

## 13.6: The Standard Gibbs Free Energy Change and Equilibrium in Ideal Gas Reactions

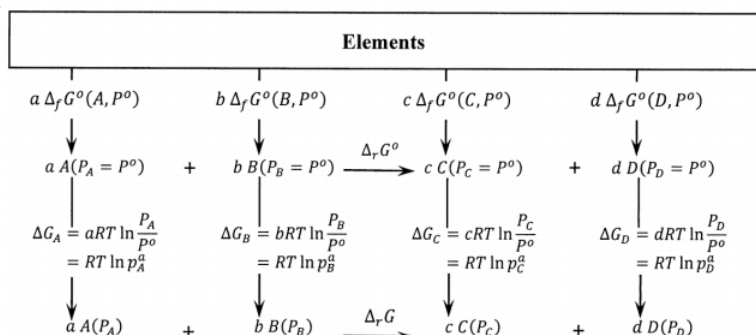


Figure 5. Cycle demonstrating the relationship between  $\Delta_r G$  and  $\Delta_r G^\circ$ .

The relationship between  $\Delta_r G$  and  $\Delta_r G^\circ$  is evident from the cycle in Figure 5. Since we have shown that  $\Delta_{sep} G(P_A, P_B, P_C, P_D) = \Delta_r G(P_A, P_B, P_C, P_D)$ , we can consider the bottom equation in this cycle to represent the reaction occurring in a mixture while calculating its free energy change as the free energy difference between pure products and pure reactants. Since  $\Delta_{cycle} G = 0$ ,

$$\Delta_{cycle} G = \Delta_r G^\circ - \Delta_r G + RT(\ln p_C^c + \ln p_D^d - \ln p_A^a - \ln p_B^b) = 0$$

which can be rearranged to the result obtained in §2:

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

$\Delta_r G$  is the Gibbs free energy change for one unit of the reaction occurring in a system whose composition is specified by  $P_A$ ,  $P_B$ ,  $P_C$ , and  $P_D$ . In this spontaneously reacting system, the molar Gibbs free energy of ideal gas  $A$  is

$$\bar{G}_A(P_A) = \Delta_f G^\circ(A, P^\circ) + RT \ln p_A$$

If the system is at equilibrium,  $P_A$ ,  $P_B$ ,  $P_C$ , and  $P_D$  are equilibrium pressures; these values characterize an equilibrium state. Then  $\Delta_r G$  is the free energy change for a reaction occurring at equilibrium at constant pressure and temperature, and  $\Delta_r G$  is zero. The equation

$$0 = \Delta_r G^\circ + RT \ln \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

is exact. We have, when the partial pressures are those for a system at equilibrium,

$$\Delta_r G^\circ = -RT \ln \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

Since  $\Delta_r G^\circ$  is a constant, it follows that

$$\frac{p_C^c p_D^d}{p_A^a p_B^b}$$

is a constant. It is, of course, the equilibrium constant. We have

$$K_P = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

and

$$\Delta_r G^\circ = -RT \ln K_P$$

or, solving for  $K_P$

$$K_P = \exp\left(+\frac{\Delta_r G^\circ}{RT}\right)$$

Note that the value of the equilibrium constant is calculated from the Gibbs free energy change at standard conditions, not the Gibbs free energy change at equilibrium, which is zero.

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