

Chemical Potential Reference States

Chemical Potentials for Liquid/Solid Mixtures

Ideal Reference State

$$\mu_i(T,P,x_i) = \mu_i^*(T,P) + RT \ln a_i$$

Ideal-Dilute Reference State

$$\mu_j(T,P,x_j) = \mu_j^{**}(T,P) + RT \ln a_j$$

Ideal-Dilute (molality) Reference State

$$\mu_j(T,P,m_j) = \mu_j^{***}(T,P) + RT \ln\left(\frac{a_j}{m^o}\right)$$

Ideal-Dilute (molarity) Reference State

$$\mu_j(T,P,c_j) = \mu_j^\square(T,P) + RT \ln\left(\frac{a_j}{c^o}\right)$$

Reference State Definitions

Ideal Reference State

$$\begin{aligned}\mu_i^*(T,P) &= \frac{G_i(T,P)}{n} \\ &= \text{Molar Gibbs Free Energy of the Pure Liquid/Solid}\end{aligned}$$

Ideal-Dilute Reference State

$$\begin{aligned}\mu_j^{**}(T,P) &= \lim_{x_j \rightarrow 0} [\mu_j(T,P,x_j) - RT \ln x_j] \\ &= \text{Hypothetical Molar Gibbs Free Energy of Pure Liquid/Solid} \\ &\quad \text{Behaving as if Perfectly Dilute}\end{aligned}$$

Ideal-Dilute (molality) Reference State

$$\begin{aligned}\mu_j^{***}(T,P) &= \lim_{m_j \rightarrow 0} \left[\mu_j(T,P,m_j) - RT \ln\left(\frac{m_j}{m^o}\right) \right] \\ &= \text{Hypothetical Molar Gibbs Free Energy of Pure Liquid/Solid} \\ &\quad \text{Behaving as if Perfectly Dilute at } m^o\end{aligned}$$

Ideal-Dilute (molarity) Reference State

$$\begin{aligned}\mu_j^\square(T,P) &= \lim_{c_j \rightarrow 0} \left[\mu_j(T,P,c_j) - RT \ln\left(\frac{c_j}{c^o}\right) \right] \\ &= \text{Hypothetical Molar Gibbs Free Energy of Pure Liquid/Solid} \\ &\quad \text{Behaving as if Perfectly Dilute at } c^o\end{aligned}$$

Notes:

- Reference States are not Standard States. For example, the Ideal Reference State is the Pure Liquid/Solid at T and P:

$$\mu_i^*(T,P) = \text{Reference State}$$

The Standard State is defined as the Molar Gibbs Free Energy of the Pure Liquid/Solid at T and P⁰:

$$\mu_i^\circ(T,P^0) = \text{Standard State}$$

These are related as:

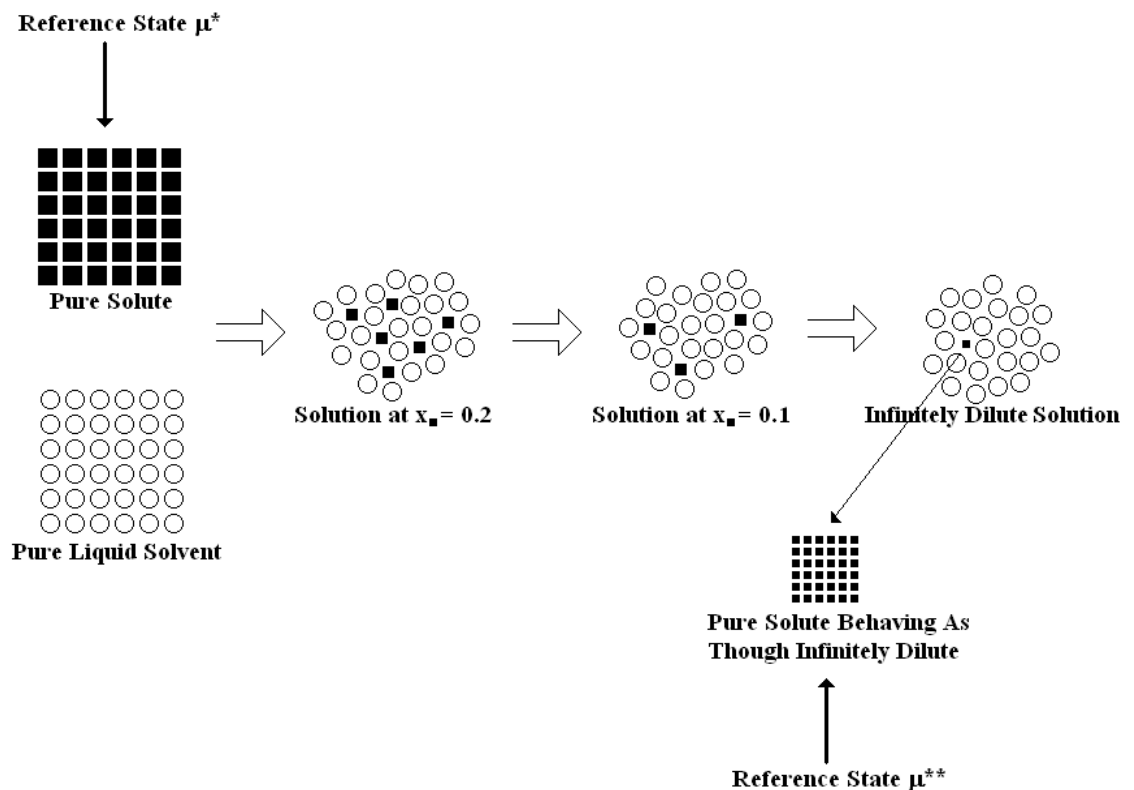
$$\mu_i^*(T,P) = \mu_i^\circ(T,P^0) + \int_{P^0}^P \bar{V}_i dP$$

For most cases, because the molar volume of a liquid or solid is small and the pressure difference is small, the integral term is negligible.

$$\mu_i^*(T,P) \sim \mu_i^\circ(T,P^0)$$

However, at high pressures, or when great accuracy is required, the integral term must be included.

- A pictorial representation of the Ideal-Dilute Reference State:

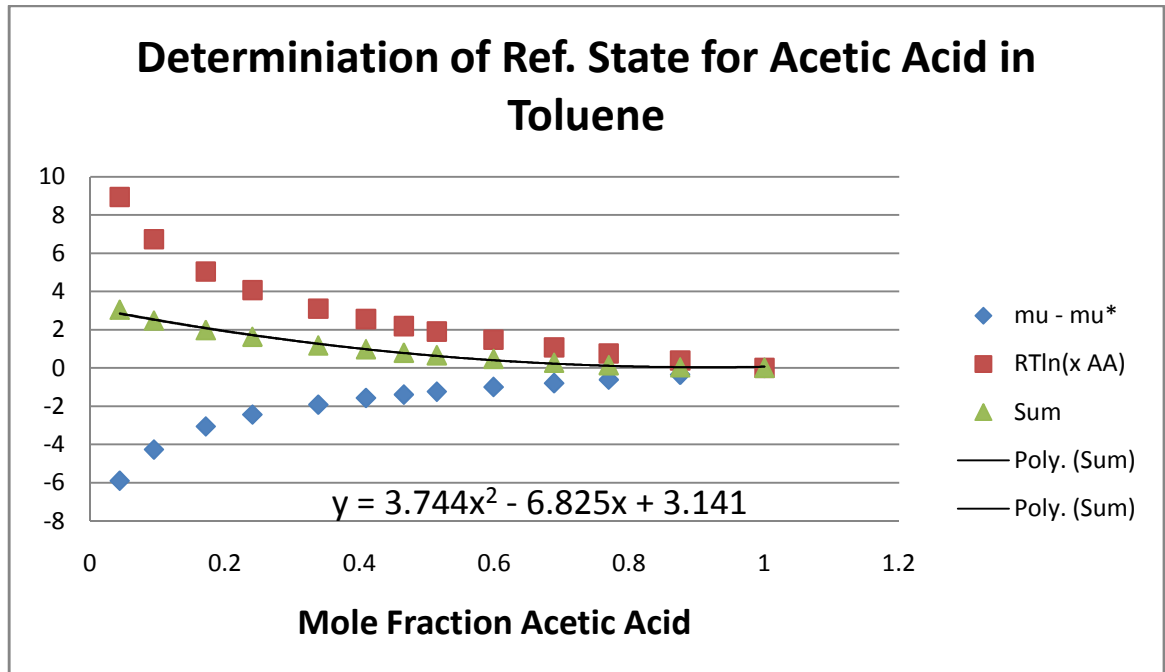


- 3) Determination of μ_{AA}^{**} for Acetic Acid in a Toluene solvent at 69.9°C. Vapor Pressure data is used to calculate $\mu_{AA} - \mu_{AA}^*$.

x_{AA}	P_{AA} [Torr]	$\mu_{AA} - \mu_{AA}^*$ [kJ/mol]	$-RT \ln x_{AA}$ [kJ/mol]
0.0435	17.2	- 5.8948	8.941
0.0942	30.5	- 4.2646	6.7373
0.1711	46.5	- 3.0585	5.0354
0.2403	57.8	- 2.4382	4.0667
0.3380	69.3	-1.9183	3.0937
0.4088	78.2	- 1.5713	2.5513
0.4651	83.7	- 1.3914	2.1833
0.5140	88.2	- 1.2390	1.8982
0.5981	95.7	- 0.9939	1.4660
0.6879	103.0	- 0.7952	1.0670
0.7690	110.8	- 0.6100	0.7491
0.8750	120.5	- 0.3524	0.3808
1.0000	136.0	- 0.0000	0.0000

The sum of the last two columns is plotted and extrapolated to zero Mole Fraction. This is then:

$$\mu_{AA}^{**} - \mu_{AA}^* = \lim_{x_{AA} \rightarrow 0} [(\mu_{AA} - \mu_{AA}^*) - RT \ln x_{AA}]$$



For This Case:

$$\mu_{AA}^{**} - \mu_{AA}^* = 3.14 \text{ kJ/mol}$$

Reference States for a Volatile System

Ideal Reference State

$$\mu_i^*(T,P) = \mu_i^{\circ}(T) + RT \ln\left(\frac{P_i^*}{P^{\circ}}\right)$$

Ideal-Dilute Reference State

$$\mu_j^{**}(T,P) = \mu_j^{\circ}(T) + RT \ln\left(\frac{K_j}{P^{\circ}}\right)$$

Ideal-Dilute (molality) Reference State

$$\mu_j^{***}(T,P) = \mu_j^{\circ}(T) + RT \ln\left(\frac{K_j}{P^{\circ}}\right) + RT \ln(M m^{\circ})$$

Ideal-Dilute (molarity) Reference State

$$\mu_j^{\square}(T,P) = \mu_j^{\circ}(T) + RT \ln\left(\frac{K_j}{P^{\circ}}\right) + RT \ln\left(\frac{M \tilde{c}^{\circ}}{\rho}\right) \quad \text{where } \tilde{c}^{\circ} = c^{\circ} [\text{mol/m}^3]$$

Notes:

- 1) For the Ideal Reference State, it is assumed the Total Pressure over the Liquid/Solid is P. However, this is usually not the case. It is instead typically P_i^* . Because the change in Gibbs Free Energy is negligible for Pressure changes for condensed phases, we have:

$$\mu_i^*(T,P) \sim \mu_i^*(T,P_i^*)$$

However, $\mu_i^*(T,P)$ is the preferred reference state.

- 2) For the Ideal-Dilute References States, it is assumed the Total Pressure over the Solution when K_j , the Henry's Law Constant, is determined is P. However, this is usually not the case. Hence P is not well defined. Because the change in Gibbs Free Energy is negligible for Pressure changes for condensed phases, this is usually not of concern.
- 3) The difference between $\mu_j^{\square}(T,P)$ and $\mu_j^{***}(T,P)$ is not very large for Aqueous systems at Room Temperature. For these systems:

$$\begin{aligned}\tilde{c}^{\circ} &= 10^3 \text{ mol/m}^3 \\ m^{\circ} &= 1 \text{ mol/kg} \\ \rho &= 997.044 \text{ kg/m}^3\end{aligned}$$

So,

$$\begin{aligned}\mu_j^{\square}(T,P) - \mu_j^{***}(T,P) &= RT \ln\left(\frac{\tilde{c}^{\circ}}{\rho m^{\circ}}\right) \\ &= (8.314)(298.15) \ln\left(\frac{10^3}{997.044 \times 1}\right) = 7.339 \text{ J/mol}\end{aligned}$$

4) A pictorial representation of the Reference States for volatile systems.

