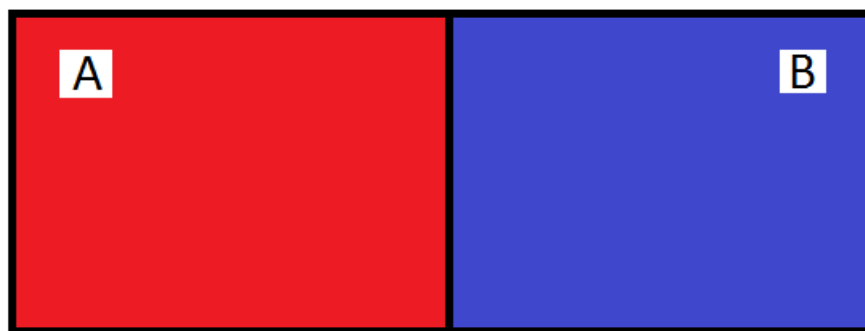


Chapter 7: Mixtures and Solutions

Up until this point, we have conserved single-component systems which do not change in composition. By and large, nature consists of much more complicated systems, containing many components and continually undergoing changes in composition through phase changes or chemical reactions or both! In order to expand our thermodynamic toolbox, we will begin by discussing mixtures.

Thermodynamics of mixing

A natural place to begin a discussion of mixtures is to consider a mixture of two gases. Consider samples of the two gases filling two partitions in a single container, both at the same pressure, temperature, having volumes V_A and V_B .



After being allowed to mix isothermally, the partial pressures of the two gases will drop by a factor of 2 (although the total pressure will still be the original value) and the volumes occupied by the two gases will double.



Enthalpy of Mixing

Assuming ideal behavior, so that interactions between individual gas molecules are unimportant, it is fairly easy to calculate ΔH for each gas, as it is simply an isothermal expansion. The total enthalpy of mixing is then given by

$$\Delta H_{mix} = \Delta H_A + \Delta H_B$$

And since the enthalpy change for an isothermal expansion of an ideal gas is zero,

$$\Delta H_{mix} = 0$$

is a straight-forward conclusion. This will be the criterion for an **ideal mixture**.

In general, real mixtures will deviate from this limiting ideal behavior due to interactions between molecules and other concerns. Also, many substances undergo chemical changes when they mix with other substances. But for now, we will limit ourselves to discussing mixtures in which no chemical reactions take place.

Entropy of Mixing

The entropy change induced due to isothermal mixing (assuming again no interactions between the molecules in the gas mixture) is again going to be the sum of the contributions from isothermal expansions of the two gases. Fortunately, entropy changes for isothermal expansions are easy to calculate for ideal gases.

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

If we use the initial volumes V_A and V_B for the initial volumes of gases A and B, the total volume after mixing is $V_A + V_B$, and the total entropy change is

$$\Delta S_{mix} = n_A R \ln \left(\frac{V_A + V_B}{V_A} \right) + n_B R \ln \left(\frac{V_A + V_B}{V_B} \right)$$

Noting that the term $\left(\frac{V_A + V_B}{V_A} \right)$ is $\frac{1}{x_A}$ (where x_A is the mole fraction of A after mixing), and that n_A can be expressed as the product of x_A and the total number of moles, the expression can be rewritten

$$\Delta S_{mix} = n_{tot} R [-x_A \ln(x_A) - x_B \ln(x_B)]$$

It should be noted that because the mole fraction is always between 0 and 1, that $\ln(x_i)$ is always a negative number. As such, the entropy change for a system undergoing isothermal mixing is always positive, as one might expect (since mixing will make the system less ordered.)

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Free Energy of Mixing

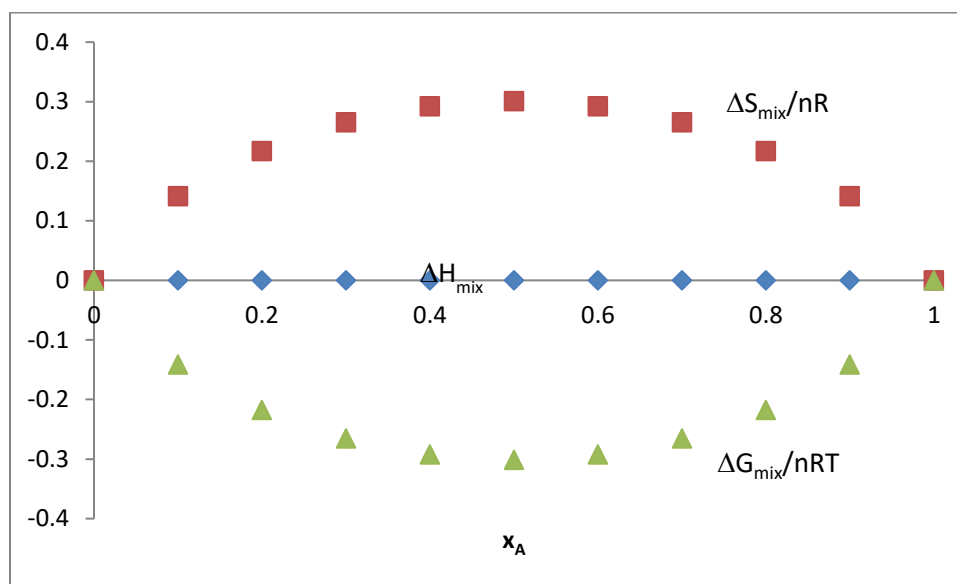
Calculating ΔG_{mix} should be no more difficult than calculating ΔS_{mix} . For isothermal mixing,, and constant total pressure

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

and so it follows from above that for the isothermal mixing of two gases at constant total pressure

$$\Delta G_{\text{mix}} = n_{\text{tot}}RT[x_A \ln(x_A) + x_B \ln(x_B)]$$

The relationships describing the isothermal mixing of two ideal gases A and B is summarized in the graph below.



Again, because $\ln(x_i)$ is always negative, ΔG_{mix} is also always negative, implying that mixing is always a spontaneous process. This is true for gases. But for many combinations of liquids or solids, the strong intermolecular forces may make mixing unfavorable (for example in the case of vegetable oil and water.) Also, these interactions may make the volume non-additive as well (as in the case of ethanol and water.)

Partial Molar Volume

The **partial molar volume** of compound A in a mixture of A and B can be defined as

$$V_A = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B}$$

Using this definition, a change in volume for the mixture can be described using the total differential of V:

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

or

$$dV = V_A dn_A + V_B dn_B$$

And integration yields

$$\begin{aligned} V &= \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B \\ &= V_A n_A + V_B n_B \end{aligned}$$

This result is important as it demonstrates an important quality of partial molar quantities. Specifically, if ξ_i represents the partial molar property X for component i of a mixture, The total property X for the mixture is given by

$$X = \sum_i \xi_i n_i$$

It should be noted that while the volume of a substance is never negative, the partial molar volume can be. An example of this appears in the dissolution of a strong electrolyte in water. Because the water molecules in the solvation sphere of the ions are physically closer together than they are in bulk pure water, there is a volume decrease when the electrolyte dissolves. This is easily observable at high concentrations where a larger fraction of the water in the sample is tied up in solvation of the ions.

Chemical Potential

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound *i* in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_{j \neq i}}$$

This particular partial molar function is of particular importance, and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. And since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function. In general, the total change in the Gibbs function (dG) can be calculated from

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_{j \neq i}} dn_i$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives as was done in chapter 6:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions U, H, A, or G:

$dU = TdS - pdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}}$
$dH = TdS + VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j \neq i}}$
$dA = -pdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j \neq i}}$
$dG = Vdp - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j \neq i}}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function is the most commonly used, and perhaps the most useful. As the partial most Gibbs function, it is easy to show that

$$d\mu = Vdp - SdT$$

Where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

And so at constant temperature

$$\int_{\mu^o}^{\mu} d\mu = \int_{p^o}^p V dp$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (κ_T is very small)

$$\begin{aligned}\int_{\mu^o}^{\mu} d\mu &= V \int_{p^o}^p dp \\ \mu - \mu^o &= V(p - p^o)\end{aligned}$$

Or

$$\mu = \mu^o + V(p - p^o)$$

Where p^o is a reference pressure (generally the standard pressure of 1 atm) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas

$$V = \frac{RT}{p}$$

And so at constant temperature

$$\int_{\mu^o}^{\mu} d\mu = RT \int_{p^o}^p \frac{dp}{p}$$

Or

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

The Gibbs-Duhem equation

For a system at equilibrium, the Gibbs-Duhem equation must hold:

$$\sum_i n_i d\mu_i = 0$$

This relationship places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition.

This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities,

$$G_{tot} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

But dG can also be expressed as

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

Setting these two expressions equal to one another

$$\sum_i n_i d\mu_i + \sum_i \mu_i dn_i = Vdp - SdT + \sum_i \mu_i dn_i$$

And after canceling the $\sum_i \mu_i dn_i$ term, one gets

$$\sum_i n_i d\mu_i = Vdp - SdT$$

For a system at constant temperature and pressure

$$Vdp - SdT = 0$$

This results in the **Gibbs-Duhem equation**,

$$\sum_i n_i d\mu_i = 0$$

This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium. So for a binary system, consisting of components A and B (the two most often studied compounds in all of chemistry)

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

Fugacity

The relationship for chemical potential

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

was derived assuming ideal gas behavior. But for real gases that deviate widely from ideal behavior, the expression has only limited applicability. In order to use the simple expression on real gases, a “fudge” factor is introduced called **fugacity**. Using fugacity instead of pressure, the chemical potential expression becomes

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

where f is the fugacity. Fugacity is related to pressure, but contains all of the deviations from ideality within it. To see how it is related to pressure, consider that a change in chemical potential for a single component system can be expressed as

$$d\mu = Vdp - SdT$$

And so

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V$$

Differentiating the expression for chemical potential above with respect to pressure at constant volume results in

$$\left(\frac{\partial \mu}{\partial p} \right)_T = \left\{ \frac{\partial}{\partial p} \left[\mu^o + RT \ln \left(\frac{f}{f^o} \right) \right] \right\}_T$$

which simplifies to

$$\left(\frac{\partial \mu}{\partial p} \right)_T = RT \left[\frac{\partial \ln(f)}{\partial p} \right]_T = V$$

Multiplying both sides by p/RT gives

$$p \left[\frac{\partial \ln(f)}{\partial p} \right]_T = \frac{pV}{RT} = Z$$

where Z is the compression factor as discussed in Chapter 2. Now, we can use the expression above to obtain the **fugacity coefficient** γ , as defined by

$$f = \gamma p$$

Taking the natural logarithm of both sides yields

$$\ln f = \ln \gamma + \ln p$$

Or

$$\ln \gamma = \ln f - \ln p$$

Using some calculus and substitutions from above,

$$\int \left(\frac{\partial \ln \gamma}{\partial p} \right)_T dp = \int \left(\frac{\partial \ln f}{\partial p} - \frac{\partial \ln p}{\partial p} \right)_T dp = \int \left(\frac{Z}{p} - \frac{1}{p} \right)_T dp$$

Finally, integrating from 0 to p yields

$$\ln \gamma = \int_0^p \left(\frac{Z - 1}{p} \right)_T dp$$

If the gas behaves ideally, $\gamma = 1$. In general, this will be the limiting value as $p \rightarrow 0$ since all gases behave ideal as the pressure approaches 0. The advantage to using the fugacity in this manner is that it allows one to use the expression

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

to calculate the chemical potential, insuring that

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V$$

even for gases that deviate from ideal behavior!

Colligative Properties

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

Solution – a homogeneous mixture.

Solvent – The component of a solution with the largest mole fraction

Solute – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous (aerosols are examples of gas-phase solutions) forms. For the most part, this discussion will focus on liquid-phase solutions.

Freezing Point Depression

In general (and as will be discussed in Chapter 8 in more detail) a liquid will freeze when

$$\mu_{solid} \leq \mu_{liquid}$$

As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent. As it turns out, the chemical potential of the solvent is reduced by the presence of a solute.

In a mixture, the chemical potential of component A can be calculated by

$$\mu_A = \mu_A^o + RT \ln x_A$$

And because x_A is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

The condition under which the solvent will freeze is

$$\mu_{A,solid} = \mu_{A,liquid}$$

where the chemical potential of the liquid is given by

$$\mu_A = \mu_A^o + RT \ln x_A$$

Rearrangement yields

$$\frac{\mu_A - \mu_A^o}{RT} = \ln x_A$$

In order to evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T} \left(\frac{\mu_A - \mu_A^o}{RT} \right) \right]_p = \left(\frac{\partial \ln x_A}{\partial T} \right)_p$$

$$-\frac{(\mu_A - \mu_A^o)}{RT^2} + \frac{1}{RT} \left[\left(\frac{\partial \mu_A}{\partial T} \right)_p - \left(\frac{\partial \mu_A^o}{\partial T} \right)_p \right] = \left(\frac{\partial \ln x_A}{\partial T} \right)_p$$

Recalling that

$$\mu = H - TS$$

and

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -S$$

The previous equation becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT} [-S_A + S_A^o] = \left(\frac{\partial \ln x_A}{\partial T} \right)_p$$

And noting that in the case of the solvent freezing, H_A^o is the enthalpy of the pure solvent in solid form, and H_A is the enthalpy of the solvent in the liquid solution. So

$$H_A^o - H_A = \Delta H_{fus}$$

The previous equation becomes

$$\frac{\Delta H_{fus}}{RT^2} - \frac{-S_A + S_A^o}{RT} + \frac{-S_A + S_A^o}{RT} = \left(\frac{\partial \ln x_A}{\partial T} \right)_p$$

or

$$\frac{\Delta H_{fus}}{RT^2} = \left(\frac{\partial \ln x_A}{\partial T} \right)_p$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^T \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln x_A$$

where T^o is the freezing point of the pure solvent and T is the temperature at which the solvent will begin to solidify in the solution. After integration

$$-\frac{\Delta H_{fus}}{R} \left(\frac{1}{T} - \frac{1}{T^o} \right) = \ln x_A$$

This can be simplified by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o}$$

where ΔT is the difference between the freezing temperature of the pure solvent and that of the solvent in the solution. Also, for small deviations from the pure freezing point, TT^o can be replaced by the approximate value $(T^o)^2$. So the expression becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2} \Delta T = \ln x_A$$

Further, for dilute solutions, for which x_A , the mole fraction of the solvent is very nearly 1, values of x_A ,

$$\ln x_A \approx -(1 - x_A) = -x_B$$

where x_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{RT^{o2}}{\Delta H_{fus}} \right) x_B$$

The factor $\left(\frac{RT^{o2}}{\Delta H_{fus}} \right)$ can be replaced by K_f , which is the **cryoscopic constant** for the solvent.

$$\Delta T = K_f x_B$$

ΔT gives the magnitude of the reduction of freezing point for the solution. Since ΔH_{fus} and T^o are properties of the solvent, the freezing point depression property is independent of the solute and is a property based solely on the nature of the solvent. Further, since x_B was introduced as $(1 - x_A)$, it represents the sum of the mole fractions of all solutes present in the solution.

It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of ΔT will change as the freezing process continually removes solvent from the liquid phase of the solution.

Boiling Point Elevation

The derivation of an expression describing boiling point elevation is similar to that for freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, cause it to favor the liquid phase over the vapor phase. As sch, the temperature must be increased to increase the chemical potential of the solvent in the liquid

solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b x_B$$

where

$$K_b = \left(\frac{RT^{\circ 2}}{\Delta H_{vap}} \right)$$

is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes.

A very elegant derivation of the form of the models for freezing point depression and boiling point elevation has been shared by F. E. Schubert (Schubert, 1983).

Cryoscopic and ebullioscopic constants are generally tabulated using molality as the unit of solute concentration rather than mole fraction. In this form, the equation for calculating the magnitude of the freezing point decrease or the boiling point increase is

$$\Delta T = K_f \cdot m \quad \text{or} \quad \Delta T = K_b \cdot m$$

where m is the concentration of the solute in moles per kg of solvent. Some values of K_f and K_b are shown in the table below.

Substance	K_f ($^{\circ}\text{C kg mol}^{-1}$)	T_f° ($^{\circ}\text{C}$)	K_b ($^{\circ}\text{C kg mol}^{-1}$)	T_b° ($^{\circ}\text{C}$)
Water	1.86	0.0	0.51	100.0
Benzene	5.12	5.5	2.53	80.1
Ethanol	1.99	-114.6	1.22	78.4
CCl₄	29.8	-22.3	5.02	76.8

Example:

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of CCl₄ raises the boiling point to 81.5 $^{\circ}\text{C}$. What is the molar mass of the compound?

Solution:

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(81.5^{\circ}\text{C} - 76.8^{\circ}\text{C}) = \left(5.02 \frac{^{\circ}\text{C kg}}{\text{mol}} \right) m$$

$$m = 0.936 \frac{\text{mol}}{\text{kg}}$$

Using the number of kg of solvent, one finds the number of moles of solute:

$$\left(0.936 \frac{\text{mol}}{\text{kg}}\right) (0.025 \text{ kg}) = 0.0234 \text{ mol}$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00 \text{ g}}{0.0234 \text{ mol}} = 128 \frac{\text{g}}{\text{mol}}$$

Vapor Pressure Lowering

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{\text{vapor}} = \mu_{\text{solvent}}$$

If the solute is not volatile, the vapor will be pure. And so (assuming ideal behavior)

$$\mu_{\text{vap}}^o + RT \ln \frac{p'}{p^o} = \mu_A^o + RT \ln x_A$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu_A^o = \mu_{\text{vap}}^o + RT \ln \frac{p_A}{p^o}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substitution of the second expression into the first yields

$$\mu_{\text{vap}}^o + RT \ln \frac{p'}{p^o} = (\mu_{\text{vap}}^o + RT \ln \frac{p_A}{p^o}) + RT \ln x_A$$

The terms for μ_{vap}^o cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln x_A$$

Subtracting $RT \ln(p_A/p^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln x_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln x_A$$

Dividing both sides by RT and exponentiating the result yields

$$\frac{p'}{p_A} = x_A$$

or

$$p' = x_A p_A$$

This last result is Raoult's Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

Example:

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

Solution:

Using Raoult's Law:

$$p_A = (0.400)(150 \text{ Torr}) = 60.0 \text{ Torr}$$

$$p_B = (0.600)(300 \text{ Torr}) = 180 \text{ Torr}$$

$$p_{tot} = p_A + p_B = 240 \text{ Torr}$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

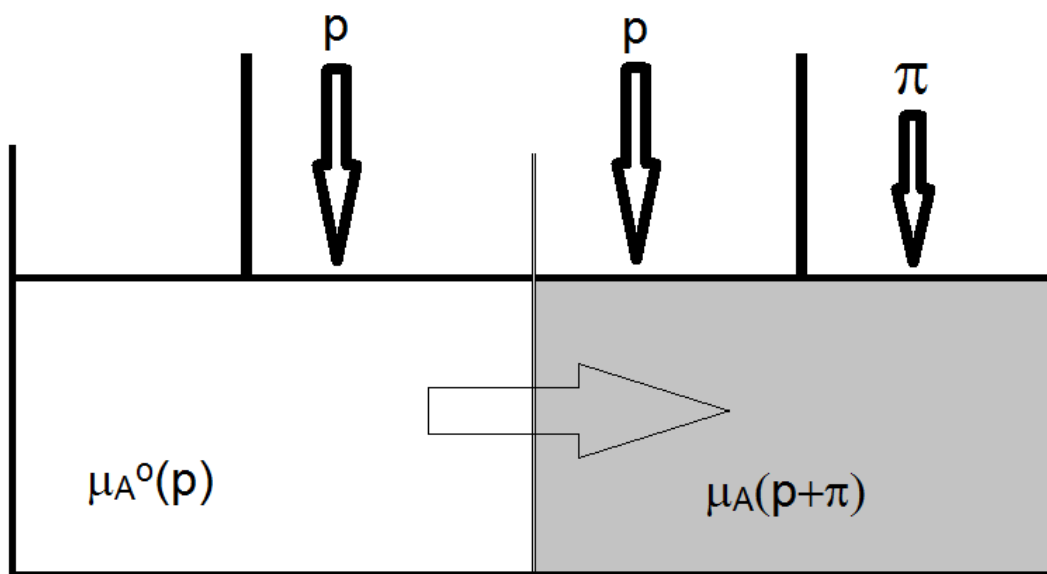
$$x_A = \frac{p_A}{p_{tot}} = \frac{60.0 \text{ Torr}}{240 \text{ Torr}} = 0.250$$

$$x_B = \frac{p_B}{p_{tot}} = \frac{180 \text{ Torr}}{240 \text{ Torr}} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

Osmotic Pressure

Osmosis is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln x_A$$

And since $x_A < 1$, the chemical potential of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying

pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(x_B, p + \pi)$$

To solve the problem to determine the magnitude of π , the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure π must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = -RT \ln x_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p + \pi) = \mu(p) + \int_p^{p+\pi} \left(\frac{\partial \mu}{\partial p} \right)_T dp$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial p} \right)_T = V$$

where V is the molar volume of the substance. Combining these expressions results in

$$-RT \ln x_A = \int_p^{p+\pi} V dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of κ_T – which is the case for most liquids) the term on the right becomes.

$$\int_p^{p+\pi} V dp = V[p]_p^{p+\pi} = V\pi$$

Also, for values of x_A very close to 1

$$\ln x_A \approx -(1 - x_A) = -x_B$$

So, for dilute solutions

$$x_B RT = V\pi$$

Or after rearrangement

$$\pi = \frac{x_B RT}{V}$$

again, where V is the molar volume of the solvent. And finally, since x_B/V is the concentration of the solute B for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure π is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

Solubility

The maximum solubility of a solute can be determined using the same methods we have used to describe colligative properties. The chemical potential of the solute in a liquid solution can be expressed

$$\mu_B(\text{solution}) = \mu_B^o(\text{liquid}) + RT \ln x_B$$

If this chemical potential is lower than that of a pure solid solute, the solute will dissolve into the liquid solvent (in order to achieve a lower chemical potential!) So the point of saturation is reached when the chemical potential of the solute in the solution is equal to that of the pure solid solute.

$$\mu_B^o(\text{solid}) = \mu_B^o(\text{liquid}) + RT \ln x_B$$

Since the mole fraction at saturation is of interest, we can solve for $\ln(x_B)$.

$$\ln x_B = \frac{\mu_B^o(\text{solid}) - \mu_B^o(\text{liquid})}{RT}$$

The difference in the chemical potentials is the molar Gibbs function for the phase change of fusion. So this can be rewritten

$$\ln x_B = \frac{-\Delta G_{fus}^o}{RT}$$

It would be convenient if the solubility could be expressed in terms of the enthalpy of fusion for the solute rather than the Gibbs function change. Fortunately, the Gibbs-Helmholtz equation gives us a means of making this change. Noting that

$$\left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_p = \frac{\Delta H}{T^2}$$

Differentiation of the above expression for $\ln(x_B)$ with respect to T at constant p yields

$$\left(\frac{\partial \ln x_B}{\partial T} \right)_p = \frac{1}{R} \frac{\Delta H_{fus}}{T^2}$$

Separating the variables puts this into an integrable form that can be used to see how solubility will vary with temperature:

$$\int_0^{\ln x_B} d \ln x_B = \frac{1}{R} \int_{T_f}^T \frac{\Delta H_{fus} dT}{T^2}$$

So if the enthalpy of fusion is constant over the temperature range of T_f to the temperature of interest,

$$\ln x_B = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right)$$

And x_B will give the mole fraction of the solute in a saturated solution at the temperature T . The value depends on both the enthalpy of fusion, and the normal melting point of the solute.

Activity

The bulk of the discussion in this chapter dealt with ideal solutions. However, real solutions will deviate from this kind of behavior. So much as in the case of gases, where fugacity was introduced to allow us to use the ideal models, **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute is related to its concentration by

$$a_B = \gamma \frac{m_B}{m^o}$$

where γ is the **activity coefficient**, m_B is the molality of the solute, and m^o is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, insuring that dilute solutions behave ideally. The use of activity to describe the solute

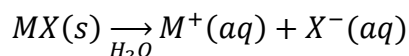
allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_B = \mu_B^o + RT \ln a_B$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration.

Activity Coefficients for Ionic Solutes

For an ionic substance that dissociates upon dissolving



the chemical potential of the cation can be denoted μ_+ and that of the anion as μ_- . For a solution, the total molar Gibbs function of the solutes is given by

$$G = \mu_+ + \mu_-$$

where

$$\mu = \mu^* + RT \ln a$$

where μ^* denotes the chemical potential of an ideal solution, and a is the activity of the solute. Substituting this into the above relationship yields

$$G = \mu_+^* + RT \ln a_+ + \mu_-^* + RT \ln a_-$$

Using a molal definition for the activity coefficient

$$a_i = \gamma_i m_i$$

The expression for the total molar Gibbs function of the solutes becomes

$$G = \mu_+^* + RT \ln \gamma_+ m_+ + \mu_-^* + RT \ln \gamma_- m_-$$

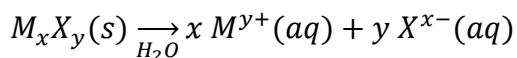
This expression can be rearranged to yield

$$G = \mu_+^* + \mu_-^* + RT \ln m_+ m_- + RT \ln \gamma_+ \gamma_-$$

where all of the deviation from ideal behavior comes from the last term. Unfortunately, it is impossible to experimentally deconvolute the term into the specific contributions of the two ions. So instead, we use a geometric average to define the **mean activity coefficient**, γ_{\pm} .

$$\gamma_{\pm} = \sqrt{\gamma_+ \gamma_-}$$

For a substance that dissociates according to the general process



the expression for the mean activity coefficient is given by

$$\gamma_{\pm} = (\gamma_+^x \gamma_-^y)^{\frac{1}{x+y}}$$

Debye-Hückel Law

In 1923, Debye and Hückel (Debye & Hückel, 1923) suggested a means of calculating the mean activity coefficients from experimental data. Briefly, they suggest that

$$\log \gamma_{\pm} = -\frac{1.824 \cdot 10^6}{(\epsilon T)^{\frac{3}{2}}} |z_+ z_-| \sqrt{I}$$

where ϵ is the dielectric constant of the solvent, T is the temperature in K, z_+ and z_- are the charges on the ions, and I is the **ionic strength** of the solution. I is given by

$$I = \frac{1}{2} \frac{(m_+ z_+^2 + m_- z_-^2)}{m^o}$$

For a solution in water at 25 °C,

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

References

- Debye, P., & Hückel, E. (1923). Zur Theorie der Electrolyte. *Physikalische Zeitschrift*, 24, 185-206.
- Schubert, F. E. (1983). Depression of Freezing Point and Elevation of Boiling Point. *Journal of Chemical Education*, 60(1), 88. doi:10.1021/ed060p87.2

Vocabulary and Concepts

activity.....	175	chemical potential	160
activity coefficient	175	cryoscopic constant.....	168

ebullioscopic constant.....	169	osmosis.....	172
enthalpy of mixing	158	osmotic pressure.....	172
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Learning Objectives

After mastering the material in this chapter, one will be able to

1. Describe the thermodynamics of mixing and calculate ΔH , ΔS , and ΔG of mixing for an ideal solution.
2. Define chemical potential, and calculate its value as a function of pressure and composition.
3. Derive expressions for the colligative properties and perform calculations using the relationships.
4. Estimate the maximum solubility of a solute in a solvent based on the concept equality of chemical potential at saturation.
5. Define fugacity and activity.
6. Calculate the mean activity coefficients of ions in solution based on the ionic strength of the solution.

Problems

1. The compression factor (Z) for O_2 at 200 K is measured to have the following values:

p (atm)	Z
1.000	0.9970
4.000	0.9880
7.000	0.9788
10.000	0.9700

Using numerical integration, calculate the fugacity constant for O_2 at 200 K from these data.

2. The normal boiling point of ethanol is 78.4 °C. Its enthalpy of vaporization is 38.6 kJ/mol. Estimate the vapor pressure of ethanol at 24.4 °C.

- When 20.0 grams of an unknown nonelectrolyte compound are dissolved in 500.0 grams of benzene, the freezing point of the resulting solution is 3.77 °C. The freezing point of pure benzene is 5.444 °C and the cryoscopic constant (K_f) for benzene is 5.12 °C/m. What is the molar mass of the unknown compound?
- Consider a mixture of two volatile liquids, A and B. The vapor pressure of pure liquid A is 324.3 Torr and that of pure liquid B is 502.3 Torr. What is the total vapor pressure over a mixture of the two liquids for which $x_B = 0.675$?
- Consider the following expression for osmotic pressure

$$\pi V = x_B RT$$

where π is the osmotic pressure, V is the molar volume of the solvent, x_B is the mole fraction of the solute, R is the gas law constant, and T is the temperature (in Kelvin).

The molar volume of a particular solvent is 0.0180 L/mol. 0.200 g of a solute (B) is dissolved in 1.00 mol of the solvent. The osmotic pressure of the solvent is then measured to be 0.640 atm at 298 K. Calculate the molar mass of the solute.

- At 300 K, the vapor pressure of HCl(g) over a solution of HCl in GeCl₄ are summarized in the following table.

x_{HCl}	P_{HCl} (kPa)
0.005	32.0
0.012	76.9
0.019	121.8

Calculate the Henry's Law constant for HCl based on these data.

- Consider the mixing of 1.00 mol of hexane (C₆H₁₂) with 1.00 mole of benzene (C₆H₆). Calculate ΔH , ΔS , and ΔG of mixing, if the mixing occurs ideally at 298 K.