

# 7

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## Chemical Reactions

*Better things for better living, through chemistry*

DuPont Co. slogan

The changes of thermodynamic quantities in chemical reactions are calculated from tabulated values of absolute entropies and heat capacities. However, enthalpies and free energies of formation reactions are used. Such quantities can be measured in calorimetric experiments, such as those using the bomb calorimeter, which is used for combustion reactions. Alternatively, generic bond dissociation energies or group additivity relations may be employed to estimate thermodynamic quantities. At equilibrium, the Gibbs free energy change of a reaction is zero, allowing equilibrium constants to be calculated from standard free-energy changes. Because the free energies of condensed phases are approximately pressure independent, these species do not enter into equilibrium-constant expressions, except at high pressure. The Gibbs phase rule specifies the number of degrees of freedom of a system at equilibrium. Calculations of equilibrium concentrations are most systematically performed using a single variable, the extent of reaction, to express the concentrations of reactants and products at equilibrium. The enthalpy change of a reaction is used to convert its equilibrium constant from one temperature to another.

## 7.1 Nomenclature

We write a general chemical reaction as



Therefore, a chemical reaction is a process in which the initial state is the reactants and the final state is the products of the reaction. Reactions may involve changes in temperature and pressure. However, for simplicity of calculation, we usually consider the reactants and products to be at the same  $T$  and  $P$ , and correct to the actual  $T$  and  $P$  in a separate step, using the energy released in the reaction. As discussed in [Chapter 3](#), the standard pressure chosen for compilation of thermodynamic data is  $1.0 \text{ bar} \equiv 10^5 \text{ Pa}$ ,<sup>1</sup> and it is designated by a degree sign, so we can write a standard reaction as



In terms of individual reagents, a reaction may be written as



where  $a$ ,  $b$ ,  $c$ , and  $d$  are the reagent numbers of the reaction, usually written as integer numbers. (Sometimes, fractional values are used.) Because, in regard to conservation of mass, atomic species, and energy, a chemical reaction implies equality of reactants and products, we choose to convert the arrow (“is converted to”) in this reaction into an equal sign. The reactants are then brought over to the product side of the equality to give

$$0 = \sum_i \nu_i A_i \quad (4)$$

where  $i$  ranges over reactants and products and  $\nu_i$  is the *stoichiometric coefficient*, positive for products and negative for reactants.

During a reaction, the change in the amount of any reactant or product is proportional to its stoichiometric coefficient, and a single variable is sufficient to specify the production of products and consumption of reactants. This variable,  $\xi$ , is the number of moles of product with unit stoichiometric coefficient that is formed and is called the *extent of the reaction*. The change in the number of moles of any reactant or product is given by

$$\Delta n_i = n_i - n_i(t=0) = \nu_i \xi \quad (5)$$

The change of a property in a reaction is that property of the products minus that property of the reactants. The symbol  $\Delta_{rxn}$  indicates the change in the property when molar amounts of reactants indicated by their stoichiometric coefficients form molar amounts of products indicated by their stoichiometric coefficients. It is important to always give the balanced equation of the reaction being considered, including the phase of each reactant and product if these are not

evident. If the reagents and products are noninteracting (e.g., ideal gases), the change of any extensive property can be calculated from molar properties of the individual reactants and products. For example, for the volume change on reaction

$$\Delta_{rxn}V = cV_{m,c} + dV_{m,d} + \cdots - (aV_{m,a} + bV_{m,b} + \cdots) = \sum_i \nu_i V_{m,i} \quad (6)$$

At temperature  $T$  and the standard pressure, we have

$$\Delta_{rxn}V^\circ(T) = \sum_i \nu_i V_{m,i}^\circ(T) \quad (7)$$

which is called the standard volume change of the reaction (the volume change at the standard pressure).

## 7.2 Thermochemistry

Using the procedure of Eq. (7), the entropy change of chemical reaction (2) can be written as

$$\Delta_{rxn}S(T) = \sum_i \nu_i S_{m,i}(T) \quad (8)$$

This is a useful equation because the third law sets the zero of entropy for every pure substance and thus permits calculations of absolute entropies at temperature  $T$  by Eq. (5) of [Chapter 4](#).

Equations similar to Eq. (8) can also be written for  $U$ ,  $H$ ,  $A$  and  $G$ . For example,

$$\Delta_{rxn}H(T) = \sum_i \nu_i H_{m,i}(T) \quad (9)$$

and

$$\Delta_{rxn}G(T) = \sum_i \nu_i G_{m,i}(T) \quad (10)$$

An alternative form for Eq. (10), which is also applicable for systems in which there exist interactions between species, is from Eq. (11) of [Chapter 6](#):

$$\Delta_{rxn}G(T) = \sum_i \nu_i \mu_i(T) \quad (11)$$

Equations like Eqs. (9)–(11) are of little value for calculations, however, because we have no way of determining absolute values for thermodynamic functions that have an energy component. Even though absolute values of energy can be defined by using Einstein's  $E = mc^2$  to convert mass into energy, there are both theoretical and practical difficulties in dealing with absolute energy-like quantities: theoretical because the definitions of potential and kinetic energies require the choice of zero-energy position and velocity reference; practical

because the Einstein energy or even the total electrostatic energies of molecules are so huge that their uncertainties mask chemically interesting energies. We can circumvent this difficulty by arbitrarily choosing a reference state and measuring changes in thermodynamic properties with respect to this reference state. Taking the enthalpy change as an example, we have, according to Fig. 1,

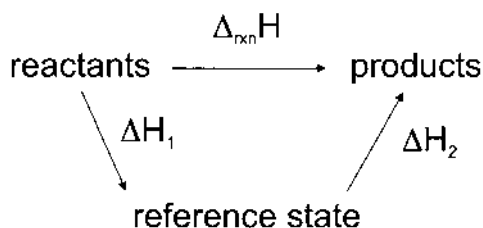
$$\Delta_{rxn}H = \Delta H_1 + \Delta H_2 \quad (12)$$

Equation (12) follows from enthalpy being a state function, which means that its change is independent of the path taken in going from reactants to products. The enthalpy change of a reaction is known as the *heat of the reaction*, and Eq. (12) is an example of *Hess' law*, which is the procedure of calculating the change of a thermodynamic property of a process by using an alternative path to go from the initial to the final state of the process. At temperature  $T$  and the standard pressure, Eq. (12) becomes

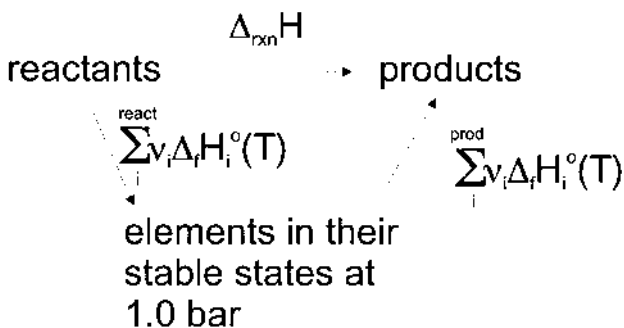
$$\Delta_{rxn}H^\circ(T) = \Delta H_1^\circ(T) + \Delta H_2^\circ(T) \quad (13)$$

where  $\Delta_{rxn}H^\circ(T)$  is the standard enthalpy change or standard heat of the reaction at temperature  $T$ .

In choosing a reference state, we are allowed to make a choice for each element, because elements cannot be transformed into each other by chemical means. The choice usually made for the reference state of an element is the form in which it is stable at temperature  $T$  and the standard pressure = 1.0 bar. For example, at most temperatures, for  $O_2$  this would be gaseous diatomic molecules; for iron, it would be the solid metal, and for bromine, it would be the diatomic in the liquid state below  $59^\circ C$  and in the gaseous state above  $59^\circ C$ . We call the standard enthalpy change of the reaction in which 1 mol of compound  $i$  is formed from its component elements in their reference states the *heat of formation* of compound  $i$ ,  $\Delta_f H_i^\circ(T)$ . The heat of reaction is related to heats of formation as



**Figure 1** Hess' law.



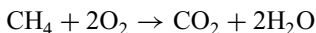
**Figure 2** Using heats of formation.

shown in Fig. 2. (Note that  $v_i$  for the reactants are negative numbers.) Because enthalpy is a state function,

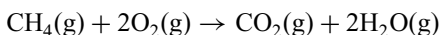
$$\Delta_{rxn}H^\circ(T) = \sum_i v_i \Delta_f H_i^\circ(T) \quad (14)$$

where the sum extends over both reactants and products. In [Appendix B](#), heats of formation are tabulated for a variety of compounds at 298 K, which allows the heat of reaction to be calculated for many reactions at 298 K by Eq. (14). The entries for the heats of formations of elements in this table are, of course, zero, because the reaction to form them from the elements are null reactions (reactions in which nothing happens). Note the efficiency of tabulating thermodynamic data in this form. For  $n$  compounds, each of which can react with any other, roughly  $n^2$  heats of reaction can be calculated. Care must be taken in using the data that values are chosen for compounds in the state of interest. This is illustrated in Example 1.

**Example 1.** Calculate  $\Delta_{rxn}H^\circ(298.15 \text{ K})$  of the reaction

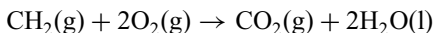


*Solution:* The solution depends on whether the water is formed in the liquid or gaseous state. Gaseous water will result if water is formed with a partial pressure less than its vapor pressure of 23.7 torr at 298.15 K. In this case,



$$\begin{aligned} \Delta_{rxn}H^\circ(298.15) &= 2(-241.8) + (-393.5) - [(-74.8) + 2(0)] \\ &= -802.3 \text{ kJ/mol} \end{aligned}$$

“mol” in the result implies that it is for the reaction *as written* in molar quantities. If the water is formed in the liquid state,<sup>2</sup> we have



$$\begin{aligned}\Delta_{\text{rxn}}H^\circ(298.15) &= 2(-285.8) + (-393.5) - [(-74.8) + 2(0)] \\ &= -890.3 \text{ kJ/mol}\end{aligned}$$

Appendix B also includes values for  $S^\circ(298.15)$  and  $\Delta_f G^\circ(298.15)$ , from which entropies of reaction and Gibbs free energies of reactions can be calculated at 298.15 K from

$$\Delta_{\text{rxn}}S^\circ(T) = \sum_i \nu_i S_i^\circ(T) \quad (15)$$

and

$$\Delta_{\text{rxn}}G^\circ(T) = \sum_i \nu_i \Delta_f G^\circ(T) \quad (16)$$

Because absolute entropies, rather than entropies of formation, are tabulated, the entries for entropies of elements are not zero and must not be neglected in using Eq. (15).

In most tabulations of thermochemical data, such as that of Appendix B, values for the thermodynamic functions are given only at a single temperature, usually 298.15K.<sup>3</sup> In order to convert standard heats of reaction to other temperatures, temperature variations at constant pressure must be considered. From Eq. (9),

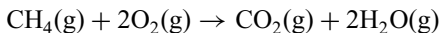
$$\left(\frac{\partial \Delta_{\text{rxn}}H^\circ}{\partial T}\right)_P = \sum_i \nu_i \left(\frac{\partial H_{m,i}^\circ}{\partial T}\right)_P = \sum_i \nu_i C_{P,m,i}^\circ \equiv \Delta_{\text{rxn}}C_P^\circ \quad (17)$$

where  $\Delta_{\text{rxn}}C_P^\circ$  is the standard heat capacity change for the reaction. Integration gives

$$\Delta_{\text{rxn}}H^\circ(T) = \Delta_{\text{rxn}}H^\circ(298.15) + \int_{298.15}^T \Delta_{\text{rxn}}C_P^\circ dT \quad (18)$$

Temperature corrections are usually not too large, due to partial cancellation of the heat capacities of the reactants and products. If the temperature of interest is not too different from 298.15 K, it is usually sufficient to use temperature-independent heat capacities, such as those obtained from Appendix B, and remove  $\Delta_{\text{rxn}}C_P^\circ$  from under the integral sign.

**Example 2.** Calculate the heat of the reaction at 50°C for



*Solution:* Since we only have to make a temperature correction over a range of 25 K, we can consider the heat capacities to be constant at the

values given in [Appendix B](#):

$$\Delta_{rxn}C_p^\circ = 37.11 + 2(33.58) - [35.31 + 2(29.36)] = 10.44 \text{ J/K mol}$$

Using the value of  $\Delta_{rxn}H^\circ(298.15)$  from Example 1,

$$\begin{aligned}\Delta_{rxn}H^\circ(323.15) &= \Delta_{rxn}H^\circ(298.15) + (25 \text{ K})\Delta_{rxn}C_p^\circ \\ &= -802.3 \frac{\text{kJ}}{\text{mol}} + 10.44 \frac{\text{J}}{\text{K mol}} (25 \text{ K}) \frac{\text{kJ}}{1000 \text{ J}} = -802.0 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

A common error is to omit the final transformation from joules to kilojoules.

Entropies can be transformed to temperatures other than 298.15 K using Eq. (17) of [Chapter 3](#):

$$\Delta_{rxn}S^\circ(T) = \Delta_{rxn}S^\circ(298.15) + \int_{298.15}^T \frac{\Delta_{rxn}C_p^\circ}{T} dT \quad (19)$$

or

$$\Delta_{rxn}S^\circ(T) = \Delta_{rxn}S^\circ(298.15) + \Delta_{rxn}C_p^\circ \ln\left(\frac{T}{298.15}\right) \quad (20)$$

if a temperature-independent  $\Delta_{rxn}C_p^\circ$  can be used.

Gibbs free energies can be calculated as

$$\Delta_{rxn}G^\circ(T) = \Delta_{rxn}H^\circ(T) - T\Delta_{rxn}S^\circ(T) \quad (21)$$

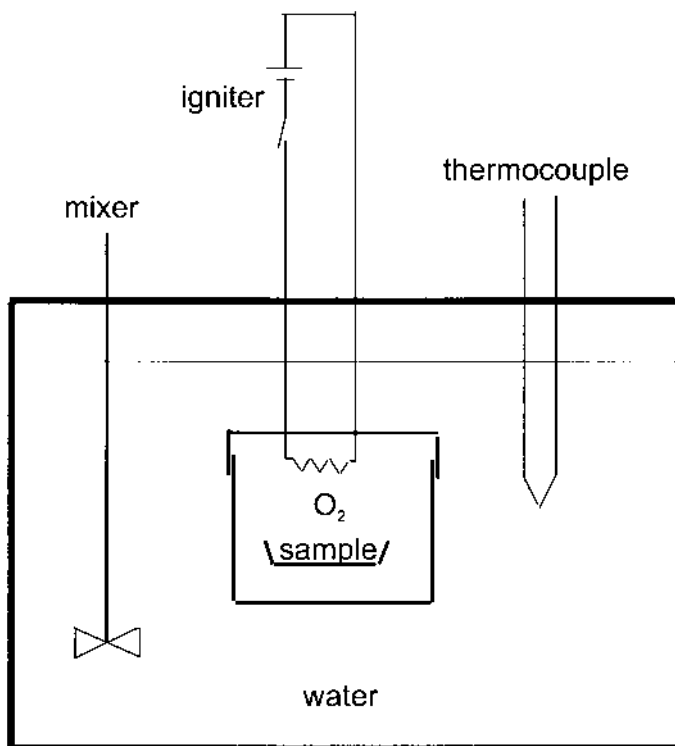
A common error is to use  $\Delta_{rxn}H^\circ(298.15)$  and  $\Delta_{rxn}S^\circ(298.15)$  in Eq. (21) for calculating  $\Delta_{rxn}G^\circ(T)$  at a temperature other than 298.15 K.

## 7.3 Calorimetry

Calorimetry is the determination of thermodynamic properties (enthalpies, free energies, heat capacities, etc.) by measuring the energy released or absorbed in a process. Usually, this is achieved by carrying out the process *adiabatically* (i.e., in a system to which negligible heat is transferred during the measurement). For systems of constant volume, no work is done, and the temperature change is directly related to the change in  $U$  of the system.

A diagram of a constant-volume adiabatic calorimeter, called a bomb calorimeter, used for measuring the  $\Delta U$  of combustion reactions is shown in [Fig. 3](#).

Adiabaticity is achieved by insulating the calorimeter and studying reactions that occur over a short period of time (because time is required for heat transfer). It is also useful to be able to control the starting time of the reaction and study reactions that go to completion, so that the extent of the reaction does not



**Figure 3** Adiabatic bomb calorimeter.

have to be experimentally determined. Combustion reactions are ideal for study in this manner. They proceed at a negligible rate, until *ignited* by an externally controlled ignition source. When initially pressurized with excess oxygen, the reaction proceeds almost instantaneously, converting hydrocarbons to CO<sub>2</sub> and H<sub>2</sub>O (which is almost entirely in the liquid state at the final temperature of the calorimeter). Sulfur is converted to SO<sub>2</sub> and nitrogen to N<sub>2</sub> (and a little nitric acid, which may have to be titrated and corrected for). The calorimetry experiment involves igniting the mixture and measuring the increase in temperature,  $\Delta T$ , of the calorimeter. Because the calorimeter is adiabatic and does no work, we can write, for an infinitesimal amount of reaction,

$$dU = 0 = U_{\text{prod+cal}}(T_i + dT) - U_{\text{react+cal}}(T_i)$$

$$= d_{\text{rxn}} U(T_i) + C dT \quad (22)$$

$$d_{\text{rxn}} U(T_i) = -C dT \quad (23)$$



where  $C$  is the heat capacity of the calorimeter and the products of the reaction. Measurements are usually performed with temperature changes small enough that heat capacities can be considered constant; thus, we can write

$$\Delta_{rxn}U = -C\Delta T \quad (24)$$

where  $\Delta_{rxn}U$  is the internal energy change of the reaction.  $C$  can be determined by using a resistor to add a known amount of energy ( $I^2Rt$ ) to the calorimeter and measuring its temperature increase, or by running the calorimeter with a measured amount of a compound of known heat of combustion. Benzoic acid is convenient for calibration.  $C$  is almost all due to the heat capacity of the metallic parts and the water of the calorimeter. In practice, the energy added for ignition and for mixing must be taken into account.

The difference between the heat (enthalpy change) of a reaction and  $\Delta_{rxn}U$  results from the work that must be done in moving the atmosphere to make room for gas that is formed in the reaction. We can write

$$\Delta_{rxn}H = \Delta_{rxn}U + \Delta_{rxn}(PV) = \Delta_{rxn}U + RT\Delta_{rxn}n_{\text{gas}} \quad (25)$$

where  $\Delta_{rxn}n_{\text{gas}}$  is the change in the number of moles of gas in the reaction.

An alternative way of determining some thermodynamic functions is by measuring the position and temperature shift of equilibrium. The relation between thermodynamics and the equilibrium of chemical reactions will be explored later in this chapter.

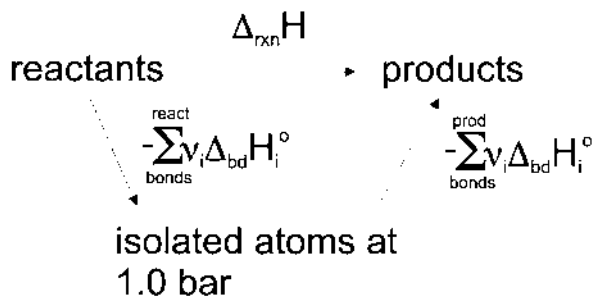
## 7.4 Estimating the Thermodynamics of Reactions

An alternative reference state from which to tabulate thermodynamic functions is that of isolated atoms. The use of this reference state is shown in Fig. 4, where  $\Delta_{\text{bd}}H_i$  is a bond dissociation enthalpy in a reactant or product molecule. (Remember that the  $\nu_i$ 's are negative for reactants.) The heat of reaction is then given by

$$\Delta_{rxn}H = - \sum_i \nu_i \Delta_{\text{bd}}H_i \quad (26)$$

This equation is for reactions involving only gaseous reactants and products. If some species are in condensed phases, appropriate heats of vaporization or sublimation must be included.

Compared to Eq. (14), the negative sign in Eq. (26) results from bond dissociation energies being enthalpies required to pull molecules apart. Bond dissociation energies are positive. Larger bond dissociation energies of product molecules than reactant molecules are characteristic of exothermic reactions (negative  $\Delta_{rxn}H$ ). The calculation indicated by Fig. 4 is as exact as that indicated

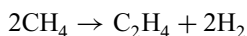


**Figure 4** Using bond dissociation energies.

by Fig. 2. However, in order to achieve comparable accuracy in calculation, bond dissociation enthalpies specific for the bonds in each particular reactant and product molecule are required. These quantities are not generally available and would require values for every bond in each molecule, a much more difficult task to measure and tabulate than just the  $\Delta H_f$  of molecules.

Equation (26) is often used with *generic bond dissociation enthalpies*, assuming that it takes the same energy to break the same type (single, double, or triple) bond between the same two atoms. With this assumption, a further simplification in tabulating thermodynamic data is achieved: The heats of a huge number of reactions can be calculated with the few quantities listed in Table 1. Unfortunately, the strength of similar bonds do vary in different molecules, and large errors can be made in using generic bond dissociation enthalpies, as illustrated in Example 3.

**Example 3.** Calculate  $\Delta_{\text{rxn}} H$  of the gaseous reaction



from heats of formation and from generic bond dissociation enthalpies.

**TABLE 1** Generic Bond Dissociation Enthalpies (kJ/mol)

H—H	436	O=O	498	C=C	615	N≡N	946
C—H	415	C—O	350	C≡N	890	N—N	159
C—C	344	C=O	725	O—H	463	N=N	418
C=C	615	C—N	292	N—H	391	C—F	441
C≡C	812	C=N	615	O—O	143	C—Cl	328

*Solution:* With heats of formation taken from [Appendix C](#),

$$\Delta_{rxn}H = 52.26 - 2(-74.81) = 201.88 \text{ kJ/mol}$$

with generic bond dissociation enthalpies,

$$\Delta_{rxn}H = 8(415) - [2(436) + 615 + 4(415)] = 173 \text{ kJ/mol}$$

Obviously, in this example, there is a very significant difference.

Perhaps recognizing that generic bond dissociation enthalpies are so approximate that corrections to energies are unwarranted, the quantities in [Table 1](#) are often called *generic bond dissociation energies* or just *bond dissociation energies*. Reactions that form strong bonds, such as those between C and O or between H and O, release considerable energy in forming product molecules and are likely to be strongly exothermic. Combustion processes are the prototypes of such reactions.

A considerable improvement in the accuracy of estimating thermodynamic quantities is achieved by the use of the method of *group additivities*,<sup>4</sup> which include the effect of nearest-neighbor interactions. In this method, thermodynamic quantities are decomposed into contributions from multibonded atoms (called groups). Each of these atoms is identified by its bonding type (e.g., single-, double-, or triple-bonded carbon atoms) and the identity of the atoms to which it is bonded, which is written in parentheses. For example, C<sub>d</sub>-(C)(H) refers to a doubly-bonded carbon, attached to a non-multiply-bonded carbon (*sp*<sup>3</sup>) and a hydrogen. The method will be illustrated for calculation of  $\Delta_f H^\circ$  of some hydrocarbons, using the group properties in Table 2. However, group properties for the calculation of all thermodynamic properties of a wide variety of

**TABLE 2** Group Values for  $\Delta_f H^\circ$  (kJ/mol) of Nonaromatic Hydrocarbons

C-(H) <sub>3</sub> (C)	-42.68	C-(C <sub>d</sub> )(C)(H) <sub>2</sub>	-19.92
C-(H) <sub>2</sub> (C) <sub>2</sub>	-20.63	C-(C <sub>d</sub> ) <sub>2</sub> (H) <sub>2</sub>	-7.95
C-(H)(C) <sub>3</sub>	-7.95	C-(C <sub>t</sub> )(C)(H) <sub>2</sub>	-19.79
C-(C) <sub>4</sub>	2.09	C-(C <sub>d</sub> )(C) <sub>2</sub> (H)	-6.19
C <sub>d</sub> -(H) <sub>2</sub>	26.19	C-(C <sub>t</sub> )(C) <sub>2</sub> (H)	-7.20
C <sub>d</sub> -(H)(C)	35.94	C-(C <sub>d</sub> )(C) <sub>2</sub>	7.03
C <sub>d</sub> -(C) <sub>2</sub>	43.26	C <sub>t</sub> -(H)	112.68
C <sub>d</sub> -(C <sub>d</sub> )(H)	28.37	C <sub>t</sub> -(C)	115.27
C <sub>d</sub> -(C <sub>d</sub> )(C)	37.15	C <sub>t</sub> -(C <sub>d</sub> )	122.17
C <sub>d</sub> -(C <sub>t</sub> )(H)	28.37	C <sub>a</sub>	143.1
C <sub>d</sub> -(C <sub>d</sub> ) <sub>2</sub>	19.25		

*Note:* C<sub>d</sub> = double-bonded carbon; C<sub>t</sub> = triple-bonded carbon; C<sub>a</sub> = allenic carbon. Corrections are also provided for non-nearest-neighbor interactions, such as for *cis* isomers, *gauche* conformers, and ring systems. (See Note 4.)

compounds are available. The reader is referred to Benson's book for more detailed use of the method. The accuracy of the method is demonstrated by the following example.

**Example 4.** Use the group additivity method to estimate the heats of formation of isobutane and 1-butene. Compare your result with the literature values of 134.7 kJ/mol and -0.5 kJ/mol, respectively.

*Solution:* Isobutane: The contributing groups are  $3[\text{C}-(\text{C})(\text{H})_3] + \text{C}-(\text{C})_3(\text{H})$ :

$$\Delta_f H^\circ = 3(-42.68) - 7.95 = 136.0 \text{ kJ/mol}$$

1-Butene: The contributing groups are  $\text{C}_d-(\text{H})_2 + \text{C}_d\text{H}(\text{C}) + \text{C}-(\text{H})_2(\text{C})_2 + \text{C}-(\text{H})_3(\text{C})$ :

$$\Delta_f H^\circ = 26.19 + 35.94 - 20.63 - 42.68 = -1.18 \text{ kJ/mol}$$

The agreement with the literature values is quite impressive.

## 7.5 Chemical Equilibrium

We have considered the change of properties of a system in which a chemical reaction occurs with an extent of reaction,  $\xi$ . We also need ways to determine just what extent of reaction will occur in a particular system. In many cases, this question will be answered by stoichiometry, namely by assuming that the reaction will proceed until *essentially* all the limiting reagent is converted into product, a situation that is called a reaction *going to completion*.

There are two reasons for reactions not going to completion. The first is that they may be kinetically inhibited, as illustrated by a mixture of  $\text{H}_2$  and  $\text{O}_2$  gas, which is stable at ambient conditions. We know that such a mixture has a *tendency* to form  $\text{H}_2\text{O}$ , as can be observed by igniting the system with a spark. Without the spark, however, the system reacts at negligible rate. Rates of chemical reactions are the subject of chemical kinetics, which will not be dealt with in this book.

The second reason for a reaction not going to completion is that it proceeds to a state of material equilibrium in which both reactants and products exist. This is the case for all gas-phase reactions, because free energy minimizes in gas mixtures when some of each component is present. (See Problem 16 in [Chapter 4](#).) In fact, even in the case of the spark-initiated  $\text{H}_2$ - $\text{O}_2$  reaction discussed earlier, some  $\text{H}_2$  and  $\text{O}_2$  will remain after the reaction. Equilibrium is more evident with the gaseous molecule  $\text{NO}_2$ , a fraction of which exists as the dimer,  $\text{N}_2\text{O}_4$ , near ambient conditions. This fraction depends on the temperature and pressure and rapidly adjusts to changes in these variables, indicating that there is

no kinetic inhibition in this system. The system is described by an *equilibrium constant*,  $K(T)$ . Because, once equilibrium is established, there is no further change in the concentrations in the system, the rates of the forward and reverse reaction must be equal at equilibrium, and  $K(T)$  can be obtained from this condition. However, equilibrium constants can also be calculated from thermodynamic data, by defining the equilibrium condition as that in which there is no tendency for change. This latter approach will be the subject of this section.

At equilibrium, the change in any thermodynamic property resulting from an infinitesimal change in the extent of a reaction,  $d\xi$ , can be calculated by the two different paths shown in Fig. 5.

Using the internal energy as an example, for the direct reaction path, no material enters or leaves the system and it may be considered closed. By the first and second laws, for a closed system at (mechanical, thermal, and material) equilibrium, performing no non- $PV$  work, we have

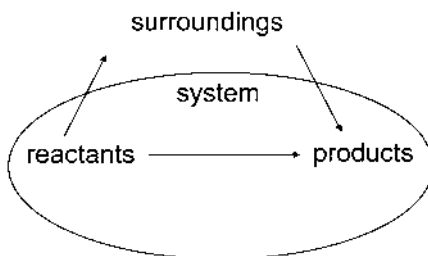
$$dU = \delta q + \delta w \stackrel{\text{m.e.}}{=} T dS - P dV \quad (27)$$

The system can also undergo the same change by allowing  $dn_i = v_i d\xi$  of each reactant or product to pass into the system. (Because the  $v_i$  are negative for the reactants, the reactants actually pass out of the system.) The system must be open for this to occur, and its change in internal energy is given by Eq. (4) of [Chapter 6](#):

$$dU = T dS - P dV + \sum_i \mu_i dn_i \quad (28)$$

These two expressions describe the same change of state of the system and must be equal, requiring that

$$\sum_i \mu_i dn_i = \sum_i \mu_i v_i d\xi \stackrel{\text{m.e.}}{=} 0 \quad (29)$$



**Figure 5** Reaction at equilibrium.

Because  $d\xi$  may be brought outside the summation sign and is not zero, this gives as the general condition for chemical equilibrium:

$$\sum_i \nu_i \mu_i = \Delta_{rxn} G \stackrel{m.e.}{=} 0 \quad (30)$$

At equilibrium, a condition such as Eq. (30) must hold for each *independent* reaction that can occur in a system (i.e., for every reaction that cannot be written as a linear combination of other reactions).

## 7.6 Direction of Chemical Reactions

From Eq. (7) of [Chapter 6](#), for a chemical reaction occurring in a system at constant  $T$  and  $P$ ,

$$dG = \sum_i \mu_i dn_i = \left( \sum_i \mu_i \nu_i \right) d\xi = \Delta_{rxn} G d\xi \quad (31)$$

Because processes will be spontaneous in closed systems at constant  $T$  and  $P$  if they lower the Gibbs free energy ( $dG/d\xi < 0$ ), we see that the criterion for a spontaneous reaction in a system at constant  $T$  and  $P$  is

$$\sum_i \nu_i \mu_i = \Delta_{rxn} G < 0 \quad (32)$$

The quantity  $A \equiv -\sum_i \nu_i \mu_i = -\Delta_{rxn} G$  is often called the *affinity* of the chemical reaction. It is the thermodynamic driving force of the reaction.

In a similar manner, a process occurring at constant  $T$  and  $V$  will be spontaneous if it lowers the Helmholtz free energy, which from Eq. (6) of Chapter 6 also gives  $\sum_i \mu_i dn_i < 0$  and Eq. (32). In [chapter 10](#), it is shown that the criterion for spontaneity, Eq. (32), is perfectly general and must hold, regardless of the conditions under which the reaction is conducted. The Gibbs free energy of reaction always decreases in a spontaneous chemical reaction.

## 7.7 Concentration Dependence of Free Energy

Combining Eq. (11) with Eq. (47) of Chapter 6, we have

$$\begin{aligned} \Delta_{rxn} G &= \sum_i \nu_i (\mu_i^\circ + RT \ln a_i) = \sum_i \nu_i \mu_i^\circ + RT \sum_i \ln a_i^{\nu_i} \\ &= \Delta_{rxn} G^\circ + RT \ln \prod_i a_i^{\nu_i} \end{aligned} \quad (33)$$

where the  $\ln$  of a product has been substituted for the sum of  $\ln$ 's.  $\Delta_{rxn} G^\circ$  is the Gibbs free-energy change of the reaction under standard condition (the *standard free-energy change of the reaction*), and we define the product as

$$Q_a \equiv \prod_i a_i^{v_i} \quad (34)$$

where  $Q_a$  is the *proper quotient of activity coefficients for the reaction*. For example, for the reaction:  $2\text{CO} + \text{O}_2 \leftrightarrow 2\text{CO}_2$ ,  $Q_a = a_{\text{CO}_2}^2 / a_{\text{CO}}^2 a_{\text{O}_2}$ . The concentration dependence of activities thus determines  $\Delta_{rxn} G$  by the equation

$$\Delta_{rxn} G = \Delta_{rxn} G^\circ + RT \ln Q_a \quad (35)$$

**Example 5.** For the reaction:  $9\text{H}_2(\text{g}) + \text{C}_6\text{H}_6(\text{liq}) \leftrightarrow 6\text{CH}_4(\text{g})$ :

- Calculate the standard enthalpy change and the standard Gibbs free energy change at  $25^\circ\text{C}$ .
- Calculate  $\Delta G$  for the reaction at  $25^\circ\text{C}$  when the partial pressure of hydrogen is 0.1 bar and the partial pressure of  $\text{CH}_4$  is 50 bar.

*Solution:*

$$\begin{aligned} \text{(a)} \quad \Delta H^\circ(298) &= 6(-74.81) - (49.1) = -498.0 \text{ kJ/mol} \\ \Delta G^\circ(298) &= 6(-50.72) - (124.5) = -428.8 \text{ kJ/mol} \end{aligned}$$

- The ideal gas approximation is very good at 298 K and the pressures of this problem. Activities of  $\text{CH}_4$  and  $\text{H}_2$  can therefore be taken as their pressures in bar. The activity of liquid benzene can be taken as 1.0. This will be discussed in detail in Section 7.8.1.

$$\begin{aligned} Q_a &= \frac{P_{\text{CH}_4}^6}{P_{\text{H}_2}^9} = \frac{(50)^6}{(0.1)^9} = 1.56 \times 10^{19} \\ \Delta G &= \Delta G^\circ + RT \ln Q_a = -428.8 \text{ kJ/mol} \\ &\quad + \frac{8.314 \text{ J}}{\text{mol K}} (298 \text{ K}) \frac{\text{kJ}}{1000 \text{ J}} \ln(1.56 \times 10^{19}) \\ &= -428.8 + 109.5 = -319.3 \text{ kJ/mol} \end{aligned}$$

## 7.8 Equilibrium Constants

From Eq. (30), at equilibrium,  $\Delta_{rxn} G = 0$ . (There is no driving force for the reaction in either direction.) We have from Eq. (35), at equilibrium,

$$\Delta_{rxn} G^\circ = -RT \ln K_a \quad (36)$$

where  $K_a$ , the *activity equilibrium constant*, is the value of  $Q_a$  at equilibrium. It is the product of the equilibrium activities of reactants and products, each raised to their appropriate stoichiometric coefficient. Because the stoichiometric coefficients of the reactants are negative, the reactant terms can be written in the denominator with positive coefficients, as is more commonly done for equilibrium constants. Equation (36) can also be written as

$$K_a = \exp\left(-\frac{\Delta_{rxn}G^\circ}{RT}\right) = \exp\left(\frac{\Delta_{rxn}S^\circ}{R}\right) \exp\left(-\frac{\Delta_{rxn}H^\circ}{RT}\right) \quad (37)$$

which shows that reactions that increase entropy and decrease enthalpy have large equilibrium constants and tend to go to completion.

For equilibria involving ideal gases, whose activities are  $P/P^\circ$ , or just the numerical value of the pressure (in bars), we can write

$$\Delta_{rxn}G^\circ = -RT \ln \prod_i \left(\frac{P_i}{P^\circ}\right)^{v_i} = -RT \ln K_P \quad (38)$$

where  $K_P$  is an equilibrium constant involving the numerical values of pressures (in bars) (or to a very good approximation, in atmospheres). In Eq. (38), different pressures are used on the left-hand and right-hand sides of the equation.  $\Delta_{rxn}G^\circ$  is calculated with all reactants and products at 1.0 bar, the standard pressure at which we choose to tabulate thermodynamic functions. The equilibrium constant, of course, generally involves partial pressures different from 1.0 bar. Although this often creates some confusion, it results from converting free energies from the standard pressure to the equilibrium partial pressures. The free-energy change at the equilibrium pressures does not enter into Eq. (38) because it is zero.

Also, note that because the left-hand side of Eq. (38) is independent of the total pressure of the system, the equilibrium constant must also be pressure independent in the ideal gas regime. This does not mean, however, that the partial pressures of individual components are pressure independent, as shall be seen when we do some calculations with equilibrium constants.

For real gases, we can use Eq. (51) of [Chapter 6](#) to write

$$\Delta_{rxn}G^\circ = -RT \ln \prod_i \left(\frac{f_i}{P^\circ}\right)^{v_i} = -RT \ln K_f \quad (39)$$

where  $K_f$  is an equilibrium constant involving the numerical values of fugacity (in bars). Alternatively, using Eq. (55) of [Chapter 6](#), we can write

$$\Delta_{rxn}G^\circ = -RT \ln \prod_i \left(\frac{\phi_i P_i}{P^\circ}\right)^{v_i} = -RT \ln K_P K_\phi \quad (40)$$

where  $K_\phi$  is an equilibrium constant formed from fugacity coefficients. If conditions can be found where measurable amounts of reactants and products



coexist at equilibrium, Eqs. (38)–(40) provide a means to determine  $\Delta_{rxn}G^\circ$  without making any calorimetric measurements.

In order to avoid confusion, it is very important to clearly state the balanced chemical reaction to which a given equilibrium constant applies. This is illustrated in Example 6.

**Example 6.** Write down the form of the equilibrium constant that applies to the Haber process for the production of ammonia.

*Solution:* The Haber process is one of the most important industrial chemical reactions. The reaction describing the process can be written as



or alternatively as



The form of  $K_a$  for reaction I is  $K_a(\text{I}) = a_{\text{NH}_3}/a_{\text{N}_2}^{1/2}a_{\text{H}_2}^{3/2}$ , whereas that for reaction II is  $K_a(\text{II}) = a_{\text{NH}_3}^2/a_{\text{N}_2}a_{\text{H}_2}^3 = [K(\text{I})]^2$ . (When you double the reaction, you square the equilibrium constant.) In terms of fugacities (which would be used at the high pressures at which the Haber process is carried out), the rate constant is

$$K_f(\text{I}) = \frac{f_{\text{NH}_3}P^\circ}{f_{\text{N}_2}^{1/2}f_{\text{H}_2}^{3/2}} \quad \text{and} \quad K_f(\text{II}) = \frac{f_{\text{NH}_3}^2P^{\circ 2}}{f_{\text{N}_2}f_{\text{H}_2}^3}$$

Both of these forms are in agreement with Eq. (38), because  $\Delta_{rxn}G^\circ(\text{II})$  is twice  $\Delta_{rxn}G^\circ(\text{I})$ .

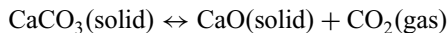
## 7.8.1 Equilibria Involving Condensed Phases

Because, at constant temperature,  $dG_m = V_m dP$  and the molar volumes of condensed phases are very small, it is usually sufficiently accurate to take their molar free energy as pressure independent and the same as that at the 1.0-bar standard state. This is equivalent to setting the activity of pure, condensed phases equal to unity. (See Problem 9.) The activity of a condensed phase is also independent of just how much of the phase is present. As a result of these considerations, no variable describing the condensed phase appears in the equilibrium constant and the equilibrium is independent of just how much condensed phase is present.

Because the activity of condensed phases is not appreciably affected by the amount of the condensed phase or the pressure, equilibria involving condensed phases are achieved by variation of gas-phase concentrations. For example, in the equilibrium  $\text{NH}_4\text{Cl}_{(\text{solid})} \leftrightarrow \text{NH}_3_{(\text{gas})} + \text{HCl}_{(\text{gas})}$ , if the amounts of  $\text{NH}_3$  and  $\text{HCl}$

are too low for  $a_{\text{NH}_3}a_{\text{HCl}} = K_a = \exp(-\Delta G^\circ/RT)$ , the equilibrium will not hold and there will be no solid  $\text{NH}_4\text{Cl}$  in the system.

**Example 7.** Show the form of Eq. (36) for the reaction



*Solution:* Because  $\nu_{\text{CaCO}_3} = -1$ ,  $\nu_{\text{CaO}} = 1$ , and  $\nu_{\text{CO}_2} = 1$ ,  $K_a = a_{\text{CO}_2}a_{\text{CaO}}/a_{\text{CaCO}_3}$ ,  $\text{CaO}$  and  $\text{CaCO}_3$  are condensed phases; their activities are unity and they do not enter into the equilibrium expression (as long as some of these materials are present). The activity of  $\text{CO}_2$  is  $a_{\text{CO}_2} = f_{\text{CO}_2}/P^\circ$ , which, at pressures where  $\text{CO}_2$  behaves ideally, is just the partial pressure of  $\text{CO}_2$  in units of bar. Equation (36) then becomes

$$\Delta_{\text{rxn}} G^\circ = -RT \ln\left(\frac{P_{\text{CO}_2}}{P^\circ}\right) \quad \text{or} \quad \frac{P_{\text{CO}_2}}{P^\circ} = \exp\left(-\frac{\Delta_{\text{rxn}} G^\circ}{RT}\right)$$

## 7.9 General Considerations Involving Multicomponent and Multiphase Equilibrium: The Gibbs Phase Rule

A *component* is a particular chemical substance. A chemical reaction at equilibrium is therefore a *multicomponent system*. In discussing the equilibria of multicomponent systems, it is important to be aware of what constitutes a complete and sufficient specification of the system. If too few variables are specified, the system is not completely defined; if too many are specified, the values of these variables may be inconsistent with equilibrium. It is possible to waste much time considering improperly specified systems.

The *Gibbs phase rule* allows  $f$ , the number of *degrees of freedom* of a system, to be determined.  $f$  is the number of intensive variables that can and must be specified to define the *intensive state* of a system at equilibrium. By intensive state is meant the properties of all phases in the system, but not the amounts of these phases. Phase equilibria are determined by chemical potentials, and chemical potentials are intensive properties, which are independent of the amount of the phase that is present. The overall concentration of a system consisting of several phases, however, is not a degree of freedom, because it depends on the amounts of the phases, as well as their concentration. In addition to the intensive variables, we are, in general, allowed to specify one extensive variable for each phase in the system, corresponding to the amount of that phase present.

We will consider the number of degrees of freedom,  $f$ , of a system consisting of  $c$  components and  $p$  phases. Two intensive variables,  $T$  and  $P$ , are needed to specify the state of thermal and mechanical equilibrium of the system. In order to determine the state of material equilibrium of the system, it is necessary to know the chemical potential of each component of every phase. At a given temperature and pressure, chemical potentials are functions of the concentrations in the phase, so we can consider specifying the  $c \times p$  concentrations of each component in every phase. However, this value for the degrees of freedom,  $c \times p + 2$ , is too large. First, the concentrations of the  $c$  components of each phase cannot be independently specified, because there is a relation between them, most easily written as the sum of the mole fractions in each phase being unity [Eq. (44) of [Chapter 1](#)]. This reduces the number of degrees of freedom by the number of phases,  $p$ . Second, we have seen that the general condition for phase equilibrium is that the chemical potential of each component be the same in every phase. For example, if there are three phases, we have

$$\begin{aligned}\mu_{i\alpha} &= \mu_{i\beta} \\ \mu_{i\beta} &= \mu_{i\gamma}\end{aligned}\tag{41}$$

Note that these two restrictions mathematically require that  $\mu_{i\alpha} = \mu_{i\gamma}$ , which is, therefore, not an independent restriction.

In general, the number of independent restricting equations for phase equilibrium will be one less than the number of phases for each component. The degrees of freedom of the system then become

$$f = c \times p + 2 - p - c \times (p - 1) = c - p + 2\tag{42}$$

This relation is called the *Gibbs phase rule*. However, as indicated next,  $c$  should be limited to the number of *independent components*.

Chemical reactions reduce the number of degrees of freedom of a system. For each independent chemical reaction that can occur in a system,  $\Delta_{rxn} G = 0$  is required. If  $r$  is the number of independent reactions at equilibrium in the system, this reduces the degrees of freedom by  $r$ .

Other restrictions on the system may result from stoichiometric considerations. A very common stoichiometric restriction occurs in ionic solutions where *charge neutrality* must hold. Other restrictions can result if two species are produced only by the decomposition of the same molecule. If the number of stoichiometric restrictions is  $a$ , the degrees of freedom of the system become

$$f = c - p + 2 - r - a\tag{43}$$

Usually, the combination  $c - r - a$  is called the *number of independent components*,  $c_{ind}$ , and the phase rule is written as

$$f = c_{ind} - p + 2\tag{44}$$

For one-component systems, such as have been considered in [Chapter 6](#), Eq. (44) becomes

$$f = 3 - p \quad (45)$$

Thus, temperature and pressure can both be varied while remaining in a region of a single phase, whereas only temperature or pressure can be varied (e.g., on a vapor–pressure curve) while retaining equilibrium between two phases. The triple point is completely invariant. More interesting applications of the phase rule are obtained with multicomponent systems, as indicated in the following examples.

**Example 8.** Ethanol–water.

*Discussion:* Ethanol does not react with water, so the two components are independent:  $c_{\text{ind}} = 2$ . They are completely miscible, so a single liquid phase exists, which, when in equilibrium with vapor, gives  $p = 2$ . From Eq. (44), there are two degrees of freedom, usually taken as the temperature and composition, which determine the vapor pressure of the solution. If the solution is exposed to the atmosphere, air is present and is a third component. There are now three degrees of freedom and the pressure is that of the atmosphere.

**Example 9.** Sodium chloride–water.

*Discussion:* There are two ways of treating this system and they should give identical results. If we consider NaCl as a single un-ionized substance, the system has two independent components, which form a solution (assuming that we have not exceeded the solubility limit). There is, thus, two degrees of freedom, just as in the ethanol–water system. Alternatively, we can treat NaCl as an electrolyte, which is completely ionized in solution. Then, there are actually three components,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$  in the system. However, charge neutrality requires that  $[\text{Na}^+] = [\text{Cl}^-]$ , which reduced  $c_{\text{ind}}$  to 2, giving the same result in this example. If more NaCl is added to the system than will dissolve, a third phase, solid NaCl, appears. The system then has a single degree of freedom, and fixing the temperature determines the concentration of the solution and the vapor pressure of water above the solution.

**Example 10.** Acetic acid–water.

*Discussion:* Acetic acid is soluble in water and partially ionized, resulting in four components:  $\text{HAc}$ ,  $\text{Ac}^-$ ,  $\text{H}^+$ , and  $\text{H}_2\text{O}$ . However, now there is a reaction,  $\text{HAc} \leftrightarrow \text{H}^+ + \text{Ac}^-$ , which gives an equilibrium relationship,  $K_a = a_{\text{H}^+}a_{\text{Ac}^-}/a_{\text{HAc}}$ , as well as the charge neutrality condition.  $c_{\text{ind}} = 2$ , yielding  $f = 2$  for the solution in equilibrium with its vapor, the same results as for ethanol–water.

**Example 11.** Silver chloride–water.

*Discussion:* The components are  $\text{H}_2\text{O}$ ,  $\text{AgCl}$ ,  $\text{Ag}^+$  and  $\text{Cl}^-$ , but the solubility equilibrium of  $\text{AgCl}$  and charge neutrality reduces  $c_{\text{ind}}$  to 2. Because  $\text{AgCl}$  is only slightly soluble, in equilibrium with water vapor this system has three phases and, therefore, only a single degree of freedom. Specification of the temperature, for example, determines all intensive variables in the system (but not the amounts of the phases). Note that considering  $\text{H}^+$  and  $\text{OH}^-$  from the ionization of water introduces two additional components, but also two addition constraints: the ionization equilibrium of water and the requirement that  $[\text{H}^+] = [\text{OH}^-]$ , so that  $c_{\text{ind}}$  and  $f$  are unchanged.

**Example 12.**  $\text{CaCO}_3$ – $\text{CaO}$ – $\text{CO}_2$ 

*Discussion:* At high temperature, equilibrium is established among these three components, so this system has  $c_{\text{ind}} = 3 - 1 = 2$ . Usually, crystalline solids exist as pure components, so there will be two solid and one gaseous phase present. With  $p = 3$ ,  $f = 1$ . Specification of the temperature will therefore determine the pressure of  $\text{CO}_2$ , but not its volume, nor the amounts of the two solid phases.

It might occur that  $\text{CaO}$  and  $\text{CaCO}_3$  form a solid solution or a mixture in which the particles are so small that it is preferred to consider them as constituting a single solid phase. The system then has two phases and two degrees of freedom. The additional degree of freedom is now the concentration of the solid phase, which is analogous to the relative amounts of the two solid phases when they are considered as separate phases. We are free to set either of these quantities.

In general, the calculated degrees of freedom will be independent of decisions that we make regarding just what substances are dissociated, or whether solids are single or mixed phases.

## 7.10 Concentrations at Equilibrium

Although free energies are related to equilibrium constants, it is concentrations that are either ultimately desired or experimentally determined. There are many ways to perform equilibrium calculations. We will approach such calculations through the extent of reaction,  $\xi$ , defined in Eq. (5), because all concentrations can be expressed in terms of this single variable. In addition, use of the extent of the reaction allows us to perform equilibrium calculations in a very systematic manner. At equilibrium, the extent of reaction becomes  $\xi_e$ , the extent of reaction at equilibrium. An intermediate step in the calculation is expressing the mole

fractions,  $x_i$ , in the gas in terms of  $\xi_e$ . The activities of condensed phase species can almost always be taken as unity; therefore, these species do not enter into the equilibrium constant. In terms of mole fractions, the equilibrium constant may be written as

$$K_P(T) = \prod_{\text{gas}} \left( \frac{P_j}{P^\circ} \right)^{v_j} = \prod_{\text{gas}} \left( \frac{x_j P}{P^\circ} \right)^{v_j} = \prod_{\text{gas}} \left( \frac{P}{P^\circ} \right)^{v_j} \prod_{\text{gas}} x_j^{v_j} = \left( \frac{P}{P^\circ} \right)^{\Delta v_{\text{gas}}} K_x(T, P) \quad (46)$$

$\Delta v_{\text{gas}}$  is the change in the number of moles of gas in the reaction and  $K_x$  is the equilibrium constant in terms of mole fractions of gaseous reactants and products, which can be seen to be a function of both temperature and pressure:

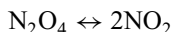
$$K_x(T, P) = K_P(T) \left( \frac{P}{P^\circ} \right)^{-\Delta v_{\text{gas}}} \quad (47)$$

For a reaction with positive gas mole change, Eq. (47) indicates that  $K_x$  decreases with pressure. Because  $\xi_e$  is a monotonically increasing function of  $K_x$ , the equilibrium extent of a reaction with positive  $\Delta v_{\text{gas}}$  always decreases as pressure is increased. This is an example of Le Chatelier's principle, which states that a reaction at equilibrium shifts in response to a change in external conditions in a way that moderates the change. In this case, because the reaction increases the number of moles of gas and thus the pressure, the reaction shifts back to reactants. The isothermal compressibility of a reactive system can, therefore, be much greater than that of a nonreactive system. This effect can be dramatic in systems with condensed phases. For example, in the calcium carbonate dissociation discussed in Example 12, if the external pressure is raised above the dissociation pressure of  $\text{CO}_2$ , the system will compress down to the volume of the solid. Of course, a similar effect is observed in simple vaporization or sublimation equilibrium. As the pressure on water at  $100^\circ\text{C}$  is increased above 1.0 atm, all vapor is removed from the system.

The use of  $\xi_e$  in equilibrium calculations will be illustrated by a number of examples.

**Example 13.** Find the fraction of  $\text{N}_2\text{O}_4$  that is dissociated into  $\text{NO}_2$ , as a function of the total pressure of the mixture of these two gases at 298 K.

*Solution:*  $\text{N}_2\text{O}_4$  dissociates into  $\text{NO}_2$  (the compound that sometimes gives the air over Los Angeles its brown color) by the equation



At 298 K, we have, from [Appendix B](#),

$$\begin{aligned}\Delta G^\circ &= 2(51.31) - 97.89 = 4.73 \text{ kJ/mol} \\ K_P &= \exp\left(-\frac{4.73 \text{ kJ}}{\text{mol}} \left| \frac{1000 \text{ J}}{\text{kJ}} \right| \left| \frac{\text{mol K}}{8.314 \text{ J}} \right| \left| \frac{1}{298 \text{ K}} \right| \right) \\ &= \exp(-1.91) = 0.148\end{aligned}$$

The system has two components that are related by one chemical reaction, and, therefore,  $c_{\text{ind}} = 1$ . There is a single phase and therefore two degrees of freedom. At a fixed temperature, 298 K, the single remaining degree of freedom can be taken as the pressure. We can also specify one extensive variable, which we choose to be  $n_{\text{init}}$ , the initial number of moles of  $\text{N}_2\text{O}_4$ . We choose  $n_{\text{init}} = 1$ , so that  $\xi_e$  is directly the fraction of  $\text{N}_2\text{O}_4$  dissociated.

To find  $\xi_e$ , we construct a table giving the initial, reacting, and equilibrium number of moles, mole fractions, and partial pressures.

	$\text{N}_2\text{O}_4$	$\text{NO}_2$	Total
Initial	1	0	1
Reacting	$-\xi_e$	$+2\xi_e$	$\xi_e$
Equilibrium	$1 - \xi_e$	$2\xi_e$	$1 + \xi_e$
Mole fraction	$\frac{1 - \xi_e}{1 + \xi_e}$	$\frac{2\xi_e}{1 + \xi_e}$	1
Partial pressure	$\left(\frac{1 - \xi_e}{1 + \xi_e}\right)P$	$\left(\frac{2\xi_e}{1 + \xi_e}\right)P$	$P$

Assuming the pressure is low enough to use unit fugacity coefficients, the equilibrium constant is (with  $P$  in bars)

$$\begin{aligned}K_P &= \left(\frac{2\xi_e}{1 + \xi_e}\right)^2 P^2 \left[\left(\frac{1 - \xi_e}{1 + \xi_e}\right)P\right]^{-1} = \frac{4\xi_e^2 P}{1 - \xi_e^2} \\ \xi_e &= \sqrt{\frac{K_P}{4P + K_P}} = \sqrt{\frac{0.148}{4P + 0.148}}\end{aligned}$$

$P$  in this expression includes only the pressures of the “active” species  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  (see Problem 13). Even in the polluted air of Los Angeles, these are quite low, and  $\text{N}_2\text{O}_4$  is essentially completely dissociated.

**Example 14.** A mixture is prepared at 298 K by opening the stopcock between two 500-mL flasks; one containing 600 torr of NO, the other 300 torr of Br<sub>2</sub>. Due to the presence of photodissociating light, equilibrium is rapidly established between Br<sub>2</sub>, NO, and NOBr. What are the equilibrium partial pressures of each of the compounds?

*Solution:* There are three components in a single phase. One chemical reaction,  $2\text{NO} + \text{Br}_2 \leftrightarrow 2\text{NOBr}$ , reduces the number of independent components to two. The number of degrees of freedom is  $2 - 1 + 2 = 3$ , one of which is the fixed temperature of 298 K. The other two can be taken as the ratio of the initial pressure of NO to that of Br<sub>2</sub> and the total final pressure. First, we calculate the equilibrium constant:

$$\Delta G^\circ = 2(82.4) - 2(86.6) = -8.4 \text{ kJ/mol}$$

$$K_P = \exp\left(\frac{8.4 \text{ kJ}}{\text{mol}} \left| \frac{1000 \text{ J}}{\text{kJ}} \right| \frac{\text{mol K}}{8.314 \text{ J}} \left| \frac{1}{298 \text{ K}} \right| \right) = \exp(3.4) = 30$$

Because we have decided that the result depends only on the ratio of NO to Br<sub>2</sub> and the pressure, we can choose the initial moles of Br<sub>2</sub> = 1 and of NO = 2. Preparing a table similar to that of Example 13:

	NO	Br <sub>2</sub>	NOBr	Total
Initial	2	1	0	3
Change	$-2\xi_e$	$-\xi_e$	$+2\xi_e$	$-\xi_e$
Equilibrium	$2 - 2\xi_e$	$1 - \xi_e$	$2\xi_e$	$3 - \xi_e$
Mole fraction	$\frac{2 - 2\xi_e}{3 - \xi_e}$	$\frac{1 - \xi_e}{3 - \xi_e}$	$\frac{2\xi_e}{3 - \xi_e}$	1
Partial pressure	$\left(\frac{2 - 2\xi_e}{3 - \xi_e}\right)P$	$\left(\frac{1 - \xi_e}{3 - \xi_e}\right)P$	$\left(\frac{2\xi_e}{3 - \xi_e}\right)P$	$P$

The initial pressure (after the stopcock is opened, but before reaction) is 450 torr. The final pressure is lower due to the reduction in the number of moles by the reaction  $\{P = 450 \text{ torr}[(3 - \xi_e)/3]\}$ . Substituting into the equilibrium constant and converting pressure to bars gives

$$\begin{aligned}
 30 &= \left(\frac{2\xi_e}{3 - \xi_e}\right)^2 P^2 \left[ \left(\frac{2 - 2\xi_e}{3 - \xi_e}\right)^2 P^2 \left(\frac{1 - \xi_e}{3 - \xi_e}\right) P \right]^{-1} \\
 &= \frac{4\xi_e^2(3 - \xi_e)}{(2 - 2\xi_e)^2(1 - \xi_e)} \frac{760(3)}{450(3 - \xi_e)1.01}
 \end{aligned}$$



or

$$\xi_e^2 - 5.98(1 - \xi_e)^3 = 0$$

This cubic equation can be solved by a number of methods, including trial and error, to give  $\xi_e = 0.605$ . The final total pressure is then 359 torr and the partial pressures are  $P_{\text{NO}} = 119$ ,  $P_{\text{Br}_2} = 59$ , and  $P_{\text{NOBr}} = 181$  torr, values which, when substituted into the equilibrium constant, give the required value of 30.

**Example 15.** Water gas, a combustible mixture of  $\text{CH}_4$  and  $\text{CO}$ , is made by the reaction of water with coke at elevated temperature. This reaction can be written as  $3\text{C}_{\text{gr}} + 2\text{H}_2\text{O}_{(\text{g})} \leftrightarrow \text{CH}_{4(\text{g})} + 2\text{CO}_{(\text{g})}$  and has an equilibrium constant of 118 at  $1000^\circ\text{C}$  (see Problem 13). What is the ratio of the partial pressure of  $\text{CO}$  to that of  $\text{H}_2\text{O}$  in the gas mixture formed at  $1000^\circ\text{C}$  and 10 atm pressure by passing steam over coke?

*Solution:* There are four components in the system related by one chemical equation. There is also a stoichiometric equation resulting from the fact that all of the hydrogen and oxygen come from water and, therefore,  $P_{\text{CO}}/P_{\text{CH}_4} = 2$ . The number of independent components is therefore  $4 - 2 = 2$ . With two phases, there are two degrees of freedom. These can be taken as the temperature and pressure of the system. A table is formed as in the two previous examples. (Graphite, a solid, is assumed to have unit activity and does not enter into the equilibrium constant.) The initial amount of water is arbitrarily chosen as 1.0 mol. (An extensive variable characterizing the amount of gas phase can be specified.)

	$\text{H}_2\text{O}$	$\text{CH}_4$	$\text{CO}$	Total
Initial	1	0	0	1
Change	$-2\xi_e$	$\xi_e$	$2\xi_e$	$\xi_e$
Equilibrium	$1 - 2\xi_e$	$\xi_e$	$2\xi_e$	$1 + \xi_e$
Mole fraction	$\frac{1 - 2\xi_e}{1 + \xi_e}$	$\frac{\xi_e}{1 + \xi_e}$	$\frac{2\xi_e}{1 + \xi_e}$	1
Partial pressure	$\left(\frac{1 - 2\xi_e}{1 + \xi_e}\right)P$	$\left(\frac{\xi_e}{1 + \xi_e}\right)P$	$\left(\frac{2\xi_e}{1 + \xi_e}\right)P$	$P$

Substituting into the equilibrium constant gives

$$K_a = \left( \frac{\xi_e}{1 + \xi_e} \right) P \left( \frac{2\xi_e}{1 + \xi_e} \right)^2 P^2 \left[ \left( \frac{1 - 2\xi_e}{1 + \xi_e} \right)^2 P^2 \right]^{-1}$$

$$= \frac{4\xi_e^3 P}{(1 + \xi_e)(1 - 2\xi_e)^2}$$

With  $K_a = 118$  and  $P = 10$ ,

$$11.8(1 + \xi_e)(1 - 2\xi_e)^2 = 4\xi_e^3$$

This cubic equation has three real roots:  $\xi_e = -1.04$ ,  $0.431$ , and  $0.609$ .

Only the central root gives positive values for all the concentrations.

Thus,  $\xi_e = 0.431$  and

$$\frac{P_{\text{CO}}}{P_{\text{H}_2\text{O}}} = \frac{2\xi_e}{1 - 2\xi_e} = 6.2$$

## 7.11 Temperature Dependence of the Equilibrium Constant

Multiplying Eq. (36) by  $T^{-1}$  and taking the derivative with respect to  $T^{-1}$ ,

$$\frac{d(T^{-1}\Delta_{rxn}G^\circ)}{dT^{-1}} = -R \frac{d \ln K_a}{dT^{-1}} \quad (48)$$

Because the derivatives are of pressure-independent quantities, we can use Eq. (29) of [Chapter 4](#) to give

$$\frac{d \ln K_a}{dT^{-1}} = -\frac{\Delta_{rxn}H^\circ}{R} \quad (49)$$

Equation (49) provides a means of determining the heat of a reaction without performing any calorimetric measurements. If an equilibrium can be established for the reaction with measurable amounts of reactants and products over a range of temperature, then  $\Delta_{rxn}H^\circ$  can be obtained from the slope of a graph of the logarithm of the equilibrium constant versus  $T^{-1}$ . Equation (49) can also be written as

$$\frac{d \ln K_a}{dT} = \frac{\Delta_{rxn}H^\circ}{RT^2} \quad (50)$$

showing that the equilibrium constant of an exothermic reaction decreases with increasing temperature. As heat is added to such a system, the equilibrium shifts back toward reactants (the extent of reaction decreases). The shift of the equilibrium absorbs some of the added heat, and the system's temperature rise

is not as large as it would be otherwise. Reaction systems at equilibrium therefore can have very large heat capacities and are useful as heat storage media. This is another example of Le Chatelier's principle, that if a stress (temperature increase, in this case) is put on a system at equilibrium, reactions in the system will shift to moderate the stress (reduce the temperature increase).

The above equations are useful for converting equilibrium constants from one temperature to another. Separating variables and integrating gives

$$\ln K_a(T_2) - \ln K_a(T_1) = -\frac{1}{R} \int_{T_1}^{T_2} \Delta_{rxn} H^\circ d(T^{-1}) = \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta_{rxn} H^\circ}{T^2} dT \quad (51)$$

If  $\Delta_{rxn} H^\circ$  can be considered temperature independent (either because the heat capacity of the products is close to that of the reactants or because  $T_1$  does not differ much from  $T_2$ ), it can be taken out of the integral, giving

$$\ln K_a(T_2) = \ln K_a(T_1) - \frac{\Delta_{rxn} H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (52)$$

A common occurrence is that the equilibrium constant is known at 298 K, because free energies of formation are tabulated at that temperature.  $T_1$  is then taken as 298 K:

$$\ln K_a(T) = \ln K_a(298) - \frac{\Delta_{rxn} H^\circ}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \quad (53)$$

If  $|T_2 - T_1|$  is large enough that Eq. (53) is not an adequate approximation, the next level of approximation, assuming temperature-independent heat capacities, is used:

$$\Delta_{rxn} H^\circ(T) = \Delta_{rxn} H^\circ(298) + \Delta_{rxn} C_P(T - 298) \quad (54)$$

Substituting into Eq. (51) and integrating gives

$$\begin{aligned} \ln K_a(T) = \ln K_a(298) - \frac{\Delta H_{rxn}(298) - 298 \Delta_{rxn} C_P}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \\ + \frac{\Delta_{rxn} C_P}{R} \ln \left( \frac{T}{298} \right) \end{aligned} \quad (55)$$

In higher-order approximations, the temperature variation of heat capacities (See [Table 1](#) of [Chapter 2](#)) is considered.

**Example 16.** Calculate  $K_a$  for the reaction  $2\text{SO}_2 + \text{O}_2 \leftrightarrow 2\text{SO}_3$  at 500 K. You may use temperature-independent heat capacities.

*Solution:* At 298 K, we find, from [Appendix B](#),

$$\Delta_{rxn} H^\circ = 2(-395.72) - [2(-296.83)] = -191.78 \text{ kJ/mol}$$

$$\Delta_{rxn} G^\circ = 2(-371.06) - [2(-300.19)] = -141.73 \text{ kJ/mol}$$

$$\Delta_{rxn} C_p^\circ = 2(50.67) - [2(39.87) + 29.36] = -7.76 \text{ J/mol K}$$

From these, we calculate, from Eq. (36),

$$\begin{aligned} \ln K_a(298) &= -\frac{\Delta_{rxn} G^\circ(298)}{R(298 \text{ K})} = \frac{141.73 \text{ kJ}}{\text{mol}} \frac{1000 \text{ J}}{\text{kJ}} \frac{1}{8.314 \text{ J/mol K}} \frac{1}{298 \text{ K}} \\ &= 57.2 \\ K_a &= 6.9 \times 10^{24} \end{aligned}$$

Substituting into Eq. (55),

$$\begin{aligned} \ln K_a(500) &= \ln K_a(298) + \frac{[-191,780 - 298(-7.765)] \text{ J/mol K}}{8.314 \text{ J/mol K}} \\ &\quad \times \left( \frac{1}{298} - \frac{1}{500} \right) \frac{1}{\text{K}} + \frac{-7.765 \text{ J/mol K}}{8.314 \text{ J/mol K}} \ln \left( \frac{500}{298} \right) \\ \ln K_a(500) &= 57.2 - 30.89 - 0.48 = 25.8 \\ K_a &= 1.6 \times 10^{11} \end{aligned}$$

For this highly exothermic reaction, the equilibrium shifts strongly toward reactants as the temperature is increased.

## 7.12 Equilibrium Constant in Terms of Partition Function

For reactions of ideal gases, we can write

$$\Delta G^\circ = \sum_i \nu_i \mu_i^\circ = \sum_i \nu_i G_{m,i}^\circ \quad (56)$$

Using Eq. (38) of [Chapter 5](#),

$$\Delta G^\circ = \sum_i \nu_i \left[ U_{0,i}^\circ - RT \ln \left( \frac{q_i^\circ}{N_A} \right) \right] = \Delta U_0^\circ - RT \ln \prod_i \left( \frac{q_i^\circ}{N_A} \right)^{\nu_i} \quad (57)$$

With Eq. (36), we obtain

$$-RT \ln K_p = \Delta U_0^\circ - RT \ln \prod_i \left( \frac{q_i^\circ}{N_A} \right)^{\nu_i} \quad (58)$$

from which

$$K_P = \prod_i \left( \frac{q_i^\circ}{N_A} \right)^{v_i} \exp \left( -\frac{\Delta U_0^\circ}{RT} \right) \quad (59)$$

Note similarities and differences to Eq. (37).

## Questions

1. Write the equation for the Haber process synthesis of ammonia from hydrogen and nitrogen in the form of Eq. (4). For an initial 1 mol of nitrogen and 3 mol of hydrogen and an extent of reaction,  $\xi = 0.3$ , how much ammonia is formed? How much hydrogen is consumed?
2. How is the equilibrium constant of a reverse reaction (products going to reactants) related to the equilibrium constant of the forward reaction?
3. Can equations analogous to Eq. (12) be written for the following?
  - (a) The entropy change of a reaction
  - (b) The volume change of a reaction
  - (c) The heat released in a reaction
4. What would be an acceptable reference state from which to calculate atomic energies in nuclear physics, where elements can be transmuted?
5. State whether each of the following is true or false in regard to the measured value of the equilibrium constant,  $K_a$ , of a gaseous chemical reaction:
  - (a) The same value should be obtained whether starting from reactants or products.
  - (b) The value obtained should be independent of time.
  - (c) The value obtained should be independent of total pressure.
  - (d) The value obtained should be independent of temperature.
6. For each of the following reactions, indicate whether  $\Delta H^\circ$  is greater, less, or just about equal to  $\Delta U^\circ$ :
  - (a)  $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)}$
  - (b)  $\text{H}_{2(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{HCl}_{(g)}$
  - (c) The electrolysis of liquid water
  - (d) The rusting of iron
7. In a table of standard thermodynamic properties of compounds at 298 K, indicate whether each of the following is always zero, always positive, always negative, or none of the above (do this without looking at such a table and be able to explain your answer):
  - (a)  $\Delta G_f^\circ$  of an element
  - (b)  $S^\circ$  of an element
  - (c)  $\Delta G_f^\circ$  of a non-elemental compound
  - (d)  $C_P^\circ$  of an element

8. Decide whether each of the following quantities is usually zero, positive, or negative:
  - (a)  $\Delta_{rxn} H^\circ$  of a dissociation reaction
  - (b)  $\Delta_{rxn} H^\circ$  of a combustion reaction
  - (c)  $\Delta_{rxn} S^\circ$  of a dissociation reaction
  - (d)  $\Delta_{rxn} C_p^\circ$  of a dissociation reaction
9. As mentioned, the reference-state for elemental bromine changes from liquid to gas at  $59^\circ\text{C}$ . Which of the following is discontinuous at  $59^\circ\text{C}$ ? Why?
  - (a) The heat of formation of atomic bromine
  - (b) The heat of the reaction  $\text{Br}_{(g)} + \text{Cl}_{2(g)} \rightarrow \text{BrCl}_{(g)} + \text{Cl}_{(g)}$
10.  $K_p$  for the reaction  $3\text{O}_2 \leftrightarrow 2\text{O}_3$  is  $10^{-57}$  at 298 K.
  - (a) What is the  $K_p$  for the reaction  $\frac{3}{2}\text{O}_2 \leftrightarrow \text{O}_3$ ?
  - (b) What is the  $K_p$  for the reaction  $\text{O}_3 \leftrightarrow \frac{3}{2}\text{O}_2$ ?
  - (c) Given the low value of the rate constant in part (a), how could you explain the presence of parts per million concentration of ozone in the stratosphere? This stratospheric ozone layer is largely responsible for shielding life on Earth from the deleterious effects of solar ultraviolet radiation in the range 200–300 nm.
11. Consider a mixture of ice in salt water. How many degrees of freedom has the system under each of the following conditions:
  - (a) It is open to the atmosphere,
  - (b) It is allowed to come to equilibrium with its vapor in the absence of air.
  - (c) In part (b), enough NaCl is added, so that solid NaCl is present.
12. How many degrees of freedom has each of the following systems:
  - (a) Solid  $\text{NH}_4\text{Cl}$  in the presence of gaseous  $\text{NH}_3$  and HCl
  - (b) Solid  $\text{NH}_4\text{Cl}$  heated in a sealed evacuated container
13. How many degrees of freedom has a system consisting of an aqueous solution of acetic acid and sodium acetate, in equilibrium with its vapor?
14. Consider an aqueous titration of NaOH by HCl in a vessel exposed to air (which can be taken as a single component). What are the components of this system? How many independent components and phases are there? How many degrees of freedom does the system have?
15. Show that both exothermic and endothermic reactions follow Le Chatelier's principle and moderate the effect of heat added to a reactive system at equilibrium.
16. Compare chemical reactions with phase transitions for use as thermal storage media for capturing sunlight during the day and releasing heat during the night.
17. Plot  $\Delta_{rxn} G$  and  $A$  (the affinity) for a reversible reaction as a function of  $\xi$ , in a region around  $\xi_e$ .

18. For which of the following reactions does  $K_a$  increase with temperature?
- The dissociation of ethane into methyl radicals
  - The reaction of hydrogen and oxygen to form water
  - $3\text{O}_2 \rightarrow 2\text{O}_3$
19. An aerogel is a solid with a density comparable to a gas. In a reaction involving an aerogel as reactant, should a term involving the aerogel be included in the equilibrium constant?
20. Discuss similarities and differences between the two forms for the equilibrium constant of an ideal gas reaction, Eqs. (37) and (59).
21. Show that Eq. (36) holds for the Haber process, regardless which of the equations of Example 6 are used to describe the process.

## Problems

- In the limit in which gases may be considered ideal and condensed-phase volumes neglected, show that  $\Delta_{rxn} V^\circ(T) = \Delta v_{\text{gas}} RT/P^\circ$ .
- Write the formation reaction for each of the following compounds at 298 K (indicate the phase of all species):  $\text{NH}_3$  (gas),  $\text{CH}_4$  (gas),  $\text{NH}_4\text{Br}$  (solid).
- In a constant-volume bomb calorimeter with a heat capacity of 13.418 kJ/K, 1.17 g of naphthalene,  $\text{C}_{10}\text{H}_8$ , is burned. Fifty-two joules of energy are required to ignite the sample. If the temperature rise of the calorimeter is 3.318 K, what is the  $\Delta U$  and  $\Delta H$  of combustion of naphthalene? What is the  $\Delta H_f$  of naphthalene? (You may assume that all water is formed in the liquid phase.)
- Using the data in [Appendix C](#), calculate  $\Delta_{rxn} H^\circ$  from heats of formation,  $\Delta_{rxn} S^\circ$  from absolute entropies and  $\Delta_{rxn} G^\circ$  from free energies of formation for the reaction  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  at 298 K. Verify that your results satisfy  $\Delta_{rxn} G^\circ = \Delta_{rxn} H^\circ - T\Delta_{rxn} S^\circ$ .
- Calculate  $\Delta_{rxn} H^\circ$  for the reaction  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  from generic bond dissociation energies and compare with the value obtained from heats of formation in Problem 4.
- Compare the values calculated for  $\Delta_{rxn} H^\circ$  of the reaction  $2\text{C}_2\text{H}_4 \rightarrow 1\text{-butene}$  using heats of formation, generic bond dissociation energies, and group additivities. (See Example 4.)
- At 298 K, the heat of formation and Gibbs free energy of formation of  $\text{CaCl}_2$  (solid) are  $-795.8$  kJ/mol and  $-748.1$  kJ/mol, respectively.
  - Using information in Appendix C, calculate  $\Delta_{rxn} H$  and  $\Delta_{rxn} G$  for the reaction  $\text{CaCl}_2(\text{solid}) + \text{H}_2(\text{gas}) \leftrightarrow 2\text{HCl}(\text{gas}) + \text{Ca}(\text{solid})$ .
  - Using your result from part (a), calculate  $S^\circ(\text{CaCl}_2(\text{solid}))$  at 298 K. Compare your result with that given in Appendix C.

8. What is the affinity (driving force) of the reaction  $\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$  in the atmosphere, where concentrations (by volume) are approximately 21%  $\text{O}_2$ , 300 ppm (parts per million)  $\text{CO}_2$ , and 100 pb (parts per billion)  $\text{CO}$ ?

9. Show that the activity of a condensed phase at high pressure is  $a = \exp((P - P^\circ)V_m/RT)$ . Calculate the activity of water at 100 atm ( $\approx 100$  bar pressure).

10.\* Using the results worked out in Example 13 for the equilibrium  $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$  at 298 K, write an expression for the volume as a function of pressure. You can assume that the gas behaves ideally. Find an expression for the isothermal compressibility,  $-(1/V)(\partial V/\partial P)_T$ . Show that this quantity is always greater than the compressibility of a constant number of moles of ideal gas.

11. Calculate  $K_a$  of the reaction  $\text{PCl}_3 + \text{Cl}_2 \leftrightarrow \text{PCl}_5$  at 25°C. Assuming temperature-independent heat capacities, calculate  $K_a$  at 300°C.

12. Using your result from problem 11, calculate the fraction of  $\text{PCl}_5$  that is dissociated at 25°C and 300°C.

13. Coke and steam react at a high temperature to produce a combustible mixture of CO and  $\text{CH}_4$  called water gas. Calculate  $K_a$  at 1000°C for this reaction, using the following:

- (a) The approximation of a temperature-independent heat of reaction
- (b) The approximation of temperature-independent heat capacities.

14. One of the most important industrial processes is the Haber process, based on the reaction  $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$ . Calculate the equilibrium constant of this reaction at 298 K and, using temperature-independent heat capacities, at 1000 K. In light of your result, can you guess why the reaction is carried out at a high temperature?

15. Using the value of  $K_a$  (1000 K) calculated in Problem 14 for the reaction  $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$ , calculate the mole fraction of  $\text{NH}_3$  produced at equilibrium in a reactor at 1000 K into which a 3 to 1 mixture of  $\text{H}_2$  to  $\text{N}_2$  is introduced.

16.\* Consider the dissociation of  $\text{N}_2\text{O}_4$  in the presence of an inert gas pressure  $P_{\text{inert}}$ . Considering  $\text{N}_2\text{O}_4$  as an ideal gas, it is obvious that the inert gas cannot influence the extent of its dissociation reaction. By reconstructing the table for Example 13, with an additional column for the inert gas, show that the inert gas changes  $K_x$  but not  $K_p$  or  $\xi_e$ .

17.  $\text{Fe}_2\text{O}_3$  (hematite) can be reduced to iron by reaction with the reducing agent CO. Calculate the ratio of the partial pressures of CO to  $\text{CO}_2$  in a mixture equilibrated by the reaction  $\text{Fe}_2\text{O}_3(\text{solid}) + 3\text{CO}(\text{gas}) \leftrightarrow 2\text{Fe}(\text{solid}) + 3\text{CO}_2(\text{gas})$  for the following:

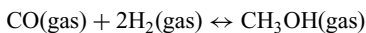
- (a) at 25°C
- (b) at 1000°C
- (c) Do these results depend on pressure? Explain your answer.

18.\* In the blast furnace, the iron oxides  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and FeO, are successively reduced to iron by CO produced by the reaction of coke with air. Calculate  $\Delta G^\circ$  at 1500 K for the reaction  $\text{FeO}(\text{solid}) + \text{CO}(\text{gas}) \leftrightarrow \text{Fe}(\text{solid}) + \text{CO}_2(\text{gas})$ , the final stage of reduction of iron oxide in the blast furnace, using the constant heat capacity approximation.



What does this equilibrium constant imply is necessary to reduce FeO(solid) to Fe(solid) at this temperature in the blast furnace? How is this brought about?

19. Consider the following reaction as a route to synthesize methanol:



- (a) Calculate the heat of this reaction and its equilibrium constant at 298 K. What partial pressure of CH<sub>3</sub>OH would exist in equilibrium with partial pressures of 5.0 atm each of CO and H<sub>2</sub> at this temperature?
  - (b) Using the constant heat capacity approximation, calculate the equilibrium constant of the reaction at 500 K. What partial pressure of CH<sub>3</sub>OH would exist in equilibrium with partial pressures of 5.0 atm each of CO and H<sub>2</sub> at this temperature?
20. Calculate  $\Delta C_p^\circ(298)$  for each of the following gas-phase reactions:
- (a)  $\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$
  - (b)  $\text{H}_2 + \text{Cl}_2 \leftrightarrow 2\text{HCl}$
  - (c)  $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$
  - (d)  $\text{C}_2\text{H}_4 + \text{H}_2 \leftrightarrow 2\text{CH}_4$
  - (e) From the results of your calculation, can you guess a generalization for when  $\Delta C_p^\circ$  might be small enough for a gas-phase reaction, so that the constant heat of reaction approximation could be used in making temperature corrections to the equilibrium constant?
  - (f) From what you have learned about heat capacities in [Chapter 5](#), can you offer any explanation for your result?

## Notes

1. In earlier compilations, a pressure of 1.0 atm was often chosen as the standard pressure. Because 1.0 atm = 1.01325 bar, the difference between the two compilations is usually negligible for all applications except those requiring the highest accuracy.
2. Some gaseous water will always form, due to its vapor pressure. If the volume is not too large, this may be negligible due to the low density of the vapor.
3. In the *JANAF Thermochemical Tables* [U.S. National Bureau Standards, NSRDS-NBS Pub. 37 (1971 and later)], thermodynamic data are tabulated at many different temperatures.
4. SW Benson. *Thermochemical Kinetics*. New York: Wiley, 1976.