

Thermodynamics of solutions

Partial molar quantities

Partial molar volume

Chemical potential

Gibb-Duhem Equation

NC State University

Total derivative for two components

We consider the thermodynamics of two-component systems. The ideas discussed here are easily generalized to multicomponent systems. For a solution consisting of n_1 moles of component 1 and n_2 moles of component 2, the Gibbs energy is a function T and P and the two mole numbers n_1 and n_2 . The dependence on these variables is indicated by writing $G = G(T, P, n_1, n_2)$. The total derivative of G is given by

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2} dP + \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1} dn_2$$

Gibbs energy at fixed composition

If the composition of the solution is fixed then we have $dn_1 = dn_2 = 0$, and the last two terms are zero. In this case the functional form of the Gibbs energy is exactly the same as we have seen previously

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2} dP$$

where

$$\left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2} = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2} = V$$

The chemical potential in a mixture

The chemical potential is defined as

$$\mu_1 = \mu_1(T, P, \mu_2) = \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2} = G_{T, P, n_2}$$

for component 1 and an analogous equation holds for component 2. In general there may be a greater number of components and each will have an associated chemical potential that is the derivative of the Gibbs energy with respect to the mole number of that component. It is also evident that the chemical potential is a molar Gibbs energy for one component and for more than one component it is a partial molar Gibbs energy. This is an intensive property and is just the Gibbs energy per mole.

General Gibbs energy for a mixture

For a binary solution the Gibbs energy is

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2$$

At constant T and P we have

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

A general expression for the Gibbs energy is

$$G = \mu_1 n_1 + \mu_2 n_2$$

For a one component system $G = \mu n$ consistent with the statements made previously that μ is a molar Gibbs energy.

Other thermodynamic quantities have associated partial molar values. The easiest to see physically is the partial molar volume $V_{j,m} = (\partial V / \partial n)_j$.

Partial molar volume

For a two component mixture the volume is

$$V = V_{1,m}n_1 + V_{2,m}n_2$$

For example, when 1-propanol and water are mixed, the final volume, V of the solution is not equal to the volumes of pure 1-propanol and water. The mixture of two components that can interact in a non-ideal fashion leads to a solution volume that is greater or less than that of the pure components. The partial molar volumes allow this to be quantified.

Other thermodynamic quantities can also be expressed as partial molar derivatives. In general for the j th component we have

$$d\mu_j = -\bar{S}_j dT + \bar{V}_j dP$$

Gibbs-Duhem Equation

Starting with $G = \mu_1 n_1 + \mu_2 n_2$ we can differentiate to obtain

$$dG = d\mu_1 n_1 + d\mu_2 n_2 + \mu_1 dn_1 + \mu_2 dn_2$$

Comparison with the above equation $dG = \mu_1 dn_1 + \mu_2 dn_2$

leads to

$$n_1 d\mu_1 + n_2 d\mu_2 = 0.$$

If we divide both sides by $n_1 + n_2$ we have

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

where x_1 and x_2 are mole fractions.

These last two equations are two forms of the Gibbs-Duhem equation. The Gibbs-Duhem equation is important because it tells that if we know the chemical potential of one component as a function of composition, we can determine the other.

Gibbs-Duhem Equation

For example, the chemical potential of substance 1 in a two component mixture is

$$\mu_1 = \mu_1^* + RT \ln x_1$$

Where $0 \leq x_1 \leq 1$. The superscript * is the IUPAC notation for a property of a pure substance. We can differentiate with respect to x_1 and substitute into the Gibbs-Duhem equation to obtain

$$\begin{aligned} d\mu_2 &= -\left(\frac{x_1}{x_2}\right)d\mu_1 = -RT\left(\frac{x_1}{x_2}\right)d \ln x_1 \\ &= -RT\left(\frac{x_1}{x_2}\right)\frac{dx_1}{x_1} = -RT\left(\frac{dx_1}{x_2}\right) \end{aligned}$$

and since $dx_1 = -dx_2$ we have

$$d\mu_2 = RT \left(\frac{dx_2}{x_2} \right)$$

or

$$\mu_2 = \mu_2^* + RT \ln x_2$$

Thus, we have shown that one can derive the chemical potential of substance 2 from substance 1.

The expression $\mu_j = \mu_j^* + RT \ln x_j$ implies that we can determine the chemical potential of any substance based on the knowledge of the chemical potential of the pure substance and the mole fraction x_j . One of our goals in the study of non-ideal solutions will be to prove this.

Recall that if two phases are in equilibrium their chemical potentials are equal. We can use this fact to our advantage. At any given temperature a liquid has a vapor pressure. This means that the chemical potential of the vapor above the liquid must equal the chemical potential of the liquid itself. This is just another way of saying that the liquid and its vapor are in chemical equilibrium.

$$\mu_j^{\text{sln}} = \mu_j^{\text{vap}}$$

If the pressure of the vapor phase is low we can consider it to be ideal. Thus we have

$$\mu_j^{\text{sln}} = \mu_j^{\text{vap}} = \mu_j^{\circ}(T) + RT \ln P_j$$

where we have simply stated the chemical potential of the j th component of the liquid relative to that of its standard state of 1 bar of pressure $\mu_j^{\circ}(T)$.

Chemical potential of a solution

For pure component j the equation becomes

$$\mu_j^*(l) = \mu_j^*(\text{vap}) = \mu_j^\circ(T) + RT \ln P_j^*$$

Thus

$$\mu_j^{\text{sln}} = \mu_j^* + RT \ln P_j/P_j^*.$$

This is a central result for the study of liquid. This result uses information from the vapor phase chemical potential above the liquid to give us information on the chemical potential in the liquid.