CPSS 4273

FIRST PUBLIC EXAMINATION

Long Vacation 2000

Preliminary Examination in Physical Sciences

SUBJECT 3: CHEMISTRY 3: PHYSICAL CHEMISTRY

also

Preliminary Examination in Molecular and Cellular Biochemistry

Monday, 18th September 2000, 2.30 p.m. to 5.00 p.m.

Time Allowed 2 ½ hours

*Candidates should answer **all** questions in Section A and any **two** questions in Section B.*

(The numbers in square brackets indicate the weight that the Examiners expect to assign to each part of the question)

Molar gas constant, R	$= 8.314\ J\ K^{-1}\ mol^{-1}$
Planck constant, h	$= 6.626 \times 10^{-34}\ J\ s$
Boltzmann constant, k_B	$= 1.381 \times 10^{-23}\ J\ K^{-1}$
Speed of light, c	$= 2.998 \times 10^{8}\ m\ s^{-1}$
Avogadro number, N_A	$= 6.022 \times 10^{23}\ mol^{-1}$
$p^{\ominus}$	$= 1\ bar = 1 \times 10^{5}\ Pa$
Electron mass, m_e	$= 9.110 \times 10^{-31}\ kg$
Elementary charge, e	$= 1.602 \times 10^{-19}\ C$
Faraday constant, F	$= 9.648 \times 10^{4}\ C\ mol^{-1}$
Atomic mass unit, m_u	$= 1.661 \times 10^{-27}\ kg$
Molar volume, V_m	$= 24.79\ dm^{3}\ mol^{-1}$ at 298K
1 electron volt	$= 1.6022 \times 10^{-19}\ J$

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

Section A

Answer **all six** questions in this section

1. The First Law of Thermodynamics can be expressed as:

$$đU = đq + đw.$$

(i) Explain what the symbols stand for. [2]

(ii) Explain what is meant by U being a state function. [3]

(iii) Show that for an isothermal reversible expansion of a perfect gas at constant pressure from a volume V_i to a volume V_f

$$w = -nRT\ln\frac{V_f}{V_i}.$$

Why is this not equal to the change in the internal energy of the system? [4]

2. Consider a chemical reaction in which a reactant is transformed into a product by heat.

(i) Draw and label an appropriate energy diagram for this process. [2]

(ii) How may the activation energy of the reaction be determined? [4]

(iii) If the reaction proceeds to equilibrium, what determines the position of equilibrium? Define any thermodynamic terms you introduce. [4]

3 The term symbols of the four lowest energy states of the hydrogen atom are $^2S_{1/2}$, $^2S_{1/2}$, $^2P_{1/2}$ and $^2P_{3/2}$. These result from the $1s^1$, $2s^1$ and $2p^1$ electron configurations.

(i) Explain the conventions for writing these term symbols. [2]

(ii) Why do two ^2P states result from a single electron configuration and why does the $^2P_{1/2}$ state have the lower energy? [3]

(iii) Can spectral transitions be observed from the lowest state to all the three other states? [2]

4. (i) What is a radial distribution function? Sketch those for the 1s and 2s orbitals of the hydrogen atom and comment on their differences. [3]

(ii) What is meant by penetration and shielding? [3]

(iii) What is the significance of the *l* and *m* quantum numbers obtained from the solution of the Schrödinger equation for the H atom? [3]

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5. The equipartition principle predicts that the heat capacity at constant volume of a monatomic gas is 3R/2, and of a diatomic gas 7R/2, both independent of temperature.

Why is this, and does experiment confirm these predictions? [7]

6. Comment on the following, explaining the terms used:

(i) Helium is almost an ideal gas at room temperature but ammonia is not. **[4]**

(ii) A solution of naphthalene in benzene is almost ideal but one in n-hexane is not. **[4]**

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Section B

Answer **two** questions from this section.

7. In an experiment a flash of light dissociates molecules dissolved in a solvent instantaneously into two identical free radicals:

$$\text{R-R} \rightarrow \text{R}^{\bullet} + \text{R}^{\bullet}.$$

The concentration of these radicals, which is very low, is then monitored as a function of time after the flash.

(i) Is it possible to predict what the order of the reaction with respect to disappearance of the radicals will be? **[2]**

(ii) Typical reactions of free radicals are for them to abstract an H-atom from the solvent (SH) or to recombine to form the starting material. Explain why, if the solvent is inert, the radical decay is observed to be second order whilst if it is reactive then first order behaviour is observed. [5]

(iii) In such an experiment the concentration (c) of free radicals was found to vary with time (t) after the flash as follows:

c/arbitrary unit	10.0	3.67	1.35	0.49	0.18
$t/10^{-6}$s	0	1	2	3	4

What is the order of the reaction and what is its rate constant? [8]

(iv). In a further series of experiments an inert substance is used to dilute SH which however remains in much greater concentration than the radicals.

Explain how this can be used to obtain the order of reaction with respect to S. [5]

With [SH] = 5 mol dm^{-3} the observed rate constant is 0.1×10^{6} s^{-1}; with [SH] = 2 mol dm^{-3} it is 0.04×10^{6} s^{-1}. What is the order of the reaction with respect to the solvent?

[5]

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8. The phase rule is summarised in the formula

$$P + F = C + 2$$

where C is the number of components, P is the number of phases present and F is the number of independent variables (e.g. temperature and pressure).

(i) Sketch the one component phase diagram for water over the pressure range where there is only one solid phase (normal ice). Label the phases clearly and mark in the normal freezing point, the normal boiling point, the triple point and the critical point.

[8]

(ii) Explain what the lines represent and why a triple point exists. [6]

(iii) What is the thermodynamic condition for equilibrium between two phases? Show from first principles how this leads to the Clapeyron equation for the slopes of the phase boundaries, explaining carefully what the symbols mean,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_m}{\Delta V_m}.$$

[8]

(iv) Why is the slope of the line separating the solid and liquid phases negative for water?

[3]

9. (i) What is meant by wave-particle duality and what is its significance within the atom?

[3]

(ii) Give one example of an electron exhibiting particle properties, and one exhibiting wave properties. [2]

(iii) What is a wave function, ψ? Does it have physical significance? [2]

(iv) What is the physical significance of $|\psi^2|\,\mathrm{d}\tau$, where $\mathrm{d}\tau$ is a small element of space in which the wave function is ψ? [3]

(v) What conditions ("boundary conditions") apply to restrict the solutions of the Schrödinger equation to ensure that they have physical significance? [5]

(vi) The wave functions and energies of an electron of mass m travelling in one dimension in free space may be written

$$\psi = A\sin kx + B\cos kx \text{ and } E = \frac{k^2\hbar^2}{2m}$$

where A, B and k are constants. *(continued on next page).*

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9(vi) *continued*

If the electron is now enclosed in a box of length L, such that the potential energy inside the box is zero but rises abruptly to infinity at $x = 0$ and $x = L$, show that the boundary conditions imply that the energy of the electron is quantised, and derive an expression for this energy. **[10]**

10. (i) What is meant by the standard electrode potential of a half cell and how is it measured ? [5]

(ii) A cell consists of the hydrogen electrode and a silver/silver chloride electrode dipping into a solution of hydrochloric acid:

$$Pt \mid H_2(g)\ (p = p^{\varnothing}) \mid HCl\ (aq., a) \mid AgCl \mid Ag$$

Write the cell reaction and the Nernst equation for the cell. [5]

How would the electromotive force (emf) change if (a) the pressure of hydrogen was increased and (b) sodium nitrate was added to the solution? [4]

(iii) Why does the emf of the cell change if the temperature is changed, and what can be deduced from this observation? [5]

(iv) To a reasonable approximation the variation of the standard emf of the cell measured in volts (V) with absolute temperature (T) is given by

$$E^{\varnothing}/V = 0.237 - 4.07\times 10^{-6}\ T/K$$

Calculate $\Delta G^{\varnothing}$, $\Delta H^{\varnothing}$ and $\Delta S^{\varnothing}$ for the cell reaction at 298K.

(1J =1CV)

[6]

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