Solution to problem 2.1

The first step is to calculate the equilibrium constant at 723 K. This constant can be determined from the standard free energy of reaction, as given by:

$$\Delta G_R^\circ = -R_g T \ln K$$

First calculate ΔG_R° at 298 K from ΔG_f° data (at 298 K). The following data are taken from the Appendix 1. The constants a, b, c and d are constants in the heat capacity polynomial.

Formula	ΔH_f° kJ/mol	ΔG_f° kJ/mol	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
N_2	0	0	28.85	-0.1569	0.8067	-2.868
H_2	0	0	29.06	-0.1913	0.3997	-0.8690
NH_3	-46.22	-16.6	27.524	2.5603	0.98911	-6.6801

The free energy of formation of NH_3 is –16.6 kJ/mol. This value is equal to ΔG_R° because the free energies of formation of nitrogen and hydrogen are equal to zero. Therefore, at 298 K:

$$K_{298} = \exp\left(\frac{-\Delta G_R^\circ}{R_g T}\right) = \exp\left(\frac{-16.6 \times 10^3}{8.314 \times 298}\right) = 812$$
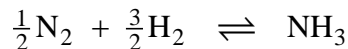
To calculate K at 723 K use the relationship:

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_R^\circ}{R_g T^2}$$

This equation requires an expression for ΔH_R° as a function of T, which in turn depends on the difference in heat capacities between reactants and products, according to the equation:

$$\frac{\partial \Delta H_R^\circ}{\partial T} = \Delta C_P$$

The calculations are based on a reaction stoichiometry of one mole of NH_3.

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3$$

Using the data from Appendix 1 (given above), we can obtain an expression for the change in heat capacity. The general formula is:

$$\Delta C_P = \Delta a + \Delta b T + \Delta c T^2 + \Delta d T^3$$

Substituting the values from the above table gives:

$$\Delta C_P = -30.49 + 2.926 \times 10^{-2} T + 1.889 \times 10^{-5} T^2 - 3.943 \times 10^{-9} T^3$$

The enthalpy of reaction at 298 K is equal to the enthalpy of formation of NH_3, or

$\Delta H^{\circ}_{R,298} = -46.22 \times 10^3$ J/mol. By integration we then obtain the general equation:

$$\Delta H^{\circ}_R = \Delta H^{\circ}_{R,298} + \int_{298}^{T} \Delta C_P \, dT$$

Substitution and integration gives the following equation:

$$\Delta H^{\circ}_R = -46.22 \times 10^3 + \left[-30.49 T + \frac{2.926 \times 10^{-2}}{2} T^2 + \frac{1.889 \times 10^{-5}}{3} T^3 - \frac{3.943 \times 10^{-9}}{4} T^4 \right]_{298}^{T}$$

Simplify to give the following equation:

$$\Delta H^{\circ}_R = -3.86 \times 10^4 - 30.49 T + 1.463 \times 10^{-3} T^2 + 6.297 \times 10^{-6} T^3 - 9.86 \times 10^{-10} T^4$$

The equilibrium constant at 723 K can now be computed:

$$\ln\left(\frac{K_{723}}{K_{298}} \right) = \frac{1}{R_g} \int_{298}^{723} \frac{\Delta H^{\circ}_R}{T^2} \, dT$$

Substitution and integration gives:

$$\ln\left(\frac{K_{723}}{812} \right) = \frac{1}{8.314} \left[\frac{3.86 \times 10^4}{T} - 30.49 \ln(T) + 1.463 \times 10^{-3} T + \frac{6.297 \times 10^{-6}}{2} T^2 - \frac{9.86 \times 10^{-10}}{3} T^3 \right]_{298}^{723}$$

Substitution of the limits and simplification gives $K_{723} = 4.153 \times 10^{-3}$. The equilibrium constant can be expressed in terms of the mole fractions, fugacity coefficients and total pressure:

$$K = \frac{K_{\phi} K_y}{K_{f^{\circ}}} P^{\Sigma \nu_j}$$

where $\quad K_y = \dfrac{y_{NH_3}}{y_{N_2}^{0.5}\, y_{H_2}^{1.5}}$ $\quad$ and $\quad K_\phi = \dfrac{\phi_{NH_3}}{\phi_{N_2}^{0.5}\, \phi_{H_2}^{1.5}}$.

The sum of the stoichiometric coefficients is:

$$\sum v_i = 1 - \tfrac{3}{2} - \tfrac{1}{2} = -1$$

The fugacity coefficient ϕ is defined as:

$$\phi = \frac{f}{P}$$

Therefore the three fugacity coefficients are:

$$\phi_{H_2} = \frac{1350}{1000} = 1.35, \quad \phi_{N_2} = \frac{1380}{1000} = 1.38 \;\; \text{and} \;\; \phi_{NH_3} = \frac{860}{1000} = 0.86$$

Therefore:

$$K_\phi = \frac{0.86}{(1.38)^{.5}(1.35)^{1.5}} = 0.467$$

The mole fractions in K_y refer to equilibrium mole fractions. Take a basis of 100 moles of feed

and let w moles of N_2 react. The following mole table then can be constructed:

Component	Initial Moles	Equilibrium Moles
N_2	21	21 - w
H_2	63	$63 - 3w = 3(21\text{-}w)$
NH_3	0	2w
Ar	16	16
Total	100	$100 - 2w$

Express K_y in terms of equilibrium moles.

$$K_y = \left(\frac{2w}{100-2w}\right)\left(\frac{100-2w}{3(21-w)}\right)^{1.5}\left(\frac{100-2w}{21-w}\right)^{0.5}$$

Now substitution of K, K_ϕ and P gives:

$$K = K_y K_\phi P^{-1} \quad \text{or} \quad 4.153\times10^{-3} = K_y (0.467)(1000)^{-1}$$

Solving gives $K_y = 8.893$. The value of w can then be determined. Simplification gives a quadratic equation:

$$w^2 - 42.64w + 405.9 = 0$$

This equation can be solved using the quadratic formula. It has two roots, $w = 15.36$ and $w = 27.28$. As w must be less than 21, it follows that the realistic solution is $w = 15.36$. Therefore, the equilibrium mole fractions at 1000 atm and 723 K are:

$$N_2 = \frac{21 - 15.36}{100 - 2 \times 15.36} = 0.0814$$

$$H_2 = \frac{3(21 - 15.36)}{100 - 2 \times 15.36} = 0.244$$

$$NH_3 = \frac{2 \times 15.36}{100 - 2 \times 15.36} = 0.443$$

$$Ar = \frac{16}{100 - 2 \times 15.36} = 0.231$$

Comments: High pressure favours conversion because there is a decrease in moles on reaction. The reaction is exothermic and therefore a low temperature would give a more favourable conversion. However, a high temperature is used to give a high reaction rate.

Part (a)

The first step is to calculate the equilibrium constant at 1023 K. For this purpose the equilibrium constant is first calculated at 298 K using the free energy of reaction:

$$\Delta G_R^\circ = -R_g T \ln K$$

K is then calculated at 1023 K using the van't Hoff equation:

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_R^\circ}{R_g T^2}$$

The Gibbs free energy of reaction is calculated from the data in Appendix 1. The data, including heat capacity data for the species present are:

Formula	ΔH_f° kJ/mol	ΔG_f° kJ/mol	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
H_2	0	0	29.06	-0.1913	0.3997	-0.8690
C_2H_6	-84.72	-32.9	6.889	17.24	-6.395	7.273
C_2H_4	52.32	68.17	3.95	15.61	-8.331	17.64

Therefore the free energy of reaction at 298 K is:

$$\Delta G_{R,298}^\circ = \Delta G_{f,298}^\circ(C_2H_4) - \Delta G_{f,298}^\circ(C_2H_6)$$

$$\Delta G_{R,298}^\circ = 68.05 \times 10^3 - (-32.90 \times 10^3) = 100.95 \times 10^3 \frac{J}{mol}$$

The equilibrium constant at 298 K is then calculated to be $K_{298} = 1.9373 \times 10^{-18}$. To compute K_{1023} it is first necessary to calculate ΔH_R° as a function of temperature. For this purpose use the following relationship:

$$\frac{\partial \Delta H_R^\circ}{\partial T} = \Delta C_P$$

The difference in heat capacity between products and reactants is calculated from the above data. The general formula is:

$$\Delta C_P = \Delta a + \Delta b T + \Delta c T^2 + \Delta d T^3$$

Substituting the values from the above table gives:

$$\Delta C_P = 25.5 - 1.222 \times 10^{-2} \, T - 2.788 \times 10^{-5} \, T^2 + 16.45 \times 10^{-9} \, T^3$$

The enthalpy change with reaction at 298 K is:

$$\Delta H^{\circ}_{R,298} = \Delta H^{\circ}_{f,298}(C_2H_4) - \Delta H^{\circ}_{f,298}(C_2H_6)$$

$$\Delta H^{\circ}_{R,298} = 52.25 \times 10^3 - (-84.60 \times 10^3) = 136.9 \times 10^3 \, \frac{J}{mol}$$

The general expression for ΔH°_R is thus derived by integration:

$$\Delta H^{\circ}_R = \Delta H^{\circ}_{R,298} + \int_{298}^{T} \Delta C_P \, dT$$

For the cracking of ethane, substitution of the values and integration gives:

$$\Delta H^{\circ}_R = 130,007 + 25.5 \, T - 6.11 \times 10^3 \, T^2 - 9.293 \times 10^{-6} \, T^3 + 4.113 \times 10^{-9} \, T^4$$

The general equation for the equilibrium constant in integral form is:

$$\ln K = \ln K_{298} + \frac{1}{R_g} \int_{298}^{T} \frac{\Delta H^{\circ}_R}{T} \, dT$$

Substitution of ΔH°_R and integration with a limit of 1023 K gives a value of $K_{1023} = 0.4916$.

The equilibrium constant is related to the composition by:

$$K = \frac{K_\phi \, K_y}{K_{f^{\circ}}} \, P^{\Sigma v_j}$$

where
$$K_y = \frac{y_{H_2} \, y_{C_2H_4}}{y_{C_2H_6}}$$
and
$$K_\phi = \frac{\phi_{H_2} \, \phi_{C_2H_4}}{\phi_{C_2H_6}} = 1.$$

The sum of the stoichiometric coefficients is:

$$\Sigma v_i = 1 + 1 - 1 = 1$$

Therefore:

$$K = K_y P = \frac{y_{H_2} \, y_{C_2H_4}}{y_{C_2H_6}} \, P$$

with P in atm. $P = 120/100 = 1.2$ bar. Take a basis of 1 mole of ethane and let X moles react (X is therefore the fractional conversion).

Compound	Initial Moles	Final Moles
C_2H_6	1	$1-X$
C_2H_4	0	X
H_2	0	X
Total	1	$1+X$

Substitute for the mole fractions:

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

Therefore, the equilibrium conversion is given by:

$$0.4916 = \frac{X^2}{\left(1-X^2\right)}1.2$$

Solve for $X = 0.539$. The conversion of ethane is 53.9 % at equilibrium.

Part (b)

In part (a) a general expression for ΔH_R° was derived. Substituting 1023 K into this equation gives $\Delta H_R^\circ = 144255$ J/mol. This number is positive which indicates that 144,255 J must be transferred to the reactor for each mole of ethane that cracks.

Solution to problem 2.3

The equilibrium constant at 500 ºC has a value of 85. The relationship between composition and the equilibrium constant K is:

$$K = \frac{K_y \, K_\phi}{K_{f_i^\circ}} P^{\sum v_i}$$

From the reaction stoichiometry the change in moles on reaction is:

$$\sum v_i = 1 - 1 - \tfrac{1}{2} = -\tfrac{1}{2}$$

Because the fugacity coefficients are equal to one, it follows that $K_\phi = 1$. Using a standard state of 1 bar gives:

$$K = K_y \, P^{-0.5} \qquad \text{where } P \text{ is in bar}$$

The mole fractions at equilibrium must be expressed in terms of the number of moles present at equilibrium. Take a basis of 100 moles of original mixture and let X be the fractional conversion at equilibrium. That is,

$$X = \frac{N_{SO_2,0} - N_{SO_2}}{N_{SO_2,0}}$$

Construct a stoichiometric table on the 100 mole basis:

Compound	Moles Initial	Moles Final
SO_2	8	$8(1-X)$
SO_3	0	$8X$
O_2	11	$11 - \frac{8}{2}X$
N_2	81	81
Total	100	$100 - 4X$

Substitute into the equation for K:

$$K = K_y P^{-0.5} = \frac{y_{SO_3}}{y_{SO_2} y_{O_2}^{0.5}} \times 1^{-0.5} = \frac{\left(\dfrac{8X}{100-4X}\right)}{\left(\dfrac{8(1-X)}{100-4X}\right)\left(\dfrac{11-4X}{100-4X}\right)^{0.5}} = 85$$

Simplify:

$$85 = \frac{X}{1-X}\left(\frac{100-4X}{11-4X}\right)^{0.5}$$

The above equation is solved numerically to get a value of $X = 0.9587$. Therefore at equilibrium 95.87% of the original SO_2 is converted to SO_3.

At 2 bar pressure the equation becomes:

$$85 = 2^{-0.5} \frac{X}{1-X}\left(\frac{100-4X}{11-4X}\right)^{0.5}$$

Solving numerically gives a value of $X = 0.97$. Note that an increase in pressure gives an increase in conversion.

Solution to problem 2.4

The reactor is adiabatic so the energy released by the reaction heats up the process stream. Take a basis of 100 moles of mixture. First calculate ΔC_P for the reaction using the values supplied.

$$\Delta C_P = (C_P)_{SO_3} - \tfrac{1}{2}(C_P)_{O_2} - (C_P)_{SO_3} = 64.0 - \tfrac{1}{2}32.6 - 47.7 = 0$$

It is seen that $\Delta C_P = 0$ which means that the heat of reaction is constant (it does not change with temperature) and the heat capacity of the feed may be used to represent the mean heat capacity of the mixture. Let X be the fractional conversion of SO_2, then the mole balance table is

Compound	Moles Initial	Moles Final
SO_2	8	$8(1-X)$
SO_3	0	$8X$
O_2	11	$11-4X$
N_2	81	81
Total	100	$100-4X$

The heat released on reaction is the product of the enthalpy of reaction and the moles of SO_3 that react, or $8X(-\Delta H_R)$. The heat capacity of 100 moles of feed is

$$\overline{C}_P = 8 \times 47.7 + 11 \times 32.6 + 81 \times 28.8 = 3073 \, J$$

The energy balance therefore gives:

$$(-\Delta H_R)8X = \int_{673}^{T} \overline{C}_P \, dT = 3073(T-673)$$

Substitute for $-\Delta H_R$, X and simplify to give the adiabatic reaction line:

$$T = 255.6X + 673 \tag{1}$$

where T is in Kelvin. The relationship between composition and the equilibrium constant K is:

$$K = \frac{K_y \, K_\phi}{K_{f_i^\circ}} P^{\Sigma \nu_i}$$

From the reaction stoichiometry the change in moles on reaction is:

$$\sum \nu_i = 1 - 1 - \tfrac{1}{2} = -\tfrac{1}{2}$$

The fugacity coefficients are equal to one, therefore $K_\phi = 1$. With a standard state of 1 bar:

$$K = K_y P^{-0.5} \qquad \text{where } P \text{ is in bar}$$

The mole fractions at equilibrium must be expressed in terms of the number of moles present at equilibrium. Take a basis of 100 moles of original mixture and let X be the fractional conversion at equilibrium. That is:

$$X = \frac{N_{SO_2,0} - N_{SO_2}}{N_{SO_2,0}}$$

Substitute into the equation for K:

$$K = K_y P^{-0.5} = \frac{y_{SO_3}}{y_{SO_2} y_{O_2}^{0.5}} \times 1^{-0.5} = \frac{\left(\dfrac{8X}{100-4X}\right)}{\left(\dfrac{8(1-X)}{100-4X}\right)\left(\dfrac{11-4X}{100-4X}\right)^{0.5}}$$

Simplify:

$$K = \frac{X}{1-X}\left(\frac{100-4X}{11-4X}\right)^{0.5} \qquad\qquad (2)$$

The temperature dependence of K is given by:

$$\frac{d \ln K}{dT} = \frac{\Delta H_R^\circ}{R_g T^2}$$

As ΔH_R° is assumed constant, this equation can be integrated to give:

$$\ln \frac{K_2}{K_1} = \frac{(-\Delta H_R^\circ)}{R_g}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or, by rearrangement:

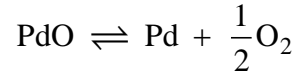$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{R_g}{(-\Delta H_R^\circ)} \ln\left(\frac{K_2}{K_1}\right)$$

Substitute the known value of $K = 85$ at 500°C.

$$\frac{1}{T} = \frac{1}{773} + \frac{8.314}{98.2 \times 10^3} \ln\left(\frac{K}{85}\right) \qquad\qquad (3)$$

Equations (1), (2), and (3) can be solved numerically to give $X = 0.798$ and $T_2 = 876.9 \ K$.

Solution to problem 2.5

The reaction is represented as:

$$PdO \rightleftharpoons Pd + \frac{1}{2}O_2$$

The composition at equilibrium depends on the activities of the three species. Thus:

$$K = \frac{a_{Pd}a_{O_2}^{0.5}}{a_{PdO}}$$

Both palladium oxide and palladium metal are solids and therefore their activities are equal to one. The equilibrium constant thus reduces to:

$$K = a_{O_2}^{0.5}$$

At low to moderate pressure the fugacity coefficient of oxygen equals one, and the activity of the oxygen is given by its partial pressure:

$$K = P_{O_2}^{0.5}$$

The equilibrium constant is related to the free energy change of reaction:

$$-\Delta G_R^o = R_g T \ln(K)$$

Combining the two equations:

$$\frac{-\Delta G_R^o}{R_g} = T \ln(P_{O_2}^{0.5})$$

The free energy change of reaction is given by:

$$\frac{\Delta G_R^o}{R_g} = 11273 + T[2.89 \log_{10}(T) - 18.57]$$

Combining the two equations:

$$T \ln(P_{O_2}^{0.5}) = 11273 + T[2.89 \log_{10}(T) - 18.57]$$

Substitution of 0.2 bar for the oxygen partial pressure gives a temperature of about 1063 K. At 1 bar the temperature is about 1175 K.

Solution to problem 2.6

Take a basis of 6 moles of mixture, that is, 5 moles of water and 1 mole of methane. Assume ideal gas behaviour. The equilibrium constants are then related to the composition by the relationship:

$$K_P = K_y P^{\Sigma \nu_j} = P^{\Sigma \nu_j} \prod_{j=1}^{n} y_j^{\nu_j}$$

Let x be the number of moles of CO_2 formed and let w be the moles of CO formed. The mole balance table can then be written:

Species	Initial	Final
CH_4	1	$1 - x - w$
H_2O	5	$5 - 2x - w$
CO	0	w
H_2	0	$3w + 4x$
CO_2	0	x
Total	6	$6 + 2w + 2x$

For reactions 1 and 2 the change in stoichiometric coefficients is $\Sigma \nu_j = 2$. The mole fractions of the species are given by:

$$y_{CH_4} = \frac{1 - x - w}{6 + 2w + 2x}; \quad y_{H_2O} = \frac{5 - 2x - w}{6 + 2w + 2x}; \quad y_{CO} = \frac{w}{6 + 2w + 2x}$$

$$y_{H_2} = \frac{3w + 4x}{6 + 2w + 2x}; \quad y_{CO_2} = \frac{x}{6 + 2w + 2x}$$

Therefore the K_P are given by:

$$(K_P)_1 = P^2 \frac{y_{CO} \, y_{H_2}^3}{y_{CH_4} \, y_{H_2O}} = 4 \frac{w(3w + 4x)^3}{(1 - x - w)(5 - 2x - w)(6 + 2w + 2x)^2} = 0.41$$

$$\left(K_P\right)_2 = P^2 \frac{y_{CO_2} \, y_{H_2}^4}{y_{CH_4} \, y_{H_2O}^2} = 4 \frac{x(3w+4x)^4}{(1-x-w)(5-2x-w)^2(6+2w+2x)^2} = 1.09$$

These two equations are solved numerically for w and x using a suitable method. In this case, the

solutions were generated using the POLYMATH software. The solutions thus found are:

$$w = 0.18 \quad \text{and} \quad x = 0.60$$

The final values on the mole balance table can then be calculated by substitution:

Species	Mole fraction	Moles
CH_4	0.029	0.22
H_2O	0.479	3.62
CO	0.024	0.18
H_2	0.389	2.94
CO_2	0.079	0.60
Total	1.000	7.56

There is an increase in the total number of moles on reaction.

Solution to problem 2.7

The first step is to calculate an expression for the equilibrium constant. At a temperature of 298 K we can write:

$$\frac{-\Delta G^0_{R,298}}{T} = R_g \ln K_{298}$$

Substitute:

$$\frac{-134,300}{298.15} = 8.314 \ln K_{298}$$

Solving the equation gives: $K_{298} = 2.954 \times 10^{-24}$ or $\ln(K_{298}) = -54.18$. The temperature dependence of K is given by:

$$\frac{\partial(\ln K)}{\partial T} = \frac{\Delta H^0_R}{R_g T^2}$$

The temperature dependence of the enthalpy of reaction must be determined. The relationship is:

$$\frac{\partial\left(\Delta H^0_R\right)}{\partial T} = \Delta C_P$$

The solid heat capacities are given. The heat capacity of CO_2 is obtained from the appendix.

$$\left(C_P\right)_{CO_2} = 22.22 + 5.97 \times 10^{-2} T - 3.459 \times 10^{-5} T^2 + 7.475 \times 10^{-9} T^3 \, \frac{J}{mol \cdot K}$$

The difference is:

$$\Delta C_P = \left(C_P\right)_{CO_2} + \left(C_P\right)_{CaO} - \left(C_P\right)_{CaCO_3}$$

Substitute the numbers:

$$\Delta C_P = -18.24 + 3.021 \times 10^{-2} T - 3.459 \times 10^{-5} T^2 + 7.475 \times 10^{-9} T^3 + \frac{8.35 \times 10^5}{T^2} \, \frac{J}{mol \cdot K}$$

Substitute into:

$$\int_{298}^{T} d\left(\Delta H_R^0\right) = \int_{298}^{T} \Delta C_P \, dT$$

Substitute, solve and simplify:

$$\left(\Delta H_R^0\right) = 1.879 \times 10^5 - 18.24T + 1.511 \times 10^{-2} T^2 - 1.165 \times 10^{-5} T^3 + 1.869 \times 10^{-9} T^4 - \frac{8.35 \times 10^5}{T} \frac{J}{mol}$$

We must substitute again into the expression:

$$\left(\ln K\right) = \left(\ln K\right)_{298} + \int_{298}^{T} \frac{\Delta H_R^0}{R_g T^2} dT$$

Substitute, solve and simplify:

$$\left(\ln K\right) = 33.07 - \frac{2.26 \times 10^4}{T} - 2.194 \ln(T) + 1.817 \times 10^{-3} T - 7.01 \times 10^{-7} T^2 + 7.493 \times 10^{-11} T^3 + \frac{5.022 \times 10^4}{T^2}$$

The equilibrium constant is expressed in terms of the activities of the species at equilibrium:

$$K = \left(\frac{a_{CaO} \, a_{CO_2}}{a_{CaCO_3}}\right)$$

The activities of the solids are equal to one. At low pressure the activity of carbon dioxide can be

approximated by the partial pressure, therefore:

$$K = P_{CO_2}$$

At a temperature of 1000 K, the equilibrium constant has a value of

$$K \equiv P_{CO_2} = 3.192 \times 10^{-2} \text{ bar} \equiv 31.92 \text{ kPa}$$

When the pressure equals 1 bar, then it follows that $K = 1$. Substitute into the expression for K

and solve for the temperature. The answer is $T = 1199$ K.