Thermodynamics -2

For a spontaneous reaction, the entropy of the universe must increase.

Reactions with large negative ΔH values (exothermic reactions) tend to be spontaneous (Thermodynamically favored).

The spontaneity of a reaction seems to involve two thermodynamic concepts, enthalpy and entropy.

The equilibrium position in a spontaneous process is given by the minimum free energy available to the system. The free energy decreases until it reaches this minimum value.

In a spontaneous process at constant temperature and pressure, the free energy always decreases.

Free Energy and Temperature

The sign of ΔG tells us if the reaction is spontaneous (thermodynamically favored).

$$\Delta G = \Delta H - T\Delta S$$

If $\Delta H < 0$ and $-T\Delta S < 0$. Then ΔG will always be < 0. Thus, the reaction will be spontaneous.

If $\Delta H > 0$ and $-T\Delta S > 0$. Then ΔG will always be > 0. Thus, the reaction will not be spontaneous.

If ΔH and $-T\Delta S$ have different signs. The sign of ΔG will depend on the sign and magnitude of the other terms.

Thermodynamics gives us the direction of a spontaneous process. It does not give us the rate of the process.

Free Energy and the Equilibrium Constant

and K_{eq} (equilibrium constant) apply to standard conditions.

and Q (equilibrium quotient) apply to any conditions.

It is useful to determine whether substances will react under specific conditions.

$$\Delta G = \Delta G^o + RT \ln Q$$

At equilibrium, $Q = K_{eq}$ and $\Delta G = 0$ so:

$$0 = \Delta G^o + RT \ln K_{eq}$$

$$\Delta G^o = -RT \ln K_{eq} = -2.303 \, RT \log K_{eq}$$

R = 8.314 J/mol K

$$K_{eq} = e^{-\Delta G^o / RT}$$
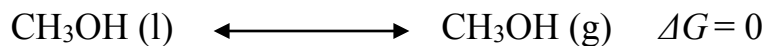
From the above, we can conclude:

If $\Delta G^o < 0$, then $K_{eq} > 0$
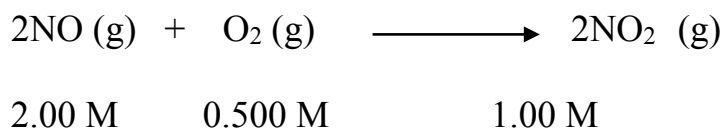
If $\Delta G^o = 0$, then $K_{eq} = 1$

If $\Delta G^o > 0$, then $K_{eq} < 1$

When a phase change is occurring, the value for ΔG is always zero ($\Delta G = 0$) as no real chemical reaction is occurring.

$$CH_3OH \, (l) \longleftrightarrow CH_3OH \, (g) \quad \Delta G = 0$$

Example 1:

Calculate ΔG for the following at 500 K:

$$2NO\ (g)\ +\ O_2\ (g)\ \longrightarrow\ 2NO_2\ (g)$$

$$2.00\ M \qquad 0.500\ M \qquad\qquad 1.00\ M$$

$\Delta G^o{}_f =$ 86.71 kJ/mol   0.00 kJ/mol.   51.84 kJ/mol

ΔG^o rxn = 2(51.84) - [2(86.71) + 0.00] = -69.74 kJ/mole

$$\Delta G = \Delta G^o\ rxn + RT\ ln\ Q$$

$$Q = [NO_2]^2\ /\ [NO]^2\ [O_2]$$

$$= (1.00)^2\ /\ (2.00)^2\ (0.50)$$

$$= 1/2$$

$\Delta G = \Delta G^o\ rxn + RT\ ln\ Q$

$\Delta G = (-69.74\ \text{x}\ 1000)\ J + 8.314\ J/mol\ K\ x\ 500\ K\ ln\ 1/2 = -7.262\ x\ 10^4\ J/mol$

Example 2:

$$N_2\ (g) + 3H_2\ (g)\ \longrightarrow\ 2\ NH_3\ (g)$$

$\Delta G = \Delta G^o\ rxn + RT\ ln\ Q$

$\Delta G = \Delta G^o\ rxn + RT\ ln\ (P_{NH3}\ )^{\ 2}\ /\ (P_{N2})\ (\ P_{H2})^{\ 3}$

Example 3:

$$2\ O_3\ (g) \quad \longleftrightarrow \quad 3\ O_2\ (g) \qquad K_{eq} = 4.17 \times 10^{14}$$
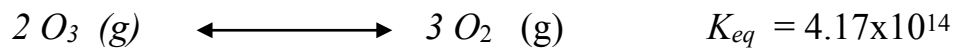
The system is at equilibrium, then $\Delta G = 0$

$\Delta G = \Delta G^o + RT \ln K_{eq}$

$0 = \Delta G^o + RT \ln K_{eq}$

$\Delta G^o = -RT \ln K_{eq} = -2.303\ RT \log K_{eq}$

$\Delta G^o = -RT \ln K_{eq} = -2.303\ RT \log K_{eq}$

$\Delta G^o = -RT \ln K_{eq} = -8.314\ \text{J/mol K}\ (298)\ \ln\ 4.17 \times 10^{14} = -8.34\ \text{J/mol}$

Domain of thermodynamics (the initial and final states)

Domain of kinetics (the reaction pathway)
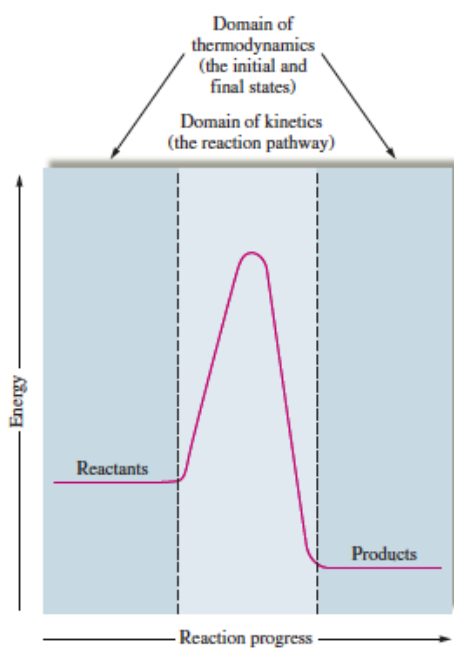
Energy

Reactants

Products

— Reaction progress —

TABLE 16.6   Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

$\Delta G°$	K
$\Delta G° = 0$	$K = 1$
$\Delta G° < 0$	$K > 1$
$\Delta G° > 0$	$K < 1$

Substance	$S°$ (J/K · mol)
$Al_2O_3(s)$	51
$H_2(g)$	131
$Al(s)$	28
$H_2O(g)$	189