GX332

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SEMESTER 1 2001

SECOND YEAR CHEMISTRY

Physical Chemistry (CH 203)

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 K Waugh
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. Explain what is meant by a *state function*.

[5 marks]

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 of liquid water at 273.15 K.

$C_p(H_2) = 27.3 + 3.26 \times 10^{-3} T$

$C_p(O_2) = 29.9 + 4.18 \times 10^{-3} T$

$C_p(H_2) = 75.5$

[20 marks]

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2. Calculate the entropy change of the system and of the surroundings for the reversible isothermal expansion of 1 mole of and ideal gas from a pressure of 10 atm to 1 atm.

[13 marks]

If the above expansion had taken place into a vacuum, what would the corresponding entropy changes be

[6 marks]

and what important principle does your answer illustrate?

[6 marks]

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3. Derive the following expression for the mean free path.

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N}$$

[12 marks]

At what pressure does the mean free path of Ar at 25 °C become comparable with the diameter of the atoms themselves? The collision cross-section σ is 0.36 nm^2.

[13 marks]

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4. What is Raoult's Law?

[10 marks]

The vapour pressures of each component in a mixture of acetone, (A) and chloroform, (C) were measured at 35 °C with the following results:

x_C	0	0.20	0.40	0.70	0.80	0.97	1.00
P_C/mm Hg	0	35	82	165	219	284	293
P_A/ mm Hg	347	270	185	65	37	4.9	0

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component.

[15 marks]

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5. Conductivities are often measured by comparing the resistance of a cell filled with the sample to its resistance when filled with some standard solution, such as aqueous potassium chloride. The conductivity of water is $76 \times 10^{-3}\ \Omega^{-1}m^{-1}$ at 298K and the conductivity of 0.10 mol dm^{-3} KCl (aq) is $1.164\ \Omega^{-1}m^{-1}$. A cell had a resistance of 33.21Ω when filled with 0.10 mol dm^{-3} KCl (aq) and 300.0Ω when filled with 0.10 mol dm^{-3} CH_3COOH.
What is the molar conductance (Λ) of acetic acid at that concentration and temperature?
[9 marks]

(a) If the limiting molar conductance (Λ^0) for acetic acid is $39.05 \times 10^{-3}\ \Omega^{-1}\,m^2\,mol^{-1}$, estimate the pK_a for the acid. **[8 marks]**

Calculate the pH of 0.05 mol dm^{-3} acetic acid. **[8 marks]**

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6. Answer (a) and (b).

From thermodynamic calculations the applied potential required to begin the decomposition of water into hydrogen and oxygen is 1.23V. However under experimental conditions decomposition does not begin until the potential is at least 1.83V. Account for this extra voltage requirement. **[10 marks]**

A solution is 0.05M in BiO^+ and 0.04M in Co^{2+} and has a pH of 2.5.
What is the concentration of the more readily reduced cation at the onset of deposition of the less redoucable one? **[9 marks]**
What is the potential of the cathode when the concentration of the more easily reduced species is 1.0×10^{-6}M. **[6 marks]**

$BiO^+ + 2H^+ + 3e^- \rightarrow Bi + H_2O \quad E^0 = +0.32V$

$Co^{2+} + 2e^- \rightarrow Co \quad E^0 = -0.028V$

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7. The fundamental vibration wavenumber of gaseous nitric oxide, $^{14}N^{16}O$, is 1,904 cm^{-1}.

a) Calculate the force constant, *k*, for nitric oxide. **[20 marks]**

b) When complexed with hemoglobin A an absorption is observed at 1,615 cm^{-1}; why do you think this happens? **[5 marks]**

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8. The antibiotic penicillin loses activity on storage at 298 K; show that the data in the Table below are consistent with a first-order process with a rate law of:

$$-\frac{dA}{dt} = k\,A$$

You may assume that the activity, A, is directly related to the concentration of penicillin.

[20 marks]

Time (weeks)	*Activity*
0	10,100
1	8,180
2	6,900
3	5,380

After what length of time would the penicillin show one half of its initial acitivity?

[5 marks]