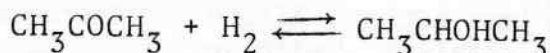


## CHAPTER 2

### THERMODYNAMICS OF CHEMICAL REACTIONS

#### Problem 2.1 Solution



For this reaction the standard enthalpy change is given by

$$\begin{aligned}\Delta H^0 &= \sum v_i \Delta H_{f,i}^0 \\ &= (1)(-261.30) - 1(0) - 1(-216.83) \\ &= -44.47 \text{ kJ/mole} \quad (\text{A})\end{aligned}$$

The standard Gibbs free energy change is given by

$$\begin{aligned}\Delta G^0 &= \sum v_i \Delta G_{f,i}^0 \\ &= (1)(-159.94) - 1(0) - 1(152.61) \\ &= -7.33 \text{ kJ/mole}\end{aligned}$$

The reaction velocity and the conversion achieved in a short time at the start of the reaction will be affected by process variables which affect the reaction rate. Normally the rate will increase with increasing temperature and with increasing reactant concentrations. In some cases mass transfer effects may also influence reaction rates.

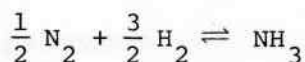
The equilibrium constant and the equilibrium degree of conversion are governed by thermodynamic considerations. Equation A indicates that the reaction is exothermic. Hence the equilibrium constant will decrease with increasing temperature. For the reaction under consideration equation 2.7.1 becomes

$$\frac{n_{\text{alcohol}}}{n_{\text{H}_2} n_{\text{acetone}}} = \frac{K_a}{K_{f/P}} \left( \frac{P}{n_{\text{alcohol}} + n_{\text{H}_2} + n_{\text{acetone}} + n_{\text{inerts}}} \right)$$

The considerations in Section 2.7 indicate that the effects of the various variables are as indicated in the table below.

| Variable<br>Effect on     | T<br>increase | p<br>increase        | Less active<br>catalyst | Dilute<br>with argon | Increase in<br>$N_{Re}$ |
|---------------------------|---------------|----------------------|-------------------------|----------------------|-------------------------|
| Reaction<br>velocity      | increase      | probable<br>increase | decrease                | probable<br>decrease | indeterminate           |
| $K_a$                     | decrease      | no effect            | no effect               | no effect            | no effect               |
| equilibrium<br>conversion | decrease      | increase             | no effect               | decrease             | no effect               |
| initial<br>conversion     | increase      | probable<br>increase | decrease                | probable<br>decrease | indeterminate           |

#### Problem 2.2 Solution



Temperature = 450°C

Pressure = 101.3 MPa  $\approx$  1000 atm

In this problem we are given input composition data and are asked to evaluate the effluent composition if equilibrium prevails.

If we choose as a basis 100 moles of entering gas mixture the following mole table may be constructed:

|        | In  | Out             |
|--------|-----|-----------------|
| $N_2$  | 20  | $20 - (\xi/2)$  |
| $H_2$  | 60  | $60 - (3\xi/2)$ |
| A      | 20  | 20              |
| $NH_3$ | 0   | $\xi$           |
| Total  | 100 | $100 - \xi$     |

The equilibrium constant for the reaction may be written in terms of standard states of unit fugacity as

$$K_a = \frac{(\hat{f}_{NH_3}/1)}{\left(\frac{\hat{f}_{H_2}}{1}\right)^{3/2} \left(\frac{\hat{f}_{N_2}}{1}\right)^{1/2}} \quad (A)$$

For component  $i$

$$\hat{f}_i = \left( \frac{n_i}{n_{\text{Total}}} \right) \left( \frac{f}{P} \right)_i P_{\text{Total}} \quad (\text{B})$$

where  $n_i$  is the mole number of species  $i$ , where  $\left( \frac{f}{P} \right)_i$  is the fugacity coefficient of species  $i$  evaluated at the total pressure of the reaction mixture, and where  $P_{\text{Total}}$  is the total pressure in atmospheres. The product  $\left[ \left( \frac{f}{P} \right)_i P_{\text{Total}} \right]$  represents the fugacity of pure  $i$  at the total pressure in question.

The fugacity coefficients of nitrogen and ammonia may be evaluated using the corresponding states plot in Appendix B and critical property data from Appendix A.

|          | Critical<br>temperature<br>(°K) | Reduced<br>temperature<br>at 450°C | Critical<br>Pressure<br>(atm) | Reduced<br>Pressure<br>at 1000 atm | $\frac{f}{p}$                 |
|----------|---------------------------------|------------------------------------|-------------------------------|------------------------------------|-------------------------------|
| Nitrogen | 126.2                           | 5.73                               | 33.5                          | 29.9                               | 1.38                          |
| Ammonia  | 405.6                           | 1.783                              | 112.5                         | 8.89                               | 0.865                         |
| Hydrogen | ---                             | ---                                | ---                           | ---                                | $\frac{136.8}{101.3} = 1.350$ |

Combination of equations A and B and substitution of numerical values from the problem statement and the tables gives

$$K_a = 8.75 \times 10^{-3} = \frac{\left( \frac{\xi}{100-\xi} \right) (0.865)}{\left[ \left( \frac{60-1.5\xi}{100-\xi} \right) 1.350 \right]^{3/2} \left[ \left( \frac{20-0.5\xi}{100-\xi} \right) (1.38) \right]^{1/2} 1000}$$

or

$$\frac{\xi(100-\xi)}{(60-1.5\xi)^{3/2} (20-0.5\xi)^{1/2}} = 18.64 = \frac{\xi(100-\xi)}{3^{3/2} (20-0.5\xi)^2}$$

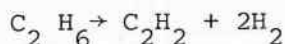
Thus  $96.85(20-0.5\xi)^2 = 100\xi - \xi^2$

or  $25.21\xi^2 - 2037\xi + 38,741 = 0$

Thus  $\xi = \frac{2037 \pm \sqrt{(2037)^2 - 4(25.21)(38,741)}}{2(25.21)} = 40.40 \pm 9.77$

The positive root may be neglected since all mole numbers must be positive.  
Hence

|                 |              |               |
|-----------------|--------------|---------------|
|                 | $\xi = 30.6$ |               |
|                 | mole number  | mole per cent |
| N <sub>2</sub>  | 4.7          | 6.8           |
| H <sub>2</sub>  | 14.1         | 20.3          |
| A               | 20           | 28.8          |
| NH <sub>3</sub> | 30.6         | 44.1          |
| Total           | 69.4         | 100.0         |

Problem 2.3 Solution

A. From equation 2.2.6

$$\begin{aligned}\Delta G^0 &= \sum v_i \Delta G_{f,i}^0 \\ &= 1(209.340) + 2(0) - 1(-32.908) \\ &= 242.248 \text{ kJ/mole}\end{aligned}$$

B. From equation 2.2.5

$$\begin{aligned}\Delta H^0 &= \sum v_i \Delta H_{f,i}^0 \\ &= 1(226.899) + 2(0) - 1(-84.724) \\ &= 311.623 \text{ kJ/mole}\end{aligned}$$

C.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Thus

$$\Delta S^0 = \frac{311.623 - 242.248}{298.16} = 0.23268 \frac{\text{kJ}}{\text{mole} \cdot ^\circ\text{K}}$$

Now

$$\Delta S^0 = \sum v_i S_i^0$$

Thus in consistent units

$$232.68 = 1(200.95) + 2S_{\text{H}_2}^0 - 1(229.65)$$

or

$$S_{\text{H}_2}^0 = 130.7 \text{ J/mole} \cdot ^\circ\text{K}$$

D. At 25°C, from equation 2.4.7

$$\begin{aligned}K_a &= e^{-\Delta G^0/RT} = \exp \left[ \frac{-242.248 \times 10^3}{(8.31)(298.16)} \right] \\ &= 3.45 \times 10^{-43}\end{aligned}$$

E. Integration of equation 2.5.3 for  $\Delta H^0$  independent of temperature gives

$$\ln \left( \frac{K_2}{K_1} \right) = - \frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

At 827°C = 1100°K

$$\ln \left( \frac{K_2}{K_1} \right) = - \frac{311,623}{8.31} \left[ \frac{1}{1100.16} - \frac{1}{298.16} \right]$$

or

$$K_2 = 6.58 \times 10^{39} K_1 = 2.27 \times 10^{-3}$$

(A)

F. For the indicated choice of standard states and the reactor conditions cited, the gases will behave ideally. The equilibrium constant may then be written as

$$K_a = \frac{P_{C_2H_2} P_{H_2}^2}{P_{C_2H_6}} = \frac{y_{C_2H_2} y_{H_2}^2}{y_{C_2H_6}} \left( \frac{101.3}{101.3} \right)^2 \quad (B)$$

where the  $P_i$  refer to partial pressures in atmospheres.

If we choose as a basis 100 moles of feed, the following mole table may be constructed

|          | In  | Out          |
|----------|-----|--------------|
| $C_2H_6$ | 100 | $100 - \xi$  |
| $C_2H_2$ | 0   | $\xi$        |
| $H_2$    | 0   | $2\xi$       |
| Total    | 100 | $100 + 2\xi$ |

Equation B may now be rewritten as

$$K_a = 2.27 \times 10^{-3} = \frac{\left( \frac{\xi}{100 + 2\xi} \right) \left( \frac{2\xi}{100 + 2\xi} \right)^2}{\left( \frac{100 - \xi}{100 + 2\xi} \right)}$$

or

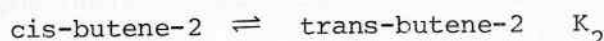
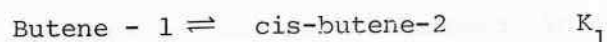
$$\frac{4\xi^3}{(100 + 2\xi)^2 (100 - \xi)} = 2.27 \times 10^{-3}$$

If we recognize that  $0 < \xi < 100$ , a trial and error procedure gives the desired result

$$\xi = 8.96$$

The effluent composition is then

|          | Mole numbers | Mole per cent |
|----------|--------------|---------------|
| $C_2H_6$ | 91.04        | 77.2          |
| $C_2H_2$ | 8.96         | 7.6           |
| $H_2$    | 17.92        | 15.2          |
|          | <hr/> 117.92 | <hr/> 100.0   |

Problem 2.4 Solution

We are given equilibrium data at two temperatures and values of  $\Delta G_f^0$  and  $\Delta H_f^0$  for butene-1. We are asked to evaluate  $\Delta G_f^0$  and  $\Delta H_f^0$  for the two butene-2 isomers.

Since the pressures involved are below one atmosphere, the gases will behave ideally and the equilibrium constants for the two reactions may be written as

$$K_1 = \frac{y_B}{y_A} \quad K_2 = \frac{y_C}{y_B}$$

where B refers to cis-butene-2, C to trans-butene-2, and A to butene-1.

At 25°C

$$K_1 = \frac{0.219}{0.030} = 7.30 \quad K_2 = \frac{0.751}{0.219} = 3.43$$

At 127°C

$$K_1 = \frac{0.288}{0.081} = 3.56 \quad K_2 = \frac{0.631}{0.288} = 2.19$$

For reaction 1 equations 2.4.7 and 2.2.6 indicate that

$$\Delta G_1^0 = \Delta G_{f,B}^0 - \Delta G_{f,A}^0 = -RT \ln K_1$$

At 25°C = 298.16°K

$$\Delta G_{f,B}^0 - 72,100 = -8.31(298.16) \ln(7.30)$$

or

$$\Delta G_{f,B}^0 = 67,174 \text{ J/mole}$$

If the heat of reaction is assumed to be independent of temperature, equation 2.5.3 indicates that

$$\frac{-\Delta H_1^0}{R} = \frac{\ln \left( \frac{K_1 \text{ at } T_2}{K_1 \text{ at } T_1} \right)}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)} = \frac{\ln \left( \frac{3.56}{7.30} \right)}{\left( \frac{1}{400.16} - \frac{1}{298.16} \right)}$$

$$\Delta H_1^0 = -8.31(840) = -6980 \text{ J/mole.}$$

From equation 2.2.6

$$\Delta H_{f,B}^0 = -6980 + 1172 = -5808 \text{ J/mole.}$$

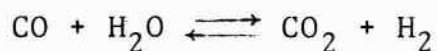
In similar fashion using the data for the second reaction and the thermochemical values tabulated above, it can be shown that

$$\Delta G_{f,C}^0 = 64.12 \text{ kJ/mole}$$

and

$$\Delta H_{f,C}^0 = -10.17 \text{ kJ/mole}$$

### Problem 2-5 solution



$$\text{At } 900^\circ\text{F} \quad K_a = 5.62$$

For reaction at  $900^\circ\text{F}$  and  $75 \text{ atm}$ , determine the mole ratio of  $\text{H}_2\text{O}/\text{CO}$  which gives 90% conversion of  $\text{CO}$  to  $\text{CO}_2$ .

Let  $R$  = desired ratio

If we choose as a basis one mole of entering  $\text{CO}$ , the following mole table may be prepared

|                  | Moles in | Moles out |
|------------------|----------|-----------|
| CO               | 1.00     | 0.10      |
| H <sub>2</sub> O | R        | R - 0.90  |
| CO <sub>2</sub>  | 0.00     | 0.90      |
| H <sub>2</sub>   | 0.00     | 0.90      |
| Total            | 1.00 + R | 1.00 + R  |

The equilibrium constant for the reaction can be written as

$$K_a = \left( \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} \right) \frac{(f/P)_{\text{CO}_2} (f/P)_{\text{H}_2}}{(f/P)_{\text{CO}} (f/P)_{\text{H}_2\text{O}}} = 5.62 \quad (\text{A})$$

The fugacity coefficients may be evaluated using the corresponding states correlation given in Appendix B. Thus at  $75 \text{ atm}$  and  $900^\circ\text{F}$  ( $755^\circ\text{K}$ )

| Species          | $T_c (^{\circ}\text{K})$ | $P_c (\text{atm})$ | Reduced pressure | Reduced temperature | $f/P$ |
|------------------|--------------------------|--------------------|------------------|---------------------|-------|
| CO               | 133                      | 34.5               | 2.17             | 5.68                | 1.00  |
| CO <sub>2</sub>  | 304.2                    | 72.9               | 1.03             | 2.48                | 0.98  |
| H <sub>2</sub> * | 33.3                     | 12.8               | 5.86             | 22.69               | 1.05  |
| H <sub>2</sub> O | 647                      | 218.3              | 0.343            | 1.17                | 0.95  |

Equation A may be rewritten in terms of the tabular entries as

$$\frac{\left(\frac{0.9}{1+R}\right)^2 (0.98)(1.05)}{\left(\frac{R-0.9}{1+R}\right) \left(\frac{0.1}{1+R}\right) (1.00)(0.95)} = 5.62$$

or 
$$\frac{(0.9)^2}{(0.1)(R-0.9)} = 5.19$$

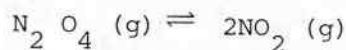
Solving for the desired ratio

$$R = 0.9 + \frac{(0.9)^2}{0.1(5.19)} = 2.46$$

If one assumes that the fugacity coefficients are all unity, he finds that  $R = 2.34$ .

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\*Pseudocritical values should actually be used for hydrogen. However the reduced temperature is so high that we are effectively out of the range of the chart anyway.



A. We are asked to calculate the equilibrium composition for this system. This requires a knowledge of the equilibrium constant for this reaction which in turn requires thermochemical data for  $\text{N}_2\text{O}_4$ . From the Handbook of Chemistry and Physics, 53d edition:

|                        | $\Delta G_f^0$ (kcal/mole) | $\Delta H_f^0$ (kcal/mole) |
|------------------------|----------------------------|----------------------------|
| $\text{NO}_2$          | 12.39                      | 8.09                       |
| $\text{N}_2\text{O}_4$ | 23.49                      | 2.31                       |

For the above reaction equation 2.2.6 indicates that

$$\Delta G^0 = 2(12.39) - 1(23.49) = 1.29 \text{ kcal/mole.}$$

From equation 2.4.7

$$K_a = e^{-1290/(1.987)(298.16)} = 0.1133$$

For standard states at one atmosphere (101.3 kPa) and ideal gas behavior:

$$K_a = \frac{y_{\text{NO}_2}^2}{y_{\text{N}_2\text{O}_4}} = \frac{y_{\text{NO}_2}^2}{(1 - y_{\text{NO}_2})} = 0.1133$$

Thus

$$y_{\text{NO}_2} = 0.285$$

B. To calculate the Gibbs free energy of mixtures of these two substances at the indicated pressure and temperature, we can recognize that

$$G_{\text{MIXTURE}} = n_{\text{NO}_2} G_{f,\text{NO}_2}^0 + n_{\text{N}_2\text{O}_4} G_{f,\text{N}_2\text{O}_4}^0 + \Delta G_{\text{MIXING}} \quad (\text{A})$$

where  $G_{f,\text{NO}_2}^0$  and  $G_{f,\text{N}_2\text{O}_4}^0$  are the Gibbs free energies of pure  $\text{NO}_2$  and pure  $\text{N}_2\text{O}_4$  at 101.3 kPa and 25°C. The  $n_i$  are the mole numbers.

$$\text{Now} \quad \Delta G_{\text{MIXING}} = \Delta H_{\text{MIXING}} - T\Delta S_{\text{MIXING}}$$

For an ideal gas mixture the last equation reduces to

$$\Delta G_{\text{MIXING}} = -T\Delta S_{\text{MIXING}} = RT \sum n_i \ln y_i \quad (\text{B})$$

Combination of equations (A) and (B) gives

$$G_{\text{MIXTURE}} = n_{\text{NO}_2} G_{f,\text{NO}_2}^0 + n_{\text{N}_2\text{O}_4} G_{f,\text{N}_2\text{O}_4}^0 + RT n_{\text{N}_2\text{O}_4} \ln \left( \frac{n_{\text{N}_2\text{O}_4}}{n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}} \right) + RT n_{\text{NO}_2} \ln \left( \frac{n_{\text{NO}_2}}{n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2}} \right)$$

For a mixture containing 2 gram atoms of nitrogen

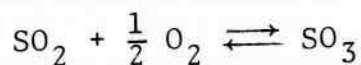
$$n_{\text{NO}_2} + 2n_{\text{N}_2\text{O}_4} = 2.0$$

With  $RT = 1.987(298.16) = 0.5924$  kcal/mole and the thermochemical data tabulated in part A, the following table may be constructed.

| $n_{\text{NO}_2}$ | $n_{\text{N}_2\text{O}_4}$ | $y_{\text{NO}_2}$ | $G_{\text{MIXTURE}}$ (kcal) |
|-------------------|----------------------------|-------------------|-----------------------------|
| 0                 | 1.0                        | 0.0000            | 23.490                      |
| 0.2               | 0.9                        | 0.1818            | 23.310                      |
| 0.3               | 0.85                       | 0.2609            | 23.2925                     |
| 0.35              | 0.825                      | 0.2979            | 23.2918                     |
| 0.4               | 0.8                        | 0.3333            | 23.296                      |
| 0.6               | 0.7                        | 0.4615            | 23.345                      |
| 0.8               | 0.6                        | 0.5714            | 23.440                      |
| 1.0               | 0.5                        | 0.6667            | 23.569                      |
| 1.2               | 0.4                        | 0.7500            | 23.731                      |
| 1.4               | 0.3                        | 0.8235            | 23.924                      |
| 1.6               | 0.2                        | 0.8889            | 24.150                      |
| 1.8               | 0.1                        | 0.9474            | 24.422                      |
| 2.0               | 0.0                        | 1.00              | 24.780                      |

The Gibbs free energy of the mixture is plotted versus mole fraction  $\text{NO}_2$  in Figure 2.S.1. The minimum in the curve corresponds to the equilibrium mole fraction calculated in part (A).

### Problem 2-7 solution



- (a) For standard states given, equation 2.4.8 indicates that

$$K_a = e^{-\Delta G^0/RT}$$

with  $\Delta G^0 = -70,040$  J/mole

$$T = 25 + 273.16 = 298.16^\circ\text{K}$$

$$R = 8.317 \text{ J/mole-}^\circ\text{K}$$

The indicated pressure is equivalent to 1 atmosphere.

Thus  $K_a = 1.846 \times 10^{12}$  since unit fugacity is equivalent to 101.3 kPa.