# Mixtures

CHEM 361A: Introduction to Physical Chemistry

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Lecture 9

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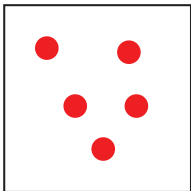   - Activity
   - Henry's Law

Learning Objective: Define the chemical potential for components in mixtures in order to discuss their properties.

References:

- Atkins and de Paula Focus 4C and 4D
- Chang §7.1 - §7.5
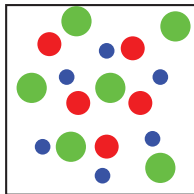
# The Chemical Potential

Single Component System



$$G = n\, G_m$$

where:

$$G_m = \frac{G}{n}$$

Multi Component System



$$G = n_R \mu_R + n_B \mu_B + n_G \mu_G$$

where:

$$\mu_J = \left( \frac{\partial G}{\partial n_J} \right)_{T, P, n_{other}}$$

## Applying Chemical Potentials to Mixtures of Gases Setup

We previously determined that the molar Gibbs Free Energy for a pure gas at constant Temperature varies with pressure according to

$$G_m(p_f) = G_m(p_i) + RT \ln\left(\frac{p_f}{p_i}\right)$$

We will set

- $p_f$ to p: the pressure of interest
- $p_i$ to $p^{\ominus}$: 1 bar
- $G_m(p_i)$ to be $G_m^{\ominus}$

which gives:

$$G_m(p) = G_m^{\ominus} + RT \ln\left(\frac{p}{p^{\ominus}}\right)$$

# Applying Chemical Potentials to Mixtures of Gases

For a mixture of gases, we use the chemical potential to describe gas J's contribution to the total Gibbs Free energy according to:

$$\mu_J(g) = \mu_J^{\ominus}(g) + RT \ln\left(\frac{p_J}{p^{\ominus}}\right)$$

where $p_J$ is interpreted to be the *partial pressure* of gas J.



So the more of gas J that's in the system, the larger its chemical potential and the more potential for that component to contribute chemically.
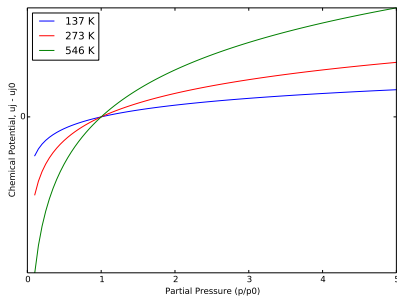
## Chemical Potential Examples

1. Suppose that the partial pressure of a perfect gas falls from 100 kPa to 50 kPa as it is consumed in a reaction at $25°C$. What is the change in chemical potential of the substance?

2. Suppose we have two gases at the same pressure and temperature in a box separated by an impermeable membrane. Show that it is spontaneous that the gases will mix.
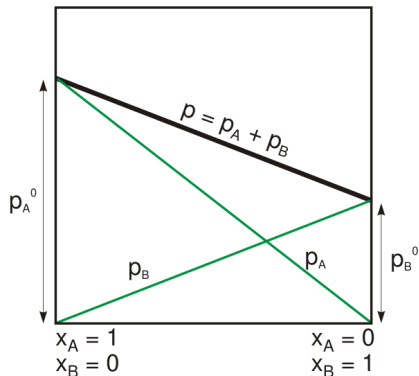
## Ideal Volatile Solutions

Ideal solutions follow Raoult's Law:

### Raoult's Law:

The partial vapour pressure of a substance in a liquid mixture is proportional to its mole fraction in the mixture and its vapour pressure when pure:

$$p_J = x_J p_J^*$$

where $p_J^*$ is the vapour pressure of the pure substance.

## Raoult's Law and Chemical Potentials

Raoult's law allows us to quantify the chemical potential, $\mu_J$, of each component of a solution based on their vapour pressure. Starting from pure components (denoted by the asterisk) and assuming that the vapour and liquid phases are at equilibrium:

$$\mu_J^*(l) = \mu_J^*(g) = \mu_J^{\ominus}(g) + RT \ln \frac{p_J^*}{p^{\ominus}}$$

Rearranging this to solve for $\mu_J^{\ominus}$ gives

$$\mu_J^{\ominus} = \mu_J^*(l) - RT \ln \frac{p_J^*}{p^{\ominus}}$$

For each component in a binary mixture, as we vary the mole fraction

$$\mu_J(l) = \mu_J(g) = \mu_J^{\ominus}(g) + RT \ln \frac{p_J}{p^{\ominus}}$$

## Raoult's Law and Chemical Potentials (cont.)

Since $\mu_J^\ominus$ is the same in both cases (pure and mixed) then

$$\mu_J(l) = \mu_J^*(l) - RT \ln \frac{p_J^*}{p^\ominus} + RT \ln \frac{p_J}{p^\ominus}$$
$$= \mu_J^*(l) + RT \ln \frac{p_J}{p_J^*}$$

According to Raoult's Law

$$x_J = \frac{p_J}{p_J^*}$$

Therefore,

$$\mu_J(l) = \mu_J^*(l) + RT \ln x_J$$

Further reading on Raoult's Law:
LibreText - Raoult's Law 1
LibreText - Raoult's Law 2

## Ideal Solution Examples

1. What is the change in chemical potential of benzene at $25^\circ$C caused by a solute that is present at a mole fraction of 0.10?

2. Show that the mixing of an ideal solution is spontaneous.

## Real Solutions

Raoult's Law is only valid for a small number of mixtures (typically those whose components are very similar).

To account for the deviation from ideal conditions we will define something called its **activity**, in the context of Raoult's Law, as

$$a_J = \gamma_J x_J = \gamma_J \frac{p_J}{p_J^*}$$

where $\gamma_J$ is the activity coefficient (deviation from ideal conditions for gases) of component J.



Since Raoult's Law is based on the pure component, in real solutions it is only applicable when $x_J \approx 1$.
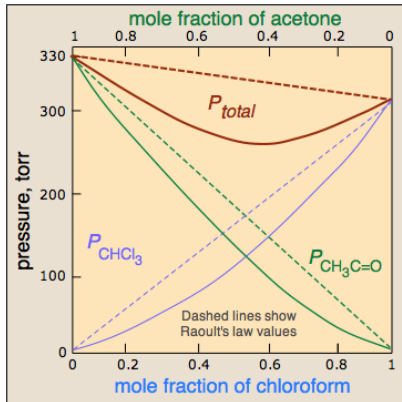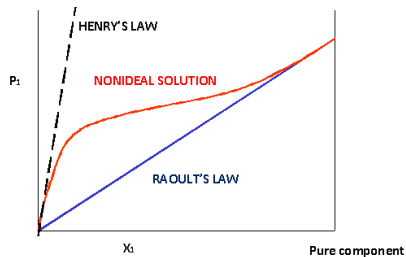
# Henry's Law

Given that Raoult's Law does not describe very dilute components in real solutions, the relationship between mole fraction and partial pressure is quantified by **Henry's Law**

## Henry's Law

The vapour pressure of a volatile solute J is proportional to its mole fraction in a solution:

$$p_J = a_J K_H$$

where $K_H$ is characteristic of the solute and chosen so that the straight line predicted by Henry's Law is tangent to the experimental curve at $a_J = 0$.

## Henry's Law Example

Calculate the molal solubility of carbon dioxide in water at 298 K and a $CO_2$ pressure of $3.3 \times 10^{-4}$ atm, which corresponds to the partial pressure of $CO_2$ in air. Assume $K_H = 1.63 \times 10^3$ atm.

## Chemical Potential of Dilute Solutions

Henry's law allows us to quantify the chemical potential, $\mu_J$, of the dilute component of a solution based on their vapour pressure. Starting from pure components (denoted by the dagger) and assuming that the vapour and liquid phases are at equilibrium:

$$\mu_J^\dagger(l) = \mu_J^\dagger(g) = \mu_J^\ominus(g) + RT \ln \frac{K_{H,J}}{p^\ominus}$$

Where according to Henry's Law, the pressure of pure component J is $K_{H,J}$. Rearranging this to solve for $\mu_J^\ominus$ gives

$$\mu_J^\ominus = \mu_J^\dagger(l) - RT \ln \frac{K_{H,J}}{p^\ominus}$$

For each component in a binary mixture as we vary the mole fraction

$$\mu_J(l) = \mu_J(g) = \mu_J^\ominus(g) + RT \ln \frac{p_J}{p^\ominus}$$

## Chemical Potentials of Dilute Solutions (cont.)

Since $\mu_J^{\ominus}$ is the same in both cases (pure and mixed) then

$$\mu_J(l) = \mu_J^{\dagger}(l) - RT \ln \frac{K_{H,J}}{p^{\ominus}} + RT \ln \frac{p_J}{p^{\ominus}}$$

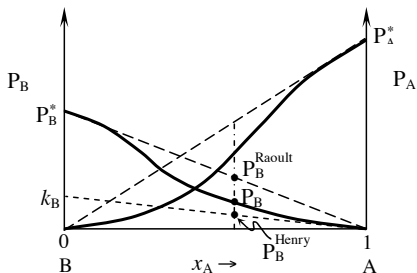According to Henry's Law

$$p_J = a_J K_{H,J}$$

Then

$$\mu_J(l) = \mu_J^{\dagger}(l) - RT \ln \frac{K_{H,J}}{p^{\ominus}} + RT \ln \frac{a_J K_{H,J}}{p^{\ominus}}$$

$$= \mu_J^{\dagger}(l) - RT \ln \frac{K_{H,J}}{p^{\ominus}} + RT \ln \frac{K_{H,J}}{p^{\ominus}} + RT \ln a_J$$

Therefore,

$$\mu_J(l) = \mu_J^{\dagger}(l) + RT \ln a_J$$

# Difference Between $\mu^*$ and $\mu^\dagger$



- $\mu^*$ assumes the pressure of the pure component is $p^*$ (Raoult's Law)
- $\mu^\dagger$ assumes the pressure of the pure component is $K_{H,J}$ (Henry's Law)

Both $\mu^*$ and $\mu^\dagger$ are standard states under different conditions.

## Chemical Potential of Dilute Components

For dilute components we will write chemical potential in reference
to the Henry's Law standard chemical potential using the standard
notation:

$$\mu_J(l) = \mu_J^{\ominus}(l) + RT \ln a_J$$

It is convenient to define the activity using molality since the mass
of the solution does not change with temperature:

$$a_J = \gamma_J \frac{m_J}{m^{\ominus}}$$

where $\gamma_J$ is the activity coefficient (ie deviation from ideal
conditions for concentrations) and $m^{\ominus}$ is 1 kg mol$^{-1}$.

## Summary

- The molar Gibbs Free Energy of each component of a multi-component system is quantified by the chemical potential, $\mu$
- When calculating the chemical potential under certain conditions, we calculate the deviation from a reference/standard chemical potential of the component

$$\mu_J(g) = \mu_J^{\ominus}(g) + RT \ln \left( \frac{p_J}{p^{\ominus}} \right)$$

- Raoult's Law defines the partial pressure of components in ideal mixtures as

$$p_J = x_J p_J^*$$

- Henry's Law defines the partial pressure of dilute components in real mixtures as

$$p_J = x_J K_H$$

## Summary (cont.)

- Since both Raoult's Law and Henry's Law are linear extrapolations in pure and dilute situations, to account for the real nature in mixtures, we use activity instead of mole fraction

$$a_J = \gamma_J x_J$$

- For dilute components, the Henry's Law constant that relates molality to partial pressure can be used instead so the chemical potential is defined as

$$\mu_J(l) = \mu_J^{\ominus}(l) + RT \ln a_J$$

where

$$a_J = \gamma_J \frac{m_J}{m^{\ominus}}$$