

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY I

Friday, 6 June 1997, 9.30 a.m. to 12.30 p.m.

Candidates should answer *five* questions

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

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Speed of light, $c$	$= 2.998 \times 10^8 \text{ m s}^{-1}$
Planck's constant, $h$	$= 6.626 \times 10^{-34} \text{ J s}$
Boltzmann's constant, $k_B$	$= 1.381 \times 10^{-23} \text{ J K}^{-1}$
Molar gas constant, $R$	$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro's number, $N_A$	$= 6.022 \times 10^{23}$
1M	$= 1 \text{ mol dm}^{-3}$
$p^\ominus$	$= 1 \text{ bar} = 10^5 \text{ Pa} \approx 1 \text{ atm}$
Atomic mass unit, $u$	$= 1.661 \times 10^{-27} \text{ kg}$

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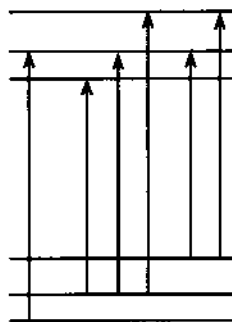
1. a) The lowest energy level of the silicon atom has the term symbol  $\underline{^3P_2}$ . Explain the meaning of this notation.

What is the degeneracy of this level? [4]

- b) Discuss the origins of the selection rule for change of the  $l$  quantum number for a radiative electronic transition of an atom. [5]

- c) The figure below illustrates the origin of the fine structure (due to spin orbit coupling) of a transition between two terms of the silicon atom, neither of which is the ground state. The upper and lower states arise from the configurations  $3s^23p\ nl$ , where  $n = 6$ , and  $3s^23p4p$  respectively, and the spin-orbit coupling constant has the same sign for each state. State the selection rules applying and hence deduce the term symbols and the  $J$  values of the levels for the upper and lower states. [5]

Note that *all* the allowed transitions are shown.



- d) Which of the possible electronic configurations for the upper state would be consistent with your assignment of the term symbols in c)? [2]

- e) The average energy of the upper state levels relative to the ground state is  $59333.4\text{ cm}^{-1}$  whereas that for the lower state is  $49092.4\text{ cm}^{-1}$ . The ionization energy is  $67543.0\text{ cm}^{-1}$ . Calculate the average quantum defects for the upper and lower levels, and comment on your answer in relation to the assignment of the upper state configuration. [4]

[Rydberg constant,  $\mathcal{R} = 109737\text{ cm}^{-1}$ ]

2. a) Simple LCAO molecular orbitals of the form

$$\Psi_{\text{M.O.}} = c_a\phi_a + c_b\phi_b$$

are often used to describe the electronic structure of a diatomic molecule AB. Outline the procedure, based on the variational theorem, by which the coefficients  $c_a$  and  $c_b$  are calculated. [5]

Describe and explain the variations in the relative magnitudes of  $c_a$ ,  $c_b$ , as the electronegativity of atom A increases relative to atom B. [3]

- b) The molar internal energy of formation of  $\text{BrCl}(\text{g})$  at 0 K from  $\text{Br}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  is  $-0.64 \text{ kJ mol}^{-1}$  and the bond dissociation energies of bromine and chlorine are  $239 \text{ kJ mol}^{-1}$  and  $190 \text{ kJ mol}^{-1}$  respectively. Electronic transitions from the ground vibrational and electronic state of  $\text{BrCl}$  to vibrational levels  $\nu'$  of an excited state, are observed at the following energies

state $\nu'$	3	4	5	6	7	8	9	10
energy ( $\text{cm}^{-1}$ )	17343	17533	17713	17881	18036	18180	18310	18428

- (i) Calculate the dissociation energy of  $\text{BrCl}$  in its electronic ground state. [2]

- (ii) Deduce the electronic states of the halogen atoms produced in the dissociation of  $\text{BrCl}$  from the observed excited electronic state. It is known that  $\text{BrCl}$  dissociates in its ground state to produce ground-state atoms and the ( $^2\text{P}_{1/2} \leftarrow ^2\text{P}_{3/2}$ ) excitation energies of  $\text{Cl}$  and  $\text{Br}$  are  $881 \text{ cm}^{-1}$  and  $3685 \text{ cm}^{-1}$ . [6]

$$[1 \text{ kJ mol}^{-1} = 83.594 \text{ cm}^{-1}]$$

- (iii) Explain why the molecular orbital approximation often provides a relatively poor description of diatomic molecules close to their dissociation limit. [4]

3. Answer both parts A and B.

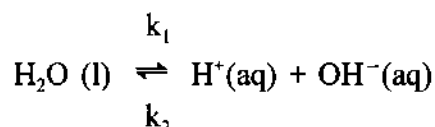
A. Explain both the following results, providing a quantitative analysis where appropriate and identifying any assumptions which you make in your analysis:-

(i) Irradiation of an equimolar, gaseous mixture of azomethane ( $\text{CH}_3\text{N}_2\text{CH}_3$ ) and azomethane- $\text{d}_6$ , with ultra-violet light produced  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{CD}_3$  and  $\text{C}_2\text{D}_6$  in the ratio 1:2:1. When a similar experiment was conducted in an inert liquid solvent,  $\text{CH}_3\text{CD}_3$  could no longer be detected among the reaction products. [5]

(ii) When azomethane only, was irradiated in an equimolar mixture of cyclo-hexane and cyclohexane- $\text{d}_6$ , at  $25^\circ\text{C}$ , both  $\text{CH}_4$  and  $\text{CH}_3\text{D}$  were detected among the reaction products, in the ratio  $\text{CH}_4 : \text{CH}_3\text{D} \approx 7:1$ . [5]

[Force constant of the C-H bond is ca.  $450 \text{ N m}^{-1}$ ]

B. When the equilibrium



was perturbed, by suddenly increasing the temperature of a sample of pure water from  $20^\circ\text{C}$  to  $25^\circ\text{C}$ , its conductivity relaxed exponentially, towards a new equilibrium value, with a relaxation time  $\tau = 3.7 \times 10^{-5} \text{ s}$ . If the concentration of  $\text{OH}^-$  at time  $t$  is given by  $[\text{OH}^-]_{\text{eq}} + x$ , where  $[\text{OH}^-]_{\text{eq}}$  is the equilibrium concentration at the new temperature,  $25^\circ\text{C}$ , show that for small values of  $x$

$$-\frac{dx}{dt} = \{k_2([\text{H}^+]_{\text{eq}} + [\text{OH}^-]_{\text{eq}}) + k_1\}x$$

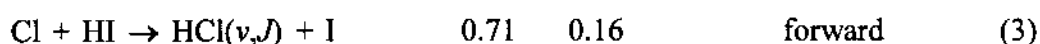
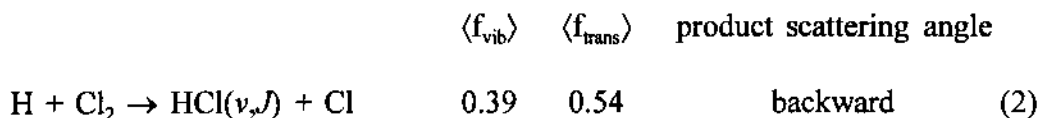
Hence estimate the magnitudes of the rate constants  $k_2$  and  $k_1$ . [10]

[At  $25^\circ\text{C}$ ,  $\text{pK}_w = 14.07$  ( $\text{H}_2\text{O}$ );  $[\text{H}_2\text{O}] = 55.5 \text{ mol dm}^{-3}$ ]

4. a) Briefly outline experimental strategies currently available for measuring the partitioning of energy between vibration, rotation and translation, in the products of an exothermic atom transfer reaction [5]



- b) How may the propensities for vibrational and translational energy disposal be influenced by the topography of the potential energy surface over which the reaction proceeds and by the masses of the atoms involved? Illustrate your answer by reference to the data, determined at 300 K, for the following reactions:- [8]



[ $\langle f_{\text{vib}} \rangle$  and  $\langle f_{\text{trans}} \rangle$  are the mean fractions of the total energy disposed into vibration and translation, respectively]

- c) Explain how the constraints imposed by the conservation of angular momentum influence the disposal of rotational energy in reaction (4) below



Reaction (4) has been studied under crossed beam conditions, at a mean reagent collision velocity,  $\langle v \rangle = 976 \text{ m s}^{-1}$ ; the rotational state distribution in the product, BaI was found to peak at the value  $\langle J \rangle = 420$ . Given the orbital angular momentum of the reagents in reaction (4) is  $L = \mu_{\text{Ba-HI}} \langle v \rangle b$ , estimate the mean impact parameter,  $b$ , and the reaction cross section. [7]

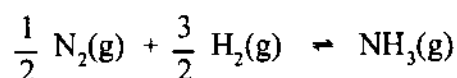
[The relative atomic masses of Ba = 137.3, H = 1.0, I = 126.9 ;  
 $h/2\pi = 1.055 \times 10^{-34} \text{ J s}$ ]

5. a) Starting from an expression which relates changes in the Gibbs Free Energy of a system to changes in temperature and pressure, derive an expression relating the molar Gibbs Free Energy of an ideal gas at pressure  $p$ , to that at the standard pressure  $p^\ominus$ , and hence show that

$$\Delta G^\ominus = -RT \ln K_p$$

for a chemical reaction involving ideal gases. [4]

- b) Assuming ideal gas behaviour, show, by deriving expressions for the partial pressures of the reacting species, that the equilibrium constant for the reaction



can be expressed in the form

$$K_p = \frac{x(\text{NH}_3)}{(1 - x(\text{NH}_3))^2} \frac{p^\ominus}{p} \frac{16}{3\sqrt{3}}$$

if the equilibrium mixture is produced by the dissociation of pure ammonia.  $x(\text{NH}_3)$  is the mole fraction of ammonia in the equilibrium mixture and  $p$  is the total pressure. [6]

- c) For such an equilibrium mixture,  $x(\text{NH}_3) = 0.25$  when  $p = 100$  bar and the temperature is 673 K.  $K_p$  is found to change by a factor of 0.24 when the temperature is raised from 623 K to 723 K.

Calculate  $\Delta G^\ominus$ ,  $\Delta H^\ominus$  and  $\Delta S^\ominus$  at 673 K, assuming  $\Delta H^\ominus$  does not vary with temperature. [5]

Is this likely to be a valid assumption? [2]

- d) Explain why the heterogeneously catalysed synthesis of ammonia from stoichiometric nitrogen and hydrogen mixtures is normally conducted at high pressures and moderately high temperatures. [3]

6. a) Give a qualitative description of the electrical double layer that exists on the surface of a colloidal particle in a lyophobic sol, such as AgI suspension in water. Sketch the electrostatic potential  $\phi$ , as a function of distance  $r$ , from the surface. [4]
- b) Sketch the potential energy curve representing the interaction of two AgI particles in aqueous solution in a stable colloidal dispersion, and discuss the physical factors underlying the shape of the potential energy diagram. [5]
- c) Explain why the addition of an inert electrolyte such as  $\text{KNO}_3$  to the AgI suspension could lead to coagulation. [3]
- d) Predict and explain the effect of (i) increasing temperature, and (ii) the addition of a soluble polymer such as polyethylene oxide, on the stability of the colloid. [5]
- e) The AgI particles have no surface charge when the  $p_{\text{Ag}} (\equiv -\log_{10}[\text{Ag}^+])$  is equal to 5.5. Discuss the effect on colloid stability of adding  $\text{AgNO}_3$  to a solution in which the  $p_{\text{Ag}}$  is initially 6.5 and decreases to 4.5. [3]

7. a) The hydroxyl radical, OH, is one of the key intermediates in the homogeneous gas phase chemistry of the troposphere. How is the formation of the free radical promoted by the introduction of urban atmospheric pollutants? [3]
- b) What factors control the daytime levels of ozone in urban atmospheres? [3]
- c) How do reactions of OH promote the oxidation of hydrocarbons present in urban atmospheres? [8]
- d) How may the nitrate radical,  $\text{NO}_3$ , be generated in urban atmospheres and how does it contribute (i) to the oxidation of hydrocarbons and (ii) to the production of acid rain? [6]



8. a) State the relationship between the translational energy of a particle inside a cubic container, the mass  $m$  of the particle, the dimension  $L$  of the container, and the associated quantum numbers. [2]

By using this relationship, show that the translational partition function  $q_{tr}$  is given by the expression

$$q_{tr} = \frac{V}{\Lambda^3} \quad \text{where} \quad \Lambda = \frac{h}{(2\pi mk_B T)^{1/2}}$$

and  $V = L^3$ . [3]

- b) Consider  $N$  identical non-interacting particles moving in a constant volume  $V$ . Starting from basic statistical mechanical relationships for the internal energy, Helmholtz free energy and entropy, show that the following relationships apply

i)  $U_T - U_0 = \frac{3}{2} Nk_B T$  ( $U_T$  is the internal energy at temperature  $T$ ) [3]

ii)  $pV = Nk_B T$  ( $p = - \left[ \frac{\partial A}{\partial V} \right]_T$  is the pressure) [3]

iii)  $S = Nk_B \ln \frac{e^{5/2} k_B T}{p \Lambda^3}$  ( $S$  is the entropy) [3]

iv)  $\mu_T = \mu_0 - RT \ln \frac{V}{\Lambda^3 N}$  ( $\mu_T$  is the chemical potential at temperature  $T$ ) [3]

- c) Explain why the expression for  $q_{tr}$  is invalid for small values of  $L$  and estimate the dimension where the invalidity will become significant for oxygen molecules at 298 K. [3]

$$\left[ \int_0^{\infty} \exp(-ax^2) dx = \frac{1}{2} \left[ \frac{\pi}{a} \right]^{1/2} ; \text{ relative atomic mass of oxygen} = 16.0 \right]$$

**End of paper**