

FULL NAME:

STUDENT ID:

SIGNATURE:

University of Canterbury

Mid Year Examination and Test Period 2009

Prescription Number(s):	CHEM 111
Paper Title:	General Chemistry A

Time Allowed: 2.5 HOURS

Number of pages: 18 pages
2 pages (formulae and periodic table)

Answer **ALL** questions

Total marks = 120

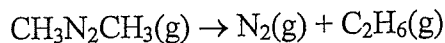
NOTE: There is a page of formulae and a periodic table with atomic masses at the end of this paper.

For examiners use only

1,2	3,4	5	6,7	8-12	13,14	Total/120

1. (13 marks)

Azomethane decomposes as follows:



At 305 °C this occurs with a rate constant of $k = 0.2310 \text{ min}^{-1}$.

- (a) The reaction is first-order. How could you have deduced this from the information above?

From the units of the rate constant (a first-order reaction has a rate constant with dimensions of inverse time).

- (b) For an experiment at 305 °C, the partial pressure of azomethane is initially 317.5 mm Hg.

Calculate the following after 120 s:

- (i) The partial pressure of azomethane

$$\begin{aligned} \text{First-order} \Rightarrow p_A &= p_{A,0} \exp(-kt) \\ &= 317.5 \text{ mm Hg} \times \exp(-0.2310 \text{ min}^{-1} \times 2.00 \text{ min}) \\ &= 317.5 \text{ mm Hg} \times \exp(-0.4620) \\ &= 200.0 \text{ mm Hg} \end{aligned}$$

- (ii) The change in the pressure of $\text{N}_2(\text{g})$

From reaction stoichiometry:

$$\Delta p_{\text{N}_2} = -\Delta p_A = -(200.0 \text{ mm Hg} - 317.5 \text{ mm Hg}) = +117.5 \text{ mm Hg}$$

(iii) The change in the total pressure

From reaction stoichiometry:

$$\Delta p_{\text{total}} = \Delta p_{\text{N}_2} = + 117.5 \text{ mm Hg}$$

(c) How long would it take for half of the azomethane to have decomposed?

$$\begin{aligned} \text{First-order} \Rightarrow t_{1/2} &= \frac{\ln 2}{k} = \frac{\ln 2}{0.2310 \text{ min}^{-1}} \\ &= 3.001 \text{ min} \end{aligned}$$

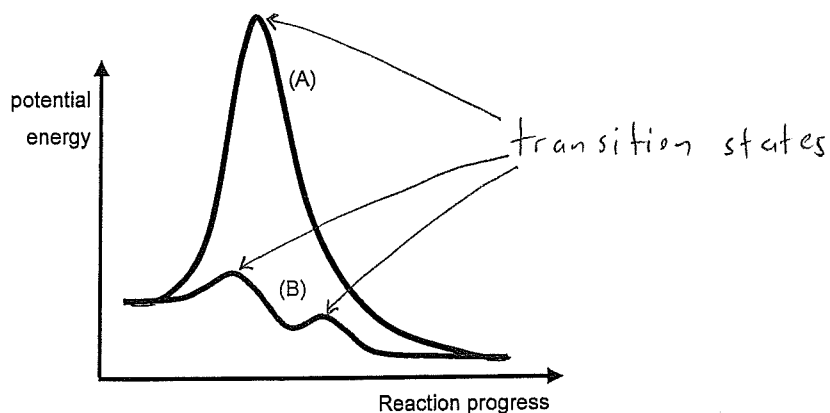
(d) At 325 °C the rate constant is found to have increased to $k = 0.5323 \text{ min}^{-1}$. What is the activation energy for the reaction?

$$[R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}; 0 \text{ °C} = 273.15 \text{ K}]$$

$$\begin{aligned} \ln \left(\frac{k_2}{k_1} \right) &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \Rightarrow E_a &= \frac{R \times \ln \left(\frac{k_2}{k_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \\ &= \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{0.5323 \text{ min}^{-1}}{0.2310 \text{ min}^{-1}} \right)}{\left(\frac{1}{578.15 \text{ K}} - \frac{1}{598.15 \text{ K}} \right)} \\ &= \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 0.8348}{5.783 \times 10^{-5} \text{ K}^{-1}} \\ &= 120.0 \times 10^3 \text{ J mol}^{-1} \\ &= 120.0 \text{ kJ mol}^{-1} \end{aligned}$$

2. (7 marks)

The diagram below relates to two possible pathways for a reaction.



(a) Is pathway (A) that of an *elementary* or *complex* reaction? Explain your answer.

Elementary.

Because the pathway has only one hump, which means there is only one reaction in the mechanism.

(b) Is pathway (B) that of an *elementary* or *complex* reaction? Explain your answer.

Complex.

Because the pathway has two humps, which means there are two reactions in the mechanism.

(c) Which of (A) or (B) represents the pathway of a *catalyzed* reaction? Explain your answer.

(B).

The height of the highest hump is the activation energy (E_a). So (B) has lower E_a , meaning it is catalyzed.

(d) Indicate the location of a *transition state* on the above diagram.

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3. (14 marks)

Nitrous acid (HNO_2) is a weak acid with $K_a = 4.5 \times 10^{-4}$. [$K_w = 1.00 \times 10^{-14}$.](a) What is the $\text{p}K_a$ of nitrous acid?

$$\begin{aligned} \text{p}K_a &= -\log_{10} K_a = -\log_{10} (4.5 \times 10^{-4}) \\ &= 3.35 \end{aligned}$$

(b) What is the pH of a $0.0500 \text{ mol L}^{-1}$ solution of nitrous acid?

$$\begin{aligned} [\text{H}_3\text{O}^+] &\approx \sqrt{K_a \times C_A} \\ &= \sqrt{4.5 \times 10^{-4} \times 0.05} \\ &= 4.74 \times 10^{-3} \end{aligned} \quad \left. \begin{array}{l} \text{"exact" sol}^5 \\ 4.52 \times 10^{-3} \\ 2.34 \end{array} \right\}$$

$$\therefore \text{pH} = 2.32$$

(c) What is the $\text{p}K_b$ of the nitrite anion (NO_2^-)?

For conjugate acid/base pair

$$\text{p}K_a(\text{Acid}) + \text{p}K_b(\text{Base}) = 14$$

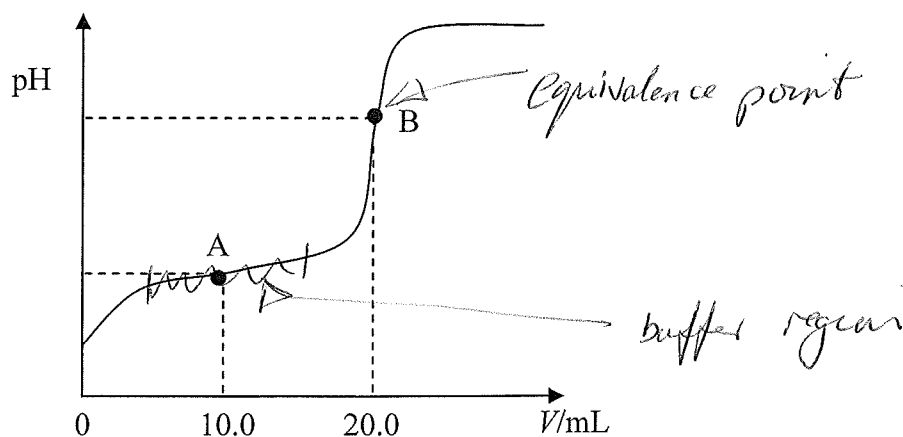
$$\therefore \text{p}K_b(\text{NO}_2^-) = 14 - \text{p}K_a(\text{HNO}_2)$$

$$= 10.65$$

(d) What is the pH of a $0.0250 \text{ mol L}^{-1}$ solution of sodium nitrite (NaNO_2)?

$$\begin{aligned} [\text{OH}^-] &= \sqrt{K_b \times C_B} = \sqrt{2.22 \times 10^{-11} \times 0.025} \\ &= 7.45 \times 10^{-7} \\ \text{pOH} &= 6.13 \\ \therefore \text{pH} &= 14 - \text{pOH} \\ &= 7.87 \end{aligned}$$

- (e) The plot below was obtained from a titration involving $0.0500 \text{ mol L}^{-1}$ solutions of nitrous acid and sodium hydroxide.



- (i) Tick the box that correctly describes the titration:

Nitrous acid solution is being added to sodium hydroxide solution

OR sodium hydroxide solution is being added to nitrous acid solution

- (ii) Indicate and clearly label the following on the above plot:

- The equivalence point
- The buffer region

- (iii) Using your answers to earlier parts of this question, what is the pH corresponding to point A of the plot? **Provide an explanation for your answer.**

In buffer region

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{NO}_2^-]}{[\text{HNO}_2]}$$

= $\text{p}K_a$ at point A which is half-way to equivalence

= 3.35 & $[\text{NO}_2^-] = [\text{HNO}_2]$

(= part (a))

(6)

- (iv) Using your answers to earlier parts of this question, what is the pH corresponding to point B? *Provide an explanation for your answer.*

At B all HNO_2 is converted
to NO_2^- by reaction

$$\text{HNO}_2 + \text{OH}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$$
 Volume is doubled $\therefore [\text{NO}_2^-] = 0.025 \text{ M}$
 $\therefore \text{pH} = 7.87$ (= part (d))

4. (10 marks)

(a) Provide definitions of the following terms in the context of acid-base equilibria:

(i) A Brønsted acid

A proton donor

(ii) A Brønsted base

A proton acceptor

(6)

(iii) A salt

Product of a (neutralisation) reaction between an acid & a base



(iv) A buffer solution

Solution which contains significant and comparable amounts of both a weak acid + a weak base conjugate pair. Such a solution reduces the pH range if acids or bases are added..

(b) A 0.10 mol L^{-1} solution of caffeine has a pH of 11.8. Circle, below, two words that best describe the acid-base properties of caffeine:

STRONG

WEAK

ACID

BASE

5. (12 marks)

(a) Give brief definitions of the following thermodynamic terms:

(i) first law of thermodynamics;

The total energy of the universe is conserved. Energy can be converted from one form to another and shifted from one place to another. But it can't be created or destroyed. For a system, $\Delta U = q + w$

(ii) entropy;

A quantifiable, thermodynamic measure of disorder. It can also be described in terms of the dispersion of energy or the number of equivalent microstates

(iii) surroundings;

2 The part of the universe that is outside of the system.

(iv) spontaneity;

2 A spontaneous process is one that occurs under the prevailing conditions of the system - that is, without requiring a change of the state of the system. For $\Delta G < 0$ forward dir
For $\Delta G > 0$ reverse dir

(v) equilibrium.

2 A system is at equilibrium when its state (as defined by state functions) does not change with time. (its state is constant). $\Delta G = 0$ for a process

(b) Give the names of the functions G , T and Q in the equation:

$$\Delta G = \Delta G^\circ + RT \log_e Q$$

G = Gibbs free energy

T = Absolute temperature

Q = reaction quotient

6. (12 marks)

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{H}_2\text{S}(\text{g})$	-20.6	205.8
$\text{O}_2(\text{g})$	0	205.1
$\text{SO}_2(\text{g})$	-296.8	248.2
$\text{H}_2\text{O}(\text{g})$	-241.8	188.8

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

(a) For the reaction: $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
use the thermodynamic data above to calculate the following:

(i) The standard molar enthalpy change, ΔH° ;

$$\begin{aligned} \Delta H^\circ &= 2\Delta H_f^\circ(\text{SO}_2(\text{g})) + 2\Delta H_f^\circ(\text{H}_2\text{O}(\text{g})) - 2\Delta H_f^\circ(\text{H}_2\text{S}(\text{g})) - 3\Delta H_f^\circ(\text{O}_2(\text{g})) \\ &= (2 \times (-296.8) + 2 \times (-241.8) - 2 \times (-20.6)) \text{ kJ mol}^{-1} \\ &= -1036 \text{ kJ mol}^{-1} \end{aligned}$$

(ii) The standard molar entropy change, ΔS° ;

$$\begin{aligned} \Delta S^\circ &= 2S^\circ(\text{SO}_2(\text{g})) + 2S^\circ(\text{H}_2\text{O}(\text{g})) - 2S^\circ(\text{H}_2\text{S}(\text{g})) - 3S^\circ(\text{O}_2(\text{g})) \\ &= (2 \times 248.2 + 2 \times 188.8 - 2 \times 205.8 - 3 \times 205.1) \text{ J mol}^{-1} \text{K}^{-1} \\ &= -152.9 \text{ J mol}^{-1} \text{K}^{-1} \end{aligned}$$

(iii) ΔG° for the reaction at 25°C ;

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -1036 \text{ kJ mol}^{-1} - 298 \times (-152.9 \text{ J mol}^{-1} \text{K}^{-1}) \\ &= -1036 \text{ kJ mol}^{-1} + 45.56 \text{ kJ mol}^{-1} \\ &= -990 \text{ kJ mol}^{-1} \end{aligned}$$

(iv) The equilibrium constant, K , for the reaction at 25°C .

$$\begin{aligned} K &= e^{-\Delta G^\circ / RT} = e^{990 \times 10^3 \text{ J mol}^{-1} / (8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298)} \\ &= e^{400} \quad \text{huge!} \end{aligned}$$

(b) For the reaction in (a) predict, with an explanation of your reasoning, whether K would *increase*, *decrease*, or *remain unchanged* when the temperature is raised to 100°C .

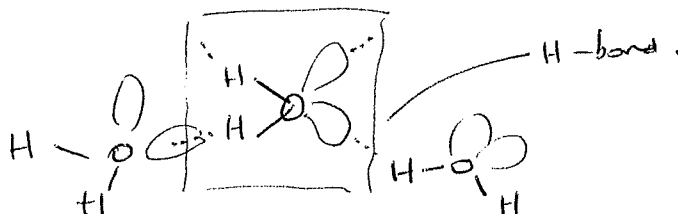
System will adjust in the endothermic direction. Since $\Delta H^\circ < 0$, the endothermic direction is the reverse direction. A shift in the reverse direction means lower K . So K will decrease

**Question 7 has not been added because it is
no longer in the 2010 syllabus**

8. (3 marks)

The hydrogen bond energy for water is 25 kJ mol^{-1} . What is a hydrogen bond (why is it formed)?

The H_2O molecule has a bent structure (104.5°) with 2 lone pairs making up the tetrahedron. Due to the separation of charge (H is $\delta+$, lone pairs $\delta-$) H_2O has a large dipole moment (1.85D). H-bonds are 'electrostatic' interactions between the $\delta+$ H atoms of one molecule and the electron pairs of neighbours. ~~plus~~ This gives a 3D array as shown



9. (2 marks)

The oceans, covering 72% of Earth's surface, exercise a moderating influence on the climate that limits high temperatures in summer and low temperatures in winter. Explain.

Summer

Because H_2O is H-bonded (high heat capacity) as the temperature increases into summer heat is absorbed and disrupts (breaks) H-bonding with little rise in ocean temp (molecular speed) - moderates ocean temp in summer.

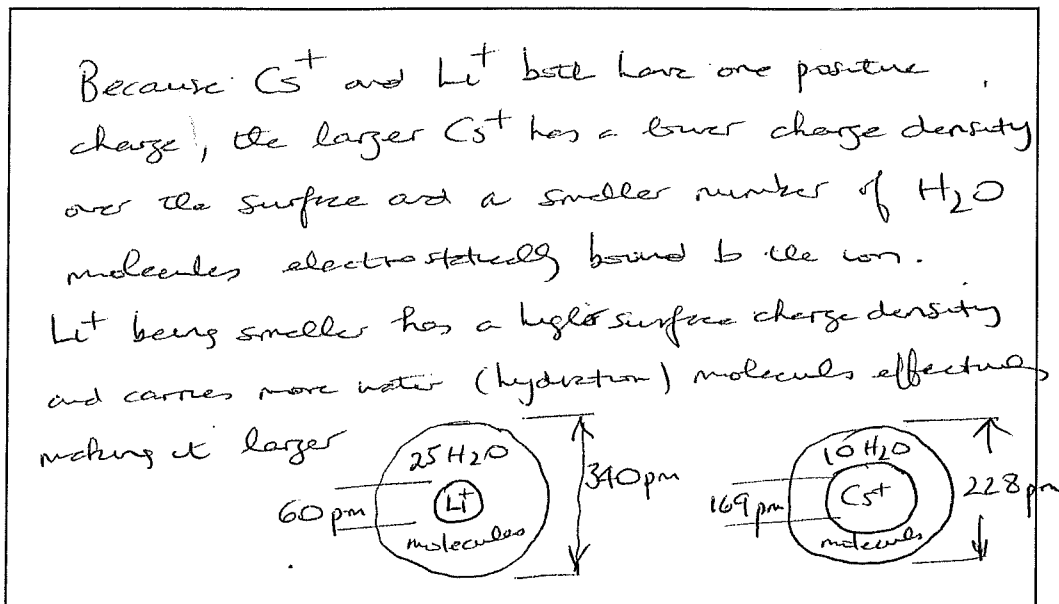
Winter

As temp decreases towards winter heat is released as H-bonds broken in summer reform this precluding excessive falls in temperature.

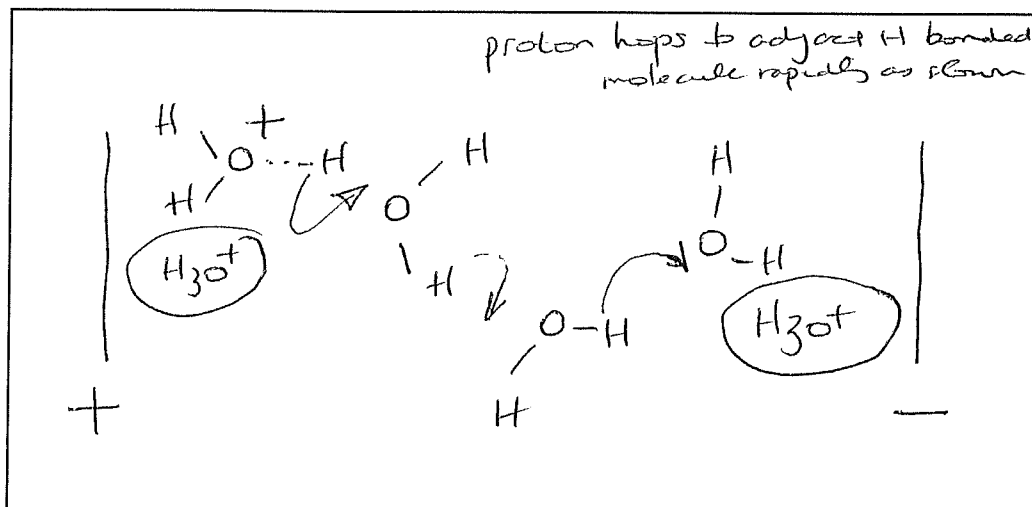
10. (4 marks)

- (a) The mobility of alkali metal cations in aqueous solution under the influence of an electric field **increases** with **increasing** ion size, i.e., Cs^+ is more mobile than Li^+ . Explain.

I don't expect all this detail

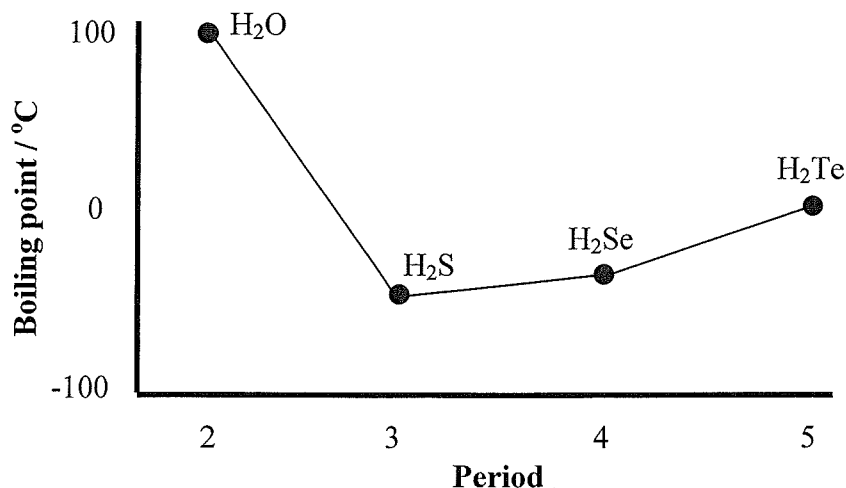


- (b) Despite the trend in (a), the H_3O^+ (H^+) ion in aqueous solution exhibits a much higher mobility than expected. Use a sketch to illustrate the mechanism responsible for this apparent anomaly.



11. (4 marks)

Using the plot below



(a) Explain why the boiling points increase from H₂S to H₂Te?

Molecular size increases from H₂S → H₂Te
 Polarizability increases
 Van der Waals attraction stronger
 Energy required to break electrostatic attraction and facilitate boiling increases

(b) Explain why the boiling point for water appears to deviate so drastically from the trend evident in going from H₂Te to H₂Se to H₂S.

H₂O has huge dipole moment and forms a 3D array of H-bonds
 Energy required to break H-bonds before molecules can gain energy to break free of liquid - increased boiling point

12. (3 marks)

Complete the Table below to qualitatively indicate the solubility of the salts made up from the cations and anions given. Use 1 for soluble, 2 for sparingly soluble and 3 for insoluble.

solubility	Mg ²⁺	Ca ²⁺	Ba ²⁺
OH ⁻	3	1	1
CO ₃ ²⁻	2	(2 or 3)	2
SO ₄ ²⁻	1	1	3

13. (9 marks)

(a) Explain the difference between *static equilibria* and *dynamic equilibria*.

Equilibrium means no change in the state of the system. In static equilibria, no processes occur. In dynamic equilibria, process occurring in opposite directions cancel out.

(b) Are chemical equilibria dynamic or static?

Dynamic

(c) Consider the chemical equilibrium given by equation (1):



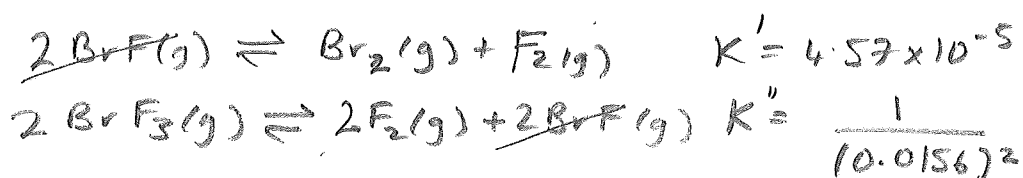
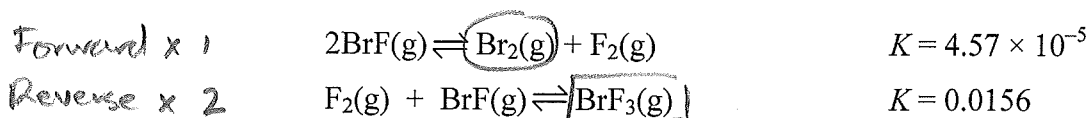
(i) Give an expression for the thermodynamic equilibrium constant for reaction (1), K_1 , in terms of the activities of the reaction components.

$$K_1 = \frac{a_{\text{Br}_2} (a_{\text{F}_2})^3}{(a_{\text{BrF}_3})^2}$$

- (ii) Give an expression for K_1 in terms of the partial pressures of the reaction components.

$$K_1 = \frac{P_{\text{Br}_2} (P_{\text{F}_2})^3}{(P_{\text{BrF}_3})^2}$$

- (iii) Using the data below, calculate the value of K_1 .



$$\frac{2\text{BrF}_3(g) \rightleftharpoons \text{Br}_2(g) + 3\text{F}_2(g)}{K_1 = K' K'' = \frac{4.57 \times 10^{-5}}{(0.0156)^2} = 0.188}$$

14. (9 marks)

- (a) Explain the difference between a *reaction quotient* and an *equilibrium constant*.

For $\text{react} \rightleftharpoons \text{prod}$

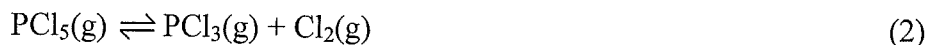
Reaction quotient $Q = \frac{a_{\text{prod}}}{a_{\text{react}}}$

where the activities relate to the conditions prevailing at that time.

Equilibrium $K = Q_{\text{eq}}$

where the activities relate to the conditions once the system has reached its equilibrium state.

- (b) For the reaction given by equation (2), the equilibrium constant is $K_2 = 1.05$ at 25°C .



- (i) Calculate the reaction quotient for a mixture of 1.0 atm $\text{PCl}_5(\text{g})$, 1.0 atm $\text{PCl}_3(\text{g})$ and 0.5 atm $\text{Cl}_2(\text{g})$.

$$Q_2 = \frac{a_{\text{Cl}_2} a_{\text{PCl}_3}}{a_{\text{PCl}_5}} = \frac{0.5 \times 1.0}{1.0} = 0.5$$

- (ii) For the mixture in (i), predict, *with reasoning*, the direction in which reaction (2) will proceed (at constant temperature and volume).

$Q_2 = 0.5$; $K_2 = 1.05$ $Q_2 < K_2$ so the reaction will proceed in the forward direction.

- (iii) Some time after preparing the mixture in (i), the total pressure was measured to be 2.70 atm. Calculate the partial pressures of each of the three reaction components.

component	initial	final	
PCl_5	1.0	$1.0 - x$	= 0.8 atm
PCl_3	1.0	$1.0 + x$	= 1.2 atm
Cl_2	0.5	$0.5 + x$	= 0.7 atm
		$2.5 + x$	
P_{Total}	$2.5 + x = 2.70$	$\Rightarrow x = 0.20$	

- (iv) At the time of the measurement in (iii), has the reaction reached equilibrium? Give your reasoning.

$$Q_2 = \frac{0.7 \times 1.2}{0.8} = 1.05 = K_2$$

Since $Q_2 = K_2$ the system is at equilibrium

END OF PAPER

(Physical Chemistry Formulae and Periodic Table on following pages)