17.6: The Gibbs-Duhem Relation

In a mixture of several components kept at constant temperature and pressure, the chemical potential μ_i of a particular component (which, under conditions of constant T and P, is also its partial molar Gibbs function, g_i) depends on how many moles of each species i are present. The Gibbs-Duhem relation tells us how the chemical potentials of the various components vary with composition. Thus:

We have seen that, if we keep the pressure and temperature constant, and we increase the number of moles of the components by N_1, N_2, N_3, the increase in the Gibbs function is

$$dG = \sum \mu_i dN_i. \tag{17.6.1}$$

We also pointed out in section 17.5 that, provided the temperature and pressure are constant, the chemical potential μ_i is just the partial molar Gibbs function, g_i, so that the total Gibbs function is

$$G = \sum g_i N_i = \sum \mu_i N_i, \tag{17.6.2}$$

the sum being taken over all components. On differentiation of equation 17.7.2 we obtain

$$dG = \sum \mu_i dN_i + \sum N_i d\mu_i. \tag{17.6.3}$$

Thus for any process that takes place at constant temperature and pressure, comparison of equations 17.6.1 and 17.6.3 shows that

$$\sum N_i d\mu_i = 0, \tag{17.6.4}$$

which is the *Gibbs-Duhem* relation. It tells you how the chemical potentials change with the chemical composition of a phase.