CPSS 4273

FIRST PUBLIC EXAMINATION

Long Vacation 1997

Preliminary Examination in Physical Sciences

SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY

TUESDAY 23rd SEPTEMBER 1997   9.30 a.m. - 12.00 noon

Time allowed: $2\frac{1}{2}$ hours

Candidates should answer **FOUR** *questions only*

The numbers in the margin indicate the approximate weight the Moderators expect to assign to each part of the question

$R = 8.3145$ J K^{-1} mol^{-1}

$k = 1.3807 \times 10^{-23}$ J K^{-1}

$N_A = 6.0221 \times 10^{23}$ mol^{-1}

$h = 6.6261 \times 10^{-34}$ J s

$c = 2.9979 \times 10^8$ m s^{-1}

$F = 9.6485 \times 10^4$ C mol^{-1}

1 u $= 1.6605 \times 10^{-27}$ kg

1 bar $= 10^5$ Pa

You must not open this paper until instructed to do so by an invigilator.

1 (a) Derive the expression

$$dG = V\,dp - S\,dT$$

from the relations $dU = dq + dw$ and $dS = dq_{rev}/T$, and explain why the expression applies to irreversible as well as to reversible processes. [10]

(b) Show how the expression derived in (a) may be used to account for the principal features of the phase diagrams of (i) carbon dioxide, (ii) water. [2 × 4]

(c) Show how the melting point of an incompressible liquid depends on the pressure and the quantities $\Delta_{fus}G^{\ominus}$ and $\Delta_{fus}V^{\ominus}$. [7]

2 (a) How is the standard cell potential (emf), $E^{\ominus}$, related to $\Delta_r G^{\ominus}$, $\Delta_r S^{\ominus}$, and $\Delta_r H^{\ominus}$ for the corresponding cell reaction? [6]

(b) Measurements performed on the cell

$$Mg(s)|MgSO_4(aq, m_1)\|CuSO_4(aq, m_2)|Cu(s)$$
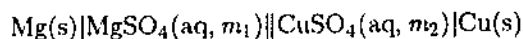
at 298 K yielded the values $E^{\ominus} = +2.71$ V and $dE^{\ominus}/dT = 7.2 \times 10^{-5}$ V K^{-1}.

(i) What is the significance of the symbol $\|$ in this cell notation? [2]

(ii) Write down the cell reaction in terms of half-reactions. [3]

(iii) Evaluate $\Delta_r G^{\ominus}$, $\Delta_r S^{\ominus}$, and $\Delta_r H^{\ominus}$ and the equilibrium constant for the cell reaction at 298 K. [6]

(c) (i) Write down the Nernst equation for the cell in (b). [3]

(ii) Calculate E for the cell at $m_1 = 1.00 \times 10^{-4}$ mol kg^{-1} and $m_2 = 1.00 \times 10^{-2}$ mol kg^{-1}. Assume the solutions to be ideal. ($RT/F = 0.0257$ V at 298 K.) [5]

3 A particle of mass m is constrained to move in a one-dimensional potential well with $V(x) = 0$ for $0 \le x \le L$ and $V(x)$ infinite elsewhere.

(a) Show that the function

$$\psi(x) = a\cos(n\pi x/L) + b\sin(n\pi x/L)$$

(where a and b are constants and n is a number) is a solution of the Schrödinger equation for the system. [5]

(b) Using the boundary conditions at $x = 0$ and L, show that $a = 0$ and find the allowed values of n and the corresponding energies. [5]

(c) Evaluate the constant b that ensures correct normalization of the wavefunction $\psi(x)$. [5]

(d) Sketch $\psi(x)$ and $\psi(x)^2$ for the lowest three values of n. Comment on the physical significance of $\psi(x)$ and $\psi(x)^2$. [5]

(e) An electron is confined to a one-dimensional box of length 15 nm. How many energy levels lie between 3.5 and 8.0 kJ mol^{-1}? ($m_e = 9.110 \times 10^{-31}$ kg.) [5]

4 (a) State the selection rules applicable to the emission spectra of hydrogenic atoms. [3]

(b) The first transition in the Lyman series of the emission spectrum of a hydrogen atom is observed at 82 258 cm^{-1}. Predict the wavenumbers of the next three lines in this series. [4]

(c) Four lines of another series of lines in the emission spectrum of a hydrogen atom are observed at 5331.5, 7799.3, 9139.8, and 9948.0 cm^{1}. Assign these lines, explaining your procedure. [4]

(d) Would the energy required to ionize the 2s electron in the ground state of a lithium atom be greater or less than that required to ionize a hydrogen atom with configuration 2s^1? Give your reasons. [6]

(e) Discuss the differences between the series of lines arising from $np \rightarrow$ 2s transitions in the emission spectra of hydrogen and lithium atoms. [8]

5 (a) Explain the terms (i) reaction order, (ii) overall order, and (iii) molecularity. [3 × 2]

(b) Explain what is meant by the *steady-state approximation* in chemical kinetics. Why is it useful, and under what conditions is it valid? [4]

(c) The following mechanism has been proposed for the thermal decomposition of ozone:

$$O_3 \longrightarrow O_2 + O \qquad k_a$$
$$O_2 + O \longrightarrow O_3 \qquad k_a'$$
$$O_3 + O \longrightarrow O_2 + O_2 \qquad k_b$$
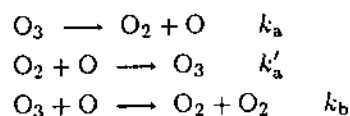
(i) Derive an expression for the rate of decomposition of O_3 in terms of the concentrations of O_3 and O_2 and of the three rate constants k_a, k_a', and k_b. [7]

(ii) Discuss the conditions under which the overall reaction will exhibit kinetics that are (a) first-order with respect to O_3 and (b) second-order with respect to O_3. [4]

(iii) Interpret the rate equation you have derived, and in particular explain the role of O_2. [4]

6 (a) Derive *Kirchhoff's law* for the temperature-dependence of standard reaction enthalpies. What modification would be made to apply the rule to standard reaction internal energies $(\Delta_r U^\ominus)$? [5 + 2]

(b) State the *equipartition principle* for the average energy of a mode of motion at a temperature T, and use it to predict the molar constant-pressure heat capacity of a gas of diatomic molecules (with vibration ignored). [5]

(c) The standard enthalpy of formation of ammonia gas is $-46.11 \text{ kJ mol}^{-1}$ at 298.15 K. Estimate (by drawing on the equipartition principle to estimate the molar heat capacities) the standard enthalpy of formation at 500 K. [6]

(d) The molar constant-pressure heat capacity of graphite and diamond both obey an expression of the form $C_{p,m} = aT^3$ at low temperatures, with different values of a. Devise an expression for the standard entropy of the graphite → diamond phase transition at low temperatures. [7]

7 (a) Derive the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_{trs}H}{T\Delta_{trs}V}$$

and use it to account for the features of a typical one-component phase diagram. [8]

(b) Label the regions in the two-component phase diagram below:
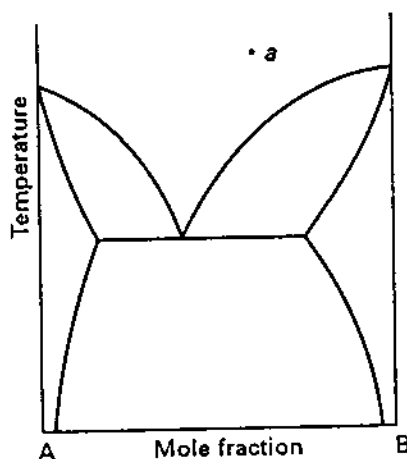
Explain, in as much detail as possible, what you would expect to observe as the system is allowed to cool from the point a. [9]

(c) The following expression was found empirically to describe the temperature dependence of the vapour pressure of a volatile solid over a limited range of temperatures:

$$\ln(p/\text{Torr}) = 16.255 - \frac{2511}{(T/\text{K})}$$

Suggest an interpretation of this empirical result, and interpret the numerical constants. [8]