**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 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**

# ADVANCED CHEMISTRY THEORY IIA

## Physical Chemistry

**Tuesday 12th January 2010, 09:30-11:00**

**Answer ONE question from each attended course**

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

**Year 2/0110** **Turn Over**

## 2.P1 – Interfacial Thermodynamics

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

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

$$dU = dq_{rev} - pdV$$

i) Define all terms in the above equation.

(2 marks)

ii) Starting from the above equation, derive an expression for the entropy change $\Delta S$ for a perfect gas as a function of temperature and volume.

Hint: integrate $dS = \frac{dq_{rev}}{T}$ and use $C_V = \left(\frac{\partial U}{\partial T}\right)_V$.

(5.5 marks)

iii) Hence calculate $\Delta S$ if 1 mole of a perfect gas is expanded isothermally from a volume of 20 dm$^3$ to 100 dm$^3$.

(2.5 marks)

iv) Use your expression from part (ii) to calculate $\Delta S$ if 1 mole of a perfect gas is heated at constant volume from 295 to 335 K.

Hint: $C_v$ = 5/2 R for a perfect gas.

(2.5 marks)

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

One form of the Fundamental equation, for a single-component system, reads:

$$d\mu = V_m dp - S_m dT$$

i) Define each term in this equation

(2.5 marks)

ii) Explain what it tells us about the pressure-dependence and temperature-dependence of $\mu$.

(3 marks)

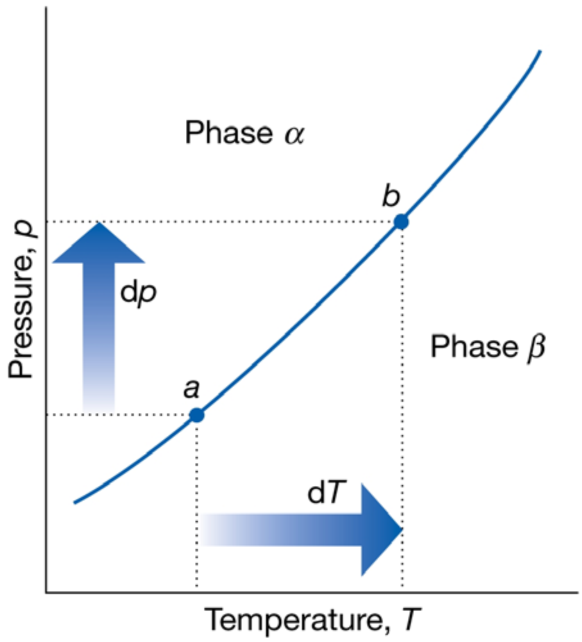
QUESTION CONTINUED OVERLEAF

iii) A small part of a two-phase coexistence curve (where $\mu(\alpha) = \mu(\beta)$) is shown in the Figure below. By equating $d\mu(\alpha)$ and $d\mu(\beta)$, derive an expression for $dp/dT$ (the Clapeyron equation).

(4 marks)

iv) At one point on the coexistence curve, at a temperature of 372.78 K, it is found that $dp/dT = 3{,}600$ Pa K$^{-1}$, and the enthalpy of the $\alpha$-$\beta$ transition at that point is $\Delta H = 40.7$ kJ mol$^{-1}$. Hence calculate the volume change $\Delta V$ of the transition. (The data refers to the boiling point of water at $10^5$ Pa).

(3 marks)




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

The figure below shows a temperature-composition phase diagram for a mixture of two partially immiscible liquids A and B.

i) State the Gibbs Phase rule for a binary system, and explain which degrees of freedom there are within single phase, and biphasic, regions of the phase diagram.

(3 marks)

ii) State what phases are found in regions m, n, o, p and q.

(4 marks)

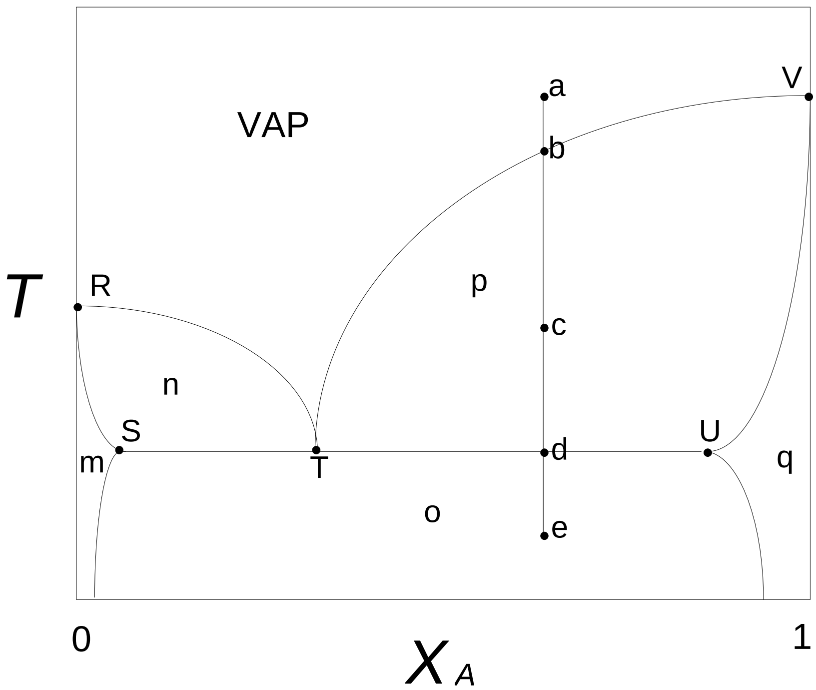
QUESTION CONTINUED OVERLEAF

iii) Explain the significance of points S, T, and U.

(3 marks)

iv) If a tie-line were drawn through point c, explain what information it would yield.

(2.5 marks)



## 2.P3 – Electronic Properties of Solids

Answer part a) and **EITHER** part b) or part c)

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

In a written exercise, students were asked to write down an expression for the total number of electrons, $N_e$, in a three-dimensional conductor at room temperature. The equation below was a popular, yet incorrect answer:

$$N_e = \int_0^{E_F} DOS(E)\,dE \qquad \text{(Equation 1)}$$

DOS(E) is the Density-Of-States function, E is the energy and $E_F$ is the Fermi energy.

i) Suggest the (two) required modifications to be made to equation (1) and explain why equation (1) in its present form is incorrect, in terms of the question asked. Write down the corrected form of the equation.

(6 marks)

ii) Draw the DOS(E) for the one-, two- and three-dimensional case in one diagram. Specify the functional dependence between the DOS and the energy for all three cases.

(6 marks)

iii) The Fermi energy $E_F$ decreases from Na (3.1 eV), K (2.1 eV), Rb (1.8 eV) to Cs (1.5 eV), which can be rationalized based on free electron theory. Write down an equation for $E_F$ and explain the observed behaviour.

(4 marks)

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

This question relates to the effective mass concept and the nearly free electron theory.

i) Draw the dispersion relation E(k) for an s-band within the 'free electron theory' and the 'nearly free electron theory' in one diagram. Why are the two curves different?

(3 marks)

QUESTION CONTINUED OVERLEAF

ii) Write down the definition of the effective mass and define all parameters.

(2 marks)

iii) Comment on the sign of the effective mass as a function of the wave vector k in the free electron theory and in the nearly free electron theory, respectively. Can the effective mass be negative? If so, what does this mean with regard to the nature of the charge carriers?

(4 marks)

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

The heat capacity of a solid (at constant volume) can be written as

$$C_V = \gamma \cdot T + A \cdot T^3$$

i) What are the two contributions to $C_V$ on the right-hand-side of the equation? Explain the underlying physical mechanism by which they affect $C_V$.

(3 marks)

ii) In which temperature range does the first term ($\gamma \cdot T$) dominate the magnitude of $C_V$ and why?

(2 marks)

QUESTION CONTINUED OVERLEAF

iii) Experimental values for the heat capacity of potassium as a function of temperature T are given in the table below. Linearize the equation for $C_V$, plot the data points accordingly and read the value for $\gamma$ off the plot. State the result including an estimated error.

(4 marks)

| **Temperature/[K]** | **Heat capacity $C_V$/[mJ/(mol·K)** |
|---|---|
| 1.1606 | 6.519 |
| 1.2392 | 7.585 |
| 1.3243 | 8.898 |
| 1.5274 | 12.75 |
| 1.9978 | 26.14 |
| 2.1300 | 31.36 |
| 2.4205 | 45.44 |

(from Lien & Phillips, Phys. Rev. 1964, 133, A1370)