

DCHA 2705

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY I

Thursday, 4th June 1998, 9.30 a.m. to 12.30 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, $c$	=	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck constant, $h$	=	$6.626 \times 10^{-34} \text{ J s}$
Boltzmann 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 number, $N_A$	=	$6.022 \times 10^{23}$
1M	=	$1 \text{ mol dm}^{-3}$
$p^\ominus$	=	$1 \text{ bar} = 10^5 \text{ Pa} \simeq 1 \text{ atm}$
$V_m^\ominus$	=	$24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K
Elementary charge, $e$	=	$1.602 \times 10^{-19} \text{ C}$
Atomic mass unit, $u$	=	$1.661 \times 10^{-27} \text{ kg}$

---

2705 DCHA

Turn over

1. Write notes on **four** of the following statements [25% each]:

- (a) The lines in the rotational spectrum of a diatomic molecule are nearly equally spaced by  $2B$ .
- (b) The force constants for bond stretching of HCl and DCl are essentially identical, even though the vibrational frequencies  $\omega_e$  are not.
- (c) The rotational constant  $B_e$  of HI is almost exactly twice that of DI.
- (d) The rotational constant of a diatomic molecule measured in different vibrational levels decreases steadily with increasing  $v$ .
- (e) The  $v = 2 \leftarrow 0$  vibration-rotation overtone band of a diatomic molecule is much weaker than the  $v = 1 \leftarrow 0$  fundamental band.
- (f) The vibrational Raman spectrum of  $F_2$  shows an intensity alternation in its rotational structure ( $^{19}F$  has a nuclear spin of  $\frac{1}{2}$ ).

2. Draw a schematic diagram to show the relative energies of the ground state and excited electronic states of a polyatomic molecule, and the possible radiative and non-radiative transitions between them. [20%]

For most molecules which fluoresce in liquid solution, the fluorescence quantum yield, emission spectrum and lifetime are independent of the absorbed wavelength. Explain why this is so. [20%]

Show that the quantum yield  $\Phi_F$ , the radiative lifetime  $\tau_F$  and the observed lifetime  $\tau$  in fluorescence are related by the equation  $\Phi_F = \tau/\tau_F$ . Here  $\tau = 1/(k_F + k_{NR})$ ,  $k_F$  is the radiative rate constant and  $k_{NR}$  is the sum of rate constants for non-radiative processes depopulating the excited state. Quenching may be assumed absent. [20%]

When the fullerene  $C_{70}$ , dissolved in a solid rare gas at 20 K, is exposed to ultraviolet light, two distinct emission bands are seen. One has its origin at  $15520 \text{ cm}^{-1}$  and is approximately ten times more intense than the second, whose origin is at  $12588 \text{ cm}^{-1}$ . The lifetime of the stronger emission is 600 ps, and its fluorescence quantum yield is  $10^{-4}$ . The lifetime of the weaker emission is 50 ms. Identify the types of states involved in the emission processes, and the transitions between them. Estimate the radiative lifetime for the stronger emission and comment on its value. [20%]

Indicate how values of the rate constants for other radiative and non-radiative processes in this system might be obtained. [20%]

2705 DCHA

3. Explain the assumptions of the Langmuir isotherm for adsorption of molecules on a surface. Derive an expression for the fractional coverage of the surface as a function of gas pressure. [30%]

Using a sample of 1g of charcoal, the following volumes of gaseous  $\text{CF}_2\text{ClCF}_2\text{Cl}$  (corrected to standard pressure) are absorbed by the sample at 298 K and at the given pressure:

$p/\text{mm of Hg}$	1.0	2.0	4.0	6.0	10.0	50.0
$V/\text{cm}^3$	17.1	26.0	35.1	39.8	44.6	52.1

Derive the limiting volume adsorbed at high pressure. Using this result and the fact that the density of  $\text{CF}_2\text{ClCF}_2\text{Cl}$  is  $1.44 \text{ g cm}^{-3}$ , estimate the surface area of the sample; you may treat the molecules as cubes. Comment on your result and the validity of the assumptions made. [70%]

[RAM C=12.0, F=19.0, Cl=35.5]

4. Relative molecular masses of polymers are much more commonly determined from osmotic pressure measurements than by, say, the freezing point depression method. Explain why this is so (a detailed discussion of the equations involved is not required). [20%]

The osmotic pressure of a polymer solution of mass concentration  $c$  and relative molecular mass  $M$  is given by

$$\Pi/c = RT \{1/M + B_2 c + \dots\}.$$

Discuss the physical basis for this equation and describe in particular the various effects which contribute to the coefficient  $B_2$ . [20%]

Measurement of the osmotic pressure  $\Pi$  of a polystyrene sample in mixtures of dichloroethane (A) and cyclohexane (B) at 285 K in the A:B concentration ratios indicated gave the following values of  $\Pi$  (in Pascals) as a function of concentration  $c$  of the polymer:

		$c/\text{g dm}^{-3}$			
		1	2	3	5
Ratio (A : B) {	(65:35)	2.52	6.92	13.20	31.40
	(6:94)	1.76	3.90	6.39	12.50

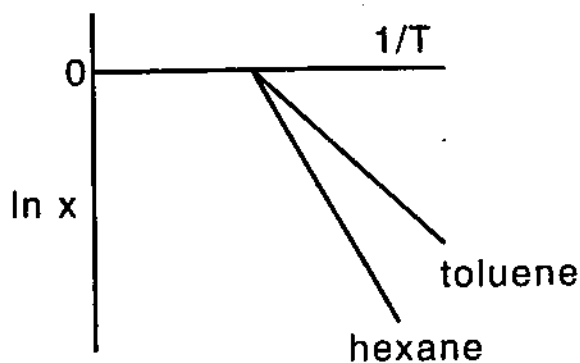
Determine the relative molecular mass of the polystyrene and the second virial coefficient in each mixed solvent. Confirm that cyclohexane is effectively a  $\theta$ -solvent ( $B_2 = 0$ ) and comment on the *quality* of dichloroethane as a solvent by comparison. You may assume that there is a linear relationship between the value of  $B_2$  and the composition of the solvent. [60%]

2705 DCHA

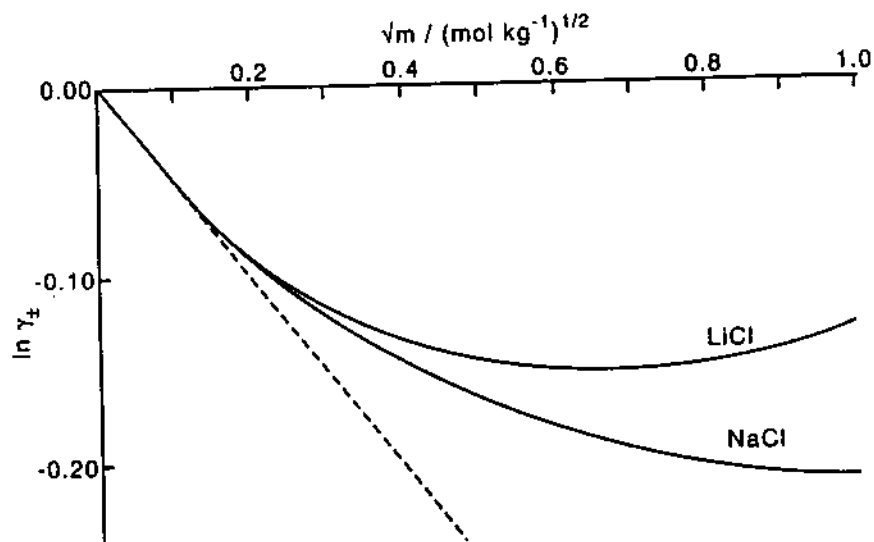
Turn over

5. Comment on the results in **three** of the following diagrams: [33% each]

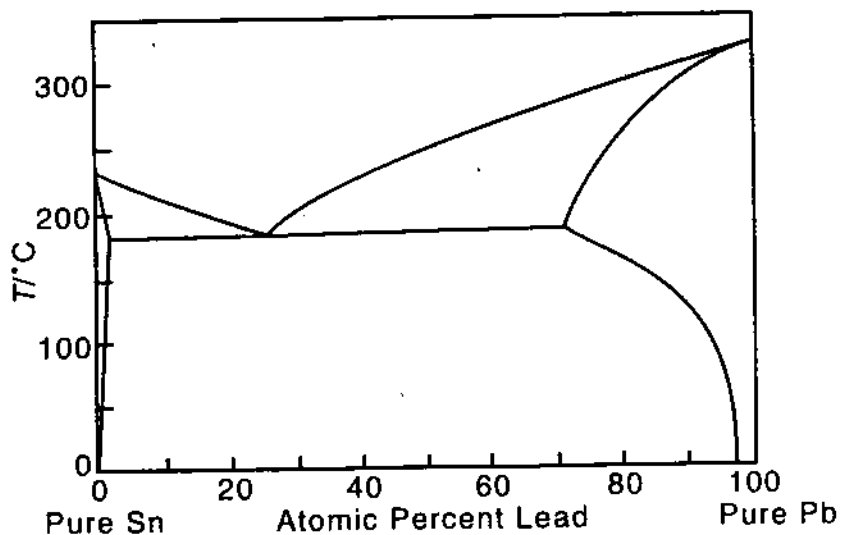
- (a) The solubility, expressed as a mole fraction  $x$ , of naphthalene in two solvents. Why are the lines linear, why do they have different slopes and why do they have the same intercept?



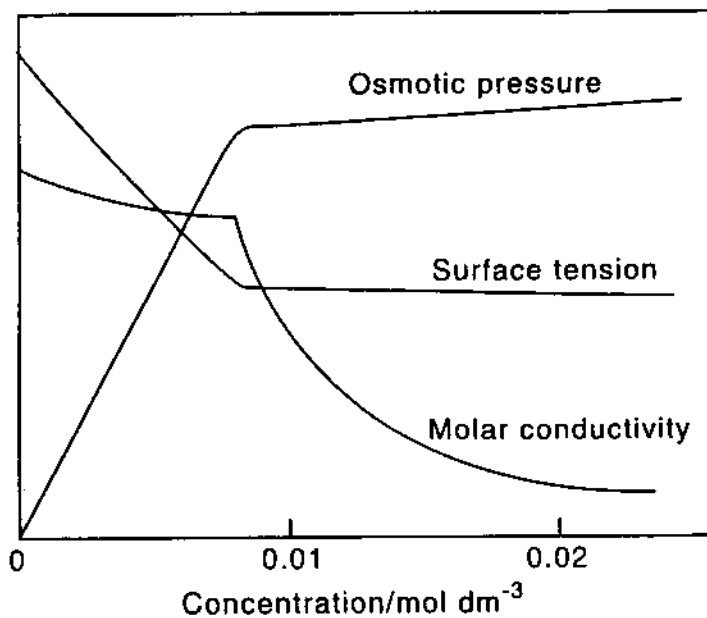
- (b) The mean activity coefficients of lithium chloride and sodium chloride as a function of molality. Why is  $\ln \gamma_{\pm}$  not a linear function of  $(\text{molality})^{1/2}$  and why do the two species differ?



- (c) The Pb-Sn phase diagram. Which are the two-phase regions? What happens when a liquid containing 80% lead and 20% tin is cooled slowly from 350°C to 100°C?



- (d) The variation of some physical properties with concentration of an aqueous solution of sodium dodecyl sulphate. Explain qualitatively the shapes of the curves and why is there an "elbow" in the properties at a concentration of approximately 0.008 mol dm<sup>-3</sup>.

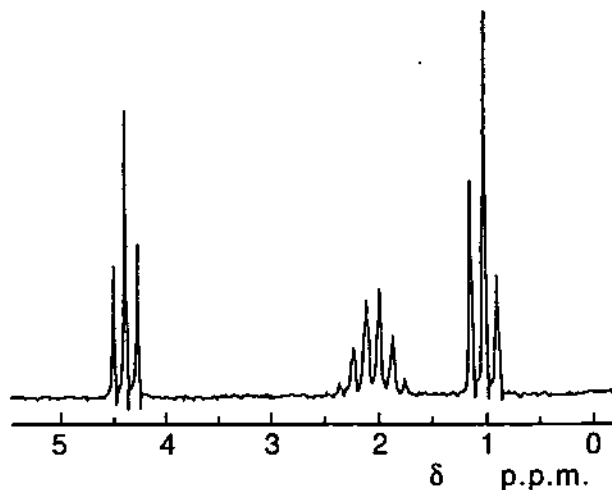


6. Answer **both** parts

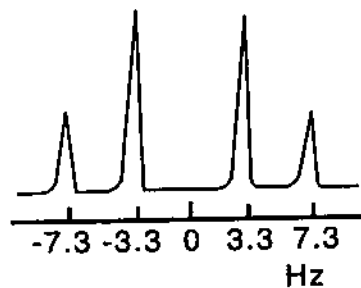
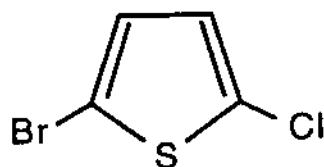
(a) Discuss *briefly* the physical origin of chemical shifts and spin-spin coupling in NMR spectroscopy. [30%]

(b) Explain the following observations in the proton NMR spectra: [70%]

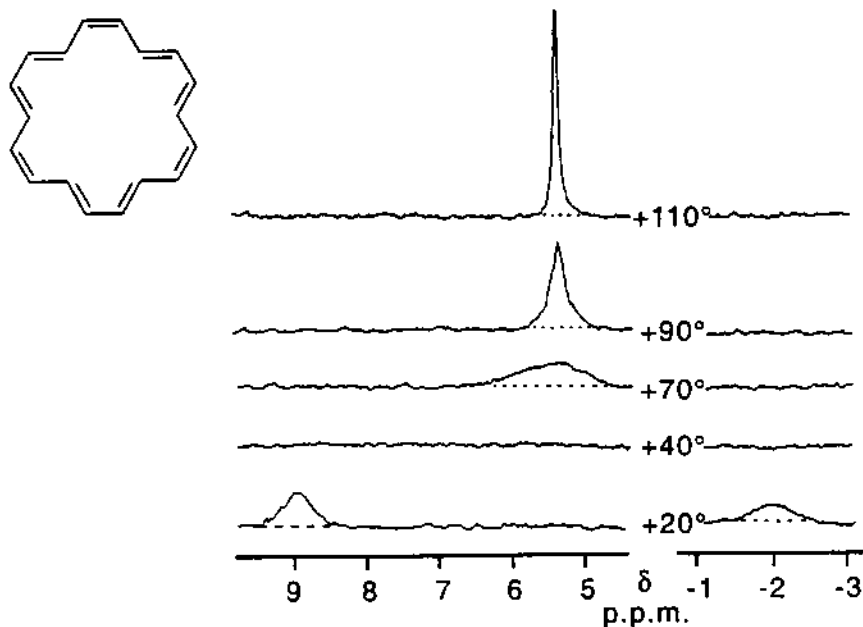
(i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$  in  $\text{CCl}_4$  at 60 MHz (relative to T.M.S.)



(ii) The spectrum of 2-chloro, 5-bromo-thiophene in  $\text{CCl}_4$  at 60 MHz relative to the centre of the spectrum. [Note that the only spin-spin coupling observed is that due to the protons].



- (iii) The temperature dependence (indicated as °C) of the NMR spectrum of [18]-annulene at 100 MHz. [Note that, at 40°C, the signal is still present but is too broad and weak to be observed above the noise].



7. Write notes on **four** of the following aspects of liquid phase reactions. [25% each]
- The activation energy of most radical recombination reactions in aqueous solution is about  $15 \text{ kJ mol}^{-1}$  but for other types of radical reaction, it can be much greater.
  - The measured rate constant for a neutral radical-radical reaction is about one quarter of the value predicted by the standard diffusion-controlled model.
  - The rate of slow reactions in solution can be measured by flow techniques; fast reactions are studied by flash photolysis methods.
  - Reactions between ions in solution sometimes show a positive entropy of activation; for neutral species, it is usually negative.
  - For some reactions in solution which involve the breaking of a C–H bond, the rate constant changes on deuteration; for others, it does not.

8. Give the definition of a Hermitian operator, in terms of an operator  $H$  and two wavefunctions  $\psi_i$  and  $\psi_j$ . Why are all operators of practical interest Hermitian? [20%]

The classical expression for the energy of a simple harmonic oscillator is

$$W = \frac{p_x^2}{2m} + \frac{1}{2} k x^2$$

where  $x$  is the displacement coordinate and  $p_x$  is the linear momentum of a particle of mass  $m$ , constrained by a force constant  $k$ . Explain the significance of the two terms and show how this expression can be transformed to the quantum mechanical operator

$$H_{sho} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} k x^2$$

Show that each term in this operator is Hermitian. [30%]

The first two eigenfunctions of  $H_{sho}$  are

$$\begin{aligned}\psi_0 &= A \exp\left(-\frac{1}{2} \alpha x^2\right) \\ \psi_1 &= B x \exp\left(-\frac{1}{2} \alpha x^2\right)\end{aligned}$$

where  $A$  and  $B$  are normalisation constants and  $\alpha$  is a constant dependent on  $k$  and  $m$ . Determine the normalisation constant  $A$  for  $\psi_0$  and show that  $\psi_0$  and  $\psi_1$  are orthogonal wavefunctions. [30%]

The classical turning points for the lowest quantum level are  $x = \pm\sqrt{(1/\alpha)}$ . Write down an expression for the probability that the quantum system lies *outside* these turning points and evaluate the probability. How would you expect the probability of lying outside the classical limits to change as  $\nu$  increases? [20%]

$$\int_{-\infty}^{\infty} e^{-\beta x^2} dx = (\pi/\beta)^{\frac{1}{2}} \qquad \int_{1/\sqrt{\beta}}^{\infty} e^{-\beta x^2} dx = 0.0786(\pi/\beta)^{\frac{1}{2}}$$

For two functions  $f(x)$  and  $g(x)$ , integration by parts states

$$\int_{-\infty}^{\infty} f^* \frac{dg}{dx} dx = \left[ f^* g \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \left( \frac{df^*}{dx} \right) g dx .$$