UNITS AND GASES

(A) Descriptive Questions

1. (a) What do you understand by the terms:
   - i) concentration;
   - ii) mole-fraction?

   What units are these quantities expressed in?

2. Draw a diagram which shows the distribution of molecular velocities in a gas and indicate the effect of temperature on the distribution.

3. What are ideal gases?

(B) Calculations

1. At what temperature will the root-mean-square speed of the nitrogen molecule be 4.000 x 10^4 cm sec^{-1}?

   The equation to use is $\sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}}$ the complete term on the left is the root-mean-square speed.

2. Calculate the root mean square velocity of a hydrogen molecule at 0.00°C.

3. At 500°C sulphur vapour effuses at 0.577 times the rate of SO_2 while at 860°C it effuses at the same rate as SO_2. (atomic mass: S = 32; O = 16)
   What is the molecular weight and formula of sulphur vapour at 500°C and 860°C?

4. Find the amount of gas (moles) that would occupy 10.2dm^3 at a pressure of 3.7 atm and a temperature of 500 K. Assume ideal behaviour.

5. Into a gas bulb of 2.83 dm^3 are introduced 0.174 g of H_2 and 1.365 g of N_2 which are assumed to behave ideally. The temperature is 0.00°C.
   (a) What are the mole-fractions of each gas?
   (b) What is the total gas pressure and what are the partial pressures of H_2 and N_2?

6. A sample of PCl_5 weighing 2.69 g was placed in a 1.00 dm^3 flask and completely vaporised at 250°C. Some of the PCl_5 dissociates and the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The total pressure at equilibrium was 1.00 atm.

What are the partial pressures and mole fractions of PCl_5, PCl_3 and Cl_2 in the reaction mixture? Assume ideal behaviour.

COLLIGATIVE PROPERTIES

(A) Descriptive Questions

1. Explain what you understand by the terms “osmosis”, “osmotic pressure” and “reverse osmosis”.

2. Explain why 0.1 mole of sodium chloride depresses the freezing point of a given mass of water twice as much as does 0.1 mole of glucose.

3. What is an ideal solution?

(B) Calculations

1. 34.2 g of sucrose (M_r = 342) are dissolved in 500 g of water giving a solution of total volume of 520 cm^3. Calculate the molarity and molality (mol kg^{-1}) of the sucrose solution and the mole fraction of both components in the mixture. What is the water potential of this solution in atmospheres in an open beaker (sea level, 20°C)?

2. Nitrobenzene freezes at 5.70°C and has a molal freezing point constant of 7.00 K kg solvent / mol solute. Calculate the molecular weight of an unknown substance from the observation that a solution of 2.05 g of unknown dissolved in 40.0 g nitrobenzene freezes at 1.10°C.

3. A solid organic compound contains 18.3% C, 0.51% H and 81.2% Br by weight. A solution of 0.793 g of the compound in 0.01480 dm^3 chloroform (with a density of 1.485 kg dm^{-3}, a boiling point of 60.30°C, and a molal boiling point constant of 3.63 K / mol solute / kg solvent) boils at 60.63°C. Find the molecular formula of the compound.

4. Members of one class of water soluble proteins are called albumins. A 1.50 g sample of a particular albumin in 0.1 dm^3 of solution had an osmotic pressure of 6255 Pa at 25^oC. Assume the solution behaves ideally. What is the molecular weight of albumin?

5. The molal freezing point constant of water is 1.86 K kg solvent/mol solute.
What would be the approximate freezing point of a solution of 0.1 mol kg^{-1} barium chloride, assuming complete dissociation?

6. A sugar mill discharges wastewater containing sucrose ($C_{12}H_{22}O_{11}$) as a major impurity which contributes to water pollution. The wastewater contains on average 34.2g sucrose /L water. The possibility exists to pre-treat the wastewater stream using reverse osmosis to remove the sucrose. What pressure must be used in the reverse osmosis (in atmospheres) to remove the sucrose completely at 20^oC? (R = 0.0821 atm L /mol K)

CHEMICAL KINETICS

Section A

1. Discuss how you would follow the rate of a chemical reaction.

2. What do you understand by the terms “order” and “molecularity” of reaction?

3. Discuss how you would determine the order and rate constant of a reaction involving two reactants.

4. Explain why the rate of a chemical reaction increases with temperature.

5. How would you measure the energy of activation and the frequency factor of a reaction?

6. How does a catalyst increase the rate of a reaction?

Section B

1. The decomposition of gaseous N_2O_5 is a first order reaction. If $k = 5 \times 10^{-4}$ sec^{-1}, how long does it take before the concentration of N_2O_5 falls to one-tenth its original value?

2. The first order rate constant for the decay of radon is 2.08 x $10^{-6}s^{-1}$. What fraction of the original material would be left after 3.38 days?

3. Measurement of the rate of decay of the radioactive element Cs-135 gave a decay constant (k) of 2.31 x 10^{-7} yr^{-1}. How long will it take for 99% of this element to disintegrate assuming first order kinetics?

4. Nitrous oxide decomposes in the presence of a heated Au wire catalyst at 990°C according to the equation $2N_2O \rightleftharpoons 2N_2 + O_2$ $t_{½}$ = 53 min. and after 100 min. 73% of the N_2O is decomposed.
Show the reaction is 1st order and calculate the specific rate constant.

5. For the reaction $C_2H_5I + OH \rightleftharpoons C_2H_5OH + I$, k = 5.03 x 10^{-2} dm^3 mol^{-1} s^{-1} at 298K and k = 6.71 dm^3 mol^{-1} s^{-1} at 333K. What is the activation energy of the reaction? What is the rate constant at 305K?

6. The data that follow show how the initial rate of the reaction

$BrO_3^- + 5Br^- + 6H^+ \rightleftharpoons 3Br_2 + 3H_2O$

varies as the concentration of the reactants are changed. What is the order of the reaction with respect to each reactant? Write the rate law for the reaction and state the overall order of the reaction.

Experiment	**Initial Concentration/mol dm^{-3}**			**Initial Rate**
	BrO_3^-	Br^-	H^+	**mol dm^{-3} s^{-1}**
1	0.10	0.10	0.10	1.2 x 10^{-3}
2	0.20	0.10	0.10	2.4 x 10^{-3}
3	0.10	0.30	0.10	3.5 x 10^{-3}
4	0.20	0.10	0.15	5.4 x 10^{-3}

THERMOCHEMISTRY

1. Explain the following terms:
   - Extensive and Intensive properties;
   - State properties;
   - Energy and enthalpy;
   - Bond enthalpy;
   - Standard state;
   - Standard enthalpy.

   How can energy and enthalpy changes be determined for chemical reactions?

   Outline the essential features, mode of operation and use of a bomb calorimeter.

2. What do you understand by the terms:
   (a) Entropy;
   (b) Free Energy.

   What is the significance of the equation $\Delta G = \Delta H - T\Delta S$?

3. Use **Appendix C** data (Brown-Le May)to calculate **:**

   (a) $\Delta H^\circ_c(C_2H_6,g,298K)$ to form $CO_2(g)$ and $H_2O(l)$.

   (b) $\Delta H^\circ_c(NH_3,g,298K)$ to form gaseous H_2O and NO.

   (c) The N-H bond energy in ammonia.

   (d) $\Delta H^\circ_c(CS_2,l)$ to form gaseous CO_2 and SO_2. (ΔH^o_f $CS_{2(l)}$ 87.9 kJ / mol)

   (e) ΔH° for $SO_2(g) + ½\, O_2(g) + H_2O(g) \rightleftharpoons H_2SO_4(l)$

   (f) ΔH° for

   (i) $NH_3(g) \rightleftharpoons ½\, N_2(g) + 3/2\, H_2(g)$

   (ii) $2H_2S(g) + 3O_2(g) \rightleftharpoons 2H_2O(l) + 2SO_2(g)$

   (g) The O-H bond energy in water.

4. Predict whether entropy increases or decreases in the following chemical reactions.

$Ba(s) + \frac{1}{2} O_2(g) \rightarrow BaO(s)$

$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$

$Br_2(g) \rightarrow 2Br(g)$

$H_2(g) + Br_2(l) \rightarrow 2HBr(g)$

5. Using **Appendix C** (Brown - Le May) calculate ΔG° values at 298K for

(a) $2C\ (\text{graphite}) + 2H_2(g) \rightarrow C_2H_4(g)$

(b) $2C\ (\text{graphite}) + 3H_2(g) \rightarrow C_2H_6(g)$

Which of these reactions is thermodynamically possible under standard conditions at 298K?

6. Metallic aluminium is an effective reaction for the reduction of oxides of some other metals as in the thermite reaction:

$$2Al(s) + Fe_2O_3(s) \rightleftharpoons 2Fe(s) + Al_2O_3(s)$$

By using the sign of the standard free energy change as a criterion and data from **Appendix C** (Brown - Le May) decide which of the following oxides cannot be reduced by aluminium:

CuO, CaO

7. Determine if the production of $SO_{3(g)}$ from $SO_{2(g)}$ and $O_{(g)}$ is a spontaneous reaction using the following data at 298K:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

	ΔH^o_f (kJ/mol)	ΔS^o(J/mol K)
$SO_2(g)$	-296.9	248.5
$SO_3(g)$	-395.2	256.2
$O_2(g)$	0	205.0

CHEMICAL EQUILIBRIUM

1 atmosphere = 1.013×10^5 Pa

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

1. 3.56 moles of H_2 and 3.90 moles of I_2 vapour were heated together at 630 K to form iodic acid (HI). The amount of free iodine at equilibrium was 0.90 moles.
What is the value of the equilibrium constant K_c for the reaction?

2. When 2 moles of PCl_5 (g) were heated to a certain temperature in a closed 2 dm^3 vessel it was found that at equilibrium 40% of the pentachloride had dissociated into PCl_3 (g) and Cl_2. Calculate K_c for the reaction.

3. Some solid ferrous sulphate ($FeSO_4$) is placed in an evacuated flask which is then heated to 929 K. The following equilibrium is established and the total gas pressure is 0.9 atm.

$$2FeSO_4\,(s) \rightleftharpoons Fe_2O_3\,(s) + SO_2\,(g) + SO_3\,(g)$$

Calculate K_p.

4. Calculate the value of K_p at 298K for the reaction

$$Fe_2O_3(s) + H_2(g) \rightleftharpoons 2FeO(s) + H_2O(g) \qquad \Delta G°(298K) = +31\text{ kJ}$$

5. Using **Appendix C** (Brown - Le May) calculate what the pressure of CO_2 is in equilibrium with a $CaCO_{3(s)}$-$CaO_{(s)}$ mixture at 298K?

6. For the reaction $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $\Delta H° = 180.5$ kJ and $K_p = 4.6 \times 10^{-31}$ at 25°C. Calculate K_p at 2127°C

ELECTROCHEMICAL CELLS

(A) Descriptive Questions

1. Sketch the glass electrode used to measure pH indicating its essential features.
Briefly discuss the mode of operation of this electrode.
What is the relationship between the potential developed by this electrode (relative to some reference electrode) and the pH of the solution?

2. Outline the chief features of

(a) a calomel electrode;
(b) the standard hydrogen electrode.

(B) Calculations

1. The e.m.f. (cell voltage) of the following cell at 298K is +0.030V.

$$\begin{array}{c|c||c|c|c} Cu_{(s)} & CuSO_{4(aq)} & \begin{array}{l} KCl_{(aq)} \\ 0.100M \end{array} & AgCl_{(s)} & Ag_{(s)} \end{array}$$

$E^o_{Cu^{2+}/Cu} = +0.340V$ $F = 96\,500\ C\ mol^{-1}$

E^o for the electrode reaction $AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$ is $+ 0.223V$.

- What is the cell reaction in the cell?
- Calculate the standard free energy change ΔG^o for the cell reaction.
- Calculate the concentration of $CuSO_{4(aq)}$ in the cell.

2. The e.m.f. of the following cell at 298K was found to be 0.8795V.

$$\begin{array}{c|c||c|c} Sn_{(s)} & \begin{array}{l} SnSO_{4(aq)} \\ c = 0.20M \end{array} & \begin{array}{l} Fe_2(SO_4)_{3(aq)} \\ c = 0.10M \\ FeSO_{4(aq)} \\ c = 0.10M \end{array} & Pt(s) \end{array}$$

$E^o_{Fe^{3+}/Fe^{2+}} = +0.7050V$ $F = 96\,500\ C\ mol^{-1}$

- What is the cell reaction?
- Calculate E^o for the $Sn^{2+}_{(aq)}/Sn_{(s)}$ couple and the standard free energy change of the cell reaction.

3. The electrode $Ag_{(s)} \mid AgCl_{(s)} \mid Cl^-_{(aq)}$, for which the half-reaction is

$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$ and $E^o = +0.223V$, can be used to measure chloride ion concentration.

The e.m.f. of the following cell is +1.059V at 298K.

$$\begin{array}{c|c||c|c|c} Zn_{(s)} & \begin{array}{l} Zn^{2+}_{(aq)} \\ c = 0.01M \end{array} & \begin{array}{l} \text{sea} \\ \text{water} \\ (Cl^-_{(aq)}) \end{array} & AgCl_{(s)} & Ag_{(s)} \end{array}$$

$E^o_{zn^{2+}/Zn} = -0.761V$ $\frac{2.3RT}{F} = 0.0592V$ at 298K $F = 96\,500\ C\ mol^{-1}$

- What is the cell reaction?
- What is the standard free energy change ΔG^o for the cell reaction?

- Calculate the concentration of chloride ion in the sea water sample.

4. The electrode

$$\begin{array}{c|c|c} Hg(l) & HgO(s) & OH^-(aq) \end{array}$$

for which the half reaction is

$$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-; E^o = +0.098V$$

can be used to measure OH^- concentration (from which pH may be calculated).

The e.m.f. of the following cell is +0.112V at 298K.

$$\begin{array}{c|l||l|c|c} Cu_{(s)} & Cu^{2+}_{(aq)} & \text{solution}_{(aq)} & HgO_{(s)} & Hg_{(l)} \\ & c = 0.01M & x = [OH^-] & & \end{array}$$

$E^o_{Cu^{2+}/Cu} = 0.340V.$ $F = 96\,500 \text{ C mol}^{-1}$

- What is the cell reaction?
- Given $pK_w = 14$.
- Calculate the pOH (using $[OH^-]$) and hence the pH of the above solution

$pH = -\log_{10}[H^+]$ $pOH + pH = 14$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF} x \log_{10} \frac{[\text{products}]^m}{[\text{reactants}]^n}$$

ACID~BASE EQUILIBRIA

1. List, giving appropriate equations, the following species in decreasing order of acid strength in aqueous solution:
   - ammonium chloride (NH_4Cl)
   - potassium nitrate (KNO_3)
   - sodium amide ($NaNH_2$)
   - sulphuric acid (H_2SO_4)
   - sodium cyanide ($NaCN$)

2. Calculate the pH of the following solutions.

   (a) 0.050 M hydrochloric acid

(b) 0.030 M potassium hydroxide

(c) 0.0010 M formic acid (HCOOH)
K_A (formic acid) = 1.8×10^{-4}

(d) 1.0 M hydrogen cyanide
$K_A(HCN) = 4.8 \times 10^{-10}$

(e) 0.0040 M ammonium chloride
$K_A(NH_4^+) = 5.62 \times 10^{-10}$

(f) 0.033 M diethylamine [$(C_2H_5)_2NH$]
pK_A (diethylammonium) = 10.98

(g) 0.137 M sodium cyanide
$K_A(HCN) = 4.8 \times 10^{-10}$

3. (a) What do you understand by the terms
(i) “BrØnsted-Lowry acid”
(ii) “buffer solution” and
Give an example of each.

(b) What do you understand by the terms
(i) “buffer capacity”
(ii) “indicator working range”?

4. (a) Calculate the pH of a solution of 0.1M propanoic acid. pK_A (propanoic acid) = 4.90

(b) Sketch the titration curve for the titration of 0.1M propionic acid with 0.125M sodium hydroxide. Indicate the equivalence point and the pH of the solution at this point.

Which of the indicators below would be most suitable for detecting the equivalence point? Give reasons.

Methyl red (pK_{In} 5.2)
Bromothymol blue (pK_{In} 6.9)
Phenol red (pK_{In} 8.0)

NUMERIC ANSWERS

N.B. *Where data from Tables in the texts have been used the final results have been calculated using the data from Silberberg "Chemistry 2^{e}". The calculated values should be close if you have used the data from Brown-Le May but they won't be exactly the same.*

Units and Gases

1. 180K
2. 1.84×10^{3} ms^{-1}
3. S_6 at 500°C, S_2 at 860°C
4. 0.92 mol
5. $x_{H_2} = 0.64$ $x_{N_2} = 0.36$ $p = 1.09 \times 10^{5}$ Pa $p_{H_2} = 6.98 \times 10^{4}$ Pa $p_{N_2} = 3.92 \times 10^{4}$ Pa
6. $p(PCl_5) = 1.09 \times 10^{4}$Pa $p(PCl_3) = 4.52 \times 10^{4}$Pa

   $p(Cl_2) = 4.52 \times 10^{4}$Pa $x(PCl_5) = 0.108$
   $x(PCl_3) = 0.446$ $x(Cl_2) = 0.446$

Colligative Properties

1. $c = 0.192$ mol dm^{-3} molality = 0.200 mol kg^{-1}

   x (sucrose) = 0.0036 x (water) = 0.9964
2. M.W. 78
3. $C_6H_2Br_4$
4. M.W. 5940
5. -0.56°C
6. $-\pi = 2.40$ atm

Chemical Kinetics

1. 4.6×10^{-3}s
2. 0.545
3. 2.0×10^{7} years
4. $k = 2.18 \times 10^{-4}$ s^{-1}
5. $E_a = 115$ kJ mol^{-1}, $k = 1.5 \times 10^{-1}$ dm^3 mol^{-1} s^{-1}
6. Rate = $k[BrO_3^-][Br^-][H^+]^2$ Reaction is overall fourth order

Electrochemical Cells

1. $Cu(s) + 2AgCl(s) \rightarrow 2Ag(s) + Cu^{2+}_{(aq)} + 2Cl^-_{(aq)}$ $\Delta G^o = 22.6$ kJ $[Cu^{2+}] = 1.1 \times 10^{-3}$ mol dm^{-3}
2. $Sn(s) + 2Fe^{3+} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$ $\Delta G^o = -162.3$ kJ $E^o(sn^{2+}/_{sn}) = -0.1361$ V
3. $Zn(s) + 2AgCl(s) \rightarrow Zn^{2+}_{(aq)} + 2Cl^-_{(aq)} + 2Ag(s)$ $\Delta G^o = -190$ kJ $[Cl^-] = 0.536$ mol dm^{-3}
4. $Cu(s) + HgO(s) + H_2O \rightarrow Hg(l) + 2OH^-_{(aq)} + Cu^{2+}_{(aq)}$ pOH = 5 pH = 9

Thermochemistry

3. (a) -1559.9 kJ mol^{-1}

(b) -226.5 kJ mol^{-1}

(c) 391 kJ mol^{-1}

(d) $\Delta H°_c(CS_2,l)$ = -1075.0 kJ mol^{-1}

(e) $\Delta H°$(298K) = -275.4kJ

(f) (i) $\Delta H°$ = 45.9 kJ

(ii) $\Delta H°$ = -1124.9 kJ

(g) 464 kJ mol^{-1}

4. ΔS= -ve, ΔS= +ve, ΔS= +ve, ΔS= +ve

5. (a) $\Delta G°$ = 68.36 kJ mol^{-1}

(b) $\Delta G°$ = -32.89 kJ mol^{-1}
Reaction (b) is spontaneous at 1 atm and 298K

6. CaO

7. $\Delta G°$ = -140.1 kJ; spontaneous

Chemical Equilibrium

1. $K_p = K_c = 71.4$
2. $K_c = 2.66 \times 10^{-1}$ mol dm^{-3}
3. K_p = 0.20 atm^2; P = 1.1 x 10^5 Pa (or 1.08 atm)
4. $K_p = 3.7 \times 10^{-6}$
5. p = 1.1 x 10^{-18} Pa
6. 2.4 x 10^{-3}

Acid-Base Equilibria

2. (a) pH = 1.30
(b) pH = 12.48
(c) pH = 3.46
(d) pH = 4.66
(e) pH = 5.82
(f) pH = 11.71
(g) pH = 11.23

4. (a) pH = 2.95

(b) Phenol Red