**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JUNE 2017, for Internal Students of the Imperial College of Science, Technology and Medicine**

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

# CHEM40003 PHYSICAL CHEMISTRY 1

**Tuesday 27th June 2017, 09:30-11:45**

**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.**

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

## Q1, Thermodynamics 1: Chemical Equilibria

Answer part a) and **EITHER** part b) **OR** part c) of this question**.**

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

i) Define what is meant by an *isothermal process* and an *adiabatic process*.

(2 marks)

ii) State the circumstances under which a process tends to proceed by each of the routes in part (i) above.

(2 marks)

iii) Sketch a graph showing the change in the entropy (S) of a sample of $H_2O$ as its temperature is raised from 173 K to 473 K. Indicate on your graph all entropy changes observed and explain why these changes occur.

(4 marks)

iv) The autoprotolysis of water is described by the following equilibrium:

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$$

The pH of water is 7 at 25 ºC and the enthalpy change (ΔH) for the reaction above is 56.1 kJ $mol^{-1}$.

Calculate the expected pH of water at 70 ºC. State all assumptions made.

(6 marks)

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

i) Explain what is meant by *chemical potential* (μ) and *standard chemical potential* ($\mu^{\ominus}$), and state how these two quantities are linked for a substance in solution.

(3 marks)

ii) Using the concept of chemical potential, describe why a gas will always expand to fill its container.

(2 marks)

QUESTION CONTINUED OVERLEAF

iii) The conversion of $SO_2$ to $SO_3$ forms a key step in the production of sulphuric acid and occurs by the equilibrium shown below.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

The standard chemical potentials of the reactants and product of this reaction are:

$$\mu^{\theta}(SO_2) = -600.4 \text{ kJ.mol}^{-1}$$
$$\mu^{\theta}(O_2) = 0.0 \text{ kJ.mol}^{-1}$$
$$\mu^{\theta}(SO_3) = -742.2 \text{ kJ.mol}^{-1}$$

The enthalpy change for the reaction is:

$$\Delta_r H = -197 \text{ kJ mol}^{-1}$$

Calculate the equilibrium constant for the reaction at 25 ºC and at the temperature used in the industrial production of sulphuric acid of 450 ºC.

Comment on the difference between the equilibrium constant at these two temperatures. What other factors need to be considered in industrial chemical production.

(6 marks)

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

Citric acid is a highly important chemical in foodstuffs, biochemistry and industrial processes. Below pH 4, it dissociates according to the following equilibrium:

$$C_5H_7O_5COOH + H_2O \rightleftharpoons C_5H_7O_5COO^- + H_3O^+$$

The pH of a 0.1 M solution of citric acid at a range of temperatures is shown in the table below.

| **Temperature / ºC** | **pH** |
|---|---|
| 25 | 2.064 |
| 30 | 2.058 |
| 37 | 2.050 |
| 42 | 2.045 |
| 48 | 2.038 |
| 53 | 2.033 |
| 60 | 2.027 |

Calculate the enthalpy change and entropy change for the dissociation of citric acid.

(11 marks)

## Q2, Thermodynamics 2: Molecular Driving Forces

Answer part a) and **EITHER** part b) **OR** part c) of this question.

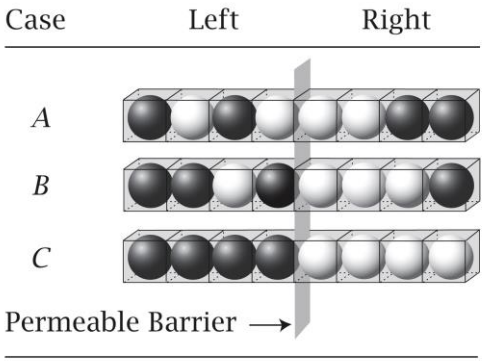
a) Answer **ALL** parts of this question

i) For a series of 4 coin tosses, which **sequence** HHHH or HTHH, where H represents heads and T tails respectively, is more probable?

(2 marks)

ii) The diagram below represents three different examples of how four white and four black balls may be arranged to represent the process of mixing. Which of the following three cases, A, B or C would be the most probable?

Your answer should be based on the multiplicity of the three systems.




(5 marks)

iii) Derive the expression for the Gibbs free energy, G = H -TS, when it is at a minimum.

Hint: you may find the following expression useful in your derivation

$$dH = TdS + Vdp + \sum_{j=1}^{M} \mu_j dN_j$$

(3 marks)

iv) The Helmholtz free energy of a pure liquid in the lattice model is given by the following equation:

$$A = U - TS = U = N\left(\frac{zw_{AA}}{2}\right)$$

Explain why the free energy can be represented by just one term. Identify the variables $N$, $z$ and $w_{AA}$. Determine the chemical potential, $\mu_C$, for the liquid.

(3 marks)

QUESTION CONTINUED OVERLEAF

v) The vapour pressure of water is 23 mm Hg at T= 300 K and 760 mm Hg at T = 373 K. Calculate the enthalpy of vapourization $\Delta H_{vap}$. Assuming that each water has z = 4 nearest neighbours, calculate the interaction energy $w_{AA}$. You may find the following equation useful:

$$ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(2 marks)

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

State the equation describing the Lennard-Jones (12,6) potential, defining all terms used. Sketch this potential for two Argon atoms, clearly identifying the attractive, repulsive and total interaction curves. Indicate on the diagram the equilibrium interaction distance and the dissociation energy.

(10 marks)

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

For an ideal gas, the entropy is $S = N\, k_B \ln V$

i) Express $\Delta S_V = S_2(V_2) - S_1(V_1)$, the entropy change upon changing the volume from $V_1$ to $V_2$, at fixed particle number $N$.

ii) Express $\Delta S_N = S_2(N_2) - S_1(N_1)$, the entropy change upon changing the particle number from $N_1$ to $N_2$, at fixed volume $V$.

iii) Write an expression for the entropy change, $\Delta S$, for a two-step process:

$$(V_1,N_1) \longrightarrow (V_2,N_1) \longrightarrow (V_2,N_2)$$

in which the volume changes first at fixed particle number, then the particle number changes at fixed volume.

iv) Show that the entropy change $\Delta S$ above is exactly the same as for the two-step process in reverse order: changing the particle number first, then the volume.

v) What is the entropy change if you double the volume from $V$ to $2V$ in a quasi-static isothermal process at temperature $T$?

(10 marks)

## Q3, Chemical Kinetics

Answer **ALL** parts of this question

a) Define what is meant by the molecularity of an elementary reaction.

(1 mark)

b) For a simple reaction A → B with a first order rate law and rate constant k, derive an expression for:

i) the concentration as a function of time

(4 marks)

ii) the time constant for the system.

(2 marks)

c) Why does varying temperature of a radical recombination reaction in the gas phase have little effect on the rate of reaction?

(3 marks)

d) With the use of a diagram explain how the flow method is used to undertake real time kinetic analysis of reactions.

(5 marks)

e) The decomposition of nitrogen pentoxide:

$$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$$

is believed to occur via the following mechanism:

| | | | | |
|---|---|---|---|---|
| Step 1: | $N_2O_5$ | → | $NO_2 + NO_3$ | Rate constant: $k_a$ |
| Step 2: | $NO_2 + NO_3$ | → | $N_2O_5$ | Rate constant: $k_a'$ |
| Step 3: | $NO_2 + NO_3$ | → | $NO_2 + O_2 + NO$ | Rate constant: $k_b$ |
| Step 4: | $NO + N_2O_5$ | → | $NO_2 + NO_2 + NO_2$ | Rate constant: $k_c$ |

Experiments have demonstrated this reaction is first order with respect to $N_2O_5$. Show that the above mechanism can account for this observation.

(10 marks)