THE COLLEGE OF THE BAHAMAS

EXAMINATION

SEMESTER 01-2009

FACULTY OF PURE AND APPLIED SCIENCES

SCHOOL OF SCIENCES AND TECHNOLOGY

X NASSAU
FREEPORT
EXUMA
ELEUTHERA

DATE AND TIME OF EXAMINATION: Wednesday, April 29, 2009, 7:00 PM, in D2

DURATION: 3 HOURS

COURSE NUMBER: CHEM 240

COURSE TITLE: Physical Chemistry

STUDENT NAME:

STUDENT NUMBER:

LECTURER'S NAME

INSTRUCTIONS TO CANDIDATES: This paper has 11 pages and 3 sections. Please follow the instructions given with each section.

SECTION I: Multiple choice questions. Answer ALL questions on this section. Read all alternatives carefully before selecting the best one. Indicate it on the answer sheet by marking the appropriate letter with a cross (X).

There is one mark for each question, making a total of 35 marks for this section.

1) Which one of the following statements is true regarding a gas whose temperature is increased?
   A The proportion of molecules with the most common velocity is increased.
   B The proportion of molecules with low velocities is increased.
   C The proportion of molecules with very high velocities is decreased.
   D The total number of molecules is increased.
   E The proportion of molecules with very high velocities is increased.*

2) Which one of the following is simultaneously true of both a real gas and an ideal gas?
   A The molecules of a gas attract each other under certain conditions.
   B The molecules of a gas repel each other under certain conditions.
   C The molecules of a gas occupy appreciable volume.
   D The molecules of a gas have appreciable mass. *
   E The molecules of a gas all have the same kinetic energy.

3) The freezing point of a 0.1 M aqueous solution of glucose is -0.18°C. The approximate freezing point of a 0.1M aqueous solution of magnesium chloride ($MgCl_2$) should therefore be
   A -0.09°C
   B -0.18°C
   C -0.06°C
   D -0.36°C
   E -0.54°C*

4) Which one of the following aqueous solutions should have the lowest vapour pressure?
   A 0.1M sucrose
   B 0.1M glucose
   C 0.1M iron(II) chloride*
   D 0.1M sodium chloride
   E pure water

   C benzoic acid is dimerized in this solution. *
   D naphthalene is dimerized in this solution.
   E benzoic acid is dissociated in this solution.

6) Two ideal aqueous solutions, S_1 and S_2, of unionized solutes have the same vapour pressure at a given temperature. Which one of the following conclusions can be drawn from this information?
   A S_1 and S_2 contain equal masses of solute per unit volume.
   B S_1 and S_2 contain equal numbers of moles of solute per unit volume. *
   C S_1 and S_2 have different osmotic pressures at the given temperature.
   D S_1 and S_2 contain the same solute.
   E S_1 and S_2 have different boiling points.

7) Which one of the following methods is the most suitable for the determination of the relative molecular mass of a polymer?
   A depression of the freezing point of a suitable solvent
   B elevation of the boiling point of a suitable solvent
   C osmotic pressure in a suitable solvent*
   D vapour pressure lowering of a suitable solvent
   E Dumas's (measurement of the density of polymer vapour)

8) In which one of the reactions represented by the following equations is the entropy change (ΔS) most likely to be positive?
   A $C_2H_5OH(g) \rightarrow C_2H_5OH(l)$
   B $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
   C $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$
   D $CuSO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + CuCl_2(aq)$
   E $CH_3CH_2CH_2CH_3(g) \rightarrow CH_3CH_3(g) + CH_2{:}CH_2(g)$ *

9) The standard Gibbs energy change (ΔG) for the

reaction is negative.
D The standard entropy change (ΔS) for the reaction is positive.
E The reaction proceeds effectively to completion under standard conditions. *

10) The enthalpy change of combustion of graphite is -393.5 kJmol^{-1} and that of diamond is -395.4 kJmol^{-1}. The enthalpy change for the reaction

$C(graphite) \rightarrow C(diamond)$

in kJ mol^{-1} is therefore
A -788.9
B -1.9
C 0
D +1.9*
E -788.9

11) In which one of the following reactions, carried out at 298 K and 1atm pressure, would ΔU be closest to ΔH?
A $CH_3COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3CH_2OCOCH_3(l) + HO(l)$ *
B $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
C $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
D $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
E $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

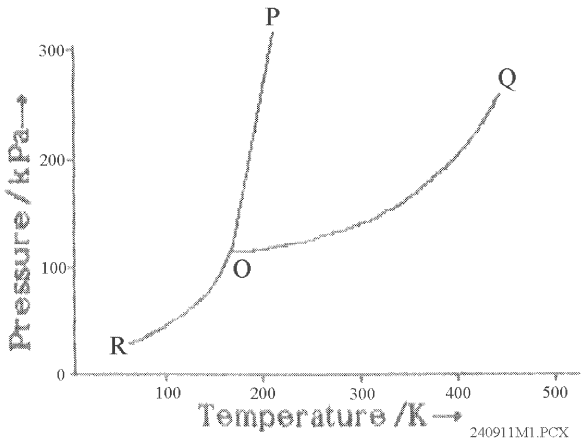
12) The internal energy of an ideal gas
A is dependent only on the volume.
B is dependent only on the temperature. *
C depends strongly on pressure.
D cannot be calculated.
E is the same as its enthalpy.

13) Many spontaneous reactions are endothermic. This is possible because
A reacting systems naturally tend towards a state of maximum enthalpy.
B "spontaneous" means that the reaction does not occur.
C the enthalpy change involved is unimportant.
D such reactions lead to a large increase in entropy. *
E an increase in enthalpy automatically leads to a decrease in free energy.

14) The temperature rise was 8.0°C, measured to a

A a beaker in which silver nitrate and sodium chloride solutions are reacting.
B a beaker containing a reacting mixture which is evolving a gas. *
C a bomb calorimeter.
D the whole universe.
E a beaker in which no reaction is occurring.

Questions 16 to 20 involve the phase diagram for an unknown substance as shown below



16) Which one of the following is represented by the point O on the diagram?
A The boiling point of the liquid.
B The melting point of the solid.
C The triple point. *
D The critical point of the liquid.
E The sublimation temperature of the solid.

17) Which one of the following correctly describes the situation for the substance at standard temperature and pressure?
A gas phase only present*
B liquid phase only present
C solid phase only present
D gas and liquid in equilibrium
E liquid and solid in equilibrium

18) Which one of the following conclusions can be drawn from the phase diagram?
A Line OP represents the variation of boiling point with pressure.
B Line RO represents the variation of the melting point with pressure.
C Curve OP represents the variation of the

approximately 100 K.
- B The boiling point of the liquid is approximately 200 K
- C The boiling point of the liquid is approximately 300 K
- D The boiling point of the liquid is approximately 400 K*
- E The liquid does not boil at this pressure.

20) At a pressure above that of its triple point the substance:
- A cannot be liquefied.
- B shows solid, liquid and gas phases depending on the temperature. *
- C exists as solid, liquid and gas phases at equilibrium.
- D has some of the properties of a liquid and some of a gas.
- E cannot be solidified.

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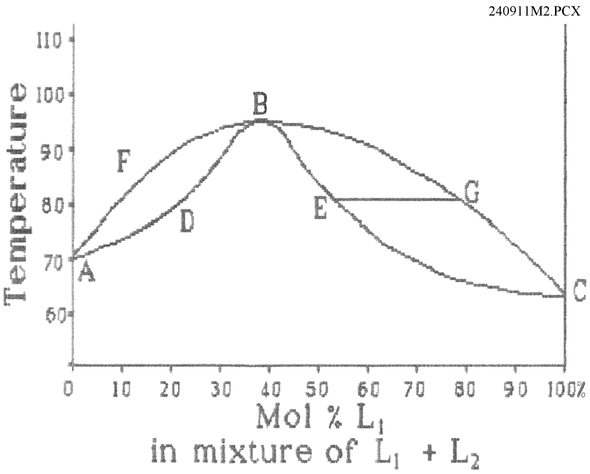
Questions 21 to 25 involve the temperature / composition diagram for a mixture of two liquids L_1 and L_2 in equilibrium with their vapour as shown below.



21) Line EG shows
- A the composition of mixtures whose boiling points are equal.
- B the composition of vapour in equilibrium with liquid at the same temperature. *
- C the range of compositions that the liquid could have at a temperature of approximately 80°C.
- D the range of compositions that the vapour could have at a temperature of approximately 80°C.
- E a mixture of vapours which cannot be liquefied.

23) A mixture of approximately 52 mol% L_1 could be fractionally distilled to yield a mixture of
- A pure L_1 as distillate and pure L_2 remaining in the distillation flask.
- B approximately 38% L_1 as distillate and pure L_1 remaining in the distillation flask.
- C pure L_1 as distillate and a mixture containing about 38% L_1 remaining in the distillation flask. *
- D Pure L_1 remaining in the distillation flask and pure L_2 as distillate.
- E pure L_2 as distillate and a mixture of about 80% L_1 remaining in the distillation flask.

24) The diagram shows the variation in boiling point with composition for a mixture of liquids which
- A show ideal behaviour.
- B show a small negative deviation from Raoult's law.
- C show a small positive deviation from Raoult's law.
- D show a large negative deviation from Raoult's law. *
- E show a large positive deviation from Raoult's law.

25) Two liquids whose mixtures would be expected to give the type of behaviour shown in the diagram are
- A ethanol and water
- B chlorobenzene and water
- C tetrachloromethane and ethanoic acid
- D hydrochloric acid and water*
- E benzene and methylbenzene

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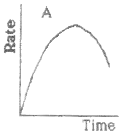
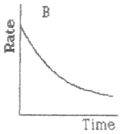
26) When an aqueous solution is shaken with an organic solvent, three-quarters of the solute is extracted. If the extraction is carried out twice, the amount remaining (as a fraction of the original amount) is:
- A one quarter.
- B three eighths.
- C one eighth.
- D three sixteenths.

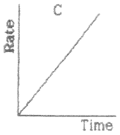
against time.

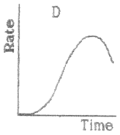
E Reciprocal of concentration of reactant against time.

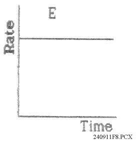
28) Which one of the following graphs best represents the change in reaction rate with time for an *autocatalysed* reaction (i.e. one catalysed by one of the products)?











D

29) The half-life for the decay of a radioisotope is constant because

A the decay of a radioisotope is a zero order process.

B the decay of a radioisotope is a first order process. *

C the decay of a radioisotope is a second order process.

D the radioisotope in question does not decay.

E only half of the radioisotope was present to start with.

30) An experiment was carried out to measure the enthalpy change for the catalytic decomposition of hydrogen peroxide. A student measured hydrogen peroxide solution into a polystyrene cup and noted its temperature at one minute intervals. On the fifth minute he added manganese(IV) oxide to start the reaction and took the temperature on the sixth and subsequent minutes until ten minutes after the reaction had ceased.
The main reason for continuing to take the temperature after reaction had ceased is

A to allow the oxygen to escape.

B that the decomposition of the hydrogen peroxide is instantaneous.

C to allow time to stir the mixture thoroughly.

D to eliminate errors in reading the thermometer.

E to allow the experimenter to compensate for heat losses while the reaction was proceeding. *

EXPERI-MENT	[A]/mol dm^{-3}	[B]/mol dm^{-3}	INITIAL RATE/ mol $dm^{-3}min^{-1}$
1	0.150	0.25	1.4×10^{-5}
2	0.150	0.50	5.6×10^{-5}
3	0.075	0.50	2.8×10^{-5}
4	0.075	0.25	7.0×10^{-6}

31) What is the order of the reaction with respect to reactant A?

A 0

B 1*

C 2

D 3

E 4

32) What is the overall order of the reaction?

A 0

B 1

C 2

D 3*

E 4

33) The internal energy of an ideal gas is given by:

A $(\frac{3}{2})R$

B $(\frac{3}{2})nR$

C $(\frac{3}{2})nRT$*

D PV

E undefined

34) When a process is spontaneous (feasible) ΔG and ΔS_{tot} ($=\Delta S_{surroundings} + \Delta S_{system}$) are:

A Both positive

B Both negative

C ΔG negative, ΔS_{tot} positive*

D ΔS_{tot} negative, ΔG positive

E Irrelevant.

35) The heat capacity of a gas at constant volume (C_v) is higher at high temperatures than at room temperature because:

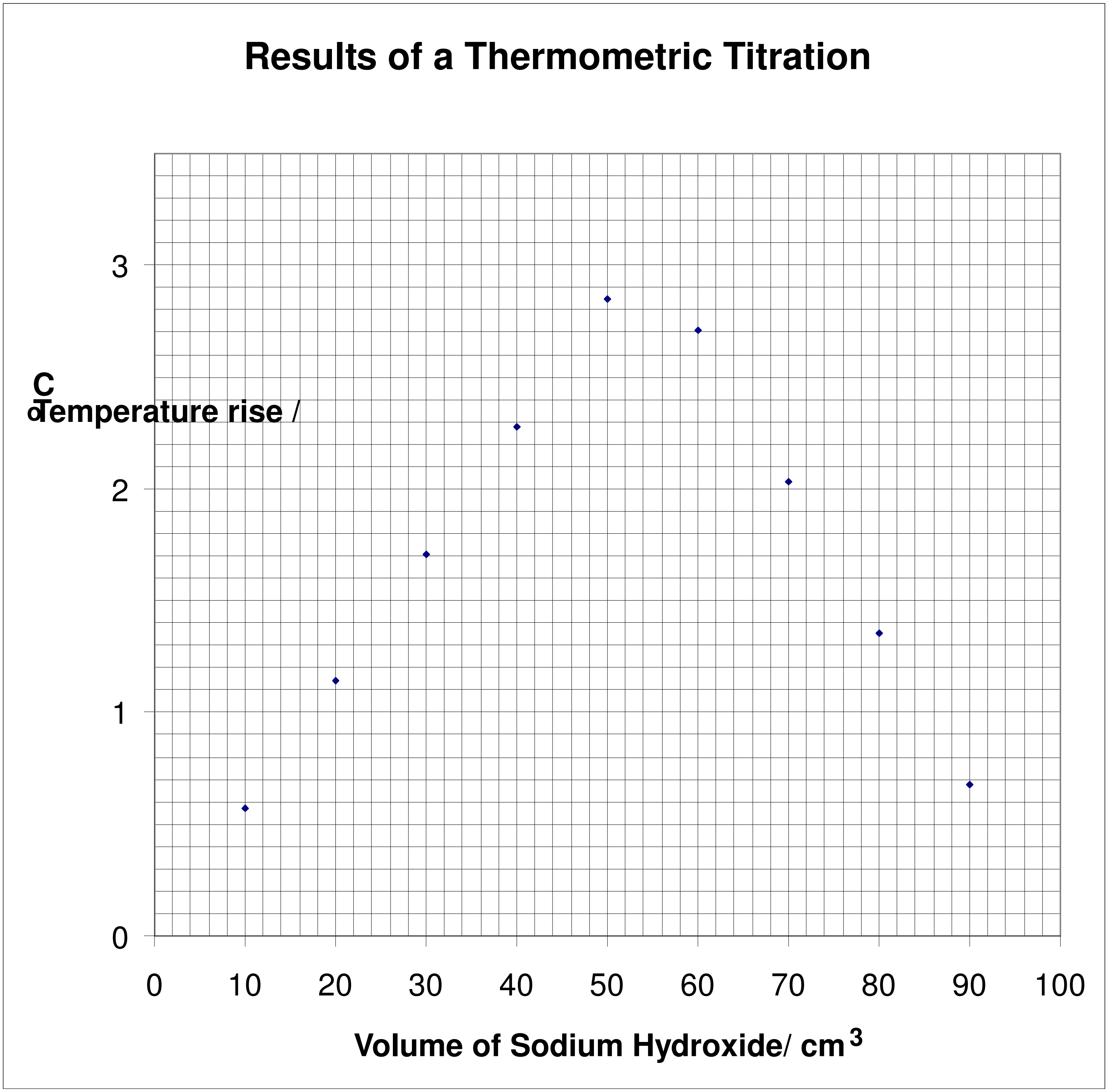
A More translational energy states are populated at high temperatures.

B More rotational energy states are populated at high temperatures.

SECTION II: ANSWER ANY FOUR QUESTIONS FROM THIS SECTION.

Use the spaces provided on the question paper.

1) This question concerns an experiment to determine the enthalpy of neutralization using sodium hydroxide titrated thermometrically with a strong acid. The concentration of the sodium hydroxide was 0.42 M. The volumes of the strong acid (of unknown concentration) and the sodium hydroxide were chosen so that the total volume of solution was always 100 cm^3. The results are as depicted below:



a) What is a thermometric titration? (2)

<u>This is a titration in which the temperature rise is monitored as varying amounts of acid are neutralised by varying amounts of base.</u>

density as 1.0 g cm^{-3}. (3)

$$q = mC\Delta T = (VD)C_s\Delta T = 100 \times 1.00 \times 4.2 \times 3.1 = 1.302 \times 10^3 \text{ J} = -\Delta H_r$$

$$\text{But \# of moles, } n = (5.43 / 1000) \times 0.42 = 2.281 \times 10^{-2}$$

$$\therefore \Delta H_{r,mol} = \Delta H_r/n = -1.302 \times 10^3 / 2.281 \times 10^{-2} = -57.09 \text{ kJ mol}^{-1}$$

e) Explain why the graph has a maximum. (4)

The amount of material is kept constant so that the amount of heat alone determines the temperature rise(1). This amount of heat is determined by the amount of the limiting reagent present. (1) As the amount of one reactant increases, the amount of the other decreases so that the limiting reagent is first one reactant and then the other.(1) In the middle, both reactants are entirely consumed, giving the maximum amount of heat and hence the maximum temperature rise.(1)

2) a) Explain the meaning of term ***entropy***. Illustrate your answer by referring to, and explaining, the relative amounts of entropy in ice at 0°C and water at 0°C, both at 1 atmosphere pressure. Which of the three states of matter has the highest entropy at a given temperature? (5)

Entropy is a measure of the disorder in a system. .(1) Thus water has more entropy than ice.(1) because in ice the molecules are in a regular lattice.(1) whereas in water there is no lattice(1) Of the three states of matter, the gaseous state has the highest entropy .(1)

b) Calculate the entropy change of the system when 1 mol of water is vaporized at 100°C and 1 atm pressure, given that $\Delta H^{\ominus}_{vap}$ for water is 40·66 $kJmol^{-1}$ at this temperature. (3)

$$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{vap}}{T} = \frac{40.66 \times 10^3}{100 + 273} = \underline{\underline{109 \text{ J K}^{-1}}}$$

c) One criterion of the feasibility of a change is that the total entropy of the system and its surroundings increases if the change is feasible.

i) Show that for the vaporization of water at 100°C and 1 atmosphere pressure, when the surroundings are at a higher temperature than the system, the total entropy of system and surroundings increases. (Assume the process is carried out reversibly.) (4)

$$\Delta S_{sys} = \frac{q_{rev}}{T_{sys}}; \Delta S_{surr} = \frac{-q_{rev}}{T_{surr}}$$

$$\text{But } T_{sur} \rangle T_{sys}$$

$$\therefore \Delta S_{sys} \rangle -\Delta S_{surr}$$

$$\therefore \Delta S_{sys} + \Delta S_{surr} \rangle 0$$

ii) Not all feasible reactions will actually occur even when the correct reactants are mixed. Give a chemical example to illustrate this and explain why it is so. (3)

When hydrogen and oxygen are mixed no reaction takes place at room temperature.(1). This is because the reaction is very slow at room temperature.(1) due to has a high energy of activation. .(1)

3) The Gibbs energy change, (ΔG) for a reaction can be used to judge the feasibility of a reaction. Explain this statement. (2)

When ΔG > 0 for a given process, the process is not feasible (spontaneous). .(1) When it is less than 0, the process is spontaneous. .(1)

assumptions have you made in determining the value at 1500 K? What would happen if calcium carbonate were heated to 1500 K? How do you know? (9)

The reaction is $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$.(1)

$$\Delta G^0 = \Delta H^o - T\Delta S^o$$

$$\text{But } \Delta H^o = \Delta H^o_f(CO_2) + \Delta H^o_f(CaO) - \Delta H^o_f(CaCO_3) = (-393) + (-635) - (-1207) = 179kJ$$

$$\text{and } \Delta S^o = S^o(CO_2) + S^o(CaO) - S^o(CaCO_3) = 213 + 39.7 - 92.9 = 159.8JK^{-1}$$

$$\Delta G^0 = 179\times10^3 - 298\times159.8 = 1314\times10^5 = 131kJ \text{ to 3 sig. figs. @ 298 K}$$

$$\Delta G^0 = 179\times10^3 - 1500\times159.8 = -6.07\times10^4 = -61kJ \text{ to 3 sig. figs. @ 1500 K}$$

(5 marks, 1 for each line)

The assumptions made are that the ΔH and ΔS values are the same at the lower and higher temperature. .(1)

If calcium carbonate were heated to 1500 K it would decompose.(1) (if the pressure were maintained at 1 atm). This is because $\Delta G^{\ominus}$ is negative, showing the process is feasible. .(1)

ii) At what temperature is $\Delta G^{\ominus}$ expected to be zero? What is the significance of this? What is the partial pressure of carbon dioxide at this temperature? (4)

$$\Delta G^0 = 179\times10^3 - T\times159.8 = 0$$

$$\therefore T = \frac{179\times10^3}{159.8} = \underline{\underline{1120K}} \qquad (2)$$

At this temperature the reaction is at equilibrium. (1) The partial pressure of carbon dioxide is 1 atm. (1)

4) a) What is meant by an ***ideal gas***? (3)

An ideal gas is a hypothetical gas which obeys all the gas laws precisely. (1) Its molecules are mathematical points (1) and there are no forces acting between them except during collisions(1), which are perfectly elastic(1). The molecules undergo random motion. (1) {Any three}

Use this concept to account for

i) the existence of gas pressure, (1)

The pressure of a gas is the force per unit area arising from collisions of the molecules with the wall of the container.

ii) the increase of pressure with increasing temperature, (2)

As temperature increases the molecules move faster(1). As a result they hit the walls more frequently (½) and more violently(½). This makes the pressure they exert greater.

iii) the fact that the pressure of a gas is the same in all directions. (1)

The motion of the molecules is completely random with no preferred direction. Hence collisions of the molecules with the walls have no preferred direction. (1)

b) State the essential differences between a real gas and an ideal gas. (2)

A real gas has molecules with finite size(1). There are also forces of attraction between them(1).

{Acceptable: real gases liquefy and solidify at low temperatures etc.}

Explain how these differences are accounted for in the van der Waals equation for 1 mole of a real gas:

$$(P + a/V^2)(V - b) = RT \qquad (2)$$

"a" accounts for attractive forces between molecules. "b" accounts for the actual size of the molecules.

c) A 1.0 litre flask containing gas A at a pressure of 1.0 atmosphere is connected by a tap to a 3.0 litre flask containing gas B at a pressure of 3.0 atmospheres. The tap is then opened. Assuming that the gases behave ideally and that the temperature remains constant throughout, calculate

i) the partial pressures of A and B. (2)

The partial pressures of the gases are governed by Boyle's law, hence

$$x_B = \frac{n_B}{n_{tot}} = \frac{P_B}{P_{tot}} = \frac{\left(\frac{3}{4}\right)}{1} = \frac{3}{4} = 0.75$$

5) a) The acid catalysed hydrolysis of an ester is a first order reaction. Write down the differential rate equation for the reaction in terms of the concentration of ester, [A]. (1)

$$\frac{d[A]}{dt} = -k[A]$$

b) Show how the expression

ln[A] = ln$[A]_0$ – kt may be derived from the differential rate equation, (where [A] represents the concentration of the reactant). (4)

As stated above:

$$\frac{d[A]}{dt} = -k[A]$$

$$\therefore \frac{d[A]}{[A]} = -kdt.....(1)$$

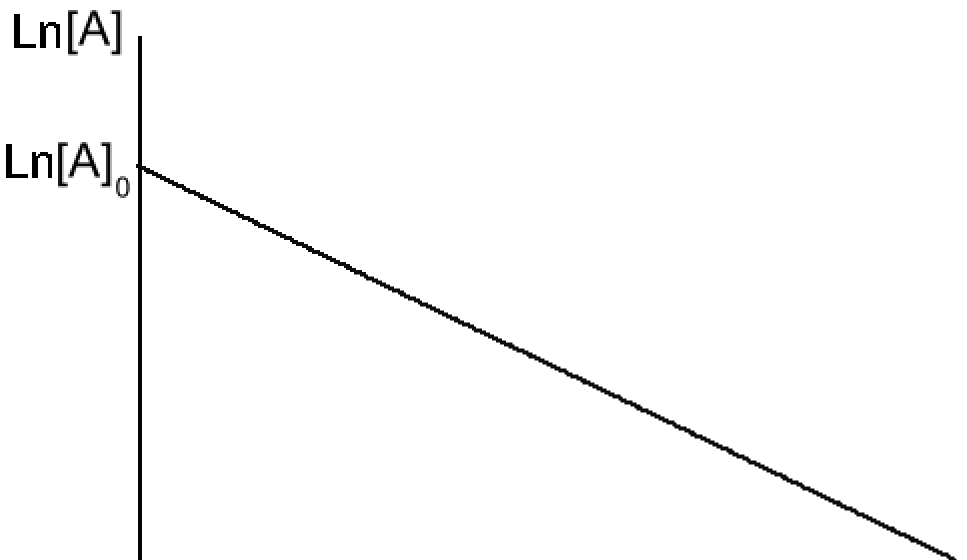
$$\int_{[A]=[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k\int_{t=0}^{t} dt.....(1)$$

$$\left[\ln[A]\right]_{[A]_0}^{[A]} = -k[t]_0^t......(1)$$

$$\ln[A] - \ln[A]_0 = -k(t-0)......(1)$$

$$\ln[A] = \ln[A_0] - kt$$

c) Sketch a graph of ln[A] against t for a first-order reaction. How could the rate constant be determined from such a plot? (3)



$\ln[A] = \ln[A]_0 - kt = \ln(0.1) - (1.0 \times 10^{-3}) \times 5 \times 60 = -2.603$

$\therefore [A] = \exp(-2.603) = 7.409 \times 10^{-2}$ 0.074 M to 2 sig. figs.

e) i) Explain the meaning of the term half-life, t_2. Why is the half-life of a first-order reaction more useful than that for a reaction of any other order? (2)

The half-life is the time required for the concentration of a reactant to fall to half of its intial value. This is particularly useful in the case of a first-order reaction because it is independent of the initial concentration of the reactant.

ii) A piece of wood from a living tree, which is slightly radioactive due to the presence of carbon-14, gives 15.0 counts per minute per gram of carbon. A piece of wood from an Egyptian mummy case gives 9.5 counts per minute per gram of carbon. The number of counts per minute is proportional to the concentration of carbon-14. How old is the case?. The half-life of C is 5600 years. (3)

Since radioactive decay is a first-order process:

$$\ln[A] = \ln[A_0] - kt.......(1)$$

$$and\ \ln\frac{[A]}{[A]_0} = -kt$$

$$\therefore \ln\frac{1}{2} = -kt_{½} = -5600k.$$

$$k = -\frac{1}{5600}\ln\frac{1}{2}.....(1)$$

$$\therefore \ln\frac{[A]}{[A]_0} = \ln\frac{9.5}{15} = -kt = \left(\frac{1}{5600}\ln\frac{1}{2}\right)t....(1)$$

$$\therefore t = \left(\ln\frac{9.5}{15}\right) \div \left(\frac{1}{5600}\ln\frac{1}{2}\right) = 3.690\times10^{3} = 3{,}700 \text{ years to 3 sig.figs......(1)}$$

6) a) Explain the meaning of the term "steam distillation". What is steam distillation used for? (2)

Steam distillation is a distillation carried out in a current of steam. It is useful for the distillation of organic chemicals which are easily oxidised.

Chlorobenzene (C_6H_5Cl) steam distils at 91°C at 1.01×10^5 Pa. At this temperature, the vapour pressure of chlorobenzene is 2.90×10^4 Pa. Calculate the percentage by mass of chlorobenzene in the distillate. (Take H=1, C=12, O=16 and Cl=35.5) (6)

The ratio of the number of moles of chlorobenzene to steam in the vapour (and hence the distillate) is given by

$$\frac{n_w}{n_c} = \frac{P_w}{P_c}................(1)$$

$$But\ P_w = P_{tot} - P_c = 7.2\times10^4\,Pa................(1)$$

$$\therefore \frac{n_w}{n_c} = \frac{P_w}{P_c} = \frac{7.2\times10^4}{2.90\times10^4} = \frac{7.2}{2.9} = 2.483..............(1)$$

$$\text{But \% by mass} = \frac{m_c}{m_w + m_c} = \frac{1}{\left(\frac{m_w}{m_c}\right)+1} \qquad (1)$$

$$\text{and} \left(\frac{m_w}{m_c}\right) = \left(\frac{n_w}{n_c}\right)\times\left(\frac{M_w}{M_c}\right) = 2.483\times\frac{18.0}{6\times12+5+35.5} = 0.3973 \qquad (1)$$

$$\therefore \text{\% by mass} = \frac{1}{\left(m_{H_2O}\right)+1} = \frac{1}{0.3973+1} = 0.7157 = \underline{\underline{71.6\%}} \text{ to 3 sig. figs.} \qquad (1)$$

Since the solute is involatile the vapour pressure only arises from the solvent. (1)

$\therefore$ Lowering of vapour pressure, $P_1^0 - P_1 = P_1^0 - P_1^0 x_1$ (1) $= P_1^0(1-x_1) = x_2 P_1^0$ (1)

c) i) Define the term *molality*. (2)

The molality of a solution is the number of moles of solute per kilogram of solvent.

ii) In terms of the molality, μ, of an undissociated solute, the freezing point depression (ΔT) is given by

$$\Delta T = -k_f \mu$$

From this, derive the equation

$$\Delta T = -k_f \frac{m}{M} \times \frac{1}{W}$$

(2)

where M is the molar mass of the solute in grams, and W is the mass of solvent in kilograms.

molality, $\mu = \dfrac{n}{W}$............(1)

But $n = \dfrac{m}{M}$..................(1)

$$\therefore \mu = \frac{m}{MW}$$

$$\therefore \Delta T = -k_f \frac{m}{MW} = -k_f \frac{m}{M} \times \frac{1}{W}$$