[Fugacity and Activity]

[Definitions]

Gibbs Free Energy: \( G \)

\[
G = H - TS = \text{[Enthalpy]} - \text{[Temperature]} \cdot \text{[Entropy]}
\]

Chemical Potential: \( \mu \)

\[
\mu = \frac{G}{n} = \bar{G}
\]

Fugacity: \( f \)

\[
\mu = RT \ln f^0 + RT \ln \frac{\Lambda^3}{RT}
\]

Fugacity has units of pressure (psia, atm)

Fugacity is "correction" to pressure

Fugacity Coefficient, \( \phi \)

\[
f^0 = \phi P_{sys}, \quad \phi = \frac{f^0}{P_{sys}}
\]

Fugacity Coefficient, \( \bar{\phi} \)

\[
\bar{\phi} = \frac{\bar{f}_i}{\bar{f}_i^0}
\]

Fugacity Coefficient, \( \phi \)

\[
\mu_i = \frac{\partial G}{\partial n_i} = \bar{G}_i
\]

\[
\mu_i = RT \ln \bar{f}_i + RT \ln \frac{\Lambda^3_i}{RT}
\]

Fugacity Coefficient, \( \bar{f}_i \)

\[
\bar{f}_i = \bar{\phi}_i \gamma_i P_{sys} \quad \bar{\phi}_i = \frac{\bar{f}_i}{\bar{f}_i^0}
\]

Activity Coefficient, \( \gamma_i \)

\[
\bar{f}_i = \gamma_i \chi_i f_i^0
\]

Activity, \( \alpha_i \)

\[
\alpha_i = \frac{\bar{f}_i}{f_i^0} = \gamma_i \chi_i
\]

Activity has units of composition

Activity is "correction" to composition

or:

\[
\alpha_i = \frac{\bar{f}_i (T, P, \chi)}{\bar{f}_i^{\text{ref}} (T, P, \chi')}
\]

\( \bar{f}_i^{\text{ref}} \): Reference fugacity at \( T', P', \chi' \).

{We can choose \( \bar{f}_i^{\text{ref}} = \) pure i fugacity: \( f_i^0 (T, P) \)}
[Available methods for calculating fugacities]:

**Pure (n)**

1. **Equations of state**
   \[ \frac{\partial G}{\partial p} \bigg|_T = V, \quad \therefore \frac{d(f^o)}{p} = \frac{z-1}{p} dp, \]

2. **Generalized \( \frac{f}{p} \) chart**

3. **steam Tables** (water only)
   \[ \mu = G = H - TS, \]

4. **...**

**Mixtures (n \_1, n \_2, \ldots, n \_c)**

1. **Equations of state**
   \[ \frac{\partial G}{\partial p} \bigg|_T = V_i \Rightarrow \frac{d(f_i)}{p} = \frac{z_i}{p} dp, \]

2. **Ideal Solutions (Y_i = 1.0)**
   (a) \( P_i = x_i P^\text{vap} \) (Raoult's Law)
   (b) \( f_i = y_i f_i^o \) (Lewis-Randall Rule)<p>22</p>
   (c) \( \bar{V}_i = V_i^o \)
   (d) \( \bar{H}_i = H_i^o \)

3. **Activity coeff. Models**
   (Nonideal Sol.)
   e.g. van Laar Model
   \[ \ln \gamma_i = \frac{A}{1 + \frac{A x_i}{x_2}} ^2, \]

4. **Ideal Gas Mixtures (Y_i = 1, Z = 1)**
   \[ PV = n_i T RT, \]
   \[ f_i = y_i P, \]
[Calculate Pure Fugacity, \( f^o \)]

1. **Steam Tables (water only)**
   a. At \( T, P \): \( G = H - TS = \mu = RT \ln f^o + C^o \),
   b. At \( T, P^* = 1 \): \( G^* = H^* - TS^* = \mu^* = RT \ln P^* + C^o \),
   c. \( RT \ln f^o - RT \ln P^* = (H - H^*) - T(S - S^*) \),
   \[ \ln \frac{f^o}{P^*} = \ln f^o = \frac{1}{RT} \left[ (H - H^*) - T(S - S^*) \right] \],

2. **van der Waals**
   \[ \ln \left( \frac{f^o}{P_{sys}} \right) = \frac{b}{v-b} - \frac{2a}{vRT} - \ln \left( \frac{P(v-b)}{RT} \right) \],

3. **Gen \( \frac{f}{P} \) chart**
   \[ T_R = \frac{T_{sys}}{T_c} \, , \, P_R = \frac{P_{sys}}{P_c} \Rightarrow \frac{f}{P} \xrightarrow{\text{chart}} \frac{f^o}{P} \]