



THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme - Level 5
Final Examination 2008/2009
CHU 3124 - Physical Chemistry

(2.5 hours)

23 June 2009

10.00 p.m - 12.30 p.m

- * There are three (3) parts A, B and C.
- * Answer **only four (4)** questions out of six (6), choosing at least one question from each part.
- * If more than four questions are answered, only the **first four relevant answers** (those selected according to the specifications given above) in the order written, will be considered for marking
- * **Indicate your choice of questions**, in order, in the space provided in the answer sheet
- * The use of a non-programmable electronic calculator is permitted.
- * Logarithm tables and graph paper will be provided
- * Mobile phones are **NOT** allowed; leave them outside.

Gas constant (R)	= 8.314 J K ⁻¹ mol ⁻¹
Boltzmann Constant (k)	= 1.380 × 10 ⁻²³ J K ⁻¹
Avogadro constant (L)	= 6.023 × 10 ²³ mol ⁻¹
Faraday constant (F)	= 96,500 C mol ⁻¹
Plancks constant (h)	= 6.63 × 10 ⁻³⁴ J s
Velocity of light (c)	= 3.0 × 10 ⁸ m s ⁻¹
Atmospheric pressure (π)	= 1 bar = 10 ⁵ Pa (N m ⁻²)
Charge of a proton (e)	= 1.602 × 10 ⁻¹⁹ C
log _e (X)	= 2.303 log ₁₀ (X)

Part A

- (1) (a) The reaction $2 \text{NO}(\text{g}) + \text{Cl}_2 \longrightarrow 2 \text{NOCl}(\text{g})$
is second order in NO and first order in Cl₂.

5 moles of NO (g) and 2 moles of Cl₂ were allowed to react in a volume of 2 dm³ and the initial rate measured was 2.5 × 10⁻³ mol dm⁻³ s⁻¹. Calculate the rate at the instance when half of the initial amount of Cl₂ has reacted

(16 marks)

- (b) A reaction of the form $\text{A} \longrightarrow \text{P}$ is said to be 25 % complete in 25 minutes. If it follows first order kinetics, what would be the concentration of A at the end of another 50 minutes given that the initial concentration of A is 2.0 × 10 mol dm⁻³.

(16 marks)

- (c) Consider a consecutive, irreversible first order reaction of the form



(where k_1 and k_2 are rate constants such that $k_1 \neq k_2 \neq 0$)

- (i) Write down the rate expression (differential form) for the disappearance of A and the corresponding integrated form given that the initial concentration of A is $[A_0]$
- (ii) Write down the differential form of the rate expression for the disappearance of B and hence, show that the concentration of B at any time, t is

$$[B] = \frac{k_1[A_0]}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

- (iii) Show that maximum value for the concentration of B is reached when

$$t = \frac{1}{[k_1 - k_2]} \ln \left(\frac{k_1}{k_2} \right)$$

- (iv) Sketch the curve showing the variation of the concentrations of A, B and C with time in the case where k_1 is approximately equal to k_2 and highlight the maxima you obtained in (iii) above.

(52 marks)

- (d) Briefly describe the following terms used in chemical kinetics.

- (i) "steady state assumption" as applied in the kinetic study of chain reactions?
(ii) a catalyst

(16 marks)

Part B

2. (a) Define the following as applied in the study of Galvanic cells.

- (i) Chemically reversible electrode.
(ii) Electromotive force
(iii) Spontaneous anode

(30 marks)

- (b) (i) Define the electrode potential of an electrode.

- (ii) A student found that the electric potential of an electrode A to be 0.322 V higher than that of a reference electrode B at 25⁰C. He also determined that the electric potential of the standard hydrogen electrode to be 0.100 V higher than that of B at 25⁰C. Deduce the electrode potential of A at 25⁰C.

(30 marks)

- (c) (i) Write down a mathematical expression for the relationship between the ionic strength of a solution of electrolytes and the concentration of ions in it. Identify all the terms in the above expression.

- (ii) A student was given a solution of silver nitrate with $[\text{AgNO}_3] = 0.10 \text{ mol dm}^{-3}$ and a sodium chloride solution with $[\text{NaCl}] = 0.20 \text{ mol dm}^{-3}$ which were labelled as A and B respectively. He mixed equal volumes of A and B and shook thoroughly to obtain a mixture (a solution and a precipitate) C. Indicating steps, estimate the ionic strength of the liquid phase of C. [You may assume that there is no volume change during mixing/precipitation of A and B and the precipitate is not soluble.]

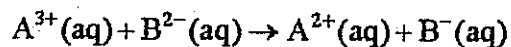
(40 marks)

3. (a) Define the following as applied to a battery.

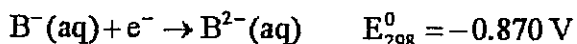
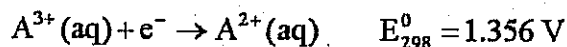
- (i) Energy density
- (ii) Capacity
- (iii) Positive terminal

(21 marks)

- (b) Ions of two compounds A and B react according to the following reaction.



The standard electrode potentials of the associated half reactions are as follows.



A student performed a potentiometric titration using a solution of $\text{A}^{3+}(\text{aq})$ as the titrand and a standard solution of $\text{B}^{2-}(\text{aq})$ as the titrant. A gold rod was used to construct the redox electrode and a saturated calomel electrode was used as the reference electrode.

- (i) Draw the half-cell diagram for the redox electrode formed before the end point.
- (ii) Draw the half-cell diagram for the redox electrode formed after the end point.
- (iii) Sketch the variation of the electrode potential of the redox electrode, during the titration, versus the volume of titrant added. Indicate the end point and the electrode potentials, of the two half reactions indicated above, on your sketch.

(30 marks)

- (c) (i) State the major difference between a fuel cell and a primary or a secondary cell.
- (ii) Ammonia could be oxidised in a fuel cell to generate electrical energy using the reaction, $4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$ in an alkaline medium. For this reaction, $\Delta G = -1400.000 \text{ kJ mol}^{-1}$, under a certain set of experimental conditions. One hundred such fuel cells are connected in series in constructing a battery which is used to power a small carpentry workshop which draws a constant current of 10 A.

- (α) Write down the spontaneous anode reaction and cathode reaction of the fuel cell.
- (β) Deduce the charge number of the fuel cell reaction.
- (γ) Calculate the emf of the battery.
- (δ) Calculate the power delivered by the battery assuming that the potential difference across the battery remained at its emf when the current is drawn.
- (λ) Calculate the rate of consumption of oxygen in the battery in mol s^{-1} .

(49 marks)

Part C

4(a) The Kelvin equation can be written in the form

$$\ln\left(\frac{P}{P^\sigma}\right) = \frac{2M\gamma}{RT\rho r}$$

- (i) Write down the **most** significant deduction that you can make from the Kelvin equation?
- (ii) State the important assumption that has been made in deriving the Kelvin equation.
- (iii) Calculate the radius r of spherical water droplets that will be necessary for the vapour pressure outside the droplet to be 1% more than the bulk at 300 K.

(For water, surface tension = $72 \times 10^{-3} \text{ N m}^{-1}$;

density = 1000 kg m^{-3}

relative molar mass = 18)

(30 marks)

(b) The surface tension (γ) of a liquid can be determined using the capillary rise method by using the expression

$$\gamma = \frac{h\rho g r}{2\cos\theta}$$

- (i) Name and define the quantity represented by the symbol θ .
- (ii) Use this expression to deduce that the level of a liquid such as mercury has to be depressed inside a capillary tube immersed in such a liquid.

(20 marks)

(c) By means of a mechanical scoop, a very thin layer of surface was skimmed off a dilute soap solution at 300 K. It was found that 6.025×10^5 mol of soap solute was present in 3.00 ml of this solution that was skimmed off $5 \times 10^{-2} \text{ m}^2$ area of the surface. 3.00 ml of soap solution in the bulk contained only 6.020×10^5 mol of soap solute.

- (i) Calculate the excess surface concentration in the thin surface layer.
- (ii) Calculate the bulk concentration (c) of the soap solution.
- (iii) Given that the surface tension (γ) of the soap solution varies with the bulk concentration, c , according to the equation

$$\gamma = 72 - bc \quad \text{where } b \text{ is a constant.}$$

calculate

- (α) the surface pressure, Π , of the given soap solution and
(β) the value of b

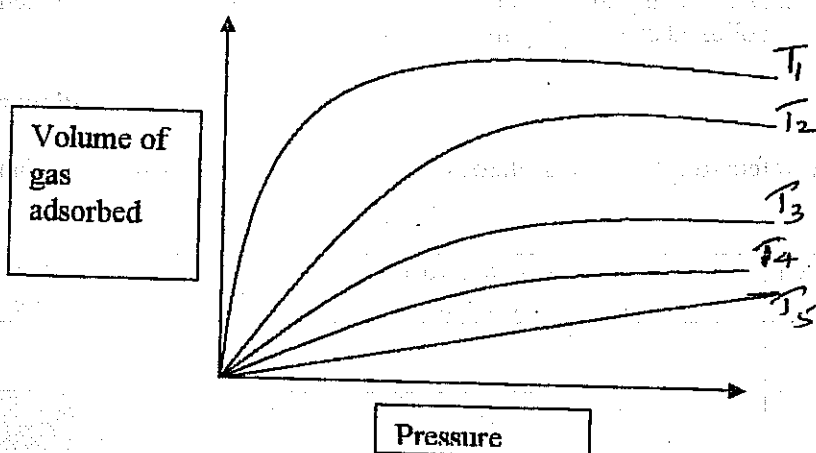
(50 marks)

5. (a) Oxygen gas (relative molecular mass = X) at a pressure C collides with a tungsten surface (area Y) at a temperature D . Given that the sticking probability = a , deduce the number of molecules that will be adsorbed on the surface in time b . Assume molecular adsorption and the oxygen behaves as an ideal gas.

[Avogadro Constant = E ; Gas Constant = F]

(Note: Your answer should **not** include any symbols/letters other than those given in the above data)

- (b) Typical adsorption isotherms obtained for a certain gas/solid system at various temperatures, T_1, T_2, T_3, T_4, T_5 are given below. (25 marks)



- (i) What can you deduce about the nature of the adsorption process?
(ii) Deduce as to which one of the following is correct:

(A) $T_1 > T_2 > T_3 > T_4 > T_5$

(B) $T_1 > T_2 > T_3 > T_4 = T_5$

(C) $T_1 < T_2 < T_3 < T_4 < T_5$

(D) $T_1 < T_2 < T_3 < T_4 = T_5$

- (iii) Give reasons for your deduction in (ii)

(iv) Who is the scientist who put forward the theory that explains the above isotherm?

(v) How can you transform the above adsorption isotherms to an equivalent set of adsorption isosteres? Give a sketch of the adsorption you are likely to obtain.

(35 marks)

(c) When nitrogen gas is adsorbed on charcoal, it is found that the adsorption amounted to 2.5 cm^3 of nitrogen on 1.5 g of charcoal under the following equilibrium conditions of pressure and temperature

P/bar	22	46
T/°C	-173	-73

- (i) Calculate the equilibrium pressure under which a similar adsorption would be obtained at $-123 \text{ }^\circ\text{C}$
- (ii) Indicate **THREE** of the most important assumptions that you have made in carrying out the above calculation.

(40 marks)

6.(a) How can you distinguish between true solutions, suspensions, and colloidal systems on the basis of molecular size.

(15 marks)

(b) Discuss briefly the most important factor that is responsible for the stability of lyophobic colloidal solutions.

(15 marks)

(c) Dialysis and Electro-Dialysis are important treatment methods in medicine for some patients. What important part does colloidal science play in such treatment.

(15 marks)

(d) The table given below refers to colloidal dispersions. Complete the table by filling the blanks appropriately.

Dispersion Medium	Dispersed Phase	General Name given to the dispersion system	One typical example	Another example
solid	gas	A	B	C
D	E	solid emulsion	F	
G	H	I	milk	J
gas	K	L	fog	smoke

Indicate in your answer sheet appropriate answers to the blanks in the table specified through the letters A, B, C, D, E, F, G, H, I, J, K, and L

(Note: some marks will be deducted for incorrect answers)

(30 marks)

(e) Explain briefly how the rate of adsorption can be used as a distinguishing criterion between physical adsorption and chemisorption.

(25 marks)