

**HONOUR SCHOOL OF NATURAL SCIENCE**

**Final Examination**

**GENERAL PHYSICAL CHEMISTRY II**

**Friday, 1st June 2001, 2.30 p.m. – 5.30 p.m.**

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*Answer **FIVE** out of nine questions*

*The numbers in square brackets indicate the approximate weight given to each part of the question.*

Your attention is drawn to the table of constants provided on page 2 of this paper.

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**Do not open this paper until instructed to do so by an invigilator.**

## Fundamental constants

Speed of light	$c$	$2.997 \times 10^8 \text{ m s}^{-1}$
Planck constant	$h$	$6.626 \times 10^{-34} \text{ J s}$
	$\hbar = h/2\pi$	$1.054 \times 10^{-34} \text{ J s}$
Boltzmann constant	$k_{\text{B}}$	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	$R$	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F$	$9.649 \times 10^4 \text{ C mol}^{-1}$
Elementary charge	$e$	$1.602 \times 10^{-19} \text{ C}$
Electron mass	$m_{\text{e}}$	$9.109 \times 10^{-31} \text{ kg}$
Proton mass	$m_{\text{p}}$	$1.673 \times 10^{-27} \text{ kg}$
Vacuum permittivity	$\epsilon_0$	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Avogadro constant	$N_{\text{A}}$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	$u$	$1.661 \times 10^{-27} \text{ kg}$
Bohr magneton	$\mu_{\text{B}}$	$9.274 \times 10^{-24} \text{ J T}^{-1}$

## Other conventions

$$\begin{aligned} p^{\ominus} &= 1 \text{ bar} = 10^5 \text{ Pa} & 1 \text{ atm} &= 101.325 \text{ kPa} = 760 \text{ Torr} \\ 1 \text{ Da} &= 1 \text{ g mol}^{-1} & 1 \text{ L} &= 1 \text{ dm}^3 & 1 \text{ M} &= 1 \text{ mol L}^{-1} \end{aligned}$$

1. *Theories of Kinetics*

- (a) For the reaction between two atoms, A and B, show how transition state theory predicts that the pre-exponential factor of the rate constant is proportional to  $T^{1/2}$ .

How does this result compare with that derived from collision theory? [8]

- (b) Explain why the rates of radical-radical reactions in the gas phase at low pressure often display third-order kinetics.

Account for the observation that the rate constants for these reactions usually decrease with increasing temperature. [4]

- (c)  $I_2$  was flash photolysed in the presence of helium buffer gas and the molecule trimethylbenzene (M). The following data were recorded for the iodine atom concentration as a function of time at different concentrations of M at 300 K.

$$[M] = 1.0 \times 10^{17} \text{ molecules cm}^{-3}$$

$t/10^{-3} \text{ s}$	0	20	40	60
$[I]/10^{14} \text{ atom cm}^{-3}$	4.00	1.54	0.952	0.690

$$[M] = 2.0 \times 10^{17} \text{ molecules cm}^{-3}$$

$t/10^{-3} \text{ s}$	0	20	40	60
$[I]/10^{14} \text{ atom cm}^{-3}$	4.00	0.952	0.541	0.377

Show that the data are consistent with the following third order reaction

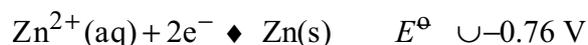


and determine the rate constant for this reaction.

Suggest a reason why trimethylbenzene is a more efficient participant in the above reaction than the helium buffer gas? [8]

## 2. *Electrochemical cells*

- (a) Explain the term *standard electrode potential* with reference to the following half cell reactions

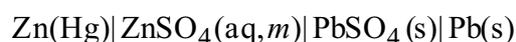


and



[4]

- (b) Explain why the *standard* emf of the cell



has a value close to +0.40 V at 298 K. The Zn(Hg) electrode is a saturated solution of Zn in Hg. Assume that ZnSO<sub>4</sub> is fully dissociated into Zn<sup>2+</sup>(aq) and SO<sub>4</sub><sup>2-</sup>(aq). [4]

- (c) Write down the Nernst equation for the cell given in part (b) when the molar concentration of zinc sulphate, assumed to be completely soluble in water, is *m*. [4]

- (d) Precise measurements at 298 K of the emf of the cell in part (b) gave a value of +0.4085 V for the *standard* emf, and a value of +0.6114 V when *m* = 0.0005 M.

Calculate the mean activity coefficient of zinc sulphate at 0.0005 M. [4]

[ $RT/F = 25.69 \text{ mV}$  at 298 K.]

- (e) Outline the factors responsible for differences between experimental values of the activity coefficients of ionic solutions and those predicted by the Debye-Hückel theory. [4]

### 3. *Atomic spectroscopy*

- (a) State the selection rules appropriate for the electronic spectra of alkali metal atoms. [3]
- (b) Explain why some transitions in the atomic spectra of alkali metal atoms are observed to be doublets and others triplets. [5]
- (c) The wavenumbers of the electronic energy levels of an alkali metal atom are given approximately by

$$\tilde{\nu}_{n,l} = -\frac{R}{(n-\delta_l)^2}$$

Explain the significance of  $n$  and  $\delta_l$ . [4]

- (d) The wavenumbers of some of the lines in the emission spectrum of caesium atoms are:

11,732	11,178	
7,357	6,803	
11,411	10,900	10,857
14,870	14,337	14,316

The lines at 11,178 and 11,732  $\text{cm}^{-1}$  are the strongest lines in the emission spectrum, and also appear strongly in absorption.

- (i) Construct an energy level diagram and assign quantum numbers to the states involved in these transitions. Only states with  $n = 6$  and 7 are involved. [The electronic configuration of Cs is {Xe}6s.] [6]
- (ii) Indicate, without calculation, how an estimate of the ionization energy of caesium could be obtained from these data. [2]

#### 4. *Electronic spectroscopy*

- (a) The vibrational energies (in  $\text{cm}^{-1}$ ) of a diatomic molecule are given approximately by

$$\varepsilon_v = T_e + (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2 \omega_e x_e$$

where  $T_e$  is the energy of the electronic state.

- (i) Explain the meaning of the symbols  $v$ ,  $\omega_e$  and  $\omega_e x_e$ . [3]
- (ii) An estimate of the number of vibrational energy levels associated with an electronic state of a diatomic molecule can be obtained using the condition  $d\varepsilon_v/dv = 0$ .

Explain why this should be so, and hence obtain the following approximate expressions for the maximum value of  $v$ , and the dissociation energy

$$v_{\max} + \frac{1}{2} = \frac{\omega_e}{2\omega_e x_e} \quad \text{and} \quad D_e = \frac{\omega_e^2}{4\omega_e x_e} \quad [5]$$

- (b) Three consecutive vibrational levels of the electronic ground state of  $\text{O}_2$  ( $T_e = 0$ ) have wavenumbers 12,563, 13,927 and 15,267  $\text{cm}^{-1}$ . The value of  $\omega_e$  for this state is 1,580  $\text{cm}^{-1}$ .

- (i) Determine  $\omega_e x_e$  and hence an estimate of  $D_e$ . [7]
- (ii) Comment on the discrepancy between this estimate and the true value, 42,050  $\text{cm}^{-1}$ . [2]

- (c) An excited electronic state of  $\text{O}_2$  with  $T_e = 33,590 \text{ cm}^{-1}$  has a dissociation energy  $D_e$  of 23,540  $\text{cm}^{-1}$ . This state dissociates into a ground state O atom ( $^3\text{P}$ ) and an excited state O atom ( $^1\text{D}$ ). The electronic ground state of  $\text{O}_2$  dissociates into two ground state atoms. Using the true value of  $D_e$  given in (b), determine the energy gap between  $\text{O}(^3\text{P})$  and  $\text{O}(^1\text{D})$ . [3]

## 5. Kinetics

- (a) The progress of a chemical reaction in the gas phase may be monitored by measuring the total pressure,  $p$ , as a function of time,  $t$ .

A reaction is found to obey the rate equation

$$\frac{dp}{dt} = -k[p - p(\infty)]$$

where  $p(\infty)$  is the final pressure, at  $t \rightarrow \infty$ .

Show that

$$p(t + T) - p(t) = [p(\infty) - p(0)][1 - \exp(-kT)]\exp(-kt)$$

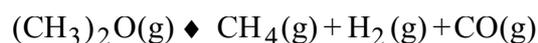
where  $T$  is a fixed time interval, and  $p(0)$  is the initial pressure. [8]

- (b) Using a value of  $T$  of 2,500 s, show that the following data for the decomposition of dimethylether at 777 K are consistent with the above rate equation, and determine a value for the rate constant  $k$ .

$t/s$	0	500	1000	2500	3000	3500
$p/\text{Torr}$	312	435	534	728	769	802

[8]

- (c) Determine the final pressure  $p(\infty)$  and discuss whether it is consistent with the following equation for the decomposition reaction



Only dimethylether is present at  $t = 0$ . [4]

## 6. Thermodynamics

- (a) Starting with the condition for equilibrium between two phases of a pure substance, show that the phase boundary is given by

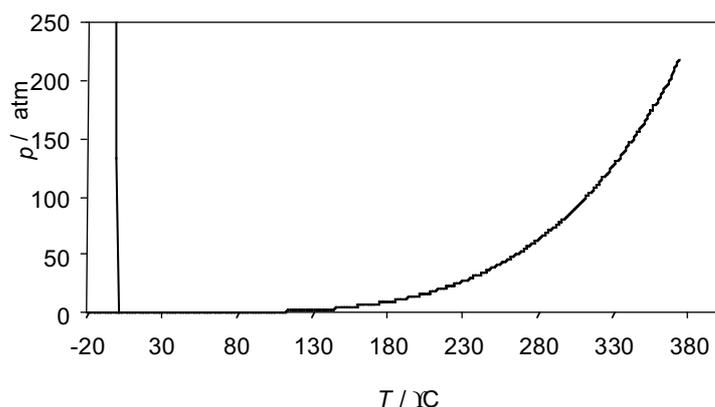
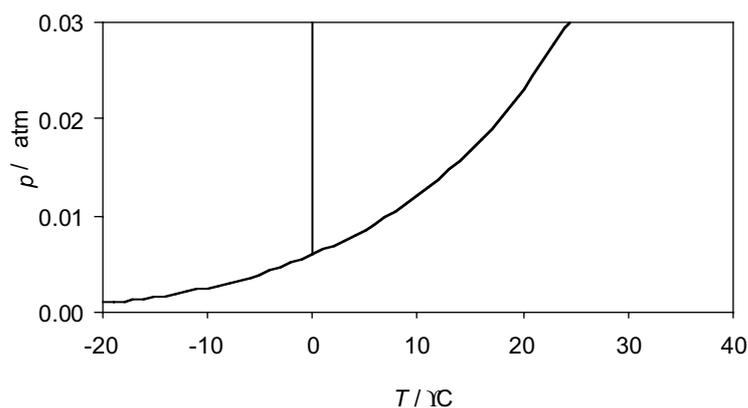
$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}}S}{\Delta_{\text{trs}}V}$$

You may use the formula  $dG = Vdp - SdT$  without proof. [3]

- (b) The phase diagram for water over two different temperature and pressure ranges is shown in the diagrams below.

Identify the main features.

Comment on the gradient of the line of equilibrium between ice and water and, using the phase boundary equation in part (a), show that ice decreases in volume when it melts. [5]



- (c) The form of ice stable at low pressure (ice I) has a residual entropy  $R\ln(3/2)$  resulting from disorder in the hydrogen bonds.

How can the presence of such a residual entropy be determined by experiment.

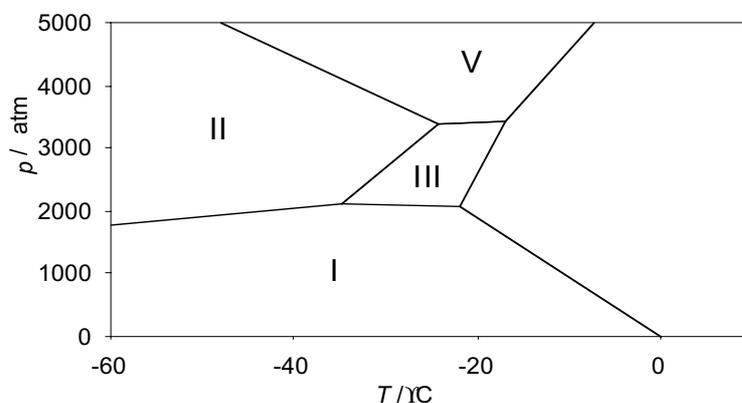
[4]

**Question continues**

(d) Part of a simplified version of the high pressure phase diagram of ice and water is shown below.

- (i) Describe what happens to ice at  $-15^{\circ}\text{C}$  as the pressure is increased from atmospheric up to 5,000 atm. [2]
- (ii) It can be shown by diffraction measurements that there is no disorder in the hydrogen bonds of ice II and hence that this form of ice has no residual entropy.

Use the equation for the phase boundary in part (a) to show that this observation is consistent with the phase boundaries between the various forms of ice in the high pressure phase diagram. Indicate the sign of the volume changes between ices I and II, and between II and V. [6]



## 7. *Molecular interactions*

- (a) Sketch a diagram of the typical behaviour of the surface tension of an aqueous solution of a surfactant over a concentration range from well below the critical micelle concentration to just above it. [5]
- (b) The adsorption of a non-ionic surface active agent at the air surface of an aqueous solution obeys the Gibbs equation

$$d\gamma = -\Gamma RTd\ln c .$$

The values of the surface tension of an aqueous solution of a soluble polymeric surfactant at concentrations just below its critical micelle concentration ( $10^{-3}$  M) at 300 K are given below

concentration/M	$5 \times 10^{-5}$	$1 \times 10^{-4}$	$5 \times 10^{-4}$	$1 \times 10^{-3}$
surface tension/ $10^{-3}$ N m <sup>-1</sup>	37.4	36.5	34.4	33.9

Use these data to calculate the surface excess of the surfactant and hence calculate the area per molecule at the air/water interface. [10]

- (c) The hydrophilic part of the polymeric surfactant in part (c) consists of a number of ethylene oxide (EO) segments. The area per molecule occupied by the small molecule surfactant  $C_{12}H_{25}(OC_2H_4)_6OH$  just below its critical micelle concentration is  $0.55 \times 10^{-18}$  m<sup>2</sup>.

Assuming that the area per EO segment is the same for the two surfactants in their saturated monolayers, estimate the number of EO groups in the polymeric surfactant.

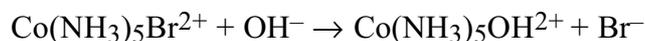
[5]

## 8. *Liquid phase kinetics*

- (a) Reactions in solution are sometimes described as *activation controlled*.

Explain what is meant by this term. [5]

- (b) Consider the following activation controlled reaction in aqueous solution:

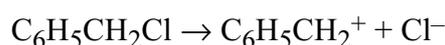


Predict the following using qualitative arguments.

- (i) The effect on the rate of changing the solvent composition in water/dioxan mixtures. [The relative permittivities of water and dioxan are 78.5 and 2.2 respectively.] [2]
- (ii) The effect on the rate of adding an inert electrolyte. [2]
- (iii) The signs of the entropy of activation and the volume of activation. [2]
- (iv) The effect on the rate of increasing the pressure. [2]
- (c) (i) Show that rate constant  $k$  of a reaction in solution depends on pressure,  $p$ , according to the expression

$$\frac{f \ln k}{f p} = - \frac{\Delta V^\ddagger}{RT}$$

- (ii) The rate constant  $k$  for the solvolysis of benzyl chloride,



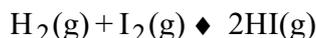
in an acetone-water mixture at 298 K depends on pressure as follows.

$p/\text{kbar}$	0.001	0.345	0.689	1.033
$k/10^{-6} \text{ s}^{-1}$	7.28	9.58	12.2	15.8

Calculate the volume of activation of the reaction and comment on its sign. [7]

## 9. *Statistical mechanics*

(a) For the reaction



statistical mechanics gives the following expression for the equilibrium constant

$$K_{\text{H}} = \frac{(q_{\text{HI}})^2}{q_{\text{H}_2}q_{\text{I}_2}} \exp \left[ -\frac{\Delta_{\text{r}}U_{0,\text{H}}}{RT} \right]$$

where  $q_{\text{X}}$  is the molecular partition function of species X, and  $\Delta_{\text{r}}U_{0,\text{H}}$  is the internal energy change of the reaction at 0 K. An analogous expression can be obtained for the equilibrium constant,  $K_{\text{D}}$ , of the reaction of  $\text{D}_2$  and  $\text{I}_2$ .

Show that the ratio of equilibrium constants is

$$\frac{K_{\text{H}}}{K_{\text{D}}} = \frac{(q_{\text{HI}})^2 q_{\text{D}_2}}{(q_{\text{DI}})^2 q_{\text{H}_2}} \exp \left[ \frac{-\Delta_{\text{r}}U_{0,\text{D}} - \Delta_{\text{r}}U_{0,\text{H}}}{RT} \right]$$

[3]

(b) The high temperature forms of the translational and rotational molecular partition functions for a diatomic molecule are given, respectively, by

$$q_{\text{trans}} = \frac{2\pi mkT}{h^2} V^{3/2} \quad \text{and} \quad q_{\text{rot}} = \frac{kT}{\sigma B}$$

where  $B = h^2/8\pi^2\mu r^2$ , and the other symbols have their usual meanings.

Stating any assumptions made, show that the ratio of the equilibrium constants can be simplified to

$$\frac{K_{\text{H}}}{K_{\text{D}}} = \frac{m_{\text{HI}}m_{\text{D}}^{1/2}}{m_{\text{DI}}m_{\text{H}}^{1/2}} \exp \left[ \frac{-\Delta_{\text{r}}U_{0,\text{D}} - \Delta_{\text{r}}U_{0,\text{H}}}{RT} \right]$$

where  $m_{\text{X}}$  is the mass of species X. [9]

(c) The vibrational wavenumbers of HI and  $\text{H}_2$  are 2,300 and 4,400  $\text{cm}^{-1}$  respectively.

Calculate the contribution of differences in zero point energies to  $\Delta_{\text{r}}U_{0,\text{H}} - \Delta_{\text{r}}U_{0,\text{D}}$ , and hence determine the value of the ratio  $K_{\text{H}}/K_{\text{D}}$  at 1000 K. [8]

[Use:  $m_{\text{H}} = 1.0 \text{ u}$ ,  $m_{\text{D}} = 2.0 \text{ u}$ ,  $m_{\text{I}} = 127.0 \text{ u}$ ]

**Last page**