Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SEMESTER II 2000

THIRD YEAR CHEMISTRY

Paper 4: Physical Chemistry (CH 313)

All questions carry equal marks.

(For a question with a choice between parts all parts of that question carry equal marks)

Answer *four* (4) questions.

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Professor R N Butler
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Time allowed : *Two* hours

Gas Constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$	Avogadro constant, $N_A = 6.022 \times 10^{23}\ mol^{-1}$
Planck's constant, $h = 6.626 \times 10^{-34}\ J\ s$	Velocity of light, $c = 2.998 \times 10^{8}\ m\ s^{-1}$
Electronic mass, $m_e = 9.109 \times 10^{-31}\ kg$	Boltzmann constant, $k = 1.381 \times 10^{-23}\ J\ K^{-1}$
Electronic charge, $e = 1.602 \times 10^{-19}\ C$	Bohr magneton, $\mu_B = 9.274 \times 10^{-24}\ J\ T^{-1}$
Faraday constant, $F = 96485\ C\ mol^{-1}$	Atmosphere $= 101325\ N\ m^{-2}$

1. The Clausius-Clapeyron equation for the vapour pressure of benzene is :

$$\ln(P_{liq} / Nm^{-2}) = -3876/T + 22.546$$

Calculate the enthalpy of vaporisation and the normal boiling point of benzene.

How could the equation be written in the form

$$\ln P_{liq} = -\left(\frac{\Delta H_{Vap}}{RT}\right) + \left(\frac{\Delta S_{Vap}}{R}\right)$$

where ΔH_{Vap} is the molar enthalpy of vaporisation and ΔS_{Vap} is the molar entropy of vaporisation?

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2. **Answer <u>EITHER</u> (a) OR (b).**

(a) Gaseous I_2 (maintained at a total pressure of 1 atm) is 1% dissociated into atoms at 873 K and is 25% dissociated at 1073 K. Calculate ΔH for the dissociation.

(b) **Answer <u>two</u> of the following:**

(i) Derive three of Maxwell's relations.

(ii) Derive the Clausius-Clapeyron equation.

(iii) Show how the Second Law of thermodynamics allows us to predict whether a reaction, which has not been carried out yet, is feasible or not.

(iv) It has been said that *Le Chatelier's Principle* is not original, but was deduced from the van't Hoff equation $\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$; show that this could be the case.

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3. **Answer (a) and (b).**

(a) What are the fundamental assumptions necessary in order to establish Boltzmann statistics?

(b) Calculate the molecular translational partition function, $\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$ for gaseous hydrogen at 1 atm and 298 K.

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4. The data in the table are for the adsorption of CO on 3.022g of charcoal at 273K. Confirm that they fit the Langmuir isotherm and find the volume adsorbed when a monolayer is formed.

P/mm Hg	100	200	300	400	500	600	700
V/cm^3 stp	10.2	18.6	25.5	31.4	36.9	41.6	46.1

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5. Answer (a) and (b).

(a) Discuss the importance of mass transport in electrode kinetics.

(b) Estimate the limiting current density at an electrode in which the concentration of Ag^+ ions is 2.5×10^{-3} mol dm^{-3} at 298K. The thickness of the Nernst diffusion layer is 0.40 mm. The molar conductance at infinite dilution of the Ag^+ ion is 6.19×10^{-3} Ω^{-1} m^2 mol^{-1} at 298K.

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6. The energy levels of an electron of mass, m_e, confined to a region along the x-axis of zero potential energy between $x = 0$ and $x = L$ are given by:

$$E_n = n^2h^2/8m_eL^2 \qquad n = 1,2,3\ldots$$

Draw a diagram, *to scale on graph paper*, showing the position of the three lowest energy levels.
How would you accommodate 4 electrons on these levels?

If $L = 695 \times 10^{-9}$ m, calculate the lowest energy transition possible.

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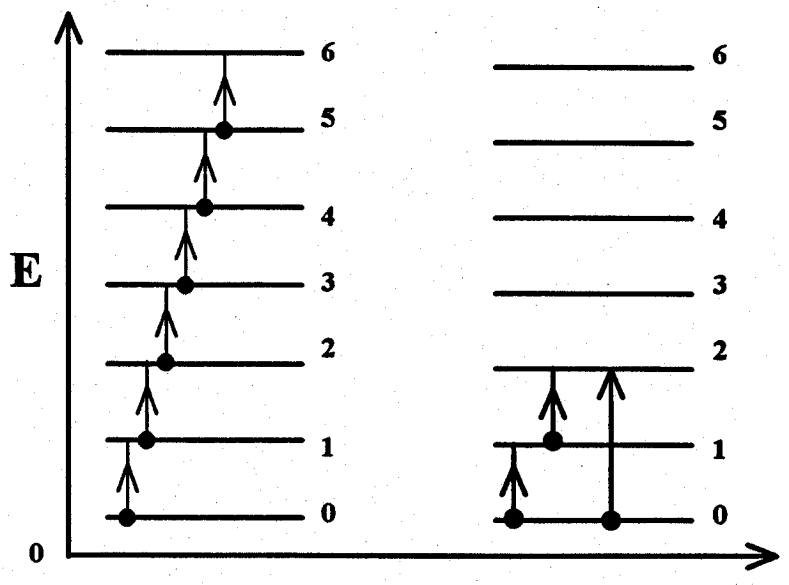
7. What do the two energy level diagrams shown in the Figure represent?

What names are usually given to the transitions shown in the right-most diagram?

Which of these transitions would normally be the most intense?

How would you increase the intensity of the 1→2 transition?



For hydrogen chloride, the observed 0→1 and 0→2 transitions occur at 2,885.9 and 5,668.1 cm^{-1} respectively. Calculate the anharmonicity term $\omega_e x_e$ given that:

$$\varepsilon_v = (v+1/2)\omega_e - (v+1/2)^2\omega_e x_e$$

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8. Write down the Arrhenius equation which shows the relationship between the rate constant, k, for a chemical reaction and the temperature, T.

The measured rate constant for the decomposition of ethyl chloride varies with temperature as:

k / s^{-1}	6.1×10^{-5}	30×10^{-5}	242×10^{-5}
T / K	700	727	765

Calculate the rate constant for this reaction at 800 K.