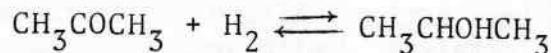


CHAPTER 2

THERMODYNAMICS OF CHEMICAL REACTIONS

Problem 2.1 Solution



For this reaction the standard enthalpy change is given by

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

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.

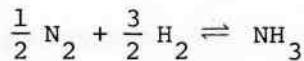
Equation A indicates that the reaction is exothermic. Hence the equilibrium constant will decrease with increasing temperature. For the reaction under consideration equation 2.7.1 becomes

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

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

Variable Effect on \	T increase	p increase	Less active catalyst	Dilute with argon	Increase in N _{Re}
Reaction velocity	increase	probable increase	decrease	probable decrease	indeterminate
K _a	decrease	no effect	no effect	no effect	no effect
equilibrium conversion	decrease	increase	no effect	decrease	no effect
initial conversion	increase	probable increase	decrease	probable decrease	indeterminate

Problem 2.2 Solution



Temperature = 450°C Pressure = 101.3 MPa = 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 - (ξ/2)
H ₂	60	60 - (3ξ/2)
A	20	20
NH ₃	0	ξ
Total	100	100 - ξ

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

$$K_a = \frac{(\hat{f}_{\text{NH}_3}/1)^3}{\left(\frac{\hat{f}_{\text{H}_2}}{1}\right)^{3/2} \left(\frac{\hat{f}_{\text{N}_2}}{1}\right)^{1/2}} \quad (\text{A})$$

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_{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 temperature (°K)	Reduced temperature at 450°C	Critical Pressure (atm)	Reduced Pressure 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 $96.85(20-0.5\xi)^2 = 100\xi - \xi^2$

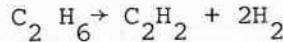
or $25.21\xi^2 - 2037\xi + 38,741 = 0$

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_2		4.7	6.8
H_2		14.1	20.3
A		20	28.8
NH_3		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

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

Now

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

Thus in consistent units

$$232.68 = 1(200.95) + 2S_{H_2}^0 - 1(229.65)$$

or

$$S_{H_2}^0 = 130.7 \text{ J/mole} \cdot \text{K}$$

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 ΔH^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

$$K_2 = 6.58 \times 10^{39} K_1 = 2.27 \times 10^{-3} \quad (A)$$

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

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

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	ξ
H_2	0	2ξ
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
$$\frac{4\xi^3}{(100 + 2\xi)^2 (100 - \xi)} = 2.27 \times 10^{-3}$$

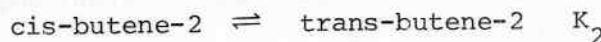
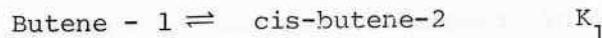
If we recognize that $0 < \xi < 100$, a trial and error procedure gives the desired result

$$\xi = 8.96$$

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
	117.92	100.0

Problem 2.4 Solution



We are given equilibrium data at two temperatures and values of ΔG_f^0 and ΔH_f^0 for butene-1. We are asked to evaluate ΔG_f^0 and ΔH_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°F and 75 atm, determine the mole ratio of H₂O/CO which gives 90% conversion of CO to CO₂.

Let R = desired ratio

If we choose as a basis one mole of entering CO, the following mole table may be prepared

	Moles in	Moles out
CO	1.00	0.10
H ₂ O	R	R - 0.90
CO ₂	0.00	0.90
H ₂	0.00	0.90
Total	1.00 + R	1.00 + R

The equilibrium constant for the reaction can be written as

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

The fugacity coefficients may be evaluated using the corresponding states correlation given in Appendix B. Thus at 75 atm and 900°F (755°K)

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Species	T _c (°K)	P _c (atm)	Reduced pressure	Reduced temperature	f/P
CO	133	34.5	2.17	5.68	1.00
CO ₂	304.2	72.9	1.03	2.48	0.98
H ₂ [*]	33.3	12.8	5.86	22.69	1.05
H ₂ O	647	218.3	0.343	1.17	0.95

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

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

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

Solving for the desired ratio

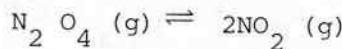
$$R = 0.9 + \frac{(0.9)^2}{0.1(5.19)} = 2.46$$

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

^{*}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.

Problem 2.6 Solution

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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 $N_2 O_4$. From the Handbook of Chemistry and Physics, 53d edition:

	ΔG_f^0 (kcal/mole)	ΔH_f^0 (kcal/mole)
NO_2	12.39	8.09
$N_2 O_4$	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:

$$K_a = \frac{y_{NO_2}^2}{y_{N_2 O_4}} = \frac{y_{NO_2}^2}{(1 - y_{NO_2})} = 0.1133$$

Thus

$$y_{NO_2} = 0.285$$

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

$$G_{\text{MIXTURE}} = n_{NO_2} G_{f,NO_2}^0 + n_{N_2 O_4} G_{f,N_2 O_4}^0 + \Delta G_{\text{MIXING}} \quad (A)$$

where G_{f,NO_2}^0 and $G_{f,N_2 O_4}^0$ are the Gibbs free energies of pure NO_2 and pure $N_2 O_4$ at 101.3 kPa and 25°C. The n_i are the mole numbers.

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

For an ideal gas mixture the last equation reduces to

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

Combination of equations (A) and (B) gives

$$G_{\text{MIXTURE}} = n_{NO_2} G_{f,NO_2}^0 + n_{N_2 O_4} G_{f,N_2 O_4}^0 + RT \sum n_{N_2 O_4} \ln \left(\frac{n_{N_2 O_4}}{n_{N_2 O_4} + n_{NO_2}} \right) + RT \sum n_{NO_2} \ln \left(\frac{n_{NO_2}}{n_{N_2 O_4} + n_{NO_2}} \right)$$

For a mixture containing 2 gram atoms of nitrogen

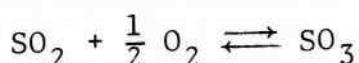
$$n_{\text{NO}_2} + 2n_{\text{N}_2\text{O}_4} = 2.0$$

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

n_{NO_2}	$n_{\text{N}_2\text{O}_4}$	y_{NO_2}	$G_{\text{MIXTURE}} (\text{kcal})$
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 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 $\Delta G^0 = -70,040 \text{ J/mole}$

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

$$R = 8.317 \text{ J/mole}^{-1}\text{K}$$

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.