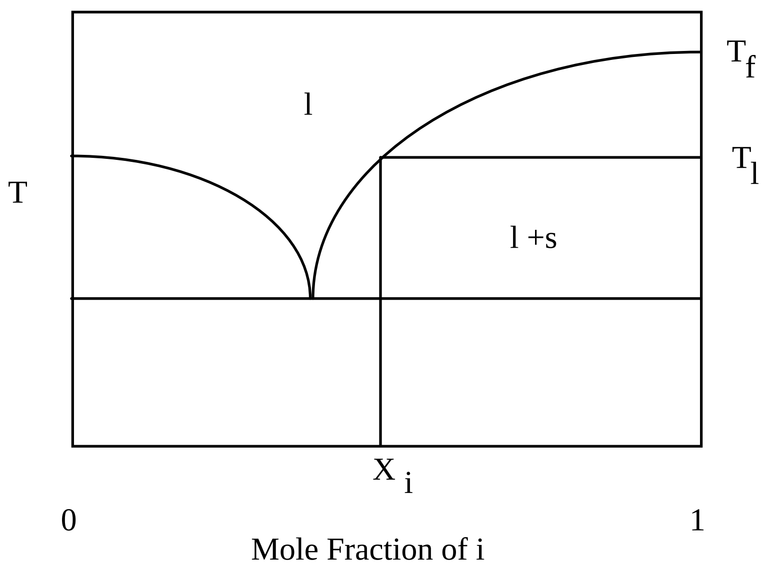
South Dakota School of Mines and Technology
Department of Materials and Metallurgical Engineering

Activities from the Phase Diagram

Required conditions

The component for which the activity is desired must be in equilibrium with a phase having a known activity of that component. The most common condition satisfying this requirement occurs when a component in liquid solution is in equilibrium with the pure, solid component. The following derivation is for this condition but it could be modified for other situations.



At temperature T_l the pure, solid i is in equilibrium with i in the liquid melt of composition X_i. The reaction describing the equilibrium is

$$i_l = i_s .$$

Where the "l" subscript denotes the liquid phase and "s" denotes the pure, solid phase.

Since the chemical potential of component i is the same in both phases,

$$\mu_i = \mu_i .$$

Substituting the definition of activity for each chemical potential gives

$$\mu_i^* + RT_l \ln a_{i,s} = \mu_i^o + RT_l \ln a_i$$

where

μ_i^* = the chemical potential of pure, solid i
μ_i^o = the chemical potential of pure, liquid i
$a_{i,s}$ = activity of i relative to pure, solid i
a_i = activity of i relative to pure, liquid i

Under the conditions stated, the activity of i relative to the pure solid is unity. Therefore,

$$\ln a_i = \frac{\mu_i^o - \mu_i^*}{-RT_l} = \frac{\Delta G^o_{fusion,T_l}}{-RT_l}$$

The Gibb's energy of fusion may be replaced with the following expression

$$\Delta G^o_{fusion,T_l} = \Delta H^o_{fusion,T_l} - T_l \Delta S^o_{fusion,T_l}$$

and $\Delta H^o_{fusion,T_l}$ and $\Delta S^o_{fusion,T_l}$ may be calculated using the following expressions

$$\Delta H^o_{fusion,T_l} = \Delta H^o_{fusion,T_f} + \int_{T_f}^{T_l} \Delta Cp dT$$

$$\Delta S^o_{fusion,T_l} = \Delta S^o_{fusion,T_f} + \int_{T_f}^{T_l} \frac{\Delta Cp dT}{T} = \frac{\Delta H^o_{fusion,T_f}}{T_f} + \int_{T_f}^{T_l} \frac{\Delta Cp dT}{T}$$

where

$$\Delta Cp = Cp_l - Cp_s$$

If the heat capacity of liquid i is assumed constant and the heat capacity of solid i is assumed to be a linear function of temperature given by the expressions

$$\text{Liquid } Cp_l = C$$

and

$$\text{Solid } Cp_s = A + BT,$$

then the following result is obtained

$$\ln a_i = \frac{\Delta H^o_{fusion,T_f}}{R}\left[\frac{1}{T_f} - \frac{1}{T_l}\right] + \frac{A - C - BT_l}{R}\left[1 - \frac{T_f}{T_l}\right] + \frac{A - C}{R}\ln\left[\frac{T_f}{T_l}\right] + \frac{B}{2RT_l}\left[T_l^2 - T_f^2\right].$$