

## 11.7: Gibbs Energy and Reaction Equilibrium

This section begins by examining the way in which the Gibbs energy changes as a chemical process advances in a closed system at constant  $T$  and  $p$  with expansion work only. A universal criterion for reaction equilibrium is derived involving the molar reaction Gibbs energy.

### The molar reaction Gibbs energy

Applying the general definition of a molar differential reaction quantity (Eq. 11.2.15) to the Gibbs energy of a closed system with  $T$ ,  $p$ , and  $\xi$  as the independent variables, we obtain the definition of the **molar reaction Gibbs energy** or molar Gibbs energy of reaction,  $\Delta_r G$ :

$$\Delta_r G \stackrel{\text{def}}{=} \sum_i \nu_i \mu_i \quad (11.7.1)$$

Equation 11.2.16 shows that this quantity is also given by the partial derivative

$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{T,p} \quad (11.7.2)$$

(closed system)

The total differential of  $G$  is then

$$dG = -S dT + V dp + \Delta_r G d\xi \quad (11.7.3)$$

(closed system)

### Spontaneity and reaction equilibrium

In Sec. 5.8, we found that the spontaneous direction of a process taking place in a closed system at constant  $T$  and  $p$ , with expansion work only, is the direction of decreasing  $G$ . In the case of a chemical process occurring at constant  $T$  and  $p$ ,  $\Delta_r G$  is the rate at which  $G$  changes with  $\xi$ . Thus if  $\Delta_r G$  is positive,  $\xi$  spontaneously decreases; if  $\Delta_r G$  is negative,  $\xi$  spontaneously increases. During a spontaneous process  $d\xi$  and  $\Delta_r G$  have opposite signs.

Sometimes reaction spontaneity at constant  $T$  and  $p$  is ascribed to the “driving force” of a quantity called the **affinity of reaction**, defined as the negative of  $\Delta_r G$ .  $\xi$  increases spontaneously if the affinity is positive and decreases spontaneously if the affinity is negative; the system is at equilibrium when the affinity is zero.

Note how the equality of Equation 11.7.3 agrees with the inequality  $dG < -S dT + V dp$ , a criterion of spontaneity in a closed system with expansion work only (Eq. 5.8.6). When  $d\xi$  and  $\Delta_r G$  have opposite signs,  $\Delta_r G d\xi$  is negative and  $dG = (-S dT + V dp + \Delta_r G d\xi)$  is less than  $(-S dT + V dp)$ .

If the system is closed and contains at least one phase that is a mixture, a state of reaction equilibrium can be approached spontaneously at constant  $T$  and  $p$  in either direction of the reaction; that is, by both positive and negative changes of  $\xi$ . In this equilibrium state, therefore,  $G$  has its minimum value for the given  $T$  and  $p$ . Since  $G$  is a smooth function of  $\xi$ , its rate of change with respect to  $\xi$  is zero in the equilibrium state. The condition for *reaction equilibrium*, then, is that  $\Delta_r G$  must be zero:

$$\Delta_r G = \sum_i \nu_i \mu_i = 0 \quad (11.7.4)$$

(reaction equilibrium)

It is important to realize that this condition is independent of whether or not reaction equilibrium is approached at constant temperature and pressure. It is a universal criterion of reaction equilibrium. The value of  $\Delta_r G$  is equal to  $\sum_i \nu_i \mu_i$  and depends on the state of the system. If the state is such that  $\Delta_r G$  is positive, the direction of spontaneous change is one that, under the existing constraints, allows  $\Delta_r G$  to decrease. If  $\Delta_r G$  is negative, the spontaneous change increases the value of  $\Delta_r G$ . When the system reaches reaction equilibrium, whatever the path of the spontaneous process, the value of  $\Delta_r G$  becomes zero.

### General derivation

We can obtain the condition of reaction equilibrium given by Eq. 11.7.4 in a more general and rigorous way by an extension of the derivation of Sec. 9.2.7, which was for equilibrium conditions in a multiphase, multicomponent system.

Consider a system with a reference phase,  $\alpha'$ , and optionally other phases labeled by  $\alpha \neq \alpha'$ . Each phase contains one or more species labeled by subscript  $i$ , and some or all of the species are the reactants and products of a reaction.

The total differential of the internal energy is given by Eq. 9.2.37:

$$dU = T^{\alpha'} dS^{\alpha'} - p^{\alpha'} dV^{\alpha'} + \sum_i \mu_i^{\alpha'} dn_i^{\alpha'} + \sum_{\alpha \neq \alpha'} \left( T^{\alpha} dS^{\alpha} - p^{\alpha} dV^{\alpha} + \sum_i \mu_i^{\alpha} dn_i^{\alpha} \right) \quad (11.7.5)$$

The conditions of isolation are

$$dU = 0 \quad (\text{constant internal energy}) \quad (11.7.6)$$

$$dV^{\alpha'} + \sum_{\alpha \neq \alpha'} dV^{\alpha} = 0 \quad (\text{no expansion work}) \quad (11.7.7)$$

For each species  $i$ :

$$dn_i^{\alpha'} + \sum_{\alpha \neq \alpha'} dn_i^{\alpha} = \nu_i d\xi \quad (\text{closed system}) \quad (11.7.8)$$

In Eq. 11.7.8,  $dn_i^{\alpha'}$  should be set equal to zero for a species  $i'$  that is excluded from phase  $\alpha''$ , and  $\nu_i$  should be set equal to zero for a species  $i''$  that is not a reactant or product of the reaction.

We use these conditions of isolation to substitute for  $dU$ ,  $dV^{\alpha'}$ , and  $dn_i^{\alpha'}$  in Eq. 11.7.5, and make the further substitution  $dS^{\alpha'} = dS - \sum_{\alpha \neq \alpha'} dS^{\alpha}$ . Solving for  $dS$ , we obtain

$$dS = \sum_{\alpha \neq \alpha'} \frac{(T^{\alpha'} - T^{\alpha})}{T^{\alpha'}} dS^{\alpha} - \sum_{\alpha \neq \alpha'} \frac{(p^{\alpha'} - p^{\alpha})}{T^{\alpha'}} dV^{\alpha} + \sum_i \sum_{\alpha \neq \alpha'} \frac{(\mu_i^{\alpha'} - \mu_i^{\alpha})}{T^{\alpha'}} dn_i^{\alpha} - \frac{\sum_i \nu_i \mu_i^{\alpha'}}{T^{\alpha'}} d\xi \quad (11.7.9)$$

The equilibrium condition is that the coefficient multiplying each differential on the right side of Eq. 11.7.9 must be zero. We conclude that at equilibrium the temperature of each phase is equal to that of phase  $\alpha'$ ; the pressure of each phase is equal to that of phase  $\alpha'$ ; the chemical potential of each species, in each phase containing that species, is equal to the chemical potential of the species in phase  $\alpha'$ ; and the quantity  $\sum_i \nu_i \mu_i^{\alpha'}$  (which is equal to  $\Delta_r G$ ) is zero.

In short, *in an equilibrium state each phase has the same temperature and the same pressure, each species has the same chemical potential in the phases in which it is present, and the molar reaction Gibbs energy of each phase is zero.*

## Pure phases

Consider a chemical process in which each reactant and product is in a separate pure phase. For example, the decomposition of calcium carbonate,



involves three pure phases if no other gas is allowed to mix with the  $\text{CO}_2$ .

The situation is different when the number of molecules changes during the reaction. Consider the reaction  $A \rightarrow 2 B$  in an ideal gas mixture. As this reaction proceeds to the right at constant  $T$ , the volume increases if the pressure is held constant and the pressure increases if the volume is held constant. Figure 11.17 shows how  $G$  depends on both  $p$  and  $V$  for this reaction. Movement along the horizontal dashed line in the figure corresponds to reaction at constant  $T$  and  $p$ . The minimum of  $G$  along this line is at the volume indicated by the open circle. At this volume,  $G$  has an even lower minimum at the pressure indicated by the filled circle, where the vertical dashed line is tangent to one of the contours of constant  $G$ . The condition needed for reaction equilibrium, however, is that  $\Delta_r G$  must be zero. This condition is satisfied along the vertical dashed line only at the position of the open circle.

This example demonstrates that for a reaction occurring at constant temperature and *volume* in which the pressure changes, the point of reaction equilibrium is not the point of minimum  $G$ . Instead, the point of reaction equilibrium in this case is at the minimum of the Helmholtz energy  $A$  (Sec. 11.7.5).

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