

## 14.4: Chemical Potentials and Stoichiometry

Let us now apply our chemical-potential equilibrium criterion,  $\sum_{j=1}^{\omega} \mu_j dn_j = 0$ , to a simple, closed system in which phases  $\alpha$  and  $\beta$  of a single component are at equilibrium. The total number of moles,  $n$ , is fixed; we have  $n = n_{\alpha} + n_{\beta}$ . Reversible change is possible while the system remains at equilibrium. However, there is a stoichiometric constraint; growth in one phase is exactly matched by shrinkage in the other;  $dn = dn_{\alpha} + dn_{\beta} = 0$ , so that  $dn_{\alpha} = -dn_{\beta}$ . The equilibrium criterion becomes  $(\mu_{\alpha} - \mu_{\beta}) dn_{\alpha} = 0$ . If reversible change occurs, we have  $dn_{\alpha} \neq 0$ , and it follows that  $\mu_{\alpha} = \mu_{\beta}$ .

We infer that this result must always be valid. That is, if a substance is present in two phases of an equilibrium system, the chemical potential of the substance is the same in each phase; no matter what other processes involving the substance may occur. This is so because all processes that occur in the system must be at equilibrium in order for the system as a whole to be at equilibrium. In our discussion of chemical kinetics, we saw this conclusion expressed as the principle of microscopic reversibility. In our development of Gibbs phase rule, we asserted that a distribution-equilibrium constant relates the concentrations of a species in any two phases. Our present conclusion that the chemical potential of a species must be the same in each phase is a more rigorous statement of the same principle.

For a process in which  $dn$  moles of a substance transfer spontaneously from phase  $\beta$  to phase  $\alpha$ , we have  $dn = dn_{\alpha} = -dn_{\beta}$ . The criterion for spontaneous change,  $\sum_{j=1}^{\omega} \mu_j dn_j < 0$ , becomes

$$\mu_{\alpha} dn_{\alpha} + \mu_{\beta} dn_{\beta} = \mu_{\alpha} dn_{\alpha} - \mu_{\beta} dn_{\alpha} < 0$$

and it follows that  $\mu_{\alpha} < \mu_{\beta}$ . We infer that this result, too, must always be valid. That is, if a substance spontaneously transfers between any two phases, the chemical potential of the transferring substance must be greater in the donor phase than it is in the acceptor phase.

While  $\sum_{j=1}^{\omega} \mu_j dn_j \leq 0$  summarizes our criteria for change, it does not specify the process that occurs in the system. In order to describe a particular chemical reaction, we must incorporate the constraints that the reaction stoichiometry imposes on the  $dn_j$ . For a description of the equilibrium system that does not require the size of the system to be specified, the position of equilibrium must be given as a function of intensive variables. While the  $\mu_j$  are intensive variables, the  $dn_j$  are not. When we include information about the stoichiometry of the equilibrium process, we obtain a criterion for equilibrium that is specific to that process.

Consider the reaction  $a A + b B \rightleftharpoons c C + d D$  in a closed system. Let  $d\xi$  be the incremental extent of reaction. Using the modified stoichiometric coefficients,  $\nu_j$ , that we introduce in [Section 13.5](#), the incremental extent of reaction becomes

$$d\xi = \frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D}$$

and we can use the stoichiometric coefficients to express the incremental composition changes,  $dn_j$ , as  $dn_j = \nu_j d\xi$ . The criteria for change become

$$\sum_{j=1}^{\omega} \mu_j \nu_j d\xi \leq 0$$

For the reaction to occur left to right, we must have  $d\xi > 0$ , so that

$$\sum_{j=1}^{\omega} \mu_j \nu_j \leq 0$$

In this form, the criteria involve only intensive variables, and the stoichiometry of the equilibrium process is uniquely specified. In most circumstances, there are additional relationships among the  $\mu_j$  for which we may have little or no specific information.

To see the nature of these additional relationships, let us consider a chemical reaction involving three species,  $A + B \rightleftharpoons C$ , at constant pressure and temperature. No other substances are present. There are two components; so there are three degrees of freedom. Pressure and temperature account for two of the degrees of freedom. The chemical potential of any one of the equilibrating species, say  $A$ , accounts for the third. Evidently, fixing pressure, temperature, and  $\mu_A$  is sufficient to fix the values of the remaining chemical potentials,  $\mu_B$  and  $\mu_C$ .  $\mu_A$  must contain information about the other chemical potentials,  $\mu_B$  and  $\mu_C$ .

If the same reaction occurs in the presence of a solvent, there are three components and four degrees of freedom. In this case, two of the chemical potentials can vary independently. Fixing pressure, temperature, and, say  $\mu_A$  and  $\mu_B$ , fixes  $\mu_C$  and the chemical

potential of the solvent. We can expect the chemical potential of the solvent to be nearly constant, and we often omit it when we write  $dG$  for this system. This omission notwithstanding, the chemical potentials of the equilibrating species include information about the chemical potential of the solvent. In general, the chemical potential of any component of an equilibrium system is a function of the chemical potentials of all of the other components.

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