CHEM 223 2005

PHYSICAL CHEMISTRY.

MID YEAR TEST

Saturday 2 July, 14.30 – 16.30

Time allowed **2 hours**

Instructions:

Answer Question 1 AND any THREE other questions.

Question 1 is worth	**36** marks
Questions 2 – 5 are worth	**28** marks
Total marks	**120**.

Useful Data:

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

$F = 96484$ C mol^{-1}

$M_R(\text{He}) = 4.00$ $M_R(\text{Na}) = 22.99$

$M_R(O_2) = 32.00$ $M_R(\text{K}) = 39.10$

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$\lambda^\circ_{H^+} = 350.1 \times 10^{-4}$ S m^2 mol^{-1}

$\lambda^\circ_{OH^-} = 199.2 \times 10^{-4}$ S m^2 mol^{-1}

$\lambda^\circ_{Na^+} = 50.1 \times 10^{-4}$ S m^2 mol^{-1}

$\lambda^\circ_{K^+} = 73.5 \times 10^{-4}$ S m^2 mol^{-1}

$\lambda^\circ_{NO_3^-} = 71.5 \times 10^{-4}$ S m^2 mol^{-1}

$\lambda^\circ_{Cl^-} = 76.4 \times 10^{-4}$ S m^2 mol^{-1}

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1. **Answer all parts.**

(a) Distinguish between the terms *molecularity* and *order of reaction* which are used to describe properties associated with chemical kinetics.

(b) Explain why a space craft filled with an atmosphere of 80% helium and 20% oxygen will lose more helium than oxygen through a small hole in the wall.

(c) Given that the enthalpy of vaporization of water at 373K and 1.0 atmosphere is +40.4 kJ mol^{-1}, calculate the boiling temperature of water in a pressure cooker at 2.5 atmospheres.

(d) Calculate the pressure that 14 g of helium gas would exert in a vessel of volume 1.5 L at 30°C. Express your answer in atmosphheres.

(e) Distinguish between the electrical behaviour of a solution of a strong electrolyte and a solution of a weak electrolyte.

(f) What is so special about the half-life of a first-order reaction?

(g) Given that the ionic radius of a sodium ion is smaller than that of a potassium ion, explain why the molar ionic conductivity in aqueous solution of the sodium ion is less than that of the potassium ion.

(h) Distinguish between the terms *chemisorption* and *physisorption* which are used in connection with a description of the adsorption of molecules on catalysts.

(i) With reference to Enzyme Kinetics what is meant by the terms *non-competitive* and *competitive inhibition.*

2. (a) Define the following terms which relate to the reaction:

$N_2 + 3H_2 \rightarrow 2NH_3$

(i) the rate of reaction

(ii) the rate law

(iii) the rate constant

(b) A gas phase reaction of the type $2A \rightarrow B$ is monitored at 298K by measuring the **total** pressure ($P_t = P_A + P_B$).

t/s	0	100	200	300	400
P_t/Torr	400	322	288	268	256

Note: At t = 0, the pressure is due to A only.

(i) Derive an expression that gives the partial pressure of A, P_A, in terms of the total pressure, P_t.

(ii) Show that the given data are consistent with a second order reaction.

(iii) Show that the rate constant at 298 K is $k_2 = 8.06 \times 10^{-6}$ $Torr^{-1}s^{-1}$.

(iv) If the rate constant at 37°C is $k_2 = 1.73 \times 10^{-5}$ $Torr^{-1}s^{-1}$

show how to calculate the activation energy of the reaction.

Note: **You do not need to calculate the activation energy: just set up an expression with <u>all</u> the appropriate numbers substituted.**

3. (a) (i) Derive the Langmuir isotherm

$$\theta = \frac{KP}{1 + KP}$$

which describes adsorption of a gas onto a surface.

Here θ is the fraction of the surface covered by the adsorbate and P is the pressure of the gas.

(ii) List the assumptions made in this derivation and discuss their validity

(b) Show that the above isotherm can be rearranged to give

$$\frac{P}{m} = \frac{P}{m_\infty} + \frac{1}{Km_\infty}$$

where m_∞ is the mass of gas absorbed at complete coverage..

(c) A certain solid adsorbs 0.44 mg of CO when the pressure is 36.0 kPa and 0.19 mg when the pressure is 3.0 kPa. In both cases the temperature was 300 K.

Assuming that the Langmuir isotherm describes the absorption of CO, calculate:

(i) the mass of gas required for complete monolayer coverage

(ii) the fractional coverage at 26.0 kPa.

(d) If the temperature is raised to 400 K will the mass of gas absorbed be greater or less than at 300 K? Explain.

(e) If the surface catalysed reaction

$$A + B \rightarrow \text{Products}$$

occurs by a mechanism where one reactant, A, is adsorbed on the catalyst surface and the other, B, is not, show that at high pressure of reactant B the observed rate of reaction will be first order, whereas at low pressure the observed rate of reaction will appear to be second order.

4. The thermal decomposition of acetaldehyde occurs according to the stoichiometric equation

$$CH_3CHO \rightarrow CH_4 + CO$$

The observed kinetic law is $$-\frac{d[CH_3CHO]}{dt} = k_{obs}[CH_3CHO]^{3/2}$$

The reaction may take place by the simple chain mechanism.

$$CH_3CHO \longrightarrow \dot{C}HO + \dot{C}H_3 \quad (1)$$

$$\dot{C}HO \longrightarrow CO + \dot{H} \quad (2)$$

$$\dot{H} + CH_3CHO \longrightarrow H_2 + \dot{C}H_2CHO \quad (3)$$

$$\dot{C}H_3 + CH_3CHO \longrightarrow CH_4 + \dot{C}H_2CHO \quad (4)$$

$$\dot{C}H_2CHO \longrightarrow \dot{C}H_3 + CO \quad (5)$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6 \quad (6)$$

(a) List the transient radical species present in the system and indicate which of these are postulated attacking acetaldehyde.

(b) State any assumptions necessary to apply the steady state treatment to this set of equations.

(c) Write down the appropriate equations for steady state and find the steady state concentrations in terms of $[CH_3CHO]$ and the various elementary rate constants (k_1, k_2, k_3, and k_4) involved.

(d) Show that this mechanism predicts that the rate of destruction of acetaldehyde is of the form

$$-\frac{d[CH_3CHO]}{dt} = 2k_1[CH_3CHO] + k_4\left(\frac{k_1}{k_6}\right)^{1/2}[CH_3CHO]^{3/2}$$

(e) Compare the result in (d) to the observed kinetic law given above. What can you say about the relative importance of the two terms in this expression?

5. (a) Explain the meaning of the following terms relating to the passage of electricity through an ionic solution and, where applicable, give the appropriate SI units.

(i) Conductivity, κ_i

(ii) limiting molar ionic conductivity, λ_i°

(iii) drift speed s_i° and mobility, μ_i°

(iv) transport number, t_i.

(b) 10 mL of a NaOH solution of unknown concentration was titrated with 0.0100 M HCl solution in a conductivity cell which has a cell constant of 36.5 m^{-1}. After the addition of 15.00 mL of the 0.0100 M HCl it was realised that too much HCl had been added. (That is, the equivalence point or end point of the titration had been passed.)

At this stage the resistance of the solution was 332 Ω.

(i) List the ions present in significant concentration after the addition of the excess HCl.

(ii) Calculate the concentration of the NaOH solution.

(iii) Calculate the conductivity at the end point.

(iv) Assuming that the concentration of the concentration of the NaOH solution was 0.012 M, calculate the transport number of the sodium ion at the end point.