

Full Name:

Student ID #:

UNIVERSITY OF CANTERBURY

Mid-Year Examinations 2005

Prescription Number(s): CHEM 111

Paper Title: General Chemistry A

Time Allowed: TWO HOURS

Number of pages: 19

Before commencing work, read the instructions on this page.

1. This is both your examination paper and your answer book. You may use the blank page opposite for any additional working pertaining to that question.
2. Please ensure that your name and student ID number have been entered in the appropriate spaces above.
3. **ANSWER ALL QUESTIONS.**

Total marks = 120: you should allocate about 1 minute per mark.

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

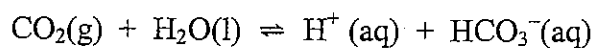
Please write your answers in the boxes provided

For examiners use only

1-2	3	4-5	6-7	8
9	10-11	12-13	Total	

1. (4 marks)

For the reaction



- (a) Give a mathematical expression for the thermodynamic equilibrium constant (K) in terms of the **activities** of the reaction components.

$$K = \frac{(a_{\text{H}^+})(a_{\text{HCO}_3^-})}{(a_{\text{CO}_2})(a_{\text{H}_2\text{O}(\text{l})})}$$

- (b) Give the working rules for estimating the activities of the reaction components.

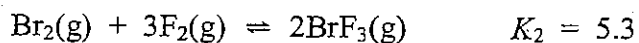
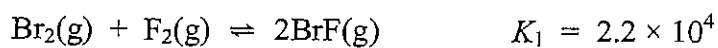
$$a_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{1 \text{ atm}}$$

$$a_{\text{H}_2\text{O}} = 1$$

$$a_{\text{H}^+} = \frac{[\text{H}^+]}{1 \text{ mol L}^{-1}}$$

$$a_{\text{HCO}_3^-} = \frac{[\text{HCO}_3^-]}{1 \text{ mol L}^{-1}}$$

2. (4 marks)

Use the data below to calculate the equilibrium constant (K_3) for the reaction

$$K_3 = \frac{(P_{\text{BrF}})(P_{\text{F}_2})}{(P_{\text{BrF}_3})}$$

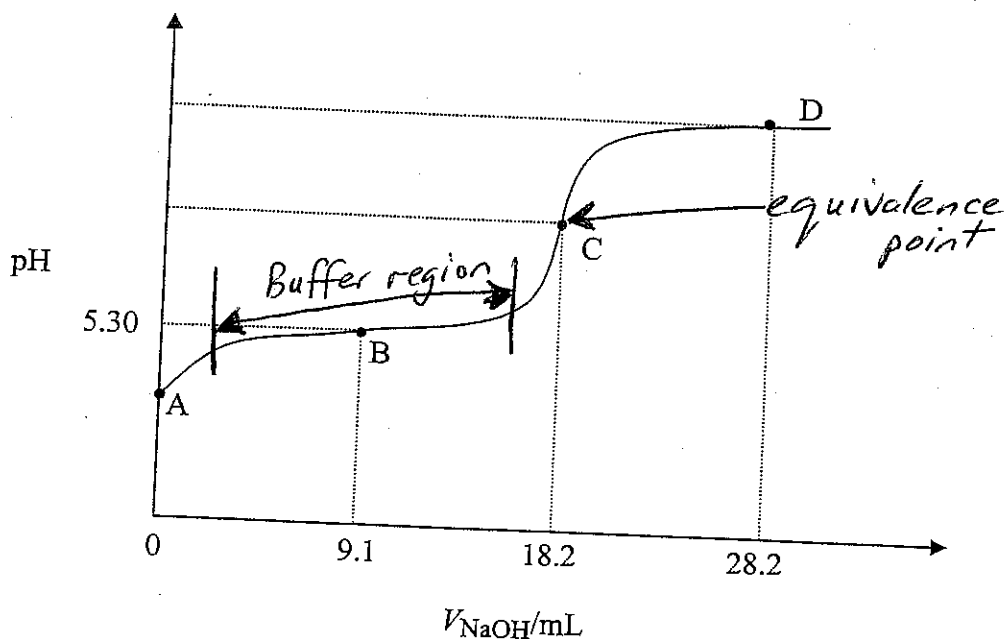
$$K_1 = 2.2 \times 10^4 = \frac{(P_{\text{BrF}})^2}{(P_{\text{Br}_2})(P_{\text{F}_2})}$$

$$K_2 = \frac{(P_{\text{BrF}_3})^2}{(P_{\text{Br}_2})(P_{\text{F}_2})^3} = 5.3$$

$$\therefore K_3 = \frac{K_1^{\frac{1}{2}}}{K_2^{\frac{1}{2}}} = \left(\frac{2.2 \times 10^4}{5.3} \right)^{\frac{1}{2}}$$

$$\therefore K_3 = 64.4$$

3. (24 marks)



The figure above shows the titration curve obtained (using a pH meter) when a 20.0 mL sample of a solution of weak acid, HA, of unknown concentration, C_{HA} , is titrated with standardised NaOH solution. The NaOH solution has a concentration of 0.110 mol L^{-1} and V_{NaOH} represents the volume in mL of NaOH which has been added. [Data: $K_w = 1.00 \times 10^{-14}$.]

(a) What pieces of laboratory equipment would be used to measure out:

(i) the volume of HA solution?

Pipette

(ii) the added volume of NaOH, V_{NaOH} ?

Burette

(b) On the figure above, clearly indicate and label the following:

(i) the equivalence point;

(ii) a buffer region.

(c) Calculate C_{HA} .

At equivalence

$$n_{HA} = n_{OH^-}$$

$$C_{HA} V_{HA} = C_{NaOH} V_{NaOH}$$

$$C_{HA} = C_{NaOH} V_{NaOH} / V_{HA}$$

$$= 0.110 \times \frac{18.2}{1000}$$

$$\frac{20.0}{1000}$$

$$= 0.100$$

mol L^{-1}

Question 3 continued on following page

Question 3 continued

- (d) Using the given pH value for the solution at point B (5.30), calculate K_a (the acid ionisation constant) for HA.

3

At point B the HA is half-neutralised ($V_{NaOH} = 9.1 = \frac{18.2}{2}$)
 $\therefore n_{HA} = n_{A^-}$ and this is a buffer system
 \therefore since $pH = pK_a + \log_{10}\left(\frac{n_{A^-}}{n_{HA}}\right)$ and $\log_{10}(\dots) = 0$
 $\therefore pK_a = pH = 5.30 \quad \therefore K_a = 10^{-5.30}$
 $= 5.01 \times 10^{-6}$

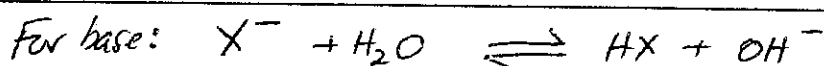
- (e) What is the pH at point A?

3

At point A we have a solution of weak acid HA
 $\therefore [H_3O^+] \approx \sqrt{K_a(HA) \cdot C_{HA}}$
 $= \sqrt{5.01 \times 10^{-6} \times 0.100}$
 $= 7.08 \times 10^{-4}$
 $\therefore pH = -\log_{10}[H_3O^+]$
 $= 3.15$

- (f) Prove the **general result** that K_b (base ionisation constant) for the base X^- (i.e. conjugate base of the acid, HX) is given by

$$K_b(X^-) = K_w / K_a(HX)$$



$$K_b(X^-) = \frac{[HX][OH^-]}{[X^-]}$$

$$= \frac{[HX][OH^-]}{[X^-]} \times \frac{[H_3O^+]}{[H_3O^+]}$$

$$= \frac{K_w}{K_a(HX)}$$

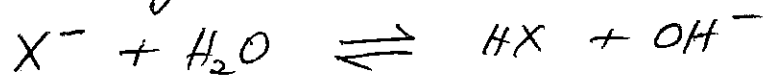
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Since $K_a(HX) = \frac{[H_3O^+][X^-]}{[HX]}$ for $HX + H_2O \rightleftharpoons H_3O^+ + X^-$

Question 3 continued

- (g) Calculate the pH at the equivalence point in the titration.

At point C (essentially) all HX has reacted \rightarrow X^-
 \therefore have a weak base (X^-) solution for which
 the pOH is governed by



Here $[OH^-] \approx \sqrt{K_b(X^-) \cdot C_{X^-}}$

$$K_b(X^-) = K_w / K_a(HX)$$

$$= 10^{-14} / 5.01 \times 10^{-6}$$

and $C_{X^-} = \frac{n_{X^-}}{\text{Total Vol.}} = \frac{n_{HX}}{\text{Total volume}}$

$$= \frac{\frac{20}{1000} \times 0.100}{\frac{20 + 18.2}{1000}} \quad (= 0.0524)$$

substituting

$$[OH^-] = \sqrt{\frac{10^{-14} \times 20 \times 0.100}{5.01 \times 10^{-6} \times (20 + 18.2)}}$$

$$= 1.023 \times 10^{-5}$$

$$\therefore pOH = 4.99$$

$$\therefore pH = 14.00 - pOH$$

$$= 9.01$$

4

Question 3 continued

- (h) The endpoint of this titration could be detected using an indicator. Of the indicators listed below, which would be the most suitable? Explain the reason for your choice.

Indicator	pK_a (indicator)
Lacmoid	5.3
Brilliant yellow	7.2
<i>o</i> -Cresolphthalein	9.0
2,4,6-Trinitrotoluene	12.3

Ideally an indicator should have a pK_a value as close as possible to the pH at the equivalence point (C) which is 9.01

Therefore *o*-Cresolphthalein is the best choice

- (i) What is the pH at point D?

At point D the surplus OH^- (from NaOH) governs the pH

$$[OH^-] = \frac{(\text{Total moles NaOH}) - (\text{Moles HX})}{\text{Total volume}}$$

$$= \frac{\left(\frac{28.2}{1000} - \frac{18.2}{1000}\right) \times 0.110}{\frac{28.2 + 20}{1000}}$$

$$= \frac{10 \times 0.110}{48.2} = 0.0228$$

$$\therefore pOH = 1.64$$

$$\therefore pH = 14 - pOH = 12.36$$

4. (12 marks)

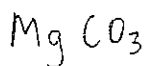
Data: $K_{sp}(\text{BaCO}_3) = 8.1 \times 10^{-9}$

$$K_{sp}(\text{MgCO}_3) = 4.0 \times 10^{-5}$$

$$K_{sp}(\text{PbCO}_3) = 3.3 \times 10^{-14}$$

$$K_{sp}(\text{SrCO}_3) = 1.6 \times 10^{-9}$$

(a) Which of the above four carbonate salts has the **greatest** molar solubility in water?



(b) In **one sentence**, explain your answer for (a).

All 4 salts have the same stoichiometry, so one can say without doing any calculations that the salt with the highest K_{sp} has the greatest molar solubility.

(c) A solution contains a mixture of Ba^{2+} and Mg^{2+} ions obtained by adding $\text{Ba}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ to pure water: $[\text{Ba}^{2+}] = 0.12 \text{ mol L}^{-1}$ and $[\text{Mg}^{2+}] = 0.50 \text{ mol L}^{-1}$. Solid sodium carbonate (Na_2CO_3) is slowly dissolved into the mixed solution until a precipitate starts to form.

What is the **first solid to precipitate** (BaCO_3 or MgCO_3) and how many **moles of sodium carbonate** will have been added **per litre of solution** when this precipitate is **first** observed? (It may be assumed that there is negligible change to the solution volume as sodium carbonate is added.)

A salt precipitates when Q (the ionic product) = K_{sp} .

So BaCO_3 precipitates when $\frac{[\text{Ba}^{2+}]}{1 \text{ M}} \frac{[\text{CO}_3^{2-}]}{1 \text{ M}} = K_{sp}(\text{BaCO}_3)$

$$\Rightarrow [\text{CO}_3^{2-}] / 1 \text{ M} = 8.1 \times 10^{-9} / 0.12 = 6.75 \times 10^{-8}$$

MgCO_3 precipitates when $\frac{[\text{Mg}^{2+}]}{1 \text{ M}} \frac{[\text{CO}_3^{2-}]}{1 \text{ M}} = K_{sp}(\text{MgCO}_3)$

$$\Rightarrow [\text{CO}_3^{2-}] / 1 \text{ M} = 4.0 \times 10^{-5} / 0.5 = 8.0 \times 10^{-5}$$

The lower value is that first reached in adding Na_2CO_3 , so

BaCO_3 is the first solid to precipitate and it does so when

$[\text{CO}_3^{2-}] = 6.8 \times 10^{-8} \text{ M}$, ie when 6.8×10^{-8} moles of Na_2CO_3 have been added per L of solution.

5. (4 marks)

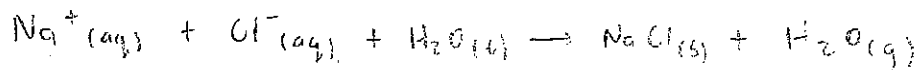
Name **TWO** industrial applications of precipitation equilibria. For each of the named processes, write a balanced, central chemical equation which describes the precipitation of a solid from solution.

Two of many possible examples (see lecture notes) are:

(a) Name of process:

Harvesting of 'table salt' from sea-water

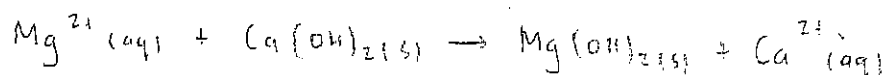
Equation:



(b) Name of process:

Recovery of magnesium from sea-water by adding slaked lime

Equation:



6. (6 marks)

(a) Provide a definition (in words) of a **state function**.

A state function is a variable that is uniquely determined by the state of a system, regardless of how that condition was achieved.

(b) Give the names of each of the state functions in the expression

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

G: Gibbs free energy

H: enthalpy

T: temperature

S: entropy

Question 6 continued on following page

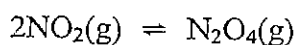
Question 6 continued

- (c) What do the delta (
- Δ
-) signs in equation (1) represent?

Δ means "change in value of"

7. (6 marks)

For the reaction

the equilibrium constant at 25°C is $K = 1.9 \times 10^{-4}$.

- (a) Calculate
- ΔG°
- at 25°C.

$$\begin{aligned} \Delta G^\circ &= -RT \ln K \\ &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln(1.9 \times 10^{-4}) \\ &= +21279 \text{ J mol}^{-1} \\ &= 21 \text{ kJ mol}^{-1} \end{aligned}$$

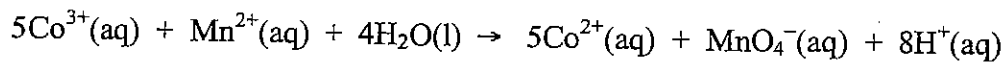
- (b) Given
- $P_{\text{NO}_2} = 0.1 \text{ atm}$
- and
- $P_{\text{N}_2\text{O}_4} = 0.2 \text{ atm}$
- , calculate the value of
- ΔG
- at 25°C.

$$Q = \frac{a_{\text{N}_2\text{O}_4(\text{g})}}{(a_{\text{NO}_2(\text{g})})^2} = \frac{P_{\text{N}_2\text{O}_4} / 1 \text{ atm}}{(P_{\text{NO}_2} / 1 \text{ atm})^2} = \frac{0.2}{(0.1)^2} = 20$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= 21279 \text{ J mol}^{-1} + (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln 20 \\ &= 21279 \text{ J mol}^{-1} + 7422 \text{ J mol}^{-1} \\ &= 28651 \text{ J mol}^{-1} \\ &= 29 \text{ kJ mol}^{-1} \end{aligned}$$

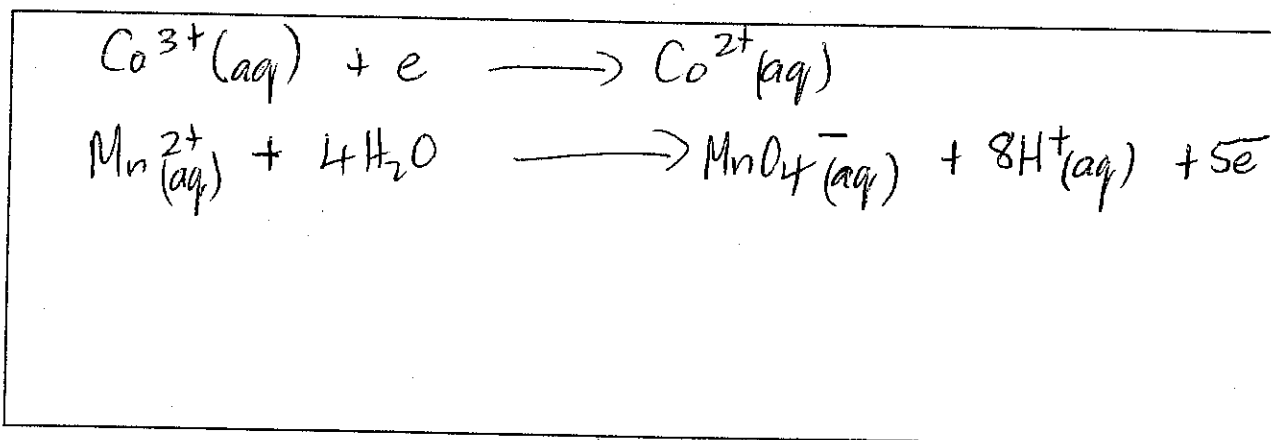
8. (16 marks)

An electrochemical cell comprising (i) a mixed solution of Co^{3+} and Co^{2+} ions and (ii) an acidified solution of potassium permanganate (MnO_4^-) and Mn^{2+} has the cell equation



For this cell, using the relevant data in the table below,

(a) write down the two half-cell equations;



(b) calculate the standard EMF of the cell, E° ;

$$\begin{aligned} E^\circ &= E^\circ_{\text{RHS}} - E^\circ_{\text{LHS}} \quad \text{each written as reduction potentials} \\ &= E^\circ_{\text{Co}^{3+}/\text{Co}^{2+}} - E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.81\text{V} - 1.51\text{V} \\ &= 0.30\text{V} \end{aligned}$$

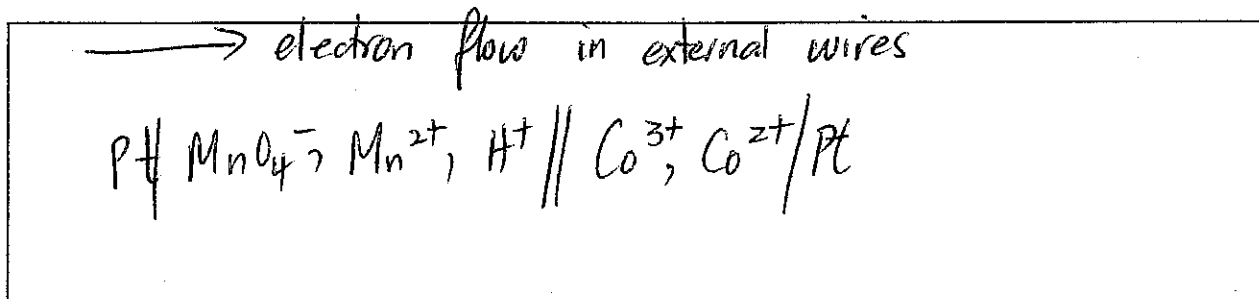
Selected values of Standard Electrode Potentials at 25°C (aqueous species unless specified otherwise).

Element	Reaction	E°/V
Cobalt (3d ⁷ 4s ²)	$\text{Co}^{3+} + e \rightleftharpoons \text{Co}^{2+}$	1.81
	$\text{Co}(\text{NH}_3)_6^{3+} + e \rightleftharpoons \text{Co}(\text{NH}_3)_6^{2+}$	0.1
	$\text{Co}^{2+} + 2e \rightleftharpoons \text{Co}(\text{s})$	-0.28
	$\text{Co}(\text{NH}_3)_6^{2+} + 2e \rightleftharpoons \text{Co}(\text{s}) + 6\text{NH}_3$	-0.43
Manganese (3d ⁵ 4s ²)	$\text{MnO}_4^- + e \rightleftharpoons \text{MnO}_4^{2-}$	0.564
	$\text{MnO}_4^- + 4\text{H}^+ + 3e \rightleftharpoons \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	1.70
	$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}(\text{l})$	1.51
	$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2e \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}(\text{l})$	1.23
	$\text{Mn}^{3+} + e \rightleftharpoons \text{Mn}^{2+}$ (in 7.5 mol L ⁻¹ H ₂ SO ₄)	1.49
	$\text{Mn}^{2+} + 2e \rightleftharpoons \text{Mn}(\text{s})$	-1.18

Question 8 continued on following page

Question 8 continued

- (c) Draw a conventional cell diagram for the cell which has the given cell reaction. Show on your diagram which electrode is positive and the direction of electron flow in the external wires.



- (d) How many moles of electrons are transferred per mole of the cell reaction as it is written above?

$$n = 5$$

- (e) Calculate the EMF of the cell under reversible conditions at 25°C when $[\text{H}^+] = 1.20 \text{ mol L}^{-1}$; $[\text{Co}^{3+}] = 1 \times 10^{-2} \text{ mol L}^{-1}$; $[\text{Co}^{2+}] = 0.10 \text{ mol L}^{-1}$; $[\text{MnO}_4^-] = 0.50 \text{ mol L}^{-1}$ and $[\text{Mn}^{2+}] = 0.10 \text{ mol L}^{-1}$.

$$\begin{aligned} E &= E^0 - \frac{RT}{5F} \ln \frac{(a_{\text{Co}^{2+}})^5 (a_{\text{MnO}_4^-}) (a_{\text{H}^+})^8}{(a_{\text{Mn}^{2+}}) (a_{\text{Co}^{3+}})^5} \\ &= 0.30 - \frac{0.0257}{5} \ln \frac{(0.10)^5 (0.50) (1.20)^8}{(1 \times 10^{-2})^5 (0.10)} \\ &= 0.30 - [5.14 \times 10^{-3} \times \ln (2.15 \times 10^6)] \\ &= 0.30 - (5.14 \times 10^{-3} \times 14.58) \\ &= 0.23 \text{ V} \end{aligned}$$

The following data may be useful: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $F = 96489 \text{ C mol}^{-1}$; $\frac{RT}{F} = 0.0257 \text{ V}$ at 25°C.

- (f) **Giving reasons**, predict whether the reaction will proceed spontaneously in the forward or reverse direction when the concentrations are as given in (e).

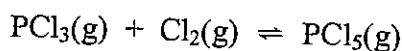
As the cell EMF in (e) is +ve, the $\Delta G < 0$ ($\Delta G = -nEF$)
As ΔG is -ve, the reaction will proceed spontaneously in the forward direction.

9. (12 marks)

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
$\text{PCl}_3(\text{g})$	-320	-272	217
$\text{PCl}_5(\text{g})$	-375	-305	365

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

(a) For the reaction

predict the sign of ΔS° (do not attempt to calculate but provide an explanation).

-ve

Decrease in the number of gaseous species

(b) Using the table above, calculate (at 298 K):

(i) ΔH° ;

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(\text{PCl}_5(\text{g})) - \Delta H_f^\circ(\text{PCl}_3(\text{g})) \\ &= -375 - (-320) \\ &= -55 \text{ kJ mol}^{-1} \end{aligned}$$

(ii) ΔG° .

$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{PCl}_5(\text{g})) - \Delta G_f^\circ(\text{PCl}_3(\text{g})) \\ &= -305 - (-272) \\ &= -33 \text{ kJ mol}^{-1} \end{aligned}$$

(c) Use your answers in (b) to calculate:

(i) ΔS° (at 298 K);

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \Delta S^\circ &= (\Delta H^\circ - \Delta G^\circ) / T \\ &= (-55 - (-33)) \times 1000 / 298 \\ &= -73.8 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

(ii) $S^\circ(\text{Cl}_2(\text{g}))$ (at 298 K).

$$\begin{aligned} \Delta S^\circ &= S^\circ(\text{PCl}_5(\text{g})) - S^\circ(\text{PCl}_3(\text{g})) - S^\circ(\text{Cl}_2(\text{g})) \\ S^\circ(\text{Cl}_2(\text{g})) &= S^\circ(\text{PCl}_5(\text{g})) - S^\circ(\text{PCl}_3(\text{g})) - \Delta S^\circ \\ &= 365 - 217 - (-73.8) = 221.8 \\ &= 222 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

10. (6 marks)

With reference to the compounds listed in the table opposite, answer the following.

	$\Delta H^\circ_{\text{vap}}/\text{kJ mol}^{-1}$
CH ₄	9.2
NH ₃	23.3
H ₂ O	40.8
HF	27.2

(a) Why does CH₄ have the lowest enthalpy of vaporisation?

2 *marks*

CH₄ molecules are tetrahedral and non-polar. Also as C has no lone pairs, no hydrogen-bonding can occur. Therefore interactive forces are small, ∴ lowest $\Delta H^\circ_{\text{vap}}$

(b) Why is the enthalpy of vaporisation greater for H₂O than that for NH₃ or HF?

4

Hydrogen-bonding occurs in H₂O which can be extensive and in 3-dimensions. This is because there are 2 lone pairs on the O (and also 2 O-H bonds).
Some H-bonding is possible in NH₃ and HF but → linear chains only (NH₃ has 1 lone pair, and HF one F-H bond, only) in contrast to 3-dimensional "clusters" in H₂O

11. (6 marks)

(a) Define what is meant by a Brønsted acid.

1 A species which loses or donates a proton

(b) Define what is meant by a Brønsted base.

1 A species which gains or accepts a proton

(c) In the following reaction, label the components as acids or bases:



Acid

Base

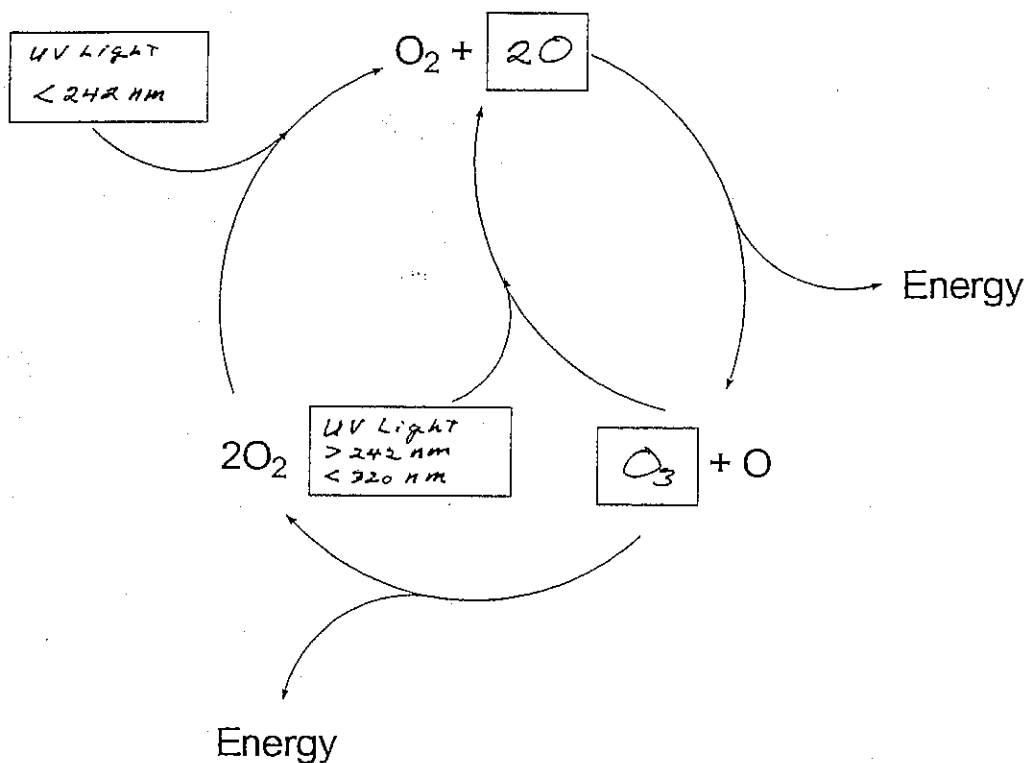
Base

Acid

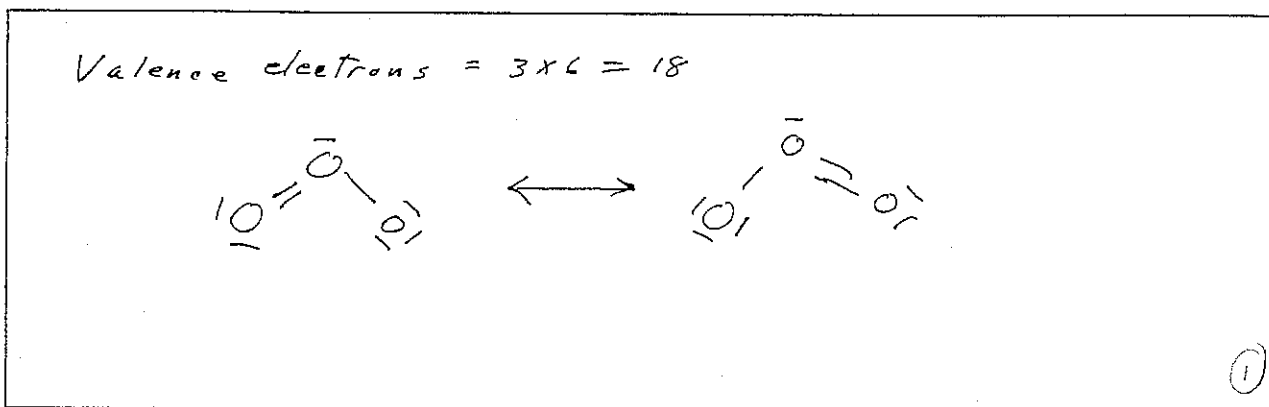
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12. (11 marks)

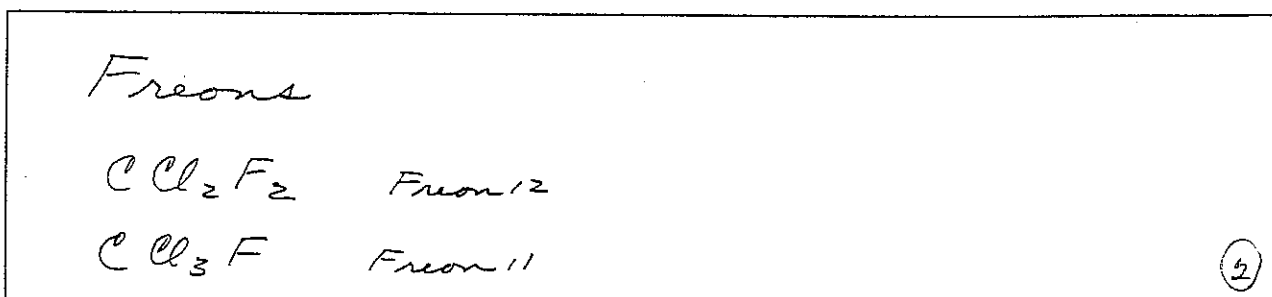
- (a) Complete the following diagram for the ozone cycle in the upper atmosphere by filling in the four blanks:



- (b) Draw a Lewis structure for ozone.

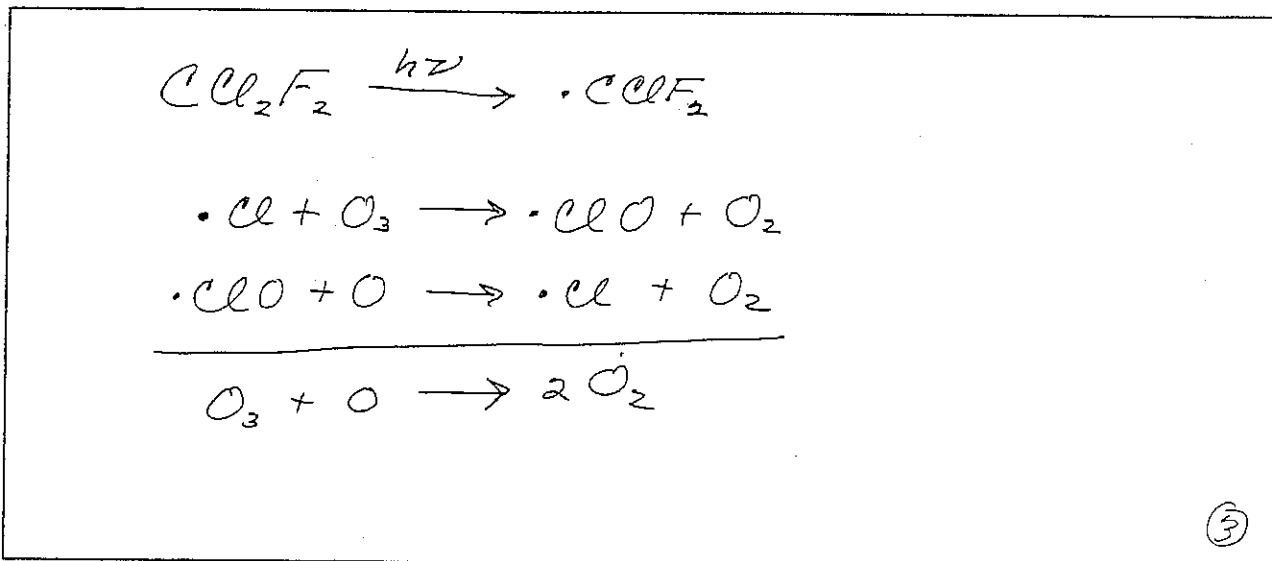


- (c) What is the class of compounds that is the major source of the chlorine atoms in the upper atmosphere which lead to ozone depletion? Provide the chemical formula for one of these compounds.



Question 12 continued

- (d) Show the mechanism of the series of reactions between chlorine-containing molecules or atoms and ozone that leads to ozone loss in the upper atmosphere.



- (e) In what months does the Antarctic ozone "hole" appear?

September Through November. Can Extend into December ①

13. (9 marks)

- (a) List the name and approximate mole percent for each of the **four** most abundant gases in the atmosphere at sea level.

Nitrogen	78%	Specifically 78.08
Oxygen	21%	20.95
Argon	1%	0.934
Carbon dioxide	0.033	0.033

②

- (b) The pH scale is used to measure the acidity of the rainfall in those countries where acid rain is a problem. Unlike most such measures, a higher number (i.e. a higher pH) means less acid rain. Explain why a higher number is better.

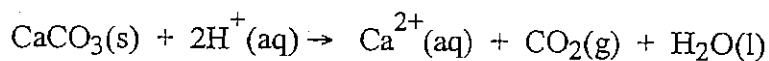
pH measures $[\text{H}^+]$ and is a reverse scale. The higher the pH, the smaller the $[\text{H}^+]$. Since $\text{pH} = -\log[\text{H}^+]$, consider

$[\text{H}^+]$	pH
10^{-4}	4
10^{-5}	5

②

Question 13 continued

- (c) Assume that new industrial pollution causes the average pH of the rain falling on a hectare of land to decrease from an expected value of 5.50 to 4.20. Assume also that the average annual rainfall is 1.00 m. Determine the mass of CaCO_3 that would be needed, per hectare per year, to neutralize the additional acid. The pertinent chemical reaction is



One hectare is $10,000 \text{ m}^2$ and one cubic metre contains $1000 \text{ L (dm}^3\text{)}$. The molar mass of CaCO_3 is 100.1 g mol^{-1} .

Find increase in $[\text{H}^+]$ due to acid rain

$$\begin{aligned} \Delta[\text{H}^+] &= 10^{-4.20} - 10^{-5.50} = 0.000063096 - 0.000003162 \\ &= 5.993 \times 10^{-5} \text{ moles/L} \end{aligned}$$

$$\text{mass CaCO}_3 = (10,000 \text{ m}^2)(1 \text{ m})(10^3 \text{ L/m}) \left(5.993 \times 10^{-5} \frac{\text{mole H}^+}{\text{L}} \right) \left(\frac{1 \text{ mole CaCO}_3}{2 \text{ moles H}^+} \right) \times$$

$$\rightarrow 100.1 \frac{\text{g CaCO}_3}{\text{mole CaCO}_3}$$

$$= 3.000 \times 10^4 \text{ g CaCO}_3$$

$$= 30.0 \text{ kg CaCO}_3$$

(5)