Example 1

Five kmole of CO, three of O_2, and four of CO_2 are instantaneously mixed at 3000 K and 101 kPa at the entrance to a reactor. Determine the reaction direction and the values of F_R, F_P, and G. What is the equilibrium composition of the gas leaving the reactor? How is the process altered if seven kmole of inert N_2 is injected into the reactor?

Solution

We assume that if the following reaction occurs in the reactor:

$$CO + 1/2\ O_2 \rightarrow CO_2, \text{ then} \quad (A)$$

$$F_R > F_P \quad (B)$$

so that the criterion $dG_{T,P} < 0$ is satisfied. The reaction potential for this reaction is

$$F_R = (1)\ \mu_{CO} + (1/2)\ \mu_{O_2}, \text{ and} \quad (C)$$

$$F_P = (1)\ \mu_{CO_2}. \quad (D)$$

For ideal gas mixtures,

$$\mu_{CO} = \hat{g}_{CO} = \bar{g}(T,P) + \bar{R}T \ln X_{CO} = \bar{g}_{CO}(T,p_{CO}). \quad (E)$$

The larger the CO mole fraction, the higher the value of μ_{CO} and, hence, F.

$$\bar{g}_{CO}(T,P) = \bar{h}_{CO}(T,P) - T\,\bar{s}_{CO}(T,P)$$

$$= [\bar{h}_{f,CO}^{0} + (\bar{h}_{t,3000K} - \bar{h}_{t,298K})_{CO}] - 3000\times(\bar{s}^{o}_{CO}(3000) - 8.314(\ln\times P/1))$$

$$= [-110530+93541] - 3000\times 273.508 - 8.314\times\ln 1)$$

$$\bar{g}_{CO} = -837513 \text{ kJ per kmole of CO.} \quad (F)$$

Similarly, at 3000K and 1 bar,

$$\bar{g}_{O_2} = -755099 \text{ kJ kmole}^{-1}, \text{ and } \bar{g}_{CO_2} = -1242910 \text{ kJ kmole}^{-1}. \quad (G)$$

The species mole fractions

$$X_{CO} = 5\div(5+3+4) = 0.417,\ X_{O_2} = 3\div(5+4+3) = 0.25, \text{ and } X_{CO_2} = 0.333. \quad (H)$$

Further,

$$\mu_{CO} = \hat{g}_{CO}(3000K, 1 \text{ bar}, X_{CO} = 0.417)$$

$$= \bar{g}_{CO}(3000K, 1 \text{ bar}) + 8.314\times 3000\times\ln(0.417)$$

$$= -837513 + 8.314 \times 3000 \times \ln 0.467$$

$$= -856504 \text{ kJ kmole}^{-1} \text{ of CO in the mixture.} \quad (I)$$

Similarly,

$$\mu_{O_2} = (3000K, 1 \text{ bar}, X_{O_2}=0.25) = -789675 \text{ kJ per kmole of } O_2. \quad (J)$$

$$\mu_{CO_2} = (3000K, 1 \text{ bar}, X_{CO_2}=0.333) = -1270312 \text{ kJ per kmole of } CO_2. \quad (K)$$

Therefore, based on the oxidation of 1 kmole of CO,

$$F_R = -856504 + 1/2(-789675) = -1254190 \text{ kJ, and} \quad (L)$$

F_P =–1270312 kJ, i.e., (M)

$F_R > F_P$, (N)

which implies that assumed direction is correct and hence CO will oxidize to CO_2.
The oxidation of CO occurs gradually. As more and more moles of CO_2 are

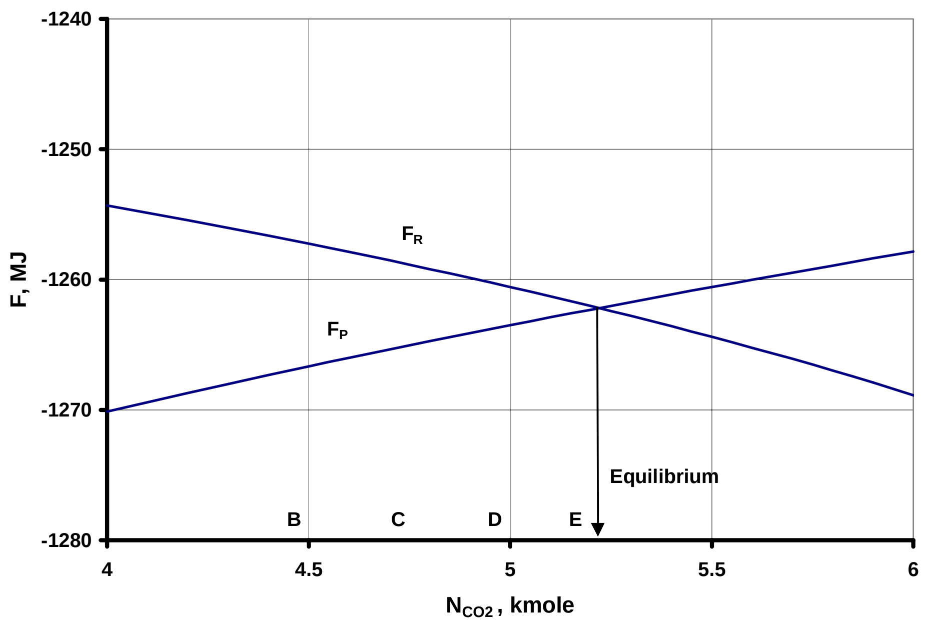

Figure 1: The reaction potential with respect to the number of moles of CO_2 produced.

produced, its molecular population increases, increasing the potential F_P. Simultaneously, the CO and O_2 populations decrease, thereby decreasing the reaction potential F_R until the reaction ceases when chemical equilibrium is attained. Thus chemical equilibrium is achieved when $F_R = F_P$, i.e., $dG_{T,P}=0$. This is illustrated in Figure 1. The corresponding species concentrations are

$$N_{CO_2} = 5.25 \text{ kmole}, N_{CO} = 3.75 \text{ kmole, and } N_{O_2} = 2.375 \text{ kmole.}$$

(Recall evaporation example discussed in Chapter 07 where A reaches a minimum at given T and V and G reaches a minimum at given T and P. From a thermodynamic perspective, chemical reaction is a similar problem. In evaporation of water from a cup into bone dry air, evaporation occurs due to $g_{H2O(\ell)} > g_{H2O(g)}$. The evaporation will continue to occur with $dG_{T,P} < 0$; but after a finite amount of water is transformed into the vapor, evaporation will cease(From a thermodynamic perspective, this problem is similar to placing a cup of cold water in bone dry air. Evaporation will occur when $dG_{T,P} < 0$, but after a finite amount of water is transformed into the vapor, evaporation will cease at which $g_{H2O(\ell)} = g_{H2O(g)}$ and $dG_{T,P} = 0$.)
The Gibbs energy at any section

$$G = \Sigma\mu_k N_k = \mu_{CO} N_{CO} + \mu_{O_2} N_{O_2} + \mu_{CO_2} N_{CO_2}.$$

Using the values, the G is computed as

G = -856504*5 -789675*3-1270312*4 = -11,732,793 kJ. Fig. 2 plots G vs N_{CO2}. The plot in Figure 2shows that G reaches a minimum at same point as F_R=F_P.

Nitrogen does not participate in the reaction. Therefore, $dN_{N_2} = 0$ and, so, the expressions for F_R and F_P are unaffected. However, the mole fractions of the reactants change so that the values of F_R and F_P are different, as is the equilibrium composition. Further, the G expression is modified as

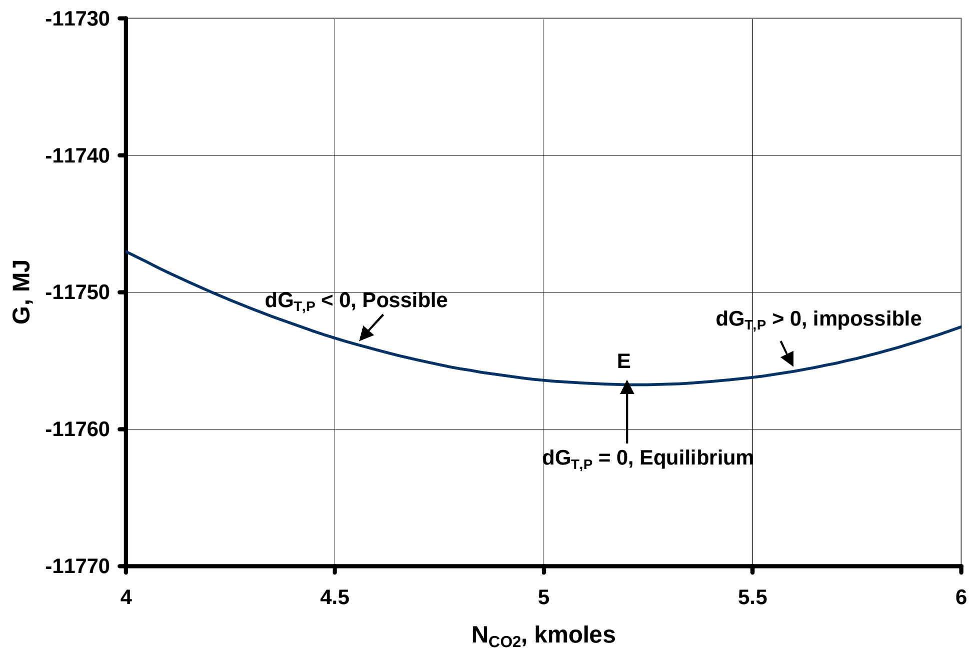

Figure 2: Illustration of the minimization of the Gibbs energy at equilibrium with respect to the number of moles of carbon dioxide produced.

$$G = \Sigma\mu_k N_k = \mu_{CO} N_{CO} + \mu_{O_2} N_{O_2} + \mu_{CO_2} N_{CO_2} + \mu_{CO_2} N_{CO_2} + \mu_{N2} N_{N2}$$

Remarks

The overall reaction has the form

$$5\ CO + 3\ O_2 + 4\ CO_2 \rightarrow 3.75\ CO + 2.375\ O_2 + 5.25\ CO_2.$$

The assumed direction (i.e., $CO + 1/2\ O_2 \rightarrow CO_2$) is possible if $dG_{T,P} < 0$ or $F_R > F_P$. The mixture is at equilibrium if $dG_{T,P} = 0$ (as illustrated in Figure 2) or $F_R = F_P$. If $dG_{T,P} > 0$ or $F_R < F_P$, the reverse reaction $CO_2 \rightarrow CO + 1/2\ O_2$ becomes possible.

19. *Example 2*

Consider the reactions

$$C\,(s) + 1/2\ O_2 \rightarrow CO, \text{ and} \quad \text{(I)}$$

$$C(s) + O_2 \rightarrow CO_2 \quad \text{(II)}$$

Which of the two reactions is more likely when 1 kmole of C reacts with 50 kmole of O_2 in a reactor at 1 bar and 298 K. Assume that $\bar{c}_{p,C}/\bar{R}$ = $1.771+0.000877\ T–86700/T^2$ in SI units and T is in K. Assume ideal mixture.

Solution

If $|(F_R - F_P)|_I > |(F_R - F_P)|_{II}$, then the first reaction dominates and vice versa. Note that the reaction potentials are functions of the species populations and hence vary as a reaction proceeds. Using Eq.(23),

$$F_R = \bar{g}_C(T,P) + \bar{R}T \ln \hat{\alpha}_k . \quad \text{(A)}$$

Since solid carbon (C(s)) is a pure component and hence the activity $\hat{a}_{C(s)} = 1$. Further,

$$\bar{h}_C = \bar{h}^o_{f,C} + \int_{298K}^{T} \bar{c}_{p,C} dT .$$

$$\text{where } \bar{h}^o_{f,C} = 0 \text{ kJ kmole}^{-1}, \text{ and} \quad \text{(B)}$$

$$\bar{s}_C = \bar{s}^o_C(298K) + \int_{298K}^{T} (\bar{c}_{p,C} / T) dT .$$

Now,

$$\bar{s}^o_C\ (298K) = 5.74 \text{ kJ kmole}^{-1} \text{ K}^{-1}. \quad \text{(C)}$$

Hence, using Eqs. (B) and (C), $\bar{g}^o_C = \bar{g}_C(298K, 1 \text{ bar}) = \bar{h}_{298K} - 298 \times \bar{s}_C\ (298K)$, i.e.,

$$\bar{g}^o_C = 0 - 298 \times 5.74 = -1711 \text{ kJ kmole}^{-1}. \quad \text{(D)}$$

For solids and liquids, $\bar{g}_k(T,P) \approx \bar{g}^o_k(T)$. Assume that 0.001 moles of C(s) react with 0.0005 moles of O_2 to produce 0.001 moles of CO. Hence,

$p_{O_2} = X_{O_2} P = (50 - 0.0005) \div (0.001+(50-0.0005)) = 0.9999\ P = 0.9999$ bar.

Therefore,

$\bar{s}_{O_2} = 205.03 - 8.314 \times \ln 0.9999 \times 205.03 \text{ kJ K}^{-1} \text{ kmole}^{-1}$, i.e.,

$$\bar{g}_{O_2}(298K, 1 \text{ bar}) = 0 - 298 \times 205.03 = -61099 \text{ kJ kmole}^{-1}. \quad \text{(E)}$$

Similarly,

$X_{CO} = 0.001 \div (0.001 + 49.995) \approx 0.00002$, and

$\bar{s}_{CO}(T, p_{CO}) = 197.54 - 8.314 \times \ln (0.00002) = 287.5 \text{ kJ K}^{-1} \text{ kmole}^{-1}$, so that

$$\bar{g}_{CO}(298K, 1 \text{ bar}) = -110530 - 298 \times 287.5 = -196205 \text{ kJ kmole}^{-1}. \text{(F)}$$

Employing Eqs. (D) and (E),

$F_R = \bar{g}_C + 1/2\ \bar{g}_{O_2} = -1710 + 0.5 \times (61099) = -32260$ kJ, and

$F_P = F_{CO} = -196205 \text{kJ kmole}^{-1}$, i.e.,

$F_R - F_P = -32260 + 196205 = 163945$ kJ.

For reaction I,

$(dG/|dN_C|)_I = (dG/|d\xi|)_I = -(F_R - F_P)_I = -163945$ kJ.

For reaction (II), the corresponding amount of O_2 consumed is 0.0001 kmole

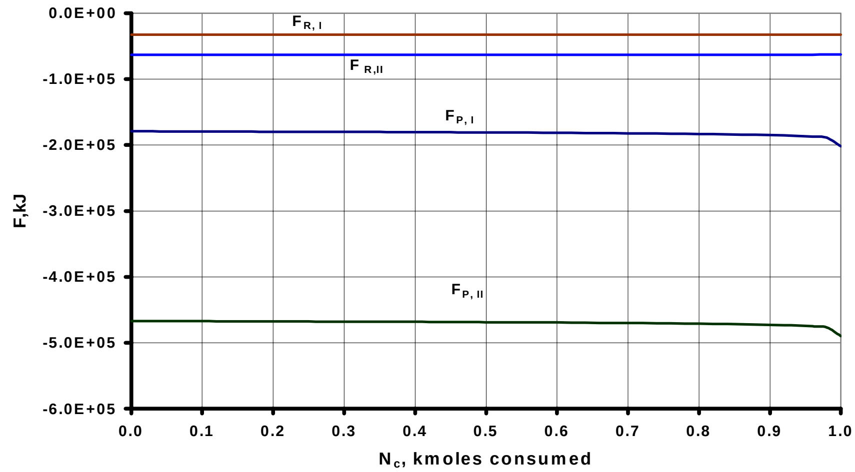

Figure 3: The reaction potentials for reactions I and II with respect to the number of moles of carbon that are consumed.

while 0.0001 kmole of CO_2 is produced. Therefore,

$N_{O_2} = 50 - 0.001 = 49.999$,

$X_{O_2} = 0.999 \times (0.0001 + 49.999) = 0.999$,

$X_{CO_2} = 0.001 \times (0.001 + 49.999) \approx 0.00002$, and

Consequently,

$$\bar{s}_{O_2} = 205.03 - 8.314 \times \ln(0.999) \approx 205.03 \text{ kJ K}^{-1} \text{ kmole}^{-1},$$
$$\bar{s}_{CO2} = 213.74 - 8.314 \times \ln(0.0002) \approx 303.70 \text{ kJ K}^{-1} \text{ kmole}^{-1},$$

$\bar{g}_{O_2} = -61099$ kJ kmole^{-1}, and

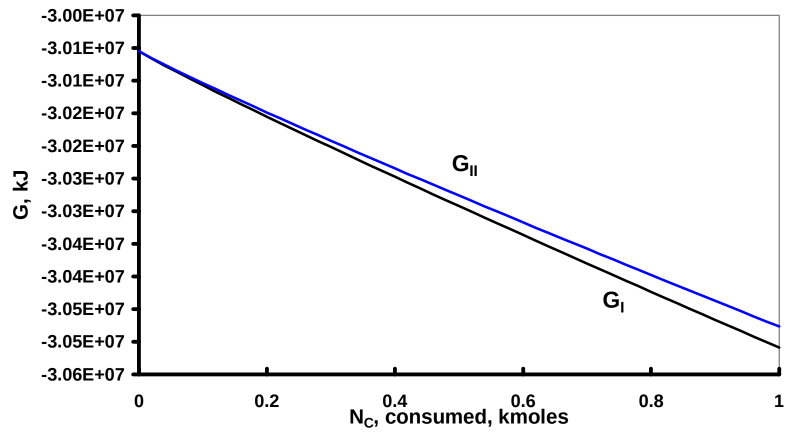

Figure 5: Variation in G_I and G_{II} with respect to the number of moles of carbon consumed for reactions I and II at 3500 K.

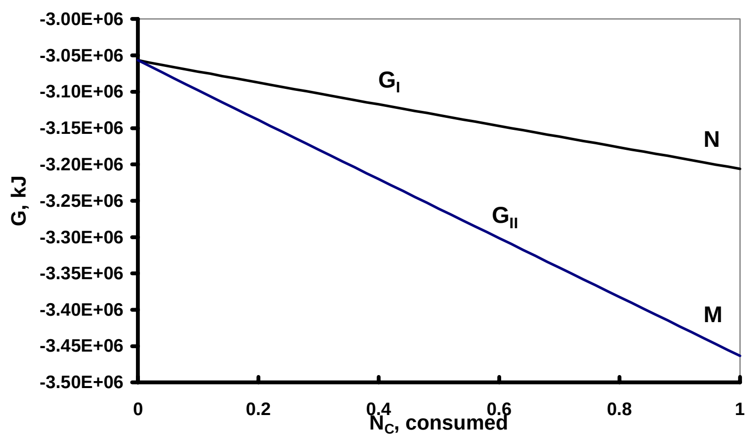

Figure 4: Variation in G_I and G_{II} with respect to the number of moles of carbon consumed for reactions I and II at 298 K.

$\bar{g}_{CO_2}$ = -393546- 298 * 303.70 = –484048 kJ kmole^{-1}.

For this reaction

F_R = –1710+(–61099) = –62810 kJ, and F_P = = –484048 kJ $kmole^{-1}$, i.e., (G)

$$F_R - F_P = -62810 + 484048 = 421238 \text{ kJ.}$$

Hence,

$$(dG/|dN_C|)_{II} = (dG/d\xi)_{II} = (F_R - F_P)_{II} = -394390 \text{ kJ.}$$

The variations in the reaction potentials for reactions I and II with respect to the number of moles of carbon that are consumed at a reactant temperature of 298 K are presented in Figure 3, and the corresponding variation in G_I and G_{II} in Figure 4At 298 K CO_2 production dominates. The analogous variations in G_I and G_{II} at 3500 K are presented in Figure 5 At the higher temperature CO formation is favored.

Remarks

Since

$$\bar{g}_k(T, P, X_k) = \bar{h}_k - T\bar{s}_k = \bar{h}_k - T(\bar{s}_k^o - \bar{R}\ln P X_k/1)$$
$$= \bar{h}_k - T(\bar{s}_k^o - \bar{R}/1)) + \bar{R}T \ln X_k$$
$$= \bar{g}_k(T,P) + \bar{R}T \ln X_k,$$

in general, the values of $\bar{g}_k(T, P, X_k)$ are a function of the species mole fractions. If we assume that $|\bar{g}_k(T,P)| \gg |\bar{R}T \ln X_k,|$, then $\bar{g}_k(T, P, X_k) \approx \bar{g}_k(T,P)$.
This offers an approximate method of determining whether reaction I or II is favored. For instance, if the reactions are assumed to go to completion, $\Delta G_I = \bar{g}_{CO} - (\bar{g}_C + 1/2\,\bar{g}_{O_2})$. Likewise, we can evaluate ΔG_{II} to determine whether $|\Delta G_{II}| > |\Delta G_I|$;if so, the CO_2 production reaction is favored. Values of $\Delta G(T,P)$ at 1 bar, i.e., $\Delta G^o(T)$ are tabulated. (Tables 27A and 27B at T= 298 K)

In addition to reactions I and II, consider the following reactions:

$$C(s) + CO_2 \rightarrow 2\,CO, \quad \text{(III)}$$

$$CO + 1/2\,O_2 \rightarrow CO_2, \text{ and} \quad \text{(IV)}$$

$$H_2 + 1/2\,O_2 \rightarrow H_2O. \quad \text{(V)}$$

For instance, for reaction III, ΔG^o (298 K) = $2\bar{g}_{CO} - (\bar{g}_C + \bar{g}_{CO_2})$ = 120080 kJ, which a positive number or $F_R = \bar{g}_{CO2} + \bar{g}_C < F_P = 2\bar{g}_{CO}$. This implies that the reaction cannot proceed in the indicated direction. In case of reaction III, the reaction potential of the products (F_P) is initially low and the value of F_R is higher. However, the equilibrium state is reached at a very low CO concentration when $dG_{T,P} = 0$, i.e., $F_R = F_P$. Thereafter, $F_P > F_R$ or $dG_{T,P} > 0$, and the reaction does not proceed. In other words, $\Delta G^o > 0$ implies that

$$C + CO_2 \rightarrow \text{large amounts of leftover C and CO + small amounts of CO.} \quad (H)$$

On the other hand for reaction II, $\Delta G^o < 0$ implies that

$$C + O_2 \rightarrow \text{small amounts of leftover C and } O_2 + \text{large amounts of } CO_2. \quad (I)$$

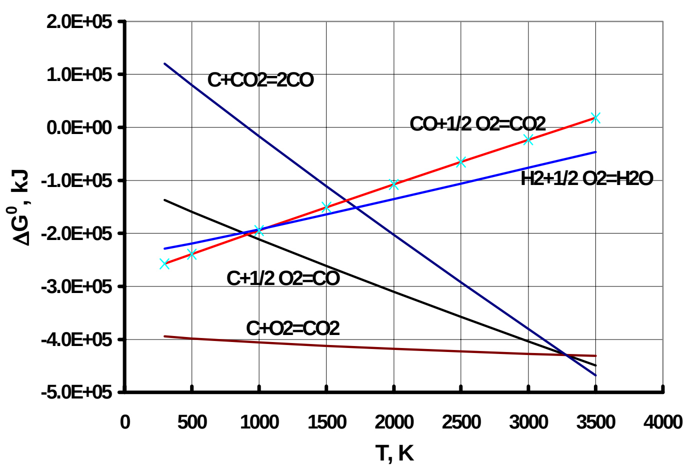

Figure 6. The variation in the value of ΔG^o with respect to the temperature for several reactions.

Generally, the value of ΔG^o for a reaction indicates the extent of completion of that reaction. A relatively large negative value of ΔG^o implies that $F_R \gg F_P$, and this requires the largest decrease in the reactant population (or extent of completion of reaction) before chemical equilibrium is reached. Normally, a positive value for ΔG implies that the reaction will produce an insignificant amount of products (reaction III).

We will now show that the value of ΔG^o for Reaction IV can be obtained in terms of the corresponding values for reactions I and II. For reactions I, II, and IV, respectively

$$\Delta G^o_I (298\text{ K}) = \bar{g}_{CO} - (\bar{g}_C + 1/2\,\bar{g}_{O_2}), \quad (J)$$

$$\Delta G^o_{II} (298\text{ K}) = \bar{g}_{CO_2} - (\bar{g}_C + \bar{g}_{O_2}), \text{and} \quad (K)$$

$$\Delta G^o_{IV} (298\text{ K}) = \bar{g}_{CO_2} - (\bar{g}_{CO} + 1/2\,\bar{g}_{O_2}), \quad (L)$$

where the $\bar{g}_k$'s are evaluated at 298 K, i.e., $\bar{g}_k = \bar{g}_k^o$. Equation (L) assumes the form

$$\Delta G^o_{IV} \text{ (298 K)} = \bar{g}_{CO_2} - (\bar{g}_C + \bar{g}_{O_2}) - \bar{g}_{CO} - (\bar{g}_C + 1/2\, \bar{g}_{O_2}) = \Delta G^o_{II} - \Delta G^o_I. \text{(M)}$$

We can arbitrarily set $\bar{g}_k^o = 0$ for the elemental species C and O_2 at T=298 K so that

$\Delta G^o_{\ I}$ (298 K)= $\bar{g}^0_{f,,CO}$ (298 K), $\Delta G^o_{\ II}$ (298 K)= $\bar{g}^0_{f,,CO2}$ (298 K) where $\bar{g}^0_{f,,k}$ is called Gibbs' function of formation of species k from elements in natural form.

$$\Delta G^o_{IV}\text{(298 K)} = \Delta G^o_{\ II} - \Delta G^o_{\ I} = \bar{g}_{CO_2}\text{(298 K)} - \bar{g}_{CO}\text{(298 K)}$$
$$= -394390 + 137137 = -257253 \text{ kJ.}$$

Example 4

Consider a mixture with the following composition at 1800 K and 2 MPa, i.e., N_{CO_2} = 1.2 kmole, N_{O_2} = 0.6 kmole, N_{CO} = 3.6 kmole, and N_{N_2} = 6.6 kmole. In which direction will the following reaction proceed: $CO + 1/2\, O_2 \rightarrow CO_2$, or $CO_2 \rightarrow CO + 1/2\, O_2$ if we maintain T and P?

Solution

Consider one of the directions for the reaction, say,

$CO_2 \rightarrow CO + 1/2\, O_2$,

$$\bar{g}_k^{\,0}\text{ (T)} = \bar{h}_k^{\,0}\text{(T)} - T\, \bar{s}_k^{\,0}\text{(T)}$$

Using Tables A-8,

$\bar{g}^o_{CO}$ = –110530 + 49517 – 1800 × 254.8 = –519650 kJ kmole^{-1}.

Similarly, Table A-9

$\bar{g}^o_{O_2}$ = 51660 - 1800 x 264.701 = -424800 kJ kmole^{-1}, and

from Table A-19

$\bar{g}^o_{CO_2}$ = – 393546 +79399 – 1800 × 302.892 = -859355 kJ kmole^{-1}.

ΔG^o = (1)×(–519650)+(1/2)×(–424800)+(–1)×(–859355)= 127305 kJ, and

{If one uses the "g' values in Tables A-8,A-9,A-19, then ΔG^o = (1)×(–269164)+(1/2)×(0)+(–1)×(–396425)= +127261 kJ, almost same as previous method}

K^o(T) = exp {–127305÷ (8.314×1800) } = 0.00020.

From Tables A-28 B and item # 7, at given temperature log 10 {K^0(T)} = -3.696 and hence K^0(T) = 0.0002.

If reaction $CO_2 \rightarrow CO + 1/2\, O_2$, occurs, then eq. (46) must be satisfied.

At given composition,

X_{CO} = 3.6/12 = 0.3, pCO = 0.3 * 20 = 6 bars; Similarly p_{O2}= 1 bar, p_{CO2} = 2 bars

$\bar{s}_{CO}$ = 254.8 – 8.314 × ln (20 × 0.3 ÷ 1) = 239.9 kJ K^{-1} kmole^{-1}, and

The ratios of the partial pressures

$(p_{CO}/1)^1\ (p_{O_2}/1)^{1/2}/(p_{CO_2}/1)^1 = (6/1)^1\ (1/1)^{1/2}/(2/1)^1 = 3,$

and the criterion

$K^o(T) = 0.0002 \geq (p_{CO}/1)^1\ (p_{O_2}/1)^{1/2}/(p_{CO_2}/1)^1$

or

$(p_{CO}/1)^1\ (p_{O_2}/1)^{1/2}/(p_{CO_2}/1)^1 \quad \leq K^o(T)=0.0002$

is violated. Hence, CO will oxidize to CO_2, i.e., the reverse path is favored.

Example 5

5 kmole of CO, 3 of O_2, 4 of CO_2, and 7 of N_2 are introduced into a reactor at 3000 K and 2000 kPa. Determine the equilibrium composition of gas leaving reactor, assuming that the outlet (product) stream contains CO, O_2, N_2, and CO_2. Will the equilibrium composition change if the feed is altered to 6 kmole of CO, 3 kmole of CO_2, 3.5 kmole of O_2, and 7 kmole of N_2 enter the reactor? Assume that the outlet stream contains the same species. Will the CO concentration at the outlet change if the pressure changes, say to 101 kPa?

Solution

Assume that the chemical reaction proceeds according to the reaction

$CO_2 \rightarrow CO + 1/2\ O_2$

so that

$K^o(T) = ((p_{CO}/1)(p_{O_2}/1)^{1/2})/(p_{CO_2}/1)$, where

$p_{CO} = X_{CO}\ P = (N_{CO}/N)\ P$, and

$N = N_{CO} + N_{O_2} + N_{CO_2}$.

Therefore,

$$K^o(T) = (N_{CO}N_{O_2}^{1/2})(P/(1\times N))^{1/2}/N_{CO_2}. \qquad (A)$$

The conservation of C and O atoms provide two additional equations. The overall balance equation in terms of the three unknown concentrations is

$$5CO + 3O_2 + 4CO_2 + 7N_2 \rightarrow N_{CO}CO + N_{O_2}O_2 + N_{CO_2}CO_2 + N_{N2}\ N_2 \qquad (B$$

There are 4 unknowns N_{CO}, NCO_2 and NO_2) and we have three atom balance equations.

$$\text{Carbon atoms: } 5 + 4 = N_{CO} + N_{CO2} \qquad (C)$$

$$\text{Oxygen atoms: } 5 *1 + 3*2 + 4 *2 = N_{CO} *1 + N_{CO_2} * 2 + N_{O_2} * 2 \qquad (D)$$

$$\text{Nitrogen atoms : } 7* 2 = N_{N2}* 2 \qquad (D')$$

The fourth equation is given by equilibrium condition at 3000 K: $CO_2 \Leftrightarrow CO + 1/2\ O_2$ reaction, $\log_{10}K = -0.48$. Using this value in Eq. (A)

$$0.327 = (N_{CO}N_{O_2}^{1/2})(P/(1\times N))^{1/2}/N_{CO_2}. \qquad (E)$$

Using Eq. (C),

$$N_{CO} = N_C - N_{CO_2},\ \text{i.e., } N_{CO} = 9 - N_{CO_2}. \qquad (F)$$

Further, using Eqs. (D) and (F),

$$N_{O_2} = (N_O - N_C - N_{CO_2})/2, \text{ i.e.,} \quad (G)$$

$$N_{O_2} = (19 - 9 - N_{CO_2})/2. \quad (H)$$

Therefore, the number of moles at the exit

$$N = N_{CO} + N_{O_2} + N_{CO_2} + N_{N2} = (N_C - N_{CO_2}) + (N_O - N_C)/2 + N_{CO_2}$$

$$= N_{N2} + (N_O + N_C - N_{CO_2})/2 = 21 - N_{CO_2}/2 \quad (I)$$

Applying Eqs. (A) and (G)–(I), at 20 bar, at the exit

N_{CO_2} = 6.96 kmole, and

N_{CO} = 2.04 kmole, N_{O_2} = 1.52 kmole, and N = 17.52 kmole.

When the feed stream is altered to react 6 kmole of CO, 3 kmole of CO_2, 3.5 kmole of O_2, and 7 kmole of N_2, the respective inputs of C, O and N atoms remain unaltered at 9, 19 and 14 respectively. Therefore, the equilibrium composition is unchanged. This indicates that it does not matter in which form the atoms of the reacting species enter the system. The same composition, for instance, could be achieved by reacting a feed stream containing 9 kmole of C(s) (solid carbon, such as charcoal), 9.5 kmole of O_2 and 7 kmole of N_2 (which is treated as an inert in this problem).

From Eq. (A) we note that for a specified temperature, the value of $K^o(T)$ is unique. Therefore, if the pressure changes, but the temperature does not.. Eq. (E) dictates that the composition is altered and more CO_2 is produced as the pressure is increased.

Example 6

Consider a PCW assembly that is immersed in an isothermal bath at 3000 K. It initially consists of 9 kmole of C atoms and 19 kmole of O atoms (total mass = 9*12.01+ 19*16 = 412 kg) is allowed to reach chemical equilibrium at 3000 K and 1 bar. What is the equilibrium composition? What is the value of the Gibbs energy? If we keep placing sand particles one at a time on the piston so that one achieves a final pressure of 4 bar; i.e. we allowed sufficient time to reach chemical equilibrium at that pressure, what is the resulting equilibrium composition and Gibbs energy?

Solution

We leave it to the reader to show that at equilibrium

$$N_{CO_2} = 5.25 \text{ kmole}, N_{CO} = 3.7 \text{ kmole, and } N_{O_2} = 2.37 \text{ kmole.} \quad (A)$$

Therefore,

$$N = \Sigma N_k = 11.37 \text{ kmole.} \quad (B)$$

The Gibbs energy,

$$G = N_{CO_2}\hat{g}_{CO_2} + N_{CO}\hat{g}_{CO} + N_{O_2}\hat{g}_{O_2}, \text{ where} \quad (C)$$

$$\hat{g}_{CO_2} = \bar{g}^o_{CO_2}(T) + \bar{R}T\ln(p_{CO_2}/1) = \bar{h}^o_{f,CO_2} + (\bar{h}_{t,T} - \bar{h}_{t,298K}) + \bar{R}T\ln(X_{CO_2}P/1), \text{ and} \quad (D)$$

$X_{CO_2} = N_{CO_2}/N = 0.462.$

At 3000 K and 1 bar, = –1262000 kJ kmole^{-1}, CO = –865200 kJ kmole^{-1} and = –794400 kJ kmole^{-1}. Hence,

G = – 11,753,000 kJ,

which at this equilibrium state must be at a minimum value.

At a temperature of 3000 K and a pressure of 4 bar, the equilibrium composition changes to

N_{CO_2} = 6.4 kmole, N_{CO} = 2.6 kmole, and N_{O_2} = 1.8 kmole, and (D)

N = ΣN_k = 10 kmole, and G = –11374000 kJ. (E)

Remarks

There is no entropy generated since there is no irreversibility. The difference in the minimum Gibbs free energies (i.e at equilibrium states) between the two states (3000,10 to (3000, 4) is given as

$dG = -SdT + VdP$, $dG_T = VdP = (N\bar{R}T/P)\,dP$

G_2 (3000,1) $-G_1$ (3000, 4) = (–11374000) – (–11757000) = 383000 kJ.

If N ≈ constant ≈ (11.37+10)/2 = 10.69 kmoles, , then $dG_T = (N\bar{R}T/P)\,dP$; integrating, G_2-G_1 ≈ $(N\bar{R}T \ln \{P_2/P_1\}$ = 369455 kJ

The relations dU= T dS- P dV, dH = T dS + V dP , dG = -S dT + V dP etc for closed systems can be applied even for chemical reactions as long as we connect a reversible path between the two equilibrium states; however these equations can not be applied during irreversible chemical reaction. Such a statement is also true for non-reacting systems.

When we compressed the products say very slowly from 1 to 4 bars, 3000 K, the reaction tends to produce more CO_2, i.e., N_{CO2} increased from 5.25 to 6.4 k moles. Suppose we perform compression to 4 bar very rapidly say by placing a large weight on the piston and then you analyze the contents. In the first few milliseconds, you won't see a significant change from composition at 1 bar, i.e., the products will be almost frozen at N_{CO2} = 5.25, N_{CO} = 3.75, N_{O2} = 2.37 even though the mass is at 3000 K, P = 4 bar. Thus products at the time of 1 ms are in non-equilibrium State. The G value at this state is computed as G_{Frozen} . 5.25 * g_{CO2}(3000, 4 bar, 5.25/11.37) + $\hat{g}_{CO}$(3000, 4 bar, 3.75/11.37) + $\hat{g}_{O2}$(3000, 4 bar, 3.75/11.37) = 5.25 * (-1,227,400) + 3.75 * (-830,600) + 2.37 * (-759,800) = -11,360,000 kJ which is higher than G = -11,374,000 kJ at the equilibrium composition corresponding to 3000K, 4 bar. Suppose we allow more time at 3000 K, 4 bars and look at the composition say after 20000 s, then chemical equilibrium is reached. Thus G approaches a minimum value of -11,360,000 kJ, at fixed T and P i.e 4 bar and 3000 K.

Similar phenomenon occurs when reacting gases flow at slowest possible velocity through a diffuser where pressure at exit of diffuser is say 4 bars. If we follow the 412 kg mass when it flows through diffuser, it will reach equilibrium composition given by Eq. (D). However if the same mass flows at high velocity, the composition at exit of diffuser may be almost same as those at inlet!

Example 7

Determine the relations between the partial pressures and temperature for the following scenarios: pure $H_2SO_4(l)$ dissociating upon evaporation, $H_2SO_4(l) \rightarrow H_2O(g) + SO_3(g)$, and an ideal mixture of 40% volatile $H_2SO_4(l)$ and 60% nonvolatile liquid or solid participating in the same reaction. Assume that $\bar{g}_{H_2SO_4}$ = –690013 kJ kmole^{-1}, $\bar{g}_{H_2O(g)}$ = –228572 kJ kmole^{-1}, $\bar{g}_{SO_3(g)}$ = –371060 kJ kmole^{-1} at 298 K and 1 bar. Estimate $(p_{H_2O(g)})(p_{SO_3(g)})$ at 298 K for pure $H_2SO_4(l)$ and for an ideal mixture of 40% volatile $H_2SO_4(l)$ and 60% nonvolatile liquid.

Solution

Pure $H_2SO_4(l)$

The problem involves a mixture of phases. We will select the standard state to be the liquid state for $H_2SO_4(l)$. Then from Eq. (35a),

$$K^o(T) = \Pi(f_k(T,P)\,\hat{\alpha}_k/f_k(T, 1\text{ bar}))^{\nu_k}.$$

The gaseous species are assumed to be ideal so that

$$f_{k(g)}(T, P) = P,\ f_{k(g)}(T, 1\text{ bar}) = 1,\text{ and } \hat{\alpha}_{k(g)}(T, P, X_k) = X_k.$$

In the liquid phase at 1 bar

$$f_{H_2SO_4}(T, P)/f_{H_2SO_4}(T, 1\text{ bar}) \approx 1.$$

Further, since the liquid is pure,

$$\hat{\alpha}_{H_2SO_4} = 1,\text{ and}$$

$$K^o(T) = (p_{H_2O(g)}/1)^1(p_{SO_3(g)}/1)^1.$$

At 298 K, when $X_{H_2SO_4} = 1$

$$(p_{H_2O(g)})(p_{SO_3(g)}) = 1.44\times10^{-16},$$

which indicates that the partial pressures are very low, i.e., there is negligible dissociation.

Ideal Liquid Mixture

Since the liquid phase is in an ideal mixture, the activity of $H_2SO_4(l) = X_{H_2SO_4}$, and

$$K^o(T) = (P\,X_{H_2O(g)}/1)^1\,(P\,X_{SO_3(g)}/1)^1/X_{H_2SO_4}$$

$$= (p_{H_2O(g)}/1)(p_{SO_3(g)}/1)/X_{H_2SO_4},\text{ i.e.,}$$

$$(p_{H_2O(g)})(p_{SO_3(g)}) = X_{H_2SO_4}K^o(T).$$

The Gibbs energy change

$$\Delta G^o(T) = \bar{g}_{H_2O(g)} + \bar{g}_{SO_3(g)} - \bar{g}_{H_2SO_4}$$

$$= -228572 - 371060 + 690013 = 90381\text{ kJ kmole}^{-1},\text{ and}$$

$$\ln K^o(T) = -\Delta G^o(T)/\bar{R}T = -36.48,\text{ i.e.,}$$

$$K^o(T) = 1.44\times10^{-16}.$$

At 298 K, when X = 0.4,

$$(p_{H_2O(g)})(p_{SO_3(g)}) = 0.4\times1.44\times10^{-16} = 0.576\times10^{-16}.$$

Remarks:

During the vaporization of $H_2SO_4(l)$ it is possible to produce H_2O, SO_2, SO_3, and O_2, rather than $H_2SO_4(g)$. The pertinent reactions are

$$H_2SO_4(l) \rightarrow H_2O(g) + SO_2(g) + 1/2\ O_2(g), \text{ and}$$

$$H_2SO_4(l) \rightarrow H_2O(g) + SO_3(g)$$

At equilibrium, can you determine the SO_2 and SO_3 concentrations?

Example 8

One kmole each of C(s) and O_2 enter a reactor at 298 K. The species CO, CO_2, and O_2 leave the reactor at 3000 K and 1 bar at equilibrium. Find value of the equilibrium composition at the exit. What is the heat transfer across the boundary? What will happen if the inlet stream is altered to contain 1/2 kmole of oxygen and one kmole of CO. Also explain what happens if the outlet contains C(s), CO, and O_2.

Solution

The overall chemical reaction is

$$C(s) + O_2 \rightarrow a\ CO_2 + b\ CO + c\ O_2. \qquad \text{(A)}$$

The species leaving the reactor are in an equilibrium state so that the following reaction must be in equilibrium, namely,

$$CO_2 \rightarrow CO + 1/2\ O_2. \qquad \text{(B)}$$

From an atom balance,

$$\text{C atoms } 1 = a + b \qquad \text{(C)}$$

$$\text{O atoms: } 2 = 2a + b + 2c. \qquad \text{(D)}$$

Therefore,

$$b = 1 - a, \text{ and } c = (1 - a)/2. \qquad \text{(E,F)}$$

The total moles leaving the reactor are

$$N = a + b + c = (3 - a)/2. \qquad \text{(G)}$$

The exit equilibrium condition requires that

$$K^o(T) = p_{CO}\ p_{CO_2}^{1/2}/p_{O_2}\ . \qquad \text{(H)}$$

For the carbon dioxide dissociation reaction at 3000 K,

$K^o(3000\text{ K}) = 0.327$.

Since,

$X_{CO} = b/N$, $X_{CO_2} = a/N$, $X_{O_2} = c/N$, and $p_k = X_k \times 1$ bar,

Solving the three unknowns a,b and c from Eqs. (B), (C) and (H)

a = 0.563, b = 0.437, and c = 0.219.

Applying the First Law

$$dE_{cv}/dt = \dot{Q}_{cv} - \dot{W}_{cv} + \Sigma_{,k}\ \dot{N}_{ik}\ \hat{h}_{i,k} - \Sigma_k\ \dot{N}_{e,k}\ \hat{h}_{e,k}, \qquad \text{(I)}$$

Under steady state, $dE_{cv}/dt = 0$. No work transfer. Thus for every kmole of C(s),

$$\bar{q} = \frac{\dot{Q}}{\dot{N}_{c(s)}} == 0.563\,\bar{h}_{CO_2}(3000\text{ K}) + 0.437\,\bar{h}_{CO}(3000\text{ K}) + 0.219\,\bar{h}_{O_2}(3000\text{ K}) -$$

$$\bar{h}_{C(s)}(298\text{ K}) - 1/2\,\bar{h}_{O_2}(298\text{ K}) = 121426 \text{ kJ per kmole of C(s) consumed.} \quad (J)$$

If the inlet stream is altered to contain 1/2 kmole of oxygen and one kmole of CO, the atom balance remains unchanged. Therefore, the outlet composition will remain unaltered. However, the heat transfer will change, since the inlet stream containing CO and O_2 has a lower enthalpy as compared to the mixture of C(s) and O_2. Hence, the value of Q will be lower.

If C(s) is present at the outlet, the overall chemical reaction is

$$C(s) + 1\,O_2 \rightarrow b\,CO + c\,O_2 + d\,C(s) \quad (K)$$

There are two atom balance equations, and we will also consider the following reaction to be in equilibrium, i.e.,

$$C(s) + 1/2\,O_2 \rightarrow CO, \text{ so that} \quad (L)$$

$K^o(T) = p_{CO}/1/((p_{O_2}/1)^{1/2}\,(f_{C(s)}(T,P)/f_{C(s)}(T,1)))$

Since $(f_{C(s)}(T,P) \approx f_{C(s)}(T,1))$,

$K^o(T) = p_{CO}/1/((p_{O_2}/1)^{1/2}) = (X_{CO}/X_{O_2})\,(P/1)^{1/2}$.

Hence,

$b + d = 1$, $b + 2c = (2–a)1/2$, and $N = (b + 2)/2$, so that

$(b = 2/((P/2)^{1/2}/K^o(T) + 1)) < 1$, and $d = 1 – b$.

For tbe $C(s) + 1/2\,O_2 \rightarrow CO$,

$K^o(3000\text{ K}) = 10^{6.4}$.

Since $K^o(3000\text{ K})$ is relatively large, Eq. (M) suggest that $X_{O_2} \approx 0$, i.e., almost all of the oxygen is consumed and converted into product.

Example 9

Determine the equilibrium constant for the reaction $NH_4HSO_4(l) \rightarrow NH_3(g) + H_2O(g) + SO_3(g)$. At 298 K, $\Delta H^o = 336500$ kJ kmole^{-1} and $\Delta S^o = 455.8$ kJ kmole^{-1} K. Determine the transition temperature (i.e. at which $K^0(T) = 1$)..

Solution

Recall from Eq.(65) that

$$K^o(T) = K^o(T_o)\exp[-\Delta H^o/\bar{R}\,(1/T - 1/T_o)], \quad (A)$$

where $K(T_0) = \exp(-\Delta G^o/\bar{R}T_0)$ and

$\Delta G^o = \Delta H^o - T\Delta S^o = 336500 - 298\times455.8 = 200672$ kJ kmole^{-1}, i.e.,

$$K^o(T_o) = \exp(-\Delta G^o/\bar{R}T_o) = 6.67\times10^{-36}, \text{ or} \quad (B)$$

$$K^o(T) = 6.67\times10^{-36}\exp(-\,336500/8.314(1/T - 1/298))) \quad (C)$$

By setting $K^o(T) = 1$, the transition temperature $T_{trans} = 336500 \div 456 = 738$ K.

Remarks

Since,

$$K^o(T) = (p_{NH_3}/1\ (p_{H_2O}/1)\ (p_{SO_3}/1), \qquad (D)$$

and K^o increases with temperature, decomposition is also favored at higher temperatures.

Example 10

Derive the Clausius–Clapeyron Relation from the van't Hoff equation by considering the equilibrium of liquid and vapor.

Solution

Consider an isothermal and isobarically maintained air duct into which water droplets are injected. The chemical potentials of the liquid drops and the vapor are different, which cause a transfer of species from one phase into the other (from liquid to vapor during evaporation). The liquid droplets will eventually reach equilibrium with the vapor. At the equilibrium condition

$$H_2O(\ell) \rightarrow H_2O(g), \text{ and} \qquad (A)$$

$$K^o(T) = p_{H_2O\,(g)}/1 \qquad (B)$$

If the equilibrium constant is known at a reference temperature T_{ref},

$$K^o{}_{ref}(T) = p_{H_2O\,,ref(g)}/1, \text{ and} \qquad (C)$$

from the van't Hoff equation

$$\ln \{K^o / K^o_{ref}\} = -(\Delta H^o_R/\bar{R})\ (1/T - 1/T_{ref}). \qquad (D)$$

For the vaporization process,

$$\Delta H^o_R = \bar{h}_g - \bar{h}_f, \text{ or } \Delta H^o_R = \bar{h}_{fg}, \text{ i.e.,} \qquad (E)$$

$$\ln (p_{H_2O\,(g)}/p_{H_2O\,(g),ref}) = -(\bar{h}_{fg}/\bar{R})\ (1/T - 1/T_{ref}), \qquad (F)$$

which is a relation for the change in the partial pressure of the vapor as the temperature changes. This is almost same as the Clausius–Clapeyron Relation

Example 11

Consider the reaction

$$CO_2 \rightarrow CO + 1/2\ O_2. \qquad (A)$$

That occurs in an isobaric and isothermal reactor. Discuss the effect on the equilibrium composition when the temperature is increased at a specified pressure and vice versa.

Solution

Recall that

$$d(\ln K^o)/dT = \Delta H^o_R/\bar{R}T^2, \qquad (B)$$

where $\Delta H^o_R > 0$ for the reaction. Hence, $d(\ln K^o)/dT > 0$, and the value of K increases with an increase in the pressure. Consequently, since

$$K^o(T) = (p_{CO}/1)\,(p_{O_2}/1)^{0.5}/(p_{CO_2}/1), \quad \text{(C)}$$

The value of p_{CO_2} decreases (as does that of X_{CO_2}). The effect of increasing the temperature is to dissociate more CO_2.
Simplifying Eq. (C),

$$K^o(T) = X_{CO}(X_{O_2})^{0.5}\,(P/1)^{0.5}/X_{CO_2}\,. \quad \text{(D)}$$

The value of K^o is a function of temperature alone. Therefore, increasing the pressure should cause the value of X_{CO_2} to increase, i.e., a relatively lower amount of dissociation will occur. Since each mole of CO_2 that dissociates produces 1.5 moles of the other two species, a lower dissociation results in a smaller amount of product (in terms of moles), thereby lowering the pressure (which counteracts the pressure increase). This is an example of the Le Chatelier principle which states that any inhomogeneity or disturbance that is introduced into a system must result in a process which counteracts that inhomogeneity or disturbance.

Example 12

Consider the stoichiometric combustion of one kmole of CH_4 with air. The products are at 2250 K and 1 bar stream and contain CO_2, CO, H_2O, H_2, O_2, N_2, and OH. Determine the equilibrium composition.

Solution

The overall chemical reaction is

$$CH_4 + 2(O_2 + 3.76\,N_2) \rightarrow$$

$$N_{CO_2}\,CO_2 + N_{CO}\,CO + N_{H_2O}\,H_2O + N_{H_2}\,H_2 + N_{O_2}\,O_2 + N_{N_2}\,N_2 + N_{OH}\,OH. \quad \text{(A)}$$

There are seven species of unknown composition. The four atom conservation equations for C, H, N, and O atoms are:

$$\text{C atoms: } 1 = N_{CO_2} + N_{CO}, \quad \text{(B)}$$

$$\text{H atoms: } 4 = 2\times N_{H_2O} + 2\times N_{H_2} + N_{OH}, \quad \text{(C)}$$

$$\text{N atoms: } 7.52\times 2 = 2\times N_{N_2}, \text{ and} \quad \text{(D)}$$

$$\text{O atoms: } 2\times 2 = 2\times N_{CO_2} + N_{CO} + N_{H_2O} + 2\times N_{O_2} + N_{OH}. \quad \text{(E)}$$

We, therefore, require three additional relations. At equilibrium, for the reactions

$$CO_2 \rightarrow CO + 1/2\,O_2,\ K^o_{CO_2} = p_{CO}(p_{O_2})^{0.5}/(p_{CO_2}), \quad \text{(F)}$$

$$H_2O \rightarrow H_2 + 1/2\,O2,\ K_{H_2O} = (p_{H_2})(p_{O_2})^{0.5}/(p_{H_2O}), \text{ and} \quad \text{(G)}$$

$$OH \rightarrow 1/2H_2 + 1/2\,O_2,\ K_{OH} = (p_{H_2})^{0.5}(p_{O_2})^{0.5}/(p_{OH}). \quad \text{(H)}$$

Assume for example N_{CO}, N_{O2}, N_{CO2}. Solve for other species from Eqs. (B) to (E). Then check whether Eqs. (F) to (H) are satisfied. If not iterate. One of the authors had developed spreadsheet based program which presents solution for all species at any given T and P, and any given air composition. The results (in terms of one kmole of methane consumed) are

N_{CO_2} = 0.910, N_{CO} = 0.09, N_{H_2O} = 1.96, N_{H_2} = 0.04, N_{O_2} = 0.064, and N_{N_2} = 7.52

Remark

If it exists in trace amounts, the NO concentration at equilibrium can be determined during combustion by considering the following reactions, i.e.,

$$NO \rightarrow 1/2\ N_2 + 1/2\ O_2, \text{ for which} \quad \text{(I)}$$

$$K_{NO} = (p_{H_2}/1)^{0.5}(p_{O_2}/1)^{0.5}/(p_{NO}/1). \quad \text{(J)}$$

Example 13

A piston–cylinder assembly contains two kmole of O_2 at 1 bar and 3000 K. The pressure and temperature are maintained constant. Chemical reaction proceeds and O atoms are formed at the expense of O_2. Determine the equilibrium composition.

Solution

The O atom conservation equation is

$$2\ N_{O_2} + N_O = 4 \quad \text{(A)}$$

The Gibbs energy of the species O, O2 must keep decreasing as the reaction proceeds and equilibrium is achieved when it is at the minimum.

$$G = \Sigma\mu_k\ N_k, \text{ i.e.,} \quad \text{(B)}$$

$$G = G(T, P, N_{O_2}, N_O) = \mu_{O_2} N_{O_2} + \mu_O N_O. \quad \text{(C)}$$

We will minimize Eq. (C) at the specified pressure and temperature subject to the atom balance constraint Eq. (A). Using the LaGrange multiplier scheme

$$F = G(T,P,N_{O_2},N_O) + \lambda\ (2N_{O_2} + N_O - 4) = 0, \text{ and } \partial F/\partial N_{O_2} = 0,\ \partial F/\partial N_O = 0. \quad \text{(D)}$$

From Eq. (D),

$$\partial F/\partial N_{O_2} = \partial G/\partial N_{O_2} + 2\lambda = 0, \text{ i.e., } \mu_{O_2} + 2\lambda = 0 \text{ (and } \mu_O + \lambda = 0).\text{(E)}$$

Assuming the ideal mixture model to apply,

$$\mu_{O_2} = \hat{g}_{O_2} = \bar{g}_{O_2}(T,P) + \bar{R}T \ln X_{O_2}. \quad \text{(F)}$$

Further, assuming ideal gas behavior,

$$\bar{g}_{O_2}(T,P) = \bar{g}^o_{O_2} + \bar{R}T \ln (P/1). \quad \text{(G)}$$

Therefore,

$$\mu_{O_2} = \bar{g}^o_{O_2} + \bar{R}T \ln (p_{O_2}/1), \text{ and} \quad \text{(H)}$$

$$\mu_O = \bar{g}^o_O + \bar{R}T \ln (p_O/1), \text{ so that} \quad \text{(I)}$$

$$(\bar{g}^o_{O_2} + \bar{R}T \ln (p_{O_2}/1)) + 2\lambda = 0, \text{ and} \quad (J)$$

$$(\bar{g}^o_O + \bar{R}T \ln (p_O/1)) + \lambda = 0. \quad (K)$$

Multiplying Eq. (K) by 2 and subtracting it from Eq. (J),

$$\bar{g}^o_{O_2} - 2\,\bar{g}^o_O + \bar{R}T \ln (p_{O_2}/1) - 2\bar{R}T \ln (p_O/1) = 0, \text{ i.e.,}$$

$$(p_O/1)^2/(p_{O_2}/1) = \exp(-(2\bar{g}^o_O - \bar{g}^o_{O_2})/(\bar{R}T)) \text{ or } (N_O)^2(P/N)^{(2-1)}/N_{O_2} = K^o, \text{ where} \quad (L)$$

$$N = N_{O_2} + N_O. \quad (M)$$

The equilibrium constant

$$K = \exp(-\Delta G^o/\bar{R}T), \text{ where } \Delta G^o = 2\bar{g}^o_O - \bar{g}^o_{O_2}. \quad (N)$$

With the values $N_O = 4 - 2N_{O_2}$ and $N = 4 - 2N_{O_2} + N_{O2} = 4 - N_{O_2}$,

$$(4 - 2N_{O_2})^2(P/(1(4 - N_{O_2})))/N_{O_2} = K^o. \quad (O)$$

the pressure P = 1 bar,

$$(N_{O_2})^2 - 4\,N_{O_2} + 4^2/(4+K^o) = 0. \quad (P)$$

Now,

$\bar{g}^o_{O_2} = -755102$ kJ kmole^{-1}, and $\bar{g}^o_O = -323359$ kJ kmole^{-1}.

We can solve for N_{O_2} and selecting the root, such that $N_{O_2} > 0$ and $N_O > 0$, i.e.,

$N_{O_2} = 1.8875$, $N_O = 0.225$, and $G_{min} = -1.52\times10^6$.

Example 14

A steady flow reactor is fired with 1 kmole of $C_{10}H_{20}$, with 10 % excess air. The species (1 to 5) leaving are CO, CO_2, H_2 , H2O, OH, O2, NO, and N2 at T= 2500 K , 1 bar. Determine equilibrium composition of species leaving the reactor. Assume idea gas behavior.,

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Solution

The stoichiometric O2 can be determined to be :

$$(C_{10}H_{20}) + 15\,\{O_2 + 3.76\,N_2\} = 10\,CO_2 + 10\,H_2O + 56.4\,N_2$$

With 10 % excess air, O2 supplied = 16.5 kmoles , N2 supplied 62.04 kmoles

$$(C_{10}H_{20}) + 16.5\,\{O_2 + 3.76\,N_2\} \rightarrow CO, CO_2, H2, H2O, OH, O2, NO, N2$$

This system is an open system. Now we follow a fixed mass (140+528+ 1737= 2405 kg) as it travels the reactor. Suppose this mixture is instantaneously heated to 2500 K at 1 bar and then calculate assuming various values for the moles of 8 species CO, CO2 etc subject to satisfaction of atom conservation for C, H, N, and O and select the composition at which G is minimum at same T and P. We use Larange multiplier method to arrive at the composition.

The four elements C,H,N and O are denoted by subscript j and eight species denoted by subscript k. The coefficients d_{jk}, i.e., $d_{11} = 1$, $d_{12} = 1$, … are provided in the following table:

Coefficients d_{jk}

Element j→ **Species k ↓**	C	H	N	O
CO	1			1
CO2	1			2
H2		2		
H2O		2		1
NO			1	1
N2			2	
OH		1		1
O2				2

The atom conservation equations ($\Sigma_k d_{jk} N_k - A_j$) (see Eq. (81)) yield the relations:

j = 1 (C atoms): $1N_{CO} + 1N_{CO_2} + 0N_{H_2} + 0N_{H_2O} + 0N_{NO} + 0N_{N2}+0N_{OH} + 0N_{O2} - 10 = 0$, (A)

j = 2 (H atoms): $0\, N_{CO} + 0\, N_{CO_2} + 2\, N_{H_2} + 2\, N_{H_2O} + 0N_{NO} + 0N_{N2}+1N_{OH} + 0N_{O2} - 20 = 0$, (B)

j = 3 (O atoms): $1N_{CO} + 2\, N_{CO_2} + 0\, N_{H_2} + 1\, N_{H_2O} + 1N_{NO} + 0N_{N2}+1N_{OH} + 2N_{O2} - 31.6 = 0$, (C)

j = 4 (N atoms): $0N_{CO} + 0\, N_{CO_2} + 0N_{H_2} + 0\, N_{H_2O} + 1N_{NO} + 2N_{N2}+0N_{OH} + 0N_{O2} - 118.6 = 0$, (D)

Dividing these equations by the total moles ($N= \Sigma N_k$), we obtain the relations

$1X_{CO} + 1X_{CO_2} + 0X_{H_2} + 0X_{H_2O} + 0X_{XO} + 0X_{N2}+0X_{OH} + 0X_{O2} - 10/N = 0$, (E)

$0\, X_{CO} + 0\, X_{CO_2} + 2\, X_{H_2} + 2\, X_{H_2O} + 0X_{NO} + 0X_{N2}+1X_{OH} + 0X_{O2} - 20/N = 0$, (F)

$1X_{CO} + 2\, X_{CO_2} + 0\, X_{H_2} + 1\, X_{H_2O} + 1X_{NO} + 0X_{N2}+1X_{OH} + 2X_{O2} - 31.6/N= 0$, (G)

$0X_{CO} + 0\, X_{CO_2} + 0X_{H_2} + 0\, X_{H_2O} + 1X_{NO} + 2X_{N2}+0X_{OH} + 0X_{O2} - 118.6/N = 0$,(H)

where N is solved from the identity

$$\Sigma X_k = 1 \quad \text{(I)}$$

$$G = G(T,P,N_1, N_2, \ldots, N_K). \quad \text{(J)}$$

Multiplying Eqs. (A)–(D), respectively by λ_C, λ_H, λ_N and λ_O, and adding with Eq. (J) we form a function

$F = G + \lambda_C (N_{CO} + N_{CO_2} – 10) + \lambda_H(2N_{H_2} + 2N_{H_2O} + N_{OH} - 20) +$

$\lambda_O(N_{CO} + 2N_{CO_2} + N_{H_2O} + N_{OH}+ N_{NO}+ 2 N_{O2} – 31.6) + \lambda_N (N_{NO} + 2 N_{N2} –118.6)$ (K)

that is minimized at equilibrium, i.e.,

$$\partial F/\partial N_{CO} = (\partial G/\partial N_{CO})_{T,P} + \lambda_C + \lambda_O = 0, \quad (L)$$

$$\partial F/\partial N_{CO2} = (\partial G/\partial N_{CO2})_{T,P} + \lambda_C + 2\lambda_O = 0, \text{ and} \quad (M)$$

$$\partial F/\partial N_{H_2} = (\partial G/\partial N_{H_2})_{T,P} + 2\lambda_H = 0. \quad (N)$$

Rewrite Eqs. (L) to (N as :

$$\mu_{CO} + \lambda_C + \lambda_O = 0, \quad (O)$$

$$\mu_{CO2} + \lambda_C + 2 \lambda_H = 0, \text{ and} \quad (P)$$

$$\mu_{H_2} + 2\lambda_H = 0. \quad (Q)$$

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where $\mu_k = (\partial G/\partial N_k)_{T,P}$

Recall that for an ideal mixture of gases or ideal mix of liquids or solids

$$\mu_k = \hat{g}_k = \bar{g}_k(T,P) + \bar{R}T \ln (X_k). \quad (R)$$

Divide by $\bar{R}T$; then

$$\mu_k / \bar{R}T = \{ \bar{g}_k(T,P)/ \bar{R}T \} + \ln (X_k1). \quad (R')$$

Divide Eqs (O) ..(Q) by $\bar{R}T$ and using (R')

$$\{ \bar{g}_{CO}(T,P)/ \bar{R}T \} + \ln (X_{CO}).+ \lambda_C' + \lambda_O' = 0, \quad (S)$$

$$\{ \bar{g}_{CO2}(T,P)/ \bar{R}T \} + \ln (X_{CO2}).+ \lambda_C' + 2 \lambda_H' = 0, \text{ and} \quad (T)$$

$$\{ \bar{g}_{H2}(T,P)/ \bar{R}T \} + \ln (X_{H2}) + 2\lambda_H' = 0 \quad (U)$$

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where $\lambda_j' = \lambda_j / \bar{R}T$

the values of ln $\{X_k\}$ can be determined from the linear equations (S) to (U) for assumed values of modified Legrange multipliesr of λ_C', λ_H', λ_N', and λ_O'. Then we check whether these four multipliers satisfy the four-element conservation equations (E) to (H). Thus knowing μ_k, X_k can be determined from linear equations like Eq. (R).Irrespective of the number of unknown species, one makes assumptions only for the La Grange multipliers which are equal to number of atom balance equations. Good starting values can be obtained by assuming complete combustion, estimate mole fractions and hence obtain initial guessing values for using Eqs. (S) to (U). Thus for T = 2500 K and P = 1 bar. Then

$$\bar{g}_k = \bar{h}_k - T\bar{s}_k, \text{ and}$$

$$\bar{g}_{CO} = -701455 \text{ kJ kmole}^{-1}, \bar{g}_{H_2} = -419840 \text{ kJ kmole}^{-1},$$

$$\bar{g}_{CO_2} = -1078464 \text{ kJ kmole}^{-1}, \ldots\ldots \text{ so on} \qquad \text{(S)}$$

and good starting values could be λ_C', λ_H ' , λ_N ', and λ_O' = 19.7, 12.5, 14.0, 17.1 . The converged solutions are given below:

N_{CO} = 2.04 kmoles , N_{CO_2} = 7.96, N_{H_2} = 0.42, N_{H_2O} = 9.24, N_{NO} = 0.57, N_{N2} = 59, N_{OH} = 0.69 , N_{O2} = 1.52 , N = ΣN_k = 81.4 kmoles . The NASA equilbrium code uses descent Newton-Raphson method with typical number of iterations 8-12