IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2010, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

PHYSICAL CHEMISTRY IIB

Monday 14th June 2010, 14:00-16:30

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

2.P2 – Electrochemistry and Electrochemical Kinetics

Answer any **TWO** of the three parts a), b) and c)

a) Answer **ALL** parts of this question.

i) State the Debye-Hückel Limiting Law. Explain all terms.

(3.5 marks)

ii) The table below shows the value of the difference between experimentally measured activity coefficients ($\gamma_{\pm}$(expt.)) and those calculated from the Debye-Hückel Limiting Law ($\gamma_{\pm}$ (calc)) for three electrolyte solutions, labelled A, B and C. Each electrolyte has a concentration of 0.05 mol kg^{-1} and their general formulae are MX, MX_2 and MX_3. Which general formula corresponds to A, which to B and which to C? Explain the reasoning behind your answer.

Electrolyte	($\gamma_{\pm}$(expt.) - $\gamma_{\pm}$ (calc))
A	0.0600
B	0.218
C	0.0537

(3 marks)

iii) Two electrolyte solutions, LiOH and LiF, have the same concentration. In which electrolyte would you expect the transport number for Li^+ to be largest? Explain the reasoning behind your answer.

(3 marks)

iv) When it spins at 50Hz, a rotating disc electrode has a diffusion layer thickness, δ, of 7.50×10^{-6} m. At a given potential the bulk concentration of the reactant is 0.25 mmol dm^{-3}, the diffusion coefficient of the reactant is 5.6×10^{-10} m^2s^{-1} and the flux of reactant towards the surface of the electrode is 1.12×10^{-5} mol m^{-2} s^{-1}. What is the surface concentration of the reactant? You may assume that the concentration gradient is linear.

(3 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts of this question.

i) In many electrochemical textbooks, cell potentials are calculated using concentrations rather than activities (i.e. non-ideal effects are ignored). For the half-cell listed below, what is the value of the difference between the equilibrium potential calculated using activity and that calculated using concentration. Assume that the temperature is 25°C.

Ag| $AgNO_3$ (0.01M)
$\gamma_{\pm}$ (Ag^+) = 0.892
E° = 0.7996V

(3.5 marks)

ii) Tollen's reagent is ammoniacal silver nitrate and is used as a test for the identification of aldehydes. The presence of an aldehyde leads to the production of a "silver mirror" when the reagent is added to a solution of the aldehyde in a test tube. The underlying chemistry of the process is an oxidation/ reduction reaction. Taking the example of glucose as the aldehyde, the relevant half cell reactions are as shown below (note that the addition of ammonia to silver nitrate converts the silver ion to the diammine silver (I) complex).

$$C_6H_{12}O_7 + 2H^+ + 2e^- \rightarrow C_6H_{12}O_6 + H_2O \quad - E^\circ = 0.050V$$

$$Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3 \quad - E^\circ = 0.373V$$

Calculate the difference between the two half cell potentials if the pH is 11 and the concentration of $Ag(NH_3)_2^+$ is 0.3moldm^{-3} (assume that all other concentrations are at their standard values and that the temperature is 25°C). You may neglect any non-idealities.

(7 marks)

iii) Suppose that you wished to try to <u>measure</u> the potential of the system shown in part ii). Write down (in the conventional notation i.e. as shown in part i)) an electrochemical cell which would allow you to do this. Briefly explain your answer.

(2 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of this question.

i) The oxidation of methanol is a reaction of great interest in the development of fuel cells.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

Comment on the likely size of overpotential (you may wish to refer to other electrode reactions for relative comparison) needed to obtain a significant current for this reaction and briefly explain your answer.

(2 marks)

ii) An electrode process is found to have a symmetry factor that is 0.7. What are the relative sizes of the oxidation and reduction component currents for this process at an electrode potential of 0.75V if the equilibrium potential is 0.66V and the temperature is 25^0C.

(7.5 marks)

iii) At a rotating disc electrode rotating at constant speed, an oxidation process is taking place and the potential is in a region where further increases in potential no longer have any effect on the current, which remains constant. What would you expect to happen to the current passed if the speed of rotation of the electrode was decreased? Explain your answer.

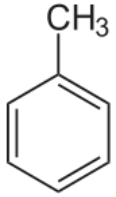
(3 marks)

2.P4 – Statistical Thermodynamics

Answer part (a) and **EITHER** part (b) **OR** part (c).

a) Answer **ALL** parts of this question

i) Consider a crystal of toluene. Estimate the residual entropy of 1 mol of crystal assuming the methyl group can occupy any position in the aromatic ring.



(2.5 marks)

ii) The Boltzmann distribution provides a route to estimate the fraction of particles in an energy level.

What are the main assumptions used to derive this probability distribution?

Under which conditions is it an accurate approximation? Justify your answer.

(3 marks)

iii) Spectroscopic measurements indicate that the vibrational temperature of water is larger than 2000 K and the rotational temperature is of the order of 25 K.

Use the equipartition principle to estimate the heat capacity of water vapour at 398 K. Compare your result with the experimental measurement 26 J K^{-1} mol^{-1}. Justify all the approximations you make.

(5 marks)

iv) Consider the following rotational temperatures of diatomic molecules: $\theta_r(N_2) = 2.9K, \theta_r(HD) = 64.7K$

Assuming classical behaviour, estimate the number of accessible rotational energy levels at 290 K. In which case would the classical approximation be accurate? Justify your answer.

(2.5 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts of this question

The translational partition function of one nitrogen molecule moving in 3 dimensions is given by, $q = \left[\sum_{n=1}^{\infty} \exp\left(\frac{-n^2h^2}{8mL^2}\frac{1}{k_BT}\right)\right]^3$.

i) Show that the classical limit approximation for the translational partition function is given by:

$$q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

Explain all your working.

Use the following integral: $\int_0^{\infty} \exp(-ax^2)dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$

(5 marks)

ii) 1 mol of Nitrogen undergoes a reversible expansion at 298 K, from 1 cm^3 to 100 cm^3. Using appropriate statistical thermodynamics expressions in the canonical ensemble, estimate the work associated with the expansion of the gas.

How much heat would be exchanged with the reservoir?

Explain all your working.

(7 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of this question

The vibrational partition function of one diatomic molecule is:

$$q = \frac{e^{-\frac{\theta_v}{2T}}}{1 - e^{\frac{-\theta_v}{T}}},$$

i) Show that the vibrational internal energy of 1 mol of molecules is:

$$U = \frac{N_A k_B \theta_v}{2} + R \frac{\theta_v}{(\exp(\theta_v / T) - 1)}$$

(7 marks)

ii) Sketch the dependence of the internal energy and heat capacity with temperature. Indicate clearly in your answer the limiting behaviour of these properties in the limits, $T \to 0$, and, $\mathrm{T} \to \infty$.

(5 marks)

M4C2 – Theoretical Methods

Answer part (a) and **EITHER** part (b) **OR** part (c).

a) Answer **ALL** parts of this question

Into which of the following classifications:- symmetric, Hermitian, orthogonal, or unitary do the following matrices fit?

i) $\mathbf{A} = \begin{pmatrix} 1 & i \\ -i & 0 \end{pmatrix}$

(1.5 marks)

ii) $\mathbf{B} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ -i & -1 \end{pmatrix}$

(1.5 marks)

iii) $\mathbf{C} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$

(1.5 marks)

iv) $\mathbf{D} = \begin{pmatrix} 1 & -1 \\ -1 & 0 \end{pmatrix}$

(1.5 marks)

v) Find $\mathbf{B}^{-1}$

(3.5 marks)

vi) Check your results by demonstrating that

$\mathbf{B}^{-1}\mathbf{B} = \mathbf{E}_2$

(1.5 marks)

b) Answer **ALL** parts of this question

i) Find the approximate asymptotic expression for the integral $I(p,n) = \int_0^\infty dx \frac{x e^{-px^2}}{(1+x^2)^n}$ for large positive p

(11.5 marks)

QUESTION CONTINUED OVERLEAF

ii) Under what conditions is your approximation expected to be accurate?
(2.5 marks)

c) Answer **ALL** parts of this question

[Hint: This questions concerns dimensionality (scaling) analysis]

i) List the parameters that determine the ground state of the hydrogen atom.
(1.5 marks)

ii) Compose the expression for Bohr radius, based on a combination of these parameters (product/ratio/powers) that has dimensionality of length, explaining why these parameters appear in the nominator or denominator.
(8.5 marks)

iii) Find the combination of parameters that describes the electron velocity on the first Bohr orbit.

[Hint: in addition to the dimensionality analysis, make use of the Bohr quantization principle]

(4 marks)