

## Thermodynamics of Mixtures

### Ideal Mixture

Ideal mixtures obey Amagat's law

$$V_m = \sum_{i=1}^k x_i V_{m,i}$$

The same additivity relation is valid for internal energy, enthalpy, heat capacity. For entropy, Gibbs energy and Helmholtz energy of ideal mixture holds

$$S_m = \sum_{i=1}^k x_i S_{m,i} - R \sum_{i=1}^k x_i \ln x_i \quad G_m = \sum_{i=1}^k x_i G_{m,i} + RT \sum_{i=1}^k x_i \ln x_i \quad F_m = \sum_{i=1}^k x_i F_{m,i} + RT \sum_{i=1}^k x_i \ln x_i$$

### Mixing Properties

Mixing properties are defined for any extensive variable  $Y$

$$Y_m = \sum_{i=1}^k x_i Y_{m,i} + Y^M$$

### Excess Properties

$$Y_m = Y_{m,\text{id. smes}} + Y^E$$

Both mixing and excess properties can be used for expression of real behavior of mixtures. More appropriate for this purpose are the excess properties that do not include ideal mixing terms for  $S$ ,  $G$ ,  $F$ .

### Partial Molar Properties (PMP)

PMP correspond to a property of a component in mixture. The definition is

$$\bar{Y}_i = \left( \frac{\partial Y}{\partial n_i} \right)_{T,p,n_{i,j}}$$

PMPs can be treated in the same way as pure compound properties. Partial molar Gibbs energy is often called **chemical potential** or **chemical affinity** (symbol  $\mu_i$ ). PMPs are not mutually independent, in a system with  $k$ -components there are only  $k-1$  independent PMPs. E.g. for a binary mixture

$$\bar{Y}_1 = Y_m + x_2 \left( \frac{\partial Y_m}{\partial x_1} \right)_{T,p} \quad \bar{Y}_2 = Y_m - x_1 \left( \frac{\partial Y_m}{\partial x_1} \right)_{T,p}$$

For evaluation of PMPs only the relation  $Y_m = Y_m(x_1)$  is needed, functional dependence on  $x_2$  follows from the above equations. Such functions are typically stated for the excess Gibbs energy. E.g. the Redlich-Kister equation for a binary system is

$$G^E = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots]$$

If parameters  $C$ ,  $D$ , ... are equal to zero, Redlich-Kister equation is reduced to so-called regular solution. Parameters must be evaluated from experimental data and change with temperature and pressure. Common thermodynamic relations are valid also for excess properties, e.g. excess volume from the Redlich-Kister equation is

$$V^E = \left( \frac{\partial G^E}{\partial p} \right)_T = x_1 x_2 \left[ \left( \frac{\partial B}{\partial p} \right)_T + \left( \frac{\partial C}{\partial p} \right)_T (x_1 - x_2) + \left( \frac{\partial D}{\partial p} \right)_T (x_1 - x_2)^2 + \dots \right]$$

### Chemical Potential

Dependence of  $\mu_i$  on temperature and pressure is analogous to the Gibbs energy of pure substances

$$\left( \frac{\partial \mu_i}{\partial T} \right)_p = -\bar{S}_i \quad \left( \frac{\partial \mu_i}{\partial p} \right)_T = \bar{V}_i$$

Considering the ideal gas EOS for partial molar volume ( $\bar{V}_i = RT/p_i$  with  $p_i$  the partial pressure), we get

$$d\mu_i = RT \frac{dp}{p_i} \quad \text{and its integral} \quad \mu_i - \mu_i^\circ = RT \ln \frac{p_i}{p_i^\circ}$$

Lewis suggested generalization of the last equation: replacing partial pressure by some other related property, the equation will be valid for real systems as well. This property was named **fugacity**

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$$\mu_i - \mu_i^\circ = RT \ln \frac{f_i}{f_i^\circ}$$

Chemical potential depends on fugacity of a given component and on its fugacity in some selected standard state (index  $^\circ$ ). Equivalently, the above equation can be re-written using **activity**

$$\mu_i - \mu_i^\circ = RT \ln a_i$$

Activity is dimensionless number, expressing the relation of component behavior at the conditions of interest to the behavior of this component in the selected standard state. Activity therefore depends on the selection of the standard state and this information must always accompany any published values of activity.

### Standard States

The selection of appropriate standard state should comply with several requirements: the properties in the standard state such as  $\mu_i^\circ$  should be well-known, and at the same time standard state should be close to the actual state of a component. These practical considerations lead to different choice of a standard state for different systems:

- For **gaseous mixtures** it is the pure component in ideal gas state at the same temperature as the system of interest. Standard fugacity is in this case equal to standard pressure and activity is

$$a_i = \frac{f_i}{f_i^\circ} = \frac{x_i p}{p^\circ} \gamma_i \quad \lim_{\substack{x_i \rightarrow 1 \\ p \rightarrow p^\circ}} \gamma_i = 1$$

The factor  $\gamma_i$  is activity coefficient, which is a measure of the difference between behavior of a component in ideal gas state and in the real mixture. For gaseous mixtures the value of activity is often neglected as it is close to unity at most situations.

- For **liquid or solid mixtures** standard state corresponds to a pure component at the same temperature and pressure as the system of interest

$$a_i = x_i \gamma_i \quad \lim_{x_i \rightarrow 1} \gamma_i = 1$$

For pure solids and liquids this choice of standard state leads to unit activity.

- For **solutions** (mixtures with one prevailing component – solvent – and minor component(s) – solute(s)) the standard state corresponds to a solution at unit concentration, extrapolated to infinite dilution. This choice of standard state is *asymmetric* (for solvent we use the standard state of a pure component) and *hypothetic* (solution of unit concentration, behaving as infinitely dilute solution, cannot be realized experimentally)

$$a_i = X_i \gamma_i^{[X]} \quad \lim_{X_i \rightarrow 0} \gamma_i^{[X]} = 1$$

where  $X$  is (dimensionless) concentration unit – molar fraction, molarity or molality (number of moles of solute per kilogram of a solvent). Activity defined at different concentration scales can be recalculated.

### Activity Coefficients

Besides the properties at standards states, activity coefficients are needed for the description of real-system behavior. Experimental information is commonly obtained from the data on phase equilibria. The results can be generalized e.g. with the help of Redlich-Kister equation: from the relations for the excess Gibbs energy and for chemical potential we obtain for the activity coefficient

$$\bar{G}_i^E = RT \ln \gamma_i$$

Estimation Methods: UNIFAC group contribution method is commonly used for liquid mixtures Gmehling J., Li J., Schiller M.: Ind. Eng. Chem. Res., 32, 178, 1993.

Mean activity coefficient of dilute electrolyte solutions is estimated from Debye-Hückel theory

$$\ln \gamma_{\pm}^{[m]} = -|z_+ z_-| A_\phi \left( \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right)$$

where  $A_\phi$  is parameter dependent on  $T$ ,  $p$  and the solvent (for water at 25 °C  $A_\phi = 0,3915$  (kg/mol)<sup>1/2</sup>), parameter  $b$  is according to Pitzer constant,  $b = 1,2$  (kg/mol)<sup>1/2</sup>.  $I$  is the ionic strength,  $I = 1/2 \sum m_i z_i^2$ .