

Homework Set #5

- 5.12 Which of the following has a higher chemical potential? If neither, answer "same." (a) $\text{H}_2\text{O}(s)$ or $\text{H}_2\text{O}(l)$ at water's normal melting point, (b) $\text{H}_2\text{O}(s)$ at -5°C and 1 bar or $\text{H}_2\text{O}(l)$ at -5°C and 1 bar, (c) benzene at 25°C and 1 bar or benzene in a 0.1 M toluene solution in benzene at 25°C and 1 bar.

The less stable species of a pair has a higher chemical potential. When both substances in a pair are at equilibrium, then they have the same chemical potential.

(a) Same

(b) $\text{H}_2\text{O}(l)$ at -5°C and 1 bar

(c) Benzene at 25°C and 1 bar. This is because $x_{\text{benzene}} < 1$ in the following relation:

$$\mu_{\text{benzene}}(l) = \mu_{\text{benzene}}^*(l) + RT \ln x_{\text{benzene}}$$

Therefore,

$$\mu_{\text{benzene}}(l) < \mu_{\text{benzene}}^*(l)$$

- 5.18 The solubility of N_2 in blood at 37°C and a partial pressure of 0.80 atm is $5.6 \times 10^{-4} \text{ mol L}^{-1}$. A deep-sea diver breathes compressed air with a partial pressure of N_2 equal to 4.0 atm. Assume that the total volume of blood in the body is 5.0 L. Calculate the amount of N_2 gas released (in liters) when the diver returns to the surface of water, where the partial pressure of N_2 is 0.80 atm.

Assuming N_2 is an ideal gas, the volume of N_2 released can be readily calculated from the number of moles of N_2 released, which in turn is related to the number of moles of N_2 dissolved in blood when the partial pressures of N_2 are 4.0 atm and 0.80 atm, respectively.

According to Henry's law, the solubility of a substance is proportional to the applied pressure. Therefore,

$$\frac{\text{Solubility of } \text{N}_2 \text{ when } P_{\text{N}_2} \text{ is 4.0 atm}}{\text{Solubility of } \text{N}_2 \text{ when } P_{\text{N}_2} \text{ is 0.80 atm}} = \frac{4.0 \text{ atm}}{0.80 \text{ atm}} = 5.0$$

$$\text{Solubility of } \text{N}_2 \text{ when } P_{\text{N}_2} \text{ is 4.0 atm} = 5.0 \left(5.6 \times 10^{-4} \text{ mol L}^{-1} \right) = 2.80 \times 10^{-3} \text{ mol}$$

When $P_{\text{N}_2} = 0.80 \text{ atm}$,

$$\text{Number of moles of } \text{N}_2 \text{ in blood} = \left(5.6 \times 10^{-4} \text{ mol L}^{-1} \right) (5.0 \text{ L}) = 2.80 \times 10^{-3} \text{ mol}$$

When $P_{\text{N}_2} = 4.0 \text{ atm}$,

$$\text{Number of moles of } \text{N}_2 \text{ in blood} = \left(2.80 \times 10^{-3} \text{ mol L}^{-1} \right) (5.0 \text{ L}) = 1.40 \times 10^{-2} \text{ mol}$$

When the diver returns to the surface of water,

$$\text{Number of moles of } \text{N}_2 \text{ released} = 1.40 \times 10^{-2} \text{ mol} - 2.80 \times 10^{-3} \text{ mol} = 1.12 \times 10^{-2} \text{ mol}$$

and therefore,

$$\text{Volume of } \text{N}_2 \text{ released} = \frac{(1.12 \times 10^{-2} \text{ mol}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (310 \text{ K})}{0.80 \text{ atm}} = 0.36 \text{ L}$$

- 5.28 A common antifreeze for car radiators is ethylene glycol, $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$. How many milliliters of this substance would you add to 6.5 L of water in the radiator if the coldest day in winter is -20°C ? Would you keep this substance in the radiator in the summer to prevent the water from boiling? (The density and boiling point of ethylene glycol are 1.11 g cm^{-3} and 470 K , respectively.)

The molality of ethylene glycol that can depress the freezing point by 20°C or 20 K is

$$m_2 = \frac{\Delta T}{K_f} = \frac{20\text{ K}}{1.86\text{ K mol}^{-1}\text{ kg}} = 10.75\text{ mol kg}^{-1}$$

Assuming the density of water is 1 kg L^{-1} , the mass of water in the radiator is 6.5 kg , which, together with the molality of ethylene glycol, gives the number of moles of ethylene glycol.

$$\text{Number of moles of ethylene glycol} = (10.75\text{ mol kg}^{-1})(6.5\text{ kg}) = 69.88\text{ mol}$$

which corresponds to a volume of

$$V = \frac{(69.88\text{ mol})(62.07\text{ g mol}^{-1})}{1.11\text{ g cm}^{-3}} = 3.91 \times 10^3\text{ cm}^3 = 3.91 \times 10^3\text{ mL}$$

Since it has a higher boiling point, ethylene glycol can also elevate the boiling point of water. With a 10.75 m solution, the boiling point of water will be elevated by

$$\Delta T = K_b m_2 = (0.51\text{ K mol}^{-1}\text{ kg})(10.75\text{ mol kg}^{-1}) = 5.5\text{ K}$$

Therefore, keeping ethylene glycol in the radiator in the summer will increase the boiling point by 5.5°C .

- 5.48 The following data give the pressures for carbon disulfide–acetone solutions at 35.2°C . Calculate the activity coefficients of both components based on deviations from Raoult's law and Henry's law. (*Hint*: First determine Henry's law constants graphically.)

x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
$P_{\text{CS}_2}/\text{torr}$	0	272	390	438	465	512
$P_{\text{C}_3\text{H}_6\text{O}}/\text{torr}$	344	291	250	217	180	0

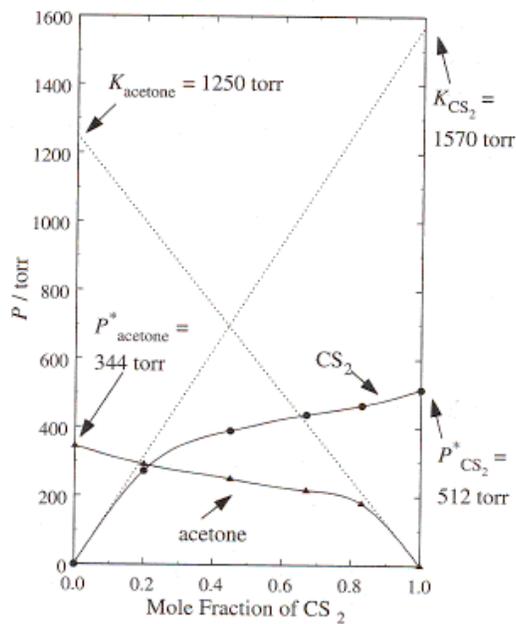
From a graph of the vapor pressure data, Henry's law constants may be obtained from the limiting slopes of the curves as they approach their respective infinite dilution (mole fraction equals zero) limits. (Note that the graph pictured is scaled to show the $x = 1$ intercept of each Henry's law line. In making the actual determination of the limiting slopes it is better to use an expanded scale that shows the limiting behavior in detail.) The Henry's law constants obtained from these data are $K_{\text{CS}_2} = 1570\text{ torr}$ and $K_{\text{C}_3\text{H}_6\text{O}} = 1250\text{ torr}$. The activity coefficient of the i^{th} component accounts for deviations from Henry's law as

$$P_i = K_i \gamma_i x_i$$

or

$$\gamma_i = \frac{P_i}{K_i x_i}$$

The necessary data to find the Henry's law activity coefficients, $\gamma_i(\text{H})$ are in the table. (Note that $x_{\text{C}_3\text{H}_6\text{O}} = 1 - x_{\text{CS}_2}$.)



x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
$P_{\text{CS}_2}/\text{torr}$	0	272	390	438	465	512
$P_{\text{C}_3\text{H}_6\text{O}}/\text{torr}$	344	291	250	217	180	0
$\gamma_{\text{CS}_2}(\text{H})$	1.00	0.87	0.55	0.42	0.36	0.33
$\gamma_{\text{C}_3\text{H}_6\text{O}}(\text{H})$	0.28	0.29	0.36	0.53	0.85	1.00

The Raoult's law activity is found through deviations from Raoult's law via

$$P_i = \gamma_i x_i P_i^*$$

or

$$\gamma_i = \frac{P_i}{x_i P_i^*}$$

The tabulated data are used once again, noting that the vapor pressures of the pure components are included, namely $P_{\text{CS}_2}^* = 512$ torr and $P_{\text{C}_3\text{H}_6\text{O}}^* = 344$ torr. The Raoult's law activity is denoted $\gamma_i(\text{R})$, and is not defined at zero mole fraction.

x_{CS_2}	0	0.20	0.45	0.67	0.83	1.00
$P_{\text{CS}_2}/\text{torr}$	0	272	390	438	465	512
$P_{\text{C}_3\text{H}_6\text{O}}/\text{torr}$	344	291	250	217	180	0
$\gamma_{\text{CS}_2}(\text{R})$	—	2.66	1.69	1.28	1.09	1.00
$\gamma_{\text{C}_3\text{H}_6\text{O}}(\text{R})$	1.00	1.06	1.32	1.91	3.08	—

The activities determined from the two laws differ because the standard state is chosen differently in the two cases.

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- 5.52** Consider a binary liquid mixture A and B, where A is volatile and B is nonvolatile. The composition of the solution in terms of mole fraction is $x_A = 0.045$ and $x_B = 0.955$. The vapor pressure of A from the mixture is 5.60 mmHg, and that of pure A is 196.4 mmHg at the same temperature. Calculate the activity coefficient of A at this concentration.

The activity of A is

$$a_A = \frac{P_A}{P_A^*} = \frac{5.60 \text{ mmHg}}{196.4 \text{ mmHg}} = 2.851 \times 10^{-2}$$

The activity coefficient of A is

$$\gamma_A = \frac{a_A}{x_A} = \frac{2.851 \times 10^{-2}}{0.045} = 0.63$$

- 5.21** A mixture of ethanol and *n*-propanol behaves ideally at 36.4° C. (a) Determine graphically the mole fraction of *n*-propanol in a mixture of ethanol and *n*-propanol that boils at 36.4° C and 72

mmHg. (b) What is the total vapor pressure over the mixture at 36.4° C when the mole fraction of *n*-propanol is 0.60? (c) Calculate the composition of the vapor in (b). (The equilibrium vapor pressures of ethanol and *n*-propanol at 36.4° C are 108 mmHg and 40.0 mmHg, respectively.)

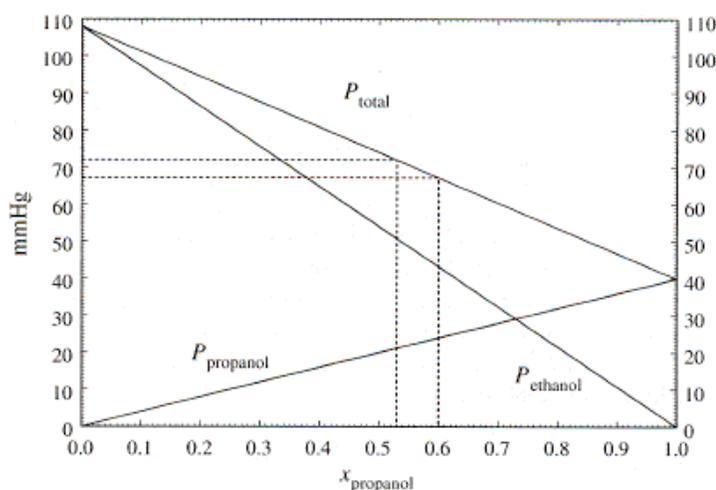
(a) The vapor pressure of ethanol, P_{ethanol} , the vapor pressure of propanol, P_{propanol} and the total vapor pressure, P_{total} , can each be expressed as a function of the mole fraction of ethanol, x_{ethanol} :

$$P_{\text{ethanol}} = x_{\text{ethanol}} P_{\text{ethanol}}^* = x_{\text{ethanol}} (108 \text{ mmHg}) = (1 - x_{\text{propanol}}) (108 \text{ mmHg})$$

$$P_{\text{propanol}} = x_{\text{propanol}} P_{\text{propanol}}^* = x_{\text{propanol}} (40.0 \text{ mmHg})$$

$$P_{\text{total}} = P_{\text{ethanol}} + P_{\text{propanol}}$$

These relations are plotted below.



The vapor pressure of the mixture is the same as the external pressure when it boils. According to the graph, when the total vapor pressure is 72 mmHg, the mole fraction of propanol is 0.53 and the mole fraction of ethanol is $1 - 0.53 = 0.47$.

(b) According to the graph, when the mole fraction of propanol is 0.60, the total vapor pressure is 67.2 mmHg.

(c) The vapor pressure of each component can be written in terms of (1) its mole fraction in the vapor and the total pressure or (2) its mole fraction in the solution and the vapor pressure of the pure component.

$$P_{\text{ethanol}} = x_{\text{ethanol}}^{\text{v}} P_{\text{total}} = x_{\text{ethanol}} P_{\text{ethanol}}^*$$

$$P_{\text{propanol}} = x_{\text{propanol}}^{\text{v}} P_{\text{total}} = x_{\text{propanol}} P_{\text{propanol}}^*$$

Take the ratio between P_{ethanol} and P_{propanol} :

$$\frac{P_{\text{ethanol}}}{P_{\text{propanol}}} = \frac{x_{\text{ethanol}}^{\text{v}} P_{\text{total}}}{x_{\text{propanol}}^{\text{v}} P_{\text{total}}} = \frac{x_{\text{ethanol}} P_{\text{ethanol}}^*}{x_{\text{propanol}} P_{\text{propanol}}^*}$$

$$\frac{x_{\text{ethanol}}^{\text{v}}}{x_{\text{propanol}}^{\text{v}}} = \frac{(0.40) (108 \text{ mmHg})}{(0.60) (40.0 \text{ mmHg})} = 1.80$$

$$x_{\text{ethanol}}^{\text{v}} = 1.80 x_{\text{propanol}}^{\text{v}} = 1.80 (1 - x_{\text{ethanol}}^{\text{v}})$$

$$2.80 x_{\text{ethanol}}^{\text{v}} = 1.80$$

$$x_{\text{ethanol}}^{\text{v}} = 0.64$$

$$x_{\text{propanol}}^{\text{v}} = 1 - 0.64 = 0.36$$