

Chapter 3: Dissociation and Equilibrium

Objectives

The objectives of this Chapter are:

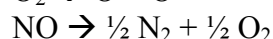
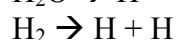
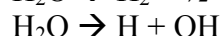
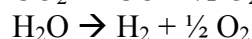
- To present the concept of dissociation.
- To introduce the concept of equilibrium constants.
- To calculate the composition of combustion products at equilibrium.
- To illustrate the practical relevance of equilibrium calculations.

Introduction

We use combustion in order to release heat and then, for example, to drive a turbine or move a piston. As engineers, we want to know the temperature that the combustion products will have. An estimate was done in Chapter 1, by using the products of complete combustion. Unfortunately, chemical equilibrium of the flame products affects the species mass fractions and hence, by virtue of the First Law, the adiabatic flame temperature will be different than that calculated by assuming complete combustion. Hence the products composition needs to be studied in detail. In this way, we can also make an estimate of the amount of major pollutants (NO and CO) released from combustion.

Dissociation

At high temperatures, the main products of combustion will decompose or *dissociate* into other species. For example, complete combustion of hydrocarbons with air gives CO₂, H₂O, N₂ (and O₂ if lean) as products. But dissociation of these and reactions between the resultant species from the dissociation may lead to many other species, for example O, H, OH, N, NO, and others. Important dissociation reactions are:



and we will use some of these to introduce the concept of equilibrium later. Dissociation of a molecule occurs at high temperatures because it is only then that significant numbers of the molecules have enough kinetic energy during a collision to break one or more internal bonds. At typical combustion temperatures, dissociation affects mostly CO₂ and H₂O, although other species will also be affected at higher temperatures. The presence of CO and H₂ in the products means that oxidation is not complete and hence that the final temperature is less than the adiabatic flame temperature calculated in Chapter 1 based on the products of complete combustion.

Chemical equilibrium

Description of the concept

Consider an adiabatic closed box filled with CO and O₂ in stoichiometric proportion. No other species are present initially. As the reaction proceeds, more and more CO₂ will appear. Experiment, however, shows that the reaction stops before all the CO and O₂ disappears, because dissociation of CO₂ (back towards O₂ and CO) begins. Hence there is a point where reactants and products coexist in equilibrium and their concentrations do not change any more. In the language of Chemical Kinetics, equilibrium is defined as the state where $w_i=0$ for all species i .

In the language of Thermodynamics, chemical equilibrium is a Second-Law concept. For the system above, the equilibrium point will be the one that gives the maximum entropy of the whole mixture. For constant pressure and temperature systems, often seen in practice, a slightly different approach, based on equilibrium constants, is easier. This is the main topic of this Chapter.

Equilibrium constants

Consider a fixed-mass isothermal, constant pressure system with many species. The criterion for equilibrium is

$$dG_{mix}=0 \text{ at constant } P, T \text{ and mass} \quad (3.1)$$

with $G=H-TS$, the *Gibbs free energy* or *Gibbs function*. For a mixture of N species containing n_i kmols of each,

$$G_{mix} = \sum_{i=1}^N n_i \bar{g}_i \quad (3.2)$$

with

$$\bar{g}_i = \bar{g}_i^0 + R^0 T \ln(P_i / P^0) \quad (3.3)$$

\bar{g}_i^0 is the molar Gibbs function at the *standard state* P^0 , usually taken as 1bar. Hence \bar{g}_i^0 is independent of pressure but depends on the temperature and is known for each species i . P_i is the partial pressure.

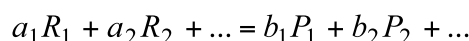
Using Eqs. (3.2) and (3.3) in (3.1), the condition for equilibrium of the mixture becomes

$$d \sum_{i=1}^N n_i \bar{g}_i = 0 \Leftrightarrow \sum_{i=1}^N dn_i [\bar{g}_i^0 + R^0 T \ln(P_i / P^0)] + \sum_{i=1}^N n_i d[\bar{g}_i^0 + R^0 T \ln(P_i / P^0)] = 0 \quad (3.4)$$

The second term is zero since the pressure and temperature are constant and hence (3.4) becomes

$$\sum_{i=1}^N dn_i [\bar{g}_i^0 + R^0 T \ln(P_i / P^0)] = 0 \quad (3.5)$$

Now, we bring in the fact that the species are engaged in a chemical reaction. Take the general equilibrium reaction



The changes dn_i in the number of moles of each species are not independent. They are directly proportional to the species stoichiometric coefficient in the reaction, or

$$dn_{R1} = -(\omega V) a_1, \quad dn_{R2} = -(\omega V) a_2, \quad dn_{P1} = (\omega V) b_1, \quad dn_{P2} = (\omega V) b_2 \text{ etc.}$$

V is the volume, ω the reaction rate (in kmol/m³/s). Substituting in (3.5), we obtain

$$\begin{aligned} & (b_1 \bar{g}_{P1}^0 + b_2 \bar{g}_{P2}^0 + \dots) - (a_1 \bar{g}_{R1}^0 + a_2 \bar{g}_{R2}^0 + \dots) \\ & - R^0 T (b_1 \ln(P_{P1} / P^0) + b_2 \ln(P_{P2} / P^0) + \dots - a_1 \ln(P_{R1} / P^0) - a_2 \ln(P_{R2} / P^0)) \\ & \Leftrightarrow -\frac{\Delta G^0}{R^0 T} = \ln \left[\frac{(P_{P1} / P^0)^{b_1} (P_{P2} / P^0)^{b_2} \dots}{(P_{R1} / P^0)^{a_1} (P_{R2} / P^0)^{a_2} \dots} \right] \\ & \Leftrightarrow -\frac{\Delta G^0}{R^0 T} = \ln K_p \end{aligned} \quad (3.6)$$

with the definitions

$$\Delta G^0 = (b_1 \bar{g}_{P1}^0 + b_2 \bar{g}_{P2}^0 + \dots) - (a_1 \bar{g}_{R1}^0 + a_2 \bar{g}_{R2}^0 + \dots)$$

and

$$K_p = \frac{(P_{P1} / P^0)^{b_1} (P_{P2} / P^0)^{b_2} \dots}{(P_{R1} / P^0)^{a_1} (P_{R2} / P^0)^{a_2} \dots} \quad (3.7)$$

The quantity K_p is called the *equilibrium constant* for the particular reaction. So the mixture will be in equilibrium if the partial pressures obey Eq. (3.7).

Features of K_p

From Eq. (3.6), since the standard Gibbs functions are a function of temperature only, the equilibrium constant K_p is also a function of temperature only (given a choice of P^0). Usually, P^0 is 1 bar (e.g. Thermofluids Tables) but 1 atm is also used in some books. It is tabulated for various reactions (not only for dissociation reactions). Sometimes, K_p is calculated directly from tabulated values of the Gibbs function through Eq. (3.6). Note that an *exactly* equivalent definition of the equilibrium constant is

$$K'_p = \frac{(P_{P1})^{b_1} (P_{P2})^{b_2} \dots}{(P_{R1})^{a_1} (P_{R2})^{a_2} \dots}$$

i.e. without normalizing the partial pressures by the standard pressure P^0 (1 bar). This form is easier to remember than Eq. (3.7), but it is K_p from Eq. (3.7) that is tabulated. Note that the equilibrium constant depends on the way the reaction is written (i.e. “products” appear in the numerator, “reactants” in the denominator).



K_p and the reaction rates

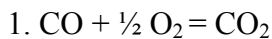
If a reaction is in equilibrium, its forward and backward rates must be the same. Hence the equilibrium constant can relate the reaction rate constants of the forward and backward reactions. For example: if the dissociation reaction $O_2 = 2O$ is in equilibrium, we have that $k_f[O_2] = k_b[O]^2$, and hence $[O]^2/[O_2] = k_f/k_b$. If we now express the concentrations in terms of mole fractions, we have that

$$\begin{aligned} [O]^2/[O_2] &= k_f/k_b && \Leftrightarrow (X_O P/R^0 T)^2 / (X_{O_2} P/R^0 T) = k_f/k_b \\ &&& \Leftrightarrow P_O^2/P_{O_2} = R^0 T \ k_f/k_b \\ &&& \Leftrightarrow (P_O/P^0)^2 / (P_{O_2}/P^0) P^0 = R^0 T \ k_f/k_b \\ &&& \Leftrightarrow K_p = R^0 T/P^0 \ k_f/k_b \end{aligned}$$

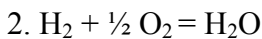


Since K_p is a known function of temperature (e.g. from Tables), so is k_f/k_b . This analysis supplies the necessary rates in our NO mechanism (Chapter 2, Eq. 2.10) by knowledge of the equilibrium constant of the O_2 dissociation reaction.

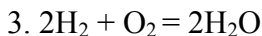
Examples of K_p for some reactions



$$\begin{aligned} K'_p &= P_{CO_2} / [(P_{CO}) (P_{O_2})^{1/2}] \\ K_p &= (P_{CO_2}/P^0) / [(P_{CO}/P^0) (P_{O_2}/P^0)^{1/2}] \\ \text{At 2000K, } \ln(K_p) &= 6.634 \text{ (Tables, Reaction 7).} \end{aligned}$$



$$\begin{aligned} K'_p &= P_{H_2O} / [(P_{H_2}) (P_{O_2})^{1/2}] \\ K_p &= (P_{H_2O}/P^0) / [(P_{H_2}/P^0) (P_{O_2}/P^0)^{1/2}] \\ \text{At 2000K, } \ln(K_p) &= 8.145 \text{ (Tables, Reaction 5).} \end{aligned}$$



$$\begin{aligned} K'_p &= (P_{H_2O})^2 / [(P_{H_2})^2 (P_{O_2})] \\ K_p &= (P_{H_2O}/P^0)^2 / [(P_{H_2}/P^0)^2 (P_{O_2}/P^0)] = (K_p \text{ of ex. above})^2 \end{aligned}$$

Further discussion and comments

Depending on the temperature and pressure, some dissociation reactions will advance more than others. For example, dissociation of H_2O into H_2 and O_2 is more pronounced than the dissociation of H_2O into H_2 and OH , as can be seen by comparing the equilibrium constants for reactions (5) and (6) from the Thermochemical Data Book. If conditions change, the equilibrium point will shift in a way so as to minimize the change. This is the *principle of Le Châtelier*. For example, the reaction $CO + \frac{1}{2} O_2 = CO_2$ will shift to the right (less dissociation, fewer moles) if the pressure is increased. It will shift to the left if the temperature is increased (towards the endothermic direction). This principle allows us to predict qualitatively the direction a system will move to reach a new equilibrium if the pressure or temperature changes.

Usage

We have managed to produce algebraic relations between the species partial pressures, and hence mole fractions, at the equilibrium point. Hence, if we know (or assume) which reaction is to be equilibrated, Eq. (3.7) provides a relation between mole fractions. This, together with atom balances, allows the calculation of combustion products (see Examples 3-1 and 3-2). For rich

combustion, we use the equilibrium of the water-gas shift reaction to determine the relative amounts of CO and H₂ in the products. For lean combustion, a larger number of possibilities arise. In progressive order of appearance as the temperature increases, we get dissociation of CO₂, dissociation of H₂O into H₂ and O₂, dissociation of H₂O into H₂ and OH, and then the dissociation of H₂ and O₂ into their respective atoms.

Refinement of adiabatic flame temperature calculation

We have seen that dissociation will shift the products composition towards the reactants side, for example some CO and H₂ will be present. This means that not all of the heat of combustion of the fuel can be utilised and hence the flame temperature will be lower than our estimates in Chapter 1. We cannot calculate the proper adiabatic flame temperature with the methods used in Chapter 1 because the Heat of Combustion is the heat released when the products have not dissociated. A more complete method is outside the purposes of this course and numerical methods are necessary to find simultaneously the temperature and composition, satisfying both the First Law and the equilibrium conditions. See “Internet-based Learning” for an example of a computer code that does exactly that.

Are combustion products in real life in equilibrium?

Not very often, but it could happen in long residence-time furnaces of very high temperatures. The reason is that usually it takes significant amount of time to establish full equilibrium and it is not too often that the fluid is left at high temperature conditions for a long time. (Why would an engineer want to do that? Once combustion has occurred, the reasonable thing to do is to use the heat of the products as quickly as possible!) One exemption is glass and cement kilns, where very intense heating rates are needed for a long time to melt the solids to be processed.

In most engines (internal-combustion, gas turbines), the products are “frozen” at some stage before full equilibrium is reached because the temperature or pressure decreases quickly after combustion has occurred. However, for many flames the equilibrium composition is a good approximation of the final products and hence it must be studied. For example, the CO emitted from engines as a function of equivalence ratio is well represented by the equilibrium CO of the corresponding flame. See “Internet-based Learning” for more details.

Summary of main points

- The dissociation of combustion products leads to a lowering of the flame temperature.
- Dissociation and other reactions can be in equilibrium. This state is governed by Thermodynamics and is described by the concept of equilibrium constants (Eq. 3.7). These depend on the reaction, the way the reaction is written, and on the temperature.
- The principle of Le Châtelier can be used to predict qualitatively the direction the system will move once the conditions (e.g. pressure or temperature) change.
- Employing equilibrium constants and atom conservation, we can calculate the equilibrium composition of the products of combustion.

Suggested reading

Turns:

Ch. 2 (Equilibrium)

Glassman:

Ch. 1 (pp. 8-20)

Worked examples

Example 3-1. Calculate the equilibrium mole fraction of NO in atmospheric air at 2000K and 1bar.

The reaction is $a_1 \text{O}_2 + a_2 \text{N}_2 = b_1 \text{NO} + b_2 \text{O}_2 + b_3 \text{N}_2$. We want to find the products composition, i.e. b_1, b_2, b_3 . Then, we can use them to express the composition in terms of mole fractions. The solution sequence follows these steps:

Step 1: Identify the reactants.

Since the l.h.s. is atmospheric air, we can take $a_1=0.21$ and $a_2=0.79$.

Step 2: Write down atom conservation equations.

For O: $2a_1 = 2b_2 + b_1$

For N: $2a_2 = 2b_3 + b_1$

Step 3: Identify the equilibrium reaction.

In this case, NO appears in the equilibrium reaction $2\text{NO}=\text{N}_2+\text{O}_2$ (Tables, Reaction 4).

Step 4: Write down equilibrium constants.

Let the total number of kmols in the products be $n = b_1 + b_2 + b_3$. The partial pressure P_i is then Pn_i/n . Hence the equilibrium constant can be written as

$$K_p = \frac{(P_{\text{O}_2}/P^0)(P_{\text{N}_2}/P^0)}{(P_{\text{NO}}/P^0)^2} = \frac{(b_2/n)(b_3/n)}{(b_1/n)^2} \frac{(P/P^0)(P/P^0)}{(P/P^0)^2} = \frac{b_2 b_3}{b_1^2}$$

From Tables, $\ln(K_p)=7.824$ (at 2000K), hence $K_p=2499.88$.

Step 5: Numerical solution

We have 3 equations (2 from atom conservation, one from equilibrium) in three unknowns (b_1, b_2 , and b_3). The system can be solved by various means. In this particular example, the atom conservation equations can be solved for b_2 and b_3 to give

$$K_p = \frac{(a_1 - b_1/2)(a_2 - b_1/2)}{b_1^2} \Leftrightarrow b_1^2 \left(K_p - \frac{1}{4} \right) + b_1 \left(\frac{a_1}{2} + \frac{a_2}{2} \right) - a_1 a_2 = 0$$

The solution is

$b_1 = 0.000805$.

$b_2 = 0.2060$ and

$b_3 = 0.7860$.

The second solution for b_1 is unrealistic, as it is negative. Hence

$X_{\text{NO}} = b_1/(b_1 + b_2 + b_3) = 0.000805$.

Notes:

- The amount of NO created is small. A good approximation in most combustion problems to treat NO as a tracer, without disturbing the major species mole fractions.
- In Step 3, the reaction has to be written in the convention of the Tables: to the right are the species with +ve sign in the Tables, to the left the species with -ve sign.
- We could have added more species (e.g. O) to the right. Then, we would need an extra equilibrium equation, e.g. $2\text{O}=\text{O}_2$. The system of equations would be more complicated to solve, but still closed.
- In this example, there is no pressure effect, as the number of moles in the reactants is equal to the number of moles in the products of the equilibrium reaction.

Example 3-2. Calculate the equilibrium composition of methane combustion at $\phi=1.25$, 1600K and 10 bar, assuming that the only species present are CO_2 , CO , H_2 , H_2O , N_2 .

This is an example of rich combustion and hence it makes sense to assume no oxygen in the products list. The combustion reaction is

$\text{CH}_4 + \frac{2}{\phi}(\text{O}_2 + \frac{0.79}{0.21}\text{N}_2) \rightarrow b_1\text{CO}_2 + b_2\text{CO} + b_3\text{H}_2\text{O} + b_4\text{H}_2 + b_5\text{N}_2$, where we have used the form given in Eq. (1.7). The atom conservation equations become:

$$\text{For O: } 4/\phi = 2b_1 + b_2 + b_3$$

$$\text{For C: } 1 = b_1 + b_2$$

$$\text{For H: } 4 = 2b_3 + 2b_4$$

$$\text{For N: } \frac{2 \cdot 0.79}{\phi \cdot 0.21} = b_5$$

We have five unknowns and four equations, so we need one equilibrium reaction. As this is rich combustion and the products are at low temperature, we take the water gas shift reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ (Reaction 8 in Tables). Hence

$$K_p = \frac{(P_{\text{CO}_2}/P^0)(P_{\text{H}_2}/P^0)}{(P_{\text{CO}}/P^0)(P_{\text{H}_2\text{O}}/P^0)} = \frac{(b_1/n)(b_4/n)}{(b_2/n)(b_3/n)} \frac{(P/P^0)(P/P^0)}{(P/P^0)(P/P^0)} = \frac{b_1 b_4}{b_2 b_3}$$

From Tables, $\ln(K_p) = -1.091$ (at 1600K), hence $K_p = 0.33588$. Algebraic manipulation (relatively tough, hence left as an exercise!) results in a quadratic equation for one of the unknowns. The final solutions are:

$$b_1 = 0.58494$$

$$b_2 = 0.41506$$

$$b_3 = 1.61506$$

$$b_4 = 0.38492$$

$$b_5 = 6.01905$$

Using $n = b_1 + b_2 + b_3 + b_4 + b_5$, the mole fractions ($X_i = b_i/n$) can be calculated:

$$X_{\text{CO}_2} = 0.0649$$

$$X_{\text{CO}} = 0.0460$$

$$X_{\text{H}_2\text{O}} = 0.1791$$

$$X_{\text{H}_2} = 0.0427$$

$$X_{\text{N}_2} = 0.6674$$

Notes:

- The pressure does not enter the calculation because, as in Example 3-1, there is an equal number of kmols in the reactants and in the products of the equilibrium reaction.
- It may be that both solutions of the quadratic are positive (and hence we cannot tell which one to reject). A discrepancy, however, will surface somehow down the calculation, as one of the b 's will become negative. In general, equilibrium systems have unique solutions.
- The water-gas shift reaction is very important in the chemical industry. It is used in hydrogen production and in gasification processes (e.g. gaseous fuel production from coal or biomass).

Software in the DPO

In the DPO, a software package written by Dr. Lewins of the Engineering Department has been installed which calculates the degree of progress of the reactions in the ThermoFluid Tables. To use it, start Matlab and then type “gibbs”. There is extensive on-line help. Select one of the equations (e.g. CO₂ dissociation), a pressure and a temperature and examine the degree of dissociation. Change the temperature and pressure and see if the principle of Le Châtelier is satisfied. This exercise is not obligatory, but it will help you understand better the concepts of dissociation and equilibrium.

Internet-based learning

Go to <http://www.wiley.com/college/ferguson/>

This is a companion site to the book “Internal Combustion Engines” by Ferguson & Kirkpatrick, 2nd Edition, 2000. Java applets concerning calculations of equilibrium and flame temperature for various fuels can be found in this site. The following applets illustrate some of the principles discussed in this Chapter. The exercise below should not take you more than 20 minutes. This material is not examinable.

On the left side of the page, click on “Student”, then on “On-line resources for students”, then on “IC engines applets”, and then on “Adiabatic Flame Temperature”. Now select a fuel, a pressure, an equivalence ratio and set “residual mass fraction” to zero. Click “Enter”. Hence find the adiabatic flame temperature for a range of ϕ , e.g. for methane for $0.5 < \phi < 1.5$. This temperature does not assume complete combustion (as we have done in chapter 1), but uses the equilibrium composition, which is simultaneously calculated but unfortunately not shown in this applet. To see the equilibrium composition, go back, and click on “Equilibrium Combustion Solver”. Select the same pressure and fuel and for each of the previous conditions of ϕ , type-in the temperature you have just calculated to obtain the equilibrium products. Plot the CO, NO and temperature against ϕ . These curves will prove to be very useful for understanding pollution generation from combustion.

Compare the adiabatic flame temperature at full equilibrium with a calculation assuming complete combustion (Q2, Examples Paper 1) at the same conditions (fuel, ϕ , pressure, temperature). The difference is due to dissociation and equilibrium. Experiment by changing the pressure and see if the principle of Le Châtelier is satisfied.

Run the “Equilibrium Combustion Solver” applet for the conditions of Example 3-2. The very small differences you will observe are due to round-off errors in our calculation and the fact that in our example, we neglected the presence of atomic species while in the full calculation (i.e. using many equilibrium reactions) these are included.