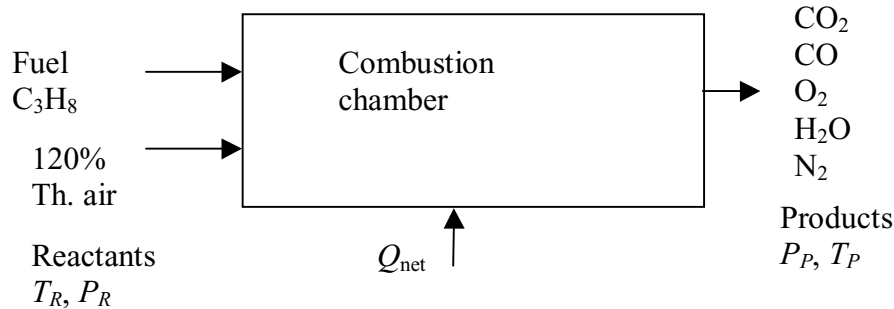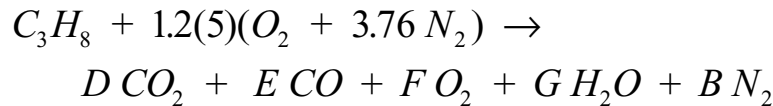# Chapter 15: Chemical and Phase Equilibrium

Consider the combustion of propane with 120 percent theoretical air.

The combustion equation is

$$C_3H_8 + 1.2(5)(O_2 + 3.76\,N_2) \rightarrow$$
$$D\,CO_2 + E\,CO + F\,O_2 + G\,H_2O + B\,N_2$$

Conservation of mass for each species yields

$$C: \quad 3 = D + E$$
$$H: \quad 8 = 2\,G \quad or\ G = 4$$
$$O: \quad (5)(A)(2) = 2\,D + E + 2\,F + G$$
$$N_2: \quad B = (3.76)(5)(1.2)$$

Since the percent theoretical air is known, the N_2 balance gives B. The H balance gives G. Then the C and O balances give two equations that relate the remaining three unknowns D, E, and F. Therefore, we need one more equation.

To obtain this last equation relating the mole numbers of the products, we assume that the products are in chemical equilibrium.

To develop the relations for chemical equilibrium, consider placing the product gases in a system maintained at constant T and P. The constant T

and *P* are achieved if the system is placed in direct contact with a heat reservoir and a work reservoir. In particular, let's consider that CO_2, CO, and O_2 form a mixture in chemical equilibrium.

$$CO + O_2 \rightarrow CO_2$$

Heat
Reservoir
At T

δQ

δW_b

Work
Reservoir
At P

System of Product
Gases At T and P
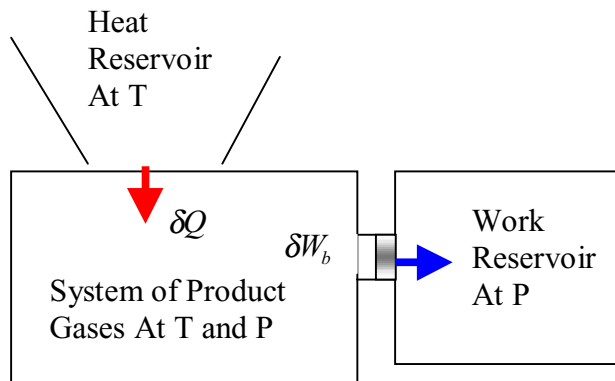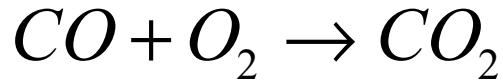
Taking the positive direction of heat transfer to be to the system, the increase of entropy principle for a reacting system is

$$ds_{sys} \geq \frac{\delta Q_{sys}}{T}$$

If the reaction takes place adiabatically, then $ds_{sys} \geq 0$. A reaction taking place adiabatically does so in the direction of increasing entropy.
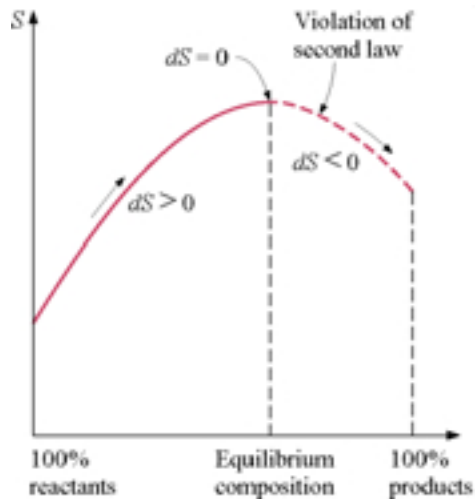
If we apply both the first law and the second law for the fixed mass system of reacting gases for fixed T and P where there is both heat transfer and work, we obtain

$$\delta Q - W_b = dU$$

$$W_b = PdV$$

$$dS \geq \frac{\delta Q}{T}$$

$$T\,dS \geq \delta Q$$

$$T\,dS \geq dU + PdV$$

$$0 \geq dU + P\,dV - T\,dS$$

$$or$$

$$dU + P\,dV - T\,dS \leq 0$$

Now, we define a new (for us anyway) thermodynamic function, the Gibbs function, as

$$G = H - TS$$

The differential of the Gibbs function when T and P are constant is

$$dG = dH - T\,dS - S\,dT$$
$$= (dU + P\,dV + V\,dP^{\,0}) - T\,dS - S\,dT^{\,0}$$
$$= dU + P\,dV - T\,dS$$
$$\leq 0 \text{ at constant } T \text{ and } P$$

The chemical reaction at constant temperature and pressure will proceed in the direction of decreasing Gibbs function. The reaction will stop and chemical equilibrium will be established when the Gibbs function attains a minimum value. An increase in the Gibbs function at constant T and P would be a violation of the second law.
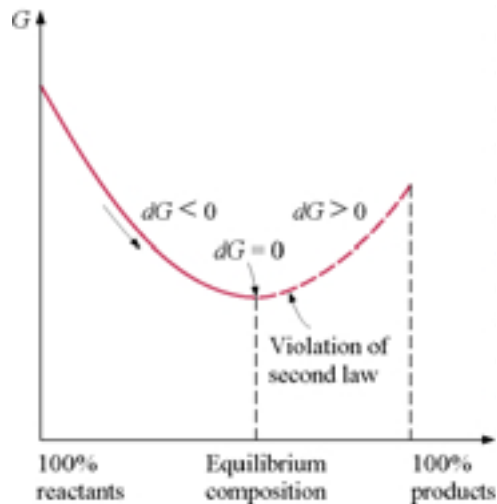

The criterion for chemical equilibrium is expressed as

$$(dG)_{T,P} = 0$$

Consider the equilibrium reaction among four reacting components A and B as reactants and C and D as products. These components will have mole numbers as N_A, N_B, N_C, and N_D. As differential amounts of A and B react to

form differential amounts of C and D while the temperature and pressure remain constant, we have the following reaction to consider.

$$dN_A A + dN_B B \rightarrow dN_C C + dN_D D$$
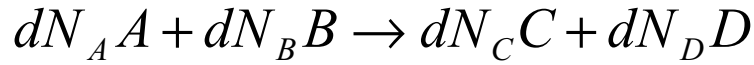
For equilibrium the Gibbs function of this mixture must be a minimum. This yields

$$(dG)_{T,P} = \sum (dG_i)_{T,P} = \sum (\bar{g}_i \, dN_i)_{T,P} = 0$$

$$\bar{g}_D \, dN_D + \bar{g}_C \, dN_C + \bar{g}_A \, dN_A + \bar{g}_B \, dN_B = 0$$

Here $\bar{g}_i$ is the molar Gibbs function for component i (also called the chemical potential).

To find a relation among the dN's, we select a corresponding stoichiometric reaction. For the CO, CO_2, O_2 reaction, the stoichiometric or theoretical reaction is

$$CO_2 \Leftrightarrow CO + \frac{1}{2} O_2$$
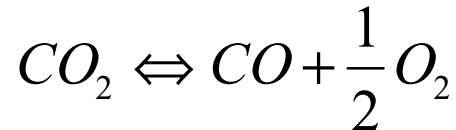
The change in moles of the components is related to their stoichiometric coefficients, 1, 1, ½ for CO_2, CO, and O_2, respectively. If 0.01 mole of CO_2 disassociates, 0.01 mole of CO and 0.005 mole of O_2 are formed. For the four general components in equilibrium, A, B, C, and D, the corresponding stoichiometric equation is

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$$
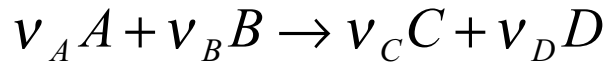
where the ν's are the stoichiometric coefficients.

The change in mole numbers of the reacting components is proportional to the stoichiometric coefficients by

$$dN_A = -\varepsilon v_A \qquad dN_C = \varepsilon v_C$$

$$dN_B = -\varepsilon v_B \qquad dN_D = \varepsilon v_D$$

where ε is the proportionality constant and represents the extent of reaction. A minus sign is added to the dN_A and dN_B because the number of moles of A and B decrease as the reaction takes place. Now, we substitute these into the requirement for equilibrium and cancel the ε's.

$$\bar{g}_D(\varepsilon v_D) + \bar{g}_C(\varepsilon v_C) + \bar{g}_A(-\varepsilon v_A) + \bar{g}_B(-\varepsilon v_B) = 0$$

$$v_D\bar{g}_D + v_C\bar{g}_C - v_A\bar{g}_A - v_B\bar{g}_B = 0$$

This last result is known as the **criterion for chemical equilibrium**. It is this last equation that we use to relate the mole numbers of the reacting components at equilibrium. Now let's see how the mole numbers are imbedded in this equation. First we assume that the mixture of reacting components is an ideal gas. Then we need the Gibbs function for ideal gases.

Specific Gibbs Function for Ideal Gases

Recall that $g = h - Ts$. Then

$$dg = dh - T\,ds - s\,dT \quad and \quad dh = T\,ds + v\,dP$$

$$dg = (T\,ds + v\,dP) - T\,ds - s\,dT$$

$$= v\,dP - s\,dT$$

Consider an isothermal process with T = constant and on a mole basis

$$dg = \bar{v}\, dP$$

For an ideal-gas mixture undergoing an isothermal process, the Gibbs function for the ith component, $\bar{g}_i$, on a mole basis is found by

$$\int_{T,P_o}^{T,P_i} d\bar{g}_i = \int_{P_o}^{P_i} \bar{v}_i dP_i' = \int_{P_o}^{P_i} \frac{R_u T}{P_i'} dP_i' = R_u T \ln \frac{P_i}{P_o}$$

$$\bar{g}_i(T,P_i) = \bar{g}_i(T,P_o) + R_u T \ln \frac{P_i}{P_o}$$

Let's take P_o to be one atmosphere and measure the component partial pressure P_i in atmospheres. Let $\bar{g}_i^*$ be the Gibbs function for any component at the temperature T and a pressure of 1 atm. Then the Gibbs function becomes

$$\bar{g}_i(T,P_i) = \bar{g}_i^*(T) + R_u T \ln P_i$$

We substitute $\bar{g}_i(T,P_i)$ into the criterion for chemical equilibrium.

$$v_D \bar{g}_D + v_C \bar{g}_C - v_A \bar{g}_A - v_B \bar{g}_B = 0$$

$$v_C[\bar{g}_C^*(T) + R_u T \ln P_C] + v_D[\bar{g}_D^*(T) + R_u T \ln P_D]$$
$$- v_A[\bar{g}_A^*(T) + R_u T \ln P_A] - v_B[\bar{g}_B^*(T) + R_u T \ln P_B] = 0$$

Remember that we are trying to find a way to calculate the mole numbers of components in the product gases for equilibrium at fixed T and P. Do you see where the mole numbers are hidden in this equation?

The mole numbers are contained in the expression for the partial pressures.

$$P_i = y_i P = \frac{N_i}{N_{total}} P$$

Now, let's put the last result into a workable form. We define the standard-state Gibbs function change as

$$\Delta G^*(T) = v_C \bar{g}_C^*(T) + v_D \bar{g}_D^*(T) - v_A \bar{g}_A^*(T) - v_B \bar{g}_B^*(T)$$

Substituting we get

$$\Delta G^*(T) = -R_u T (v_C \ln P_C + v_D \ln P_D - v_A \ln P_A - v_B \ln P_B)$$

$$= -R_u T \ln \frac{P_C^{v_C} P_D^{v_D}}{P_A^{v_A} P_B^{v_B}}$$

We define the **equilibrium constant** $K_P(T)$ as

$$\ln K_P(T) = -\frac{\Delta G^*(T)}{R_u T} = \ln \frac{P_C^{v_C} P_D^{v_D}}{P_A^{v_A} P_B^{v_B}}$$

$$K_P(T) = \exp \left[-\frac{\Delta G^*(T)}{R_u T} \right]$$

or

$$K_P(T) = \frac{P_C^{v_C} P_D^{v_D}}{P_A^{v_A} P_B^{v_B}}$$

Table A-28 gives $\ln K_P(T)$ for several equilibrium reactions as a function of temperature.

Now, let's write $K_P(T)$ in terms of the mole numbers of the reacting components in the real product gas mixture. Using the definition of partial pressure given above, $K_P(T)$ becomes

$$K_P(T) = \frac{N_C^{v_C} N_D^{v_D}}{N_A^{v_A} N_B^{v_B}} \left(\frac{P}{N_{total}} \right)^{\Delta v}$$

where

$$\Delta v = v_C + v_D - v_A - v_B$$

Clearly the equilibrium constant is a function of the mole numbers, temperature, and pressure at equilibrium as well as the stoichiometric coefficients in the assumed equilibrium reaction. N_{total} is the total moles of all components present in the equilibrium reaction, including any inert gases.

For values of $\ln K_P(T)$ given in Table A-28 for several equilibrium reactions, we make the following observations. Again consider the typical equilibrium reaction

$$v_A A + v_B B \rightarrow v_C C + v_D D$$
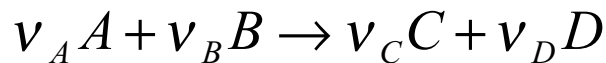
If

$$\ln K_P(T) < 0 \quad then \quad K_P(T) < 1$$
$$\ln K_P(T) > 0 \quad then \quad K_P(T) > 1$$

When $\ln K_P(T) < -7$, ($K_P(T) \ll 1$), the components are so stable that the reaction will not occur (left to right).

When $\ln K_P(T) > 7$, ($K_P(T) \gg 1$), the components are so active that the reaction will proceed to completion (left to right).

Review the discussion of the equilibrium constant given in Section 15-3.

Example 15-1

Consider the disassociation of H_2

$$H_2 \rightarrow xH_2 + yH$$

The equilibrium reaction is assumed to be

$$H_2 \Longleftrightarrow 2H$$
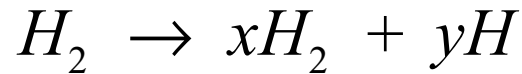
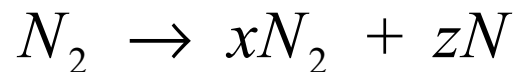For $T < 2400$ K, $\ln K_P(T) < -8.276$, and the reaction does not occur. $x \cong 1$ and $y \cong 0$.

For $T > 6000$ K, $\ln K_P(T) > 5.590$, and the reaction occurs so rapidly that the products will be mostly H with traces of H_2. $x \cong 0$ and $y \cong 2$.

Example 15-2

Determine the amount of N_2 that dissociates into monatomic N at 1 atm when the temperature is 3000 K and 6000 K.
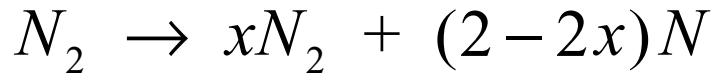
The reaction equation is

$$N_2 \rightarrow xN_2 + zN$$

The nitrogen balance yields

$$N: \quad 2 = 2X + Z$$

or

$$Z = 2 - 2X$$

The balanced reaction equation becomes

$$N_2 \rightarrow xN_2 + (2-2x)N$$

The total moles of products is

$$N_{total} = x + z = x + (2-2x) = 2-x$$

To solve for x (or to get a second equation that relates x and z), we assume the product gases N_2 and N to be in chemical equilibrium. The equilibrium reaction is assumed to be

$$N_2 \Leftrightarrow 2N$$

Assuming ideal gas behavior, the equilibrium constant $K_P(T)$ is defined by

$$K_P(T) = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

or

$$K_P(T) = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}}\right)^{\Delta\nu}$$

$$K_P(T) = \frac{z^2}{x^1} \left(\frac{P}{2-x}\right)^{(2-1)}$$

$$= \frac{(2-2x)^2}{x^1} \left(\frac{P}{2-x}\right)^{(2-1)}$$

This becomes

$$(4+\frac{K_P(T)}{P})x^2 - (8+\frac{2K_P(T)}{P})x+4=0$$

The solution to the above equation is the well-known quadratic formula; or, the solution can be found by trial and error. Note both x and z must be greater than zero or negative moles will result. For $z \geq 0$, $x \leq 1$. So a trial-and-error solution would be sought in the range $0 < x < 1$. Recall $P = 1$ atm.

Using Table A-28 at $T = 3000$ K, ln $K_P(T) = -22.359$ and $K_P(T) = 1.948\text{x}10^{-10}$.

Solving for x and then z, we find

$$x = 1.0 \qquad \text{and} \qquad z = 0.0$$

The balanced combustion equation when the product temperature is 3000 K is

$$N_2 \rightarrow 1\,N_2 + 0\,N$$

At $T = 6000$ K, ln $K_P(T) = -2.865$ and $K_P(T) = 5.698\text{x}10^{-2}$.

Solving for x and then z, we find

$$x = 0.881 \qquad \text{and} \qquad z = 0.238$$

The balanced combustion equation when the product temperature is 6000 K is
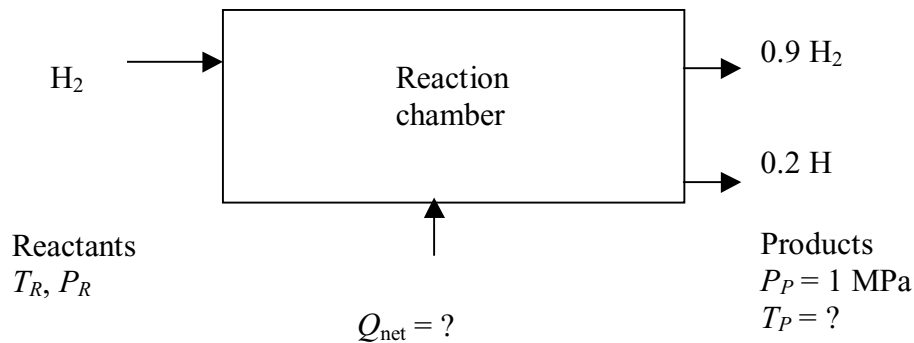
$$N_2 \rightarrow 0.881\,N_2 + 0.238\,N$$

Notice that the product gas mixture at equilibrium has the following composition

$$y_{N_2} = \frac{0.881}{0.881 + 0.238} = 0.787 \ \ or \ \ 78.7\%$$

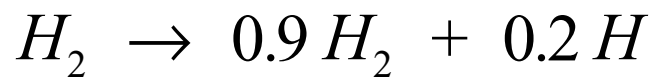$$y_{N} = \frac{0.238}{0.881 + 0.238} = 0.213 \ \ or \ \ 21.3\%$$

Example 15-3

Determine the product temperature for the following when the product pressure is 1 MPa.

The product pressure in atmospheres is 1 Mpa(1 atm/0.1 Mpa) = 10 atm.

The balanced reaction equation is

$$H_2 \ \rightarrow \ 0.9 \, H_2 \ + \ 0.2 \, H$$

The total moles of products are

$$N_{total} \ = \ 0.9 + 0.2 = 1.1$$

The equilibrium reaction is assumed to be

$$H_2 \Leftrightarrow 2H$$

Assuming ideal gas behavior, the equilibrium constant $K_P(T)$ is defined by

$$K_P(T) = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}} \right)^{\Delta \nu}$$

$$K_P(T) = \frac{(0.2)^2}{(0.9)^1} \left(\frac{10}{1.1} \right)^{(2-1)}$$

$$= 0.404$$

$$\ln K_P(T) = -0.9063$$

For this value of the equilibrium constant, the product temperature is found in Table A-28 as

$$T_P = 3535 \text{ K}$$

If we were to consider the influence of product temperature on the disassociation of H_2 at 10 atm, the following results for the mole fraction of monatomic hydrogen in the products are found.
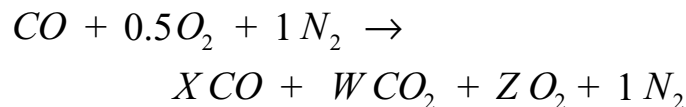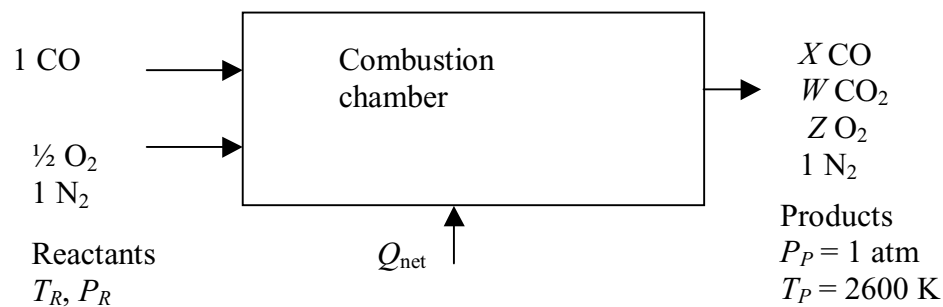
T (K)	$K_P(T)$	Mole Fraction of H
1000	5.17×10^{-18}	0.00
2000	2.65×10^{-6}	0.16
3000	2.5×10^{-1}	14.63
3535	4.04×10^{-1}	18.18
6000	$2.68 \times 10^{+2}$	99.63

These data show that the larger the product temperature, the larger the equilibrium constant, and the more complete the reaction for the disassociation of H_2.

Effect of Inert Gases on Equilibrium

Example 15-4

One kmol of CO is combusted with one-half kmol O_2 and one kmol of N_2. The products are assumed to consist of CO_2, CO, O_2, and N_2 when the product temperature is 2600 K and the product pressure is 1 atm. Write the balanced combustion equation.

1 CO	Combustion chamber	X CO
		W CO_2
½ O_2		Z O_2
1 N_2		1 N_2

Reactants T_R, P_R Q_{net} Products $P_P = 1$ atm $T_P = 2600$ K

$$CO + 0.5\,O_2 + 1\,N_2 \rightarrow$$
$$X\,CO + W\,CO_2 + Z\,O_2 + 1\,N_2$$

The nitrogen does not react with the other components and is inert. Note that the moles of a given component must be ≥ 0, so X, W, and Z all must be ≥ 0.

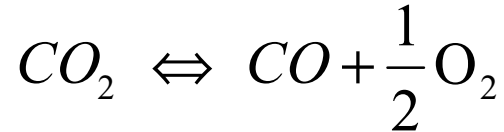$$C\text{: } 1 = X + W, \quad W = 1 - X, \qquad X \leq 1$$
$$O\text{: } 1 + 0.5(2) = X + W(2) + Z(2), \quad Z = 0.5X, \quad X \geq 0$$

The moles of CO at equilibrium must be such that $0 \leq X \leq 1$.

The total number of moles of product gases at equilibrium is

$$N_{total} = X + W + Z + 1 = X + (1 - X) + 0.5 X + 1 = 0.5 X + 2$$

The equilibrium reaction is assumed to be

$$CO_2 \iff CO + \frac{1}{2} O_2$$

Assuming ideal gas behavior, the equilibrium constant $K_P(T)$ is defined by

$$K_P(T) = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}} \right)^{\Delta\nu}$$

$$K_P(T) = \frac{X^1 Z^{1/2}}{W^1} \left(\frac{1}{0.5X + 2} \right)^{(1 + \frac{1}{2} - 1)}$$

$$= \frac{X^1 (0.5X)^{1/2}}{(1 - X)^1} \left(\frac{1}{0.5X + 2} \right)^{(1/2)}$$

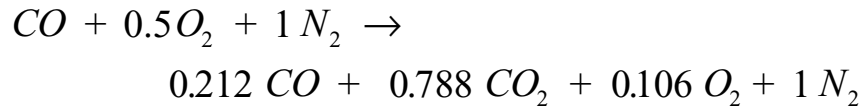At $T = 2600$ K, $\ln K_P(T) = -2.801$ and $K_P(T) = 0.06075$.

$$0.06075 = \frac{X^1 (0.5X)^{1/2}}{(1 - X)^1} \left(\frac{1}{0.5X + 2} \right)^{(1/2)}$$

Using a trial-and-error method to solve for X and then W and Z, we find

$$X = 0.212$$
$$W = 0.788$$
$$Z = 0.106$$

The balanced reaction equation becomes

$$CO + 0.5O_2 + 1\,N_2 \rightarrow$$
$$0.212\,CO + 0.788\,CO_2 + 0.106\,O_2 + 1\,N_2$$

Note: If in the last example, the initial moles of CO were changed from 1 to 2, then the solution for X would be in the range $1 \le X \le 2$.

What is the heat transfer per unit kmol of CO for this reaction?

How do we find the adiabatic flame temperature of a reacting system when chemical equilibrium is required?

Simultaneous Reactions

When all the products that are not inert but present in the reacting mixture cannot be expressed in terms of one equilibrium reaction, we must consider simultaneous equilibrium reactions are occurring.

Example 15-5

Find the equilibrium composition when CO_2 disassociates into CO, O_2, and O at 3000 K, 1 atm, according to the following reaction equation:

$$CO_2 \rightarrow a\,CO_2 + b\,CO + c\,O_2 + d\,O$$
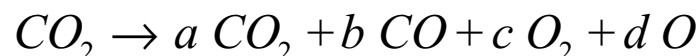
We assume the equilibrium reactions to be

$$CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$$

$$O_2 \Leftrightarrow 2O$$
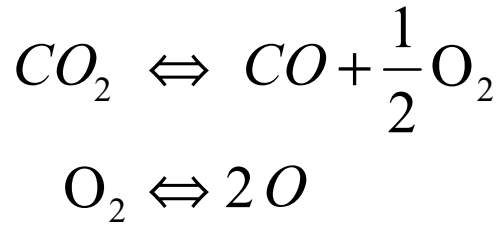
We note that there are four unknowns, a, b, c, and d so we need four equations relating them. These equations are the species balance equations for C and O and the equilibrium constant equations for the two assumed equilibrium reactions.
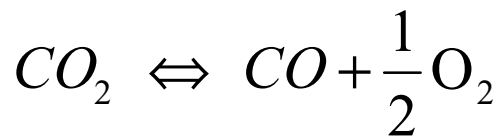
$$C: \ 1 = a + b, \qquad b = 1 - a, \qquad a \leq 1$$
$$O: \ 2 = 2a + b + 2c + d, \quad a = 1 - 2c - d, \quad b \geq 0$$

The moles of each component at equilibrium must be such that the mole numbers are greater than or equal to zero.

The total number of moles of product gases at equilibrium is

$$N_{total} = a + b + c + d = (1 - 2c - d) + (2c + d) + c + d$$
$$= 1 + c + d$$

For the first assumed stoichiometric reaction

$$CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$$

and assuming ideal-gas behavior, the equilibrium constant $K_{P1}(T)$ is defined by

$$K_{P1}(T) = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}} \right)^{\Delta\nu}$$

$$K_{P1}(T) = \frac{b^1 c^{1/2}}{a^1} \left(\frac{1}{a+b+c+d} \right)^{(1+\frac{1}{2}-1)}$$

For the second assumed stoichiometric reaction

$$O_2 \Leftrightarrow 2\,O$$

and assuming ideal-gas behavior, the equilibrium constant $K_{P2}(T)$ is defined by

$$K_{P2}(T) = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}} \right)^{\Delta\nu}$$

$$K_{P2}(T) = \frac{d^2}{c^1} \left(\frac{1}{a+b+c+d} \right)^{(1+\frac{1}{2}-1)}$$

Therefore, we have four unknowns (a, b, c, d) and four equations that may be solved by trial and error.

So,

$$a = 1 - 2c - d$$

$$b = 1 - a = 1 - (1 - 2c - d) = 2c + d$$

$$N_{total} = a + b + c + d = 1 + c + d$$

$$K_{P1}(T) = \frac{(2c+d)^1 c^{1/2}}{(1-2c-d)^1} \left(\frac{1}{1+c+d}\right)^{(1+1/2-1)}$$

$$K_{P2}(T) = \frac{d^2}{c^1} \left(\frac{1}{1+c+d}\right)^{(2-1)}$$

At 3000 K, $K_{P1}(T) = 0.327$ and $K_{P2}(T) = 0.0126$.

Since $K_{P2}(T)$ is small, we expect d to be small; and since a $\leq$ 1, c $\leq$ 1/2.
So guess c, solve for d from $K_{P2}(T)$, and check both values in $K_{P1}(T)$.
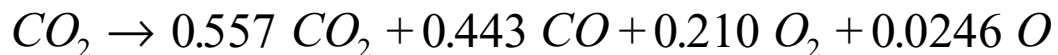Repeat until $K_{P1}(T)$ is satisfied within some small error. The results are
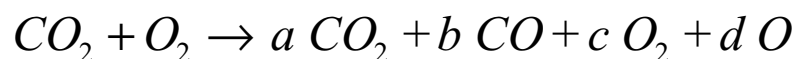
$$a = 0.557$$
$$b = 0.443$$
$$c = 0.210$$
$$d = 0.0246$$

and the balanced reaction equation is

$$CO_2 \rightarrow 0.557 \ CO_2 + 0.443 \ CO + 0.210 \ O_2 + 0.0246 \ O$$

How do we find the adiabatic flame temperature of a reacting system when simultaneous chemical equilibrium is required as in the following reaction?

$$CO_2 + O_2 \rightarrow a \ CO_2 + b \ CO + c \ O_2 + d \ O$$

Phase Equilibrium

The criterion that the Gibbs be a minimum also applies to equilibrium between phases. Consider the equilibrium of saturated liquid water and saturated water vapor at 100°C. Let g be the specific Gibbs function per unit mass, G/m.

$$G = m_f g_f + m_g g_g$$

At a fixed T, the g_f and g_g are constant, and the Gibbs function changes because mass is changing between the liquid and the vapor states.

$$dG = g_f \, dm_f + g_g \, dm_g$$

and, by conservation of mass,

$$dm = dm_f + dm_g = 0$$
$$dm_g = -dm_f$$

At equilibrium for constant T and P, $dG = 0$

$$dG = (g_f - g_g) \, dm_f$$
$$g_f = g_g$$

Example 15-6

Show that the Gibbs functions for saturated liquid water and saturated water vapor at 100°C are equal.

$$g_f = h_f - Ts_f = 419.04 \frac{kJ}{kg} - 373.15K(1.3069 \frac{kJ}{kg \cdot K})$$

$$= -68.6 \frac{kJ}{kg}$$

$$g_g = h_g - Ts_g = 2676.14 \frac{kJ}{kg} - 373.15K(7.3549 \frac{kJ}{kg \cdot K})$$

$$= -68.4 \frac{kJ}{kg}$$

The saturated liquid and saturated vapor specific Gibbs functions are in close agreement. Some property table preparers use the equality of the saturated liquid and saturated vapor Gibbs functions as another property relation in the required calculations for generating the table values.