CHAPTER 10

CHEMICAL REACTIONS AND CHEMICAL EQUILIBRIUM

10.1 Introduction

(NOTE: This chapter is incomplete; consult the hand-written notes I passed out in class.)

Chemically-reacting flows are vital to many engineering applications, including almost all aerospace and terrestrial propulsion systems, and all systems which produce power by burning fossil fuels. Solving current technological problems, such as how to reduce undesirable pollutant emission from these devices, requires an understanding of some of the chemistry occurring in these systems.

10.2 The Reaction $A + B \rightleftharpoons AB$

Consider a mixture of 2 chemically-reactive elemental species, A and B. Suppose that these can react with one another to form a molecule AB:

$$A + B \rightarrow AB$$
. (10.1)

Once an AB molecule is formed, it may break up again via

$$AB \rightarrow A + B.$$
 (10.2)

We can write a short-hand notation for these two reactions as follows:

$$A + B \rightleftharpoons AB.$$
 (10.3)

Suppose we introduce $N_{A,0}$ moles of A and $N_{B,0}$ moles of B into a container with volume V at time t=0. We allow the system to evolve with no interaction with the surroundings (isolated). As time proceeds, we find that the mole numbers change, due to formation of AB molecules. If we wait long enough, the mole numbers come to steady-state values, which we will denote N_A^* , N_B^* , and N_{AB}^* . Evidently, once steady state is reached, the rate at which AB is formed by reaction (10.1) just balances the rate at which it is destroyed by reaction (10.2).

When this condition is reached, we say the system is in *chemical equilibrium*. Depending on the nature of the chemical reaction, and also on the temperature

and pressure, chemical equilibrium may be reached in microseconds (explosions) or may take thousands of years. Determining the rate at which the reaction proceeds is the subject of chemical kinetics. However, the final state achieved at long times does not depend on kinetics, but only on the thermodynamic properties of the atoms or molecules involved.

To determine the condition for chemical equilibrium, we apply the same basic principle we have used to determine other equilibrium conditions: the system will attain the state for which the entropy is maximal, compared to all other possible states with the same total $U, V, N_{A,0}$, and $N_{B,0}$.

In our previous discussions of equilibrium, we have imagined a system divided by a partition, which can pass energy, volume, or molecules. For the present problem, the "constraint" we will relax is somewhat different. Let us imagine that we can turn a knob on the system which can (somehow) stop the reaction from occurring, or can run it in the forward direction [reaction (10.1)] or in the reverse direction [reaction (10.2)]. We will turn the knob back and forth, calculating the entropy of the system for each set of conditions, and find the state which maximizes S. This then must be the equilibrium state the system will come to when "unconstrained."

Suppose we initially set the knob so that the reaction is stopped, and the mole numbers are N_A , N_B , and N_{AB} . We now turn the knob to allow the reaction to proceed infinitesimally in the forward direction, and then reset it to stop the reaction at this new condition. We find that N_{AB} has increased by an amount dN_{AB} . Since the only way to increase N_{AB} is by consuming an equivalent amount of A and B atoms, we must have that

$$dN_A = -dN_{AB} (10.4)$$

$$dN_B = -dN_{AB}. (10.5)$$

How much has $S(U, V, N_A, N_B, N_{AB})$ changed? Using the chain rule,

$$dS = \left(\frac{\partial S}{\partial N_A}\right)_{U,V,N_B,N_{AB}} dN_A + \left(\frac{\partial S}{\partial N_B}\right)_{U,V,N_A,N_{AB}} dN_B + \left(\frac{\partial S}{\partial N_{AB}}\right)_{U,V,N_A,N_B} dN_{AB}.$$
(10.6)

We know that the chemical potential is defined by

$$\left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_i} = -\frac{\mu_i}{T}.$$
(10.7)

Therefore, if we also use equations (10.4) and (10.5) to substitute for dN_A and dN_B , Eq. (10.6) becomes

$$dS = \frac{1}{T} \left[\mu_A + \mu_B - \mu_{AB} \right] dN_{AB}. \tag{10.8}$$

At the equilibrium state, S will be maximal with respect to N_{AB} , and therefore dS = 0. The chemical equilibrium condition for this reaction is then

$$\mu_{AB} - \mu_A - \mu_B = 0. \tag{10.9}$$

This equilibrium condition is very general, and applies whatever type of solution the species A, B, and AB form. For example, it could be a liquid or even a solid solution. By using the form for the chemical potential appropriate for the phase of the mixture, we can develop an explicit condition for equilibrium in terms of experimental parameters, such as the mole numbers, temperature, and pressure.

It is worth noting that, although we imagined an isolated system to derive Eq. (10.9), now that we have this equation we no longer need to restrict our attention only to isolated systems. The condition expressed by Eq. (10.9) must be satisfied at the equilibrium state, no matter how this state was reached. It could have been reached in an isolated system (constant U and V) or, for example, by allowing the reaction to proceed at constant T and T0, adding or removing heat as necessary to keep T1 constant, and allowing the volume to change to keep T2 constant.

10.3 Reactions in Ideal Gases

If the mixture of A, B, and AB is an ideal gas mixture, then we have already derived the form of the equation for the chemical potential. In this case, recall that

$$\mu_i = \hat{g}(T, P_i) = \hat{g}^0(T) - \hat{R}T \ln\left(\frac{P_i}{P_0}\right)$$
 (10.10)

That is, the chemical potential of species i in the mixture is the molar Gibbs free energy (of the pure species i) evaluated at the partial pressure P_i .

Substituting this expression into Eq. (10.9), we have

$$\ln\left[\frac{(P_A/P_0)(P_B/P_0)}{(P_{AB}/P_0)}\right] = -\frac{\hat{g}_A^0 B(T) - \hat{g}_A^0(T) - \hat{g}_B^0(T)}{\hat{R}T}$$
(10.11)

or

$$\frac{P_A P_B}{P_{AB}} = P_0 e^{-\Delta G^0(T)/\hat{R}T},\tag{10.12}$$

where

$$\Delta G^{0}(T) = \hat{g}_{AB}^{0}(T) - \hat{g}_{A}^{0}(T) - \hat{g}_{B}^{0}(T)$$
(10.13)

is the *standard free energy of reaction* for this reaction. We can re-write this equation in terms of mole numbers as

$$\frac{N_A^* N_B^*}{N_{AB}^*} = \left(\frac{P_0 V}{\hat{R}T}\right) e^{-\Delta G^0(T)/RT}.$$
 (10.14)

This equation provides us with one equation for the 3 unknowns N_A^* , N_B^* , and N_{AB}^* . The remaining 2 equations come from the *atom conservation* conditions:

$$N_A^* + N_{AB}^* = N_{A,0} (10.15)$$

and

$$N_B^* + N_{AB}^* = N_{B,0}. (10.16)$$

These equations simply state that the number of moles of A atoms (independent of whether they appear as free A atoms or in AB molecules) is the same as initially placed in the container, and similarly for B. These three equations together allow solving uniquely for the values of N_A^* , N_B^* , and N_{AB}^* at equilibrium.

10.4 A General Reaction

The above results are easily generalized to any chemical reaction. Let's consider a reaction such as

$$2H_2 + O_2 \rightleftharpoons 2H_2O. \tag{10.17}$$

We may write this reaction (or any other one) symbolically as

$$\sum_{j} \nu_j \mathbf{A}_j = 0, \tag{10.18}$$

where A_j stands for the chemical symbol of the jth species (e.g., " H_2 ", " O_2 ", or " H_2O ") and ν_j is the *stoichiometric coefficient* for species j. The stoichiometric coefficient is defined to be positive for products (H_2O) and negative for reactants (H_2 and O_2). Therefore, for this reaction

$$\nu(H_2) = -2 \tag{10.19}$$

$$\nu(O_2) = -1 \tag{10.20}$$

$$\nu(H_2O) = +2$$
 (10.21)

To find the equilibrium condition for a general reaction such as reaction (10.18), we again maximize the entropy at fixed U and V as we did above. For

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the general case, the stoichiometric relation among the mole numbers as the reaction proceeds forward or backward is:

$$\frac{dN_j}{\nu_j} = d\tilde{N}. (10.22)$$

That is, each mole number changes by an amount equal to ν_j multiplied by the change in a species-independent "extent of reaction" variable \tilde{N} . Note that for the simple A + B \rightleftharpoons AB reaction considered above, Eq. (10.22) reduces to equations (10.4) and (10.5).

The condition that S is maximal with respect to \tilde{N} then leads to

$$\sum_{j=1}^{r} \mu_j \nu_j = 0. (10.23)$$

This is the general form of the condition for chemical equilibrium for a single reaction. (Note that ν_j is non-zero only for those species in the mixture which participate in the reaction.)

For ideal gases, we can again substitute in the known form of the chemical potential. This leads us to the generalization of Eq. (10.12):

$$\prod_{j=1}^{r} \left(\frac{P_j}{P_0}\right)^{\nu_j} = e^{-\Delta G^0(T)/\hat{R}T},\tag{10.24}$$

where

$$\Delta G^{0}(T) = \sum_{j=1}^{r} \hat{g}_{j}^{0}(T)\nu_{j}$$
 (10.25)

is again the standard free energy of reaction. Equation (10.24) is known as the law of mass action.

Since the right-hand side of Eq. (10.24) is a function only of temperature, it is convenient to give it a symbol. We define the equilibrium constant $K_p(T)$ as

$$K_p(T) = e^{-\Delta G^0(T)/\hat{R}T}.$$
 (10.26)

We can write the law of mass action in terms of mole fractions, since $P_j = X_j P$. Making this substitution into Eq. (10.24), we have

$$\prod_{j=1}^{r} X_{j}^{\nu_{j}} = \left(\frac{P_{0}}{P}\right)^{\sum_{j=1}^{r} \nu_{j}} K_{p}(T).$$
 (10.27)

We can also write the law of mass action in terms of mole numbers or concentrations $C_j = N_j/V$ as follows:

$$\prod_{j=1}^{r} C_{j}^{\nu_{j}} = \left(\frac{P_{0}}{\hat{R}T}\right)^{\sum_{j=1}^{r} \nu_{j}} K_{p}(T), \tag{10.28}$$

and

$$\prod_{j=1}^{r} N_{j}^{\nu_{j}} = \left(\frac{P_{0}V}{\hat{R}T}\right)^{\sum_{j=1}^{r} \nu_{j}} K_{p}(T).$$
(10.29)

All of the forms (10.27), (10.28), and (10.29) of the law of mass action have an additional factor in front of $K_p(T)$, which arises due to the conversion from pressure to mole fraction, concentration, or mole number units. The exponent this factor is raised to is the *net* change in mole numbers as the reaction proceeds from pure reactants to pure products. For example, for the reaction $A+B \rightleftharpoons AB$, $\sum_{j=1}^r \nu_j = -1$. On the other hand, for a reaction of the type $A+B \rightleftharpoons C+D$, this sum is zero, and the factor in front of $K_p(T)$ does not appear.

Remember that P_0 is the reference pressure at which the thermodynamic properties are computed, not the actual pressure of the problem. It might seem odd that P_0 appears in the law of mass action, since the equilibrium composition can't depend on our choice of the reference pressure. In fact, it does not, since $\Delta G^0(T)$ depends on P_0 in just such a way that it cancels the P_0 factor multiplying $K_p(T)$. (Recall that $\hat{g}(T, P)$ has an $\hat{R}T \ln P$ term in it.)

If the reference pressure $P_0 = 1$ atm, then

$$\frac{P_0}{\hat{R}T} = 40.62 \left(\frac{300}{T}\right) \quad \text{moles/m}^3.$$
 (10.30)

Let us see how this works in practice by looking at a simple example.

Example 10.1 Suppose oxygen gas (O_2) is heated to 2500 K. We wish to know the mole fraction of atomic oxygen O which forms at chemical equilibrium.

The reaction forming O is

$$O_2 \rightleftharpoons 2O.$$
 (10.31)

Therefore,

$$\Delta G^0 = 2\hat{q}(O) - \hat{q}(O_2). \tag{10.32}$$

We can look up the molar Gibbs functions in a table such as the JANAF tables, or calculate them from polynomial fits (using $\hat{g} = \hat{h} - T\hat{s}$). Doing this, we find that for T = 2500 K,

$$\hat{q}(O) = -219.13 \text{ kJ/mole}$$
 (10.33)

$$\hat{g}(O_2) = -614.67 \text{ kJ/mole.}$$
 (10.34)

Therefore,

$$\Delta G^0(2500) = 176.41 \text{ kJ/mole}$$
 (10.35)

and

$$K_{\nu}(2500) = 2.06 \times 10^{-4}.$$
 (10.36)

The law of mass action then becomes

$$\frac{X_{\rm O}^2}{X_{\rm O_2}} = \left(\frac{P_0}{P}\right)^{+1} K_p(T). \tag{10.37}$$

The atom conservation condition, expressed in mole fraction units, is simply

$$X_{\rm O} + X_{\rm O_2} = 1. (10.38)$$

Therefore,

$$\frac{{X_{\rm O}}^2}{1 - {X_{\rm O}}} = 2.06 \times 10^{-4} \left(\frac{P_0}{P}\right). \tag{10.39}$$

We can solve this simple quadratic equation for the atomic oxygen mole fraction if the pressure is specified. As P increases, the atomic oxygen mole fraction decreases. For example, at P=1 atm at 2500 K, we have that $X_{\rm O}=0.0142$. But at P=0.01 atm, $X_{\rm O}=0.133$.

The pressure dependence seen in Example 10.1 occurs because the mole numbers change by +1 in this reaction. A reaction of the type $A + B \rightleftharpoons C + D$, in which the mole numbers do not change, would have no pressure dependence to the equilibrium mole fractions, since the term (P_0/P) in the law of mass action would not appear (the exponent would be zero).

This is one example of *Le Chatlier's Principle*, which states that when a change is imposed on a system (such as increasing the pressure), the system will respond in such a way to try to counteract the change. In this case, as the pressure is increased, some O atoms recombine to O_2 in order to reduce the total number of moles, and therefore reduce the system pressure compared to what it would be if the composition remained constant.