UNIVERSITY OF TECHNOLOGY, JAMAICA

DEPARTMENT OF SCIENCE AND MATHEMATICS

SEMESTER II FINAL EXAMINATION

GROUP: Sci. Ed. 2 **DATE:** APRIL/MAY, 2008

MODULE: PHYSICAL CHEMISTRY (CHY2007) **DURATION:** 2 HRS

INSTRUCTIONS: ANSWER **FOUR** (4) QUESTIONS

$R = 0.08206$ L atm mol^{-1} K^{-1} = 8.314 J K^{-1} mol^{-1}; 1 atm = 760 mm Hg = 760 bar = 101325 Pa = 1.01325×10^5 N m^{-2}; 1 J = 1 N m

QUESTION NO. 1

(a) Three gases – H_2, CO_2 and Ar each weighing 50 g, are contained in a 1.0 L flask at 25.0 °C.

(i) Calculate the number of moles of each gas and hence the mole fraction of each gas in the mixture. **[4]**

(ii) Calculate the total pressure of the mixture and hence the partial pressure exerted by each gas. **[3]**

(b) (i) State which assumptions of the kinetic molecular theory for an ideal gas become invalid under conditions of extremely high pressure and extremely low temperatures. **[2]**

(ii) Explain why these assumptions become invalid at conditions of extremely high pressures and extremely low temperatures. **[6]**

(c) Using the assumptions of the kinetic molecular theory explain, the following:

(i) Charles' Law

(ii) Avogadro's Law **[2.5 × 2 = 5]**

Total = 20 marks

QUESTION NO. 2

(a) The following reaction is important in the manufacture of sulphuric acid:

$$SO_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightleftharpoons SO_3\,(g)$$

At 900 K, 0.0216 mol of SO_2 and 0.0148 mol of O_2 are sealed in a 1.00 dm^3 reaction vessel. When equilibrium is reached, the concentration of SO_3 is determined to be 0.0175 M. Calculate K_c and K_p for the reaction. **[6]**

(b) The solubility product K_{sp}, for lead(II) iodide, PbI_2, is 7.9×10^{-8} mol^3 dm^{-9}. Calculate the solubility (in mol dm^{-3} and g dm^{-3}) of PbI_2 in:

(i) pure water and, **[3]**

(ii) 0.10 mol dm^{-3} sodium iodide (NaI) solution. **[4]**

(iii) Why is your answer in b (ii) so different from that obtained in b (i)? **[2]**

(c) (i) Explain why an aqueous solution containing equal concentrations of propanoic acid (CH_3CH_2COOH) and its sodium salt constitutes a buffer system. **[3]**

(ii) **Briefly** explain how the buffer system in (i) is able to minimise the effect of added H_3O^+ ions. **[2]**

Total = 20 marks

QUESTION NO. 3

(a) Explain how Hess's Law of heat summation depend on the fact that enthalpy is a state function. **[3]**

(b) (i) Determine the heat absorbed during the complete reaction of 2.614 moles of carbon with SO_2 (g) to form CS_2 (l) and CO (g) at constant pressure?

$$5C\ (s) + 2SO_2\ (g) \rightarrow CS_2\ (l) + 4\ CO\ (g)$$ **[1]**

(ii) If the reaction occurs at STP, what is the internal energy change ΔU for the reaction? Assume volume change, due to solid and liquid reactants, to be constant. **[5]**

(c) Use the given average bond dissociation energies (BE) to estimate ΔH for the hydrogenation of ethyne, C_2H_2 (g):

$$H{-}C{\equiv}C{-}H\ (g) + 2H_2\ (g) \rightarrow C_2H_6\ (g)$$

Bond	BE/ kJ mol^{-1}
C≡C	835
C—H	410
C—C	350
H—H	436

[4]

(d) (i) Define the terms "lattice energy" and "enthalpy of ionisation". **[2]**

(ii) Using the following data, construct a Born-Haber cycle for potassium chloride and use it to calculate the electron affinity of chlorine. **[5]**

	ΔH/kJ mol^{-1}
1st ionisation energy of potassium	+ 419
Enthalpy of atomisation of potassium	+ 89.2
Enthalpy of atomisation of chlorine	+ 121.7
Enthalpy of formation of KCl (s)	- 436.7
Lattice enthalpy of potassium chloride	- 711

Total = 20 marks

QUESTION NO. 4

(a) Explain how the following affect the solubility of sparingly soluble salts:
(i) pH
(ii) addition of a common ion **[3 + 3]**

(b) State Lewis' definition of acids. **[2]**

(c) The pK_a for acetic acid is 4.74. Calculate the pH and the concentration of all species present (CH_3COOH, CH_3COO^-, H_3O^+) in a 0.102 M aqueous solution of acetic acid. **[7]**

(d) Several commercial drain cleaners contain NaOH (s) and small amounts of Al (s). When one of these cleaners is added to water a reaction occurs resulting in the formation of H_2 bubbles:

$$2Al\ (s) + 2OH^-\ (aq) + 2H_2O \rightarrow 3H_2\ (g) + 2AlO_2^-\ (aq)$$

The purpose of the H_2 bubbles is to agitate the solution and thereby increase the cleansing action. According to this equation, how many liters of H_2 (g) are released when 0.200 g Al are dissolved in an excess of OH^- at 25 °C and 1.00 atm pressure? **[5]**

Total = 20 marks

QUESTION NO. 5

(a) **Discuss <u>two</u> (2)** factors that affect the rate of a reaction. **[4]**

(b) The first-order gas phase reaction, $SO_2Cl_2\,(g) \rightarrow SO_2\,(g) + Cl_2\,(g)$, has a rate constant, $k = 2.20 \times 10^{-5}\ s^{-1}$ at 593 K. What percent of a sample of SO_2Cl_2 would be decomposed by heating (at 593 K) for

(i) 1 hr,

(ii) 3 hrs? **[5]**

(c) The following data relates to the hydrolysis of t-butyl bromide (A) in a 10:90 water-acetone solution.

time/min	9.0	27.0	54.0	72.0	105.0
[A]/mol dm^{-3}	0.0961	0.0767	0.0536	0.0432	0.0270

(i) Prove that this reaction is first-order and not second-order reaction. **[8]**

(ii) Calculate the rate constant of the reaction. **[1]**

(d) Consider the reaction for the combustion of methane, CH_4,

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

If methane burns at a rate of 0.16 mol dm^{-3} s^{-1}, at what rates are CO_2 and H_2O formed? **[2]**

<u>Total = 20 marks</u>

QUESTION NO. 6

(a) Given the following data:

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad E^\circ_{red} = -0.44\ V$$
$$Ag^+ + e^- \rightarrow Ag \qquad E^\circ_{red} = 0.80\ V$$

Answer the following with respect to the reaction

$$Fe^{2+}\,(aq) + 2Ag\,(s) \rightarrow Fe\,(s) + 2Ag^+\,(aq).$$

(i) Calculate E° for the above reaction. **[1]**

(ii) Indicate whether E° for the reaction is spontaneous or not, at standard states. **[1]**

(iii) What is the value of E at equilibrium? **[1]**

(iv) What is the value of the equilibrium constant at 25 °C? **[2]**

(v) If $[Fe^{2+}] = 0.001$ M and $[Ag^+] = 0.0100$ M, what is the magnitude of E at 25 °C? **[2]**

(vi) For the reaction that is spontaneous, what is the maximum amount of work than can be performed? **[2]**

(b) How many grams of cadmium are consumed in a nickel-cadmium battery if it operates at a constant current of 0.2 amp for 30.00 sec? The half-reaction of interest is

$$Cd\,(s) + 2OH^-\,(aq) \rightarrow Cd(OH)_2\,(s) + 2e^-$$ **[3]**

(d) A mixture of gaseous hydrocarbons is produced by catalytic cracking. Three of these gases: CH_4, C_2H_6, and C_3H_8 move through a hole into a vacuum area housing a detector. Calculate the rates at which C_2H_6, and C_3H_8 reach the detector relative to CH_4. **[3]**

(e) Differentiate between:

(i) Surface tension and viscosity

(ii) Hexagonal close packing and cubic close packing of solids **[5]**

<u>Total = 20 marks</u>

****END OF PAPER****

PERIODIC TABLE OF THE ELEMENTS

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)