

A. PROBLEMS

- [1] The straight-line plot of $\ln P$ versus $1/T$ for the vapour pressure of a certain liquid whose normal boiling point is 27°C extrapolates to $P = 10^5$ atm at infinite temperature. Calculate the molar heat of vaporization of the liquid, $\overline{\Delta H}_{\text{vap}}$. [Express your answer in kcal/mol.]
- [2] While snow-shoveling after one January winter storm, a local scientist in a remote Ontario town accidentally discovered a new form of ice, called Ice IX. Its triple point is found to be at 500 mm Hg and 80°C . Ice IX is more dense than liquid water and its heat of sublimation is less than that of liquid water. This form of ice is quite different from ordinary ice, Ice I, which has a vapour pressure of 5 mm Hg at its melting point. Now, sketch a phase diagram for water substance, including the phases: vapour, liquid and both Ice IX and Ice I. Use a log scale for P from 0.1 mm Hg to 10^3 mm Hg and a linear scale for T from -50°C to 150°C . Make sure that the slopes and curvatures of various lines confer to the above data and to the general thermodynamic equations, and be sure to label all the features in the phase diagram. Use dotted lines for lines of metastable two-phase equilibria and full lines for stable ones. Explain the reasoning (steps) of the way you deduce this diagram.
- [3] A certain liquid of molecular weight 60 g/mol has a critical temperature of 400°C . Its melting point is 15.000°C as normally measured (i.e. at a pressure of 1 atm) and 14.980°C at its triple point (where the system is subjected only to its own low vapour pressure, $P \sim 0$ atm). The solid and liquid densities are 0.85 g/cm^3 and 0.80 g/cm^3 , respectively.
- Estimate $\overline{\Delta H}_{\text{vap}}$. [Express your answer in kcal/mol.] **Hint:** This can be done easily by using two semi-empirical rules: (1) Trouton's rule says that $\overline{\Delta H}_{\text{vap}} / T_b \sim 21 \text{ cal/K/mol}$ or 88 J/K/mol , where T_b is the boiling point and $\overline{\Delta H}_{\text{vap}}$ is the molar heat of vaporization. (2) The normal boiling point of a liquid is found to be about two-thirds of its critical temperature for most materials.
 - Determine $\overline{\Delta H}_{\text{sub}}$ and $\overline{\Delta H}_{\text{fus}}$. [Express your answers in kcal/mol.]
 - Estimate the vapour pressure at the triple point.
- [4] The vapour pressure of pentane ($n\text{-C}_5\text{H}_{12}$) at 25°C is 0.674 bar and that of hexane ($n\text{-C}_6\text{H}_{14}$) is 0.198 bar.
- Calculate the partial pressure of each substance and the total pressure over a solution with the composition of $\chi_{\text{pentane}} = 0.25$. Assume that these substances form an ideal solution.
 - What is the composition of the vapour phase in equilibrium with the above solution? [i.e. Work out the mole fractions for pentane and hexane in the vapour phase.]
 - Using all the available data, sketch a pressure-composition diagram for the above system. Use the mole fraction of hexane as the independent variable. Explain how you derive this plot.
- [5] Liquids A and B form an ideal solution. Suppose the mole fraction of A in a certain solution is 0.25 (i.e. $\chi_A = 0.25$), and the mole fraction of A of the vapour in equilibrium with the solution at 25°C is 0.50 (i.e. $y_A = 0.50$). The molar heat of vaporization of A is 5 kcal/mol and that of B is 7 kcal/mol.
- Calculate the ratio of the vapour pressure of pure A to that of pure B at 25°C .
 - Calculate the value of the same ratio for the solution with the same composition but at 100°C .