

PHYSICS 140A : STATISTICAL PHYSICS
HW ASSIGNMENT #8 SOLUTIONS

(1) A grocer starts his day with 4 boxes of pears, 5 boxes of oranges, and 6 boxes of apples. Each box contains 24 fruit and is initially completely filled.

- (a) At some time, the grocer notes that exactly half the pears, a third of the oranges, and a quarter of the apples have been sold. Assuming that customers take fruit from random positions in each of the boxes, find the dimensionless entropy $\ln W$ of the fruit distribution.
- (b) A clumsy customer then topples the table on which the fruit boxes rest, and all the fruit fall to the ground. The customer cleans up the mess, putting all the fruit back into the boxes, but into random locations. What is the entropy of the final state?

Solution :

(a) The grocer starts with 96 pears, 120 oranges, and 144 apples. By the time the grocer checks, 48 pears, 40 oranges, and 36 apples have been removed. The number of ways of doing this is

$$W = \binom{96}{48} \binom{120}{40} \binom{144}{36} = 8.303 \times 10^{93} .$$

Thus, $\ln W = 216.3$.

(b) There are a total of $96 + 120 + 144 = 360$ slots for the fruit, which contain the remaining 48 pears, 120 oranges, and 108 apples. The rest of the slots, which amount to $360 - 48 - 120 - 108 = 84$ in total, are empty. Therefore,

$$W' = \frac{360!}{94! \cdot 48! \cdot 120! \cdot 108!} = 1.093 \times 10^{205} ,$$

and the dimensionless entropy is $\ln W' = 472.1$.

(2) The *triple point* of a single component thermodynamic system is an isolated point (T_t, p_t) in the (T, p) plane where there is three phase coexistence between solid, liquid, and vapor. Consider three phase coexistence between a pure solid, a pure vapor, and a solution where the solute fraction is x . Find the shift $(\Delta T_t, \Delta p_t)$ as a function of x, T_t , and the quantities $s_{S,L,V}$ and $v_{S,L,V}$, *i.e.* the molar entropies and volumes of the three respective phases.

Solution :

At the triple point, we have $\mu_S(T_t, p_t) = \mu_L(T_t, p_t) = \mu_V(T_t, p_t)$, which gives two equations for the two unknowns T_t and p_t . We write $T_t = T_t^0 + \Delta T$ and $p_t = p_t^0 + \Delta p$, and we solve

$$\begin{aligned} \mu_L^0(T_t^0 + \Delta T, p_t^0 + \Delta p) - x k_B (T_t^0 + \Delta T) &= \mu_V^0(T_t^0 + \Delta T, p_t^0 + \Delta p) \\ \mu_V^0(T_t^0 + \Delta T, p_t^0 + \Delta p) &= \mu_S^0(T_t^0 + \Delta T, p_t^0 + \Delta p) , \end{aligned}$$

where the 0 superscript indicates the value for a pure phase. We now expand in the notionally small quantities ΔT and Δp , and we use

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,N} = -\left(\frac{\partial S}{\partial N}\right)_{p,T} = -\frac{s}{N_A} \quad , \quad \left(\frac{\partial\mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{p,T} = \frac{v}{N_A} ,$$

where s and v are the molar entropy and molar volume, respectively. This yields the linear system,

$$\begin{pmatrix} s_V - s_L & v_L - v_V \\ s_S - s_V & v_V - v_S \end{pmatrix} \begin{pmatrix} \Delta T \\ \Delta p \end{pmatrix} = \begin{pmatrix} xRT_t^0 \\ 0 \end{pmatrix} .$$

This yields

$$\Delta T = \frac{(v_V - v_S) \cdot xRT_t^0}{s_V(v_L - v_S) + s_L(v_S - v_V) + s_S(v_V - v_L)}$$

$$\Delta p = \frac{(s_V - s_S) \cdot xRT_t^0}{s_V(v_L - v_S) + s_L(v_S - v_V) + s_S(v_V - v_L)} .$$

Note that we do not retain terms of order $x \Delta T$, because we have assumed x is small, *i.e.* a weak solution.

(3) A solution of 4.00 g of hemoglobin in 100 mL of water was prepared and its osmotic pressure was measured to be $\pi = 0.0130$ atm at $T = 280$ K. Estimate the molecular mass of hemoglobin.

Solution :

We use the formula $\pi v = xRT$ for the osmotic pressure π of weak solutions. Here v is the molar volume of the solvent, and x is the molar fraction of solute. If M is the molar mass of hemoglobin, then

$$x = \frac{4.00 \text{ g}}{M} \bigg/ \frac{100 \text{ g}}{18 \text{ g}} = \frac{18 \text{ g}}{25 M} ,$$

since the density of water is $1.0 \text{ g/cm}^3 = 1 \text{ g/mL}$. We then have

$$M = \frac{18}{25} \text{ g} \cdot \frac{RT}{\pi v}$$

$$= \frac{18 \text{ g}}{25} \cdot \frac{(8.314 \times 10^7 \text{ erg/mol K})(280 \text{ K})}{(0.013 \text{ atm})(1.013 \times 10^6 \text{ g/cm}^2 \text{ atm})(18 \text{ cm}^3/\text{mol})} = 70710 \text{ g} .$$

The actual value is $M = 65706 \text{ g}$.