightarrow k_{\mathrm{obs}} = 1.88\cdot10^{-2}\ \mathrm{min^{-1}}$
$k_{\mathrm{obs}} = k_0 + k_{\mathrm{OH}}[\mathrm{OH^-}]$ k_0 can be neglected

$k_{\mathrm{OH}} = k_{\mathrm{obs}}/[\mathrm{OH^-}] = 1.24\ \mathrm{dm^3\cdot mol^{-1}\cdot min^{-1}}$

At pH = 1.30, $[\mathrm{H^+}] = 0.0501\ \mathrm{mol\ dm^{-3}}$
$\log(k_{\mathrm{obs}}/\mathrm{min^{-1}}) = -3.886 \Rightarrow k_{\mathrm{obs}} = 1.30\cdot10^{-4}\ \mathrm{min^{-1}}$
$k_{\mathrm{obs}} = k_{\mathrm{H}}[\mathrm{H^+}] + k_0$ k_0 cannot be neglected

$$k_{\mathrm{H}} = \frac{k_{\mathrm{obs}} - k_0}{[\mathrm{H^+}]} = \frac{3.0\cdot10^{-5}\mathrm{min^{-1}}}{0.0501\mathrm{mol\cdot dm^{-3}}}$$

$k_{\mathrm{H}} = 6.0\cdot10^{-4}\ \mathrm{dm^3\cdot mol^{-1}\cdot min^{-1}}$

6p (1p for k_0, 2p for k_{OH}, 3p for k_{H}, 0.5p penalty for wrong or no units)

k_0:　　　　　k_{OH}:　　　　　k_H:

4.3.1.　　b, c　　2p, (1p penalty for every mistake)

4.3.2. Assuming that only reactions I, II and III occur, <u>calculate</u> the value of the pH at the minimum of k_{obs}.

Your work:

$$k_{obs} = k_H[H^+] + k_0 + k_{OH}\frac{K_w}{[H^+]}$$

This is a minimum if

$$\frac{dk_{obs}}{d[H^+]} = k_H - k_{OH}\frac{K_w}{[H^+]^2} = 0$$

$$[H^+]_{min} = \sqrt{\frac{k_{OH}K_w}{k_H}} \qquad pH_{min} = \frac{1}{2}pK_W + \frac{1}{2}\log\frac{k_H}{k_{OH}} = 2.40$$

or see alternative solution without calculus

4p (3p for expression of [H⁺] at minimum, 1p for numerical result)

k_{obs} is a minimum if $k_H[H^+] + k_{OH}\frac{k_w}{[H^+]}$ is minimal.

The minimum happens when the two terms are equal. So at minimum:

$$k_H[H^+] = k_{OH}\frac{K_w}{[H^+]}$$

$$[H^+]_{min} = \sqrt{\frac{k_{OH}K_w}{k_H}} \qquad pH_{min} = \frac{1}{2}pK_W + \log\frac{k_H}{k_{OH}} = 2.40$$

pH at minimum:

Problem 1

6% of the total

Problem 1	A			B	C	Total
	A1	A2	A3			
Total	4	1	2	7	6	20
Score						

Problem 1: Production of propene using heterogeneous catalysts

Propene or propylene is one of the most valuable chemicals for the petrochemical industry in Thailand and around the world. One good example of the commercial use of propene is for the production of polypropylene (PP).

Part A.

Propene can be synthesized via a direct dehydrogenation of propane in the presence of a heterogeneous catalyst. However, such a reaction is not economically feasible due to the nature of the reaction itself. Provide a concise explanation to each of the questions below. Additional information: H_{bond}(C=C) = 1.77H_{bond}(C-C), H_{bond}(H-H) = 1.05H_{bond}(C-H), and H_{bond}(C-H) = 1.19H_{bond}(C-C), where H_{bond} refers to average bond enthalpy of the indicated chemical bond.

1-A1) What is the enthalpy change of the direct dehydrogenation of propane? Show your calculation and express your answer in terms of H_{bond}(C-C).

<u>Calculation:</u>

1-A2) It is difficult to increase the amount of propene by increasing pressure at constant temperature. Which law or principle can best explain this phenomenon? Select your answer by marking “✓” in **one** of the open circles.

○ Boyle’s law
○ Charles’ law
○ Dalton’s law
○ Raoult’s law
○ Le Chatelier’s principle

1-A3) Initially, the system is in equilibrium. Consistent with question **1-A1)**, what is/are correct set(s) of signs for the following thermodynamic variables of the system for the direct dehydrogenation of propane? Select your answer(s) by marking “✓” in any of the open circle(s).

	ΔH	ΔS	ΔG	T^*
○	-	+	+	lower
○	-	+	-	higher
○	-	-	+	lower
○	-	-	-	higher
○	+	+	+	lower
○	+	+	-	higher
○	+	-	+	lower
○	+	-	-	higher
○	None of the above is correct			

[*] Relative to the initial temperature at the same partial pressure.

Part B.

A better reaction to produce large quantity of propene is the *oxidative dehydrogenation (ODH)* using solid catalysts, such as vanadium oxides, under molecular oxygen gas. Although this type of reaction is still under intense research development, its promise toward the production of propene at an industrial scale eclipses that of the direct dehydrogenation.

1-B) The overall rate of propane consumption in the reaction is $r_{C_3H_8} = \frac{1}{\left(\frac{p^o}{k_{red}\, p_{C_3H_8}} + \frac{p^o}{k_{ox}\, p_{O_2}}\right)}$,

where k_{red} and k_{ox} are the rate constants for the reduction of metal oxide catalyst by propane and for the oxidation of the catalyst by molecular oxygen, respectively, and p^o is the standard pressure of 1 bar. Some experiments found that the rate of oxidation of the catalyst is 100,000 times faster than that of the propane oxidation. The experimental $r_{C_3H_8} = k_{obs}\frac{p_{C_3H_8}}{p^o}$ at 600 K, where k_{obs} is the observed rate constant (0.062 mol s^{-1}). If the reactor containing the catalyst is continuously passed through with propane and oxygen at a total pressure of 1 bar, determine the value of k_{red} and k_{ox} when the partial pressure of propane is 0.10 bar. Assume that the partial pressure of propene is negligible.

Calculation:

Part C.

The metal oxide catalyst contains oxygen atoms on its surface that serve as active sites for the ODH. Denoting red* as a reduced site and O(*s*) as an oxygen atom on the surface of the catalyst, one of the proposed mechanisms for the ODH in the presence of the catalyst can be written as follows:

$$C_3H_8(g) + O(s) \xrightarrow{k_1} C_3H_6(g) + H_2O(g) + \text{red*} \qquad (1)$$

$$C_3H_6(g) + 9O(s) \xrightarrow{k_2} 3CO_2(g) + 3H_2O(g) + 9\text{red*} \qquad (2)$$

$$O_2(g) + 2\text{red*} \xrightarrow{k_3} 2O(s) \qquad (3)$$

Given $\beta = \dfrac{number\ of\ reduced\ sites}{total\ number\ of\ active\ sites}$, the rate laws for the above 3 steps are:

$r_1 = k_1 p_{C_3H_8}(1-\beta)$,

$r_2 = k_2 p_{C_3H_6}(1-\beta)$,

and $r_3 = k_3 p_{O_2}\beta$.

1-C) Assuming that the amount of oxygen atoms on the surface stays constant at any time of reaction, calculate β as a function of *k₁*, *k₂*, *k₃*, $p_{C_3H_8}$, $p_{C_3H_6}$, and p_{O_2}.

Calculation:

Problem 1

6% of the total

Problem 1	A			B	C	Total
	A1	A2	A3			
Total	4	1	2	7	6	20
Score						

Problem 1: Production of propene using heterogeneous catalysts

Propene or propylene is one of the most valuable chemicals for the petrochemical industry in Thailand and around the world. One good example of the commercial use of propene is for the production of polypropylene (PP).

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1-A1) What is the enthalpy change of the direct dehydrogenation of propane? Show your calculation and express your answer in terms of H_{bond}(C-C).

Calculation:

$$\begin{aligned}\Delta H_{rxn} &= -\{H_{bond}(C{=}C)+ H_{bond}(C\text{-}C)+ 6H_{bond}(C\text{-}H)+ H_{bond}(H\text{-}H)\}\\ &\quad +\{2H_{bond}(C\text{-}C)+8H_{bond}(C\text{-}H)\} && \text{(2 points)}\\ &= -\{1.77H_{bond}(C\text{-}C)+ H_{bond}(C\text{-}C)+ 6(1.19H_{bond}(C\text{-}C)+ 1.05(1.19H_{bond}(C\text{-}C)\}\\ &\quad +\{2H_{bond}(C\text{-}C)+8(1.19H_{bond}(C\text{-}C)\}\\ &= +0.360H_{bond}(C\text{-}C) && \text{(2 points)}\end{aligned}$$

1-A2) It is difficult to increase the amount of propene by increasing pressure at constant temperature. Which law or principle can best explain this phenomenon? Select your answer by marking "✓" in **one** of the open circles.

- ○ Boyle's law
- ○ Charles' law
- ○ Dalton's law
- ○ Raoult's law
- ☑ Le Chatelier's principle

1-A3) Initially, the system is in equilibrium. Consistent with question **1-A1)**, what is/are correct set(s) of signs for the following thermodynamic variables of the system for the direct dehydrogenation of propane? Select your answer(s) by marking "✓" in any of the open circle(s).

	ΔH	ΔS	ΔG	T^*
○	-	+	+	lower
○	-	+	-	higher
○	-	-	+	lower
○	-	-	-	higher
☑	+	+	+	lower
☑	+	+	-	higher
○	+	-	+	lower
○	+	-	-	higher
○	None of the above is correct			

* Relative to the initial temperature at the same partial pressure.

If a student provides a negative enthalpy in question 1-A1, full credit will be given if the student selects the 2nd choice. If a student does not answer question 1-A1, he or she will still get full credit if either the two choices indicated above or the 2nd choice are selected.

Part B.

A better reaction to produce large quantity of propene is the *oxidative dehydrogenation (ODH)* using solid catalysts, such as vanadium oxides, under molecular oxygen gas. Although this type of reaction is still under intense research development, its promise toward the production of propene at an industrial scale eclipses that of the direct dehydrogenation.

1-B) The overall rate of propane consumption in the reaction is $r_{C_3H_8} = \dfrac{1}{\left(\dfrac{p^o}{k_{red}\,p_{C_3H_8}} + \dfrac{p^o}{k_{ox}\,p_{O_2}}\right)}$,

where k_{red} and k_{ox} are the rate constants for the reduction of metal oxide catalyst by propane and for the oxidation of the catalyst by molecular oxygen, respectively, and p^o is the standard pressure of 1 bar. Some experiments found that the rate of oxidation of the catalyst is 100,000 times faster than that of the propane oxidation. The experimental $r_{C_3H_8} = k_{obs}\dfrac{p_{C_3H_8}}{p^o}$ at 600 K, where k_{obs} is the observed rate constant (0.062 mol s^{-1}). If the reactor containing the catalyst is continuously passed through with propane and oxygen at a total pressure of 1 bar, determine the value of k_{red} and k_{ox} when the partial pressure of propane is 0.10 bar. Assume that the partial pressure of propene is negligible.

<u>Calculation:</u>

From the information given, the oxidation step is much faster than the propane reduction. Thus, $\dfrac{1}{k_{red}\,p_{C_3H_8}} >> \dfrac{1}{k_{ox}\,p_{O_2}}$. *(1 point)*

We then have $r_{C_3H_8} = k_{red}\,p_{C_3H_8}$. *(2 points)*

Therefore, $k_{obs} = k_{red} = 0.062$ *mol* s^{-1}. *(1 point)*

Since $k_{ox}\,p_{O_2} = 100{,}000 k_{red}\,p_{C_3H_8}$, *(1 point)*

$k_{ox} = 100{,}000(0.062\ mol\ s^{-1})(0.10)/(0.90) = 6.9\times10^{2}\ mol\ s^{-1}$. *(2 points)*

[Deduction of 1 point for incorrect unit(s). In any case, the total point for this question cannot be negative.]

Part C.

The metal oxide catalyst contains oxygen atoms on its surface that serve as active sites for the ODH. Denoting red* as a reduced site and O(*s*) as an oxygen atom on the surface of the catalyst, one of the proposed mechanisms for the ODH in the presence of the catalyst can be written as follows:

$$C_3H_8(g) + O(s) \xrightarrow{k_1} C_3H_6(g) + H_2O(g) + \text{red*} \qquad (1)$$

$$C_3H_6(g) + 9O(s) \xrightarrow{k_2} 3CO_2(g) + 3H_2O(g) + 9\text{red*} \qquad (2)$$

$$O_2(g) + 2\text{red*} \xrightarrow{k_3} 2O(s) \qquad (3)$$

Given $\beta = \dfrac{number\ of\ reduced\ sites}{total\ number\ of\ active\ sites}$, the rate laws for the above 3 steps are:

$r_1 = k_1 p_{C_3H_8}(1-\beta)$,

$r_2 = k_2 p_{C_3H_6}(1-\beta)$,

and $r_3 = k_3 p_{O_2}\beta$.

1-C) Assuming that the amount of oxygen atoms on the surface stays constant at any time of reaction, calculate β as a function of k_1, k_2, k_3, $p_{C_3H_8}$, $p_{C_3H_6}$, and p_{O_2}.

Calculation:

Consumption of oxygen atoms in steps 1+2 = Production of oxygen atoms in step 3

$r_1 + 9r_2 = 2r_3$ *(3 points)*

$k_1 p_{C_3H_8}(1-\beta) + 9k_2 p_{C_3H_6}(1-\beta) = 2k_3 p_{O_2}\beta$ *(1 point)*

$k_1 p_{C_3H_8} + 9k_2 p_{C_3H_6} - \beta(k_1 p_{C_3H_8} + 9k_2 p_{C_3H_6}) = 2k_3 p_{O_2}\beta$

$\beta(k_1 p_{C_3H_8} + 9k_2 p_{C_3H_6} + 2k_3 p_{O_2}) = k_1 p_{C_3H_8} + 9k_2 p_{C_3H_6}$

Thus, $\beta = \dfrac{k_1 p_{C_3H_8} + 9k_2 p_{C_3H_6}}{k_1 p_{C_3H_8} + 9k_2 p_{C_3H_6} + 2k_3 p_{O_2}}$. *(2 points)*

Problem 2

6% of the total

Problem 2	A								Total
	A1	A2	A3	A4	A5	A6	A7	A8	
Total	2	2	7	3	3	1	5	1	24
Score									

Problem 2: Kinetic isotope effect (KIE) and zero-point vibrational energy (ZPE)

Calculation of ZPE and KIE

Kinetic isotope effect (KIE) is a phenomenon associated with a change in rate constant of the reaction when one of the atoms is replaced by its isotope. KIE can be used to confirm whether a particular bond to hydrogen is broken in the reaction. Harmonic oscillator model is used to estimate the difference in the rate between C-H and C-D bond activation (D = ${}^{2}_{1}H$).

The vibrational frequency (ν) represented by harmonic oscillator model is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}},$$

where k is the force constant and μ is the reduced mass.

The vibrational energies of the molecule are given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu \ ,$$

where n is vibrational quantum number with possible values of 0, 1, 2, ... The energy of the lowest vibrational energy level (E_n at $n = 0$) is called **zero-point vibrational energy (ZPE)**.

2-A1) Calculate the reduced mass of C-H (μ_{CH}) and C-D (μ_{CD}) in atomic mass unit. Assume that the mass of deuterium is twice that of hydrogen.

Calculation:

[If students are unable to calculate the values for μ_{CH} and μ_{CD} in **2-A1)**, use $\mu_{CH} = 1.008$ and $\mu_{CD} = 2.016$ for the subsequent parts of the question. Note that the given values are not necessarily close to the correct values.]

2-A2) Given that the force constant (k) for C-H stretching is the same as that for the C-D stretching and the C-H stretching frequency is 2900 cm^{-1}, find the corresponding C-D stretching frequency (in cm^{-1}).

Calculation:

2-A3) According to the C-H and C-D stretching frequencies in question **2-A2**), calculate the zero-point vibrational energies (ZPE) of C-H and C-D stretching in kJ mol^{-1}.

Calculation:

[If students are unable to calculate the values for *ZPE* in **2-A3)**, use ZPE_{CH} = 7.23 kJ/mol and ZPE_{CD} = 2.15 kJ/mol for the subsequent parts of the question. Note that the given values are not necessarily close to the correct values.]

Kinetic isotope effect (KIE)

Due to the difference in zero-point vibrational energies, a protonated compound and its corresponding deuterated compounds are expected to react at different rates.

For the C-H and C-D bond dissociation reactions, the energies of both transition states and both products are identical. Then, the isotope effect is controlled by the difference in the ZPE's of the C-H and C-D bonds.

2-A4) Calculate the difference in the bond dissociation energy (BDE) between C-D bond and C-H bond ($\mathrm{BDE}_{\mathrm{CD}} - BDE_{CH}$) in kJ mol^{-1}.

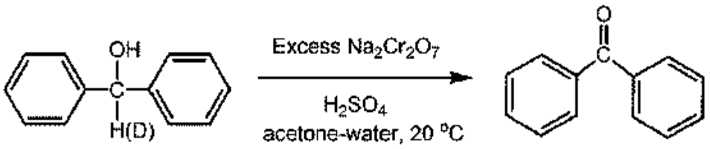
Calculation:

2-A5) Assume that the activation energy (E_a) for the C-H/C-D bond cleavage is approximately equal to the bond dissociation energy and the Arrhenius factor is the same for both C-H and C-D bond cleavage. Find the relative rate constant for the C-H/C-D bond cleavage (k_{CH}/k_{CD}) at 25 °C.

Calculation:

Using KIE to study reaction mechanism

The oxidation of nondeuterated and deuterated diphenylmethanol using an excess of chromic acid was studied.



2-A6) Let C_0 be the initial concentration of either nondeuterated diphenylmethanol or deuterated diphenylmethanol and C_t its concentration at time t. The experiment led to two plots (Figure 2a and Figure 2b), from which the first-order rate constant can be determined.

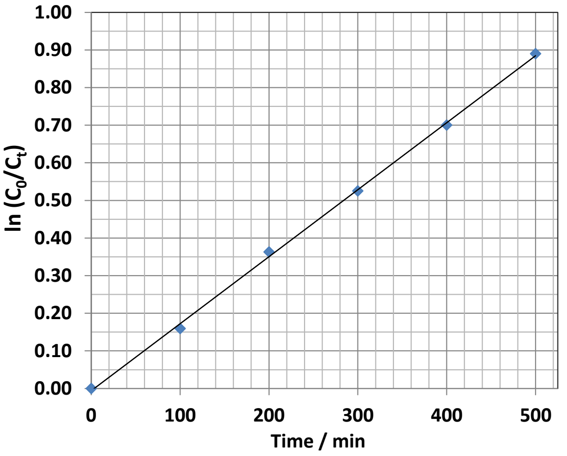


Figure 2a

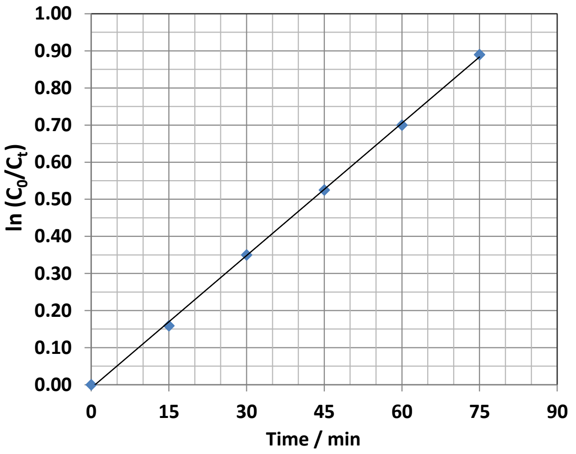


Figure 2b

Which plot should be for the oxidation of nondeuterated diphenylmethanol and which one is for the oxidation of deuterated diphenylmethanol?
For each statement, select your answer by marking "✓" in **one** of the open circles.

The oxidation of nondeuterated diphenylmethanol: ○ Figure 2a ○ Figure 2b

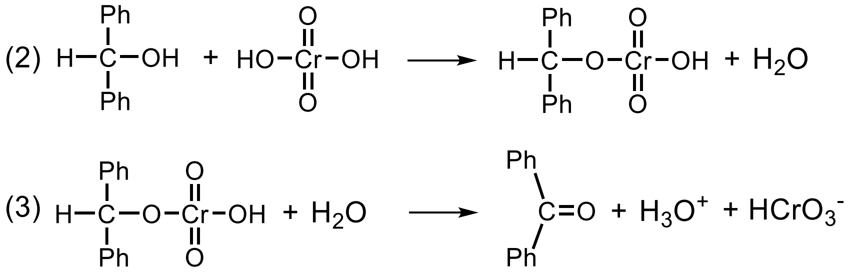
The oxidation of deuterated diphenylmethanol: ○ Figure 2a ○ Figure 2b

2-A7) Determine k_{CH}, k_{CD} (in min^{-1}), and the k_{CH}/k_{CD} of this reaction from the plots in question **2-A6)**.

Calculation:

2-A8) The mechanism has been proposed as follows:

$$(1)\quad Cr_2O_7^{2-} + H_2O + 2H^+ \rightleftharpoons 2H_2CrO_4$$



$$(2)\quad \mathrm{H{-}\overset{Ph}{\underset{Ph}{C}}{-}OH} + \mathrm{HO{-}\overset{O}{\underset{O}{Cr}}{-}OH} \longrightarrow \mathrm{H{-}\overset{Ph}{\underset{Ph}{C}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}OH} + H_2O$$

$$(3)\quad \mathrm{H{-}\overset{Ph}{\underset{Ph}{C}}{-}O{-}\overset{O}{\underset{O}{Cr}}{-}OH} + H_2O \longrightarrow \mathrm{Ph_2C{=}O} + H_3O^+ + HCrO_3^-$$

According to the information in **2-A6)** and **2-A7)**, which step should be the rate determining step?

Select your answer by marking "✓" in **one** of the open circles.

- ○ Step (1)
- ○ Step (2)
- ○ Step (3)

Problem 2

6% of the total

Problem 2	**A**								**Total**
	A1	A2	A3	A4	A5	A6	A7	A8	
Total	2	2	7	3	3	1	5	1	24
Score									

Problem 2: Kinetic isotope effect (KIE) and zero-point vibrational energy (ZPE)

Calculation of ZPE and KIE

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$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ ,$$

where k is the force constant and μ is the reduced mass.

The vibrational energies of the molecule are given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu\ ,$$

where n is vibrational quantum number with possible values of 0, 1, 2, ... The energy of the lowest vibrational energy level (E_n at n = 0) is called **zero-point vibrational energy (ZPE)**.

2-A1) Calculate the reduced mass of C-H (μ_{CH}) and C-D (μ_{CD}) in atomic mass unit. (2 points) Assume that the mass of deuterium is twice that of hydrogen.

Calculation:

Full credit will also be given using m_H = 1.00 amu, m_D = 2.014 or 2.00 amu.

$$\mu_{CH} = \frac{m_C m_H}{m_C + m_H} = \frac{(12.01)(1.008)}{12.01 + 1.008} \qquad \text{(0.5 point)}$$

$$= \frac{12.11}{13.02} = 0.9299 \ \text{amu} \qquad \text{(0.5 point)}$$

If the answer is not in atomic mass unit, 0.5 point will be deducted.

$$\mu_{CD} = \frac{m_C m_D}{m_C + m_D} = \frac{(12.01)(2\times 1.008)}{12.01 + (2\times 1.008)} \qquad \text{(0.5 point)}$$

$$= \frac{24.21}{14.03} = 1.726 \ \text{amu} \qquad \text{(0.5 point)}$$

If the answer is not in atomic mass unit, 0.5 point will be deducted.

[If students are unable to calculate the values for μ_{CH} and μ_{CD} in **2-A1)**, use μ_{CH} = 1.008 and μ_{CD} = 2.016 for the subsequent parts of the question. Note that the given values are not necessarily close to the correct values.]

2-A2) Given that the force constant (k) for C-H stretching is the same as that for the C-D stretching and the C-H stretching frequency is 2900 cm^{-1}, find the corresponding C-D stretching frequency (in cm^{-1}). (2 points)

Calculation:

1. Use the correct reduced mass.

$$\nu_{CH} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CH}}}$$

$$\nu_{CD} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CD}}}$$

$$\frac{\nu_{CH}}{\nu_{CD}} = \sqrt{\frac{\mu_{CD}}{\mu_{CH}}} = \sqrt{\frac{1.726}{0.9299}} = \sqrt{1.856} = 1.362$$ (1 point)

$$\nu_{CD} = \frac{\nu_{CH}}{1.362} = \frac{2900}{1.362} = 2129\,cm^{-1}$$ (1 point)

2. Use the reduced mass given.

$$\frac{\nu_{CH}}{\nu_{CD}} = \sqrt{\frac{\mu_{CD}}{\mu_{CH}}} = \sqrt{\frac{2.016}{1.008}} = \sqrt{2.000} = 1.414$$ (1 point)

$$\nu_{CD} = \frac{\nu_{CH}}{1.414} = \frac{2900}{1.414} = 2051\,cm^{-1}$$ (1 point)

Alternatively, full credit is given when students use $\nu_{CH} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CH}}}$ to evaluate force constant, then use the force constant to calculate ν_{CD}. In this case, if the ν_{CD} is wrong, but the force constant k is correct, only 1 point will be given.

2-A3) According to the C-H and C-D stretching frequencies in question **2-A2**, calculate the zero-point vibrational energies (ZPE) of C-H and C-D stretching in kJ mol^{-1}. (7 points)

Calculation:

$$E_n = \left(n + \frac{1}{2}\right)h\nu, \quad n = 0, 1, 2, \ldots$$

$$\mathrm{ZPE} = \mathrm{E}_{n=0} = \frac{1}{2}h\nu$$ (1 point)

$$ZPE_{CH} = \frac{1}{2}h\nu_{CH}$$

$$= \frac{1}{2}(6.6261\times 10^{-34}\ J\ s)(2900\,cm^{-1})(2.9979\times 10^{10}\ cm\,s^{-1})(6.0221\times 10^{23}\ mol^{-1})(10^{-3}\ kJ)$$

$$= 17.35\,kJ\,mol^{-1}$$ (3 points)

If either calculation error or wrong unit is found, 0.5 point will be deducted.
If one of the conversion factors is missing, 1 point will be deducted.
If one of the conversion factors is missing and either calculation error or wrong unit is found, 1.5 points will be deducted.
If two of the conversion factors are missing, 2 points will be deducted.
If two of the conversion factors are missing and either calculation error or wrong unit is found, 2.5 points will be deducted.

Either 1. or 2. below is accepted.

1. Use the correct reduced mass.

$$ZPE_{CD} = \frac{1}{2}h\nu_{CD}$$

$$= \frac{1}{2}(6.6261\times 10^{-34}\ J\ s)(2129\,cm^{-1})(2.9979\times 10^{10}\ cm\,s^{-1})(6.0221\times 10^{23}\ mol^{-1})(10^{-3}\ kJ)$$

$$= 12.73\,kJ\,mol^{-1}$$ (3 points)

2. Use the given reduced mass.

$$ZPE_{CD} = \frac{1}{2}h\nu_{CD}$$

$$= \frac{1}{2}(6.6261\times 10^{-34}\ J\ s)(2051\,cm^{-1})(2.9979\times 10^{10}\ cm\,s^{-1})(6.0221\times 10^{23}\ mol^{-1})(10^{-3}\ kJ)$$

$$= 12.27\,kJ\,mol^{-1}$$ (3 points)

If either calculation error or wrong unit is found, 0.5 point will be deducted.
If one of the conversion factors is missing, 1 point will be deducted.
If one of the conversion factors is missing and either calculation error or wrong unit is found, 1.5 points will be deducted.
If two of the conversion factors are missing, 2 points will be deducted.
If two of the conversion factors are missing and either calculation error or wrong unit is found, 2.5 points will be deducted.

[If students are unable to calculate the values for *ZPE* in **2-A3)**, use ZPE_{CH} = 7.23 kJ/mol and ZPE_{CD} = 2.15 kJ/mol for the subsequent parts of the question. Note that the given values are not necessarily close to the correct values.]

Kinetic isotope effect (KIE)

Due to the difference in zero-point vibrational energies, a protonated compound and its corresponding deuterated compounds are expected to react at different rates.

For the C-H and C-D bond dissociation reactions, the energies of both transition states and both products are identical. Then, the isotope effect is controlled by the difference in the ZPE's of the C-H and C-D bonds.

2-A4) Calculate the difference in the bond dissociation energy (BDE) between C-D bond and C-H bond ($\mathrm{BDE}_{\mathrm{CD}} - BDE_{CH}$) in kJ mol^{-1}. (3 points)

Calculation:

From the ZPE_{CH} and ZPE_{CD} in question **2-A3)**,

1. Use the correct reduced mass.

$$BDE_{CD} - BDE_{CH} = ZPE_{CH} - ZPE_{CD} \qquad \text{(1.5 point)}$$

$$= 17.35 - 12.73\ kJ\ mol^{-1}$$

$$= 4.62\ kJ\ mol^{-1} \qquad \text{(1.5 point)}$$

2. Use the given reduced mass.

$$BDE_{CD} - BDE_{CH} = ZPE_{CH} - ZPE_{CD} \qquad \text{(1.5 point)}$$

$$= 17.35 - 12.27\ kJ\ mol^{-1}$$

$$= 5.08\ kJ\ mol^{-1} \qquad \text{(1.5 point)}$$

3. Use the given ZPE.

$$BDE_{CD} - BDE_{CH} = ZPE_{CH} - ZPE_{CD} \qquad \text{(1.5 point)}$$

$$= 7.23 - 2.15\ kJ\ mol^{-1}$$

$$= 5.08\ kJ\ mol^{-1} \qquad \text{(1.5 point)}$$

The answer calculated from $BDE_{CD} - BDE_{CH} = ZPE_{CD} - ZPE_{CH}$ will be given only 1 point for question **2-A4)**.

2-A5) Assume that the activation energy (E_a) for the C-H/C-D bond cleavage is approximately equal to the bond dissociation energy and the Arrhenius factor is the same for both C-H and C-D bond cleavage. Find the relative rate constant for the C-H/C-D bond cleavage (k_{CH}/k_{CD}) at 25 °C. (3 points)

Calculation:

1. Use the correct reduced mass.

$$\frac{k_{CH}}{k_{CD}} = e^{-(ZPE_{CD} - ZPE_{CH})/RT} \qquad \text{(1 point)}$$

$$= e^{-(-4.62 \times 10^{3}\ J\ mol^{-1})/(8.3145 J\ K^{-1}\ mol^{-1})(25+273.15K)} \qquad \text{(1 point)}$$

$$= e^{1.86} \quad = 6.45 \qquad \text{(1 point)}$$

2. Use the given reduced mass or the given ZPE.

$$\frac{k_{CH}}{k_{CD}} = e^{-(ZPE_{CD} - ZPE_{CH})/RT} \qquad \text{(1 point)}$$

$$= e^{-(-5.08 \times 10^{3}\ J\ mol^{-1})/(8.3145 J\ K^{-1}\ mol^{-1})(25+273.15K)} \qquad \text{(1 point)}$$

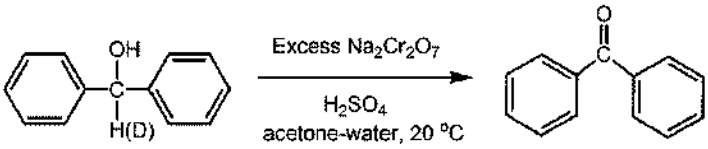
$$= e^{2.05} = 7.77 \qquad \text{(1 point)}$$

The answer calculated from $\frac{k_{CH}}{k_{CD}} = e^{-(ZPE_{CH} - ZPE_{CD})/RT}$ will be given only 1 point for question **2-A5)**.

*[The answer must be consistent with the answer in question **2-A4)**.]*

Using KIE to study reaction mechanism

The oxidation of nondeuterated and deuterated diphenylmethanol using an excess of chromic acid was studied.



2-A6) Let C_0 be the initial concentration of either nondeuterated diphenylmethanol or deuterated diphenylmethanol and C_t its concentration at time t. The experiment led to two plots (Figure 2a and Figure 2b), from which the first-order rate constant can be determined.

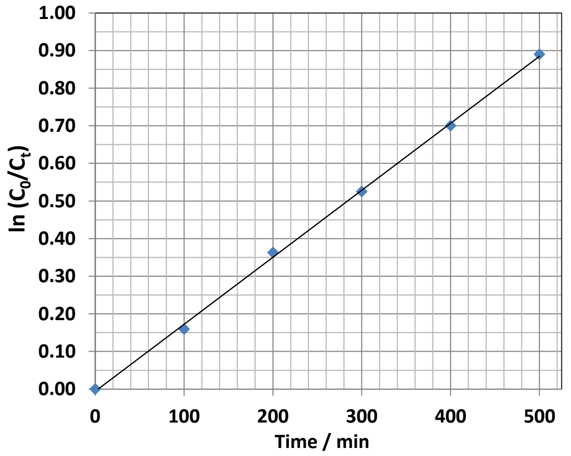


Figure 2a

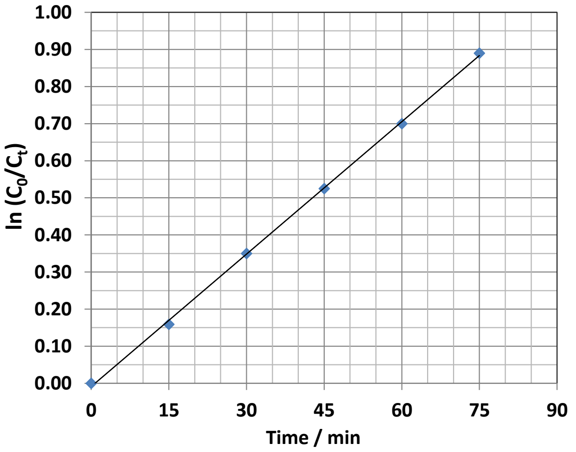


Figure 2b

Which plot should be for the oxidation of nondeuterated diphenylmethanol and which one is for the oxidation of deuterated diphenylmethanol? (1 point)
For each statement, select your answer by marking "✓" in **one** of the open circles.

The oxidation of nondeuterated diphenylmethanol: ○ Figure 2a ☑ Figure 2b

The oxidation of deuterated diphenylmethanol: ☑ Figure 2a ○ Figure 2b

[1 point for 2 correct answers; 0.5 point for 1 correct answer; 0 point for 2 wrong answer; 0 point for 1 wrong & 1 correct answer]

*[The answer must be consistent with the answer in question **2-A5)**.]*

2-A7) Determine k_{CH}, k_{CD} (in min^{-1}), and the k_{CH}/k_{CD} of this reaction from the plots in question **2-A6**. (5 points)

Calculation:

$$\ln\frac{C_0}{C_t} = k_{CH}t \qquad \ln\frac{C_0}{C_t} = k_{CD}t \qquad \text{(1 point)}$$

$$k_{CH} = 0.012 \quad \text{min}^{-1} \quad \text{(from the slope of the plot in Figure 2b)} \qquad \text{(1.5 points)}$$

Example: $k_{CH} = \dfrac{0.70-0.35}{60-30} = 0.012 \ \text{min}^{-1}$

[If kCH is calculated from the slope of the plot in Figure 2a, 1 point will be deducted.]

$$k_{CD} = 0.0018 \quad \text{min}^{-1} \quad \text{(from the slope of the plot in Figure 2a)} \qquad \text{(1.5 points)}$$

Example: $k_{CD} = \dfrac{0.70-0.35}{400-200} = 0.0018 \ \text{min}^{-1}$

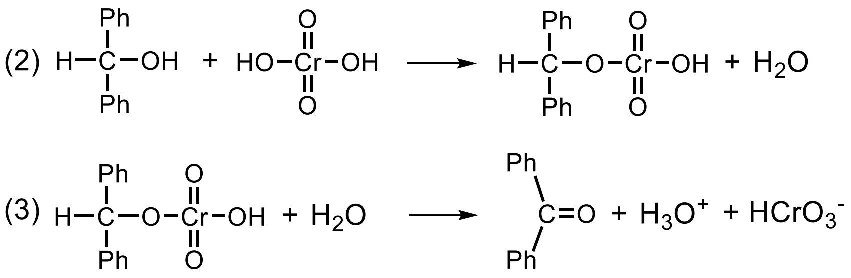
[If kCD is calculated from the slope of the plot in Figure 2b, 1 point will be deducted.]

$$\frac{k_{CH}}{k_{CD}} = \frac{0.012}{0.0018} = 6.7 \qquad \text{(1 point)}$$

*[The answer must be consistent with the answer in question **2-A6)**.]*

2-A8) The mechanism has been proposed as follows:

(1) $Cr_2O_7^{2-} + H_2O + 2H^+ \rightleftharpoons 2H_2CrO_4$



(2) $Ph_2CH{-}OH + HO{-}CrO_2{-}OH \longrightarrow Ph_2CH{-}O{-}CrO_2{-}OH + H_2O$

(3) $Ph_2CH{-}O{-}CrO_2{-}OH + H_2O \longrightarrow Ph_2C{=}O + H_3O^+ + HCrO_3^-$

According to the information in **2-A6)** and **2-A7)**, which step should be the rate determining step? (1 point)
Select your answer by marking "✓" in **one** of the open circles.

- ○ Step (1)
- ○ Step (2)
- ☑ Step (3)

Problem 3

6% of the total

Problem 3	A			B	Total
	A1	A2	A3		
Total	7	3	8	6	24
Score					

Problem 3: Thermodynamics of chemical reactions

Part A.

Methanol is produced commercially by using a mixture of carbon monoxide and hydrogen over zinc oxide/copper oxide catalyst:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g).$$

The standard enthalpy of formation (ΔH_f^o) and the absolute entropy (S^o) for each of the three gases at room temperature (298 K) and at a standard pressure of 1 bar are given as follows.

Gas	ΔH_f^o (kJ mol^{-1})	S^o (J K^{-1} mol^{-1})
$CO(g)$	-111	198
$H_2(g)$	0	131
$CH_3OH(g)$	-201	240

3-A1) Calculate ΔH^o, ΔS^o, ΔG^o, and K_p for the reaction at 298 K.

Calculation:

ΔH^o = ………….……… kJ

ΔS^o = ………………..… $J\,K^{-1}$

ΔG^o = ………….……… kJ

K_p = ….……………….

If you are unable to calculate K_p at 298 K in problem **3-A1)**, use $K_p = 9 \times 10^5$ later on.

3-A2) A commercial reactor is operated at a temperature of 600 K. Calculate the value of K_p at this temperature, assuming that ΔH^o and ΔS^o are independent of temperature.

Calculation:

K_p = …………………………..

If you are unable to calculate K_p at 600 K in problem **3-A2)**, use $K_p = 1.0\times10^{-2}$ later on.

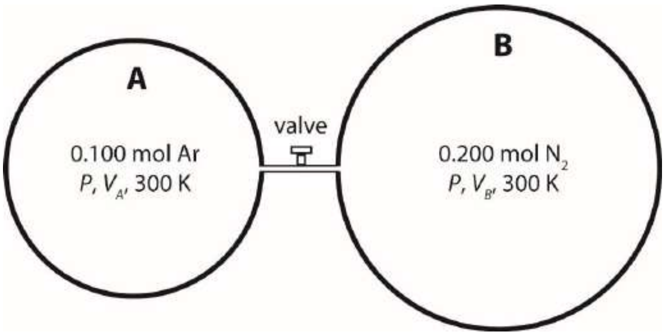
3-A3) Production of methanol in industry is based on flowing of the gas comprising 2.00 moles of H_2 for each mole of CO into the reactor. The mole fraction of methanol in the exhaust gas from the reactor was found to be 0.18. Assuming that equilibrium is established, what is the total pressure in the reactor at a high temperature of 600 K?

Calculation:

Total pressure = ………………………. bar.

Part B.

3-B) Consider the following closed system at 300 K. The system comprises 2 compartments, separated by a closed valve, which has negligible volume. At the same pressure P, compartment A and compartment B contain 0.100 mol argon gas and 0.200 mol nitrogen gas, respectively. The volumes of the two compartments, V_A and V_B, are selected so that the gases behave as ideal gases.



After opening the valve slowly, the system is allowed to reach equilibrium. It is assumed that the two gases form an ideal gas mixture. Calculate the change in Gibbs free energy at 300 K, ΔG.

Calculation:

ΔG = ………………….. J

Problem 3

6% of the total

Problem 3	**A**			**B**	**Total**
	A1	A2	A3		
Total	7	3	8	6	24
Score					

Problem 3: Thermodynamics of chemical reactions

Part A.

Methanol is produced commercially by using a mixture of carbon monoxide and hydrogen over zinc oxide/copper oxide catalyst:

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The standard enthalpy of formation (ΔH_f^o) and the absolute entropy (S^o) for each of the three gases at room temperature (298 K) and at a standard pressure of 1 bar are given as follows.

Gas	ΔH_f^o (kJ mol^{-1})	S^o (J K^{-1} mol^{-1})
$CO(g)$	-111	198
$H_2(g)$	0	131
$CH_3OH(g)$	-201	240

3-A1) Calculate ΔH^o, ΔS^o, ΔG^o, and K_p for the reaction at 298 K. (7 points)

Calculation:

ΔH^o (reaction) $= \Delta H_f^o (CH_3OH) - \Delta H_f^o (CO) - 2\Delta H_f^o (H_2)$ kJ

$= -201-(-111)-2(0)$ kJ (1 point)

ΔH^o = ………..-90 ……… kJ (0.5 point)

ΔS^o (reaction) $= S^o (CH_3OH) - S^o (CO) - 2S^o (H_2)$ J K^{-1}

$= 240-(198)-2(131)$ J K^{-1} (1 point)

ΔS^o = ………….-220…….. J K^{-1} (0.5 point)

and $\Delta G^o = \Delta H^o - T\Delta S^o$

$= -90-[(298)(-220)/1000]$ kJ (1.5 points)

ΔG^o = ………..-24…………. kJ (0.5 point)

A value for the equilibrium constant, K_p, can be found from the expression,

$\Delta G^o = -RT \ln K_p$

So that,

$K_p = \exp(-\Delta G^o/RT)$

$= \exp[24000/(8.3145)(298)]$ (1.5 point)

$= \exp(9.69)$

K_p = ….1.6×10^4…… (0.5 point)

If you are unable to calculate K_p at 298 K in problem 3-A1), use $K_p = 9 \times 10^5$ later on.

3-A2) A commercial reactor is operated at a temperature of 600 K. Calculate the value of K_p at this temperature, assuming that ΔH^o and ΔS^o are independent of temperature. (3 points)

Calculation:

To find value of K_p at 600 K, we use the van't Hoff Isochore

$$\ln K_p = \frac{-\Delta H^\circ}{RT} + \text{constant}$$

It follows that

$$\ln K_p(600) = \ln K_p(298) + \frac{\Delta H^o}{R}\left(\frac{1}{298\ K} - \frac{1}{600\ K}\right)$$

$$= \ln (1.6\times10^4) + \frac{(-90\times10^3\,\mathrm{J\ mol^{-1}})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})}\left(\frac{1}{298\ \mathrm{K}} - \frac{1}{600\ \mathrm{K}}\right) \quad \text{(2 points)}$$

K_p $= 1.8 \times 10^{-4}$

or K_p $= 1 \times 10^{-2}$ (if using $K_{p,\,298K} = 9 \times 10^5$ → fake value)

(1 point)

If you are unable to calculate K_p at 600 K in problem 3-A2), use $K_p = 1.0\times10^{-2}$ later on.

3-A3) Production of methanol in industry is based on flowing of the gas comprising 2.00 moles of H_2 for each mole of CO into the reactor. The mole fraction of methanol in the exhaust gas from the reactor was found to be 0.18. Assuming that equilibrium is established, what is the total pressure in the reactor at a high temperature of 600 K? (8 points)

Calculation:

It is helpful to consider the amounts of different species present before the reaction and during the equilibrium.

	$CO(g)$ +	$2H_2(g) \rightleftharpoons$	$CH_3OH(g)$	
				(0.5 point)
Before reaction	*1 mol*	*2 mol*	*0 mol*	
At equilibrium	*1-y mol*	*2-2y mol*	*y mol*	*(0.5 point)*

The amount of methanol, y moles, can be found from the fact that the mole fraction of methanol is 0.18, so

$$0.18 = \frac{no.mol\ CH_3OH}{no.mol\ H_2 + no.mol\ CO + no.mol\ CH_3OH}$$

$$= \frac{y}{3-2y}$$

So, $y = 0.40$ mol *(1 point)*

From the above, it is possible to find the mole fraction x of different species:

$$x(CH_3OH) = \frac{0.40}{3-(2\times 0.40)} = 0.18$$ *(0.5 point)*

$$x(CO) = \frac{1-0.40}{3-(2\times 0.40)} = 0.27$$ *(0.5 point)*

$$x(H_2) = \frac{2-(2\times 0.40)}{3-(2\times 0.40)} = 0.55$$ *(0.5 point)*

The corresponding partial pressures are

$p(CH_3OH) = 0.18\times p_{TOT}$, *(0.5 point)*
$p(CO) = 0.27\times p_{TOT}$, *(0.5 point)*
and $p(H_2) = 0.55\times p_{TOT}$, *(0.5 point)*

where p_{TOT} is the total pressure.

Since the reactor operates at 600 K,

$$K_p = 1.8\times 10^{-4} = \frac{p(CH_3OH)}{p(CO)\times p(H_2)^2}$$ *(1 point)*

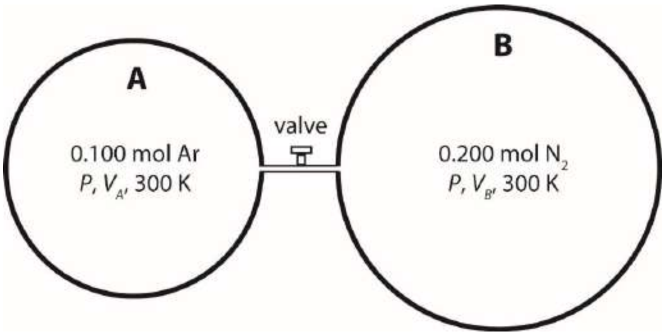
$$= \frac{0.18p_{TOT}}{0.27p_{TOT}\times(0.55p_{TOT})^2}$$ *(1 point)*

Solving this equation gives $p_{TOT} = 111$ bar
(or 15 bar if $K_p = 1.0\times 10^{-2}$ is used)

(1 point)

Part B.

3-B) Consider the following closed system at 300 K. The system comprises 2 compartments, separated by a closed valve, which has negligible volume. At the same pressure P, compartment A and compartment B contain 0.100 mol argon gas and 0.200 mol nitrogen gas, respectively. The volumes of the two compartments, V_A and V_B, are selected so that the gases behave as ideal gases.



After opening the valve slowly, the system is allowed to reach equilibrium. It is assumed that the two gases form an ideal gas mixture. Calculate the change in Gibbs free energy at 300 K, ΔG. (6 points)

Calculation:

At constant T, $\Delta U = 0$ *and* $\Delta H = 0$. (0.5 point)

ΔS *of the process can be found as described below.*

For an irreversible process (at constant pressure), $q = -w = P\Delta V$ *, while* (0.5 point)

$q = -w = nRT\ln\frac{V_2}{V_1}$ *for a reversible process (at constant temperature). The change in entropy can then be found from:* $\Delta S = \frac{q_{rev}}{T} = \frac{nRT\ln\frac{V_2}{V_1}}{T} = nR\ln\frac{V_2}{V_1}$. (0.5 point)

Therefore, for this process: $\Delta S = n_A R\ln\frac{(V_A + V_B)}{V_A} + n_B R\ln\frac{(V_A + V_B)}{V_B}$ (1 point)

$$= 0.100\,R\ln\frac{3}{1} + 0.200\,R\ln\frac{3}{2}$$ (1 point)

$= 1.59\ J\ K^{-1}$ (1 point)

Lastly, the change in Gibbs free energy can be found as follows:

$$\Delta G = \Delta H - T\Delta S = -T\Delta S$$ (0.5 point)

$$= -300 \times 1.59 = -477\ J$$ (1 point)

or $\Delta G = n_A RT\ln x_A + n_B RT\ln x_B = -477\ J$

If you are unable to calculate K_p at 298 K in problem **3-A1)**, use $K_p = 9 \times 10^5$ later on

Problem 4	A	Total

6-A2) Both Fe and **X** crystallize in the body centered cubic structure. Approximating the Fe atoms as hard-spheres, the volume taken up by the Fe atoms inside the unit cell is 1.59x10^{-23} cm^3. The volume of the unit cell of **X** is 0.0252 nm^3. A complete substitutional solid solution usually occurs when ΔR = $\left(\frac{|R_X - R_{Fe}|}{R_{Fe}}\right) \times 100$ is less than or equal to 15, where R_X and R_{Fe} are the atomic radii of **X** and Fe, respectively. Can **X** and Fe form a complete substitutional solid solution? Show your calculation. **No credit is given without calculation presented**. The volume of sphere is 4/3πr^3.

Answer (Mark ✓ in an appropriate box.)

☐ Yes (ΔR ≤ 15) ☐ No (ΔR > 15)

Calculation

R_{Fe} = ...……………...…..nm R_X = ………………….nm ΔR = ………………..…..

Part C.

^{59}Fe is a radiopharmaceutical isotope which is used in the study of iron metabolism in the spleen. This isotope decays to ^{59}Co as follows:

$$^{59}_{26}Fe \rightarrow {}^{59}_{27}Co \;+\; \mathbf{a} \;+\; \mathbf{b} \qquad (1)$$

6-C1) What are **a** and **b** in equation (1)? (Mark ✓ in the appropriate boxes.)

proton	neutron	beta	positron	alpha	gamma

6-C2) Consider equation (1), if the ^{59}Fe isotope is left for 178 days which is *n* times of its half-life ($t_{1/2}$), the mole ratio of ^{59}Co to ^{59}Fe is 15:1. If *n* is an integer, what is the half-life of ^{59}Fe in day(s)? Show your calculation.

Calculation:

Half-life of ^{59}Fe = …………………….days (1 decimal place)

6-A2) Both Fe and **X** crystallize in the body centered cubic structure. Approximating the Fe atoms as hard-spheres, the volume taken up by the Fe atoms inside the unit cell is 1.59×10^{-23} cm^3. The volume of the unit cell of **X** is 0.0252 nm^3. A complete substitutional solid solution usually occurs when $\Delta R = \left(\frac{|R_X - R_{Fe}|}{R_{Fe}}\right) \times 100$ is less than or equal to 15, where R_X and R_{Fe} are the atomic radii of **X** and Fe, respectively. Can **X** and Fe form a complete substitutional solid solution? Show your calculation. **No credit is given without calculation presented**. The volume of sphere is $4/3\pi r^3$. (8 points)

Answer (Mark ✓ in an appropriate box.)

☑ Yes ($\Delta R \leq 15$) ☐ No ($\Delta R > 15$) *(0.5 points,*Y or N relates to the calculated ΔR

Calculation

For Fe

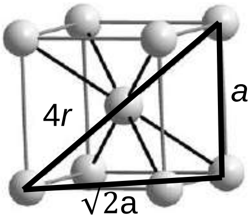
$V = 2(4/3)\pi r^3$ *("2" => 1 point, the bcc unit cell contains 2 atoms of Fe)*

$r^3 = (V*3)/(8*\pi) = (1.59 \times 10^{-23}\ \text{cm}^3*3)/(8*\pi) = 1.90 \times 10^{-24}\ \text{cm}^3$

$r = 1.24 \times 10^{-8}\ \text{cm} \times (1\ \text{nm}/10^{-7}\ \text{cm})$ *(conversion factor => 1 point)*

$r = 0.124$ nm *(2 points)*

For X



(This figure will not appear in the exam paper and no credit will be given for drawing this structure)

$V = a^3 \Rightarrow a = \sqrt[3]{V} = \sqrt[3]{0.0252} = 0.293$ nm *(1 point)*

$r = (\sqrt{3}a)/4 = (\sqrt{3} \times 0.293\ \text{nm})/4 = 0.127$ nm *(1.5 points)*

$\Delta R = \left(\frac{|R_X - R_{Fe}|}{R_{Fe}}\right) \times 100 = \left(\frac{|0.127\ nm - 0.124\ nm|}{0.124\ nm}\right) \times 100 = 2.42$, less than 15

(1 point for a correct calculation)

R_{Fe} = ...0.124........nm R_X = ...0.127.......nm ΔR = ...2.42........

6-C2) Consider equation (1), if the ^{59}Fe isotope is left for 178 days which is *n* times of its half-life ($t_{1/2}$), the mole ratio of ^{59}Co to ^{59}Fe is 15:1. If *n* is an integer, what is the half-life of ^{59}Fe in day(s)? Show your calculation.

Calculation: *(total = 4 points)*

t = 0 $^{59}Fe = N_0$ and $^{59}Co = 0$
t = 178 d $^{59}Fe = N_t$ and $^{59}Co = N_0 - N_t$

the ratio of ^{59}Co to ^{59}Fe at t = 178 d is $15 = (N_0 - N_t)/N_t$
so $\mathbf{N_t = N_0/(15+1)}$ *(2 points)*

At 178 day => $N_t = N_o/(15+1)$
$= N_0/16 = 0.0625N_0$
Suppose that $N_0 = 100\%$, so $N_t = 6.25\%$
t = 0 => $N_0 = 100\ \%$
$t = 1(t_{1/2})$ => $N_t = 50\ \%$
$t = 2(t_{1/2})$ => $N_t = 25\ \%$
$t = 3(t_{1/2})$ => $N_t = 12.5\ \%$
$t = 4(t_{1/2})$ => $N_t = 6.25\ \%$
So, *n* = 4 and $t_{1/2} = 178/4 = 44.5$ days

$\ln(N_t/N_0) = -kt$
$\ln[(N_0/16)/N_0] = -k(178\ d)$
$\ln(1/16) = -k(178\ d)$
$k = [\ln(1/16)]/(-178)\ d^{-1}$
$t_{1/2} = \ln 2/k = 44.5$ days

1 pt

Half-life of ^{59}Fe = ……44.5…….days (1 decimal place) *(1 point)*

Theoretical Problem 1	Question	1.1	1.2	1.3	1.4	1.5	1.6	**Total**
	Points	5	5	4	12	12	24	**62**
7% of the total	Score							

Problem 1. DNA

Palindromic sequences are an interesting class of DNA. In a palindromic double-stranded DNA (dsDNA) species, the sequence of one strand read in the 5′→3′ direction matches the 5′→3′ reading on the complementary strand. Hence, a palindromic dsDNA consists of two identical strands that are complementary to each other. An example is the so-called Drew–Dickerson dodecanucleotide (**1**):

5′-CGCGAATTCGCG-3′
| | | | | | | | | | | |
3′-GCGCTTAAGCGC-5′
(**1**)

1.1 How many different palindromic double-stranded DNA dodecanucleotides (i.e., dsDNA species with twelve base pairs) exist?

1.2 How many different palindromic double-stranded DNA undecanucleotides (i.e., dsDNA species with eleven base pairs) exist?

The melting temperature of dsDNA, T_m is defined as the temperature at which 50% of the original amount of DNA double strands are dissociated into separate strands.

1.3 Consider the Drew–Dickerson dodecanucleotide (**1**). Assume that a G–C nucleobase pair contributes to the DNA duplex stability more than an A–T pair does. What is the probability that its T_m increases when a single randomly selected base pair is replaced by a G–C pair?

Probability

Let us analyse the thermodynamics of formation of double-helical DNA from single strands, and its dependence on the length of the DNA and on the temperature. The equilibrium constant of association of single strands to form dsDNA differs for palindromic and non-palindromic dsDNA. A solution of dsDNA with the initial concentration of $c_{\text{init}} = 1.00 \times 10^{-6}$ mol dm^{-3} was heated to T_m and equilibrium was reached.

1.4 Calculate the equilibrium constant of **association** of single strands at T_m for both non-palindromic and palindromic DNA.

Non-palindromic dsDNA

Show your calculation:

K =

Palindromic dsDNA

Show your calculation:

K =

The mean contributions to the Gibbs energy of association of two single strands to form dsDNA were estimated over a certain range of experimental conditions, and they amount to −6.07 kJ mol^{-1} per one G–C pair, and −1.30 kJ mol^{-1} per one A–T pair present in a dsDNA.

1.5 How many base pairs are there in the **shortest** dsDNA oligonucleotide that has T_m above 330 K? At this T_m, consider the following values of the equilibrium constant of association of single strands to form a dsDNA: $K_{np} = 1.00 \times 10^6$ for a non-palindromic dsDNA, $K_p = 1.00 \times 10^5$ for a palindromic dsDNA. Is the shortest oligonucleotide palindromic or non-palindromic?

Calculation of the number of base pairs:

The required number of base pairs in non-palindromic dsDNA:

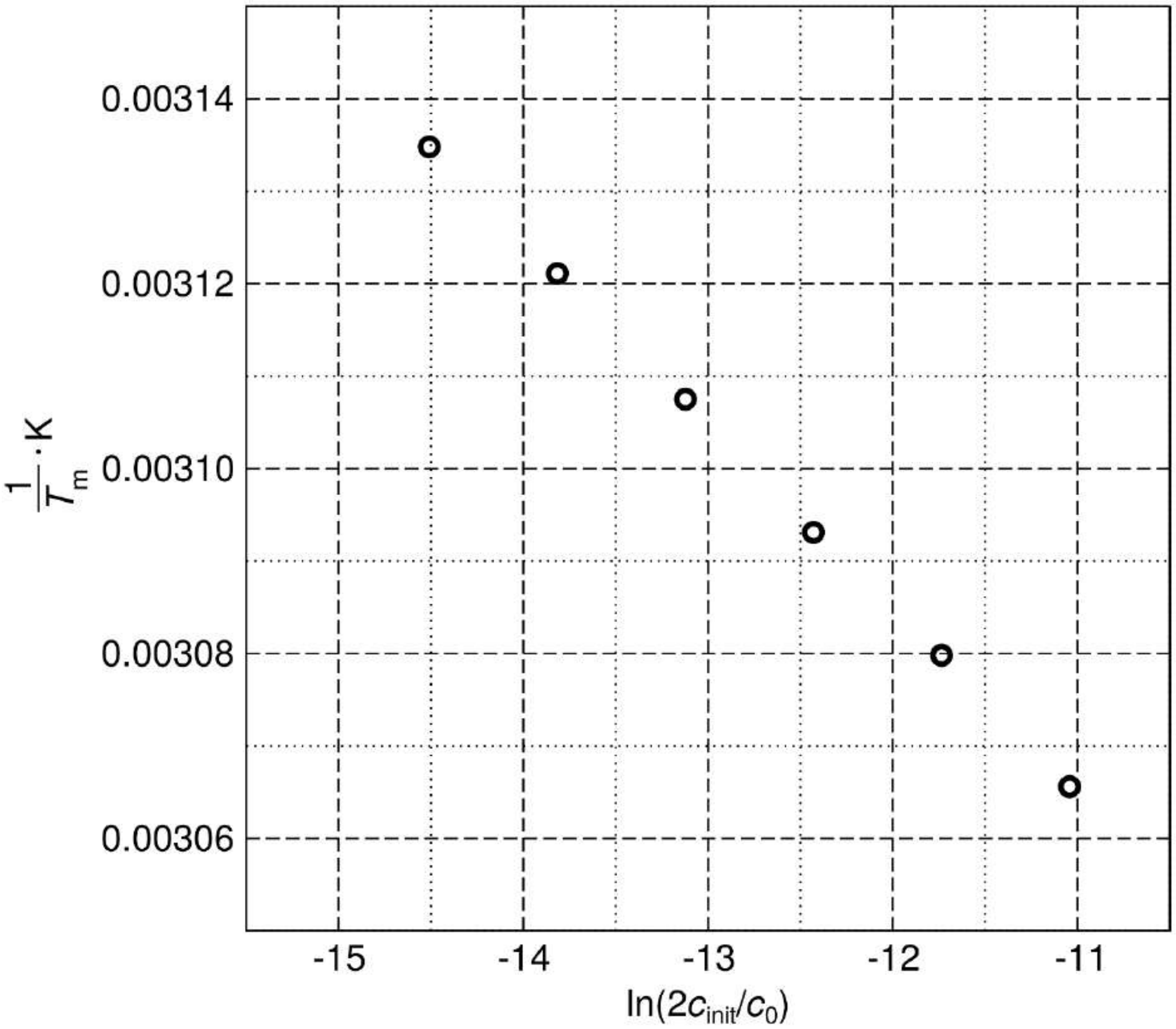
The required number of base pairs in palindromic dsDNA:

The shortest oligonucleotide is

☐ palindromic (P)

☐ non-palindromic (NP).

Finally, let us leave the simplified idea of base pairs contributing individually to the **association** of DNA strands. The Gibbs energy of this process may be considered explicitly dependent on temperature. The dependence of the inverse T_m of the Drew–Dickerson dodecanucleotide (**1**) on the logarithm of the initial duplex concentration c_{init} is shown below. (*Note*: a standard concentration c_0 = 1 mol dm^{-3} is introduced.)



c_{init} / 10^{-6} mol dm^{-3}	0.25	0.50	1.00	2.0	4.0	8.0
T_m / K	319.0	320.4	321.8	323.3	324.7	326.2

1.6 Calculate the standard enthalpy Δ*H*° and the standard entropy Δ*S*° of the association of DNA single strands to form the palindromic double-stranded Drew–Dickerson dodecanucleotide (**1**). Assume that Δ*H*° and Δ*S*° do not vary with temperature.

Show your calculation:

Theoretical Problem 1 7% of the total	Question	1.1	1.2	1.3	1.4	1.5	1.6	**Total**
	Points	5	5	4	12	12	24	**62**
	Score							

Problem 1. DNA

Palindromic sequences are an interesting class of DNA. In a palindromic double-stranded DNA (dsDNA) species, the sequence of one strand read in the 5′→3′ direction matches the 5′→3′ reading on the complementary strand. Hence, a palindromic dsDNA consists of two identical strands that are complementary to each other. An example is the so-called Drew–Dickerson dodecanucleotide (**1**):

5′-CGCGAATTCGCG-3′
| | | | | | | | | | | |
3′-GCGCTTAAGCGC-5′
(**1**)

1.1 How many different palindromic double-stranded DNA dodecanucleotides (i.e., dsDNA species with twelve base pairs) exist?

The choice of the first, second, third, fourth, fifth and sixth nucleotide in one strand is arbitrary; the seventh through twelfth nucleotides in the same strand are determined by the condition of self-complementarity. There are always 4 options (C, G, A, T) for the first through six nucleotide. Hence, the total number of palindromic DNA hexanucleotides is $4 \times 4 \times 4 \times 4 \times 4 \times 4 = 4^6 = 4\ 096$.

5 points in total
Any numerical result above scores full marks.
No explanation of the calculation is needed to score full marks as long as the result is correct.
Example of a partially correct solution:
4 points if the student writes 4 × 4 × 4 × 4 × 4 × 4 explicitly, but he/she gives an incorrect final result (e.g., due to an improper use of a calculator).
Examples of incorrect solutions that do not score any marks:
The student counts uracil as the fifth possibility, yielding 15 625 octanucleotides.
The student counts four possibilities for each of the twelve nucleotides, i.e. they ignore the condition of self-complementarity, yielding 16 777 216 dodecanucleotides.
0 points for any other result.

1.2 How many different palindromic double-stranded DNA undecanucleotides (i.e., dsDNA species with eleven base pairs) exist?

0. There is no palindromic dsDNA with an odd number of base pairs.

5 points
No explanation is needed.
0 points for any other result.

The melting temperature of dsDNA, T_m is defined as the temperature at which 50% of the original amount of DNA double strands are dissociated into separate strands.

1.3 Consider the Drew–Dickerson dodecanucleotide (**1**). Assume that a G–C nucleobase pair contributes to the DNA duplex stability more than an A–T pair does. What is the probability that its T_m increases when a single randomly selected base pair is replaced by a G–C pair?

Probability

The thermodynamic stability, and thus the melting temperature increases whenever an A–T pair is replaced by a G–C pair. The probability of randomly drawing one of the 4 A–T pairs from the Drew–Dickerson dodecanucleotide containing 12 base pairs is

4/12 = **1/3** ~ **0.333** ~ **0.33** or **33.3% ~ 33%**

4 points in total
Any of the numerical results above scores full marks.
No additional explanation is needed to score full marks.
Example of a partially correct solution:
2 points if the student declares 4/12 but they present an incorrect final result (e.g. 4/12 = 0.25).
Examples of incorrect solutions that do not score any marks:
The student counts only two A–T pairs rather than four, yielding the probability of 2/12.
The student incorrectly counts the total number of nucleotide pairs.

Let us analyze the thermodynamics of formation of double-helical DNA from single strands, and its dependence on the length of the DNA and on the temperature. The equilibrium constant of association of single strands to form dsDNA differs for palindromic and non-palindromic dsDNA. A solution of dsDNA with the initial concentration of $c_{\text{init}} = 1.00 \times 10^{-6}$ mol dm^{-3} was heated to T_m and equilibrium was reached.

1.4 Calculate the equilibrium constant of **association** of single strands at T_m for both non-palindromic and palindromic DNA.

Non-palindromic dsDNA

Calculation:

The association reaction of a non-palindromic dsDNA reads

$$\text{ssDNA1} + \text{ssDNA2} \rightleftharpoons \text{dsDNA}$$

and the equilibrium constant of association takes the form

$$K_{np} = \frac{\frac{[\text{dsDNA}]}{c_0}}{\frac{[\text{ssDNA1}]}{c_0} \times \frac{[\text{ssDNA2}]}{c_0}}$$

where c_0 is the standard concentration of 1.00 mol dm^{-3} and the lower index *np* stands for "non-palindromic".

At T_m, one half of the initial dsDNA concentration has melted to ssDNA, so

$$[\text{dsDNA}] = [\text{ssDNA1}] = [\text{ssDNA2}] = 1/2\ c_{\text{init}}$$

which yields

$$K_{np}(T_m) = \frac{\frac{1/2\, c_{init}}{c_0}}{\frac{1/2\, c_{init}}{c_0} \times \frac{1/2\, c_{init}}{c_0}} = \frac{c_0}{1/2\, c_{init}} = \frac{1.00\,\{\text{mol dm}^{-3}\}}{1/2 \times 1.00 \times 10^{-6}\,\{\text{mol dm}^{-3}\}} = \mathbf{2.00 \times 10^{6}}$$

$K =$

Palindromic dsDNA

Calculation:

The association reaction of a palindromic dsDNA reads

$$2\ \text{ssDNA} \rightleftharpoons \text{dsDNA}$$

and the equilibrium constant of association is

$$K_p = \frac{\frac{[\text{dsDNA}]}{c_0}}{\left(\frac{[\text{ssDNA}]}{c_0}\right)^2}$$

where c_0 is the standard concentration, and the lower index p stands for “palindromic”.
At T_m, one half of the initial dsDNA concentration has melted into two ssDNAs with identical sequences, so

$$[\text{dsDNA}] = 1/2\, c_{init}$$
$$[\text{ssDNA}] = 2 \times [\text{dsDNA}] = c_{init}$$

which yields

$$K_p(T_m) = \frac{\frac{1/2\, c_{init}}{c_0}}{\left(\frac{c_{init}}{c_0}\right)^2} = \frac{1/2\, c_0}{c_{init}} = \frac{1/2 \times 1 \times 1.00\ \text{mol dm}^{-3}}{1.00 \times 10^{-6}\ \text{mol dm}^{-3}} = \mathbf{5.0 \times 10^{5}}$$

$K =$

2 points for the association reactions (1 point each)
10 points for the calculation of the association constant with c_{init} (5 points each)
Some of the steps may be condensed or performed implicitly, and the association reactions may not be presented explicitly. As long as the derivation is correct, full marks are scored for all of the elementary steps.
K is considered correct if given as unitless number or with the unit of $\text{mol}^{-1}\ \text{dm}^{3}$. Thus, failure to introduce unitless concentrations explicitly does not lead to any deduction provided the result is numerically correct.
Examples of grading partially correct solutions:
Dissociation is considered rather than association, and the calculation is otherwise correct
deduction of 3 points
Wrong numeric value of $K(T_m)$ in spite of the correct symbolic result, due to, e.g., an improper use of a calculator *deduction of 2 points each*
A correct expression for K is written initially, but there is an error in the derivation
deduction of 2 pts per each K affected, max. 2 points
K is correct numerically, but the unit is wrong (e.g., mol dm^{-3})
deduction of 2 points, enforced max. once
The score for any sub-task may not be negative.

The mean contributions to the Gibbs energy of association of two single strands to form dsDNA were estimate over a certain range of experimental conditions, and they amount to −6.07 kJ mol^{-1} per one G–C pair, and −1.30 kJ mol^{-1} per one A–T pair present in a dsDNA.

1.5 How many base pairs are there in the **shortest** dsDNA oligonucleotide that has T_m above 330 K? At this T_m, consider the following values of the equilibrium constant of association of single strands to form a dsDNA: $K_{np} = 1.00 \times 10^6$ for a non-palindromic dsDNA, $K_p = 1.00 \times 10^5$ for a palindromic dsDNA. Is the shortest oligonucleotide palindromic or non-palindromic?

Calculation of the number of base pairs:

K is related to the association Gibbs energy as $\Delta G^\circ_{np} = -RT \ln K_{np}$, so the Gibbs energy at T_m is

$$\Delta G^\circ_{np}(T_m) = -RT \ln K_{np}(T_m) =$$

$$= -8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 330\ \text{K} \times \ln(1.00 \times 10^6) = \mathbf{-37.9\ kJ\ mol^{-1}}$$

The shortest oligonucleotide will be obtained if C–G-only dsDNA is considered, because C–G pairs are more stable than A–T pairs.

Then, the smallest number of base pairs is obtained by dividing the Gibbs energy by the contribution of one C–G pair, which for a non-palindromic dsDNA is:

$$n_{np} = \frac{-37.9\ \text{kJ mol}^{-1}}{-6.07\ \text{kJ mol}^{-1}} = 6.2$$

The needed length of a non-palindromic dsDNA: **7**

For a palindromic dsDNA, the Gibbs energy at T_m is

$$\Delta G^\circ_{p}(T_m) = -RT \ln K_{p}(T_m) =$$

$$= -8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 330\ \text{K} \times \ln(1.00 \times 10^5) = \mathbf{-31.6\ kJ\ mol^{-1}},$$

and the number of base pairs is

$$n_{p} = \frac{-31.6\ \text{kJ mol}^{-1}}{-6.07\ \text{kJ mol}^{-1}} = 5.2$$

The needed length of a palindromic dsDNA: **6**

The shortest oligonucleotide is

☐ palindromic (P)

☐ non-palindromic (NP).

A smaller number of base pairs was obtained under the assumption of a palindromic dsDNA. Therefore, we conclude that the shortest dsDNA that has T_m above 330 K has a palindromic sequence of 6 C–G pairs.

5 points for the calculations of Gibbs energies

2 points for the consideration of C–G-only DNA (either stated explicitly, of just considering −6.07 kJ mol^{-1} for the contribution of a single base pair to the Gibbs energy of association; not awarded if the value for A–T DNA is considered)

3 points for the calculation of the number of base pairs

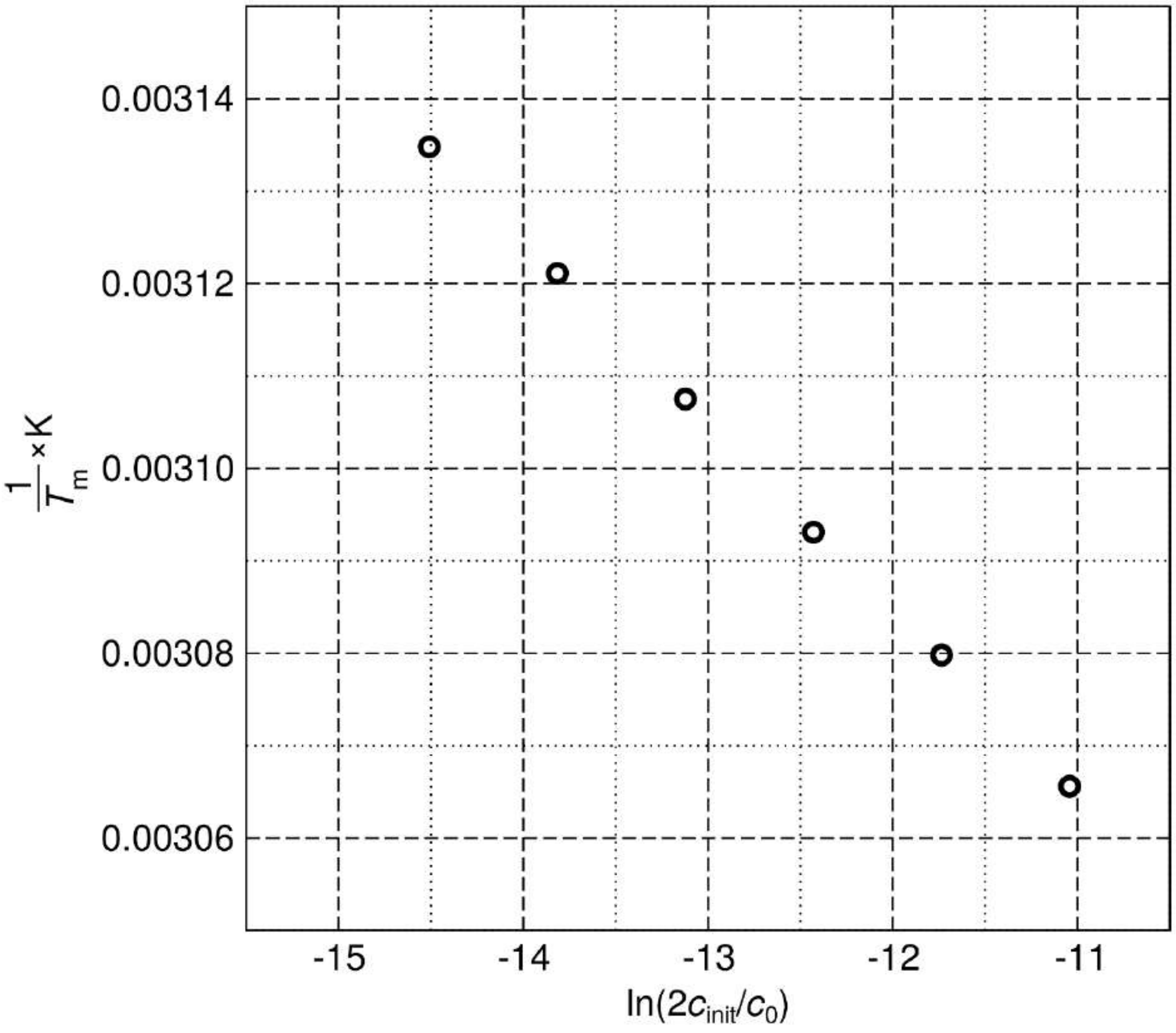
2 points for the decision on a palindromic sequence

Full marks will be given if palindromic dsDNA is considered correctly. The non-palindromic case is not required explicitly.

If only non-palindromic case is considered, 50% of the marks may be scored for the calculation (max. 5 points in total)

−2 points for the wrong numeric value of n_p in spite of the correct symbolic result and logics, e.g. due to an improper use of a calculator, or due to a gross rounding error

Finally, let us leave the simplified idea of base pairs contributing individually to the **association** of DNA strands. The Gibbs energy of this process may be considered explicitly dependent on temperature. The dependence of the inverse T_m of the Drew–Dickerson dodecanucleotide (**1**) on the logarithm of the initial duplex concentration c_{init} is shown below. (*Note*: a standard concentration c_0 = 1 mol dm^{-3} is introduced.)



c_{init} / 10^{-6} mol dm^{-3}	0.25	0.50	1.00	2.0	4.0	8.0
T_m / K	319.0	320.4	321.8	323.3	324.7	326.2

1.6 Calculate the standard enthalpy $\Delta H°$ and the standard entropy $\Delta S°$ of the association of DNA single strands to form the palindromic double-stranded Drew–Dickerson dodecanucleotide (**1**). Assume that $\Delta H°$ and $\Delta S°$ do not vary with temperature.

Calculation:

Start from the definition of $\Delta G°$ and its relation to the equilibrium constant:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta G^{\circ} = -RT\ln K$$

Combination of the expressions leads to

$$\Delta H^{\circ} - T\Delta S^{\circ} = -RT\ln K$$

Division by $T \times \Delta H°$ yields

$$\frac{1}{T} - \frac{\Delta S^{\circ}}{\Delta H^{\circ}} = -\frac{R}{\Delta H^{\circ}}\ln K$$

so that, specifically for T_m

$$\frac{1}{T_m} = \frac{\Delta S^{\circ}}{\Delta H^{\circ}} - \frac{R}{\Delta H^{\circ}}\ln K_m$$

where K_m is the equilibrium constant at the melting temperature.

For the palindromic Drew–Dickerson dodecanucleotide, the concentrations of dsDNA and ssDNA at the melting temperature may be expressed in terms of the initial duplex concentration c_{init}

$$[\text{dsDNA}] = 0.5\, c_{\text{init}}$$

$$[\text{ssDNA}] = c_{\text{init}}$$

and the equilibrium constant at the melting temperature follows as

$$K_m = \frac{0.5\frac{c_{\text{init}}}{c_0}}{\left(\frac{c_{\text{init}}}{c_0}\right)^2} = \frac{1}{2\frac{c_{\text{init}}}{c_0}}$$

This may be cast into the equation above for the inverse melting temperature, yielding a linearized concentration dependence (note the “plus” sign), which corresponds to the plot in this task directly:

$$\frac{1}{T_m} = \frac{\Delta S^{\circ}}{\Delta H^{\circ}} + \frac{R}{\Delta H^{\circ}}\ln\left(2\frac{c_{\text{init}}}{c_0}\right)$$

The slope $R/\Delta H°$ and the intercept $\Delta S°/\Delta H°$ may be obtained

- either graphically from the plot – **method 1**,
- or by solving a system of 2 linear equations using any 2 data points – **method 2**.

Method 1: The dependence in the plot is strongly linear, and it is very easy to draw a straight line passing the centre of each of the circles representing data points. Then, values of the linear function may be read, e.g., at $\ln(2\frac{c_{\mathrm{init}}}{c_0}) = -15$, ca. 0.003145 K^{-1}, and at $\ln(2\frac{c_{\mathrm{init}}}{c_0}) = -11$, ca. 0.003065 K^{-1}. From these numerical values, the slope follows as

$$\text{slope} = \frac{0.003065\ \mathrm{K}^{-1} - 0.003145\ \mathrm{K}^{-1}}{-11-(-15)} = -\,0.000020\ \mathrm{K}^{-1}$$

and the intercept has to be re-calculated to abscissa equal to zero, e.g., as

$$\text{intercept} = 0.003065\ \mathrm{K}^{-1} + (0-(-11)) \times (-0.000020\ \mathrm{K}^{-1}) = 0.002845\ \mathrm{K}^{-1}$$

Method 2: For instance, considering the first and the last point, we obtain:

the first point: $\frac{1}{T_\mathrm{m}} = \frac{1}{319.0\ \mathrm{K}} = 3.135 \times 10^{-3}\ \mathrm{K}^{-1}$ $\qquad \ln(2\frac{c_{\mathrm{init}}}{c_0}) = \ln\left(2 \times 0.25 \times 10^{-6}\right) = -14.5$

the last point: $\frac{1}{T_\mathrm{m}} = \frac{1}{326.2\ \mathrm{K}} = 3.066 \times 10^{-3}\ \mathrm{K}^{-1}$ $\qquad \ln(2\frac{c_{\mathrm{init}}}{c_0}) = \ln\left(2 \times 8.0 \times 10^{-6}\right) = -11.0$

A system of two linear equations follows as

$$3.135 \times 10^{-3}\ \mathrm{K}^{-1} = \frac{\Delta S^\circ}{\Delta H^\circ} - 14.5 \times \frac{R}{\Delta H^\circ}$$

$$3.066 \times 10^{-3}\ \mathrm{K}^{-1} = \frac{\Delta S^\circ}{\Delta H^\circ} - 11.0 \times \frac{R}{\Delta H^\circ}$$

which yields the solution

$$\frac{\Delta S^\circ}{\Delta H^\circ} = 2.849 \times 10^{-3}\ \mathrm{K}^{-1} \quad \text{and} \quad \frac{R}{\Delta H^\circ} = -\,2.0 \times 10^{-5}\ \mathrm{K}^{-1}$$

Common to Methods 1 and 2: The desired thermodynamic quantities follow from there:

$$\boldsymbol{\Delta H^\circ} = \frac{R}{\text{slope}} = \frac{8.314}{-\,0.000020}\ \mathrm{J\ mol^{-1}}\ \mathbf{= -\,416\ kJ\ mol^{-1}}$$

$$\boldsymbol{\Delta S^\circ} = R \times \frac{\text{intercept}}{\text{slope}} = 8.314 \times \frac{0.002845}{-0.000020}\ \mathrm{J\ K^{-1}\ mol^{-1}}\ \mathbf{= -1.18\ kJ\ K^{-1}\ mol^{-1}}$$

Alternative route:

It is also possible to consider the linearized dependence implicitly.

After the combination of equalities for $\Delta G°$, K_m may be expressed in terms of c_{init}:

$$\Delta H^\circ - T_\mathrm{m}\Delta S^\circ = RT_\mathrm{m} \ln(2\frac{c_{\mathrm{init}}}{c_0})$$

Then, a set of 2 such equations for 2 different concentrations

$$\Delta H^\circ - T_{\mathrm{m}1}\Delta S^\circ = RT_{\mathrm{m}1} \ln(2\frac{c_{\mathrm{init},1}}{c_0})$$

$$\Delta H^\circ - T_{m2}\Delta S^\circ = RT_{m2}\ln\left(2\frac{c_{init,2}}{c_0}\right)$$

may be solved for 2 unknowns, ΔH° and ΔS°.

For instance, multiplication of the equations with T_{m2} and T_{m1}, respectively, followed by the subtraction of equations leads to

$$\Delta H^\circ = R\frac{T_{m1}T_{m2}}{T_{m2} - T_{m1}}\ln\frac{c_{init,1}}{c_{init,2}}$$

and a plain subtraction of equations leads to

$$\Delta S^\circ = R\frac{T_{m1}\ln\left(2\frac{c_{init,1}}{c_0}\right) - T_{m2}\ln\left(2\frac{c_{init,2}}{c_0}\right)}{T_{m2} - T_{m1}}$$

Or, ΔS° may be obtained by casting ΔH° into one of the equations being solved:

$$\Delta S^\circ = \frac{\Delta H^\circ}{T_{m1}} + R\ln 2\frac{c_{init,1}}{c_0}$$

The desired quantities follow as **$\Delta H^\circ = -420$ kJ mol^{-1} and $\Delta S^\circ = -1.2$ kJ mol^{-1} K^{-1}.**

24 points in total
15 points for the symbolic derivations
3 points for the combination of the expressions for ΔG°
3 points for the rearrangement to yield the linear relationship between T_m and K_m
3 points for the concentrations of the dsDNA and ssDNA at T_m
3 points for the expression of K_m in terms of c_{init} for a palindromic sequence
3 points for the linear relationship between T_m and ln $2c_{init}$

9 points for the numerical calculations
Note: the least-squares linear fit to the data series leads to the following results including the standard deviations: slope = $(-19.97 \pm 0.08) \times 10^{-6}$, intercept = $(2.845 \pm 0.001) \times 10^{-3}$.
Method 1:
Perform a least-squares linear fit on the pocket calculator, or
read-off of the slope & intercept for the linear dependence (ref.: least-sq. linear fit)
6 points within a margin of 5σ (i.e., $-20.39 < 10^6$ slope < -19.55 & $2.840 < 10^3$ intercept < 2.850)
3 points within a margin of 10σ (i.e., $-20.81 < 10^6$ slope < -19.13 & $2.835 < 10^3$ intercept < 2.855)
partial marks will be scored in case the slope & intercept are given with different deviations or if one is missing
3 points for the calculation of ΔH° & ΔS° from the slope & intercept
Method 2:
3 points for the setup of the system of two equations
up to 6 points for the calculation of ΔH° and ΔS°, considering the accuracy requirements given above

Alternative route – symbolic derivations up to 18 points, numerical calculations up to 6 points
Symbolic derivations:
3 points for the combination of the expressions for ΔG° (a)
3 points for the concentrations of the dsDNA and ssDNA at the melting temperature (b)
3 points for the expression of K_m in terms of c_{init} for a palindromic sequence (c)

3 points for the setup of the system of two equations (d)
3 points for the expression for $\Delta H°$ (e)
3 points for the expression for $\Delta S°$ (f)
9 points for a correct application of Van ‘t Hoff equation, yielding an expression for $\Delta H°$ (a+d+e)
Numerical calculations: maximum 6 points considering the accuracy requirements given above

General remarks

Some of the steps in the derivation and in the calculation may be taken implicitly or simultaneously. As long as they are correct, full marks will be scored for each of the partial steps.
Failure to write unitless concentrations explicitly and consistently does not lead to any deduction as long as the concentrations are in mol dm^{-3} and numerically correct.

Theoretical Problem 2	Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	**Total**
	Points	1	4	4	2	6	10	17	14	**58**
8% of the total	Score									

Problem 2. Repatriation of remains in the middle ages

At ambient temperatures, racemisation is a slow reaction. As such, it can be used for dating biological objects and, moreover, for studying their thermal history. Let us take L-isoleucine (L-Ile) ((2*S*,3*S*)-2-amino-3-methylpentanoic acid) as an example. It isomerises on the α-carbon and forms (2*R*,3*S*)-2-amino-3-methylpentanoic acid, also known as D-*allo*-isoleucine. As the configuration changes on only one of the two stereogenic centres, this process is called epimerisation rather than racemisation.

2.1 Choose all true statements.

☐ D-*allo*-isoleucine and L-isoleucine have the same values of specific optical rotation but they have different melting points.

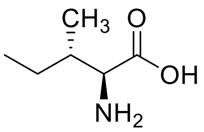
☐ D-*allo*-isoleucine has an identical absolute value of specific optical rotation as L-isoleucine but the sign is opposite. The melting point is the same for both isomers.

☐ D-*allo*-isoleucine and L-isoleucine have different values of specific optical rotation but they have the same melting points.

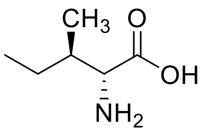
☐ D-*allo*-isoleucine and L-isoleucine have different values of specific optical rotation and different melting points.

☐ D-*allo*-isoleucine is not optically active.

2.2 Assign the absolute configurations for each stereoisomer of isoleucine.



A



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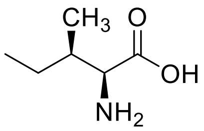
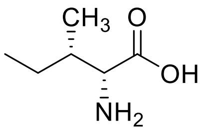


C



D

☐ 2*S*,3*R* (L-*allo*-isoleucine)

☐ 2*R*,3*S* (D-*allo*-isoleucine)

☐ 2*S*,3*S* (L-isoleucine)

☐ 2*R*,3*R* (D-isoleucine)

2.3 The equilibrium constant K_{ep} for L-isoleucine epimerisation has the value of 1.38 (at 374 K). Setting the molar Gibbs free energy of L-isoleucine G°_{m} = 0 kJ mol^{-1}, determine the Gibbs free energies for all structures **A–D** from question 2.2 at 374 K.

A kJ mol^{-1}

B kJ mol^{-1}

C kJ mol^{-1}

D kJ mol^{-1}

2.4 If we take into account stereoisomerism at all stereocentres, what is the maximum possible number of the stereoisomers of the tripeptide Ile-Ile-Ile?

The number of stereoisomers is

At the start of the epimerisation, we can neglect the reverse reaction. The epimerisation then follows the first-order kinetics:

$$\text{L-isoleucine} \xrightarrow{k_1} \text{D-}\textit{allo}\text{-isoleucine}$$

The value of the rate constant at 374 K is k_1(374 K) = 9.02 × 10^{-5} h^{-1} and at 421 K it is k_1(421 K) = 1.18 × 10^{-2} h^{-1}.

In the following calculation, shorten the concentration of L-isoleucine to [L] and of D-*allo*-isoleucine to [D].

We can define a quantity *de* (diastereomeric excess):

$$de = \frac{[\text{L}] - [\text{D}]}{[\text{L}] + [\text{D}]} \times 100(\%).$$

2.5 Let us boil L-isoleucine for 1 943 hours at 374 K. What is the value of *de* (with three significant figures) for L-isoleucine a) before boiling and b) after boiling?

a) Before boiling

Show your calculation:

de = % (with 3 significant figures)

b) After boiling

Show your calculation:

de = % (with 3 significant figures)

2.6 How long does it take to convert 10% of L-isoleucine to D-*allo*-isoleucine at 298 K?

Show your calculation:

t = years

In fact, the reverse reaction cannot be neglected. The correct kinetic scheme is expressed as

$$\text{L-isoleucine} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{D-}\textit{allo}\text{-isoleucine}$$

Let us define the deviation of concentration from its equilibrium value $[\mathrm{L}]_{\mathrm{eq}}$

$$x = [\mathrm{L}] - [\mathrm{L}]_{\mathrm{eq}}$$

It is possible to derive that x evolves with time according to the following equation:

$$x = x(0) \times \mathrm{e}^{-(k_1 + k_2)t},$$

where $x(0)$ is the deviation from equilibrium at $t = 0$ h.

2.7 Let us boil 1.00 mol dm^{-3} L-isoleucine solution for 1 943 hours at 374 K. The rate constant for the forward reaction is $k_1(374\ \mathrm{K}) = 9.02 \times 10^{-5}\ \mathrm{h}^{-1}$, K_{ep} for L-isoleucine epimerisation has the value of 1.38 (at 374 K). In the following calculation, shorten the concentration of L-isoleucine to [L] and of D-*allo*-isoleucine to [D]. Evaluate (with three significant figures) a) $[\mathrm{L}]_{\mathrm{eq}}$, b) diastereomeric excess (*de*) after boiling.

a) Show your calculation:

$[L]_{eq}$ = mol dm^{-3}

b) Show your calculation:

de = % (with 3 significant figures)

Amino acids with a single chiral centre undergo racemisation, e.g. L-arginine racemises:

$$\text{L-arginine} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \text{D-arginine}$$

The time evolution of concentrations is governed by

$$\ln \frac{1 + \frac{[\mathrm{D}]}{[\mathrm{L}]}}{1 - \frac{[\mathrm{D}]}{[\mathrm{L}]}} = 2k_1 t + C$$

Here [D] and [L] are concentrations of D- and L-arginine at time t, k_1 is the rate constant, and the term C is set according to the initial concentrations.

Holy Roman Emperor Lothar III passed away during his journey to Sicily in 1137. To facilitate the repatriation of the remains, his body was, immediately after his death, boiled in water (at 373 K) for a certain time. Let us try to estimate the boiling time with the help of chemical kinetics. We know that the rate constant k_1 of arginine racemisation within the protein at 373 K and pH = 7 has the value of 5.10×10^{-3} h^{-1}.

In order to analyse the isomeric composition of arginine in Lothar's bones, we need to start with transferring arginine into solution. Lothar's bones were hydrolysed in a highly acidic environment for

4 hours at 383 K. The ratio of the optical isomers was $\frac{[D]}{[L]} = 0.090$. Lothar's wife Richenza was not boiled after her death. Her bones were hydrolysed using the same procedure and in this case the ratio was $\frac{[D]}{[L]} = 0.059$. (Note that the racemisation also takes place during the hydrolysis, with the rate constant k_1', different from k_1).

2.8 How long was the Holy Roman Emperor Lothar III boiled in water in 1137?

Note: The racemisation of arginine is an extremely slow process at temperatures typically encountered in graves. As both bodies are only some 880 years old, we can neglect the natural racemisation during this time.

Show your calculation:

$t_{\text{boiling}} =$ h

Theoretical Problem 2	Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	**Total**
	Points	1	4	4	2	6	10	17	14	**58**
8% of the total	Score									

Problem 2. Repatriation of remains in the middle ages

At ambient temperatures, racemization is a slow reaction. As such, it can be used for dating biological objects and, moreover, for studying their thermal history. Let us take L-isoleucine (L-Ile) ((2*S*,3*S*)-2-amino-3-methylpentanoic acid) as an example. It isomerizes on the α-carbon and forms (2*R*,3*S*)-2-amino-3-methylpentanoic acid, also known as D-*allo*-isoleucine. As the configuration changes on only one of the two stereogenic centres, this process is called epimerization rather than racemization.

2.1 Choose all true statements.

☐ D-*allo*-isoleucine and L-isoleucine have the same values of specific optical rotation but they have different melting points.

☐ D-*allo*-isoleucine has an identical absolute value of specific optical rotation as L-isoleucine but the sign is opposite. The melting point is the same for both isomers.

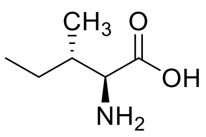
☐ D-*allo*-isoleucine and L-isoleucine have different values of specific optical rotation but they have the same melting points.

☒ D-*allo*-isoleucine and L-isoleucine have different values of specific optical rotation and different melting points.

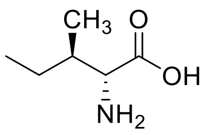
☐ D-*allo*-isoleucine is not optically active.

1 point for the correct answer
−1 point for each incorrect answer
0 points minimum score

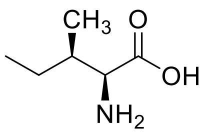
2.2 Assign the absolute configurations for each stereoisomer of isoleucine.



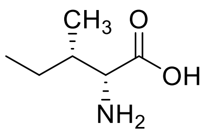
A



B



C



D

C 2*S*,3*R* (L-*allo*-isoleucine)

D 2*R*,3*S* (D-*allo*-isoleucine)

A 2*S*,3*S* (L-isoleucine)

B 2*R*,3*R* (D-isoleucine)

1 point for each correct answer

2.3 The equilibrium constant K_{ep} for L-isoleucine epimerization has the value of 1.38 (at 374 K). If we set molar Gibbs free energy of L-isoleucine G°_{m} = 0 kJ mol^{-1}, determine the Gibbs free energies for all structures **A–D** from question 2.2 at 374 K.

A kJ mol^{-1}
B kJ mol^{-1}
C kJ mol^{-1}
D kJ mol^{-1}

A $G^{\circ}_{m} = 0$ kJ mol^{-1} (L-isoleucine)

B $G^{\circ}_{m} = 0$ kJ mol^{-1} (**B** is a mirror image of **A** with identical physical properties)

C $G^{\circ}_{m} = -RT \ln K_{ep} = -1.00 \times 10^{3}$ J mol^{-1}

D $G^{\circ}_{m} = -1.00 \times 10^{3}$ J mol^{-1} (**D** is a mirror image of **C** with identical physical properties)

4 points in total, 1 point for each numerical value **A**, **B**, **C**, **D**
No explanation is needed to score full marks as long as the results are correct.
0 points for incorrect sign.

2.4 If we take into account stereoisomerism at all stereocentres, what is the maximum possible number of the stereoisomers of the tripeptide Ile-Ile-Ile?

The number of stereoisomers is 2^{N}, where N is the number of stereogenic centres.

For Ile-Ile-Ile, $N = 6$, so there are $2^{6} = 64$ stereoisomers.

2 points for the numerical result (either 2^{6} or 64). *No explanation is needed.*
1 point if the student correctly declares 2^{6} *but the final result is numerically incorrect.*
Example of an incorrect solution that do not score any marks:
The student incorrectly counts the number of stereocenters.

At the start of the epimerization, we can neglect the reverse reaction. The epimerization then follows the first-order kinetics:

$$\text{L-isoleucine} \xrightarrow{k_1} \text{D-}allo\text{-isoleucine}$$

The value of the rate constant at 374 K is $k_1(374\text{ K}) = 9.02 \times 10^{-5}$ h^{-1} and at 421 K it is $k_1(421\text{ K}) = 1.18 \times 10^{-2}$ h^{-1}.

In the following calculation, shorten the concentration of L-isoleucine to [L] and of D-*allo*-isoleucine to [D].

We can define a quantity *de* (diastereomeric excess):

$$de = \frac{[\text{L}] - [\text{D}]}{[\text{L}] + [\text{D}]} \times 100(\%).$$

2.5 Let us boil L-isoleucine for 1 943 hours at 374 K. What is the value of *de* (with three significant figures) for L-isoleucine a) before boiling and b) after boiling?

a) Before boiling

Calculation:

Before boiling, the *de* is:

$$de = \frac{[\mathrm{L}\,]_0 - [\mathrm{D}\,]_0}{[\mathrm{L}\,]_0 + [\mathrm{D}\,]_0} \times 100(\%)$$

Because $[\mathrm{D}\,]_0 = 0$, the *de* of native L-isoleucine before boiling is 100%.

de = % (with three significant figures)

b) After boiling

Calculation:

First, we have to calculate the concentration ratio $\frac{[\mathrm{L}]}{[\mathrm{L}]_0}$ from the first-order rate equation

$$\frac{[\mathrm{L}]}{[\mathrm{L}]_0} = e^{-k_1 t} = 0.839$$

$$\text{so } [\mathrm{D}] = 0.161\ [\mathrm{L}]_0$$

and $de = \frac{0.839 - 0.161}{0.839 + 0.161} \times 100\% = 67.8\%$ (with three significant figures)

de = % (with three significant figures)

Number of significant figures is not evaluated
2 points for the de before boiling
No additional explanation is needed to score full marks.
After boiling:
1 point for the equation for the concentration ratio from the first-order rate equation
1 point for the relation between the concentration of D-allo-isoleucine and L-isoleucine
2 points for the numerical result
If de is given as 0.678, full marks are scored.
Some of the steps may be performed implicitly. As long as the result is correct, full marks are scored for all elementary steps.
No points are scored if the calculations are not provided

2.6 How long does it take to convert 10% of L-isoleucine to D-*allo*-isoleucine at 298 K?

Calculation:

We need to evaluate the rate constant at 298 K. It can be evaluated from the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

We get $\ln A$ and E_a from the values of k at two temperatures (374 K and 421 K)

$$\ln k\ (374\ \mathrm{K}) = \ln 9.02 \times 10^{-5}\ [\mathrm{h}^{-1}] = -9.313 = \ln A - \frac{E_a}{R \times 374}$$

$$\ln k\ (421\ \mathrm{K}) = \ln 1.18 \times 10^{-2}\ [\mathrm{h}^{-1}] = -4.444 = \ln A - \frac{E_a}{R \times 421}$$

It follows that

$$\ln A = -9.313 + \frac{E_a}{R \times 374} = -4.444 + \frac{E_a}{R \times 421}$$

from which $E_a = 136\ \text{kJ mol}^{-1}$.

ln *A* is from the equation at 374 K

$$\ln(A[\text{h}^{-1}]) = -9.313 + \frac{E_a}{R \times 374} = 34.4$$

For *k* at 298 K we then have:

$$\ln(k(298\ \text{K})[\text{h}^{-1}]) = \ln A - \frac{E_a}{R \times 298} = 34.4 - \frac{136 \times 10^3}{R \times 298} = -20.5$$

$$k(298\ \text{K}) = 1.25 \times 10^{-9}\ \text{h}^{-1}$$

It follows from the rate equation that

$$\ln \frac{[\text{L}]}{[\text{L}]_0} = -kt$$

$$\ln 0.90 = -1.25 \times 10^{-9}\ t$$

$$t = 8.42 \times 10^{7}\ \text{h} = 9\ 610\ \text{years}$$

t = years

2 points for the formulation of the set of two equations
2 points for the correct formulae for ln A and E_A (1 point each)
2 points for the correct numerical values of ln A and E_A (1 point each)
2 points for the calculation of the rate constant at 298 K (1 point for the formula, 1 point for the numerical value)
2 points for the calculation of time
Full marks will be given if the time is calculated correctly using a wrong value of k based on the correct formula.
Some of the steps may be performed implicitly. As long as the result is correct, full marks are scored for all elementary steps. Full marks will be given for numerical calculations of time and rate constants within margins $k(298\ \text{K}) = 1.25 \times 10^{-9}\ \text{h}^{-1} \pm 0.1 \times 10^{-9}\ \text{h}^{-1}$, $t = 9\ 610$ years ± 850 years.
No points are scored if the calculations are not provided.

In fact, the reverse reaction cannot be neglected. The correct kinetic scheme is expressed as

$$\text{L-isoleucine} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{D-}\textit{allo}\text{-isoleucine}$$

Let us define the deviation of concentration from its equilibrium value $[\text{L}]_{eq}$

$$x = [\text{L}] - [\text{L}]_{eq}$$

It is possible to derive that *x* evolves with time according to the following equation:

$$x = x(0) \times e^{-(k_1 + k_2)t},$$

where *x*(0) is the deviation from equilibrium at *t* = 0 h.

2.7 Let us boil 1.00 mol dm^{-3} L-isoleucine solution for 1 943 hours at 374 K. The rate constant for the forward reaction is $k_1(374\ \text{K}) = 9.02 \times 10^{-5}\ \text{h}^{-1}$, K_{ep} for L-isoleucine epimerization has the value of 1.38 (at 374 K). In the following calculation, shorten the concentration of L-isoleucine to [L] and of D-*allo*-isoleucine to [D]. Evaluate (with three significant figures) a) $[\mathrm{L}]_{\mathrm{eq}}$, b) diastereomeric excess (*de*) after boiling.

a) Calculation:

From the definition and mass balance we know that

$$x = [\mathrm{L}] - [\mathrm{L}]_{\mathrm{eq}} = [\mathrm{D}]_{\mathrm{eq}} - [\mathrm{D}]$$

We can derive the formulae for $[\mathrm{L}]_{\mathrm{eq}}$ (and also for $[\mathrm{D}]_{\mathrm{eq}}$) in terms of $[\mathrm{L}]_0$

$$[\mathrm{L}]_0 = [\mathrm{L}]_{\mathrm{eq}} + [\mathrm{D}]_{\mathrm{eq}}$$

$$[\mathrm{D}]_{\mathrm{eq}} = [\mathrm{L}]_0 - [\mathrm{L}]_{\mathrm{eq}}$$

We also know that

$$K_{\mathrm{ep}} = \frac{k_1}{k_2} = \frac{[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{L}]_{\mathrm{eq}}}$$

from which

$$[\mathrm{D}]_{\mathrm{eq}} = \frac{k_1}{k_2}\,[\mathrm{L}]_{\mathrm{eq}}$$

The substitution for $[\mathrm{D}]_{\mathrm{eq}}$ in $[\mathrm{D}]_{\mathrm{eq}} = [\mathrm{L}]_0 - [\mathrm{L}]_{\mathrm{eq}}$ yields

$$[\mathrm{L}]_{\mathrm{eq}} = \frac{k_2}{k_1 + k_2}\,[\mathrm{L}]_0$$

The rate constant k_2 is calculated from the epimerization constant K_{ep} as

$$k_2 = \frac{k_1}{K_{\mathrm{ep}}} = \frac{9.02 \times 10^{-5}\ \mathrm{h}^{-1}}{1.38} = 6.54 \times 10^{-5}\ \mathrm{h}^{-1}$$

After the substitution of the numerical values, we get (with three significant digits)

$$[\mathrm{L}]_{\mathrm{eq}} = \frac{6.54 \times 10^{-5}\ \mathrm{h}^{-1}}{9.02 \times 10^{-5}\ \mathrm{h}^{-1} + 6.54 \times 10^{-5}\ \mathrm{h}^{-1}} \times 1\ \mathrm{mol\ dm}^{-3} = 0.420\ \mathrm{mol\ dm}^{-3}$$

$[\mathrm{L}]_{\mathrm{eq}}$ = mol dm^{-3} (with three significant figures)

b) Calculation:

de is defined as

$$de = \frac{[\mathrm{L}] - [\mathrm{D}]}{[\mathrm{L}] + [\mathrm{D}]} \times 100(\%)$$

We can express *de* in terms of the equilibrium values as

$$de = \frac{[\mathrm{L}]_{\mathrm{eq}} + x - [\mathrm{D}]_{\mathrm{eq}} + x}{[\mathrm{L}]_{\mathrm{eq}} + x + [\mathrm{D}]_{\mathrm{eq}} - x} \times 100(\%) = \frac{[\mathrm{L}]_{\mathrm{eq}} - [\mathrm{D}]_{\mathrm{eq}} + 2x}{[\mathrm{L}]_0} \times 100(\%)$$

We already have the formula for $[\mathrm{L}]_{\mathrm{eq}}$ from task a). $[\mathrm{D}]_{\mathrm{eq}}$ in terms of $[\mathrm{L}]_0$ is then

$$[\mathrm{D}]_{\mathrm{eq}} = \frac{k_1}{k_2}\,[\mathrm{L}]_{\mathrm{eq}} = \frac{k_1}{k_1 + k_2}\,[\mathrm{L}]_0$$

Finally, we need to evaluate x in terms of $[L]_0$. We know that $x(0) = [D]_{eq}$, so

$$x = [D]_{eq} \times e^{-t(k_1 + k_2)} = \frac{k_1}{k_1 + k_2}[L]_0 \times e^{-t(k_1 + k_2)}$$

We can now express *de* as

$$de = \frac{\frac{k_2}{k_1 + k_2}[L]_0 - \frac{k_1}{k_1 + k_2}[L]_0 + 2\frac{k_1}{k_1 + k_2}[L]_0 e^{-t(k_1 + k_2)}}{[L]_0} \times 100(\%) = \frac{k_2 - k_1 + 2k_1 e^{-t(k_1 + k_2)}}{k_1 + k_2} \times 100(\%)$$

$$de = \frac{6.54 \times 10^{-5} - 9.02 \times 10^{-5} + 2 \times 9.02 \times 10^{-5} e^{-1\,943\,(9.02 \times 10^{-5} + 6.54 \times 10^{-5})}}{9.02 \times 10^{-5} + 6.54 \times 10^{-5}} \times 100(\%) = 69.8\%$$

(with three significant digits)

de = % (with three significant figures)

a)
1 point for the mass balance equation
2 points for the equation for the equilibrium constant in terms of the rate constants and concentrations
2 points for the derivation of the formula for $[L]_{eq}$ *in terms of* $[L]_0$
1 point for the numerical value of k_2
1 point for the numerical value of $[L]_{eq}$
No points are scored if the calculations are not provided.
b)
2 points for the correct equation for de in terms of the equilibrium values
2 points for the derivation of the formulae for $[D]_{eq}$ *in terms of* $[L]_0$
2 points for the derivation of the formula for x in terms of $[L]_0$
2 points for the correct equation for de in terms of $[L]_0$
2 points for the correct numerical value of de based on correct formula
Some steps in the derivation may be taken implicitly or simultaneously. As long as they are correct, full marks will be scored for each of the partial steps. If the numerical calculation of k_2 *in point a) is incorrect but* k_2 *is correctly used in task b), full marks are scored in task b).*
No points are scored if the calculations are not provided.

Amino acids with a single chiral centre undergo racemization, e.g. L-arginine racemizes:

$$\text{L-arginine} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \text{D-arginine}$$

The time evolution of concentrations is governed by

$$\ln \frac{1 + \frac{[D]}{[L]}}{1 - \frac{[D]}{[L]}} = 2k_1 t + C$$

Here [D] and [L] are concentrations of D- and L-arginine at time t, k_1 is the rate constant, and the term C is set according to the initial concentrations.

Holy Roman Emperor Lothar III passed away during his journey to Sicily in 1137. To facilitate the repatriation of the remains, his body was, immediately after his death, boiled in water (373 K) for a certain time. Let us try to estimate the boiling time with the help of chemical kinetics. We know that the rate constant k_1 of arginine racemization within the protein at 373 K and pH = 7 has the value of 5.10×10^{-3} h^{-1}.

In order to analyse the isomeric composition of arginine in Lothar's bones, we need to start with transferring arginine into solution. Lothar's bones were hydrolyzed in a highly acidic environment for 4 hours at 383 K. The ratio of the optical isomers was $\frac{[D]}{[L]} = 0.090$. Lothar's wife Richenza was not boiled after her death. Her bones were hydrolyzed using the same procedure and in this case the ratio was $\frac{[D]}{[L]} = 0.059$. (Note that the racemization also takes place during the hydrolysis, with the rate constant $k_1^{'}$, different from k_1).

2.8 How long was the Holy Roman Emperor Lothar III boiled in water in 1137?

Note: The racemization of arginine is an extremely slow process at temperatures typically encountered in graves. As both bodies are only some 880 years old, we can neglect the natural racemization during this time.

Calculation:

Let us assume the following schemes for Lothar and Richenza

Lothar: $0 \xrightarrow{k_1} 1 \xrightarrow{k_1^{'}} 2$

Richenza: $0 \xrightarrow{k_1^{'}} 3$

where 0 is the state before boiling with $\frac{[D]}{[L]}$ ratio X_0, 1 corresponds to the Lothar's state after boiling in water in 1137 with the $\frac{[D]}{[L]}$ ratio X_1, 2 is the Lothar's state after the acidic hydrolysis with the $\frac{[D]}{[L]}$ ratio X_2, and 3 is the Richenza's state after the hydrolysis with the $\frac{[D]}{[L]}$ ratio X_3. k_1 is the rate constant for racemization at 373 K, $k_1^{'}$ is the rate constant for acid-catalyzed racemization at 383 K.

We can write the following equations:

$$\ln\frac{1+X_3}{1-X_3} = 2\,k_1^{'}t_{\text{hydrolysis}} \quad \text{(eq. 1)}$$

$$\ln\frac{1+X_1}{1-X_1} = 2\,k_1 t_{\text{boiling}} \quad \text{(eq. 2)}$$

$$\ln\frac{1+X_2}{1-X_2} = 2\,k_1^{'}t_{\text{hydrolysis}} + \ln\frac{1+X_1}{1-X_1} \quad \text{(eq. 3)}$$

Combining the equations leads to

$$\ln\frac{1+X_2}{1-X_2} = \ln\frac{1+X_3}{1-X_3} + 2\,k_1 t_{\text{boiling}}$$

From which the time of boiling t_{boiling} is

$$\ln\frac{(1+X_2)\,(1-X_3)}{(1-X_2)\,(1+X_3)} = 2\,k_1 t_{\text{boiling}}$$

Using the values $X_2 = 0.090$ and $X_3 = 0.059$ we get

$$t_{\text{boiling}} = \frac{1}{2 \times 5.10 \times 10^{-3}} \ln \frac{(1 + 0.090)\,(1 - 0.059)}{(1 - 0.090)\,(1 + 0.059)} = 6.11\ \text{h}$$

$t_{\text{boiling}} =$ h

8 points for rate equations describing the time evolution of the ratio between the optical isomers for Lothar and Richenza (2 points for each eq. 1 and 2; 4 points for eq. 3; 1 point for eq. 3 with an incorrect evaluation of C)

4 points for the combination of the equations to get the time of boiling

2 points for the evaluation of the boiling time

Some steps may be taken implicitly. If the correct boiling time is provided with correct assumptions in calculations, full marks will be scored.

Example of a partially correct solution:

1 point if the boiling time is derived correctly but the result is incorrect

No points are scored if the calculations are not provided.

Theoretical Problem 3 8% of the total	Question	3.1	3.2	3.3	3.4	3.5	3.6
	Points	2	6	7	3	7	8
	Score						
	Question	3.7	3.8	3.9	3.10	3.11	**Total**
	Points	6	10	5	2	6	**62**
	Score						

Problem 3. Emerging electro-mobility

Contemporary means of transportation rely on burning fossil fuels, although the efficiency of real combustion engines is inherently limited and typically ranges between 20 and 40%.

3.1 Mark the factors that can make the efficiency of a heat engine higher:

☐ Increasing the friction in the mechanical parts of the engine
☐ Increasing the burning temperature of the fuel in the engine
☐ Narrowing the working temperature interval of the engine
☐ Increasing the working pressure of the gas

Fuel cells represent a way to improve the engine efficiency for future vehicles. The engine efficiency can be improved by using hydrogen-based fuel cells.

3.2 The standard enthalpy of formation of liquid water is $\Delta_f H°(H_2O,l) = -285.84$ kJ mol^{-1}, and the standard combustion enthalpy of isooctane is $\Delta_c H°(C_8H_{18},l) = -5065.08$ kJ mol^{-1} (both at 323.15 K). Calculate the values of specific (per unit of mass) combustion enthalpy at 323.15 K of pure liquid isooctane and pure gaseous hydrogen.

$\Delta_c H_s°(C_8H_{18}) =$

$\Delta_c H_s°(H_2) =$

3.3 Calculate the standard electromotive force (EMF) of a fuel cell using gaseous oxygen and hydrogen, both ideal gases at 100 kPa and 323.15 K, to produce liquid water. Use the following entropy data for 323.15 K: $S°(H_2O,l) = 70\ J\ K^{-1}\ mol^{-1}$, $S°(H_2,g) = 131\ J\ K^{-1}\ mol^{-1}$, $S°(O_2,g) = 205\ J\ K^{-1}\ mol^{-1}$.

Show your calculation:

EMF = V

3.4 Determine the ideal thermodynamic efficiency (η) of a fuel cell producing liquid water at 353.15 K. At this temperature, the enthalpy of formation of water is $\Delta_f H°(H_2O,l) = -281.64$ kJ mol^{-1} and the corresponding reaction Gibbs energy change is $\Delta_r G° = -225.85$ kJ mol^{-1}.

η = %

3.5 A polymer membrane electrolyser facility operates at the voltage of 2.00 V and is powered by a 10.0 MW wind turbine plant which was running at full power from 10 pm to 6 am. The electrolysis yielded 1090 kg of pure hydrogen. Calculate the electrolysis yield defined as the mass of produced hydrogen divided by its theoretical produced mass.

Show your calculation:

$\eta_{\text{electrolysis}}$ = %

3.6 Calculate the mass of hydrogen required to drive the distance between Prague and Bratislava (330 km) at the average speed of 100 km h^{-1} with a car fitted with a 310 kW electric engine running on average at 15% of its maximum power. Assume that the efficiency of the hydrogen cell producing electrical energy is 75%, the efficiency of the electric engine is 95%, and the Gibbs energy change for combustion of hydrogen fuel is $\Delta_r G = -226$ kJ mol^{-1}.

Show your calculation:

m = kg

The low efficiency of hydrogen production and the safety issues connected with its storage impede spreading the hydrogen-based transportation technology. Hydrazine (N_2H_4) fuel cells might be a suitable alternative.

The following standard reduction potentials for aqueous hydrazine systems are available:

$N_2(g) + 5\ H^+(aq) + 4\ e^- \rightarrow N_2H_5^+(aq)$ $E° = -0.23$ V

$N_2H_5^+(aq) + 3\ H^+(aq) + 2\ e^- \rightarrow 2\ NH_4^+(aq)$ $E° = +1.28$ V

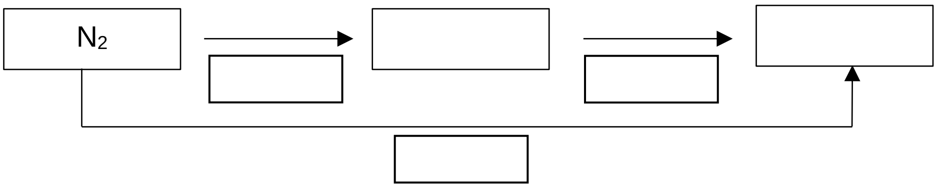
$N_2(g) + 4\ H_2O(l) + 4\ e^- \rightarrow N_2H_4(aq) + 4\ OH^-\ (aq)$ $E° = -1.16$ V

$N_2H_4(aq) + 2\ H_2O(l) + 2\ e^- \rightarrow 2\ NH_3(aq) + 2\ OH^-\ (aq)$ $E° = +0.10$ V

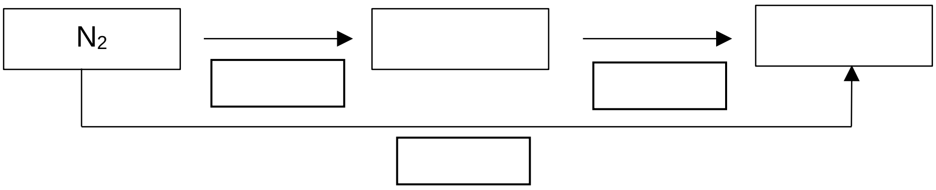
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-\ (aq)$ $E° = -0.83$ V.

3.7 Fill in the following Latimer diagrams with the forms of hydrazine and ammonia prevailing at the given conditions and write the redox potential value for each arrow representing the electrochemical half-reaction. Record all the necessary calculations.

a) Acidic environment (pH = 0)



b) Basic environment (pH = 14)



Show your calculations:

Due to the toxicity, odour and its environmental impact, it is extremely unfavourable to produce ammonia in fuel cells.

3.8 Write down the net reaction for the decomposition of hydrazine under basic conditions to (i) ammonia and nitrogen and (ii) nitrogen and hydrogen and calculate the corresponding equilibrium constants at T = 298.15 K.

Equations for hydrazine decomposition:

Show your calculations:
Hydrazine decomposition to NH_3 and N_2 in a basic environment:

K =

Hydrazine decomposition to H_2 and N_2 in a basic environment:

K =

Rechargeable lithium-based batteries are an alternative to fuel cells. Lithium-ion batteries commonly use graphite for one of the electrodes, in which lithium clusters intercalate in between the graphite sheets. The other electrode is made of lithium cobalt oxide, which can reversibly absorb lithium ions moving from one electrode to the other during the charge and discharge processes. The half-reactions relevant for the system can be formally written as:

$$(C)_n + Li^+ + e^- \rightarrow Li(C)_n \qquad E^\circ = -3.05\ V,$$

$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2 \qquad E^\circ = +0.19\ V.$$

3.9 Using the formalism given above, write down the overall chemical reaction occurring in the battery during the **discharge** process. Give the oxidation states of the cobalt atom.

3.10 Tick the boxes which are correct for the **discharge** of the lithium-based battery described in 3.9:

$Li(C)_n$ electrode is the	☐ cathode ☐ anode	☐ because lithium ions are reduced here. ☐ because lithium atoms are oxidised here.
$LiCoO_2$ electrode is the	☐ cathode ☐ anode	☐ because cobalt ions are reduced here. ☐ because cobalt ions are oxidised here.

3.11 Assume that a C_6 unit, a CoO_2 unit and Li atom form the active battery mass required to transfer one electron between the electrodes. Using the corresponding standard EMF, calculate the theoretical specific reversible charge capacity (in mAh g^{-1}) and the energy density (in kWh kg^{-1}) of such a model lithium ion battery related to the whole active battery mass.

Show your calculation:

Charge capacity ($c_{q,s}$) = mAh g^{-1}

Show your calculation:

Energy density (ρ_{el})= kWh kg^{-1}

Theoretical Problem 3 8% of the total	Question	3.1	3.2	3.3	3.4	3.5	3.6
	Points	2	6	7	3	7	8
	Score						
	Question	3.7	3.8	3.9	3.10	3.11	**Total**
	Points	6	10	5	2	6	**62**
	Score						

Problem 3. Emerging electro-mobility

Contemporary means of transportation rely on burning fossil fuels, although the efficiency of real combustion engines is inherently limited and typically ranges between 20 and 40%.

3.1 Mark the factors that can make the efficiency of a heat engine higher:

☐ Increasing the friction in the mechanical parts of the engine
☒ Increasing the burning temperature of the fuel in the engine
☐ Narrowing the working temperature interval of the engine
☒ Increasing the working pressure of the gas

2 points in total; 1 points for each correct answer (the second and fourth options in the list), −1 points for each incorrect answer, total points scored in this question may not be negative

Fuel cells represent a way to improve the engine efficiency for future vehicles. The engine efficiency can be improved by using hydrogen-based fuel cells.

3.2 The standard enthalpy of formation of liquid water is $\Delta_f H°(H_2O,l) = -285.84$ kJ mol^{-1}, and the standard combustion enthalpy of isooctane is $\Delta_c H°(C_8H_{18},l) = -5\,065.08$ kJ mol^{-1} (both at 323.15 K). Calculate the values of specific (per unit of mass) combustion enthalpy at 232.15 K of pure liquid isooctane and pure gaseous hydrogen.

$\Delta_c H_s°(C_8H_{18})$ =

$$\Delta_c H_s°(C_8H_{18}) = \frac{\Delta_c H°(C_8H_{18})}{M(C_8H_{18})} = \frac{-5\,065.08 \times 10^3\ \text{J mol}^{-1}}{114.23 \times 10^{-3}\ \text{kg mol}^{-1}} = -44.34\ \text{MJ kg}^{-1}$$

$\Delta_c H_s°(H_2)$ =

$$\Delta_c H_s°(H_2) = \frac{\Delta_c H°(H_2)}{M(H_2)} = \frac{-285.84 \times 10^3\ \text{J mol}^{-1}}{2.02 \times 10^{-3}\ \text{kg mol}^{-1}} = -141.50\ \text{MJ kg}^{-1}$$

6 points in total. Some of the steps may be condensed or performed implicitly. As long as this is performed correctly, full marks are scored for all of the elementary steps. Zero points will be scored for any numerical (sub)result given with wrong or missing units.
1 point for each numerically correct molar mass (including unit)
2 points for the correct way of calculation of the specific combustion enthalpy
1 point for each numerically correct specific combustion enthalpy (including unit)
−1 point for the wrong sign(s)

3.3 Calculate the standard electromotive force (EMF) of a fuel cell using gaseous oxygen and hydrogen, both ideal gases at 100 kPa and 323.15 K, to produce liquid water. Use the following entropy data for 323.15 K: $S°(H_2O,l) = 70\ J\ K^{-1}\ mol^{-1}$, $S°(H_2,g) = 131\ J\ K^{-1}\ mol^{-1}$, $S°(O_2,g) = 205\ J\ K^{-1}\ mol^{-1}$.

Calculations:

The oxidation of molecular hydrogen requires the transfer of $z = 2$ electrons according to the equation: $H_2 + ½\ O_2 \rightarrow H_2O$

$$\Delta_r S° = S°(H_2O,l) - \left(S°(H_2,g) + \frac{1}{2}S°(O_2,g)\right) = -164\ J\ K^{-1}\ mol^{-1}$$

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° =$$

$$= -285.84 \times 10^3\ J\ mol^{-1} + 323.15\ K \times 164\ J\ K^{-1}\ mol^{-1} = -233\ kJ\ mol^{-1}$$

$$EMF = -\frac{\Delta_r G°}{|z|F} = -\frac{-233 \times 10^3\ J\ mol^{-1}}{2 \times 96\,485\ C\ mol^{-1}} = 1.21\ V$$

EMF = V

7 points in total for the correct result calculated in any correct way. Some of the steps may be condensed or performed implicitly. As long as this is performed correctly, full marks are scored for all of the elementary steps. Zero points will be scored for any numerical (sub)result given with wrong or missing units.

1 point for the correct value of z resulting from the correctly written chemical equation

1 point for the correct formula for the reaction entropy according to the written chemical equation

1 point for the numerically correct value of the reaction entropy

1 point for the correct formula for the reaction Gibbs energy

1 point for the numerically correct value of the reaction Gibbs energy

1 point for the correct formula for the EMF

1 point for the numerically correct value of the EMF

−1 point for incorrect sign

3.4 Determine the ideal thermodynamic efficiency (η) of a fuel cell producing liquid water at 353.15 K. At this temperature, the enthalpy of formation of water is $\Delta_f H°(H_2O,l) = -281.64$ kJ mol^{-1} and the corresponding reaction Gibbs energy change is $\Delta_r G° = -225.85$ kJ mol^{-1}.

$$\eta = \frac{\Delta_r G°}{\Delta_f H°} = \frac{-225.85\ kJ\ mol^{-1}}{-281.64\ kJ\ mol^{-1}} \times 100\% = 80.19\%$$

η = %

3 points in total

2 points for the correct way of calculation

1 point for the numerically correct result

3.5 A polymer membrane electrolyzer facility operates at the voltage of 2.00 V and is powered by a 10.0 MW wind turbine plant which was running at full power from 10 pm to 6 am. The electrolysis yielded 1 090 kg of pure hydrogen. Calculate the electrolysis yield defined as the mass of produced hydrogen divided by its theoretical produced mass.

Calculations:

Electric energy produced:

$$W = P \times \tau = 10 \times 10^{6}\ \mathrm{W} \times 8 \times 3\,600\ \mathrm{s} = 2.88 \times 10^{11}\ \mathrm{J}$$

is sufficient to transfer the charge:

$$Q = \frac{W}{U} = \frac{2.88 \times 10^{11}\ \mathrm{J}}{2\ \mathrm{V}} = 1.44 \times 10^{11}\ \mathrm{C}$$

between the electrodes. Water formation is a two-electron process. Thus, the theoretical mass of hydrogen produced is:

$$m_{\mathrm{theory}} = \frac{Q\,M}{|z|\,F} = \frac{1.44 \times 10^{11}\ \mathrm{C}}{2 \times 96\,485\ \mathrm{C\ mol^{-1}}} \times 2.02 \times 10^{-3}\ \mathrm{kg\ mol^{-1}} = 1\,507\ \mathrm{kg}$$

The efficiency of the electrolysis can be evaluated as the ratio:

$$\eta_{\mathrm{electrolysis}} = \frac{m_{\mathrm{real}}}{m_{\mathrm{theory}}} \times 100\% = \frac{1\,090}{1\,507} \times 100\% = 72.3\%.$$

$\eta_{\mathrm{electrolysis}}$ = %

7 points in total for the numerically correct final result calculated in any correct way. Some of the steps may be condensed or performed implicitly. As long as this is performed correctly, full marks will be scored for all elementary steps. If only the final equation for m_{theory} is derived correctly, but its numerical value is wrong, 4 points will be scored for m_{theory}. If a wrong numerical subresult is used in subsequent steps which are performed correctly but yield a wrong numerical value, 4 points will be scored for m_{theory}. 0 points will be scored for any numerical (sub)result given with wrong or missing units.

1 point for the correct formula for W
1 point for the numerically correct value of W
1 point for the correct way of calculation of Q
1 point for the numerically correct value of Q
1 point for any correct way of calculation of the theoretical amount of hydrogen
1 point for the numerically correct theoretical amount of hydrogen
1 point for the numerically correct electrolysis efficiency

3.6 Calculate the mass of hydrogen required to drive the distance between Prague and Bratislava (330 km) at the average speed of 100 km h^{-1} with a car fitted with a 310 kW electric engine running on average at a 15% rate of its maximum power. Assume that the efficiency of the hydrogen cell producing electrical energy is 75%, the efficiency of the electric engine is 95%, and the Gibbs energy change for combustion of hydrogen fuel is $\Delta_r G = -226\ \mathrm{kJ\ mol^{-1}}$.

Calcualtions:

Driving time:

$$\tau = \frac{s}{v} = \frac{330\ \text{km}}{100\ \text{km h}^{-1} / 3\,600\ \text{s}} = 11\,880\ \text{s}$$

determines the ideal amount of energy required to cover the given distance:

$$W_{\text{ideal}} = P \times f \times \tau = 310 \times 10^3\ \text{W} \times 0.15 \times 11\,880\ \text{s} = 5.52 \times 10^8\ \text{J}.$$

Assuming the overall non-unity efficiency, the real energy required is:

$$W_{\text{real}} = \frac{W_{\text{ideal}}}{\eta_{\text{electrolysis}} \times \eta_{\text{engine}}} = \frac{5.52 \times 10^8\ \text{J}}{0.75 \times 0.95} = 7.75 \times 10^8\ \text{J}.$$

This can be combined with the standard Gibbs energy of liquid water formation to yield the amount of hydrogen:

$$m = \frac{W_{\text{real}}}{|\Delta_r G°|} \times M = \frac{7.75 \times 10^8\ \text{J}}{2.26 \times 10^5\ \text{J mol}^{-1}} \times 2.02 \times 10^{-3}\ \text{kg mol}^{-1} = 6.93\ \text{kg}.$$

m = kg

8 points in total for the numerically correct final result calculated in any correct way. Some of the steps may be condensed or performed implicitly. As long as this is performed correctly, full marks will be scored for all of the elementary steps. If only the final relation for m is derived correctly, but its numerical value is wrong, 6 points will be scored in total . If a wrong numerical subresult is used in subsequent steps which are performed correctly but yield a wrong numerical value, 6 points will be scored for m_{theory}. *0 points will be scored for any numerical (sub)result given with wrong or missing units.*

1 point for the correct formula for τ
1 point for the correct value of τ
1 point for the correct formula for W_{ideal}
1 point for the numerically correct value of W_{ideal}
1 point for the correct formula for W_{real}
1 point for the numerically correct value of W_{real}
1 point for the correct formula for m
1 point for the numerically correct value of m

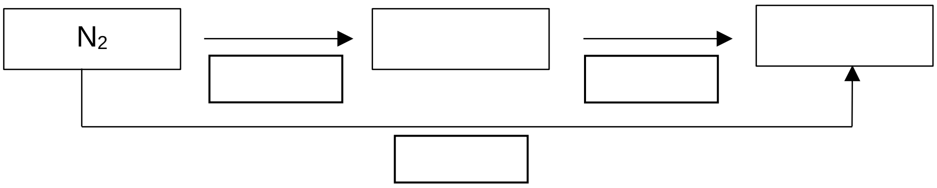
The low efficiency of hydrogen production and the safety issues connected with its storage impede spreading the hydrogen-based transportation technology. Hydrazine (N_2H_4) fuel cells might be a suitable alternative.

The following standard reduction potentials for aqueous hydrazine systems are available:

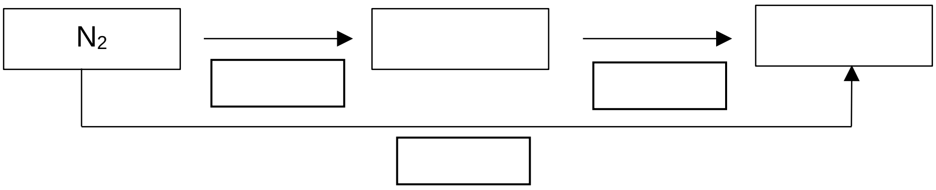
$N_2(g) + 5\ H^+(aq) + 4\ e^- \rightarrow N_2H_5^+(aq)$ $E° = -0.23$ V
$N_2H_5^+(aq) + 3\ H^+(aq) + 2\ e^- \rightarrow 2\ NH_4^+(aq)$ $E° = +1.28$ V
$N_2(g) + 4\ H_2O(l) + 4\ e^- \rightarrow N_2H_4(aq) + 4\ OH^-(aq)$ $E° = -1.16$ V
$N_2H_4(aq) + 2\ H_2O(l) + 2\ e^- \rightarrow 2\ NH_3(aq) + 2\ OH^-(aq)$ $E° = +0.10$ V
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$ $E° = -0.83$ V.

3.7 Fill in the following Latimer diagrams with the forms of hydrazine and ammonia prevailing at the given conditions and write the redox potential value for each arrow representing the electrochemical half-reaction. Record all the necessary calculations.

a) Acidic environment (pH = 0)



b) Basic environment (pH = 14)



Acidic environment:

$$\begin{tikzcd}
N_2 \arrow[r, "-0.23\ \mathrm{V}"'] \arrow[rr, bend right, "+0.27\ \mathrm{V}"'] & N_2H_5^+ \arrow[r, "+1.28\ \mathrm{V}"'] & NH_4^+
\end{tikzcd}$$

Basic environment:

$$\begin{tikzcd}
N_2 \arrow[r, "-1.16\ \mathrm{V}"'] \arrow[rr, bend right, "-0.74\ \mathrm{V}"'] & N_2H_4 \arrow[r, "+0.10\ \mathrm{V}"'] & NH_3
\end{tikzcd}$$

Calculations:

Redox potentials for N_2 to NH_4^+ and N_2 to NH_3, respectively, are calculated as follows:

$$E°(N_2/NH_4^+) = \frac{4\,E°(N_2/N_2H_5^+) + 2\,E°(N_2H_5^+/NH_4^+)}{6} = \frac{4 \times (-\,0.23) + 2 \times 1.28}{6}\ \mathrm{V} = 0.27\ \mathrm{V}$$

$$E°(N_2/NH_3) = \frac{4\,E°(N_2/N_2H_4) + 2\,E°(N_2H_4/NH_3)}{6} = \frac{4 \times (-\,1.16) + 2 \times 0.10}{6}\ \mathrm{V} = -\,0.74\ \mathrm{V}$$

6 points in total

1 point for each diagram completely correctly filled with chemical species, no partial points given if any mistake occurs

1 point for the numerically correct value of each of the standard redox potentials $E°(N_2/NH_4^+)$ and $E°(N_2/NH_3)$, no partial points given if any mistake occurs

1 point for each diagram correctly filled with the remaining standard redox potentials, no partial points given if any mistake occurs

Due to the toxicity, odour and its environmental impact, it is extremely unfavourable to produce ammonia in fuel cells.

3.8 Write down the net reaction for the decomposition of hydrazine under basic conditions to (i) ammonia and nitrogen and (ii) nitrogen and hydrogen and calculate the corresponding equilibrium constants at T = 298.15 K.

Equations for hydrazine decomposition:

$$N_2H_4(aq) \rightarrow N_2(g) + 2\ H_2(g)$$
$$3\ N_2H_4(aq) \rightarrow 4\ NH_3(aq) + N_2(g)$$

Calculations:

$$\Delta_r G^\circ = -\ RT \ln K = -\ |z|FE^\circ \rightarrow\ K = \exp\left(\frac{|z|FE^\circ}{RT}\right)$$

Hydrazine decomposition to NH_3 and N_2 in a basic environment:

$$E^\circ = E^\circ(N_2H_4/NH_3) + \left(-\ E^\circ(N_2/N_2H_4)\right) = (0.10 + 1.16)\ V = 1.26\ V$$

$$K = \exp\left(\frac{|z|FE^\circ}{RT}\right) = \exp\left(\frac{4 \times 96\,485\ C\ mol^{-1} \times 1.26\ V}{8.314\ J\ K^{-1}\ mol^{-1} \times 298.15\ K}\right) = 1.6 \times 10^{85}$$

K =

Hydrazine decomposition to H_2 and N_2 in a basic environment:

$$E^\circ = E^\circ(H_2O/H_2) + \left(-\ E^\circ(N_2/N_2H_4)\right) = (-\ 0.83 + 1.16)\ V = 0.33\ V$$

$$K = \exp\left(\frac{|z|FE^\circ}{RT}\right) = \exp\left(\frac{4 \times 96\,485\ C\ mol^{-1} \times 0.33\ V}{8.314\ J\ K^{-1}\ mol^{-1} \times 298.15\ K}\right) = 2.1 \times 10^{22}$$

K =

10 points in total

2 points for each correctly balanced reaction (4 points in subtotal)

4 points for the correct way of calculation of the equilibrium constant (2 points will be scored if the correct formula for the related standard reaction Gibbs energy is given)

1 point for each numerically correct value of equilibrium constant (2 points in subtotal), no points will be scored if a wrong value of z is used in the calculation

Rechargeable lithium-based batteries are an alternative to fuel cells. Lithium-ion batteries commonly use graphite for one of the electrodes, in which lithium clusters intercalate in between the graphite sheets. The other electrode is made of lithium cobalt oxide, which can reversibly absorb lithium ions moving from one electrode to the other during the charge and discharge processes. The half-reactions relevant for the system can be formally written as:

$$(C)_n + Li^+ + e^- \rightarrow\ Li(C)_n \qquad E^\circ = -\ 3.05\ V,$$
$$CoO_2 + Li^+ + e^- \rightarrow\ LiCoO_2 \qquad E^\circ = +0.19\ V.$$

3.9 Using the formalism given above, write down the overall chemical reaction occurring in the battery during the **discharge** process. Give the oxidation states of the cobalt atom.

Because $E^\circ_{\text{lower}} > E^\circ_{\text{upper}}$, the upper reaction occurs spontaneously in the opposite direction. Therefore, the discharge of the battery occurs when lithium leaves the graphite structure and its ions intercalate in the cobalt oxide:

$$\mathrm{Li(C)}_n + \mathrm{Co^{IV}O_2} \rightarrow \mathrm{LiCo^{III}O_2} + \mathrm{(C)}_n$$

5 points in total
1 point for each oxidation state of cobalt atom
3 points for the overall reaction
No points will be scored for the reaction written in the opposite direction.

3.10 Tick the boxes to get the correct statements which are valid for the **discharge** of the lithium-based battery described in 3.9:

$\mathrm{Li(C)}_n$ electrode is	☐ cathode ☑ anode	☐ because lithium ions are reduced here. ☑ because lithium atoms are oxidized here.
$\mathrm{LiCoO_2}$ electrode is	☑ cathode ☐ anode	☑ because cobalt ions are reduced here. ☐ because cobalt ions are oxidized here.

2 points in total
1 point for each correct pair of boxes marked

3.11 Assume that a C_6 unit, a CoO_2 unit and Li atom form the active battery mass required to transfer one electron between the electrodes. Using the corresponding standard EMF, calculate the theoretical specific reversible charge capacity (in mAh g^{-1}) and the energy density (in kWh kg^{-1}) of such a model lithium ion battery related to the whole active battery mass.

Calculations:

The transfer of 1 mol of electrons requires at least the molar mass of the active ingredients $M_{\text{total}} = 169.94\ \text{g mol}^{-1}$, meaning that the specific charge capacity is:

$$c_{q,s} = \frac{F}{M} = \frac{96\,485\ \text{C mol}^{-1}}{169.94\ \text{g mol}^{-1}} = 567.76\ \text{C g}^{-1} \approx 567.76\ \text{A s g}^{-1} \approx 157.71\ \text{mAh g}^{-1}$$

Charge capacity ($c_{q,s}$) = mAh g^{-1}

Calculations:

Assuming the standard EMF (voltage) of the battery is:

$$U = E^\circ(\mathrm{Li_{x1}CoO_2/Li_{x2}CoO_2}) - E^\circ(\mathrm{Li^+/Li^0}) = 0.19 + 3.05\ \text{V} = 3.24\ \text{V},$$

the energy density of the battery can be calculated as:

$$\rho_{\text{el}} = U \times c_{q,s} = 3.24\ \text{V} \times 567.76\ \text{C g}^{-1} = 1\,839.6\ \text{W s g}^{-1} \approx 0.511\ \text{kWh kg}^{-1}$$

Energy density (ρ_{el})= kWh kg^{-1}

6 points in total for the numerically correct final result. Some of the steps may be condensed or performed implicitly. As long as this is performed correctly, full marks will be scored for all elementary steps.
1 point will be scored if only the correct numerical value for the Gibbs energy associated with the electron transfer is given. Zero points will be scored for any numerical (sub)result given with wrong or missing units.
1 point for the numerically correct value of the active molar mass
1 point for the correct formula for the specific charge capacity
1 point for the numerically correct value of the specific charge capacity
1 point for the numerically correct value of EMF
1 point for the correct formula for the energy density
1 point for the numerically correct value of the energy density

Sommario