

DCHA 2705

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY I

Thursday, 3rd June 1999, 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.

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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, $k_B$	=	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant, $R$	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro constant, $N_A$	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
1 M	=	$1 \text{ mol dm}^{-3}$
$p^\ominus$	=	$1 \text{ bar} = 10^5 \text{ Pa}$
1 atm	=	$101.325 \text{ kPa} = 760 \text{ Torr}$
Elementary charge, $e$	=	$1.602 \times 10^{-19} \text{ C}$
Atomic mass unit, u	=	$1.661 \times 10^{-27} \text{ kg}$
Faraday constant, $F$	=	$9.6487 \times 10^4 \text{ C mol}^{-1}$
1 Da	=	$1 \text{ g mol}^{-1}$
Vacuum permittivity $\epsilon_0$	=	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Electron mass, $m_e$	=	$9.109 \times 10^{-31} \text{ kg}$
$V_m^\ominus$	=	$24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298 K

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Turn over

1. The rotational energy levels of a linear molecule in the lowest vibrational level are given by the formula:

$$F(J) = E(J)/hc = B_0J(J+1) - D_0J^2(J+1)^2 \quad \text{where } B_0 = h/8\pi^2cI$$

(a)

(i) Show that the wavenumbers of the transitions in the pure rotational spectrum are given by

$$\tilde{\nu}_J = 2B_0(J+1) - 4D_0(J+1)^3$$

where  $J$  is the quantum number of the lower state.

(ii) Describe the physical effect that gives rise to the second term involving the constant  $D_0$ . [8]

(b) The following transition wavenumbers are observed for the linear molecule OCS in the range 1.0 - 2.5  $\text{cm}^{-1}$  (note that there may be other rotational transitions outside this range).

$$1.217\,105\,4 \text{ cm}^{-1}, \quad 1.622\,800\,5 \text{ cm}^{-1}, \quad 2.028\,488\,3 \text{ cm}^{-1} \text{ and } 2.434\,170\,8 \text{ cm}^{-1}$$

Give an assignment of the upper and lower state rotational quantum numbers for each transition, and *using a graphical procedure*, deduce values for the two constants  $B_0$  and  $D_0$ .

Explain what additional data would be needed (if any) to determine the *equilibrium bond lengths* in this molecule. [12]

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2. Answer **all** parts

(A) Describe how and why the properties of fluorescence and phosphorescence differ.

Explain why there is often a mirror image relationship between the absorption and fluorescence spectra of a molecule in solution. Under what conditions would such symmetry *not* be expected?[8]

(B) Define what is meant by *quantum yield*.

A molecule is excited from its ground state to an excited singlet state in a flash photolysis experiment. Give expressions for the quantum yields of fluorescence  $\Phi_F$  and phosphorescence  $\Phi_P$  in terms of the rate constants for fluorescence  $k_F$ , phosphorescence  $k_P$ , and singlet  $\rightarrow$ triplet intersystem crossing  $k_{ISC}$ .

Hence show that the rate constant for the disappearance of the excited singlet state is equal to  $k_F/\Phi_F$ .

Assuming no chemical reactions take place, discuss the processes that could cause the sum of the two quantum yields  $\Phi_F + \Phi_P$  to be smaller than the result obtained above. [7]

(C) Continuous light ( $1.0 \times 10^{16}$  quanta  $s^{-1}$ ) falls on a cell of thickness 1.0 mm containing a solution of a fluorescent compound B. The total fluorescence was determined as a function of the concentration of B

[B]/mol dm <sup>-3</sup>	0.0030	0.030	0.300
Fluorescence/ $10^{15}$ quanta s <sup>-1</sup>	2.00	3.40	3.40

Determine the molar absorption (extinction) coefficient and the fluorescence quantum yield of B. [N.B. The fluorescence intensities at the two higher concentrations **are** identical.] [5]

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3. Answer **all** parts.

(A) Give a simple derivation of the Langmuir adsorption isotherm. Identify the assumptions made. [4]

(B) Show that the Langmuir isotherm is modified in the case where there is competitive adsorption with two species, A and B undergoing adsorption so that,

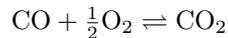
$$\theta_A = \frac{K_A[A]}{1 + K_A[A] + K_B[B]}$$

where  $\theta_A$  is the coverage of A.  $K_A$  and  $K_B$  are constants. Comment on the observation that the ethene-hydrogen reaction on a copper catalyst follows the rate law

$$rate = \frac{k[H_2][C_2H_4]}{(1 + K[C_2H_4])^2}$$

How does the rate change as the ethene pressure is increased? [6]

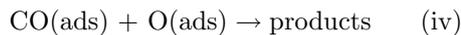
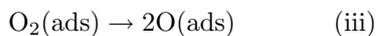
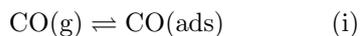
(C) The oxidation of carbon monoxide on the (111) face of a single crystal of palladium,



has been studied. Below 550 K the reaction follows the rate law

$$rate = k' \frac{[O_2]}{[CO]}$$

The following mechanism has been proposed.

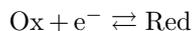


Show that the rate law is consistent with rate determining adsorption of  $O_2$  (step ii). Assume that the coverage of  $O(\text{ads})$  and  $O_2(\text{ads})$  is negligible compared to that of  $CO(\text{ads})$ . [7]

As the temperature is increased, the reaction rate passes through a maximum near 550 K; discuss qualitatively why this might occur noting that in the absence of oxygen,  $CO$  is reversibly adsorbed with an enthalpy of adsorption of  $-134.4 \text{ kJ mol}^{-1}$ . [3]

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4. For the reaction



at an electrode in an electrolytic cell, the net current flowing,  $i$ , can be shown to depend on the applied potential,  $E$ :

$$i \propto \left\{ -[\text{Ox}] \exp\left(-\frac{\alpha F}{RT}(E - E^\circ)\right) + [\text{Red}] \exp\left(\frac{\beta F}{RT}(E - E^\circ)\right) \right\}$$

where  $E^\circ$  is the standard potential of the redox couple,  $F$  is the Faraday constant and  $\alpha, \beta$  are transfer coefficients such that  $\alpha + \beta = 1$ . The first term in the equation relates to the reduction of Ox; the second term to the oxidation of Red.

(a) Show that if data can be recorded at sufficiently positive or negative values of  $E$  such that one or other of the terms in the equation can be neglected, then values of  $\alpha$  and  $\beta$  can be determined from plots of  $\ln(|i|)$  against  $E$ . [4]

(b) The following data were collected at a carbon electrode using a solution containing 0.10 M Ce(IV) and 0.010 M Ce(III).

$E/\text{mV}$	1576	1556	1536	1436	1416	1396	1376
$10^6 i/\text{A}$	+350	+230	+150	-225	-350	-475	-725

(i) Why does the current change sign as the applied potential decreases?[2]

(ii) By plotting  $\ln|i|$  against  $E$  on a single graph estimate values of  $\alpha$  and  $\beta$  for the Ce(IV)/ Ce(III) couple. [6]

[ $RT/F = 25.7$  mV at 298 K]

(iii) Use the equation above to find an expression for the potential at which no current flow occurs in terms of  $E^\circ$  and the concentrations [Ox] and [Red]. Comment on the result. [4]

(iv) Use the results of parts (ii) and (iii) to deduce a value for  $E^\circ$  for the Ce(IV)/Ce(III) couple. [4]

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5.

(a) Derive the Clapeyron equation for the temperature dependence of the pressure at which two phases are in equilibrium. You may use without proof the relationship  $dG = Vdp - SdT$  where the symbols have their usual meanings. [3]

(b) Develop the result in (a) for the case where one of the phases is gaseous to establish the Clausius-Clapeyron equation. Identify any assumptions you make. [3]

(c) Many of the higher mountains in the world have altitudes in excess of 25000 feet above sea level. At these altitudes the atmospheric pressure is around 250 Torr. Calculate the changes in (i) the freezing point and (ii) the boiling point of water at this pressure relative to normal conditions, given the following data: density of ice =  $0.92 \text{ g cm}^{-3}$ ; density of water =  $1.00 \text{ g cm}^{-3}$ ; enthalpy of fusion of ice =  $6.01 \text{ kJ mol}^{-1}$ ; enthalpy of vaporization of water at the normal boiling point =  $40.7 \text{ kJ mol}^{-1}$ ; normal freezing point of water =  $273.15 \text{ K}$ ;  $1 \text{ bar} = 760 \text{ Torr}$ ; relative atomic masses : O = 16; H = 1. [8]

(d) The single-component phase diagrams shown below relate to the following substances: water, carbon dioxide, and carbon. Identify which diagram relates to which substance and label all the phases shown. [6]

6. Answer **four** of the following parts, giving a full discussion of the *physical origins* of the interactions and effects concerned. [5 each]

(a) Comment on the diamagnetic contributions,  $\sigma_d$ , to the nuclear shielding constants for various atoms:

atom	H	D	Li	C
$\sigma_d/10^{-6}$	17.8	17.8	101.5	260.7

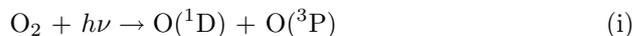
(b) Comment on the  $^1\text{H}$  chemical shifts of the compound:

(c) Comment on the observation that the  $^1\text{H}$  spin-lattice relaxation time of liquid water increases with increasing temperature.

(d) Comment on the dependence of the positions of lines in the 100 MHz  $^1\text{H}$  NMR spectrum of a mixture of water and ethanol on the concentration of hydrogen ions. (Only part of the spectrum is shown.)

(e) Comment on the pH dependence of the  $^{31}\text{P}$  chemical shift of phosphoric acid,  $\text{H}_3\text{PO}_4$ , in water.

7. In the atmosphere, molecular oxygen is photochemically decomposed as follows



The major loss processes for these atoms are



and



where M is N<sub>2</sub> or O<sub>2</sub>.

(a) By equating the rate of reaction (i) to  $I_{abs}$  and noting reaction (ii), write down a kinetic equation (net rate law) for  $\frac{d[\text{O}({}^1\text{D})]}{dt}$  [2]

(b) Using the result in (a) find an approximate expression for  $[\text{O}({}^1\text{D})]$  by applying the steady state hypothesis to the species O(<sup>1</sup>D). [2]

(c) By integration of the rate law in (a) show that

$$[\text{O}({}^1\text{D})] = (I_{abs}/k_q[\text{M}]) \{1 - \exp(-k_q[\text{M}]t)\}$$

assuming constant irradiation is applied after  $t = 0$  and that no O(<sup>1</sup>D) exists prior to this time. Under what conditions does this expression correspond to the approximate result derived in (b)? [6]

(d) In the atmosphere at an altitude of *ca* 80 km,  $[\text{M}] \simeq 3 \times 10^{14}$  molecules cm<sup>-3</sup> and the composite  $k_q$  for N<sub>2</sub> and O<sub>2</sub> is  $3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup>s<sup>-1</sup>. Estimate the minimum illumination time required for the non-steady state and steady-state concentrations to be identical to within 1%. Is the steady-state hypothesis a good approximation for the atmospheric behaviour of O(<sup>1</sup>D) where the solar intensity changes over periods of hours? [4]

(e) Neglecting reaction (ii) give steady state and non-steady state expressions for  $[\text{O}({}^3\text{P})]$  in terms of  $I_{abs}$ ,  $k_t$ ,  $[\text{M}]$  and  $[\text{O}_2]$  assuming the latter concentrations are in excess. [3]

(f) Under atmospheric conditions corresponding to part (d),  $k_t \sim 1.4 \times 10^{-33}$  cm<sup>6</sup> molecule<sup>-2</sup>s<sup>-1</sup>. Is the steady-state hypothesis a suitable approximation to apply to O(<sup>3</sup>P) in atmospheric modelling? [3]

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8.

(a) Show that the operators representing the position  $\hat{x} \equiv x$  and the momentum

$$\hat{p}_x \equiv -i\hbar \frac{d}{dx}$$

do not commute. What are the consequences of the non-commutation for the measurement of the corresponding observables?

Show that the functions

$$\psi_+ = e^{ipx/\hbar} \quad \text{and} \quad \psi_- = e^{-ipx/\hbar}$$

are eigenfunctions of the operator  $\hat{p}_x$  and comment on the implications of the commutation relationship referred to above. [8]

(b) The wavefunction for a particle moving in one dimension may be written in the general form

$$\psi = Ae^{ipx/\hbar} + Be^{-ipx/\hbar}$$

Determine the ratio of the coefficients A and B for a particle confined by a potential which is infinite for  $x \leq 0$  and zero for  $0 < x \leq \infty$ . (You do not need to normalise the wavefunction.)

Show that the wavefunction for the particle confined by the potential barrier is not an eigenfunction of the operator  $\hat{p}_x$ , but that it is an eigenfunction of the kinetic energy operator ( $\hat{p}_x^2/2m$ ).

What would be the outcome of a single measurement of the momentum of the confined particle?

Explain whether the energy for this confined particle is quantised. [7]

(c) Sketch the wavefunction for a particle moving in one dimension, if

(i) The particle is confined by the infinite potential barrier in (b).

(ii) The potential has a finite positive constant value  $V$  for  $x \leq 0$  and the value zero for  $x > 0$ . The particle has total energy  $E < V$ .

[5]

**9.**

(a) Write brief notes to explain the physical origin of the following types of intermolecular interaction:

- (i) Inductive
- (ii) Dispersive
- (iii) Repulsive.

[8]

(b) The Lennard-Jones potential for the interaction of two argon atoms may be written in the form

$$V(r) = 4\varepsilon \left[ \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right]$$

where  $r_0 = 342$  pm and  $\varepsilon = 1.712 \times 10^{-21}$  J.

(i) Sketch the form of this potential and state which of the types of force described above contribute to each term.

(ii) Derive an expression for the force between two argon atoms at an arbitrary distance  $r$ .

(iii) Calculate the radial position of the minimum in the potential and show that the well depth is equal to  $\varepsilon$ .

(iv) Assuming that in liquid argon the co-ordination number of each atom is 12, estimate the enthalpy of vaporization of liquid argon at 87 K. Describe any additional assumptions made in your calculation and compare your answer with the experimental value,  $\Delta_{\text{vap}}H = 6.28$  kJ mol<sup>-1</sup>.

[12]