

1. Prior to the discovery that freon-12 (CF_2Cl_2) was harmful to Earth's ozone layer, it was frequently used as the dispersing agent in spray cans for hair spray, etc. Its enthalpy of vaporization at its normal boiling point of -29.2°C is $20.25 \text{ kJ mol}^{-1}$. Estimate the pressure that a can of hair spray using freon-12 had to withstand at 40°C (the temperature of a can that has been standing in sunlight). Assume that $\Delta_{\text{vap}}H$ is a constant over the temperature range involved.

We use the Clausius-Clapeyron equation:
$$\ln\left(\frac{p}{p^*}\right) = -\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$p^* = 1 \text{ bar (normal boiling point)}$$

$$T^* = 273.15 - 29.2 = 243.95 \text{ K}$$

$$T = 273.15 + 40 = 313.15 \text{ K}$$

$$\ln(p/p^*) = \{-(20.25 \times 10^3 \text{ J mol}^{-1})/(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})\} \times \{1/(313.15 \text{ K}) - 1/(243.95 \text{ K})\}$$

$$= 2.20618$$

$$p = p^* \exp(2.20618) = \mathbf{9.081 \text{ bar}}$$

2. On the surface of Mars, a mean atmospheric pressure is 600 Pa, and the air mostly consists of carbon dioxide. The mole fraction of CO_2 in Martian air is 0.9532, whereas the mole fraction of O_2 is only 0.0013. If a Martian sea were to exist, what would be the molalities of CO_2 and O_2 solutions in Martian water at 298 K?

First, we determine partial vapor pressures of CO_2 and O_2 in Martian atmosphere.

$$p_{\text{CO}_2} = 0.9532 \cdot 600 \text{ Pa} = 571.92 \text{ Pa}$$

$$p_{\text{O}_2} = 0.0013 \cdot 600 \text{ Pa} = 0.78 \text{ Pa}$$

Then, we use Henry's law in terms of molality.

$$p_{\text{CO}_2} = b_{\text{CO}_2} K_{\text{CO}_2} \quad K_{\text{CO}_2} = 3.01 \cdot 10^5 \text{ kPa kg mol}^{-1}$$

$$b_{\text{CO}_2} = p_{\text{CO}_2} / K_{\text{CO}_2} = 571.92 \cdot 10^3 \text{ Pa} / 3.01 \cdot 10^5 \text{ kPa kg mol}^{-1} \\ = 1.90 \cdot 10^{-4} \text{ mol kg}^{-1}$$

$$p_{\text{O}_2} = b_{\text{O}_2} K_{\text{O}_2} \quad K_{\text{O}_2} = 1.92 \cdot 10^4 \text{ kPa kg mol}^{-1}$$

$$b_{\text{O}_2} = p_{\text{O}_2} / K_{\text{O}_2} = 0.78 \cdot 10^3 \text{ Pa} / 1.92 \cdot 10^4 \text{ kPa kg mol}^{-1} = 4.05 \cdot 10^{-4} \text{ mol kg}^{-1}$$

3. For D_2O (where D is deuterium, 2H), the normal freezing point is $3.82^\circ C$ and $\Delta_{fus}H = 6.23 \text{ kJ mol}^{-1}$.

(a) Find the freezing point depression constant K_f for D_2O .

(b) Find the freezing point of a solution of 0.954 g of CH_3COCH_3 in 100 g of D_2O .

$$K_f = \frac{R T^{*2} M_{D_2O}}{\Delta_{fus}H} = \frac{8.31447 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 276.97 \text{ K}^2}{6230 \text{ J mol}^{-1} \cdot \frac{\text{kg}}{\text{mol}}}$$

$$M_{D_2O} = 20.02 \frac{\text{g}}{\text{mol}} \quad \text{because} \quad m(D) = 2 m(H)$$

$$K_f = 2.05 \text{ K kg mol}^{-1}$$

$$n(CH_3COCH_3) = \frac{0.954 \text{ g}}{M(CH_3COCH_3)} = \frac{0.954 \text{ g}}{58 \text{ g mol}^{-1}} = 0.0164 \text{ mol}$$

$$b(CH_3COCH_3) = \frac{0.0164 \text{ mol}}{100 \text{ g}} = 0.164 \text{ mol kg}^{-1}$$

$$\Delta T = K_f b = 0.336 \text{ K}$$

Freezing point of the solution:

$$T = T^* - \Delta T = 276.63 \text{ K} = 3.48^\circ C$$

4. At 100°C benzene has a vapor pressure of 180.9 kPa, and toluene has a vapor pressure of 74.4 kPa. Assuming that these substances form ideal binary solutions with each other, calculate the composition of the solution that will boil at 1 bar at 100°C and the vapor composition. Sketch the pressure-composition phase diagram for this mixture. In each area of your diagram write down the number P of phases present, what phases are present, and F' (reduced variance). Draw the isopleth corresponding to the composition of the solution that will boil at 1 bar (which you already calculated) and the tie line, which allows to determine the corresponding vapor composition.

$$p_B = x_B \cdot p_B^* \quad p_T = x_T \cdot p_T^* = (1 - x_B) p_T^*$$

$$p_{\text{total}} = 1 \text{ bar} = 100 \text{ kPa} = p_B + p_T$$

$$100 = x_B \cdot 180.9 + (1 - x_B) \cdot 74.4$$

$$x_B = \frac{100 - 74.4}{180.9 - 74.4} = 0.24$$

$$x_T = 1 - x_B = 0.76$$

$$p_B = 0.24 \cdot 180.9 = 43.48 \text{ kPa}$$

$$p_T = 0.76 \cdot 74.4 = 56.52 \text{ kPa}$$

$$y_B = \frac{p_B}{p_{\text{total}}} = 0.4348$$

$$y_T = \frac{p_T}{p_{\text{total}}} = 0.5652$$

7. (a) Derive the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

using the expression for dH and a Maxwell relation.

(b) Use the above thermodynamic equation of state to determine $\left(\frac{\partial H}{\partial p}\right)_T$ for a perfect gas.

$$H = U + pV$$

$$(a) \quad dH = dU + d(pV) = dU + p dV + V dp$$

$$\text{Since } dU = T dS - p dV,$$

$$dH = T dS - p dV + p dV + V dp = V dp + T dS$$

Now, we divide the equation for dH by dp and impose constant temperature conditions.

$$\left(\frac{\partial H}{\partial p}\right)_T = V + T\left(\frac{\partial S}{\partial p}\right)_T$$

One of the Maxwell relations is $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$.
Replacing $\left(\frac{\partial S}{\partial p}\right)_T$ with $-\left(\frac{\partial V}{\partial T}\right)_p$ we obtain

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

(b) For a perfect gas, $pV = nRT$

$$V = \frac{nRT}{p} \quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T \frac{nR}{p} = V - \frac{nRT}{p} = V - V = 0$$