Chapter 9. Ideal and Real Solutions

Chem 231

Last term, thermodynamics of pure substances and ideal gas mixtures. But what about liquid mixtures? They are "everywhere", very important, and often strongly nonideal.

Solutions

- mixtures of **two or more different chemical components**
- form a single phase
- uniform chemical and physical properties on the microscopic scale
- a solution can be a:
  - ♦ **gas** (*e.g.*, air – N_2, O_2, H_2O, Ar, CO_2, …)
  - ♦ **liquid** (*e.g.*, NaCl dissolved in water)
  - ♦ **solid** (*e.g.*, brass – a copper/zinc alloy)

Ideal Gas Solutions

- simplest of all solutions, but very important
- no molecular interactions
- from Chem 231:

$$\Delta S_{\mathrm{mix}} = -n_{\mathrm{A}} R \ln x_{\mathrm{A}} - n_{\mathrm{B}} R \ln x_{\mathrm{B}} > 0$$

$$\Delta G_{\mathrm{mix}} = n_{\mathrm{A}} RT \ln x_{\mathrm{A}} + n_{\mathrm{B}} RT \ln x_{\mathrm{B}} < 0$$

- ideal gases always mix

Liquid Solutions

- even more important than gas solutions
- **rarely ideal**
- example: oil and water do not mix. Why?
- in addition to p, V, T, composition variables are required, such as **mole fraction** (x_i), **molality** (m_i), **molarity** (c_i)

$$x_i = \frac{n_i}{\sum_k n_k}$$

$$m_i = \frac{n_i}{\text{kilograms solvent}}$$

$$c_i = \frac{n_i}{\text{liters of solution}}$$

Chapter 9 – Liquid Solutions

Why study solution thermodynamics? To help understand:

- **vapor pressures** of solutions (and **fractional distillation**)
- **solubilities** (and purification by re-crystallization)
- **freezing point depression** (why salt melts ice)
- **osmotic pressure** (how desalination works)
- solid-liquid-vapor **phase diagrams**
- properties of **nonideal solutions**
- multicomponent phase rule $F = C + 2 - P$
- **chemical reaction equilibrium in liquid solutions**

Section 9.1 Defining Ideal Solutions

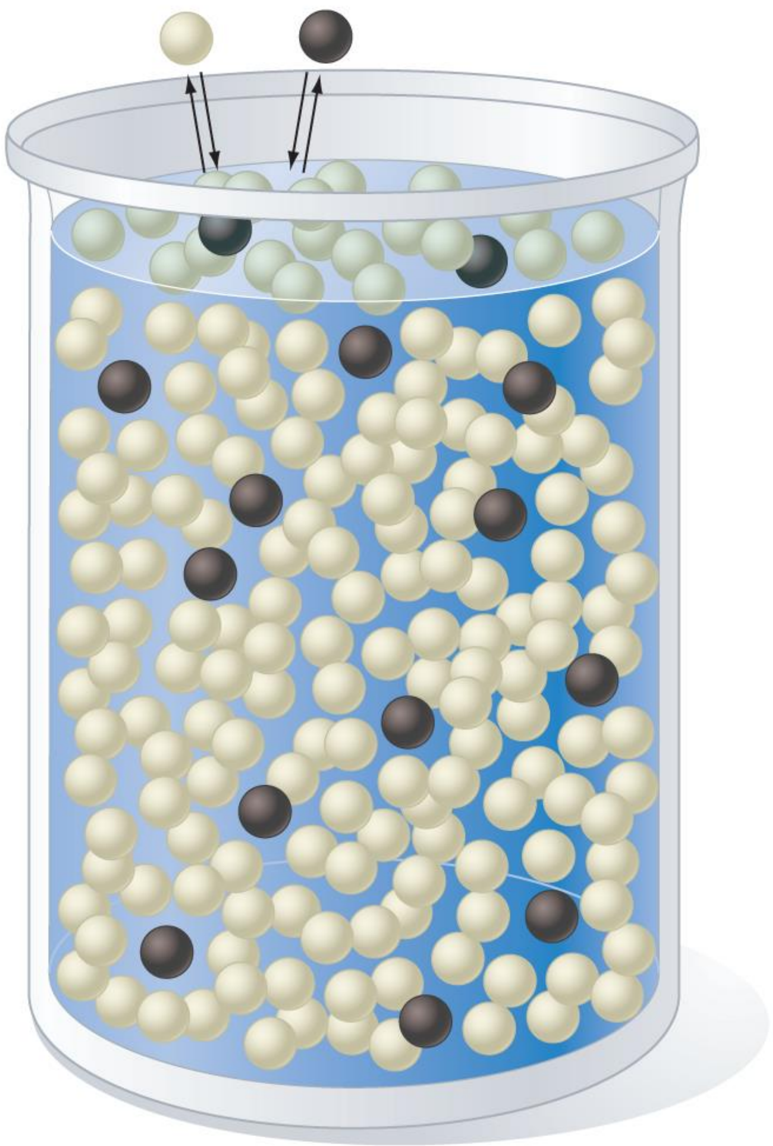
Ideal Solution of Gases A and B

- **no interactions** between molecules A and B
- a poor approximation for liquid solutions of A and B
- A and B molecules attract each other to form liquid solutions

Ideal Solution of Liquids A and B

- **equal interactions** between molecules A and B
- a reasonable approximation "similar" A and B molecules
- examples: benzene + toluene or C_6H_6 + C_6H_5D

Vapor Pressures of Ideal Liquid Solutions: **Raoult's Law**



Liquid A + B Mixtures

If A and B molecules have similar:

- sizes
- A-A, A-B and B-B interactions

expect the vapor pressures of A and B to be proportional to the mole fractions of A and B. (***Why?***)

Get:

$$p_A = x_A p_A^*$$

$$p_B = x_B p_B^*$$