SIMPLE MIXTURES
Chapter 5 Outline

HW: Questions are below. Solutions are in separate file on the course web site.

Sect.	Title and Comments	Required?
1.	Partial Molar Quantities	YES
2.	The Thermodynamics of Mixing	YES
3.	The Chemical Potentials of Liquids	YES
4.	Liquid Mixtures We will not cover Sect. 4.b on Excess Functions and Regular Solutions.	MOST
5.	Colligative Properties	YES
6.	Vapor Pressure Diagrams	NO
7.	Temperature-Compositon Diagrams	NO
8.	Liquid-Liquid Phase Diagrams	NO
9.	Liquid-Solid Phase Diagrams	NO
10.	The Solvent Activity I'll just discuss real solutions briefly, introducing activities and activity coefficients. We won't perform any calculations on real solutions.	A LITTLE
11.	The Solute Activity I'll just discuss real solutions briefly, introducing activities and activity coefficients. We won't perform any calculations on real solutions.	A LITTLE
12.	The Activities of Regular Solutions	NO
13..	The Activities of Ions in Solution	NO

Chapter 5 Homework Questions

5.1   At 25 °C, the density of a 50% by mass of an Ethanol-Water solution is 0.914 g/cm^3. Given that the Partial Molar Volume of water in the solution is 17.4 cm^3/mol, calculate the Partial Molar Volume of Ethanol in the solution.
Note: M(Ethanol) = 46. g/mol , M(Water) = 18. g/mol.

5.2   The vapor pressure of pure benzene (C_6H_6, M=78) is 53.3 kPa at 60 °C. When 19. grams of an involatile organic compound is dissolved in 500 g of Benzene, the vapor pressure drops to 51.5 kPa.

Calculate the Molar Mass of the organic compound.

5.3   The freezing point of pure CCl_4(liq) is -22.9 °C and the Freezing Point Depression constant is 30 °C. When 100 grams of an unknown organic compound is added to 750 grams of CCl_4(l), the freezing point of the mixture is -33.4 °C

Calculate the Molar Mass of the organic compound.

5.4   The boiling point of pure benzene is 80.1 °C and the Boiling Point Elevation constant is 2.13 °C/m. When a sample of napthalene ($C_{10}H_8$) is dissolved in 600. grams of Benzene, the boiling point boiling point of the mixture is 81.3 °C.

How many grams of napthalene were dissolved in the benzene.

5.5   When 0.15 grams of an unknown compound is dissolved in 100 mL of aqueous solution, the measured osmotic pressure of the solution is 0.65 kPa at 25 °C. Calculate the molar mass of the unknown compound.

5.6   Consider two containers separated by a partition. Container A is of volume 5 L, and contains N_2(g) at 2.0 atm and 30 °C. Container B is of volume 10 L, and contains H_2(g) at 2.0 atm and 30 °C.

Calculate the Entropy of mixing and the Gibbs Energy of mixing when the partition between the two partitions is removed.

5.7   Air is a mixture of primarily 3 gases with composition:
$x_{N2} = 0.78$, $x_{O2} = 0.21$, $x_{Ar} = 0.01$

Calculate the Entropy of mixing when 5 moles of air of the above composition is prepared from the above pure gases.

5.8   The freezing point of 1-butanol is 25.8 °C and its depression constant is 8.2 °C/m. When 4.0 grams of acetonitrile (CH_3CN, M = 41) is dissolved in 650 grams of 1-butanol, the freezing point of the mixture is 21.5 °C.

Calculate the activity coefficient of acetonitrile in 1-butanol.

Chapter 5

Simple Mixtures

Partial Molar Quantities

Partial Molar Volume

Imagine adding 1 mole (18 g) of $H_2O(l)$ to a very large volume of water.
The volume would increase by 18 cm^3, and we would say that

$$\frac{dV}{dn} = 18 \; cm^3 / mol$$ and would call this the Partial Molar Volume of water.

If, instead, we added 1 mole of water to a very large volume of ethanol,
the volume would increase by only 14 cm^3 because of packing effects.
Under these conditions, the Partial Molar Volume of water is 14 cm^3/mol.

Thus, the volume increase depends upon the nature of the solution; i.e.
the number of moles of the various components.

In general, the Partial Molar Volume, V_J , of a substance J is defined as:

$$V_J = \left(\frac{\partial V}{\partial n_J} \right)_{p,T,n'}$$ n' indicates that the numbers of moles of all components
except J are held constant.

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Dependence of V_{H2O} and V_{EtOH} on composition in a binary water/ethanol solution.
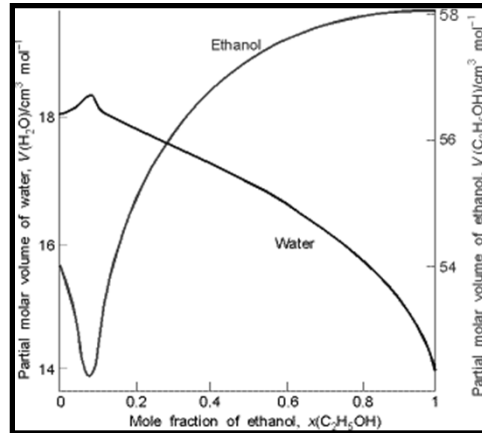
For a binary mixture of A and B, the incremental change in volume is given by:

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{T,p,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{T,p,n_A} dn_B = V_A dn_A + V_B dn_B$$

Integrate this expression under conditions of constant composition so that V_A and V_B are constant, to find that the total volume of the mixture, V, is given by:

$$V = V_A n_A + V_B n_B$$

This is may be generalized to an N component system:

$$dV = \sum_{J=1}^{N}\left(\frac{\partial V}{\partial n_J}\right)_{T,p,n'} dn_J = \sum_{J=1}^{N} V_J dn_J = V_1 dn_1 + V_2 dn_2 + ...$$

n' indicates that all $n_j \neq n_i$ are held constant

and $V = \sum_{J=1}^{N} V_J n_J = V_1 n_1 + V_2 n_2 + ...$

Example: Exer. 5.2(b)

At 20 °C, the density of a 20% by mass solution of Ethanol and Water is 0.97 g/cm^3.

Given that the Partial Molar Volume of ethanol in this solution is 52.2 cm^3/mol, what is the Partial Molar Volume of water?

Hint: Assume 1000 cm^3 of solution.

M(EtOH) = 46 g/mol
M(H$_2$O) = 18 g/mol

m(EtOH) = 194 g → n(EtOH) = 4.22 mol
m(H$_2$O) = 776 g → n(H$_2$O) = 43.1 mol
V(H$_2$O) = 18.1 cm^3/mol

Partial Molar Gibbs Energy

We introduced the Partial Molar Gibbs Energy, which is also called the Chemical Potential (μ), in Chapter 3.

$$dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i$$

where: $\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,p,n'}$ n' indicates that all $n_j \neq n_i$ are held constant

If Pressure and Temperature are held constant, then one has:

$$dG = \sum_{i=1}^{N} \mu_i dn_i = \mu_1 dn_1 + \mu_2 dn_2 + ...$$

Similar to Partial Molar Volumes, this expression can be integrated under conditions of constant composition (so that the μ_i's remain constant) to yield:

$$G = \sum_{i=1}^{N} \mu_i n_i = \mu_1 n_1 + \mu_2 n_2 + ...$$

The Gibbs-Duhem Equation

We are going to develop an expression relating changes in the chemical potentials ($d\mu_i$) of various components in a mixture.

From above, we have: $dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i = \sum_{i=1}^{N} \mu_i dn_i$

We also have: $G = \sum_{i=1}^{N} \mu_i n_i$ if T, p are constant

Taking the differential of the latter expression gives:

$$dG = \sum_{i=1}^{N} \mu_i dn_i + \sum_{i=1}^{N} n_i d\mu_i = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \ldots$$

The two equations for dG must be equal:

$$\sum_{i=1}^{N} \mu_i dn_i + \sum_{i=1}^{N} n_i d\mu_i = \sum_{i=1}^{N} \mu_i dn_i$$

which finally gives: $\sum_{i=1}^{N} n_i d\mu_i = 0$ **Gibbs-Duhem Equation**

Note: You are **not** responsible for the derivation..

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which finally gives: $\sum_{i=1}^{N} n_i d\mu_i = 0$ **Gibbs-Duhem Equation****

The significance of the Gibbs-Duhem Equation is that the Chemical Potential of one component of a mixture cannot change independently of the Chemical Potentials of the other components.

For example, in a binary mixture (components A and B), one has:

$$n_A d\mu_A + n_B d\mu_B = 0$$

This equation shows that if the chemical potential of one component increases, that of the other component must decrease; e.g.

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

The Gibbs-Duhem Equation for Chemical Potential and other quantities has important applications throughout thermodynamics.

Note: This is just a special case of the Gibbs-Duhem equation, which can be derived for any Partial Molar Quantities (e.g. the Partial Molar Volume, V_i).

The Thermodynamics of Mixing

The Chemical Potential of a Gas

In Chapter 3, we developed the following equation for the pressure dependence of the Molar Gibbs Energy of a gas:

$$G_m(p_{fin}) = G_m(p_{init}) + RT \ln\left(\frac{p_{fin}}{p_{init}}\right) \quad \text{or, remembering that } \mu \equiv G_m$$

$$\mu(p_{fin}) = \mu(p_{init}) + RT \ln\left(\frac{p_{fin}}{p_{init}}\right)$$

If we take the standard reference state as $p^o = 1$ bar, with $\mu(p^o) = \mu^o$, then the chemical potential at any other pressure, p, is:

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

It is common (and convenient) to leave off the p^o, giving:

$$\mu = \mu^o + RT \ln p$$

The Gibbs Energy of Mixing ($\Delta_{mix}G$) of Perfect Gases

Consider two containers at the same temperature and pressure, each with a pure gas, A (n_A moles) and B (n_B moles)
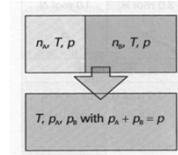
We would like to consider the Gibbs Energy change when we mix these gases. The mixture is in a new container, with $V = V_A + V_B$, and total pressure, $p = p_A + p_B$.

The initial Gibbs Energy of the two gases in their separate containers is:

$$G_{init} = n_A\mu_A + n_B\mu_B = n_A\left(\mu_A^o + RT \ln p\right) + n_B\left(\mu_B^o + RT \ln p\right)$$

After mixing, the partial pressures of the two gases are p_A and p_B, with $p_A + p_B = p$. The final Gibbs Energy of the mixture is:

$$G_{fin} = n_A\mu_A + n_B\mu_B = n_A\left(\mu_A^o + RT \ln p_A\right) + n_B\left(\mu_B^o + RT \ln p_B\right)$$

Initial: $G_{init} = n_A\left(\mu_A^o + RT\ln p\right) + n_B\left(\mu_B^o + RT\ln p\right)$

Final: $G_{fin} = n_A\left(\mu_A^o + RT\ln p_A\right) + n_B\left(\mu_B^o + RT\ln p_B\right)$

Therefore, the Gibbs Energy change of mixing is given by:

$$\Delta_{mix}G = G_{fin} - G_{init}$$
$$= \left[n_A\left(\mu_A^o + RT\ln p_A\right) + n_B\left(\mu_B^o + RT\ln p_B\right)\right]$$
$$- \left[n_A\left(\mu_A^o + RT\ln p\right) + n_B\left(\mu_B^o + RT\ln p\right)\right]$$

With simplification:

$$\Delta_{mix}G = n_A RT\left[\ln p_A - \ln p\right] + n_B RT\left[\ln p_B - \ln p\right]$$
$$= n_A RT\ln\left(\frac{p_A}{p}\right) + n_B RT\ln\left(\frac{p_B}{p}\right)$$

We can simplify this further by using: $n_A = x_A n \quad and \quad n_B = x_B n$
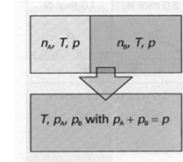
and Dalton's Law: $x_A = \frac{p_A}{p} \quad and \quad x_B = \frac{p_B}{p}$

$$\Delta_{mix}G = n_A RT\ln\left(\frac{p_A}{p}\right) + n_B RT\ln\left(\frac{p_B}{p}\right)$$

We can simplify this further by using: $n_A = x_A n \quad and \quad n_B = x_B n$

and Dalton's Law: $x_A = \frac{p_A}{p} \quad and \quad x_B = \frac{p_B}{p}$

$$\Delta_{mix}G = nRT\left[x_A\ln x_A + x_B\ln x_B\right]$$

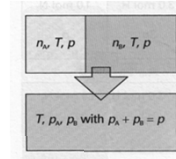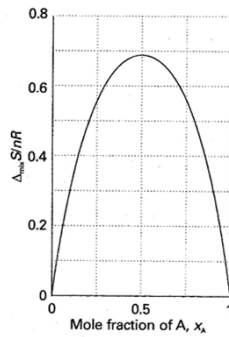| x_A	$\Delta_{mix}G/nRT$
0.1	-0.33
0.2	-0.50
0.3	-0.61
0.4	-0.67
0.5	**-0.69**
0.6	-0.67
0.7	-0.61
0.8	-0.50
0.9	-0.33

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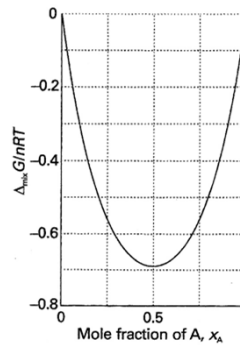
The Entropy of Mixing ($\Delta_{mix}S$) of Perfect Gases

$$dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B \quad \longrightarrow \quad -S = \left(\frac{\partial G}{\partial T}\right)_{p,n_A,n_B}$$

Therefore: $\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -\left[\frac{\partial}{\partial T}\left(nRT\left[x_A \ln x_A + x_B \ln x_B\right]\right)\right]_{p,n_A,n_B\ p,n_A,n_B}$

$$\Delta_{mix}S = -nR\left[x_A \ln x_A + x_B \ln x_B\right]$$

x_A	Δ_{mix}/nR
0.1	0.33
0.2	0.50
0.3	0.61
0.4	0.67
0.5	**0.69**
0.6	0.67
0.7	0.61
0.8	0.50
0.9	0.33

The Enthalpy of Mixing ($\Delta_{mix}H$) of Perfect Gases

$\Delta_{mix}G = nRT\left[x_A \ln x_A + x_B \ln x_B\right]$ negative for all x_A, x_B

$\Delta_{mix}S = -nR\left[x_A \ln x_A + x_B \ln x_B\right]$ positive for all x_A, x_B

$\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S \rightarrow \Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S$

$\Delta_{mix}H = nRT\left[x_A \ln x_A + x_B \ln x_B\right] + T\left\{-nR\left[x_A \ln x_A + x_B \ln x_B\right]\right\}$

$\Delta_{mix}H = 0$ It is not at all surprising the the Enthalpy of Mixing is 0, because there are no attractive or repulsive forces in Perfect Gases.
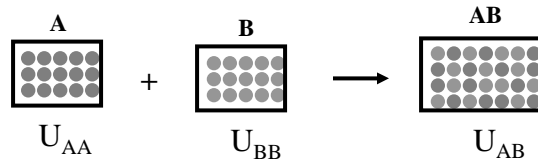
Thus, we see that the spontaneous mixing of two gases is an entropically driven process.
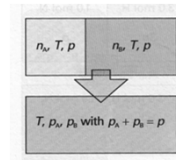
The Chemical Potential of Liquids

Ideal Solutions: Raoult's Law

A   B   AB

U_{AA} U_{BB} U_{AB}
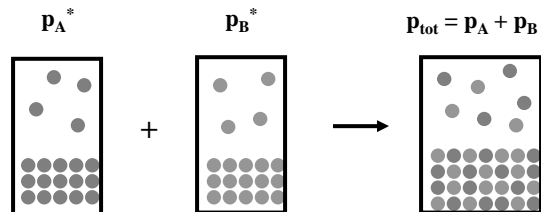
Ideal Mixture: $U_{AA} \approx U_{BB} \approx U_{AB}$

Nearly Ideal Mixtures: Benzene-Toluene
                                    Hexane-Octane

Non-Ideal Mixtures: Chloroform-Acetone
                                    Ethanol-Water

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p_A^* p_B^* $p_{tot} = p_A + p_B$

p_A^* is the vapor pressure above pure liquid A

p_B^* is the vapor pressure above pure liquid B

$p_A = x_A p_A^*$ x_A = Mole Fraction of A in mixture

$p_B = x_B p_B^*$ x_B = Mole Fraction of B in mixture

$$p_{tot} = x_A p_A^* + x_B p_B^*$$

Raoult's Law

The Chemical Potential in Ideal Solutions

We will use a superscript asterisk (*) to indicate a pure liquid. Thus the chemical potential would be denoted as μ_A^* or $\mu_A^*(l)$

Because a pure liquid must be in equilibrium with its vapor, the chemical potential of the liquid is given by:

$$\mu_A^* = \mu_A^*(l) = \mu_A(g) = \mu_A^o + RT\ln p_A^* \qquad \text{pure liquid}$$

μ_A^o is the chemical potential of the gas at $p^o = 1$ bar

p_A^* is the vapor pressure of the pure liquid

If another substance (solute) is present in the liquid, the chemical potential of the liquid is changed to μ_A and its vapor pressure is changed to p_A

$$\mu_A = \mu_A^o + RT\ln p_A \qquad \text{liquid in solution}$$

p_A is the vapor pressure of A in the solution

$$\mu_A^* = \mu_A^o + RT\ln p_A^* \qquad \text{pure liquid}$$

$$\mu_A = \mu_A^o + RT\ln p_A \qquad \text{liquid in solution}$$

We can combine the equations to eliminate μ_A^o (subtract first from second):

$$\mu_A - \mu_A^* = RT\ln p_A - RT\ln p_A^*$$

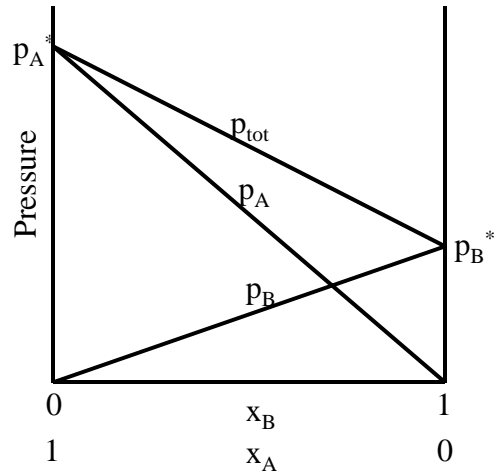or: $\quad \mu_A = \mu_A^* + RT\ln\left(p_A \Big/ p_A^*\right) = \mu_A^* + RT\ln x_A$

using Raoult's Law

Therefore, an ideal solution is one in which the chemical potential of each component is given by:
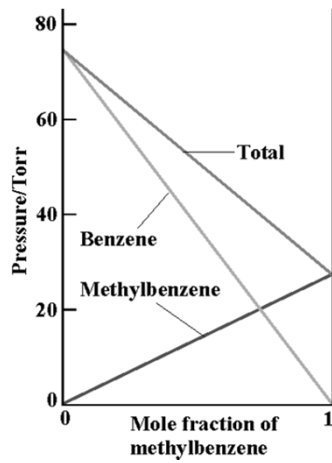
$$\mu_i = \mu_i^* + RT\ln x_i$$

The Component Vapor Pressures in an Ideal Solution
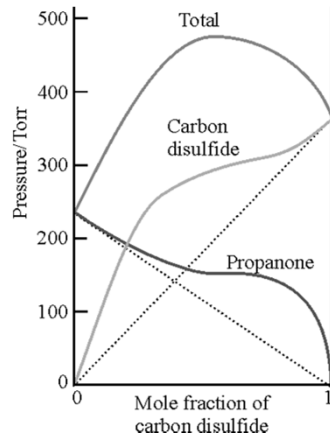

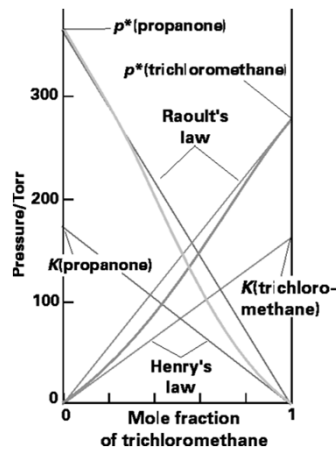$$p_{tot} = x_A p_A^* + x_B p_B^*$$

A Nearly Ideal Solution

Positive Deviations from Raoult's Law

Negative Deviations from Raoult's Law

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Ideal Dilute Solutions

Consider a solution with solvent, A, and solute, B.
If it is an ideal solution, the vapor pressures of solvent and solute are given by:

$$p_A = x_A p_A^*$$

and $p_B = x_B p_B^*$

It is found in many real dilute solutions ($x_B << x_A$) that,
while the solvent vapor pressure is given by the expression above,
the solute vapor pressure is still proportional to x_B, but the proportionality
constant is *not* p_B^*, but an empirical constant.

$$p_A = x_A p_A^*$$

and $p_B = x_B K_B$

This is called Henry's Law, and the Henry's Law constant, K_B, is a function
of the nature of the solute, B.

The Properties of Solutions

Thermodynamics of Mixing of Ideal Solutions

If we have n_A moles of A and n_B moles of B, then the initial Gibbs Energy
of the pure liquids *before* mixing is:

$$G_{init} = n_A \mu_A^* + n_B \mu_B^*$$

After mixing, the final Gibbs Energy of the solution is:

$$G_{fin} = n_A \mu_A + n_B \mu_B = n_A \left[\mu_A^* + RT \ln x_A \right] + n_B \left[\mu_B^* + RT \ln x_B \right]$$

It is straightforward to show that the Gibbs Energy of Mixing is:

$$\Delta_{mix} G = G_{fin} - G_{init} = nRT \left[x_A \ln x_A + x_B \ln x_B \right]$$

This is **identical** to the expression for the Gibbs Energy of Mixing of
Perfect Gases.

$$\Delta_{mix}G = nRT\left[x_A \ln x_A + x_B \ln x_B\right]$$

This is **identical** to the expression for the Gibbs Energy of Mixing of Perfect Gases.

Similarly, it can be shown that the expressions for $\Delta_{mix}S$ and $\Delta_{mix}H$ are the same as for Perfect Gas mixtures.

$$\Delta_{mix}S = -nR\left[x_A \ln x_A + x_B \ln x_B\right]$$

$$\Delta_{mix}H = 0$$

Excess Functions

Often, the mixing properties of Real solutions are discussed in terms of excess functions; e.g.

$$S^E = \Delta_{mix}S(\exp) - \Delta_{mix}S(ideal) = \Delta_{mix}S(\exp) - nR\left[x_A \ln x_A + x_B \ln x_B\right]$$

This is discussed in somewhat more detail in the text (Sect. 5.4b), but we will not go into excess functions any further.

Colligative Properties

Colligative properties of a solution are properties which depend only upon the number of moles of a solute, and not upon its specific nature.

- Vapor Pressure Lowering
  When an involatile (e.g. solid) solute is dissolved in a solvent, the vapor pressure drops below that of the pure solvent.

- Boiling Point Elevation
  When an involatile (e.g. solid) solute is dissolved in a solvent, the boiling point of the solution is higher than that of the pure solvent.

- Freezing Point Depression
  When a solute (usually a solid) is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent.

- Osmotic Pressure
  Solvent tends to flow from a pure solvent chamber into a solution chamber until a sufficient pressure (the "Osmotic Pressure") has developed to stop further flow.
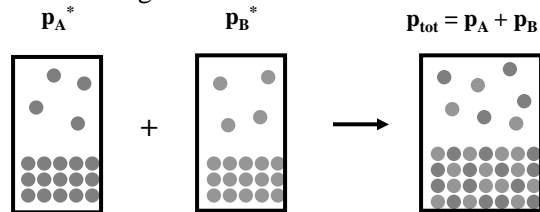
Colligative Properties

All four colligative properties are independent of the nature of the solute (B), but stem from the fact that the solute will lower the chemical potential of the solvent (A):

$$\mu_A = \mu_A^* + RT \ln x_A \; < \; \mu_A^*$$

Freezing Point Depression

Boiling Point Elevation
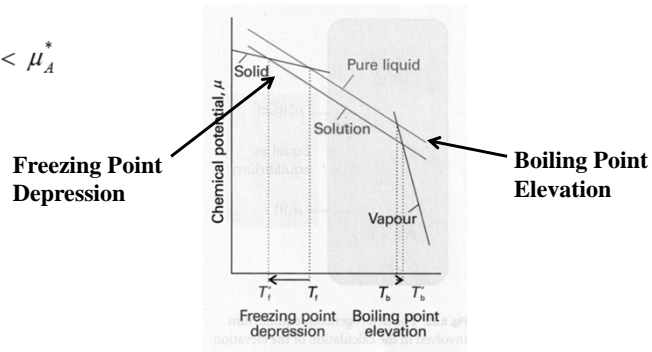
Vapor Pressure Lowering

$$p_A^* \qquad\qquad p_B^* \qquad\qquad p_{tot} = p_A + p_B$$

$p_A = x_A p_A^*$ x_A = Mole Fraction of A in mixture

$p_B = x_B p_B^*$ x_B = Mole Fraction of B in mixture

Raoult's Law: $p_{tot} = x_A p_A^* + x_B p_B^*$

In the special (but important) case that the solute, B, is non-volatile, it's pure vapor pressure will be: $p_B^* \approx 0$

In this case, Raoult's Law reduces to: $p_{tot} = p_A = x_A p_A^*$

For $x_A < 1$, $p_A < p_A^*$

Application of Raoult's Law: Determining the Molar Mass
of a compound.

Example: The vapor pressure of 2-propanol (M=60) is 50.0 Torr at 27 °C,
but fell to 49.6 torr when 8.7 g of an involatile organic compound was dissolved
in 250 g of 2-propanol.

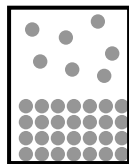Calculate the Molar Mass of the unknown compound.

$$x_{prop} = 0.992$$

$$n_X = 0.034 \text{ mol}$$
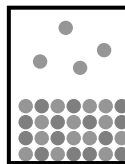
$$M_X = 260 \text{ g/mol}$$

Boiling Point Elevation

Pure Solvent	Solution

$$T = T_b^o$$
$$p = p_A^* = 1 \text{ atm.}$$
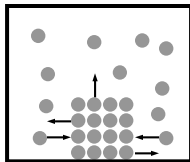
$$T = T_b^o$$
$$P = x_A p_A^* < 1 \text{ atm.}$$

Will no longer boil at T_b^o. Must raise
temperature until P rises back to 1 atm.

It can be shown (numerous texts) that the change in the boiling point, ΔT_b ,
can be expressed as a function of the solute molality, m_B .

$$\Delta T_b = T_b - T_b^o = K_b m_B$$

Freezing Point Depression

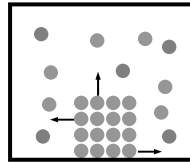Pure Solvent   Solution

$T = T_f^o$ $T = T_f^o$
Rate("pop off") = Rate("condense") Rate("pop off") > Rate("condense")

Will no longer freeze at T_f^o. Must lower
temperature until the two rates are equal.

It has been shown in various texts that the change in the freezing point, ΔT_f ,
can be expressed as a function of the solute molality, m_B .

$$\Delta T_f = T_f^o - T_f = K_f m_B$$

$$\Delta T_b = T_b - T_b^o = K_b m_B$$

$$\Delta T_f = T_f^o - T_f = K_f m_B$$

It can be shown that the Boiling Point Elevation Constant (aka the Ebullioscopic
constant) and the Freezing Point Depression Constant (Cryoscopic constant) are
given by:

$$K_b = \frac{M_A R \left(T_b^o\right)^2}{1000 \Delta_{vap} H^o} \quad \text{and} \quad K_f = \frac{M_A R \left(T_f^o\right)^2}{1000 \Delta_{fus} H^o}$$

M_A is the solvent Molar Mass
T_b^o and T_f^o are the pure solvent boiling and freezing temperatures
$\Delta_{vap} H^o$ and $\Delta_{fus} H^o$ are the solvent enthalpies of vaporization and fusion

Note that K_b and K_f depend solely upon solvent properties, and independent of
the particular solute.

Although K_f and K_b can be calculated from the above formulae, the tabulated
values in the literature are the empirical values, taken from experimental
determination using solutes of known Molar Mass.

Solvent K_f K_b

H_2O 1.86 K/m   0.51 K/m

Benzene 5.12   2.13

Phenol   7.27   3.04

CCl_4 30   4.95

Note that $K_f > K_b$. This is because $\Delta_{fus}H^o << \Delta_{vap}H^o$

$$K_b = \frac{M_A R\left(T_b^o\right)^2}{1000\Delta_{vap}H^o} \quad \text{and} \quad K_f = \frac{M_A R\left(T_f^o\right)^2}{1000\Delta_{fus}H^o}$$

Generally, the tabulated constants, K_f and K_b, are the empirical values determined from measurements with solutes of known Molar Mass.

Applications of freezing point depression and boiling point elevation measurements.

1. Determination of solute Molar Mass

2. Determination of fractional dissociation and equilibrium constants

3. Determination of solute "activity coefficients" (coming up)

Example: The addition of 5.0 g of an unknown compound to 250 g of Napthalene lowered the freezing point of the solvent by 0.78 ^{o}C

Calculate the Molar Mass of the unknown compound.

K_f (Nap) = 6.94 K/m

$m_X = 0.112$ m = 0.112 mol/kg

kg Nap = 0.25 kg

$n_X = 0.028$ mol

$M_X = 180$ g/mol

Osmotic Pressure

Lake
Pokeytenoqua

← **Wine bladder**

H_2O

H_2O →
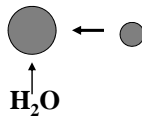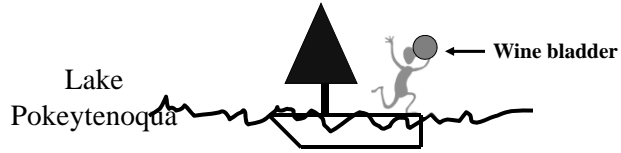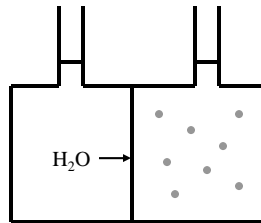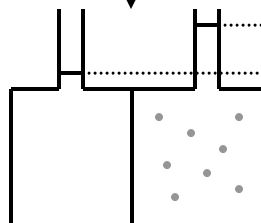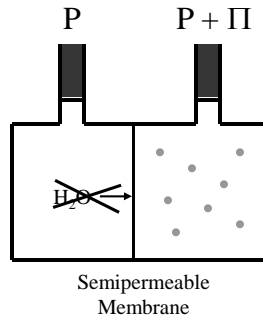
Semipermeable
Membrane

$\Pi = dgh$
= Osmotic Pressure

Static Osmometry:
Allow the two chambers
to equilibrate.

Semipermeable
Membrane

P   P + Π

Semipermeable
Membrane

Dynamic Osmometry: Apply pressure, Π, to prevent movement
of solvent between chambers.

It can be
shown that: $\boxed{\Pi V = n_B RT}$

Π = Osmotic Pressure

V = Volume of solution

n_B = Moles of Solute

R = Gas Constant

T = Temperature (in K)

Alternate form: $\Pi = (n_B/V)\, RT$

$\boxed{\Pi = [B]RT}$

[B] = Solute Molarity

A Sensitivity Comparison

Let's say that a sugar solution is prepared by dissolving 1 g of sucrose
(M = 342) in 1 L ($\approx$1 kg) of water.

The Molarity ($\approx$molality) of the solution is:

$$[Suc] \approx m_{Suc} = \frac{1g/342\,g\,/\,mol}{1L} = 2.92x10^{-3}\,M = 2.92x10^{-3}\,m$$

From K_f = 1.86 K/m, one has T_f = -0.005 °C
From K_b = 0.51 K/m, one has T_b = 100.0015 °C

Let's calculate Π (25 °C)

$$\Pi = [Suc]RT = (2.92x10^{-3}\,mol\,/\,L)(8.31kPa \cdot L\,/\,mol \cdot K)(298\,K)$$

$$= 7.23\,kPa\,x\,\frac{7.50\,torr}{1\,kPa} = 54\,torr$$

In contrast to freezing point depression, and boiling point elevation, which
are too small to be measured experimentally, the osmotic pressure can be
measured very accurately.

Application: Determination of Molar Mass from Osmotic Pressure

We will show a straightforward method for determining Molar Masses from
measured values of Π. The method is very similar to that used to calculate
Molar Mass from Freezing Point Depression or Boiling Point Elevation.

Afterwards, I will comment on the method presented in the text, which
is useful if one wishes very accurate determinations, but is not straightforward.

Example: When 2.0 g of Hemoglobin (Hb) is dissolved in 100 mL
          of solution, the osmotic pressure is 5.72 torr at 25 °C.

          Calculate the Molar Mass of Hemoglobin.   1 kPa = 7.50 torr
                                                       R = 8.31 kPa-L/mol-K

Procedure:

1. Calculate the Molarity of the unknown, [X] from Π = [X]RT
2. Determine the number of moles, n_X , using [X] and the solution volume
3. Determine the Molar Mass from: $M_X = mass_X/n_X$

Example: When 2.0 g of Hemoglobin (Hb) is dissolved in 100 mL
of solution, the osmotic pressure is 5.72 torr at 25 °C.

Calculate the Molar Mass of Hemoglobin.   1 kPa = 7.50 torr

Procedure: R = 8.31 kPa-L/mol-K

1. Calculate the Molarity of the unknown, [X] from $\Pi = [X]RT$

$$\Pi = 5.72\,torr \cdot 1\,kPa/7.50\,torr = 0.763\,kPa$$

$$[X] = \frac{\Pi}{RT} = \frac{0.763\,kPa}{(8.31\,kPa \cdot L/mol \cdot K)(298\,K)} = 3.08x10^{-4}\,mol/L$$

2. Determine the number of moles, n_X, using [X] and the solution volume

$$n_X = [X] \cdot V = (3.08x10^{-4}\,mol/L) \cdot (0.10\,L) = 3.08x10^{-5}\,mol$$

3. Determine the Molar Mass from: $M_X = mass_X/n_X$

$$M_X = \frac{mass_X}{n_X} = \frac{2.0\,g}{3.08x10^{-5}\,mol} = 6.49x10^{4}\,g/mol = 65,000\,g/mol$$

Note: The Boiling Point elevation and Freezing Point depression of the above
solution would be immeasurably small. Therefore, these techniques are useless
to determine Molar Masses of polymers.

Homework: When 3.0 g of an unknown compound is placed in 250 mL of
solution at 30 °C, the osmotic pressure is 62.4 kPa.

Calculate the Molar Mass of the unknown compound.

R = 8.31 kPa-L/mol-K

[X] = $2.48x10^{-2}$ mol/L

n_X = $6.20x10^{-3}$ mol

M_X = 480 g/mol

Note: The osmotic pressure, $\Pi = 62.4$ kPa = 470 mm Hg $\approx$ 0.50 meters,
can be measured to 0.1 % accuracy very easily.

In contrast, the freezing point depression (in aqueous solution) would be
~0.05 °C, which could only be measured to approximately 10-20% accuracy.

Note, once again, that Osmotic Pressure measurements are much more
sensitive than the other colligative properties.

FYI: Very Accurate Determination of Molar Masses from Π

Actually, the formula, $\Pi = [B]RT$, is only accurate in dilute solution.

In more concentrated solutions, one has: $\Pi = RT\left\{[J] + k[J]^2 + ...\right\}$

It is shown in the text (Example 5.4) that, writing $\Pi = \rho gh$ (hydrostatic pressure), and c = mass/Volume, one can derive the equation:

$$\frac{h}{c} = \frac{RT}{\rho ghM_X} + \left(\frac{RTk}{\rho gM^2}\right)c + ...$$

Then, an accurate value for M_X can be obtained from the intercept of a plot of h/c vs. c

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Real Solutions: Activities

Ideal Solutions

Earlier in the chapter, we showed that the solvent (A) and solute (B) chemical potentials are given by:

Solvent: $\mu_A = \mu_A^* + RT\ln\left(\frac{p_A}{p_A^*}\right) = \mu_A^* + RT\ln(x_A)$

Solute: $\mu_B = \mu_B^* + RT\ln\left(\frac{p_B}{p_B^*}\right) = \mu_B^* + RT\ln(x_B)$

Real Solutions

In solutions which are not ideal, the relatively simple formulae for the solvent and solute chemical potentials can be retained by replacing the mole fractions by activities (a_i):

Solvent: $\mu_A = \mu_A^* + RT\ln(a_A)$

Solute: $\mu_B = \mu_B^* + RT\ln(a_B)$

Real Solutions: Activities

Real Solutions

In solutions which are not ideal, the relatively simple formulae for the solvent and solute chemical potentials can be retained by replacing the mole fractions by activities (a_i):

Solvent: $\mu_A = \mu_A^* + RT \ln(a_A)$

Solute: $\mu_B = \mu_B^* + RT \ln(a_B)$

The activities can be related to the mole fractions by:
$a_A = \gamma_A x_A$ and $a_B = \gamma_B x_B$.

γ_A and γ_B are the activity coefficients, and can be calculated from thermodynamic measurements. Their deviation from $\gamma_i = 1$ characterizes the extent of non-ideality in a system.

Solute Activities in terms of molalities

In a dilute solution, it is more common to characterize solutes by their molality, rather than mole fraction in solution.

It is straightforward to show that, in a dilute solution, the molality, m_B, and mole fraction, x_B, are directly proportional:

$$x_B = \frac{n_B}{n_B + n_A} \approx \frac{n_B}{n_A} \quad (n_B \ll n_A \text{ in dilute solution})$$

If we assume an amount of solution containing 1 kg = 1000 g of solvent, then: $n_B = m_B$ and $n_A = 1000/M_A$ (solvent Molar Mass).

$$x_B \approx \frac{n_B}{n_A} = \frac{m_B}{1000 / M_A} = \left(\frac{M_A}{1000}\right) m_B \propto m_B$$

The solute chemical potential of an ideal solution, written in terms of molality rather than mole fraction, is:

$$\mu_B = \mu_B^+ + RT \ln m_B \qquad \mu_B^+ \text{ is different from the reference state, } \mu_B^\circ,$$
$$\text{when using mole fractions.}$$

For a non-ideal solute, we can then replace m_B by the activity, $a_B = \gamma_B m_B$

$$\mu_B = \mu_B^+ + RT \ln a_B = \mu_B^+ + RT \ln \gamma_B m_B$$

Activity Coefficients from Colligative Property Measurements

Earlier we discussed that the freezing point depression and boiling point elevation of a solution (assumed ideal) are given by:

$$\Delta T_f = K_f m_B \quad and \quad \Delta T_b = K_b m_B$$

If the solution is non-ideal, the solute molality, m_B, is replaced by its activity, a_B

$$\Delta T_f = K_f a_B = K_f \gamma_B m_B \quad and \quad \Delta T_b = K_b a_B = K_b \gamma_B m_B$$

Thus, the activity coefficient, γ_B, can be determined by a comparison of the measured colligative property with the value expected for an ideal solution:

$$\Delta T_f (\exp) = K_f a_B = \gamma_B \left(K_f m_B \right) = \gamma_B \Delta T_f (ideal)$$

$$\Delta T_b (\exp) = K_b a_B = \gamma_B \left(K_b m_B \right) = \gamma_B \Delta T_b (ideal)$$

Example: When 25 g of Napthalene ($C_{10}H_8$, M = 128) is placed in 500 g of benzene (K_f = 5.12 °C/m. T_f^o = 5.5 °C), the freezing point of the solution is 3.9 °C.

What is the activity coefficient of napthalene in this solution?

$$m_B = \frac{25\,g \Big/ 128\,g\,/\,mol}{0.50\,kg} = 0.391\,mol\,/\,kg = 0.391\,m$$

$$\Delta T_f(ideal) = K_f m_B = (5.12\,K\,/\,m)(0.391m) = 2.00\,K = 2.00\,^{\circ}C$$

$$\Delta T_f(\exp) = T_f^o - T_f = 5.5 - 3.9 = 1.6\,^{\circ}C$$

$$\Delta T_f(\exp) = K_f a_B = \gamma_B \left(K_f m_B \right) = \gamma_B \Delta T_f(ideal)$$

$$\downarrow$$

$$\gamma_B = \frac{\Delta T_f(\exp)}{\Delta T_f(ideal)} = \frac{1.6\,^{\circ}C}{2.0\,^{\circ}C} = 0.80$$