Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 1999

SECOND SCIENCE EXAMINATION

Chemistry: *First Paper*

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

Professor R J Donovan
Professor R N Butler
Professor B Ó Cochláin
Dr J. M. Simmie
Dr W M Carroll

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 standard enthalpy of formation of liquid water at 298.15 K is -285.8 kJ mol^{-1}. Given the following heat capacity data (J K^{-1} mol^{-1}) calculate the standard enthalpy of formation at 273.15 K.

$$C_p(H_2) = 27.3 + 3.26\times10^{-3}\,T$$
$$C_p(O_2) = 29.9 + 4.18\times10^{-3}\,T$$
$$C_p(H_2O, \text{liq}) = 75.5$$

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2. From the following heat capacity data (J K^{-1} mol^{-1}) calculate the entropy change when sulphur is heated from 300 to 410 K.

S_{rh} $\quad C_p = 15.0 + 26.2\times10^{-3}$ (298 to 368.6 K)
S_{mono} $C_p = 14.9 + 29.2\times10^{-3}$ (368.6 K to melting pt.)
S_{liq} $\quad C_p = 22.7 + 21.0\times10^{-3}$ (melting pt. to boiling pt.)
transition point (rhombic to monoclinic) = 368.6 K
melting point of monoclinic sulphur = 392 K
$\Delta H_{fusion} = 1.26$ kJ mol^{-1}
$\Delta H_{transition} = 0.361$ kJ mol^{-1}

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3. Derive an expression the mean free path of a molecule, λ and show how it depends on T. The cross sectional diameter, d of a molecule is 0.35 nm; calculate the ratio λ/d at 298 K and 1 atm pressure.

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4. Derive the barometric formula $p = p_o e^{-Mgh/RT}$ and then generalise it to obtain (i) the relationship between the vapour pressure of a liquid and temperature and (ii) the Maxwell-Boltzmann distribution of velocities of molecules in a gas.

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5. A conductivity cell has a resistance of 250 Ω when filled with 0.02M KCl at 298K and one of 10^5 Ω when filled with 6.0×10^{-3}M ammonium hydroxide solution. The conductivity of 0.02M KCl is 0.277 Ω^{-1} m^{-1} and the molar conductance at infinite dilution (Λ^0) for NH_4^+ and OH^- are 7.34×10^{-3} and 0.0198 Ω^{-1} m^2 mol^{-1} respectively. Calculate the cell constant and the degree of dissociation of the ammonium hydroxide in the 6.0×10^{-5} M solution. What would be the degree of dissociation for a 2.5×10^{-4}M solution?

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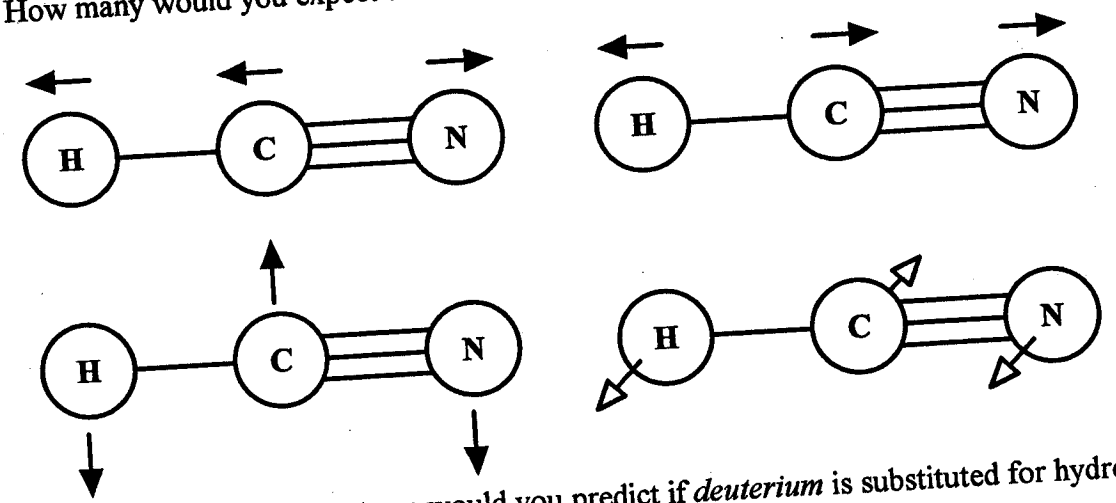
6. Answer (a) and (b).

(a) What are the significance of polarisation effects in electrochemical reactions?

(b) Write explanatory comments on the following observations. The decomposition potential ($E_{working}$) of dilute aqueous sulphuric acid is 1.8V when using platinum foil electrodes and 2.5V with a platinum foil anode and a lead foil cathode. The measurements were made at 298K at which the standard free energy of formation of water is –237.0 kJ mol^{-1}.

7. The four fundamental vibrations of the linear molecule HCN are shown below (*filled arrows represent motion in the plane of the paper, whereas unfilled arrows represent motion in and out of the plane*).

Explain why there are four vibrational modes.
How many of these vibrations are *different*?
How many would you expect to be *active in the infrared*?



What changes in the spectrum would you predict if *deuterium* is substituted for hydrogen in HCN?

8. For the reaction:

$$m\,A + n\,B = p\,X + q\,Y$$

define the *rate of reaction* in terms of a reactant, either A or B, and a product, X or Y.

What are the *units* associated with the rate of reaction?

In many cases, the rate of reaction depends upon reactant concentrations in a simple fashion. Write down this equation for the example above and state its name.

For the reaction:

$$CO + Cl_2 \rightarrow COCl_2$$

the rate law is:

$$rate = k\,[CO]\,[Cl_2]^{1/2}$$

What conclusion can you draw from this expression about the mechanism of the reaction?
What are the units associated with this k?