2006

Ollscoil na hÉireann, Gaillimh

National University of Ireland, Galway

Semester 1, Academic Year 2005–2006

Second Year Chemistry

Physical Chemistry (CH203)

All questions carry equal marks, distributed as shown

Answer *four* (4) questions

One (1) from each Section

Time allowed: *two* (2) hours

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Professor Richard N. Butler

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Gas constant, R = 8.3143 J K^{-1} mol^{-1}	Avogadro constant, N_A = 6.022 × 10^{23} mol^{-1}
Planck constant, h = 6.624 × 10^{-34} J s	Velocity of light, c = 2.998 × 10^{8} m s^{-1}
Electronic charge, e = 1.602 × 10^{-19} C	Boltzmann constant, k = 1.381 × 10^{-23} J K^{-1}
Electronic mass, m = 9.109 × 10^{-31} kg	Bohr magneton, μ_B = 9.274 × 10^{-24} J T^{-1}
Faraday constant, F = 96,485 C mol^{-1}	1 atmosphere = 101,325 N m^{-2}

Section B: Attempt *one* question from this Section

3.

Naphthalene, $C_{10}H_8$, melts at 80.2°C. If the vapour pressure of the liquid is 1.3 kPa at 85.5°C and 5.3 kPa at 119.3°C, use the Clausius-Clapeyron equation:

$$\ln p_1 = \ln p_2 + (\Delta_{\text{vap}} H / R)\left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

to calculate:

the enthalpy of vapourisation, $\Delta_{\text{vap}} H$ **[10 marks]**

the standard boiling point **[5 marks]**

and the entropy of vapourisation, $\Delta_{\text{vap}} S$, at the boiling point. **[5 marks]**

Comment on the approximations that allow transformation of the more exact Clapeyron equation:

$$\Delta p = \frac{\Delta_{\text{vap}} H}{T\,\Delta_{\text{vap}} V} \Delta T$$

into the Clausius-Clapeyron equation.

[5 marks]

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4. Answer (a), (b) and (c).

(a) When 1.158 moles of water are mixed with 0.842 moles of ethanol the volume of the solution is 68.16 cm^3 at 25°C. If $\overline{V}_{H_2O} = 16.98$ cm^3 mol^{-1} in this solution, find $\overline{V}_{C_2H_5OH}$.

[10 marks]

(b) The standard Gibbs energy of formation of $NH_3(g)$ is –16.5 kJ mol^{-1} at 298 K.
What is the reaction Gibbs energy when the partial pressures of N_2, H_2, and NH_3, treated as perfect gases, are 3 bar, 1 bar and 4 bar, respectively?

[10 marks]

(c) What is the spontaneous direction of the reaction in (b)?

[5 marks]

Section C: Attempt *one* question from this Section

5. Answer (i), (ii) and (iii).

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 33.21 Ω when filled with 0.10 mol dm^{-3} KCl (aq) and 300.0 Ω when filled with 0.10 mol dm^{-3} ethanoic (acetic) acid.

(i) What is the molar conductance (Λ) of acetic acid at that concentration and temperature?

[9 marks]

(ii) 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]

(iii) Calculate the pH of 0.05 mol dm^{-3} acetic acid.

[8 marks]

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6. Answer (a) and (b).

(a) 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]**

(b) A solution is 0.05 M in BiO^+ and 0.04 M in Co^{2+} and has a pH of 2.5.

(i) What is the concentration of the more readily reduced cation at the onset of deposition of the less reducible one?

[9 marks]

(ii) What is the potential of the cathode when the concentration of the more easily reduced species is 1.0×10^{-6} M.

[6 marks]

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

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

Section D: Attempt *one* question from this Section

7.

The Beer–Lambert law may be written as:

$$I_T = I_0\,10^{-\varepsilon \ell C}$$

By means of a diagram, or otherwise, show that you understand what each term in the above equation represents? **[10 marks]**

What effect does increasing the:

concentration of an absorbing species **[5 marks]**

pathlength of the light **[5 marks]**

wavelength of the light used **[5 marks]**

have on the transmitted intensity, for a particular experimental setup?

8.

The oxidation of nitrogen oxide: $2\,NO + O_2 \rightarrow 2\,NO_2$

is a very important reaction in the polluted atmospheres of cities because NO is emitted by vehicle exhausts and NO_2 goes on to form acid rain.

The experimental rate law for the oxidation reaction is:

$$\text{Rate,}\quad \frac{1}{2}\frac{d[NO_2]}{dt} = k\,[NO]^2\,[O_2]$$

The rate of reaction has been defined in terms of changes in the concentration of the product; write down another possible definition for the rate of this reaction.

[4 marks]

What are the units for the rate of reaction?

[4 marks]

What is the *overall order* of the oxidation reaction?

[4 marks]

If this reaction took place at the molecular level as written, what would you expect the rate law to look like for the elementary reaction?

[9 marks]

What conclusion can you draw from the fact that an experimental rate law and a theoretical rate law agree with each other?

[4 marks]
