

DCHA 2705

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY I

Monday, 12th June 2000, 9.30 a.m. - 12.30 p.m.

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.

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

1. *Equilibrium thermodynamics*

- (a) Define the quantity *chemical potential* as it applies to a pure substance. [2]
- (b) Derive the Clausius-Clapeyron equation for the vapour pressure of a pure substance as a function of temperature. Mention any approximations needed. You may use the following relationship without proof:

$$dG = Vdp - SdT .$$

[6]

- (c) At temperatures near 600 K, the vapour pressure p of Hg obeys the equation:

$$\ln p = -\frac{7073}{T} + 22.74$$

where p is in pascal and T in K.

Determine the vapour pressure of Hg at 600 K and calculate its enthalpy of vaporization at the same temperature. [4]

- (d) The approximation of a constant enthalpy of vaporization is not satisfactory over a wide temperature range.
- i. Use Kirchoff's law to show that to a better approximation, the enthalpy of vaporization can be expressed as:

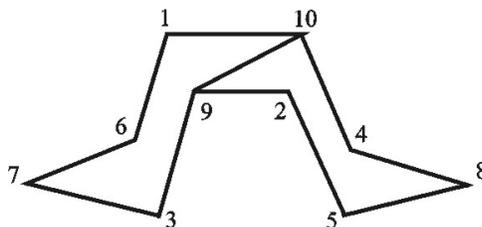
$$\Delta_{\text{vap}}H = A + BT$$

where A and B are constants. Calculate A, assuming $B = -3.9 \text{ J K}^{-1} \text{ mol}^{-1}$ at all temperatures for Hg. [4]

- ii. Using the expression for $\Delta_{\text{vap}}H$ in (d)i., obtain an improved equation for $\ln p$ as a function of temperature. Hence calculate the vapour pressure of Hg at 300 K. [4]

2. NMR

- (a)
- Summarize the factors which determine the magnitude of the *local* magnetic field experienced by a nucleus in a molecule in an applied magnetic field. [4]
 - Briefly describe two advantages of using a large applied magnetic field in NMR spectroscopy. [4]
 - Outline a mechanism by which nuclear spins can couple through bonds (as opposed to through space), for example between the protons in a CH₂ group. [3]
- (b) At elevated temperatures *cis*-decalin, C₁₀H₁₈, shown below, undergoes flips between two degenerate conformations by chair-to-chair inversions in both rings.



¹³C NMR spectra taken below 240 K consist of five lines of equal intensity. In spectra taken above 320 K only three lines appear. One of the lines is unaffected by temperature.

Note that the ¹³C NMR spectra were proton decoupled, with the result that line splittings due to couplings to the protons were not observed.

- Why are there only five lines in the NMR spectrum at low temperatures, and why does the NMR spectrum collapse to three lines at high temperatures? How might the line positions and linewidths observed in the NMR spectrum vary over the temperature range given? [5]
- If the spectrometer frequency were increased by a factor of ten, what would be the effect on the chemical shifts, transition frequencies, and the temperature dependence of the NMR spectrum? [4]

3. Kinetics

- (a) The flash photolysis (or pump-and-probe) technique is widely used in kinetic studies of reactions involving reactive intermediates. Outline the important features of this technique, including examples of methods used to follow the time-evolution of reactive intermediates. [4]
- (b) The rate of the elementary gas phase reaction



was determined using flash photolysis techniques under conditions where the molecular oxygen concentration was in large excess over that of the CH radical.

- i. Obtain an expression (in integrated form) for the time dependence of the CH radical concentration under these conditions. [4]
- ii. The CH radicals were monitored as a function of time using the technique of laser induced fluorescence. The relative fluorescence intensity, I , proportional to CH concentration, is given in the table below at different times, t .

$t/10^{-6} \text{ s}$	20	30	40	50	60	70
I	0.230	0.144	0.088	0.050	0.033	0.020

Verify that the kinetics are first-order, and determine the pseudo-first-order rate constant for the reaction. [6]

- iii. In the above experiments the molecular oxygen concentration was $8.8 \times 10^{14} \text{ molecules cm}^{-3}$. Calculate the bimolecular rate constant for the reaction. [2]
- iv. Derive an expression for the half-life of a bimolecular reaction when the two reactant concentrations are equal. What would be the half-life of the CH radicals if the O_2 and CH concentrations were initially *both* equal to $5.0 \times 10^{12} \text{ molecules cm}^{-3}$, but conditions were otherwise unchanged? [4]

4. Surfaces

- (a) Distinguish between *physisorption* and *chemisorption*. Describe the characteristic features of physisorbed and chemisorbed layers of gases on solid surfaces. [6]
- (b) The vapour pressure of N₂ in equilibrium with a layer of N₂ on rutile (TiO₂) at a constant coverage $\theta = 0.1$ varies with temperature according to

T/K	220	240	260	280	300
p/mbar	28	77	170	380	680

By plotting an appropriate graph, calculate the isosteric heat (enthalpy) of adsorption of N₂ on rutile at $\theta = 0.1$. [6]

- (c) The rate for desorption in a first-order process can frequently be fitted to an equation of the form

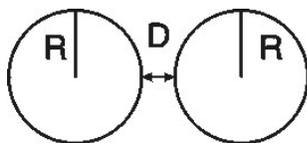
$$k = \nu e^{-E_a/k_B T}$$

where ν and E_a are constants.

- i. In a thermal desorption experiment, the rate of desorption of CO from Pd(111), at a coverage $\theta = 0.2$, was 20 times higher at 550 K than at 500 K. Estimate the enthalpy of adsorption of CO on Pd(111), noting any assumptions that you make. [4]
- ii. Estimate the average lifetimes (at the specified coverages) of nitrogen molecules on rutile and CO molecules on Pd(111) at 298 K. Comment on the lifetimes you obtain. [4]
- [Assume that the frequency factor $\nu = 10^{13} \text{ s}^{-1}$]

5. *Intermolecular forces*

- (a) Van der Waals attractions occur between molecules with and without permanent dipoles. Describe *qualitatively* the physical origins of the three principal types of attractive van der Waals interactions (i.e. those interactions whose energy varies with distance as r^{-6}). [6]
- (b) Attractive van der Waals interactions between individual molecules are usually weak ($\leq k_B T$ at room temperature) and short-range; interactions between colloidal particles are generally strong ($\gg k_B T$) and long-range. Comment on the consequences for the stability of colloids. [4]
- (c) Two polystyrene spheres with polarisability α per unit volume and radius R are separated by a distance D .



The attractive part of the pair potential for the two particles has the form

$$U = -\frac{AR}{12D} \quad \text{for } D \ll R$$

where the Hamaker constant $A = 1.0 \times 10^{-19}$ J for polystyrene spheres in a vacuum.

Estimate the interaction energy between two particles of radius $0.5 \mu\text{m}$ and separation $0.1 \mu\text{m}$. Compare the interaction energy to the thermal energy at 298 K.

[3]

Would the interaction between the two spheres be weaker or stronger in water than in a vacuum? [2]

- (d) The two spheres are placed in a uniform electric field of strength \mathcal{E} . Explain how this field gives rise to an additional interaction between the two spheres, which can be either positive or negative depending on the direction of the electric field.

Show that the repulsive interaction energy due to the field has a maximum value of

$$U = \frac{[\frac{4}{3}\pi R^3]^2 \alpha^2 \mathcal{E}^2}{4\pi\epsilon_0 (D + 2R)^3} .$$

[5]

[Note: the interaction energy between two parallel point dipoles separated by distance r in a vacuum is $U = \mu^2/(4\pi\epsilon_0 r^3)$.]

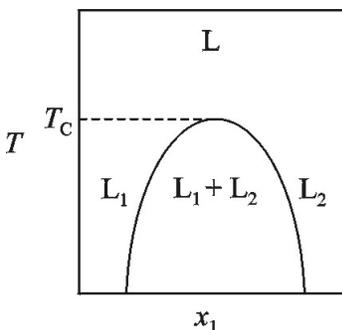
6. *Valence/Electronic and photoelectron spectroscopy*

- (a) Sketch the molecular orbital diagrams of the hydrogen and oxygen molecules, H_2 and O_2 . Give the term symbols of the ground states of each molecule, explaining the meaning of each label you use. [6]
- (b) O_2 possesses two low-lying excited electronic states, at 7900 cm^{-1} and 13200 cm^{-1} above the ground state. Give the term symbols for the two excited electronic states, and rationalize the energy ordering of the ground state and the two excited states. Why are the two low-lying excited electronic states of O_2 expected to have long radiative lifetimes? [7]
- (c) The highest electron kinetic energy features in the photoelectron spectra of H_2 and O_2 , associated with the transitions to the lowest electronic states of the ions, both display progressions of bands. For H_2 many bands are observed, and the lower bands in the progression are separated by 2300 cm^{-1} . For O_2 only a small number of bands are observed, and the bands are separated by 1900 cm^{-1} . At higher resolution each of the bands in O_2 is found to be doubled. The vibrational wavenumbers for H_2 and O_2 in their ground electronic states are 4400 cm^{-1} and 1600 cm^{-1} , respectively.

For each spectrum give the term symbol(s) for the state(s) of the ion involved. Rationalize the spectral features (both the number of bands and band separations) observed. [7]

7. Phase Diagrams

- (a) What is meant by an *ideal solution*? Write down an expression for the chemical potential in an ideal solution and hence for the molar Gibbs free energy of mixing, $\Delta_{\text{mix}}G$, in a two-component mixture. [5]
- (b) In the *regular solution* model of non-ideal mixtures, the molar entropy of mixing, $\Delta_{\text{mix}}S$, is assumed to be ideal and the molar enthalpy of mixing, $\Delta_{\text{mix}}H$, is given by $\beta x_1 x_2$, where x_1 and x_2 are the mole fractions of the two components and the constant β is independent of temperature.
- Describe a simple physical model for a non-ideal mixture that would behave as a regular solution. [3]
[A mathematical derivation is not required.]
 - The phase diagram for a mixture that behaves as a regular solution is shown below.



Sketch how $-T\Delta_{\text{mix}}S$, $\Delta_{\text{mix}}H$ and $\Delta_{\text{mix}}G$ vary with composition for mixtures at temperatures above and below the upper critical solution temperature, T_c . [6]

- Use your diagrams to explain why two liquids may only be partially miscible even though $\Delta_{\text{mix}}G < 0$ for all compositions. [3]
- Suggest reasons why real mixtures might deviate from the regular solution model. [3]

8. *Valence/Quantum mechanics*

- (a) The orbital motion of the j^{th} electron around the axis of a linear molecule can be described by the wavefunctions

$$\psi_m(j) = N e^{im\phi_j}$$

where ϕ_j is the azimuthal angle about the axis (ranging between 0 and 2π), and m is the quantum number for the orbital angular momentum along the axis.

Find the normalization constant, N , for this wavefunction, and show that the probability of locating the electron around the axis is independent of ϕ_j . [6]

- (b) Model spatial wavefunctions for two of the electronic states, A and B, arising from a π^2 electronic configuration in a linear molecule can be written

$$\Psi_A = \frac{1}{\sqrt{2}} [\psi_{+1}(1)\psi_{-1}(2) + \psi_{+1}(2)\psi_{-1}(1)]$$

$$\Psi_B = \frac{1}{\sqrt{2}} [\psi_{+1}(1)\psi_{-1}(2) - \psi_{+1}(2)\psi_{-1}(1)]$$

where the functions $\psi_m(j)$ are as defined in part (a).

- i. Explain which function, Ψ_A or Ψ_B , is associated with a singlet state, and which is associated with a triplet state. Write down the spin functions associated with each spatial wavefunction. [6]
- ii. Use the spatial functions Ψ_A and Ψ_B to show that, if electron 1 is located at $\phi_1 = 0$, the probabilities of finding electron 2 between the angles ϕ_2 and $\phi_2 + d\phi_2$ are

$$P_A(0, \phi_2)d\phi_2 = \frac{1}{2\pi^2} \cos^2 \phi_2 d\phi_2$$

$$P_B(0, \phi_2)d\phi_2 = \frac{1}{2\pi^2} \sin^2 \phi_2 d\phi_2$$

where $P_A(0, \phi_2) d\phi_2$ and $P_B(0, \phi_2) d\phi_2$ are the required probabilities for states A and B respectively. [5]

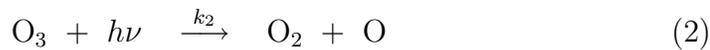
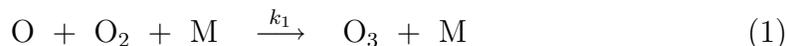
- iii. Sketch the probabilities given in part (b)ii, and hence explain why the triplet state is lower in energy than the singlet state. [3]

[Some of the following expressions may be helpful $e^{ix} + e^{-ix} = 2 \cos x$,
 $e^{ix} - e^{-ix} = 2i \sin x$, $2 \cos^2 x = 1 + \cos 2x$, and $2 \sin^2 x = 1 - \cos 2x$.]

9. *Atmospheric chemistry*

Ozone, O₃, is present in the Earth's atmosphere both at low altitudes (troposphere) and at high altitudes (stratosphere).

- (a) Explain why the presence of O₃ in the stratosphere is beneficial, whereas its presence in the troposphere is generally deleterious. [3]
- (b) Why is the majority of the O₃ found in a layer in the lower stratosphere rather than uniformly distributed at all altitudes? [3]
- (c) The two most important reactions for odd oxygen balance in the lower atmosphere are:



- i. Explain why a third body, M, is needed in (1). [2]
- ii. Obtain an expression for the steady state concentration ratio [O₃]/[O] on the basis of the two reactions. [2]
- iii. Calculate the ratio [O₃]/[O] for daytime conditions at 30 km altitude given the following:
- $k_1 = 2.0 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$;
- $[\text{O}_2] = 3.2 \times 10^{17} \text{ molecule cm}^{-3}$;
- $[\text{M}] = 1.6 \times 10^{18} \text{ molecule cm}^{-3}$;
- Rate of reaction (2) = $3.2 \times 10^{-4} \times [\text{O}_3] \text{ s}^{-1}$, where [O₃] is in molecule cm⁻³ [2]
- iv. Indicate qualitatively how the ratio [O₃]/[O] will change at night. [2]
- (d) According to a simple thermodynamic model, the temperature T of any planetary atmosphere should vary with altitude z according to

$$-\frac{dT}{dz} = \frac{g}{c_p}$$

where g is the acceleration of free fall and c_p is the constant pressure heat capacity per unit mass. (dT/dz from this equation is called the “dry adiabatic lapse rate”.)

Estimate c_p for the Earth's atmosphere below 80 km altitude, explaining the basis of your estimate and any necessary approximations. Hence calculate the dry adiabatic lapse rate using the equation given. [6]

[Take g to be 9.8 m s^{-2} .]