

Problem set 7 – Ideal Solutions, Colligative Properties and Van der Waals gas

Exercise 32

The Van der Waals equation of state for one mole ($n = 1$) is given by

$$p = \frac{RT}{V - b} - \frac{a}{V^2}.$$

- a) Explain the physical significance of the Van der Waals parameters a and b .

Below a critical temperature T_c the Van der Waals exhibits condensation, and this critical point of the van der Waals gas is defined by the conditions

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0.$$

- b) Apply the first condition to the perfect gas law, and explain that a perfect gas will never exhibit a critical point, i.e. will never condense into a liquid.
- c) Apply both of the above conditions to the Van der Waals equation of state to find the critical volume $V_c = 3b$, and hence, the critical temperature $T_c = \frac{8a}{27Rb}$.
- d) Finally, substitute the expressions for V_c and T_c back into the Van der Waals equation of state to obtain the critical pressure $p_c = \frac{a}{27b^2}$.
- e) Due to intermolecular interactions carbon dioxide cannot be treated as a perfect gas, but does obey the Van der Waals equation. Given that $a = 0.361 \text{ Jm}^3\text{mol}^{-2}$ and $b = 42.9 \cdot 10^{-6} \text{ m}^3\text{mol}^{-1}$ for CO_2 , calculate the V_c , T_c and p_c for carbon dioxide. How does it compare to the actual critical temperature (304.2 K) and critical pressure (72.9 atm) of CO_2 ?

Exercise 33

The Gibbs free energy of an ideal binary mixture – i.e. an ideal solution – is

$$G = G_{\text{unmixed}} + RT \{n_1 \ln x_1 + n_2 \ln x_2\}.$$

- a) Show that the chemical potential of the component 1 is (note: $x_i = n_i/n$ and $n = n_1 + n_2$.)

$$\mu_1 = \mu_1^* + RT \ln x_1. \quad [\text{in general: } \mu_i = \mu_i^* + RT \ln x_i \quad (i = 1, 2)].$$

- b) Show that for an ideal mixture the vapour pressure of each component i is given by Raoult's law.

$$p_i = p_i^* x_i \quad (i = 1, 2, \dots).$$

- c) A mixture of hexane and heptane forms an ideal solution to a good approximation. Both in terms of (i) number of moles and (ii) masses, in what ratio should we mix hexane and heptane to realise the largest entropy of mixing?

Exercise 34

For an aqueous solution of sucrose ($C_{12}H_{22}O_{11}$) with a molality of 0.300 mol/kg, the molarity is 0.282 mol/dm³ at 20°C and 1 atm. The density of pure water at 20°C is $\rho_{H_2O} = 0.998$ g/cm³ and the molar mass is 18 g/mol.

- a) Treating this solution as ideal, determine the osmotic pressure using the Van 't Hoff expression for the osmotic pressure of ideal solutions $\Pi = [B]RT$.

The general expression for the osmotic pressure of a solution is given by

$$\Pi = -\frac{\mu_1 - \mu_1^*}{V_{1,m}}$$

- b) Explain the meaning of the symbols in the above equation, and show that the osmotic pressure of a real (non-ideal) solution is given by

$$\Pi = -\frac{RT}{V_{1,m}} \ln a_1.$$

- c) The osmotic pressure for the sucrose solution was experimentally measured to be 7.61 atm. Determine the activity and the activity coefficient of the solvent.

Exercise 35

The expression for the elevation of boiling point due to the addition of solute is given by:

$$\Delta T = \frac{RT^{*2}}{\Delta_{\text{vap}}H} x_2.$$

When 10 g of a solid is completely dissolved in 100 g benzene, the boiling point of pure benzene (T^*) increases to 80.95 °C. The boiling point and molar mass of benzene are 80.15 °C and 78.11 g/mol, respectively, and the enthalpy of evaporation is 30.8 kJ/mol.

Calculate the molar mass of the dissolved substance.