

University of Canterbury

## End-of-year Examinations 2008

Prescription Number(s): CHEM 243

Paper Title: Physical Chemistry

Time Allowed: Two hours

Number of pages: Six  
plus answer sheet

This paper is divided into TWO sections.

Each section is worth 50% of the total marks.

Answer **ALL** questions in each section.

**TURN OVER**



## SECTION A

(Answer **ALL** questions in this section. This section is worth 50% of the total marks. Total marks = 40.)

1. [  $R=8.314 \text{ J mol}^{-1}\text{K}^{-1}$ . The listed value for the enthalpy of condensation of ammonia is  $-97.41 \text{ kJ mol}^{-1}$  at  $239.73 \text{ K}$  ]
- (a) Derive the Langmuir isotherm  $\theta = \frac{KP}{(1+KP)}$  for adsorption of a monolayer of gas on a solid surface: explain the meaning of all the symbols used, list the assumptions made, and identify the process for which the quantity  $K$  can be regarded as an equilibrium constant. (7 marks)
- (b) The adsorption of ammonia gas on charcoal is measured at  $303 \text{ K}$  and  $353 \text{ K}$ , at gas pressures such that the quantity  $KP$  is much less than 1. The pressure required for adsorption of the same weight of  $\text{NH}_3$  per gram of charcoal is found to be  $106 \text{ Torr}$  at  $303 \text{ K}$  and  $560 \text{ Torr}$  at  $353 \text{ K}$ . Calculate the isosteric heat of adsorption of  $\text{NH}_3$  on charcoal and comment on how your value compares with the latent heat of condensation that is given above. (7 marks)
- (c) Sketch a graph, showing the form of the BET isotherm that you would expect to observe with pressures of ammonia ranging from zero to much more than that required for monolayer coverage. Label the three main regions of the isotherm. (6 marks)
2. (5 marks each)
- Write brief notes on any **FOUR** of the following:
- (a) Improvements on the Langmuir isotherm.
- (b) 'Volcano' curves of catalytic activity versus atomic number for series of transition metals.
- (c) Catalysis by chiral organo-metallic compounds that are anchored within nanoporous solids.
- (d) Activated and non-activated transitions from physisorption to chemisorption.
- (e) Experimental techniques for studying the structure and composition of solid surfaces.
- (f) The Eley-Rideal mechanism of surface catalysis.
- (g) The Langmuir-Hinshelwood mechanism of surface catalysis.
- (h) The Michaelis-Menten mechanism of enzyme catalysis.

**TURN OVER**

## SECTION B

(Answer **ALL** questions in this section. This section is worth 50% of the total marks.

Each of questions 3,4,5 and 6 is worth 10 marks. Total marks = 40.)

3. The Clapeyron equation for **any** phase change may be written as

$$dP/dT = \Delta_{\text{trs}}S / \Delta_{\text{trs}}V$$

where  $\Delta_{\text{trs}}S$  is the molar entropy change for the phase change and  $\Delta_{\text{trs}}V$  is the molar volume change for the same transition.

- (a) **Show** how this equation may be modified, in the special case where the phase change is the vaporisation of a liquid, to give the Clausius-Clapeyron equation, which may be expressed as either

$$\frac{dP}{dT} = \frac{P\Delta_{\text{vap}}H}{RT^2}$$

or 
$$\frac{d(\ln P)}{d\left(\frac{1}{T}\right)} = \frac{-\Delta_{\text{vap}}H}{R}$$

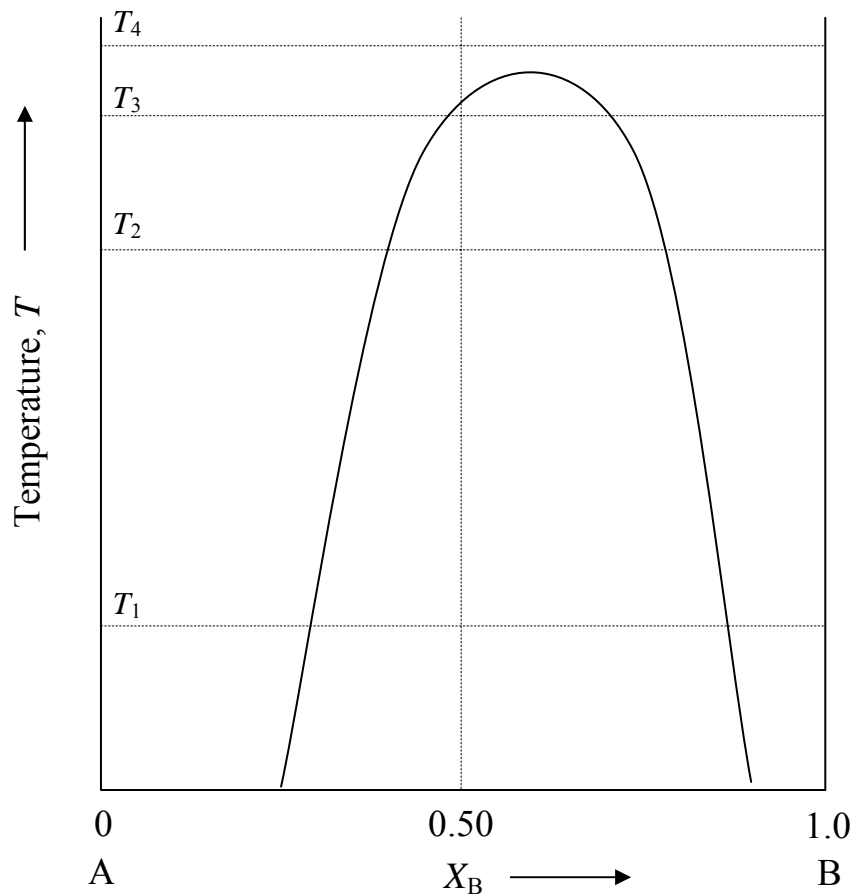
- (b) The molar volume of a solid substance, X, is  $128.0 \text{ cm}^3 \text{ mol}^{-1}$  at 101.3 kPa and its melting point of 382.42 K. At this temperature and pressure the molar volume of liquid X is  $130.4 \text{ cm}^3 \text{ mol}^{-1}$ . If the pressure is raised to 12 MPa, the melting temperature of X rises to 383.05 K.

Calculate: (i) the molar entropy of fusion,  $\Delta_{\text{fus}}S$ , for substance X, and

(ii) the molar enthalpy of fusion,  $\Delta_{\text{fus}}H$ , for substance X.

4. (a) The figure given below shows the phase diagram for two partially miscible liquids A and B at temperatures below the appearance of a vapour phase, and above the presence of solid phases. Describe what will be observed when a mixture of composition  $X_B = 0.50$  is heated.

For *each* of the temperatures  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  determine the **number**, **composition** and **relative amounts** of the phases present at equilibrium.



- (b) Sketch the general shape of, and label as appropriate, the boiling-point ( $T$ - $X$ ) diagram that you might expect to observe for the A/B system.
- (c) The A/B system has a eutectic point at  $X_B = 0.10$  at a temperature  $T_0$  (where the difference  $T_2 - T_1 \approx T_1 - T_0$ ). Sketch the general shape of an extended phase diagram. This diagram should include the equilibria which exist between liquid and solid phases. Label the various regions in your sketched diagram.

5. At 60°C, ethanol (E) has a vapour pressure of 357 Torr and methanol (M) has a vapour pressure of 625 Torr. A solution of these two compounds, which may be assumed to be an ideal solution, is made by mixing 3.77 moles of ethanol and 2.34 moles of methanol.
- (a) What are the partial pressures of each component and the total vapour pressure above the solution at 60°C?
- (b) Calculate the mole fraction of ethanol in the vapour which is at equilibrium with the above solution.
6. The figure on the answer sheet for Question 6 represents the  $T$ - $X$  phase diagram for the liquid-solid region of mixtures of C and D. Label the **seven** regions of the diagram stating **clearly** what substances will exist at equilibrium in each region. (If compound(s) are present give the formula(e).) Indicate the nature of the phase (i.e. solid or liquid).

On the right-hand figure of the answer sheet, sketch cooling curves for liquids which commence at the points a, b, c, d and e in the diagram. Label the cooling curves to indicate which phase(s) is/are present.

**END OF PAPER**

