

CHEMISTRY 311 PHYSICAL CHEMISTRY  
Homework Assignment # 7

1. Prior to the discovery that Freon-12 ( $\text{CF}_2\text{Cl}_2$ ) was harmful to the 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  $-29.2^\circ\text{C}$  is  $20.25\text{ kJ mol}^{-1}$ . Estimate the minimum pressure a can of hair spray with Freon-12 had to withstand at  $40^\circ\text{C}$ , the temperature of a can that has been standing in sunlight on a mild day. Assume that  $\Delta_{\text{vap}}H^\circ$  is constant over the temperature range considered.

**Answer**

The vapor pressure of a liquid at its normal boiling point is equal to the atmospheric pressure (1 atm or 1.01325 bar). Therefore, we set  $p_1 = 1.00\text{ atm}$ ,  $T_1 = (273.15 - 29.2)\text{ K}$ ,  $T_2 = (273.15 + 40)\text{ K}$ , and solve for  $p_2$  using the Clausius-Clapeyron equation:

$$\begin{aligned}\ln\left(\frac{p_2}{p_1}\right) &= \frac{\Delta_{\text{vap}}H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ &= \frac{20250\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}} \left(\frac{1}{243.95} - \frac{1}{313.15}\right) \frac{1}{\text{K}} \\ &= 2.2062\end{aligned}$$

Therefore,

$$\begin{aligned}p_2 &= p_1 e^{2.2062} \\ &= 9.0811\text{ atm.}\end{aligned}$$

In reality, a can has to withstand even higher pressures to provide a safety margin and to account for the air already present in the can when it is filled with the hairspray and Freon-12.

2. The vapor pressure of pure liquid A at 300 K is 575 torr, and that of pure liquid B is 390 torr. The two liquids form an ideal mixture in which the mole fraction of A in the liquid phase is 0.350. Calculate (a) the total pressure of the vapor and (b) the composition of the vapor phase, assuming that no other gases are present.

**Answer**

- (a) Using Raoult's Law, we get

$$\begin{aligned}p_A &= x_A P_A^* = 0.350 \times 575 = 201.25\text{ torr.} \\ p_B &= (1 - x_A) P_B^* = 0.650 \times 390 = 253.5\text{ torr.} \\ P &= p_A + p_B = 454.75\text{ torr.}\end{aligned}$$

- (b) Using Dalton's Law, we get the vapor composition:

$$\begin{aligned}y_A &= \frac{p_A}{P} = \frac{201.25}{454.75} = 0.4426, \\ y_B &= 1 - 0.4426 = 0.5574.\end{aligned}$$