Topic 5G - Chemical Equilibrium

Attainment of Chemical Equilibrium

FIGURE 6.2

The changes in concentrations with time for the reaction $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ when equal molar quantities of $H_2O(g)$ and $CO(g)$ are mixed.
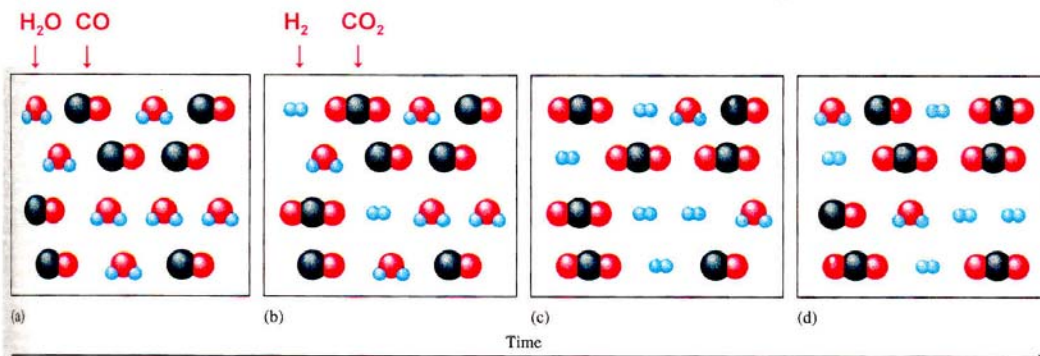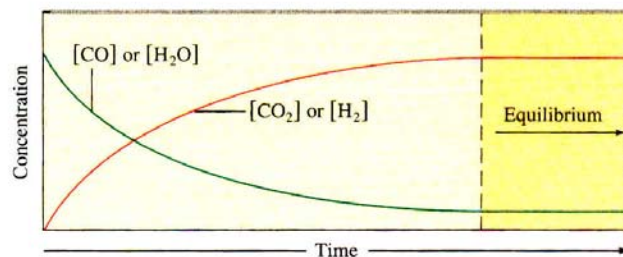
$\Delta G_r° = -28.6 \text{ kJ}$

FIGURE 6.3

(a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2. After time has passed equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time.

FIGURE 6.4

The changes with time in the rates of forward and reverse reactions for $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ when equal molar quantities of $H_2O(g)$ and $CO(g)$ are mixed. Note that the rates for the forward and reverse reactions do not change in the same way with time. We will not be concerned with the reasons for this difference at this point.
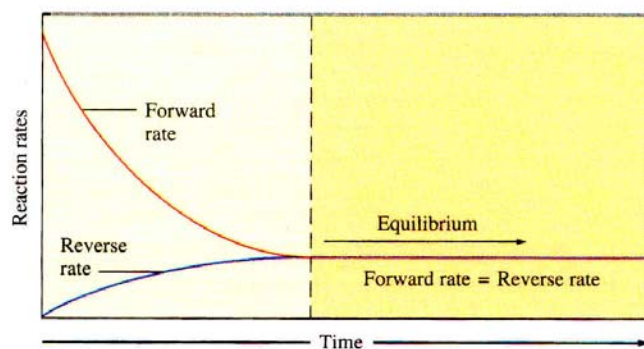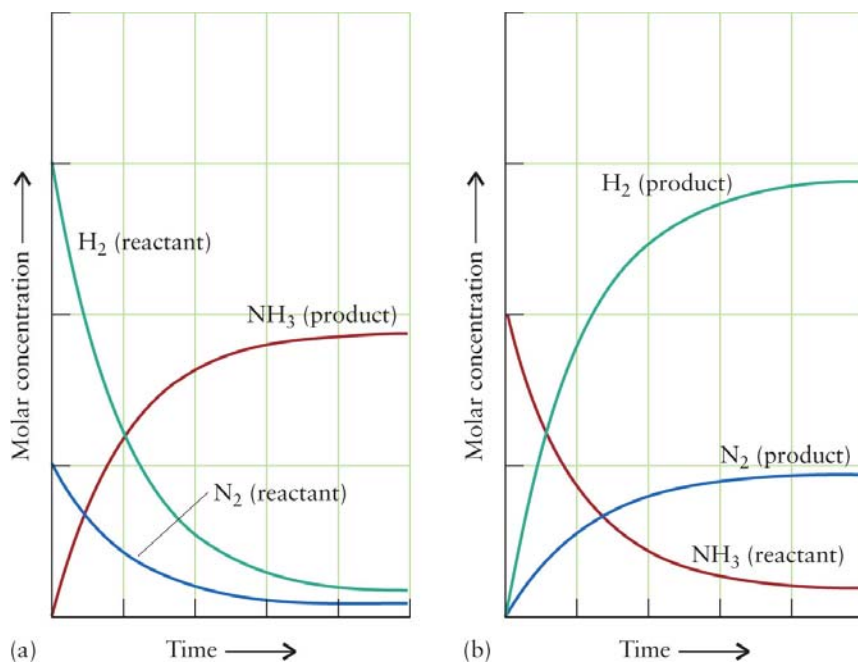
FIGURE 11.1 (a) In the synthesis of ammonia, the concentrations of N_2 and H_2 decrease with time and that of NH_3 increases until they finally settle into values corresponding to a mixture in which all three are present and there is no further net change. (b) If the experiment is repeated with pure ammonia, it decomposes, and the composition settles down into a mixture of ammonia, nitrogen, and hydrogen. (The two graphs correspond to experiments at two different temperatures, and so they correspond to different equilibrium compositions.)

Free Energy and Equilibrium

The algebraic sign of ΔG indicates the direction of spontaneous reaction, which proceeds toward a condition of <u>minimum free energy</u> (*i.e.*, equilibrium), at which point the rates of both the forward and reverse reactions are equal:

$$A + B \rightleftarrows C + D$$

The initial rate of the forward reaction (A + B → C + D) has some finite value. The initial rate of the reverse reaction (C + D → A + B) is zero, since no C or D exists initially.

After a sufficiently long time, the system will contain unchanging amounts of A, B, C, and D that are determined by the condition of minimum free energy (*i.e.*, equilibrium).

Law of Mass Action

For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$

where all reactants and products are in the gas phase, the equilibrium constant is given by:

$$K_p = \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b}$$

The dimensions of K_p are c+d-a-b, and its numerical value is a function only of the temperature.

In order to make K dimensionless, the "activity" of a dilute gas is defined as:

$$a_i = \frac{P_i}{P_{ref}}$$

where P_{ref} is usually taken to be 1 atm.

The correct expression for K_{eq} involves activities, rather than pressures, which makes it dimensionless:

$$K_{eq} = \frac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b} = \frac{\left(\dfrac{P_C}{P_{ref}}\right)^c \times \left(\dfrac{P_D}{P_{ref}}\right)^d}{\left(\dfrac{P_A}{P_{ref}}\right)^a \times \left(\dfrac{P_B}{P_{ref}}\right)^b}$$

TABLE 11.1 Equilibrium Data and the Equilibrium Constant for the Reaction
2 SO₂(g) + O₂(g) ⇌ 2 SO₃(g) at 1000. K

P_{SO_2} (bar)	P_{O_2} (bar)	P_{SO_3} (bar)	$K*$
0.660	0.390	0.0840	0.0415
0.0380	0.220	0.00360	0.0409
0.110	0.110	0.00750	0.0423
0.950	0.880	0.180	0.0408
1.44	1.98	0.410	0.0409

*Average K: 0.0413.

$$K = \frac{P^2_{SO_3}}{P^2_{SO_2} \times P_{O_2}} = \approx 0.041$$

TABLE 11.2 Equilibrium Constants for Various Reactions

Reaction	T (K)*	K	K_c†
$H_2(g) + Cl_2(g) \rightleftharpoons 2\ HCl(g)$	300	4.0×10^{31}	4.0×10^{31}
	500	4.0×10^{18}	4.0×10^{18}
	1000	5.1×10^{8}	5.1×10^{8}
$H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$	300	1.9×10^{17}	1.9×10^{17}
	500	1.3×10^{10}	1.3×10^{10}
	1000	3.8×10^{4}	3.8×10^{4}
$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$	298	794	794
	500	160	160
	700	54	54
$2\ BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$	300	377	377
	500	32	32
	1000	5	5
$2\ HD(g) \rightleftharpoons H_2(g) + D_2(g)$	100	0.52	0.52
	500	0.28	0.28
	1000	0.26	0.26
$F_2(g) \rightleftharpoons 2\ F(g)$	500	3.0×10^{-11}	7.3×10^{-13}
	1000	1.0×10^{-2}	1.2×10^{-4}
	1200	0.27	2.7×10^{-3}
$Cl_2(g) \rightleftharpoons 2\ Cl(g)$	1000	1.0×10^{-5}	1.2×10^{-7}
	1200	1.7×10^{-3}	1.7×10^{-5}
$Br_2(g) \rightleftharpoons 2\ Br(g)$	1000	3.4×10^{-5}	4.1×10^{-7}
	1200	1.7×10^{-3}	1.7×10^{-5}
$I_2(g) \rightleftharpoons 2\ I(g)$	800	2.1×10^{-3}	3.1×10^{-5}
	1000	0.26	3.1×10^{-3}
	1200	6.8	6.8×10^{-2}
$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$	298	6.8×10^{5}	4.2×10^{8}
	400	41	4.5×10^{4}
	500	3.6×10^{-2}	62
$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$	298	4.0×10^{24}	9.9×10^{25}
	500	2.5×10^{10}	1.0×10^{12}
	700	3.0×10^{4}	1.7×10^{6}
$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$	298	0.15	6.1×10^{-3}
	400	47.9	1.44
	500	1.7×10^{3}	41

*Three significant figures.
†K_c is the equilibrium constant in terms of molar concentrations of gases (Section 11.6).

Concentrations of pure solids or pure liquids do not appear in the equilibrium constant expression:

$$CaCO_3 \ (s) \ \rightleftarrows \ CaO \ (s) + CO_2 \ (g)$$

Same pressure of $CO_2(g)$

$CaCO_3(s)$

$CaO(s)$

Much $CaCO_3(s)$, little $CaO(s)$ Little $CaCO_3(s)$, much $CaO(s)$
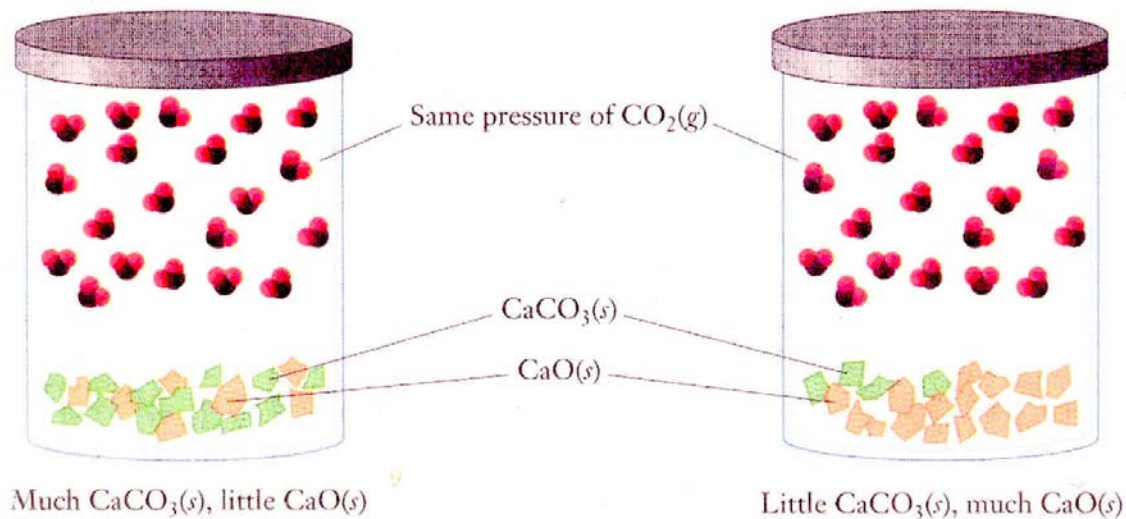
$$K = P_{CO2}$$

Effect of Pressure on Free Energy of a Gas

Since $\Delta H = 0$ when the pressure of an ideal gas is changed at <u>constant temperature</u>, then

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

The entropy change for an isothermal process of an ideal gas is given by:

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right) = -nR\ln\left(\frac{P_2}{P_1}\right)$$

Thus,

$$\Delta G = -T\Delta S = nRT\ln\left(\frac{P_2}{P_1}\right)$$

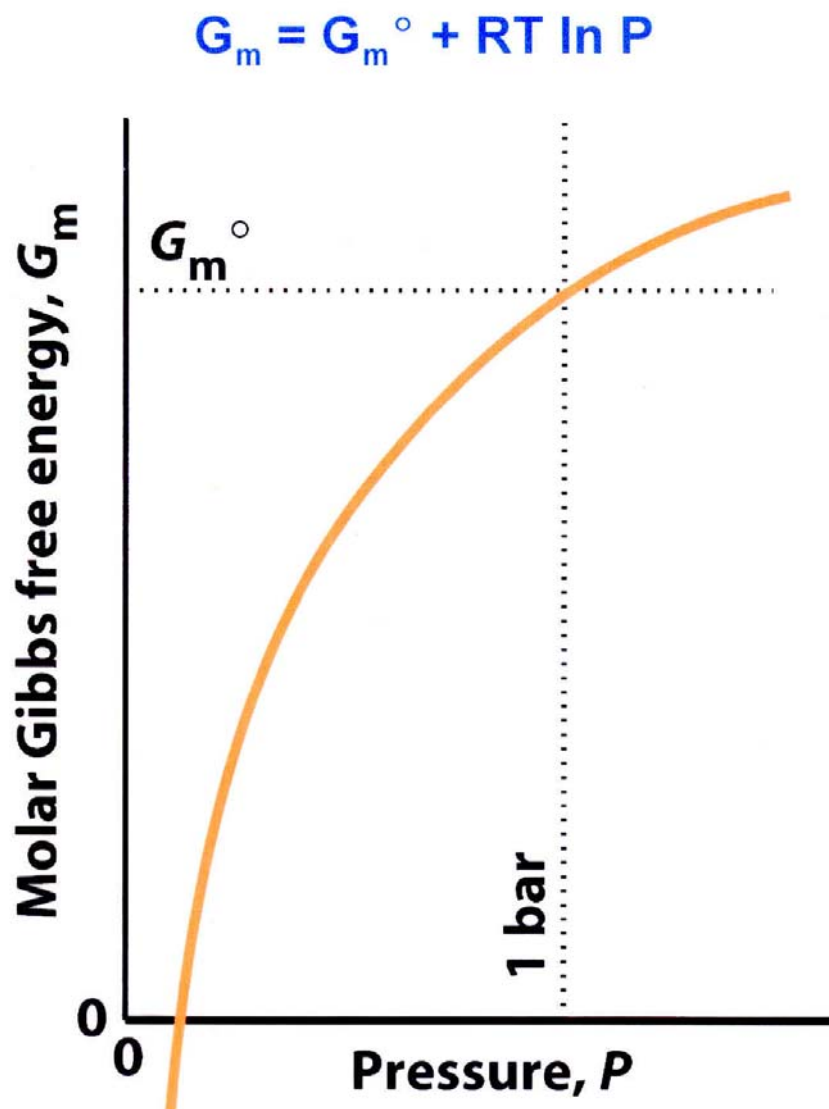Hence, the free energy of a gas at constant temperature increases with increasing pressure.

$$G_m = G_m^{\circ} + RT \ln P$$

FIGURE 8.3 The variation of the molar free energy of an ideal gas with pressure. The free energy has its standard value when the pressure of the gas is 1 bar. The value of the free energy approaches minus infinity as the pressure falls to zero.
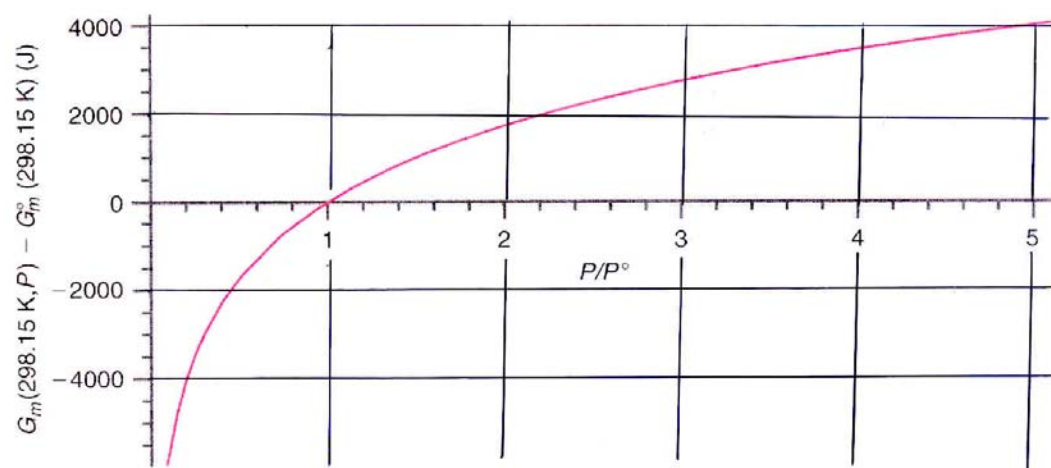
FIGURE 6.1

The molar Gibbs energy of an ideal gas
relative to its standard state value is shown
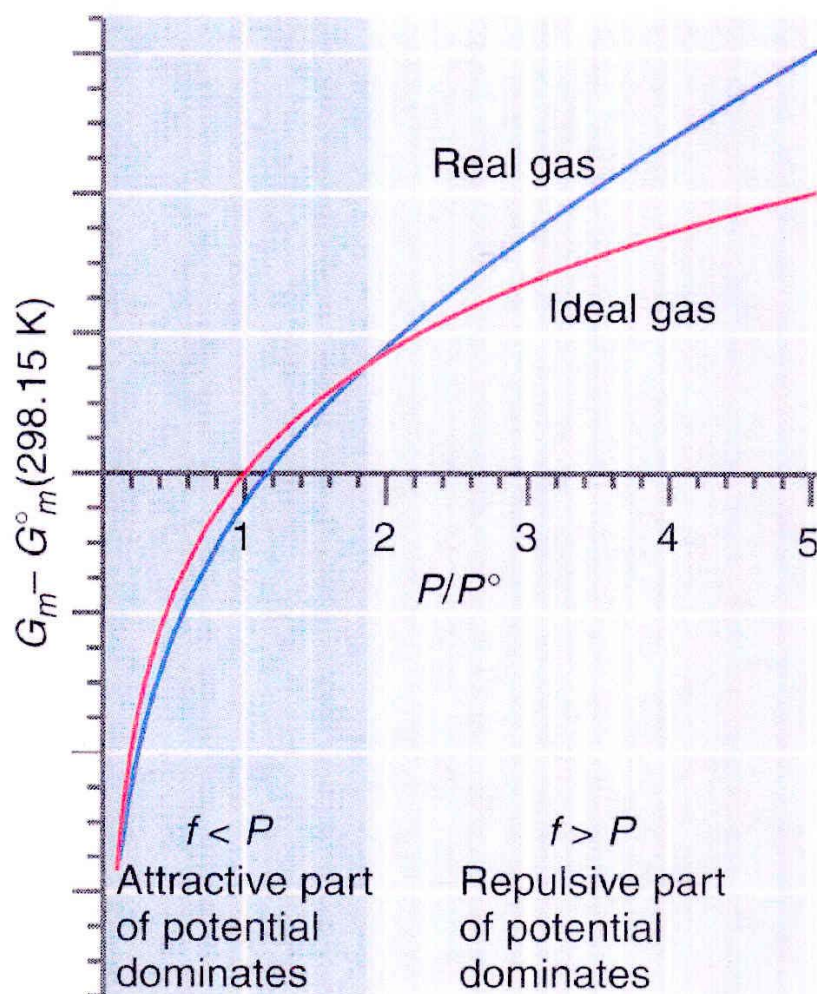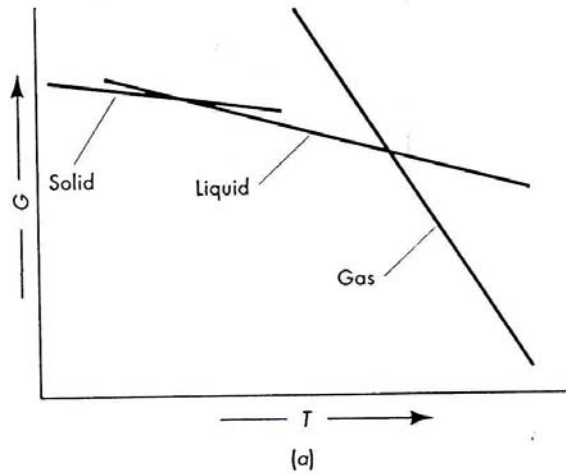as a function of the pressure at 298.15 K.

FIGURE 7.9

For densities corresponding to the attractive range of the potential, $P < P_{ideal}$. Therefore, $G_m^{real} < G_m^{ideal}$ and $f < P$. The inequalities are reversed for densities corresponding to the repulsive range of the potential.

FIGURE 5-9

The trends of free energy versus temperature for (a) the solid, liquid, and gas states of a substance, and (b) including the effect of reducing the pressure on the gas.

$$3\ NO \rightleftharpoons NO_2 + N_2O$$
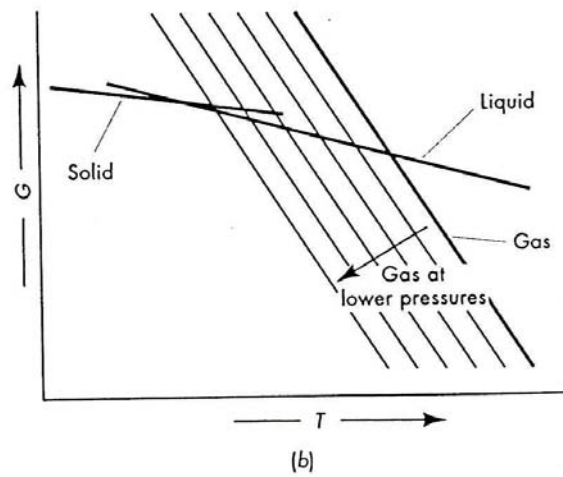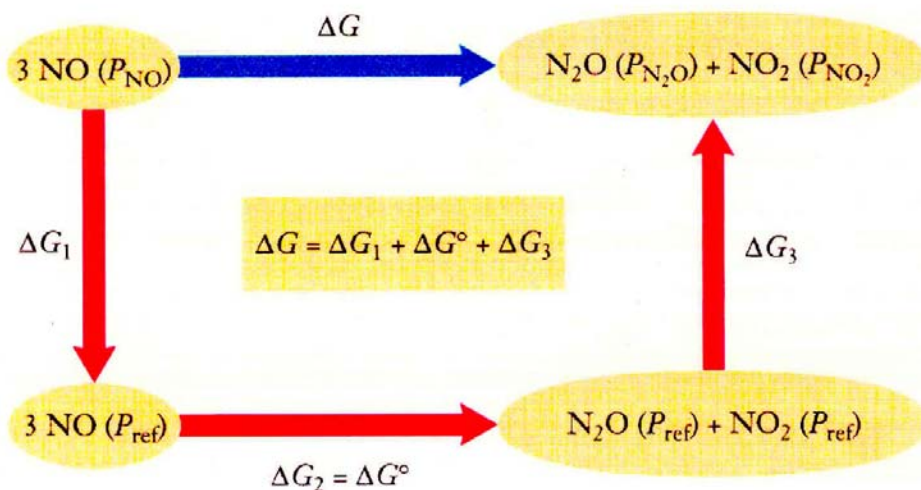
$$\Delta G_1 = 3RT\ln\left(\frac{P_{ref}}{P_{NO}}\right) = RT\ln\left(\frac{P_{ref}}{P_{NO}}\right)^3$$

$$\Delta G_2 = \Delta G^0$$

$$\Delta G_3 = RT\ln\left(\frac{P_{N_2O}}{P_{ref}}\right) + RT\ln\left(\frac{P_{NO_2}}{P_{ref}}\right) = RT\ln\left(\frac{P_{N_2O} \times P_{NO_2}}{P_{ref} \times P_{ref}}\right)$$

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 = \Delta G^0 + RT\ln\frac{\left(\frac{P_{N_2O}}{P_{ref}}\right) \times \left(\frac{P_{NO_2}}{P_{ref}}\right)}{\left(\frac{P_{NO}}{P_{ref}}\right)^3}$$

$$= \Delta G^0 + RT\ln Q$$

At equilibrium, $\Delta G = 0$ and $Q = K_{eq}$. Thus,

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

which is one of the most important equations in chemical thermodynamics, because it relates a thermodynamic state function (ΔG) to the empirical equilibrium constant.

At conditions away from equilibrium,

$$\Delta G^0 = RT \ln\left(\frac{Q}{K_{eq}}\right)$$

TABLE 10.7
Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

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

$$\Delta G^\circ = -RT \ln K_{eq}$$

Since

$$\Delta G° = -RT \ln K_{eq}$$

$$= \Delta H° - T\Delta S°$$

then

$$\ln K_{eq} = -\frac{\Delta G°}{RT} = \frac{\Delta S°_{sys}}{R} - \frac{\Delta H°}{RT}$$

and

$$K_{eq} = \exp\left(\frac{-\Delta G°}{RT}\right) = \exp\left(\frac{\Delta S°_{sys}}{R}\right) \times \exp\left(\frac{-\Delta H°}{RT}\right)$$

Thus, large values of K_{eq} are favored by positive $\Delta S°_{sys}$ (increase in randomness) and negative $\Delta H°$ (exothermicity).