CCHE 4273

FIRST PUBLIC EXAMINATION

Trinity Term 2004

Preliminary Examination in Chemistry

SUBJECT 3: PHYSICAL CHEMISTRY

Wednesday, June 9th 2004, 9.30 a.m. to 12 noon

Time allowed: 2 ½ hours

Candidates should answer **ALL** questions in Section A and any **TWO** questions in Section B.

Use **SEPARATE** booklets for your answers to Section A and Section B.

The numbers in square brackets indicate the weight that the Examiners expect to assign to each part of the question.

Fundamental Constants

Molar gas constant, R	=	8.314 J K^{-1} mol^{-1}
Planck constant, h	=	6.626×10^{-34} J s
Boltzmann constant, k_B	=	1.381×10^{-23} J K^{-1}
Speed of light, c	=	2.998×10^{8} m s^{-1}
Avogadro constant, N_A	=	6.022×10^{23} mol^{-1}
Electron mass, m_e	=	9.109×10^{-31} kg
Elementary charge, e	=	1.602×10^{-19} C
Faraday constant, F	=	9.649×10^{4} C mol^{-1}
Atomic mass unit, u	=	1.661×10^{-27} kg
Vacuum permittivity, ε_o	=	8.854×10^{-12} J^{-1} C^{2} m^{-1}
Gravitational constant, G	=	6.673×10^{-11} N m^{2} kg^{-2}

Other Conventions

$P^{\ominus}$ = 1 bar = 1×10^{5} Pa   1 atm = 101.325 kPa = 760 Torr

Do not turn this paper over until instructed to do so by an invigilator.

SECTION A

Answer all six questions in this section.

Note that the questions in this section do not all carry the same number of marks.

1. (a) When heated, calcium carbonate decomposes to give calcium oxide and carbon dioxide.

$$CaCO_3\,(s) \rightleftarrows CaO\,(s) + CO_2\,(g)$$

For the forward reaction $\Delta_r H^\ominus = 178$ kJ mol^{-1} and $\Delta_r S^\ominus = 161$ J K^{-1} mol^{-1}.

(i) Write down an expression for the equilibrium constant for the reaction.

[2]

(ii) Assuming that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ are independent of temperature, at what temperature would the equilibrium pressure of carbon dioxide be one bar?

[3]

(b) The lattice energy of an ionic solid is the energy required to vaporize 1 mole of solid to give gaseous ions:

$$MX(s) \rightarrow M^+(g) + X^-(g)$$

The hydration enthalpy is the enthalpy change when 1 mole of gaseous ions is dissolved in water.

$$M^+(g) + X^-(g) \rightarrow M^+(aq) + X^-(aq)$$

The hydration enthalpy of Na^+ is -407 kJ mol^{-1} and that of F^- is -485 kJ mol^{-1}. The lattice energy for NaF is 907 kJ mol^{-1}.

(i) Calculate the change in temperature when 0.5 mole NaF is dissolved in 1 kg of water. You may assume that the entire energy change upon dissolution is used to change the temperature of the water, which has a heat capacity of 4 J K^{-1} g^{-1}.

[4]

(ii) Comment on the expected sign of the entropy change for the process

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

[1]

2. (a) The electrostatic force between two point charges, q_1 and q_2, separated by a distance r is given by

$$F = \frac{q_1 q_2}{4\pi\varepsilon_o r^2}$$

Calculate the force between an electron and a proton separated by 0.1 nm.

[1]

(b) The gravitational force between two masses, m_1 and m_2, a distance r apart, is

$$F = -\frac{Gm_1m_2}{r^2}$$

Calculate the value of the product m_1m_2 if the gravitational force between two point masses 0.1 nm apart is equal to the force between the electron and proton calculated in part (a) above.

[2]

(c) In the light of your answer to parts (a) and (b), comment on the relative importance of gravitational and electrostatic forces in atoms.

[1]

3. (a) The ionization energy of the ground state hydrogen atom is 13.6 eV. Calculate the energy in eV required to excite the 1s electron in the He^+ ion to the 2p level.

[3]

(b) To what wavelength of light (in nm) does this energy correspond?

[2]

(c) In an approximate model the interaction energy, *V(r),* of two atoms is given by:

$$V(r) = \frac{a}{r^{12}} - \frac{b}{r^6}$$

in which r is the separation of the atoms and a and b are constants. Explain briefly the origin of this expression. [3]

(d) Determine, in terms of a and b, the distance at which the potential energy $V(r)$ is a minimum. [2]

4. (a) What is *quantum mechanical tunneling*?

[2]

(b) In what ways does the classical model of a simple harmonic oscillator differ from the quantum mechanical model of a vibrating diatomic molecule?

[3]

(c) The vibrational energy of the $H^{35}Cl$ molecule can be approximated as

$$E = (v + \frac{1}{2})h\upsilon \quad \text{joules}$$

in which

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad s^{-1} \qquad\qquad \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ kg}$$

k is the force constant for $H^{35}Cl$ and μ is its reduced mass. The energy gap between the first two vibrational levels in $H^{35}Cl$ is 5.939×10^{-20} J. Calculate the force constant of the bond in $H^{35}Cl$. [Atomic masses: H 1 u; ^{35}Cl 35 u]

[3]

5. (a) Outline the assumptions of the kinetic gas model (kinetic molecular theory of gases).

[3]

(b) Lindemann proposed the following mechanism for gas phase reactions:

$$A + A \xrightarrow{k_1} A^* + A$$
$$A^* + A \xrightarrow{k_{-1}} A + A$$
$$A^* \xrightarrow{k_2} P$$

Use the Steady State Approximation to derive an expression for the rate of production of P in terms of the concentration of reactant A.

[3]

(c) Use your expression from Part (b) to show that the order of reaction with respect to [A] may be different in the limits of low and high pressure of A.

[2]

(d) Explain qualitatively why the reaction order with respect to [A] depends upon the total pressure.

[2]

6. (a) In electrochemistry, what is meant by the term *reference electrode*? Give an example.

[2]

(b) Draw a diagram of an electrochemical cell for which the Nernst equation is

$$E = E^{o} - \frac{RT}{nF}\ln\frac{a_{Pb^{2+}}}{a_{Cd^{2+}}}$$

[2]

(c) Sketch the phase diagram for carbon dioxide and use it to explain the meaning of the following terms:

(i) critical point
(ii) sublimation
(iii) phase coexistence

[4]

SECTION B

Answer any two questions from this section – all questions carry equal marks

7. (a) What is Le Chatelier's Principle?

[3]

(b) Write down the expression for the equilibrium constant for the reaction.

$$Br_2\,(g) \rightleftarrows 2Br\,(g)$$ [1]

(c) In which direction will the equilibrium move when the pressure is increased? Explain the physical reason why the equilibrium moves in this direction.

[4]

Values for the equilibrium constant for dissociation of bromine in the gas phase are given below as a function of temperature:

T / K	K
600	6.18×10^{-12}
800	1.04×10^{-7}
1000	3.58×10^{-5}

(d) Calculate the value of $\Delta_r G^{\ominus}$ at 1000 K.

[2]

(e) Calculate the standard enthalpy of reaction, assuming that it is independent of temperature in the range 600 K to 1000 K.

[6]

(f) Calculate the value of $\Delta_r S^{\ominus}$ at 1000 K. [2]

(g) Explain what is meant by the Equipartition Principle.

[3]

(h) How would the heat capacity at constant pressure, C_p, of gaseous bromine be expected to vary:

(i) in the temperature range 298 – 1000 K;

(ii) as the temperature reaches values at which dissociation into atomic bromine becomes significant?

[4]

8. ANSWER EITHER PART A OR PART B

PART A

(a) Explain what is meant by the terms *Atomic Orbital*, *boundary condition*, *normalization*, *degenerate wavefunctions*.

[10]

(b) The general expression for the wavefunction of a particle of mass M moving along the x-axis within a region of uniform zero potential energy is

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

A particle is confined to a one-dimensional box of length L by infinitely high barriers at $x = 0$ and $x = L$. By applying the appropriate boundary conditions show that the normalized wavefunction for a particle trapped within the box is

$$\psi = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right)$$

[5]

(c) The energy of the particle in this one-dimensional box is given by

$$E^{box} = \frac{n^2 h^2}{8ML^2}$$

The energy of a particle confined to a ring is

$$E^{ring} = \frac{m^2 h^2}{8\pi^2 I}$$

in which m is a quantum number restricted to integer values and I is the moment of inertia. Show that the ratio of the energy of a particle of mass M moving in a one-dimensional box of length L to the energy of the same particle moving around a ring of circumference equal to L is

$$E^{box} / E^{ring} = \left(\frac{n}{2m}\right)^2$$

[6]

(d) The wavefunction for a particle on a ring is $\psi(\Phi)= 2\pi^{-1/2}\, e^{im\phi}$. What is the smallest value that $|\, m \,|$ can take? Explain your reasoning.

[4]

PART B OF THIS QUESTION FOLLOWS ON THE NEXT PAGE

PART B

(a) Show that the moment of inertia for a diatomic molecule consisting of point masses m_1 and m_2 separated by a distance r is

$$I = \mu r^2 \quad \text{in which} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

[4]

(b) Comment on the observation that many liquids have a similar entropy of vaporization, approximately 90 J K^{-1} mol^{-1}, at their normal boiling point (Trouton's rule).

[2]

(c) The normal boiling point of krypton is 121K. Assuming that Trouton's rule applies, determine the enthalpy of vaporization of krypton at 121K.

[2]

(d) Using a suitable model for the structure of liquid krypton, estimate the strength of the van der Waals interaction between two krypton atoms.

[4]

(e) The average rotational kinetic energy of a diatomic molecule is $k_B T$. Determine the hypothetical average angular velocity of the Kr_2 molecule at 121 K (assume a bond length of 0.39 nm. Atomic mass Kr: 84 u).

[6]

(f) The angular velocity in rad s^{-1} of a diatomic molecule is related to its force constant by

$$\omega = \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$

Determine the force constant that the Kr_2 molecule would have if it were able to rotate at the angular velocity determined in part (e) above with a bond length of 0.39 nm.

[5]

(g) Comment on the possibility of Kr_2 molecules being stable at 121K.

[2]

9. (a) The following data have been recorded for the reaction between H_2 and nitric oxide at a temperature of 1100 K.

$p_{hydrogen}$ / Torr	p_{NO} / Torr	Initial reaction rate $\Delta p_{nitrogen}$ / Torr s^{-1}
400	152	0.25
400	300	0.97
400	359	1.40
300	232	0.44
300	310	0.78
300	400	1.30
289	400	1.25
205	400	0.88

Determine the order of reaction with respect to hydrogen, the order of reaction with respect to nitric oxide and the rate constant for the reaction.

[6]

(b) A possible mechanism for this reaction is

$$NO + H_2 \xrightarrow{k_1} NOH_2$$

$$NOH_2 \xrightarrow{k_{-1}} NO + H_2$$

$$NOH_2 + NO \xrightarrow{k_2} N_2 + H_2O_2$$

$$H_2O_2 + H_2 \xrightarrow{k_3} 2H_2O$$

By applying the steady state approximation to NOH_2 and H_2O_2 derive expressions for the rate of formation of (i) nitrogen and (ii) water in terms of the concentrations of the reactants.

[7]

(c) Demonstrate that at low pressures of NO the expression derived in part (b) is in accord with the experimental rate law.

[3]

(d) Derive an expression for the half-life of a second order reaction whose rate law is:

$$\text{Rate} = k\,[A]^2$$ [5]

(e) Are there any conditions under which the expression derived in part (d) would accurately predict the half-life of the reaction between hydrogen and nitric oxide?

[4]

10. (a) Explain in detail how you would determine the standard electrode potential for the following half-cell at 298K:

$$Br^{-}(aq) \mid CuBr(s) \mid Cu(s)$$

[8]

(b) The EMF of the cell

$$Pt \mid H_2(g)\ \ (P = 1\ \text{bar}) \mid\ HBr(aq)\ \ (10^{-4}\ M) \mid CuBr \mid Cu$$

is 0.559V at 298K. The standard electrode potential for the Cu/Cu^{+} couple is 0.522V Calculate the solubility product of CuBr.

[7]

(c) Calculate the concentration of $Cu^{+}(aq)$ ions in the cell shown above.

[4]

(d) Calculate $\Delta G^{\ominus}$ for the dissolution of CuBr at 298K.

[2]

(e) By how much would the EMF of the cell change if the pressure of hydrogen were doubled? (Assume that all species in the cell behave ideally).

[4]

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