Simple Mixtures

Chapter 7 of Atkins: Sections 7.4-7.5

*The Properties of Solutions*

**Liquid Mixtures**

**Colligative Properties**
- Boiling point elevation
- Freezing point depression
- Solubility
Liquid Mixtures

Gibbs energy of mixing for two liquids is calculated the same as for gases. For two liquids A and B (note that \( \ast \) signifies pure substance):

\[
G_i = n_A \mu_A^\ast + n_B \mu_B^\ast
\]

Upon mixing, the chemical potentials are given by \( \mu_j = \mu_j^\ast + RT \ln x_j \)

\[
G_f = n_A \left( \mu_A^\ast + RT \ln x_A \right) + n_B \left( \mu_B^\ast + RT \ln x_B \right)
\]

Thus, the Gibbs energy of mixing is

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

and the entropy of the mixing of two liquids is

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

meaning that the ideal enthalpy of mixing is zero.

\[
\Delta_{mix} H = 0
\]

Same expressions as for mixing of two perfect gases. But...
Liquid Mixtures: Miscibility

Solution ideality is quite different from perfect gas behavior:

**Perfect gases**: no interactions between the molecules

**Ideal solutions**: interactions between molecules, but average of interactions between A and B molecules is same as average interactions A-A and B-B in pure liquids

**Real solutions**: Composed of molecules for which A-A, A-B, B-B interactions are all different from one another

Sometimes, molecules of one type might cluster together (additional contribution to entropy), so:

- Enthalpy change might be large and positive
- Negative entropy change
- Positive Gibbs energy for mixing

In this case, separation is spontaneous, and liquids are **immiscible** (example, CCl₄ and H₂O, which are non-polar and polar, respectively)

Liquids can also be **partially miscible**, which means that they are miscible only in certain compositions (partially dissolve in one another)
Real Solutions & Excess Functions

Thermodynamic properties of real solutions are described with *excess functions*, $X^E$

For example, the *excess entropy*, $S^E$, is the difference between the observed thermodynamic function and the function for an ideal solution:

$$S^E = \Delta_{mix}S - \Delta_{mix}S^{ideal}$$

So, the further excess energies are from zero indicates the degree to which a solution is non-ideal—a *regular solution* has $H^E \neq 0$, $S^E = 0$, with two kinds of molecules distributed randomly (like ideal solution), but having different interactions with one another

(Top) The *benzene/cyclohexane mixing*, shows that mixing is endothermic

(Bot) *Tetrachloroethane/cyclohexane* mixing shows a volume contraction at low $C_2Cl_4$ fractions, and expansion at high $C_2Cl_4$ fractions
Colligative properties literally denotes properties which depend on a collection of particles

Boiling point elevation
Freezing point depression
Solubility of liquids and solids
Osmotic pressure

Each of these properties is going to depend on the composition of the mixture (i.e., the relative mole fractions of the components)

There is no reference in these properties to the identities of the solutes and/or solvents - strictly dependent upon composition

Important Assumptions:

- Solute is not volatile, does not contribute to the chemical potential of the solvent vapor
- Solute does not dissolve in solid solvent (this is not the most common case, but does cut the mathematics down a lot!) - so pure solid solvent separates when the mixture is frozen
Colligative Properties: Common Features

All colligative properties result from lowering of the chemical potential of the solvent from the presence of a solute.

\[ \mu_A^* = \mu_A^* + RT \ln x_A \]

Remember, \( \ln x_A \) is definitely negative. So what causes the **lowering of chemical potential of a liquid**?

Not the energies of interactions between solvent and solute molecules - since lowering of energy occurs even in ideal solutions (\( \Delta_{\text{mix}} H = 0 \))

**Entropy** must be the driving force for lowering the chemical potential of a liquid once the solute has been added.
Solvents, Solutes and Entropy

There is no direct effect of the solute on the chemical potential of the solvent vapor, since solute is neither in vapor nor solid

Reduction of the chemical potential of the solution (down from that of a pure liquid) implies that:
- liquid-vapor equilibrium occurs at a higher temperature (boiling point elevation)
- liquid-solid equilibrium occurs at a lower temperature (freezing point depression)

(a) Solution with entropy $S$ & $p_A^*$, vapor pressure reflects tendency to greater $S$
(b) Solution and solute, with $S(b) > S(a)$, therefore weaker tendency to form gas, boiling $T$ elevated and $p_A < p_A^*$

Increased disorder in the liquid also opposes tendency to freeze (go to higher order), with a lower temperature required to hit solid-liquid eqb.
Boiling Point Elevation

Heterogeneous equilibrium: between solvent in solution and solvent vapor at 1 atm, where solvent is A and solute is B (involatile)

Equilibrium occurs at some temperature when:

\[ \mu_A^* (g) = \mu_A^* (l) + RT \ln x_A \]

The presence of some mole fraction \( x_B \) causes an increase in the normal boiling point from \( T^* \) to \( T^* + \Delta T \), where

\[ \Delta T = K x_B \quad K = \frac{RT^{*2}}{\Delta_v H} \]

The identity of solute is irrelevant: just the mole fraction is important, so boiling point elevation is a colligative property.

Value of \( \Delta T \) depends on the solvent, biggest changes occur for solvents with high boiling points. For practical applications, mole fraction of B is proportional to its molality, \( b \) (mol kg\(^{-1}\)), in dilute solutions, and

\[ \Delta T = K_b b \]

\( K_b \) is the empirical (& unfortunately named) ebullioscopic constant.
Freezing Point Depression

Heterogeneous equilibrium: pure solid solvent A and solution with solvent present in mole fraction $x_B$. At the freezing point:

$$
\mu^*_A(s) = \mu^*_A(l) + RT \ln x_A
$$

Only difference from boiling point elevation is the presence of $\mu^*_A(s)$ instead of $\mu^*_A(l)$. Thus,

$$
\Delta T = K' x_B
\quad K' = \frac{RT^*\Delta^*_fus H}{\Delta^*vap H}
$$

where $\Delta T$ is the freezing point depression, $T^* - T$, and $\Delta^*_fus H$ replaces $\Delta^*vap H$.

Larger depressions are observed for solvents with low $\Delta^*_fus H$ and high melting points.

If solution is dilute, mole fraction $\propto$ molality, $b$, of the solute, and

$$
\Delta T = K_f b
$$

where $K_f$ is the empirical cryoscopic constant.
Solubility

Solubility is not perfectly colligative, but may be estimated from the same techniques we’ve been discussing - but *highly questionable approximations!* If solid and liquid are in contact, solid dissolves until the solution is saturated (the equilibrium state). Chemical potentials of solid solute, $\mu_B^*$, and B in solution $\mu_B$, are equal

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$$

Since $\mu_B(l) = \mu_B^*(l) + RT \ln x_B$

then $\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$

So the question becomes:

What mole fraction of B is in solution at temperature T?
Solubility

What mole fraction of B is in solution at temperature T?

\[
\ln x_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta_{fus} G}{RT} = -\frac{\Delta_{fus} H}{RT} + \frac{\Delta_{fus} S}{R}
\]

We KNOW that at the normal freezing point, T*, that \(\Delta_{fus} G = 0\), so we can add it to the right hand side of the equation above:

\[
\ln x_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = -\frac{\Delta_{fus} G}{RT} = -\frac{\Delta_{fus} H}{RT} + \frac{\Delta_{fus} S}{R} + \frac{\Delta_{fus} H}{RT^*} - \frac{\Delta_{fus} S}{R}
\]

\[
= -\frac{\Delta_{fus} H}{RT} + \frac{\Delta_{fus} H}{RT^*}
\]

\[
= -\frac{\Delta_{fus} H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)
\]
Solubility

\[
\ln x_B = -\frac{\Delta_{fus}H}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)
\]

This relation means that the solubility of B decreases exponentially as the temperature is decreased, where \( T^* \) is the m.p.

Solute with high melting points and large enthalpies of melting have low solubilities at normal temperatures!