HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY II

Thursday, 4th June 1998, 2.30 p.m. to 5.30 p.m.

Candidates should answer *five* questions

The marks in square brackets indicate the weight the examiners expect to assign to each part of the question.

Speed of light, c	=	2.998×10^8 m s^{-1}
Planck constant, h	=	6.626×10^{-34} J s
Boltzmann constant, k_B	=	1.381×10^{-23} J K^{-1}
Molar gas constant, R	=	8.314 J K^{-1} mol^{-1}
Avogadro number, N_A	=	6.022×10^{23}
1M	=	1 mol dm^{-3}
$p^{\ominus}$	=	1 bar $= 10^5$ Pa $\simeq$ 1 atm
$V_m^{\ominus}$	=	24.79 dm^3 mol^{-1} at 298 K
Elementary charge, e	=	1.602×10^{-19} C
Atomic mass unit, u	=	1.661×10^{-27} kg
Electron mass, m_e	=	9.109×10^{-31} kg

1. Define the quantities *enthalpy* (H) and *Gibbs Free Energy* (G) and explain why they are widely used in chemistry.

[20%]

Starting from the laws of thermodynamics, derive an expression, suitable for application to solid-liquid or solid-solid equilibrium, for the slope dp/dT of any line in a one-component phase diagram.

[20%]

A partial phase diagram for sulphur, not to scale, is given below. The triple point where rhombic sulphur, monoclinic sulphur and vapour are at equilibrium is at 5×10^{-7} bar and 368.4 K. At this point the densities of rhombic and monoclinic sulphur are 2070 kg m^{-3} and 1960 kg m^{-3} respectively, and the enthalpy change in the transition is 819 J mol^{-1}. Estimate the temperature of the triple point between rhombic, monoclinic and liquid sulphur, which occurs at 1288 bar pressure, using each of the following approximations:

(i) Assume that the entropy change and volume change in the transition from rhombic to monoclinic are constant.

(ii) Assume that the enthalpy change is constant, but the volume change varies with pressure according to the equation:

$$\Delta V = \Delta V_0 (1 - aP)$$

where P is the pressure in bar, $a = 1.55 \times 10^{-5}$ bar^{-1} and ΔV_0 is the volume change at the lower triple point.

Comment on the validity of the above approximation that the enthalpy change is constant and suggest how higher accuracy might be attained.

[60%]

[RAM S = 32·06]
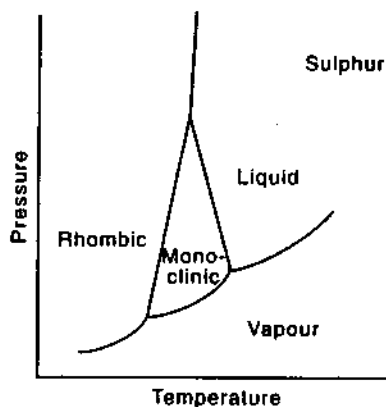
2. Define what is meant by a *molecular partition function* and discuss its use in chemistry.

[25%]

Show how the equilibrium constant for a simple isomerisation reaction can be related to the partition functions of the species involved.

[25%]

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Question continues

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For a more general reaction the expression for the equilibrium constant, K_c, is

$$K_c = \prod_j \left(\frac{q_j}{V}\right)^{\nu_j} e^{-\Delta E_0/RT}$$

where $\prod$ means the product of terms that follow, j is an index which runs over all reactants and products, ν_j is a stoichiometric factor and ΔE_0 is the difference in energy between the ground states of the products and reactants.

The energy required to ionise the rubidium atom is 403.4 kJ mol^{-1}. Calculate the equilibrium constant K_c for the ionisation and hence the fraction of atoms ionised in a flame at 2,000 K at an initial atom concentration of 6×10^{18} m^{-3}. The translational partition function for a 1-dimensional box of length l is $(2\pi mkT)^{\frac{1}{2}}l/h$. You may assume that the extent of ionisation is small. Explain any other assumptions you have made. [50%]

3. Theoretical expressions for the rate constant of a bimolecular elementary reaction step include the *Eyring* equation from transition state theory;

$$k_2 = \kappa \, \frac{k_B T}{h} \, K^{\ddagger}$$

and the collision theory result:

$$k_2 = P\sigma \left(\frac{8k_B T}{\pi\mu}\right)^{\frac{1}{2}} e^{-\frac{E_0}{k_B T}}$$

(a) Explain the significance of the terms P, κ, $K^{\ddagger}$, σ and μ in the above expressions. [20%]

(b) For what type of reaction are the predictions of the two theories identical, with P and κ equal to unity? Obtain the specific form of the Eyring equation, in terms of partition functions, for this type of reaction. [20%]

(c) Express the rate constant for the radical reaction

$$CH_3{}^{\bullet} + C_2H_6 \rightarrow CH_4 + C_2H_5{}^{\bullet}$$
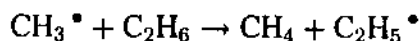
in terms of the molecular partition functions. Hence deduce how the pre-exponential factor for the radical reaction should depend on temperature. (You may assume that all vibrational partition functions are unity). [40%]

(d) When the experimental activation energy (50 kJ mol^{-1}) and the gas-kinetic collision cross-sections are used, a P factor of 0.01 is found necessary to reconcile the collision theory result with results for the radical reaction. Explain why this factor is signficantly less than one. [20%]

4. Answer **all** parts.

Explain how the Franck-Condon principle relates the vibrational structure of electronic and photoelectron spectra of molecules to geometry changes occurring in the transitions.   [30%]

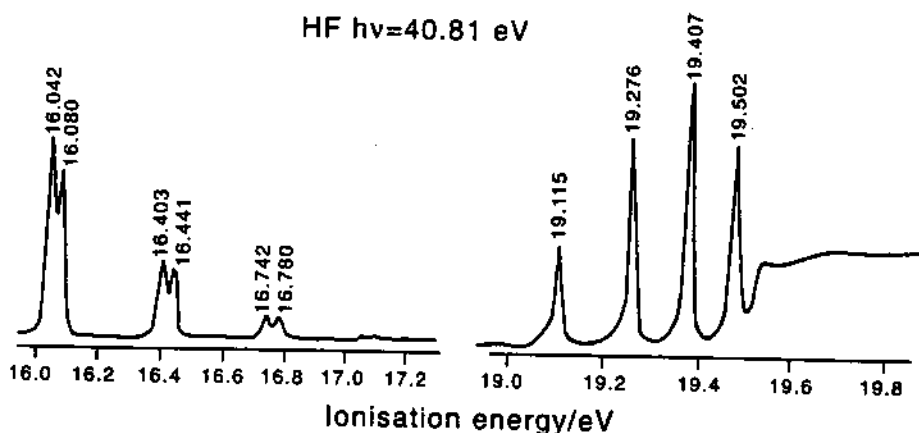The photoelectron spectrum of HF excited by 40.81 eV photons, shown below, consists of two band systems.

Sketch a molecular orbital diagram for HF. Identify the orbitals from which electrons are ejected and the states of HF^+ produced by ionisation.

Comment on the form of the lower ionisation energy band system. Determine the vibrational constants w_e and $w_e x_e$ for ions in this state.

Using the Birge-Sponer extrapolation or an equivalent method on the higher ionisation energy band system, estimate the dissociation energy of HF^+, which forms $H^+ + F$. Hence estimate the dissociation energy of neutral HF.   [50%]
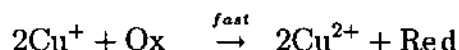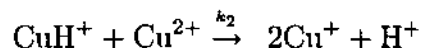
Comment on the appearance of the higher ionisation energy band system in the light of your results.   [20%]

[All energies may be given in eV. The ionisation energy of H is 13.606 eV and that of F is 17.43 eV. 1 eV = 8066 cm^{-1} = 96 kJ mol^{-1}]

HF hv=40.81 eV

16.042
16.080
16.403
16.441
16.742
16.780
19.115
19.276
19.407
19.502

16.0 16.2 16.4 16.6 16.8 17.0 17.2   19.0   19.2   19.4   19.6   19.8

Ionisation energy/eV

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5.   Explain, with examples, the meaning of the term *rate law* in chemical kinetics. Include in your answer an explanation of why the concept of overall order is not applicable to all, but only to some rate laws.   [20%]

Reductions by H_2 in aqueous solution can be catalysed by Cu^{2+} ions; the rates are independent of the concentration of the substrate being reduced. A mechanism proposed for these reactions is:

$$Cu^{2+} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuH^+ + H^+$$

$$CuH^+ + Cu^{2+} \overset{k_2}{\rightarrow} 2Cu^+ + H^+$$

$$2Cu^+ + Ox \overset{fast}{\rightarrow} 2Cu^{2+} + Red$$
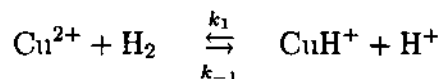
where Ox and Red represent oxidised and reduced forms of the substrate.

By treating CuH^+ as a reactive intermediate, show that the theoretical rate law for the consumption of H_2, is

$$rate = \frac{k_1 k_2 [Cu^{2+}]^2 [H_2]}{k_{-1}[H^+] + k_2[Cu^{2+}]} \quad .$$

Show that the rates given below for reaction at 100°C with a fixed Cu^{2+} concentration of 0.1 mol dm^{-3} are consistent with the mechanism, and determine the constant k_1 and the ratio k_{-1}/k_2. The Henry's law constant (solution concentration/gas pressure) for H_2 solution under the conditions of the experiment is 7.14 x 10^{-4} mol dm^{-3} bar^{-1}.   [80%]

$p(H_2)$/bar	5	10	20	20	20	20	20
$[H^+]$/mol dm^{-3}	0.01	0.01	0.01	0.1	0.2	0.4	0.5
Rate/mol dm^{-3} s^{-1}	3.5	7.0	14.0	11.48	9.57	7.18	6.38

6. What are the main assumptions and approximations in the Debye-Hückel treatment of ionic solutions? Over what typical range of concentrations is the Debye-Hückel limiting law,

$$\log_{10} \gamma^{\pm} = -A \mid z^{+}z^{-} \mid I^{\frac{1}{2}}$$

obeyed in aqueous solutions of electrolytes? [30%]

Using the Debye-Hückel limiting law, with $A = 0.509 \text{ kg}^{\frac{1}{2}}\text{mol}^{-\frac{1}{2}}$, estimate the mean activity coefficient in a 0.001 molal solution of HCl at 25°C.

Some potentials measured at 25°C are tabulated below for the cell

Ag | AgCl (s) | HCl(aq, 0.001 mol kg^{-1}) ‖ HCl(aq, m) | AgCl (s) | Ag

at different molalities m.

(a) Write down the cell "reaction" and the Nernst equation.

(b) Using the cell potentials and your estimate of $\gamma^{\pm}$ in the dilute solution, obtain the mean activity coefficients in each of the more concentrated solutions of HCl.

(c) Compare the results, either graphically or numerically, with the predictions of the Debye-Hückel limiting law. [70%]

Molality m /mol kg^{-1}	0.001	0.005	0.01	0.1	1.0
Cell potential /mV	0	-40.36	-57.50	-113.40	-173.00

$$[RT/F = 25.7 \text{ mV at } 298 \text{ K}]$$

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7. A molecular orbital ψ can be expressed as a linear combination of atomic orbitals

$$\psi = \sum_i c_i \, \phi_i.$$

Outline the procedure by which the best linear coefficients c_i and the orbital energy E can be determined. [20%]

The structure of the molecular ion H_3^+ in its ground electronic state is that of an equilateral triangle. By expressing the molecular orbitals as

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$$

where ϕ_1, ϕ_2 and ϕ_3 are 1s orbitals on each H atom, show that the orbital energies in this case are $E = \alpha - \beta, \alpha - \beta$ and $\alpha + 2\beta$ where α is $\int \phi_i^* H \phi_i \, d\tau$ and β is $\int \phi_i^* H \phi_j \, d\tau$, $i \neq j$. Determine the coefficients c_i for the lowest orbital. Overlap integrals between adjacent atoms can be neglected.

[Note that $(x^3 - 3xy^2 + 2y^3)$ factorizes as $(x - y)^2(x + 2y)$]

An alternative structure for H_3^+ is a linear, symmetric configuration. A similar calculation for this structure gives orbital energies of $\alpha + \sqrt{2}\beta$, α and $\alpha - \sqrt{2}\beta$. Show that this structure has a less stable ground state than the triangular form. [60%]

Assess critically the assumptions made in this level of treatment. [20%]

8. (a) Explain what is meant by *configurations, terms* and *levels* when applied to atoms. Determine the terms of atomic carbon which can be derived from its ground configuration. In addition, derive the terms which can be produced from promotion of one electron from a 2p orbital to a 3s orbital. [50%]

   (b) Illustrate diagrammatically the energy order of all the levels derived in (a), explaining any principles used or any assumptions made. State the selection rules and hence identify all allowed transitions between the levels derived from the two configurations. [20%]

   (c) One optical transition of carbon, at approximately 60,000 cm^{-1}, splits into three components in a magnetic field. From the splittings observed in a magnetic field, the Landé g-factors are determined to be 1.5 for each of the states involved. What are the possible assignments of the transitions?

   [The Landé g-value is given by $\{3J(J + 1) + S(S + 1) - L(L + 1)\}/2J(J + 1)$.] [30%]