

## 14.8: Gibbs-Duhem Equation

An important relationship among the differentials of the chemical potentials for a system follows from the relationships we have just developed. From the fact that the Gibbs free energy,  $G(P, T, n_A, n_B, n_C, n_D)$ , is homogeneous of order one in the composition variables, we find that the Gibbs free energy of the system is related to its partial molar derivatives by

$$G(P, T, n_A, n_B, n_C, n_D) = \mu_A n_A + \mu_B n_B + \mu_C n_C + \mu_D n_D$$

The differential of the left hand side is

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

and the differential of the right hand side is

$$dG = \mu_A dn_A + n_A d\mu_A + \mu_B dn_B + n_B d\mu_B + \mu_C dn_C + n_C d\mu_C + \mu_D dn_D + n_D d\mu_D$$

Since these differential expressions must be equal, we have

$$-SdT + VdP = n_A d\mu_A + n_B d\mu_B + n_C d\mu_C + n_D d\mu_D$$

for any change in this system.

While we have considered the particular case of a system containing the species  $A$ ,  $B$ ,  $C$ , and  $D$ , it is clear that the same arguments apply to any system. For a system that contains  $\omega$  species, we can write the result in general form as

$$-SdT + VdP = \sum_{j=1}^{\omega} n_j d\mu_j$$

This relationship is known as the chemical-potential **Gibbs-Duhem equation**. It is a constraint on the  $d\mu_j$  that must be satisfied when any change occurs in a system whose thermodynamic functions are continuous functions of its composition variables. If pressure and temperature are constant and this equation is satisfied, the system is at equilibrium—it is on a Gibbsian equilibrium manifold—and the chemical-potential Gibbs-Duhem equation becomes

$$0 = \sum_{j=1}^{\omega} n_j d\mu_j$$

In the next two sections, we develop a particularly useful expression for  $d\mu_j$ . We can obtain similar relationships for other partial molar quantities. (See problems 14.2 and 14.3.) These relationships are also called Gibbs-Duhem equations. Because the derivation requires only that the thermodynamic function be homogeneous of order one, the same relationships exist among the differentials of the partial molar derivatives of any extensive thermodynamic function. For partial molar volumes at constant pressure and temperature, we find

$$0 = \sum_{j=1}^{\omega} n_j d\bar{V}_j$$

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