

REVIEW OF CHEMICAL THERMODYNAMICS

Symbol	Description	Dimension
a	Affinity	
C	Molar concentration	N/L^3
C_P	Constant-pressure specific heat	$Q/(MT)$
C_v	Constant-volume specific heat	$Q/(MT)$
e	Specific internal energy	Q/M
e_t	Total stored energy per unit mass	Q/M
E	Stored energy	Q
f	Fugacity	F/L^2
f	Mixture fraction	
F/O	Fuel-oxidant ratio	
G	Gibbs free energy	Q
g	Gravitational acceleration	L/t^2
g_c	Factor of proportionality	ML/Ft^2
g_i	Molar specific Gibbs free energy for i th species	Q/N
H	Enthalpy	Q
\mathcal{H}	Molar specific enthalpy	Q/N
K_C	Equilibrium constant based on species concentration	$(N/L^3)^{\sum(v''_{i,e}-v'_{i,e})}$
K_n	Equilibrium constant based on moles of species	$N^{\sum(v''_{i,e}-v'_{i,e})}$

(continued overleaf)

Symbol	Description	Dimension
K_P	Partial-pressure equilibrium constant	
K_X	Mole-fraction equilibrium constant	
K_Y	Mass-fraction equilibrium constant	
KE	Kinetic energy	Q
m	Order of chemical reaction	
M	Total mass	M
M_i	Chemical symbol for species i	
m_i	Mass of species i	M
Mw_i	Molecular weight of species i	M/N
n_i	Number of moles of species i	N
n_t	Total number of moles of chemical species	N
p	Total system pressure	F/L^2
p_i	Partial pressure of species i	F/L^2
PE	Potential energy	Q
\hat{Q}	Heat	Q
R	Gas constant of gas mixture	$Q/(MT)$
R_u	Universal gas constant	$Q/(NT)$
S	Entropy	Q/T
s	Molar specific entropy	$Q/(NT)$
T	Temperature	T
t	Time	t
u_i	Velocity in the x_i -direction	L/t
U	Internal energy	Q
v	Specific volume	L^3/M
\mathbf{v}	Resultant velocity	L/t
V	Volume	L^3
\hat{W}	Work	Q
x_i	Space coordinate in the i th direction	L
X	Mole fraction	
Y	Mass fraction	
z	Elevation	L
Z	Compressibility factor, $pv = ZRT$	
$\Delta\mathcal{H}_{f,i}^o$	Standard heat of formation of species i	Q/N
ΔH_r	Heat of reaction	Q
$\Delta\mathcal{H}_v$	Heat of vaporization	Q/N
Γ	Proportionality constant f_i/p_i	
ε	Reaction progress variable	
μ	Chemical potential	Q/N
v'_i	Stoichiometric coefficient for species i appearing as a reactant	N
v''_i	Stoichiometric coefficient for species i appearing as a product	N
ρ	Density	M/L^3
ϕ	Equivalence ratio	

Symbol	Description	Dimension
<i>Superscript</i>		
$^{\circ}$	Standard-state condition (298.15 K and 1 bar)	
<i>Subscripts</i>		
g	Gas phase	
i	Index for i th species, or initial condition	
l	Liquid phase	
p	Constant-pressure process	
s	Solid phase	
v	Constant-volume process	
<i>Dimension Symbols</i>		
F	Force	
L	Length	
M	Mass	
N	Mole	
Q	Heat	
t	Time	
T	Temperature	

In this chapter, we briefly introduce and discuss some of the fundamental concepts of chemical thermodynamics and their application in solving those types of combustion problems in which only the initial and final thermodynamic states of a system are concerned. The application of a well-established chemical equilibrium calculation program (CEA), developed by Gordon and McBride^{1,2} to solve for the final equilibrium product composition and adiabatic flame temperature of a chemical system, is also discussed. Although many examples are given in this chapter to illustrate the use of chemical thermodynamic principles, the scope is too limited to provide an extensive discussion of every aspect of chemical thermodynamics. The reader is referred to the bibliography at the end of this chapter³⁻¹⁵ for broader coverage on chemical thermodynamics.

To set the scope of the chemical thermodynamics, let us first make a distinction between heat-transfer theory and thermodynamics. While heat-transfer theory deals with energy-transfer processes within a system or between a system and its surroundings due to a temperature gradient, thermodynamics deals with systems in equilibrium and therefore is applicable to phenomena involving flow and irreversible chemical reactions only when departures from equilibrium are small.

It is also important to note that the approach used in chemical thermodynamics is not a microscopic approach. Chemical thermodynamics treats matter in bulk, that is, with no regard for detailed molecular structures and microscopic events. Unlike kinetic theory, which can provide a certain amount of information about the rates of chemical processes, chemical thermodynamics can give only the final equilibrium conditions.

It is useful to define *thermodynamic equilibrium* by considering the following three distinct kinds of equilibrium:

- *Mechanical equilibrium* exists when there are no unbalanced forces in the interior of a system or between a system and its surroundings.
- *Thermal equilibrium* exists when all parts of a system are at the same temperature, which is the same as that of the surroundings.
- *Chemical equilibrium* exists when a system has no tendency to undergo a spontaneous change in chemical composition, no matter how slow.

When all three kinds of equilibrium are satisfied, the system is said to be in a state of *thermodynamic equilibrium*. Under such condition, the analysis becomes simpler, since the state variables do not change with respect to time. The state of complete equilibrium can then be described in terms of macroscopic coordinates. It is found that the thermodynamic coordinates that are independent and appropriate for combustion studies are the pressure in the system p , the volume V , and n_i , which represents the moles of all chemical species in different phases present in the system. Therefore, the symbol n_i stands for $n_{1g}, n_{2g}, \dots, n_{Ng}$ of all gas-phase species plus $n_{1l}, n_{2l}, \dots, n_{Nl}$ of all liquid-phase species and $n_{1s}, n_{2s}, \dots, n_{Ns}$ of all solid-phase species in the system.

The approach to be taken here will be that of irreversible (nonequilibrium) thermodynamics rather than classical. It is useful to understand the major difference between the two and the reason for using the nonequilibrium approach in combustion studies. First of all, classical thermodynamics can make predictions only about states of thermodynamic equilibrium; it can tell us nothing about the rates at which processes take place. When a process is followed by means of classical thermodynamics, it must be regarded as consisting of a succession of states of thermodynamic equilibrium, that is, as taking place infinitely slowly. Such processes are necessarily reversible. A *reversible* process is one that is performed in such a way that the system and its surroundings can both return to their initial states. Such a process must be carried out very slowly so that the system remains in equilibrium throughout. In the real world, we must deal with irreversible processes that are a succession of nonequilibrium states. To do this in any detail, the notions of classical thermodynamics must be supplemented.

For systems in mechanical or thermal nonequilibrium, the usual procedure is to divide the system into a large number of subsystems that are of infinitesimal size relative to the original system, but still of macroscopic size relative to the molecular structure of the medium. By assuming that each subsystem is in local equilibrium internally (but not necessarily in equilibrium with its surrounding subsystems), we can apply equilibrium thermodynamics and the concept of state variables to the subsystems. We can thus construct, by integration, a picture of the behavior of the entire nonequilibrium system. This is normally done with such success in fluid dynamics and heat transfer that it is scarcely given a second thought.

When we come to the description of a system in chemical nonequilibrium, the procedure is somewhat different. We shall assume that the system is in mechanical and thermal equilibrium and that it is homogeneous in space. We assume the system to have a definite volume V ; since it is in mechanical and thermal equilibrium, we can assign to it a definite pressure p . Furthermore, since the system is homogeneous, its composition can be specified by giving the number of moles,[†] n_i , of each of the constituent chemical species, M_i . Thus, the thermodynamic state of a system of N chemical species can be completely stated by specifying the values of $p, V, n_1, n_2, \dots, n_N$; the pressure, p , is an intensive property, while V and n_i ($i = 1, 2, \dots, N$) are extensive properties. Intensive and extensive properties are defined as follows:

An *intensive* property is one that is unchanged when the size of the system is increased by adding to it any number of systems that are identical to the original system. Some intensive properties are density, pressure, temperature, specific internal energy u , specific entropy s , chemical potential of j th species μ_j , mass fraction of k th species Y_k , and so on.

An *extensive* property is one that increases in proportion to the size of the system in such a process. Some extensive properties are volume V , mass m , total stored energy E , enthalpy H , Gibbs free energy G , kinetic energy KE, potential energy PE, and so on.

An intensive property can be formed by dividing an extensive property by another extensive property.

1 BRIEF STATEMENT OF THERMODYNAMIC LAWS

When discussing the laws of thermodynamics, it is useful to classify systems according to the exchanges of energy (heat and work) and mass that can take place across the system boundary:

- *Isolated* systems exchange neither energy nor mass with their surroundings; i.e., $\delta \hat{Q} = 0$ and $\Delta m = 0$.
- *Closed* systems exchange energy but no mass with their surroundings.
- *Open* systems exchange both energy and mass with their surroundings.

A. The Zeroth Law of Thermodynamics This states that there exists an intensive variable, the temperature

$$T = T(p, V, n_i) \quad (1-1)$$

[†] The unit g-mole is commonly used for n_i ; one g-mole designates the quantity of substance M_i whose mass in grams is equal to the molecular weight of the substance. One mole of any substance contains 6.02252×10^{23} molecules; these molecules could be in the form of atoms, ions, radicals, or undissociated molecules. This number is called Avogadro's number in honor of the Italian physicist Amedeo Avogadro. Avogadro's number can also be considered as 6.02252×10^{26} molecules/kmole.

When two bodies have the same temperature as a third body, they have the same temperature as each other and therefore will be in equilibrium if placed in thermal contact. In other words, two systems are in thermal equilibrium with each other if they have the same temperature. This seems very obvious to us because we are so familiar with the experimental result. Though formulated after the other laws, it precedes them logically, and for this reason it has been called the zeroth law. This law suggests the need for a standard scale for temperature measurements. Equation (1-1) is called the equation of state.

B. The First Law of Thermodynamics (Conservation of Energy) This states that there exists an extensive function called the stored energy E , composed of (1) internal energy U , (2) kinetic energy KE, and (3) potential energy PE:1

$$E = U + \text{KE} + \text{PE} \quad (1-2)$$

where

$$E = E(p, V, n_i) \quad (1-3)$$

The function E has the property that, for a closed system (no mass exchange with its surroundings), the heat added to the system in an infinitesimal process is related to the change of E and the work done by the system ($\delta\hat{W}$), according to

$$\delta\hat{Q} = dE + \delta\hat{W} \quad (1-4)$$

where the caret (\wedge) over a variable indicates that the variable is not a thermodynamic property, and δ indicates an inexact differential, since \hat{Q} and \hat{W} are path-dependent functions. Note that the work done by the system in chemical equilibrium can be written as $p dV$.

The first law under no change of KE and PE can be written as

$$dU = \delta\hat{Q} - p dV \quad (1-4a)$$

For a constant-volume condition, we have

$$du = \delta\hat{Q} \quad (1-4b)$$

Since the enthalpy H is defined as $H \equiv U + pV$ or $dH = dU + p dV + V dp$, the first law in the form of Eq. (1-4a) becomes

$$dH = \delta\hat{Q} + V dp \quad (1-4c)$$

For $p = \text{constant}$,

$$dH = \delta\hat{Q} \quad (1-4d)$$

The work terms in the energy conservation equation in a flow system are derived in Chapter 3. The conversion between heat and work for systems undergoing cyclic variations is discussed in the next section.

C. The Second Law of Thermodynamics This states that there exists an absolute scale for the temperature and an extensive function called the entropy:

$$S = S(p, V, n_i) \quad (1-5)$$

Thus, for an infinitesimal process in a closed system,

$$TdS \geq \delta\hat{Q} \quad (1-6)$$

where the equality is valid for reversible processes and the inequality valid for natural (irreversible) processes.

D. The Third Law of Thermodynamics According to W. H. Nernst and M. Planck, this states that the entropy of a perfect crystal is zero at the absolute zero of temperature. This is used as the base or the reference value for evaluating entropies of various substances. As stated clearly by Van Wylen and Sonntag,³ from a statistical point of view this means that the crystal structure is such that it has the maximum degree of order. It also follows that a substance that does not have a perfect crystalline structure at absolute zero but instead has a degree of randomness (such as a solid solution or a glassy solid) has a finite value of entropy at absolute zero. The experimental evidence on which the third law rests is primarily data on chemical reactions at low temperatures and measurements of the heat capacity at temperatures approaching absolute zero. The molar entropy of the substance at temperature T and 1 bar can be calculated from

$$S_T^o = S_{T_o}^o + \int_{T_o}^T \frac{\bar{C}_P}{T} dT$$

where T_o is the reference temperature, at which $S_{T_o}^o$ is known. At temperature T and pressure p , the molar entropy can be calculated from

$$S_{T,p} = S_T^o - R_u \ln \frac{p}{p_o}$$

if the assumption of ideal gas behavior along the isotherm at T yields an insignificant amount of error.

2 EQUATION OF STATE

In general, for a closed system of known material at a volume V and temperature T , there will be one set of values of n_i for which the system is in chemical equilibrium. Then,

$$n_i^* = n_i^*(V, T) \quad (1-7)$$

where the values of n_i^* are the equilibrium values. The equation of state for a system in equilibrium becomes

$$p = p(V, T, n_1^*, n_2^*, \dots, n_N^*) \quad (1-8)$$

From Dalton's law of partial pressures, we know that for a mixture of thermally perfect gases in thermodynamic equilibrium,

$$p = \frac{1}{V} \sum_{i=1}^N n_i^* R_u T \quad (1-9)$$

The pressure of the system in chemical nonequilibrium can be represented by the following equation, which has the same form as Eq. (1-9) except the asterisk has been removed from n_i :

$$p = \frac{1}{V} \sum_{i=1}^N n_i R_u T \quad (1-10)$$

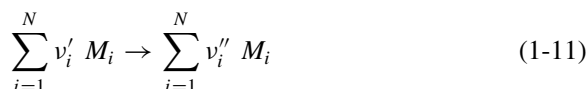
or expressed as

$$p = \frac{n_t R_u T}{V} = \frac{m R T}{V} = \frac{R T}{v} \quad (1-10a)$$

where n_t is the total number of moles of all chemical species in the system.

3 CONSERVATION OF MASS

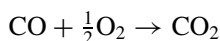
In a closed system, the total mass of the contents cannot change. If the system is under a chemical nonequilibrium situation, the amounts of the individual species will vary. A single arbitrary chemical reaction can be written as



where ν'_i is the coefficient for species i appearing as a reactant, ν''_i is the coefficient for species i appearing as a product, and M_i represents the chemical symbol for species i . Species that are not reactants have $\nu'_i = 0$, while those that do not appear as products have $\nu''_i = 0$.

Equation (1-11) implies that when $(\nu''_i - \nu'_i)$ moles of M_i are formed, $(\nu'_j - \nu''_j)$ moles of M_j disappear due to the chemical reaction (note that $j \neq i$). This reaction equation indicates a relationship between the changes in the number of moles of each species.

Example 1.1. Let us consider the oxidation of CO to form CO₂, according to



Let

$$M_1 = \text{CO}$$

$$M_2 = \text{O}_2$$

$$M_3 = \text{CO}_2$$

Then,

$$\nu'_1 = 1 \quad \nu''_1 = 0$$

$$\nu'_2 = \frac{1}{2} \quad \nu''_2 = 0$$

$$\nu'_3 = 0 \quad \nu''_3 = 1$$

When

$$\begin{aligned} v_3'' - v_3' &= 1 \text{ mole of CO}_2 \text{ is formed, } \Delta n_3 = 1 \\ v_1'' - v_1' &= 1 \text{ mole of CO disappears, } \Delta n_1 = -1 \\ v_2'' - v_2' &= \frac{1}{2} \text{ mole of O}_2 \text{ disappears, } \Delta n_2 = -\frac{1}{2} \end{aligned}$$

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This example shows that we obtained the following relationship between the changes of moles of reactants and the product species:

$$\frac{\Delta n_1}{v_1'' - v_1'} = \frac{\Delta n_2}{v_2'' - v_2'} = \frac{\Delta n_3}{v_3'' - v_3'}$$

Now let us generalize it to any elementary reaction involving an infinitesimal change. It is convenient to introduce a dimensionless single-reaction progress variable ε , so that

$$dn_i = (v_i'' - v_i') d\varepsilon \quad i = 1, 2, \dots, N \quad (1-12)$$

If $n_{i,r}$ denotes the number of moles of the various species at the same initial or reference condition at which ε is zero, the above equation can be integrated to obtain

$$n_i - n_{i,r} = (v_i'' - v_i')\varepsilon \quad i = 1, 2, \dots, N \quad (1-13)$$

It follows from Eq. (1-13) that for a closed system in which a single reaction occurs, the n_i 's in the thermodynamic state relations can be replaced by the quantities $n_{i,r}$ and the degree of reaction ε . For a system in which the composition at some reference condition is known, the thermochemical state of the system can be specified by

$$p = p(V, T, \varepsilon) \quad (1-14)$$

where the quantity ε can itself be regarded as a state variable. Chemical equilibrium for a given V and T will correspond to certain equilibrium values of n_i^* , and hence to a specific value ε^* of ε .

If m_i is the mass of the i th species and Mw_i the molecular weight of that species, then from Eq. (1-12)

$$dm_i = (v_i'' - v_i') Mw_i d\varepsilon \quad i = 1, 2, \dots, N \quad (1-15)$$

Since the total mass of a closed system is constant,

$$m = \sum_{i=1}^N m_i = \text{constant} \quad (1-16)$$

We therefore have

$$\sum_{i=1}^N dm_i = 0 \quad (1-17)$$

Substituting Eq. (1-15) into Eq. (1-17), we have

$$\sum_{i=1}^N [(v_i'' - v_i')] M w_i d\varepsilon = 0 \quad (1-18)$$

If the degree of the reaction is not zero (i.e., $d\varepsilon \neq 0$), then

$$\sum_{i=1}^N [(v_i'' - v_i')] M w_i = 0 \quad (1-19)$$

which is known as the *stoichiometric equation*. If Eq. (1-12) is differentiated with respect to time, we obtain

$$\frac{dn_i}{dt} = (v_i'' - v_i') \frac{d\varepsilon}{dt} \quad (1-20)$$

which is the rate equation.

4 THE FIRST LAW OF THERMODYNAMICS; CONSERVATION OF ENERGY

The first law of thermodynamics states that during any cycle a system undergoes, the cyclic integral of the heat is equal to the cyclic integral of work, i.e.,

$$\oint \delta \hat{Q} = \oint \delta \hat{W} \quad (1-21)$$

where $\oint \delta \hat{Q}$ is the cyclic integral of the energy transfer or the net heat transferred during the cycle, and $\oint \delta \hat{W}$ is the cyclic integral of the work or the net work done during the cycle. The first law also implies the existence of a function of state called the stored energy E of the system and relates the change of this function to the flow of energy from the surroundings.

The existence of the thermodynamic property E can be demonstrated as follows: By Eq. (1-21), we can write the cyclic integral of heat and work by taking paths a and b (Fig. 1.1). Then, we have

$$\int_{1a}^{2a} \delta \hat{Q} + \int_{2b}^{1b} \delta \hat{Q} = \int_{1a}^{2a} \delta \hat{W} + \int_{2b}^{1b} \delta \hat{W} \quad (1-22a)$$

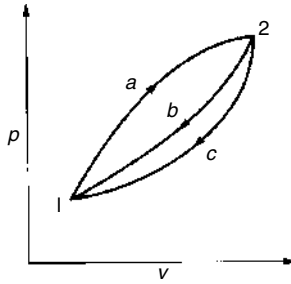


Figure 1.1 Demonstration of the existence of the thermodynamic property E .

We now consider another cycle, the system changing from state 1 to state 2 by process a , as before, and returning to state 1 by process c . Then,

$$\int_{1a}^{2a} \delta \hat{Q} + \int_{2c}^{1c} \delta \hat{Q} = \int_{1a}^{2a} \delta \hat{W} + \int_{2c}^{1c} \delta \hat{W} \tag{1-22b}$$

After subtracting the second of these equations from the first and rearranging them, we have

$$\int_{2b}^{1b} (\delta \hat{Q} - \delta \hat{W}) = \int_{2c}^{1c} (\delta \hat{Q} - \delta \hat{W}) \tag{1-23}$$

Since b and c represent arbitrary processes between states 1 and 2, $(\delta \hat{Q} - \delta \hat{W})$ is the same for all processes between 1 and 2. Therefore, $(\delta \hat{Q} - \delta \hat{W})$ depends only on the initial and final state and not on the path followed between the two states. We may conclude that $(\delta \hat{Q} - \delta \hat{W})$ is a point function and therefore is the exact differential of the system. This property is the energy of the system and is represented by the symbol E . We have

$$dE \equiv \delta \hat{Q} - \delta \hat{W} \tag{1-24}$$

where the sign preceding $\delta \hat{W}$ is negative because $\delta \hat{W}$ is the work done *by* the system.

The physical significance of the property E is that it represents all the energy of the system in the given state. This energy can be present in many forms, including thermal energy, kinetic energy, potential energy (with respect to the chosen coordinate frame), energy associated with the motion and position of molecules, energy associated with atomic structure, chemical energy (e.g., in a storage battery), electrostatic energy (e.g., in a charged capacitor), and so on.

In the study of thermodynamics, it is convenient to consider the bulk kinetic energy and potential energy separately and then to lump all other forms of energy of the system in a single property, which we shall call *internal energy* and give the symbol U . Therefore,

$$E = \text{internal energy} + \text{kinetic energy} + \text{potential energy} = U + \text{KE} + \text{PE}$$

where

$$\text{KE} = \frac{1}{2}m|\mathbf{v}|^2 \quad \text{and} \quad \text{PE} = mgz \quad (1-25)$$

In differential form, this is $dE = dU + d(\text{KE}) + d(\text{PE})$, which from Eqs. (1-24) and (1-25) may be written

$$\delta \hat{Q} = dU + d\left(\frac{1}{2}m|\mathbf{v}|^2\right) + d(mgz) + \delta \hat{W} \quad (1-26)$$

Assuming g is a constant, the above equation may be integrated between states 1 and 2 to give

$${}_1\hat{Q}_2 = (U_2 - U_1) + m \left[\frac{|\mathbf{v}_2|^2 - |\mathbf{v}_1|^2}{2} \right] + mg(z_2 - z_1) + {}_1\hat{W}_2 \quad (1-27)$$

Here, the internal energy U is an extensive property like the kinetic and potential energies, since all depend on the mass of the system.

The work term includes three forms of work. *Shaft work* (\hat{W}_s) is work done to produce an effect external to the system, that is, work that can be made to turn a shaft or raise a weight. *Flow work* is work performed to overcome pressure effects at any point on the boundary where mass flow occurs. The flow work rate can be written as

$$p \frac{dV}{dt} = \frac{p}{\rho} \left(\frac{\rho dV}{dt} \right) = \frac{p}{\rho} \dot{m} \quad (1-28)$$

Viscous work (\hat{W}_μ) is work done to overcome fluid friction effects on the boundary where mass flow occurs. The work rate can be written as

$$\frac{\delta \hat{W}}{\delta t} = \frac{\delta \hat{W}_s}{\delta t} + \frac{\delta \hat{W}_\mu}{\delta t} + \int \frac{p}{\rho} d\dot{m}_{\text{out}} - \int \frac{p}{\rho} d\dot{m}_{\text{in}} \quad (1-29)$$

For a closed system undergoing an infinitesimal reversible process, the law is usually expressed in classical (i.e., equilibrium) thermodynamics by the equation

$$dU = \delta \hat{Q} - p dV \quad (1-30)$$

where we have assumed no viscous or shaft work and no kinetic or potential energy change. $\delta \hat{Q}$ represents the amount of heat the system receives from its surroundings, and $p dV$ represents the flow work done by the system. Here, p and U are state functions related to the other variables V and T by state equations of the form

$$p = p(V, T), \quad U = U(V, T) \quad (1-31)$$

For studying chemical nonequilibrium problems, the law of conservation of energy can be applied. It is necessary, however, to redefine the state functions p and U as

$$p = p(V, T, n_1, n_2, \dots, n_N), \quad U = U(V, T, n_1, n_2, \dots, n_N) \quad (1-32)$$

When the system is in equilibrium, the n_i reduce to $n_i^*(T, V)$ and the state equations (1-32) reduce to the equilibrium relations (1-31). We can thus consider complete thermodynamic equilibrium as a special, limiting case of chemical nonequilibrium. In nonequilibrium thermodynamics, as in equilibrium thermodynamics, it is useful to define the enthalpy by the equation

$$H \equiv U + pV \quad (1-33)$$

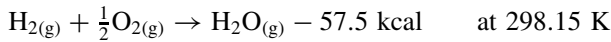
For chemical nonequilibrium cases, H is also given by a state relation of the form

$$H = H(V, T, n_1, n_2, \dots, n_N) \quad (1-34)$$

or

$$H = H(V, T, \varepsilon) \quad (1-35)$$

Example 1.2. Consider the following reaction occurring at a constant volume without any product dissociation:



For a constant-volume process, the first law becomes

$$dU = \delta \hat{Q} \quad (1-36)$$

Since the internal energy is a point function and independent of the path, the energy change equals the heat change for the chemical process, and

$$\Delta U = (\Delta \hat{Q})_v = -57.5 \text{ kcal}$$

Consider the same reaction occurring under constant pressure. The first law for this case is

$$dU = \delta \hat{Q} - p dV \quad (1-37)$$

this integrates to

$$\Delta U = (\Delta \hat{Q})_p - p(\Delta V)_p \quad (1-38)$$

If the reaction is carried out isothermally at T and a constant pressure p , then per mole of H_2O we have

$$\Delta U = (\Delta \hat{Q})_p - R_u T \Delta n$$

where $\Delta n = (n_{\text{products}} - n_{\text{reactants}})_{\text{ideal gas}} = -\frac{1}{2}$. Therefore,

$$(\Delta \hat{Q})_p = \Delta U - \frac{1}{2}R_u T = -57.796 \text{ kcal}$$

Note that this value is different from that of $(\Delta \hat{Q})_v$, since \hat{Q} is a path-dependent variable. This example further demonstrates that 0.296 kcal more heat is evolved

when the reaction is carried out at a constant pressure than at a constant volume. The additional heat, $R_u T \Delta n$, is a result of the work of the surroundings on the gas in maintaining it at a constant pressure p during the reaction, while its volume is decreasing. This shows that the heat evolved in a chemical reaction depends on the physical conditions (path-dependent) under which the reaction occurs.

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It is useful to note that the first law places no restrictions on the direction of flow of heat and work. We know from our experience that a proposed cycle that does not violate the first law does not ensure that the cycle will actually occur. It is this kind of experimental evidence that has led to the formulation of the second law of thermodynamics. Thus, a cycle³ (such as Rankine cycle, Brayton cycle, Diesel cycle, Otto cycle) will occur only if both the first and second laws of thermodynamics are satisfied.

5 THE SECOND LAW OF THERMODYNAMICS

Before we talk about the second law of thermodynamics, let us recall that a *reversible process* for a system is defined as a process that, once having taken place, can be reversed and, in so doing, leaves no change in either the system or surroundings. In general, factors that render processes irreversible include friction, heat transfer, mixing of different gases, combustion, unrestrained expansion, i^2R loss, etc.

5.1 Equilibrium Thermodynamics

The second law of thermodynamics postulates the existence of a state function called the entropy S and defines the basic properties of this function. For a closed system that undergoes a change from one state of thermodynamic equilibrium 1 to another state 2, the change in entropy is given by

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta \hat{Q}}{T} \right)_{\text{rev}} \quad (1-39)$$

where *rev* implies any reversible path between 1 and 2, $\delta \hat{Q}$ is the heat received from or added to the system, and T is the corresponding absolute temperature of the reservoir or the system. The important point to note here is that since the change in the entropy of a substance is path-independent, it is also the same for all processes. The equation given here enables us to find the change in entropy only along a reversible path, but once evaluated, the magnitude of change is the same for all processes between these two states. We may also note here that T takes the role of an integrating factor in that it has converted the inexact differential $\delta \hat{Q}$ to the exact differential $(\delta \hat{Q}/T)_{\text{rev}}$.

If the same system undergoes an irreversible or real process between the same two equilibrium end states 1 and 2, we have

$$(S_2 - S_1)_{\text{irrev}} > \int_1^2 \left(\frac{\delta \hat{Q}}{T} \right)_{\text{irrev}} \tag{1-40}$$

where $\delta \hat{Q}$ is the heat added to the system in the particular process.

The above result is arrived at by the following considerations. Consider a system that undergoes two cycles between states 1 and 2; one cycle consists of two reversible processes *a* and *b*, and the other cycle consists of path *a* and an irreversible process *c*. (See Fig. 1.2.) For the reversible cycle,

$$\oint \frac{\delta \hat{Q}}{T} = \int_{1a}^{2a} \frac{\delta \hat{Q}}{T} + \int_{2b}^{1b} \frac{\delta \hat{Q}}{T} = 0 \tag{1-41}$$

For the cycle consisting of the reversible process *a* and the irreversible process *c*, we have

$$\oint \frac{\delta \hat{Q}}{T} = \int_{1a}^{2a} \frac{\delta \hat{Q}}{T} + \int_{2c}^{1c} \frac{\delta \hat{Q}}{T} < 0 \tag{1-42}$$

which is a statement of the inequality of Clausius.³ (The inequality of Clausius is a corollary of the second law of thermodynamics. It has been demonstrated to be valid for all possible cycles.) Subtracting Eq. (1-42) from Eq. (1-41) gives

$$\int_{2b}^{1b} \frac{\delta \hat{Q}}{T} > \int_{2c}^{1c} \frac{\delta \hat{Q}}{T} \tag{1-43}$$

Since entropy is a thermodynamic property and *b* is a reversible process,

$$\int_{2b}^{1b} \frac{\delta \hat{Q}}{T} = \int_{2b}^{1b} dS = \int_{2c}^{1c} dS \tag{1-44}$$

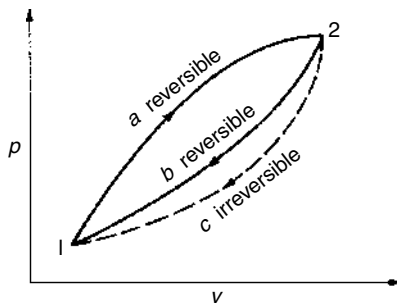


Figure 1.2 Two different cycles to demonstrate the fact that entropy is a property of a substance.

Therefore,

$$\int_{2b}^{1b} dS > \int_{2c}^{1c} \frac{\delta \hat{Q}}{T} \quad (1-45)$$

or, in general,

$$dS \geq \frac{\delta \hat{Q}}{T} \quad (1-46)$$

which when integrated between states 1 and 2 gives the desired result

$$(S_2 - S_1)_{\text{irrev}} > \int_1^2 \left(\frac{\delta \hat{Q}}{T} \right)_{\text{irrev}} \quad (1-47)$$

In both cases considered, the temperature T is the absolute temperature of the reservoir that supplies the heat $\delta \hat{Q}$. Since the temperature of the reservoir and the temperature of the system are equal in a reversible process, T in Eq. (1-39) is also the temperature of the system. For irreversible processes, however, the temperature of the system is undefined within the context of classical thermodynamics. Therefore, we have to consider the nonequilibrium thermodynamics.

5.2 Nonequilibrium Thermodynamics

Given the existence of a variable of state called the entropy S , the change in entropy, dS , in any closed system undergoing any process can be split into two parts:

$$dS = d_e S + d_i S \quad (1-48)$$

where $d_e S$ is the change in entropy resulting from interaction between the system and its surroundings (i.e., heat transfer to or from the system), and $d_i S$ is the change in entropy resulting from a process taking place within the system (e.g., chemical reaction, constant-pressure mixing of different gases). These differential quantities may also be thought of respectively as the flow of entropy into the system from the surroundings and the production of entropy by irreversible processes within the system.

The entropy change $d_i S$ is never negative:

$$d_i S = 0 \quad (\text{reversible process}) \quad (1-49)$$

$$d_i S > 0 \quad (\text{irreversible process}) \quad (1-50)$$

For a *closed* system undergoing any process, reversible or irreversible, $d_e S$ is given by

$$d_e S = \frac{\delta \hat{Q}}{T} \quad (1-51)$$

For a closed system undergoing an irreversible process, Eq. (1-48) becomes, after integration,

$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \left(\frac{\delta \hat{Q}}{T} \right) + \int_1^2 d_i S \quad (1-52)$$

For an irreversible process, $d_i S > 0$, and thus Eq. (1-52) includes the inequality of the classical statement. The latter relationship [Eq. (1-52)] is much more useful than the former [Eq. (1-47)] in that it replaces an inequality by an equality, and thus implies an ability to actually calculate $d_i S$.

For an *isolated* system, $\delta \hat{Q} = 0$; hence $d_e S = 0$ and Eq. (1-48) reduces to

$$dS = d_i S \geq 0 \quad (1-53)$$

This is equivalent to the familiar classical statement that the entropy of an isolated system can never decrease.

If mass is added to an *inert open reversible* system, the entropy associated with the additional mass can be considered to be a part of the entropy flow into the system from the surroundings. We then have

$$dS = d_e S = \frac{\delta \hat{Q}}{T} + \sum_{j=1}^N s_j d_e n_j \quad (1-54)$$

where s_j is the entropy per mole of the j th species added, and $d_e n_j$ is the change in number of moles of the j th species flowing into the system. With mass addition, the first law becomes

$$dU = \delta \hat{Q} - pdV + \sum_{j=1}^N h_j d_e n_j \quad (1-55)$$

where h_j is the enthalpy per mole associated with the j th species flowing into the system.

Let us define a new parameter μ_j in which

$$\mu_j \equiv h_j - T s_j \quad (1-56)$$

where μ_j represents the chemical potential, which will later be shown to equal the change of Gibbs free energy per mole of the i th species. [The more fundamental definition of μ_j is given by Eq. (1-80), to be discussed later in detail.] Dividing Eq. (1-55) by T , we obtain

$$\frac{\delta \hat{Q}}{T} = \frac{dU}{T} + \frac{pdV}{T} - \frac{1}{T} \sum_{j=1}^N h_j d_e n_j \quad (1-57)$$

Substituting Eqs. (1-57) and (1-56) into Eq. (1-54) gives

$$dS = d_e S = \frac{1}{T} dU + \frac{p}{T} dV - \frac{1}{T} \sum_{j=1}^N \mu_j d_e n_j \quad (1-58)$$

for an *inert open reversible* system.

Equation (1-58) is based on the assumption that all the species involved were chemically inert; hence there exist no irreversible processes resulting from chemical reactions within the system. When chemical reactions occur, the mole number of j th species may change both by mass addition from outside the system and by chemical reaction inside. Then, an infinitesimal process involving change in p , T , and n_j will, in general, be irreversible, since the system will not be in chemical equilibrium. Therefore,

$$dn_j = d_i n_j + d_e n_j \quad (1-59)$$

where $d_i n_j$ represents internal differential change of the moles of the j th species due to chemical reaction occurring inside the system, while $d_e n_j$ represents differential change of the moles of the j th species due to the exchange of j th material with its surrounding. If we further consider each species j to occupy a separate subsystem of the total system, then each subsystem can be regarded as an inert open system. This means that for each species

$$dS_j = \frac{1}{T} dU_j + \frac{p_j}{T} dV - \frac{1}{T} \mu_j dn_j \quad (1-60)$$

where p_j is the partial pressure due to species j , and U_j is the internal energy associated with species j . Summing the preceding equation over all species (i.e., over all subsystems) and noting that

$$p = \sum_{j=1}^N p_j \quad (1-61)$$

$$U = \sum_{j=1}^N U_j \quad (1-62)$$

$$S = \sum_{j=1}^N S_j \quad (1-63)$$

we obtain for the total system

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{1}{T} \sum_{j=1}^N \mu_j dn_j \quad (1-64)$$

which is the fundamental equation of chemical thermodynamics for *open irreversible chemical processes*. This is identical to Eq. (1-58) with the subscript e dropped from the d . Equation (1-64) is the result obtained by combining the first and second laws to describe an open system with chemical reactions.

From the equation of state, we have

$$S = S(U, V, n_1, n_2, \dots, n_N) \quad (1-65)$$

or in differential form

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V, n_j} dU + \left(\frac{\partial S}{\partial V}\right)_{U, n_j} dV + \sum_{j=1}^N \left(\frac{\partial S}{\partial n_j}\right)_{U, V, n'_j} dn_j \quad (1-66)$$

where the symbol n'_j in the last term indicates that all mole numbers except n_j itself are held constant when the derivative is taken. By comparing Eqs. (1-64) and (1-66) we have

$$\left(\frac{\partial S}{\partial U}\right)_{V, n_j} = \frac{1}{T} \quad (1-67)$$

$$\left(\frac{\partial S}{\partial V}\right)_{U, n_j} = \frac{p}{T} \quad (1-68)$$

and

$$-T \left(\frac{\partial S}{\partial n_j}\right)_{U, V, n'_j} = \mu_j \quad (1-69)$$

The enthalpy is defined as

$$H \equiv U + pV \quad (1-70)$$

or, in the differential form, as

$$dU = dH - p dV - V dp \quad (1-71)$$

Substituting Eq. (1-71) into Eq. (1-64), we obtain

$$dS = \frac{1}{T} dH - \frac{V}{T} dp - \frac{1}{T} \sum_{j=1}^N \mu_j dn_j \quad (1-72)$$

Similarly we can obtain

$$\mu_j = -T \left(\frac{\partial S}{\partial n_j}\right)_{H, p, n'_j} \quad (1-73)$$

Combining Eq. (1-69) with Eq. (1-73) gives

$$\left(\frac{\partial S}{\partial n_j}\right)_{H,p,n'_j} = \left(\frac{\partial S}{\partial n_j}\right)_{U,V,n'_j} \quad (1-74)$$

In the following, we shall develop the relationship between μ_j and the change of Gibbs free energy. The *Gibbs free energy* G , an extensive property, is defined by the relation

$$G \equiv H - TS = U + pV - TS \quad (1-75)$$

where G , like H , may be considered as a secondary state variable.

In differential form

$$dG = dH - T dS - S dT \quad (1-76)$$

which upon substitution into Eq. (1-72) gives

$$dG = V dp - S dT + \sum_{j=1}^N \mu_j dn_j \quad (1-77)$$

Since

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_j} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_j} dT + \sum_{j=1}^N \left(\frac{\partial G}{\partial n_j}\right)_{p,T,n'_j} dn_j$$

by comparing the coefficients of the above two equations, we can therefore write

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n_j} \quad (1-78)$$

$$S = - \left(\frac{\partial G}{\partial T}\right)_{p,n_j} \quad (1-79)$$

$$\mu_j \equiv \left(\frac{\partial G}{\partial n_j}\right)_{p,T,n'_j} = -T \left(\frac{\partial S}{\partial n_j}\right)_{H,p,n'_j} \quad (1-80)$$

where Eq. (1-80) can be taken as the definition of μ_j , which is known as the chemical potential and plays an important role in chemical thermodynamics. The chemical potential, an intensive variable, is in general a function of the state of the system, as given by p , T , and all n_j . Even though a species is not present in a system, its chemical potential need not be zero. There is always the possibility of introducing it into the system, in which case the value of G will be altered, and the value of the corresponding μ_j must therefore be different from zero.

The first law of thermodynamics for an open system can be expressed as

$$dU = \delta \hat{Q} - p dV + d_e U \quad (1-81)$$

where $d_e U$ is the internal energy carried in by mass addition. Substituting this into Eq. (1-64), we obtain

$$dS = d_e S + d_i S = \frac{1}{T} \overbrace{(\delta \hat{Q} - p dV + d_e U)}^{dU} + \frac{p}{T} dV - \frac{1}{T} \overbrace{\sum_{j=1}^N \mu_j d_e n_j - \sum_{j=1}^N \mu_j d_i n_j}^{-\frac{1}{T} \sum_{j=1}^N \mu_j d n_j}$$

Thus,

$$dS = \frac{1}{T} \left(\delta \hat{Q} + d_e U - \sum_{j=1}^N \mu_j d_e n_j \right) - \frac{1}{T} \sum_{j=1}^N \mu_j d_i n_j \quad (1-82)$$

where the two terms on the right-hand side correspond to the terms $d_e S$ and $d_i S$, respectively. Therefore,

$$d_i S = -\frac{1}{T} \sum_{j=1}^N \mu_j d_i n_j \quad (1-83)$$

which upon substitution of Eq. (1-73) becomes

$$d_i S = \sum_{j=1}^N \left(\frac{\partial S}{\partial n_j} \right)_{H,p,n'_j} d_i n_j \quad (1-84)$$

If we consider a single-step forward reaction in a closed system, then $d_i n_j$ can be given in terms of the change of the reaction progress variable, $d\varepsilon$, i.e.,

$$d_i n_j = (v_j'' - v_j') d\varepsilon \quad (1-85)$$

Substitution into Eq. (1-83) gives

$$d_i S = -\frac{1}{T} \left(\sum_{j=1}^N (v_j'' - v_j') \mu_j \right) d\varepsilon \geq 0 \quad (1-86)$$

This expression is required by the second law to be either positive, corresponding to an irreversible process, or zero, corresponding to a reversible process. Saying that a process is reversible in the present context is, however, equivalent to saying that the system is in chemical equilibrium at all times, or that the process is one of an infinitely slow succession of states of chemical equilibrium. The condition for chemical equilibrium is therefore that $d_i S$ be zero at all times, which requires

$$\sum_{j=1}^N (v_j'' - v_j') \mu_j^* = 0 \quad (1-87)$$

where μ_j^* is the value of the chemical potential at the equilibrium state. Therefore, this is the equation of reaction equilibrium. It may be regarded as a universally valid formulation of the law of mass action, since it is not restricted to gases. The quantity $-\sum_{j=1}^N (v_j'' - v_j') \mu_j$ is known in chemical literature as the *affinity* of the chemical reaction and is commonly denoted by the symbol a :

$$a \equiv - \sum_{j=1}^N (v_j'' - v_j') \mu_j \quad (1-88)$$

The chemical affinity can play a central role in chemical thermodynamics as elaborated by De Donder and his school¹⁷. In the late 1800s, van't Hoff used affinity to describe the maximum work obtainable from a chemical process in a quantitative expression. In a way, it is equivalent to interpreting the Gibbs free energy of reaction $(\Delta G)_{T,p}$ as the driving force of a reaction. Essentially, the word *affinity* is used in connection with reaction tendency. For a reaction at equilibrium, the affinity is zero.

Let us now summarize several important points and physical interpretations about the chemical potential μ_j as follows:

A. μ_j is often referred to as the partial molar Gibbs function $\mu_j \equiv \left(\frac{\partial G}{\partial n_j} \right)_{p,T,n'_j}$;

it represents the change in Gibbs free energy as an infinitesimal amount of species j is added to the system while holding pressure, temperature, and the amount of other species constant.

B. It is an intensive property and has units of energy/mole.

C. Equation (1-77) can be integrated in a "process" in which the size of the system is increased by adding systems with the same intensive properties, all intensive properties remain constant, and all extensive properties increase proportionally. Hence, $dT = 0$, $dP = 0$, and $d\mu_j = 0$ in such a process, showing that Eq. (1-77) can readily be integrated from $(G = 0, n_j = 0)$ to (G, n_j) , yielding

$$G = \sum_{j=1}^N \mu_j n_j \quad (1-89)$$

since

$$dG = \sum_{j=1}^N \mu_j dn_j + \sum_{j=1}^N n_j d\mu_j = \sum_{j=1}^N d(\mu_j n_j) = d \left[\sum_{j=1}^N \mu_j n_j \right] \quad (1-90)$$

Therefore, μ_j may be regarded as the contribution of 1 mole of that constituent to the total G value of the system. It might be imagined, in view of the above interpretation, that μ_j was equal to the value of G_j for 1 mole of the constituent j in the pure state. However, this is only true in certain limited circumstances.⁹

In general, μ_j in a solution is not equal to G_j for the pure substance, and further, the value of μ_j varies as the composition of the system changes.

D. For a closed system at constant temperature and constant pressure, it can be shown from Eqs. (1-77) and (1-90) that

$$\sum_{j=1}^N n_j d\mu_j = -S dT + V dp = 0 \quad \text{for constant } T \text{ and } p \quad (1-91)$$

This relation is called the Gibbs-Duhem equation and has many applications, especially in connection with the study of liquid-vapor equilibria.

E. For a system in chemical equilibrium at constant temperature and pressure, we have

$$\sum \mu_j dn_j = 0 \quad (1-92)$$

where the summation includes all the μdn terms for *all the phases* constituting the system. This relation forms the basis of the well-known *phase rule*.

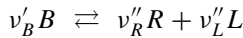
F. When a system consists of a number of components having several phases in complete equilibrium under a given temperature and pressure condition, the chemical potential of each component is the same in all the phases, i.e.,

$$\mu_{j(\text{g})} = \mu_{j(\text{l})} = \mu_{j(\text{s})} \quad \text{for all } j \quad (1-93)$$

This is shown in Ref. 9 and Example 1.3*b*.

G. If different phases of a given species in a system are not in equilibrium, the chemical potentials of this component will not be the same for different phases. There will then be a tendency for component j to pass spontaneously from a phase in which its chemical potential μ_j is higher than that with lower μ_j . In other words, matter tends to change from a state of higher chemical potential to a state of lower chemical potential. This is the reason why μ_j is given the name of chemical potential. It is a measure of the driving force tending to cause a chemical reaction to take place.

Example 1.3*a*. Consider the following chemical equilibrium reaction established in any homogeneous mixture in a closed system:



Show that

$$v'_B \mu_B^* = v''_R \mu_R^* + v''_L \mu_L^*$$

Solution: According to Eq. (1-92), the equilibrium condition is

$$\mu_B^* dn_B + \mu_R^* dn_R + \mu_L^* dn_L = 0$$

Note that the variations in the numbers of molecules are not arbitrary, but are governed by the equations

$$dn_R = \frac{v''_R}{v'_B}(-dn_B) \quad \text{and} \quad dn_L = \frac{v''_L}{v'_B}(-dn_B)$$

relating the number of product molecules formed to the number of reactant molecules consumed through appropriate coefficients. Upon substituting these equations into the first one and eliminating the common term dn_B , we have

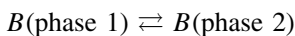
$$v'_B \mu_B^* = v''_R \mu_R^* + v''_L \mu_L^*$$

In general, the condition of homogeneous equilibrium is that the sum of chemical potentials of the reactants equals the sum of the chemical potentials of the products:

$$\sum v'_i \mu_i^* (\text{reactants}) = \sum v''_j \mu_j^* (\text{products})$$

#

Example 1.3b. Consider the following phase equilibrium established between two different phases of a chemically identical substance:



Show that $\mu_1^* = \mu_2^*$.

Solution: The condition of phase equilibrium requires that

$$\mu_1^* dn_1 + \mu_2^* dn_2 = 0$$

Since the total mass is constant, we have

$$dn_1 + dn_2 = 0$$

In order to satisfy both equations under any arbitrary amount of variation of dn_1 , we must have

$$\mu_1^* = \mu_2^*$$

#

6 CRITERIA FOR EQUILIBRIUM

Criteria for chemical equilibrium depend on the condition at which certain thermodynamic properties (or property) are kept constant. For convenience

in constant-volume processes, we introduce another secondary thermodynamic function, called the *Helmholtz free energy* A , defined by

$$A \equiv U - TS \quad (1-94)$$

Physically, A represents the available useful work other than pressure-volume work, when temperature and volume are used as independent variables. This can be seen by following Rossini's approach^{18,11} in extending the formulation of the first law by writing

$$dU = \delta \hat{Q} - p dV + d\hat{\xi} \quad (1-95)$$

where $d\hat{\xi}$ designates the work other than pressure-volume work. For work done on the system, $d\hat{\xi}$ is positive. For work done by the system, $d\hat{\xi}$ is negative. Combining Eq. (1-95) with the second law of thermodynamics, we have

$$d\hat{\xi} = dU - T dS + p dV \quad (1-96)$$

and

$$d\hat{\xi} = dA + S dT + p dV \quad (1-97)$$

It is quite obvious from Eq. (1-97) that

$$d\hat{\xi} = dA \text{ at constant } T \text{ and } V \quad (1-98)$$

Hence, dA represents the available useful work, other than pressure-volume work, at constant T and V . In particular, if dA is negative, then $d\hat{\xi}$ is negative and the system under consideration will do useful work. On the other hand, if $d\hat{\xi}$ is positive for any given process, then work must be done on the system. Finally, if $d\hat{\xi} = 0$, no useful work is done on the system or by the system and the system is at equilibrium.

By the same procedure described above, one can easily obtain the following equation written in terms of Gibbs free energy G :

$$d\hat{\xi} = dG + S dT - V dp \quad (1-99)$$

Hence,

$$d\hat{\xi} = dG \text{ at constant } T \text{ and } p \quad (1-100)$$

The general equilibrium criterion $d\hat{\xi} = 0$ leads to the results summarized in Table 1.1.

For open systems, Eq. (1-64) can be rewritten to show the change of A for an open irreversible chemical reaction process as

$$dA = -S dT - p dV + \sum_{j=1}^N \mu_j dn_j \quad (1-101)$$

Table 1.1 General Equilibrium Criteria for Closed Thermodynamic Systems¹⁸

Variables Held Constant	Thermodynamic Equilibrium Criteria for Closed Systems
p	$dH - T dS = dG + S dT = 0$
V	$dU - T dS = dA + S dT = 0$
T	$d(U - TS) + p dV = dG - V dp = dA + p dV = 0$
S	$dU + p dV = dH - V dp = 0$
p, T	$dG = 0$
V, T	$dA = 0$
P, S	$dH = 0$
V, S	$dU = 0$
S, U or A, T	$dV = 0$
A, V or G, p	$dT = 0$
U, V or H, p	$dS = 0$
G, T or H, S	$dp = 0$

Equations (1-64) and (1-72) can be rearranged to give

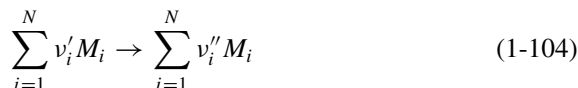
$$dU = T dS - p dV + \sum_{j=1}^N \mu_j dn_j \quad (1-102)$$

$$dH = T dS + V dp + \sum_{j=1}^N \mu_j dn_j \quad (1-103)$$

These equations together with Eq. (1-77) are very useful in chemical equilibrium studies as well as in thermochemical calculations.

7 CONSERVATION OF ATOMIC SPECIES

A generalized single-step reaction can be expressed as



Once the values of v'_i are assigned, there is a constraint on the values of v''_i ; they cannot be arbitrary. This constraint is due to the law of conservation of atomic species.

For any molecular species M_i , we can then write its chemical formula in terms of its atomic composition as

$$M_i = (A_{1a_1} A_{2a_2} A_{3a_3} \cdots)_i \quad (1-105)$$

The symbols A_1, A_2, A_3 , etc., stand for different atomic species, and a_1, a_2, a_3 are the numbers of atoms present in the particular molecular species M_i . For example,

$$M_{\text{H}_2\text{O}} = (\text{H}_2\text{O}_1) \quad (\text{for water})$$

$$M_{\text{C}_3\text{H}_8} = (\text{C}_3\text{H}_8) \quad (\text{for propane})$$

$$M_{\text{NH}_4\text{ClO}_4} = (\text{N}_1\text{H}_4\text{Cl}_1\text{O}_4) \quad (\text{for ammonium perchlorate})$$

The generalized single-step reaction can then be written as

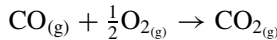
$$\sum_{i=1}^N v_i'(A_{1a_1}A_{2a_2}A_{3a_3} \cdots)_i = \sum_{i=1}^N v_i''(A_{1a_1}A_{2a_2}A_{3a_3} \cdots)_i \quad (1-106)$$

The total number of any given atomic species present in the reaction is conserved. Defining $[A_1]$ as the total number of atomic species A_1 present in the reaction, then

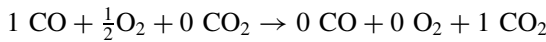
$$[A_1] \equiv \sum_{i=1}^N (v_i' a_{1i}) = \sum_{i=1}^N (v_i'' a_{1i}) = \text{constant} \quad (1-107)$$

It is important to note here that if, for example, we have five atomic species in a combustion system, five equations like Eq. (1-107) can be constructed in order to solve for the numbers of moles of products.

Example 1.4. Use the law of conservation of atomic species for the evaluation of the total numbers of atomic species in the following reaction:



Solution: In a more helpful form, the above equation can be written as



Then, the total number of carbon atoms is

$$\begin{aligned} [\text{C}] &= (1 \times 1) + (0.5 \times 0) + (0 \times 1) \\ &= (0 \times 1) + (0 \times 0) + (1 \times 1) = 1 \end{aligned}$$

Similarly, for the oxygen atoms,

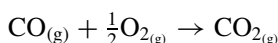
$$\begin{aligned} [\text{O}] &= (1 \times 1) + (0.5 \times 2) + (0 \times 2) \\ &= (0 \times 1) + (0 \times 2) + (1 \times 2) = 2 \end{aligned}$$

#

Given the definition of Avogadro's number as representing the number of molecules per mole (6.02252×10^{23} /mole), the molecular weight of the i th species, Mw_i , is the mass of 6.02252×10^{23} molecules and has the units of g/mole. In a gaseous mixture, the number of moles n_i of i th species is equal to the weight of the gas divided by its molecular weight Mw_i :

$$n_i = \frac{m_i g}{g_c Mw_i} \quad (1-108)$$

where g is the gravitational acceleration and g_c is the dimensional conversion factor for gravitation. The values of g_c are given in Appendix B. Then, for the reaction



we have

$$\begin{aligned} \sum_{i=1}^N \left(\frac{m_i g}{g_c} \right)_{\text{reactant}} &= \sum_{i=1}^N \left(\frac{m_i g}{g_c} \right)_{\text{product}} = v'_{\text{CO}} Mw_{\text{CO}} + v'_{\text{O}_2} Mw_{\text{O}_2} = v''_{\text{CO}_2} Mw_{\text{CO}_2} \\ &= (1 \times 28) + \left(\frac{1}{2} \times 32\right) = 1 \times 44 = 44 \end{aligned}$$

In general, the mass balance equation for any generalized single-step reaction can be written as

$$\sum_{i=1}^N v'_i Mw_i = \sum_{i=1}^N v''_i Mw_i \quad (1-109)$$

8 VARIOUS METHODS FOR REACTANT-FRACTION SPECIFICATION

The weight of the reactant is generally specified by means of fractions and ratios as follows:

8.1 Mole Fraction X and Mass Fraction Y

The mole and mass fractions of the i th species in a multicomponent system are defined by Eqs. (I-1) and (I-2) in the Introduction. It is useful to note that for N different species in a given system

$$\sum_{i=1}^N X_i = 1 \quad \text{and} \quad \sum_{i=1}^N Y_i = 1 \quad (1-110)$$

At low pressures, it is convenient to use Dalton's law to calculate partial pressures from mole fractions:

$$p_i V = n_i R_u T \quad (1-111)$$

Then,

$$p = \sum_{i=1}^N p_i = \frac{R_u T}{V} \sum_{i=1}^N n_i \quad (1-112)$$

Combining equations (1-111) and (1-112), we have

$$\frac{p_i}{p} = \frac{n_i}{\sum_{i=1}^N n_i} = X_i \quad (1-113)$$

8.2 Fuel–Oxidant Ratio F/O and Fuel–Air Ratio F/A

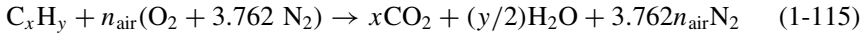
The fuel–oxidant ratio (F/O) is defined by Eq. (I-12). Similarly, the fuel–air ratio F/A can be defined as

$$F/A \equiv \frac{\text{mass of fuel}}{\text{mass of air}} \quad (1-114)$$

8.3 Equivalence Ratio ϕ

As shown in Eq. (I-13) of the Introduction, the equivalence ratio is defined as the ratio of the actual fuel–oxidant ratio (F/O) to the ratio $(F/O)_{st}$ for a stoichiometric process. Physically, a stoichiometric reaction can be considered as a unique reaction in which the oxidizer is just the amount required to completely burn the quantity of fuel in the system. It can be regarded as the most economic reaction.

Quite often the stoichiometric reaction can be written in terms of 1 mole of hydrocarbon fuel in reaction with air. For example,



where the constant 3.762 comes from the ratio of approximately 79% nitrogen to 21% oxygen by volume in the air and

$$n_{air} = x + y/4 \quad (1-116)$$

The stoichiometric air–fuel ratio can be determined as

$$(A/F)_{st} = \left(\frac{M_{air}}{M_{fuel}} \right)_{st} = \frac{4.762n_{air}}{1} \frac{Mw_{air}}{Mw_{fuel}} \quad (1-117)$$

The equivalence ratio of the fuel–air system can be evaluated from

$$\phi = \frac{(A/F)_{st}}{(A/F)} = \frac{(F/A)}{(F/A)_{st}} \quad (1-118)$$

Again, for fuel-rich mixtures, $\phi > 1$ and for fuel-lean mixtures, we have $\phi < 1$. For stoichiometric mixtures, $\phi = 1$. For a general situation, other than

stoichiometric, the mole fractions in a combustible mixture with air are calculated from Eq. (I-16).

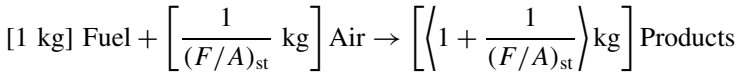
8.4 Mixture Fraction f

Mixture fraction f is a conserved scalar, which can be defined in the most general way as the mass percentage of fuel (both burned and unburned) in a gaseous mixture, i.e.,

$$f \equiv \frac{\text{mass of material having its origin in the fuel stream}}{\text{mass of mixture}} \quad (1-119)$$

Let us consider a stoichiometric combustion process of two streams of reactants (a fuel stream and an air stream, also called the first stream and the auxiliary stream) as shown in the sketch in Fig. 1.3.

In terms of mass balance, the global reaction can be written as



Let us consider the case that the reaction may not be complete due to poor mixing or low temperature conditions. Some portion of the unburned fuel and oxidizer are contained in the "mixture," containing all three types of gases (fuel, air, and product). Assume we know the local mass fractions of these three gases at a downstream location within the mixture. We now would like to find out the fraction of the original material from the fuel stream in a small local control volume in the mixture stream and call this fraction the mixture fraction, f . The next step is to determine the relationship between f , Y_F , Y_P , and $(F/A)_{st}$. Since no fuel is present in the air stream, the mass fraction of any partially burned material having its origin in the fuel stream can be written as the sum of two parts, namely

$$f = 1 \times Y_F + \frac{1}{1 + 1/(F/A)_{st}} \times Y_P$$

$$\left(\begin{array}{l} \text{Mass fraction of} \\ \text{material having} \\ \text{its origin in the} \\ \text{fuel stream} \end{array} \right) = \underbrace{\left(\frac{\text{kg fuel stream}}{\text{kg fuel}} \right) \times \left(\frac{\text{kg fuel}}{\text{kg mixture}} \right)}_{\text{fraction of unburned fuel in the mixture}} + \underbrace{\left(\frac{\text{kg fuel stream}}{\text{kg product stream}} \right) \times \left(\frac{\text{kg products}}{\text{kg mixture}} \right)}_{\text{fraction of burned fuel in the mixture}}$$

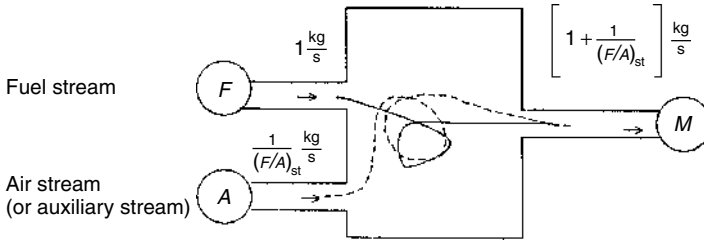


Figure 1.3 Mixing and combustion of fuel and air streams in a combustor.

Therefore, the value of mixture fracture f can be calculated from

$$f = Y_F + \left[\frac{1}{1 + (F/A)_{st}} \right] Y_P \tag{1-120a}$$

In this example, f can be considered to be a “composite” mass fraction, which is a *conserved scalar*, neither created nor destroyed by chemical reactions. As will be discussed in later chapters, the differential equation for f will not have any source terms, since it is a conserved scalar. Now let us consider the air stream that has only oxidizer; then we have

$$f = Y_F + \left[\frac{1}{1 + (F/O)_{st}} \right] Y_P \tag{1-120b}$$

It is useful to prove that the following properties are conserved scalars in this sense:

- Y_{inert} —The mass fraction of a chemically inert mixture component
- $[Y_F - (F/O)_{st} Y_O]$ —A “composite” mass fraction made of Y_F and Y_O
- $\left[Y_F + \frac{(F/O)_{st}}{1 + (F/O)_{st}} Y_P \right]$ —Another “composite” mass fraction, where Y_P is the mass fraction of combustion product
- $\left[\left(\frac{F}{O} \right)_{st} Y_O + \frac{(F/O)_{st}}{1 + (F/O)_{st}} Y_P \right]$ —Another “composite” mass fraction

It should be noted that any linear combination of conserved properties, ζ_i

$$a_0 + a_1 \zeta_1 + a_2 \zeta_2 + \dots + a_n \zeta_n$$

is also a conserved property, where a_0, a_1, \dots, a_n are constants. It can be shown in the two-stream combustion process that the mixture fraction can be expressed as

$$f = \frac{\zeta_M - \zeta_A}{\zeta_F - \zeta_A} \tag{1-121}$$

where ζ represents any conserved property¹⁹ free from sources and sinks.

Using the composite mass fraction $[Y_F - (F/O)_{st}Y_O]$ to represent the ζ for a two-stream mixing/combustion process, the fuel and oxidant mass fractions are then linked with f as follows:

$$f = \frac{[Y_F - (F/O)_{st}Y_O]_M - [Y_F - (F/O)_{st}Y_O]_A}{[Y_F - (F/O)_{st}Y_O]_F - [Y_F - (F/O)_{st}Y_O]_A} \quad (1-121a)$$

If the F stream contains only fuel and the A stream contains oxidizer but no fuel, then we have

$$\begin{aligned} [Y_F]_A &= 0, & [Y_F]_F &= 1, & [Y_O]_F &= 0 \\ f &= \frac{[Y_F - (F/O)_{st}Y_O]_M + (F/O)_{st}Y_{O,A}}{1 + (F/O)_{st}Y_{O,A}} \end{aligned} \quad (1-122)$$

If chemical reaction is complete within the mixing chamber, either fuel or oxidant will have zero concentration in the M state. Therefore, the stoichiometric value of f is

$$f_{st} = \frac{(F/O)_{st}Y_{O,A}}{1 + (F/O)_{st}Y_{O,A}} \quad (1-123)$$

and

$$\begin{aligned} f &= \frac{-(F/O)_{st}Y_{O,M} + (F/O)_{st}Y_{O,A}}{1 + (F/O)_{st}Y_{O,A}} \\ &\text{if } f < f_{st} \text{ (fuel-lean case)} \end{aligned} \quad (1-124a)$$

$$\begin{aligned} f &= \frac{Y_{F,M} + (F/O)_{st}Y_{O,A}}{1 + (F/O)_{st}Y_{O,A}} \\ &\text{if } f > f_{st} \text{ (fuel-rich case)} \end{aligned} \quad (1-124b)$$

Equation (1-124) can be rearranged to give the following values after combustion:

$$\left. \begin{aligned} Y_{F,M} &= 0 \\ Y_{O,M} &= Y_{O,A} \frac{f_{st} - f}{f_{st}} \end{aligned} \right\} \text{ for } f < f_{st} \quad (1-125a)$$

$$\left. \begin{aligned} Y_{O,M} &= 0 \\ Y_{F,M} &= \frac{f - f_{st}}{1 - f_{st}} \end{aligned} \right\} \text{ For } f > f_{st} \quad (1-125b)$$

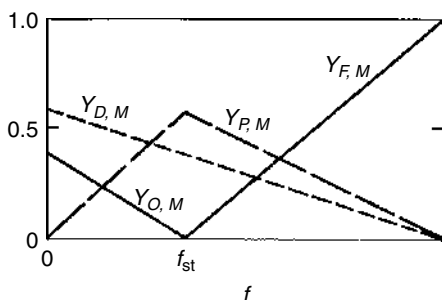


Figure 1.4 A plot of mass fractions of various species as functions of mixture fraction on the totally burned plane.

If the air stream contains some diluent gas, then we have the following relationships for any f :

$$\begin{aligned}
 Y_{D,M} &= Y_{D,A}(1 - f) \\
 Y_{P,M} &= 1 - Y_{D,M} - Y_{O,M} - Y_{F,M}
 \end{aligned}
 \tag{1-125c}$$

where $Y_{D,M}$ represents the mass fraction of diluent in the M state. The relationship between Y_O , Y_F , Y_P , Y_D , and f on the burned plane can be expressed by the graph in Fig. 1.4, which consists *entirely of straight lines*. It should be noted that this graph is not the most general form; the F stream could have some diluent, and both streams might also be contaminated with product. It would be a useful exercise for readers to construct an unburned plane of Y_O , Y_F , Y_P , and Y_D versus f and to demonstrate that the dependence of Y_i on f is totally linear. It is important to note that the mixture fraction should be distinguished quite clearly from the mass fraction of fuel, Y_F , and the fuel–oxidant ratio.

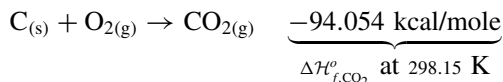
9 STANDARD ENTHALPIES OF FORMATION

The standard enthalpy of formation of the i th substance, $\Delta\mathcal{H}_{f,i}^o$ (kcal/mole), is often called the heat of formation of that substance. It is defined as the heat evolved when 1 mole of the substance is formed from its elements in their respective standard state temperature of 298.15 K and standard state pressure of 1 bar (or 100,000 N/m²). The subscript f indicates formation of the compound from elements, and the index o refers to all products and reactants in their standard states.

The *standard state of an element* is the stable form of that element at room temperature and 1 bar. The standard states of some elements are as follows: $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{N}_2(\text{g})$, $\text{Hg}(\text{l})$, $\text{C}_{(\text{s,graphite})}$. For gases, the reference state is the ideal gaseous state at a pressure of 1 bar and at a given temperature (usually 298.15 K). For

pure liquids and solids, the reference state is the actual state of the substance at 1 bar pressure and a given temperature (mostly 298.15 K). By convention, each element in its standard state is assigned an enthalpy of zero or has a standard heat of formation of zero. It is worthwhile to note that other sources may use a different reference state. One must exercise great care in this regard.

Example 1.5. As an example of the standard heat of formation, reference may be made to the reaction



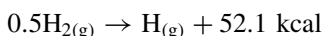
When heat is evolved (*exothermic reaction*) in the formation of the compound, then the $\Delta \mathcal{H}_f^{\circ}$ value of that compound is a negative quantity, since heat must be taken away from the system in order to maintain an isothermal reaction process. The absolute enthalpy of 1 mole of CO_2 in any other state can be found by adding the sensible enthalpy change between the standard state (298.15 K, 1 bar) and the given state (T , p) to the chemical enthalpy, associated with the heat of formation. That is,

$$H(T, p) = \Delta H_{298.15 \text{ K}, 1 \text{ bar} \rightarrow T, p} + \Delta H_f^{\circ} \times 1 \text{ mole} \quad (1-126)$$

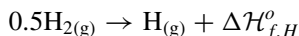
The above equation is not only valid for CO_2 but also valid for calculating the absolute enthalpy of 1 mole of any compound.

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Now let us consider another formation reaction



which can also be written as



Note that the heat of formation of hydrogen atom is a positive value equal to 52.1 kcal/g-mole. This is due to the fact that external heat must be supplied for the reaction to proceed (*endothermic reaction*). When heat is absorbed in the formation of a compound, the heat of formation of that compound is a positive quantity, since heat must be added to the system. It is useful to note that substances with large positive standard heats of formation are usually more chemically active species.

Example 1.6. Express the heat of formation of 1 mole of a given compound at 1 bar pressure and an arbitrary temperature T , in terms of the heats of formation of the compound at the standard state and the enthalpy changes of all elements involved in the formation chemical reaction.

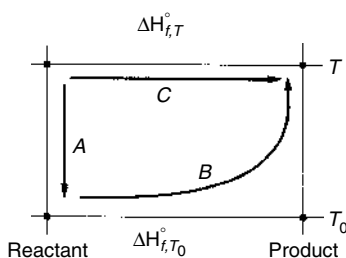


Figure 1.5 Two temperature-reaction paths.

Solution: Figure 1.5 shows that path *C* can be replaced by the sum of paths *A* and *B*; namely,

$$C = A + B = B - (-A)$$

Therefore we can write

$$\Delta \mathcal{H}_{f,T}^{\circ} = 1 \times [(\mathcal{H}_T^{\circ} - \mathcal{H}_{T_0}^{\circ}) + \Delta \mathcal{H}_{f,T_0}^{\circ}]_{\text{compound}} - \sum_{j \text{ elements}} \nu'_j (\mathcal{H}_T^{\circ} - \mathcal{H}_{T_0}^{\circ})_j$$

where the number 1 stands for 1 mole of compound formed.

#

Table 1.2 contains the standard heats of formation of various compounds at 298.15 K. More complete information can be found either from *JANAF Thermochemical Tables*,²⁰ the *Handbook of Chemistry and Physics*,¹⁶ or the users' manual of NASA CEA code developed by McBride and Gordon.²

Table 1.2 Standard Heats of Formation of Selected Substances at 298.15 K^a

Substance	$\Delta \mathcal{H}_f^{\circ}$ (kcal/mol)	Substance	$\Delta \mathcal{H}_f^{\circ}$ (kcal/mol)
B _(s)	0.00	F _{2(g)}	0.00
B _(g)	133.8 ± 2.9	F ₂ O _(g)	5.86 ± 0.38
B _{2(g)}	198.3 ± 8.0	HF _(g)	-65.14 ± 0.19
B ₂ H _{6(g)} diborane	9.8 ± 4.0	H _(g)	52.103 ± 0.001
B ₅ H _{9(l)} pentaborane	10.24 ± 1.60	H _{2(g)}	0.00
BO _(g)	0 ± 1.91	OH _(g)	9.318 ± 0.289
B ₂ O _{3(s)}	-304.0 ± 0.50	H ₂ O _(g)	-57.798 ± 0.010
BF _{3(g)}	-271.41 ± 0.41	H ₂ O _(l)	-68.315 ± 0.010
Br _(g)	26.74 ± 0.01	H ₂ O _{2(g)}	-32.530
Br _{2(g)}	7.34 ± 0.03	H ₂ O _{2(l)}	-44.880
HBr _(g)	-8.71 ± 0.04	I _(g)	25.516 ± 0.01
C _(g)	171.29 ± 0.110	I _{2(g)}	14.919 ± 0.019
C _(s,diamond)	0.45	I _{2(s)}	0.00

(continued overleaf)

Table 1.2 (continued)

Substance	ΔH_f° (kcal/mol)	Substance	ΔH_f° (kcal/mol)
C _(s,graphite)	0.0	HI _(g)	6.300 ± 0.050
CH ₂ N _{2(s)} cyanamide	14.05	Li _(g)	38.07 ± 0.240
CH _{3(g)}	34.82 ± 0.19	Li _(s)	0
CH _{4(g)}	17.895 ± 0.08	Li ₂ O _(s)	143.10 ± 0.50
C ₂ H _{6(g)}	-20.041	Li ₂ O _{2(s)}	151.20 ± 2.01
C ₃ H _{8(g)}	-25.02	LiH _(g)	33.610 ± 0.010
C ₄ H _{10(g)} <i>n</i> -butane	-30.065	LiH _(s)	-21.660 ± 0.031
C ₄ H _{10(g)} isobutene	-32.263	LiOH _(s)	115.90 ± 0.10
C ₅ H _{12(g)} <i>n</i> -pentane	-35.1	HCN _(g)	32.29
C ₆ H _{6(g)} benzene	19.81	LiF _(s)	-147.45 ± 0.191
C ₇ H _{8(g)} toluene	12.07	N _(g)	112.97 ± 0.02
C ₈ H _{10(g)} ethylbenzene	7.146	NH _{3(g)}	-10.97 ± 0.096
C ₈ H _{10(g)} <i>o</i> -xylene	4.565	N _{2(g)}	0.00
C ₈ H _{10(g)} <i>m</i> -xylene	4.135	NO _(g)	21.580 ± 0.041
C ₈ H _{10(g)} <i>p</i> -xylene	4.302	NO _{2(g)}	7.911 ± 0.191
C ₆ H ₅ NH _{2(l)} aniline	-7.553	NO _{3(g)}	17.00 ± 5.00
CH ₂ O _(g) formaldehyde	-27.7 ± 1.5	N ₂ O _(g)	19.61 ± 0.10
CH ₃ OH _(g)	-48.04	N ₂ O _{3(g)}	19.800 ± 0.191
CH ₃ OH _(l)	-57.01	N ₂ O _{4(g)}	2.17 ± 0.41
C ₃₂ H _{66(s)}	-231.65 ± 0.15	N ₂ O _{5(g)}	2.700 ± 0.311
CH ₂ O ₂ N _{4(s)}	22.14	N ₂ O _{5(s)}	-10.30
CH ₃ ON _(l) formamide	-60.71	N ₂ H _{4(l)}	12.100 ± 0.096
CH ₃ O ₂ N _(l) nitromethane	-26.91	N ₂ H ₄ · H ₂ O _(l)	-57.95
CH ₄ ON _{2(s)} urea	-79.613	Na _(g)	25.64 ± 0.17
CH ₅ N _(g) methylamine	-6.7	Na _(s)	0
CH ₅ N _{3(s)} guanidine	-13.38	Na _{2(g)}	33.956 ± 0.287
CH ₅ O ₄ N _{3(s)} urea nitrate	-114.8	NaO _{2(s)}	-62.300 ± 0.693
CH ₆ O ₃ N _{4(s)} guanidine nitrate	91.4	Na ₂ O _(s)	-99.900 ± 1.004
CO _(g)	-26.42 ± 0.04	Na ₂ O _{2(s)}	-122.66 ± 1.20
CO _{2(g)}	-94.054 ± 0.012	NaH _(g)	29.700 ± 4.590
C ₂ H _{2(g)}	54.190 ± 0.189	NaH _(s)	-13.489 ± 0.019
C ₂ H _{4(g)}	12.540 ± 0.069	NaOH _(s,II)	-101.800 ± 0.096
C ₂ H ₂ O _(g) ketene	-11.35	NaF _(s)	-137.52 ± 0.19

Table 1.2 (continued)

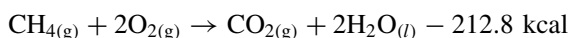
Substance	ΔH_f° (kcal/mol)	Substance	ΔH_f° (kcal/mol)
C ₂ H ₄ O _(g) ethylene oxide	-12.580 ± 0.15	HNO _{3(g)}	-32.10 ± 0.10
C ₂ N _{2(g)}	73.870 ± 0.430	NH ₂ OH _(s)	-27.29
C ₂ H ₄ O _(g) ethylene oxide	-12.580 ± 0.15	NH ₄ NO _{3(s)}	-87.38
C ₂ H ₃ N _(g) acetonitrile	17.69	NF _{3(g)}	-31.570 ± 0.270
C ₂ H ₃ N _(g) methyl isocyanide	39.08	NH ₄ Cl _(s)	-75.14
C ₂ H ₅ O ₂ N _(l) nitroethane	-34.39	NH ₄ ClO _{4(s)}	-70.58
C ₂ H ₇ N _(g) ethylamine	-11.35	O _(g)	59.553 ± 0.023
C ₂ H ₅ O ₃ N _(g) ethyl nitrite	-36.83	O _{2(g)}	0.00
C ₂ H ₅ O ₃ N _(l) ethyl nitrate	-45.51	O _{3(g)}	34.100 ± 0.406
C ₂ H ₄ O ₆ N _{2(l)} glycol dinitrate	58	P _(g)	75.619 ± 0.239
Cl _(g)	28.992 ± 0.002	PH _{3(g)}	5.471 ± 0.406
Cl _{2(g)}	0	S _(g)	66.200 ± 0.060
HCl _(g)	-22.063 ± 0.050	SO _{2(g)}	-70.947 ± 0.050
ClI _(g)	4.184 ± 0.025	SO _{3(g)}	-94.590 ± 0.170
F _(g)	18.974 ± 0.072	H ₂ S _(g)	-4.900 ± 0.191

^aConstructed from data in Refs. 2, 20, and 21.

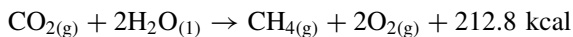
10 THERMOCHEMICAL LAWS

Pioneers A. L. Lavoisier and P. S. Laplace (1780) have been credited with the following law, stated as follows: *The quantity of heat, which must be supplied to decompose a compound into its elements, is equal to the heat evolved when the compound is formed from its elements.* A more general form of this law states that *the heat change accompanying a chemical reaction in one direction is exactly equal in magnitude, but opposite in sign, to that associated with the same reaction in the reverse direction.*

Example 1.7. Consider the following reaction occurring at 298.15 K:



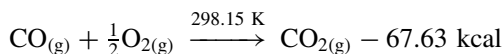
By switching the products and reactants, the sign of the heat evolved must be changed accordingly, i.e.,



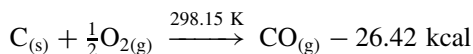
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In 1840 G. H. Hess developed empirically what is known as the law of constant heat summation. This law states that *the resultant heat change, at constant pressure or constant volume, in a given chemical reaction is the same whether it takes place in one or in several stages*. This means that the net heat of reaction depends only on the initial and final states. As a result of Hess's law, thermochemical equations can be added and subtracted just like algebraic equations. The following example demonstrates the application of this powerful law.

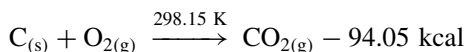
Example 1.8. Show that the standard heat of formation of carbon dioxide in the amount of -94.05 kcal/g-mole can be obtained from the known heat of formation of CO and the heat evolved from the following reaction:



Solution: Note that the heat evolved in the above reaction is not the standard heat of formation for 1 mole of $\text{CO}_2(\text{g})$, since the reactant $\text{CO}(\text{g})$ is not an element in its standard state. In the formation reaction of 1 mole of $\text{CO}(\text{g})$, we have



Adding the above two thermochemical equations like algebraic equations according to Hess's law, we have



Note that the two species on the reactant side are elements in their respective states. Therefore, this thermochemical equation is the formation reaction of 1 mole of carbon dioxide. Thus, the heat evolved is the standard heat of formation of $\text{CO}_2(\text{g})$ and

$$(\Delta H_f^o)_{\text{CO}_2(\text{g}), 298.15 \text{ K}} = -94.05 \text{ kcal/mol}$$

#

11 RELATIONSHIP BETWEEN BOND ENERGIES AND HEATS OF FORMATION

The bond energy for dissociation, $D^o(\text{R}-\text{X})$, is also known as the strength of a chemical bond between R and X of the molecule RX. When a molecule is dissociated into two parts by the reaction $\text{RX} \rightarrow \text{R} + \text{X}$, the energy required

to break the bond at 298.15 K is related to the heats of formation (also called enthalpies of formation) of the original molecule and its dissociated fragments by

$$D_{298}^{\circ}(\text{R} - \text{X}) = \Delta\mathcal{H}_{f,\text{R}}^{\circ} + \Delta\mathcal{H}_{f,\text{X}}^{\circ} - \Delta\mathcal{H}_{f,\text{RX}}^{\circ} \quad (1-127)$$

Physically, it represents the average amount of energy, per mole, required to break that kind of bond in a molecule and separate the two fragments far apart. In general, the energy required to pull two molecular fragments (R and X) apart is a function of the distance between R and X, as shown in Fig. 1.6. The bond energy corresponds to the difference between the energy level at infinity and the minimum of the potential energy curve. Some bond energies selected from Refs. 16 and 14 are tabulated in Table 1.3. These values are given at 298.15 K rather than at 0 K.

The bond strengths in many different polyatomic molecules are tabulated in Ref. 16. The enthalpies of formation of various free radicals are also given in Ref. 16. Using these tables, it is possible to estimate the standard heats of formation for compounds that have never been synthesized or are unsuitable for burning in a calorimeter.

It is useful to note that the bond energies are based on data for substances in the gaseous state and, therefore, should be used for reactions involving gases only. Also, the bond energy has the negative value of the energy required to form a particular bond. Bond energies can be used to estimate the heats of formation of certain chemical compounds. In addition to the bond energy, one should take into account the possibility of resonance in some molecules in order to estimate their heats of formation. Bond and resonance energies can also be used to estimate the heats of combustion of certain reactions. For example, the benzene molecule C_6H_6 can resonate between the five structures¹¹ shown in Fig. 1.7.

As a result of resonance, $\Delta\mathcal{H}_{f,\text{C}_6\text{H}_6}^{\circ}$ is much larger than the sum of three $\text{C}=\text{C}$, three $\text{C}-\text{C}$, and six $\text{C}-\text{H}$ bond energies. The additional energy is termed the resonance energy; it must be considered in addition to the bond energies to calculate the actual heat of formation of a given chemical compound. The resonance energy of C_6H_6 is 48.9 kcal/mol. The use of resonance energy in enthalpy of formation

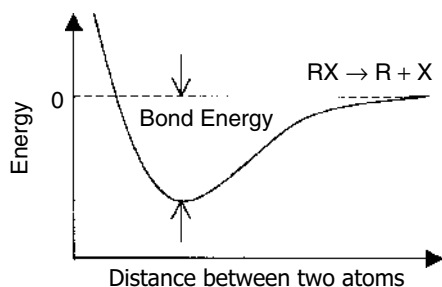


Figure 1.6 Potential energy between two molecular fragments as a function of interatomic separation distance.

Table 1.3 Some Bond and Resonance Energies*Bond Energies in Some Diatomic Molecules¹⁶*

Bond	Energy, D_{298}° (kcal/mol)	Bond	Energy, D_{298}° (kcal/mol)
H-H	104.20	C-O	≥ 141.97
F-F	37.95	C-Cl	94.89 ± 6.93
Cl-Cl	57.98	Br-C	66.92 ± 5.02
Br-Br	46.08	C-I	49.95 ± 5.02
I-I	36.11	C-F	131.93
C-H	80.88 ± 0.29	N \equiv N	225.94 ± 0.14
H-N	≤ 81.02	C=C	145.08 ± 5.02
H-O	102.20	O=O	119.11
Cl-H	103.16	Al-O	122.13 ± 0.72
Br-H	87.55	C \equiv N	180.28 ± 2.39
H-I	71.32		

Mean Bond Energies^{14,16}

Bond	Energy (kcal/mol)	Bond	Energy (kcal/mol)
Br-Br	46	H-F	135
C-C	85	H-H	103
C=C	145	H-I	72
C \equiv C	194.3	H-P	76
C-Br	67	H-S	81
C-Cl	78	I-I	36
C-F	102	N-H	88
C-H	98.1	N-N	60
C-I	64	N \equiv N	225
C-N	81	O-H	109
C \equiv N	210	O-N	150
C-O	86	O-O	33.1
C=O	173	O=O	117
C-S	64	P-Br	64
Cl-Cl	57	P-Cl	78
F-F	36	P-P	48
H-Br	88	S-Cl	60
H-Cl	103	S-S	50

Resonance Energies of Selected Compounds

Compound	Resonance Energy (kcal/mol)
Benzene, C ₆ H ₆	48.9
-COOH group (carboxyl group)	28
CO ₂	33
Naphthalene, C ₁₀ H ₈	88.0
Aniline, C ₆ H ₅ NH ₂	69.6

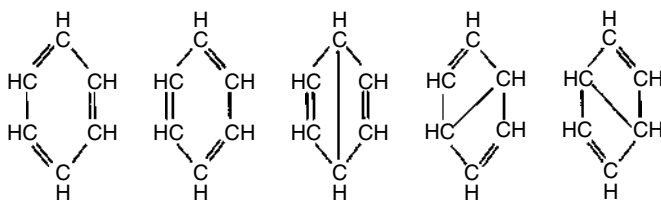


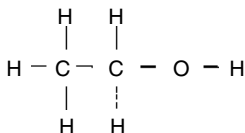
Figure 1.7 Different molecular structures of the benzene (C_6H_6) molecule.

calculation is given in Ref. ¹¹. Some examples (e.g., Example 1.11) are provided in a later section to describe the use of resonance energies.

Note that Table 1.3 has three parts. Part 1 shows the bond energies of some selected diatomic molecules, part 2 gives the mean bond energies between some selected atoms, and part 3 shows the resonance energies of some particular molecules for which different molecular structures exist; their resonance energies must be considered in the estimation of their heats of formation.

Example 1.9. Use the tabulated bond energies to estimate the heat of formation of ethanol, $C_2H_6O_{(g)}$.

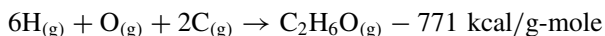
The molecular structure of $C_2H_6O_{(g)}$ is



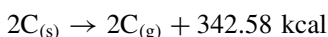
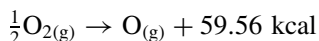
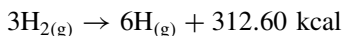
The energy required to form one mole of $C_2H_6O_{(g)}$ is

$$\begin{aligned}
 & 5(\text{C-H}) + (\text{C-C}) + (\text{C-O}) + (\text{O-H}) \\
 & = 5 \times (-98.1) + (-85.5) + (-86) + (109) = -771 \text{ kcal/mole}
 \end{aligned}$$

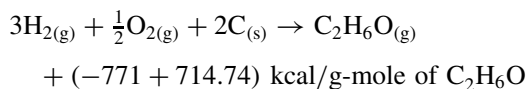
Therefore, we may write the thermochemical equation as



In order to obtain the heat of formation of $C_2H_6O_{(g)}$, we must utilize Hess's law and the thermochemical equations



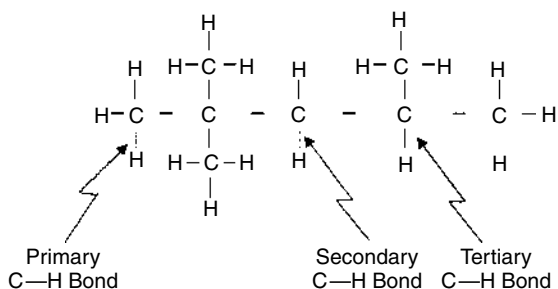
Summing up the above reaction equations, we have



Therefore, the estimated value for $\Delta\mathcal{H}_{f,\text{C}_2\text{H}_6\text{O}(\text{g})}^{\circ}$ is -56.26 kcal/mol. The actual value of heat of formation is -56.12 kcal/mol; the difference is attributed to the fact that the estimated value is based on average bond energies.

#

The previous example showed that the estimated heat of formation is very close to the actual value. However, this is not always true. It is important to note that the bond energy between the two atoms can vary significantly, depending on their respective locations in the molecule. For example, the molecular structure of iso-octane is



The bond strength ratios between primary, secondary, and tertiary bonds of iso-octane are 13, 5, and 1. Therefore, the enthalpy of formation estimated by the mean bond energy could differ significantly from the actual value. The reason for the difference in bond strengths is due to the fact that the tertiary C-H bond has a higher probability of forming antibonding orbitals than the primary and secondary C-H bonds. In antibonding orbitals, the electrons help to pull the nuclei apart rather than helping to pull them together.

12 HEATS OF REACTION FOR CONSTANT-PRESSURE AND CONSTANT-VOLUME COMBUSTION

The science of thermochemistry is concerned with the heat changes associated with chemical reaction; in other words, it deals essentially with the conversion of chemical energy into thermal energy, and vice versa.

The heat change associated with a chemical reaction, like that for any other process, is in general an *indefinite* quantity, depending on the path taken. However, once the process is specified (e.g., a constant-pressure process), the heat

change has a definite value, determined only by the initial and final states of the system. It is for this reason that heat changes of chemical reactions are usually measured under constant-pressure or constant-volume conditions.

There are a number of different ways in which a heat of reaction may be defined. One of the most general definitions is stated in the following section.

12.1 Constant-Pressure Combustion

If a closed system containing n_i moles of N different species at a given T and p is caused to undergo an isobaric process in which the values n_i are changed to prescribed final values and in which the initial and final values of T are the same, then the heat liberated by the system is the heat of reaction for the constant-pressure process.

When a system changes from one state to another, it may lose or gain energy in the form of heat and work. If, in a change from state A to state B , the energy content of the system is increased by ΔE , with the work done by the system being $\delta \hat{W}$ and the heat absorbed by the system $\delta \hat{Q}$, then by the first law of thermodynamics

$$\Delta E = \delta \hat{Q} - \delta \hat{W} \quad (1-128)$$

For chemical reactions under negligible change of kinetic energy and with no change in potential energy, $\Delta E = \Delta U$, and the first law becomes

$$\Delta U = \delta \hat{Q} - \delta \hat{W} \quad (1-128a)$$

If, in addition, the reaction occurs at a constant pressure, the first law is written as

$$\hat{Q}_p = \int (\delta \hat{Q})_p = \Delta U + p \Delta V \quad (1-128b)$$

For a change from state A to state B ,

$$\hat{Q}_p = (U_B - U_A) + p(V_B - V_A) = H_B - H_A \quad (1-129)$$

Therefore, for a constant-pressure, nonflow reaction,

$$\hat{Q}_p = \Delta H \quad (1-130)$$

For a constant-volume, nonflow reaction, on the other hand, no external work is done ($\delta \hat{W} = 0$), and the first law is

$$\hat{Q}_v = \Delta U \quad (1-131)$$

For a reacting flow, if there is insignificant amount of change in PE or KE, and no work other than that required for flow, then the net change in enthalpy is equal to the heat of reaction, i.e., $\hat{Q}_p = \Delta H$.

The notation for the heat content or enthalpy of a substance at standard state is H_T^o , where, as stated previously, the index o specifies standard state and the subscript T gives the temperature in kelvins. Therefore, H_0^o represents the enthalpy of a substance at the pressure of 1 bar and at the temperature of 0 K.

The ideal or perfect-gas equation of state is

$$pV = mRT = nR_uT \quad (1-132)$$

After inserting it into the definition of enthalpy,

$$H = U + pV$$

we have

$$H_T^o = U_T^o + (pV)^o = U_T^o + mRT = U_T^o + nR_uT \quad (1-133)$$

At $T = 0$ K,

$$H_0^o = U_0^o + mR(0) = U_0^o \quad (1-134)$$

Subtracting Eq. (1-134) from Eq. (1-133) gives a convenient way to calculate H_T^o from U_T^o , or vice versa:

$$H_T^o - H_0^o = (U_T^o - U_0^o) + mRT \quad (1-135)$$

From Eq. (1-129) we know that for a constant-pressure nonflow reaction,

$$\Delta H = \Delta U + p\Delta V \quad (1-136)$$

If V is the volume of 1 mole of any ideal gas at the constant temperature and pressure, then the change of pV is equal to $p\Delta V$. Using Eq. (1-132) for an ideal gas, one has

$$p\Delta V = (\Delta n)R_uT \quad (1-137)$$

Substituting Eq. (1-137) into Eq. (1-136), we have

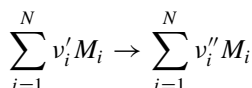
$$\Delta H = \Delta U + (\Delta n)R_uT \quad (1-138)$$

where

$$\Delta n = \left[\left(\sum_{i=1}^N n_i \right)_{\text{products}} - \left(\sum_{i=1}^N n_i \right)_{\text{reactants}} \right]_{\text{gaseous species}} \quad (1-139)$$

From Eq. (1-135) the value of the heat of reaction at constant pressure can be calculated from the value of the heat of reaction at constant volume.

Consider the generalized reaction



The heat of reaction at standard state, $\Delta H_{r,T_0}$, at T_0 is

$$\Delta H_{r,T_0} = \sum_{i=1}^N v_i'' \Delta \mathcal{H}_{f,M_i}^o - \sum_{i=1}^N v_i' \Delta \mathcal{H}_{f,M_i}^o \quad (1-140)$$

If the heat of reaction at T_1 is known, the heat of reaction at T_2 can be determined by considering the two equilibrium states as indicated in Fig. 1.8, i.e.,

$$(\text{heat change})_{\text{path } A} = (\text{heat change})_{\text{path } B}$$

or

$$\begin{aligned} \Delta H_{\text{reactants}} + \Delta H_{r,T_2} &= \Delta H_{r,T_1} + \Delta H_{\text{products}} \\ \Delta H_{\text{reactants}} &= \sum_{i=1}^N v_i' \int_{T_1}^{T_2} C_{p,M_i} dT \quad \text{and} \quad \Delta H_{\text{products}} \\ &= \sum_{i=1}^N v_i'' \int_{T_1}^{T_2} C_{p,M_i} dT \end{aligned}$$

Therefore,

$$\Delta H_{r,T_2} = \Delta H_{r,T_1} + \sum_{i=1}^N v_i'' \int_{T_1}^{T_2} C_{p,M_i} dT - \sum_{i=1}^N v_i' \int_{T_1}^{T_2} C_{p,M_i} dT \quad (1-141)$$

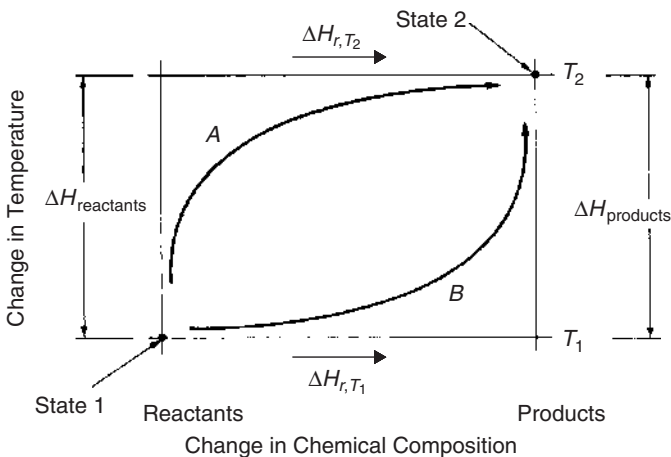


Figure 1.8 Two temperature-reaction paths, showing the relationship between heats of reaction at two different temperatures.

or

$$\Delta H_{r,T_2} = \Delta H_{r,T_1} + \sum_{\text{all products}} [H_{T_2} - H_{T_1}] - \sum_{\text{all reactants}} [H_{T_2} - H_{T_1}] \quad (1-142)$$

If we consider the reaction occurring at 1 bar pressure and set $T_1 = T_0 = 298.15$ K, $T_2 = T$, then

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \sum_{\text{products}} [H_T - H_{T_0}] - \sum_{\text{reactants}} [H_T - H_{T_0}] \quad (1-143)$$

Substituting in Eqs. (1-140) and (1-141) and changing to the appropriate integration limits gives

$$\begin{aligned} \Delta H_{r,T} = & \left[\sum_{i=1}^N v_i'' \Delta \mathcal{H}_{f,M_i}^o - \sum_{i=1}^N v_i' \Delta \mathcal{H}_{f,M_i}^o \right] \\ & + \sum_{i=1}^N v_i'' \int_{T_0}^T C_{p,M_i} dT - \sum_{i=1}^N v_i' \int_{T_0}^T C_{p,M_i} dT \end{aligned} \quad (1-144)$$

Rearranging,

$$\begin{aligned} \Delta H_{r,T} = & \sum_{i=1}^N v_i'' \left(\Delta \mathcal{H}_{f,M_i}^o + \int_{T_0}^T C_{p,M_i} dT \right) \\ & - \sum_{i=1}^N v_i' \left(\Delta \mathcal{H}_{f,M_i}^o + \int_{T_0}^T C_{p,M_i} dT \right) \end{aligned} \quad (1-145)$$

As discussed in Section 3 of Appendix A, the constant-pressure specific heat C_p is highly dependent on the temperature at relatively low pressure conditions. Methods for C_p calculation at high pressures as well as mixing rules for gas mixtures are given in the same section of Appendix A. The values of C_p^o at 1 bar can be determined from

$$\frac{C_p^o}{R_u} = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \quad (1-146)$$

where the coefficients a_1 through a_7 are tabulated in Ref. 2. In addition, C_p^o values for various gases are tabulated in the JANAF Thermochemical Tables.²⁰ For monatomic gases, the molar heat capacities at standard states, $C_p^o(T)$, are tabulated in Ref. 21. Also, expressions for C_p in terms of temperature are given in polynomial forms for 238 different gases by Andrews and Biblarz.²² These expressions, based on least-squares polynomial approximation, are very convenient for numerical computations.

Values of C_p^o (J/mol-K) for some selected gaseous chemical species covering a broad range of temperatures are given in Table 1.4. These values are compiled

Table 1.4a Molar Heat Capacities C_p^o (cal/mol-K) for Various Substances^a

T (K)	$O_{2(g)}$	$H_{2(g)}$	$N_{2(g)}$	$O_{(g)}$	$H_{(g)}$	$H^+_{(g)}$	$N_{(g)}$	$C_{(graphite)}$
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
100	6.957	6.729	6.956	5.665	4.968	4.968	4.968	0.400
200	6.961	6.560	6.957	5.434	4.968	4.968	4.968	1.196
298.15	7.021	6.892	6.961	5.237	4.968	4.968	4.968	2.036
300	7.023	6.895	6.961	5.234	4.968	4.968	4.968	2.051
400	7.196	6.974	6.991	5.134	4.968	4.968	4.968	2.824
500	7.431	6.993	7.070	5.081	4.968	4.968	4.968	3.495
600	7.670	7.009	7.196	5.049	4.968	4.968	4.968	4.026
700	7.883	7.037	7.350	5.029	4.968	4.968	4.968	4.430
800	8.062	7.080	7.513	5.015	4.968	4.968	4.968	4.739
900	8.211	7.142	7.670	5.006	4.968	4.968	4.968	4.977
1000	8.334	7.219	7.815	4.999	4.968	4.968	4.968	5.165
1100	8.437	7.309	7.945	4.994	4.968	4.968	4.968	5.316
1200	8.525	7.407	8.060	4.990	4.968	4.968	4.968	5.441
1300	8.601	7.510	8.161	4.987	4.968	4.968	4.968	5.546
1400	8.670	7.615	8.250	4.984	4.968	4.968	4.968	5.635
1500	8.734	7.719	8.328	4.982	4.968	4.968	4.968	5.713
1600	8.794	7.821	8.396	4.980	4.968	4.968	4.968	5.782
1700	8.853	7.920	8.456	4.979	4.968	4.968	4.968	5.843
1800	8.909	8.016	8.509	4.978	4.968	4.968	4.968	5.899
1900	8.965	8.106	8.555	4.978	4.968	4.968	4.968	5.950
2000	9.020	8.193	8.597	4.978	4.968	4.968	4.969	5.998
2200	9.129	8.354	8.668	4.978	4.968	4.968	4.971	6.083
2400	9.235	8.499	8.726	4.981	4.968	4.968	4.974	6.160
2600	9.337	8.631	8.775	4.986	4.968	4.968	4.982	6.231
2800	9.435	8.752	8.815	4.994	4.968	4.968	4.993	6.297
3000	9.528	8.864	8.850	5.004	4.968	4.968	5.010	6.360
3500	9.731	9.118	8.920	5.041	4.968	4.968	5.085	6.507
4000	9.900	9.349	8.975	5.091	4.968	4.968	5.212	6.645
4500	10.048	9.564	9.020	5.149	4.968	4.968	5.390	6.777
5000	10.200	9.758	9.061	5.210	4.968	4.968	5.607	6.906
5500	10.379	9.918	9.101	5.269	4.968	4.968	5.849	7.032
6000	10.609	10.030	9.148	5.323	4.968	4.968	6.100	7.157

^aCompiled and converted from the JANAF Thermochemical Tables.²⁰

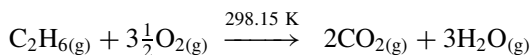
from the JANAF Tables²⁰ and Gordon and McBride's Thermodynamic Data Report.²¹ Similarly, values of the enthalpy differences ($\mathcal{H}_T^o - \mathcal{H}_{298.15}^o$) of these species are tabulated in Table 1.5 with the same temperature range as that of Table 1.4. These values are useful for equations which are expressed in terms of ($\mathcal{H}_T^o - \mathcal{H}_{298.15}^o$). The values in Tables 1.5a through 1.5f were compiled from the same sources.^{20,21}

Table 1.4b Molar Heat Capacities C_p° (cal/mol-K) for Various Substances^a

T (K)	$C_{(g)}$	$CO_{(g)}$	$NO_{(g)}$	$OH_{(g)}$	$H_2O_{(g)}$	$CO_{2(g)}$	$S_{(g)}$	$CH_{4(g)}$
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
100	5.084	6.956	7.720	7.798	7.959	6.981	5.104	7.949
200	4.996	6.957	7.271	7.356	7.971	7.734	5.590	8.000
298.15	4.980	6.965	7.133	7.167	8.028	8.874	5.658	8.518
300	4.980	6.965	7.132	7.165	8.030	8.896	5.657	8.534
400	4.975	4.862	7.157	7.087	8.189	9.877	5.553	9.680
500	4.972	7.121	7.286	7.056	8.419	10.666	5.435	11.076
600	4.971	7.276	7.466	7.057	8.682	11.310	5.339	12.483
700	4.970	7.450	7.655	7.090	8.962	11.846	5.266	13.813
800	4.970	7.624	7.832	7.150	9.255	12.293	5.210	15.041
900	4.969	7.786	7.988	7.233	9.557	12.667	5.168	16.157
1000	4.969	7.931	8.123	7.332	9.863	12.980	5.136	17.159
1100	4.969	8.057	8.238	7.439	10.166	13.243	5.111	18.052
1200	4.970	8.168	8.336	7.549	10.461	13.466	5.092	18.842
1300	4.970	8.263	8.419	7.659	10.742	13.656	5.079	19.537
1400	4.972	8.346	8.490	7.766	11.007	13.815	5.069	20.149
1500	4.975	8.417	8.552	7.867	11.233	13.953	5.064	20.687
1600	4.978	8.480	8.605	7.963	11.484	14.074	5.062	21.161
1700	4.983	8.535	8.651	8.053	11.696	14.177	5.063	21.578
1800	4.990	8.583	8.691	8.137	11.890	14.269	5.068	21.946
1900	4.998	8.626	8.727	8.214	12.069	14.352	5.075	22.272
2000	5.008	8.664	8.759	8.286	12.232	14.424	5.085	22.562
2200	5.032	8.728	8.813	8.415	12.526	14.547	5.111	23.049
2400	5.060	8.681	8.858	8.526	12.773	14.648	5.144	23.440
2600	5.094	8.825	8.895	8.622	12.985	14.734	5.181	23.757
2800	5.130	8.863	8.927	8.706	13.167	14.807	5.219	24.017
3000	5.168	8.895	8.955	8.780	13.324	14.873	5.258	24.233
3500	5.261	8.961	9.012	8.933	13.637	15.006	5.347	24.632
4000	5.345	9.014	9.058	9.055	13.870	15.118	5.418	24.900
4500	5.414	9.059	9.097	9.158	14.050	15.217	5.469	25.089
5000	5.468	9.100	9.132	9.249	14.195	15.307	5.502	25.226
5500	5.509	9.100	9.164	9.336	14.336	15.415	5.520	25.329
6000	5.540	9.175	9.194	9.422	14.477	15.525	5.527	25.408

^aCompiled and converted from the JANAF Thermochemical Tables.²⁰

Example 1.10. Assume the combustion of ethane $C_2H_{6(g)}$ with O_2 can be represented by the following global reaction without any dissociation in the final product:



Evaluate the heat of reaction of ethane.

Table 1.4c Molar Heat Capacities C_p^o (cal/mol-K) for Various Substances^a

T (K)	$C_2H_2(g)$	$C_2H_4(g)$	$Cl_2(g)$	$Br_2(g)$	$I_2(g)$	$Cl(g)$	$Br(g)$	$I(g)$
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
100	7.014	7.952	7.003	7.381	7.919	4.968	4.968	4.968
200	8.505	8.451	7.581	8.265	8.619	5.038	4.968	4.968
298.15	10.539	10.250	8.114	8.616	8.816	5.219	4.968	4.968
300	10.571	10.292	8.122	8.620	8.819	5.223	4.968	4.968
400	12.065	12.679	8.436	8.777	8.904	5.370	4.968	4.968
500	13.114	14.932	8.620	8.862	8.954	5.436	4.971	4.968
600	13.931	16.889	8.735	8.915	8.989	5.445	4.979	4.968
700	14.615	18.574	8.813	8.953	9.019	5.424	4.997	4.968
800	15.239	20.038	8.869	8.983	9.046	5.389	5.026	4.968
900	15.801	21.319	8.913	9.009	9.072	5.351	5.063	4.969
1000	16.318	22.442	8.948	9.053	9.102	5.314	5.106	4.970
1100	16.789	23.427	8.978	9.053	9.138	5.279	5.153	4.973
1200	17.221	24.289	9.004	9.073	9.185	5.248	5.199	4.977
1300	17.613	25.044	9.027	9.094	9.249	5.221	5.243	4.984
1400	17.968	25.705	9.050	9.116	9.334	5.196	5.284	4.993
1500	18.291	26.284	9.071	9.139	9.442	5.175	5.320	5.004
1600	18.582	26.793	9.092	9.165	9.572	5.156	5.351	5.006
1700	18.845	27.241	9.114	9.195	9.721	5.140	5.377	5.034
1800	19.085	27.636	9.136	9.228	9.883	5.125	5.398	5.052
1900	19.302	27.985	9.159	9.266	10.051	5.112	5.415	5.072
2000	19.504	28.295	9.185	9.308	10.217	5.101	5.428	5.093
2200	19.853	28.817	9.243	9.404	10.515	5.081	5.443	5.137
2400	20.151	29.235	9.313	9.510	10.729	5.066	5.446	5.182
2600	20.404	29.574	9.395	9.619	10.835	5.053	5.442	5.226
2800	20.625	29.852	9.485	9.721	10.832	5.043	5.432	5.267
3000	20.820	30.082	9.578	9.808	10.731	5.034	5.418	5.304
3500	21.225	30.509	9.781	9.929	10.195	5.018	5.375	5.376
4000	21.557	30.796	9.872	9.896	9.496	5.007	5.329	5.420
4500	21.835	30.998	9.811	9.738	8.819	5.000	5.287	5.442
5000	22.077	31.145	9.614	9.508	8.232	4.994	5.249	5.446
5500	22.309	31.255	9.322	9.249	7.746	4.989	5.216	5.439
6000	22.521	31.339	8.980	8.992	7.350	4.986	5.188	5.425

^aCompiled and converted from the JANAF Thermochemical Tables.²⁰*Solution:* To calculate ΔH_r at standard state conditions, we can use Eq. (1-140):

$$\begin{aligned}
 \Delta H_{r,T_0}^o &= \sum_{i=1}^N v_i'' \Delta \mathcal{H}_{f,M_i}^o - \sum_{i=1}^N v_i' \Delta \mathcal{H}_{f,M_i}^o \\
 &= 0 \Delta \mathcal{H}_{f,C_2H_6(g)}^o + 0 \Delta \mathcal{H}_{f,O_2(g)}^o + 2 \Delta \mathcal{H}_{f,CO_2(g)}^o + 3 \Delta \mathcal{H}_{f,H_2O(g)}^o \\
 &\quad - (1 \Delta \mathcal{H}_{f,C_2H_6(g)}^o + 3 \frac{1}{2} \Delta \mathcal{H}_{f,O_2(g)}^o + 0 \Delta \mathcal{H}_{f,CO_2(g)}^o + 0 \Delta \mathcal{H}_{f,H_2O(g)}^o)
 \end{aligned}$$

Table 1.4d Molar Heat Capacities C_p° (cal/mol-K) for Various Substances^a

T (K)	HCl _(g)	HBr _(g)	HI _(g)	F _{2(g)}	F _(g)	HF _(g)	(FH) _{2(g)}
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
100	6.959	6.959	6.958	6.958	5.068	6.962	8.288
200	6.961	6.961	6.961	7.095	5.403	6.962	9.507
298.15	6.964	6.965	6.968	7.481	5.436	6.964	10.725
300	6.964	6.965	6.969	7.489	5.435	6.964	10.748
400	6.973	6.984	7.010	7.885	5.361	6.967	11.879
500	7.004	7.039	7.107	8.187	5.282	6.973	12.795
600	7.069	7.139	7.253	8.393	5.218	6.986	13.512
700	7.167	7.272	7.424	8.564	5.169	7.015	14.090
800	7.288	7.422	7.600	8.685	5.132	7.063	14.579
900	7.422	7.576	7.767	8.779	5.104	7.129	15.012
1000	7.559	7.724	7.919	8.857	5.083	7.211	15.404
1100	7.693	7.863	8.056	8.923	5.065	7.303	15.763
1200	7.819	7.989	8.177	8.982	5.052	7.402	16.093
1300	7.936	8.103	8.283	9.035	5.041	7.504	16.396
1400	8.043	8.205	8.376	9.084	5.032	7.606	16.673
1500	8.141	8.296	8.459	9.130	5.024	7.705	16.926
1600	8.229	8.378	8.532	9.172	5.018	7.800	17.155
1700	8.310	8.451	8.596	9.209	5.013	7.891	17.364
1800	8.382	8.517	8.654	9.241	5.008	7.977	17.553
1900	8.448	8.576	8.706	9.266	5.005	8.058	17.724
2000	8.509	8.630	8.753	9.284	5.001	8.133	17.880
2200	8.614	8.724	8.835	9.296	4.996	8.270	18.149
2400	8.702	8.803	8.904	9.272	4.992	8.389	18.371
2600	8.778	8.870	8.964	9.213	4.988	8.493	18.556
2800	8.844	8.929	9.016	9.123	4.986	8.584	18.710
3000	8.901	8.980	9.063	9.006	4.984	8.664	18.841
3500	9.020	9.088	9.162	8.641	4.979	8.829	19.087
4000	9.115	9.176	9.246	8.234	4.977	8.958	19.257
4500	9.195	9.252	9.320	7.841	4.975	9.063	19.378
5000	9.265	9.320	9.387	7.486	4.974	9.152	19.467
5500	9.328	9.383	9.451	7.176	4.973	9.230	19.534
6000	9.388	9.442	9.512	6.900	4.972	9.300	19.586

^aCompiled from the JANAF Thermochemical Tables.²⁰

Using the heats of formation tabulated in Table 1.2, we have

$$\begin{aligned}\Delta H_{r,T_0}^\circ &= [-(2 \times 94.05) - (3 \times 57.8)] - [-(1 \times 20.04) + (3.5 \times 0)] \\ &= -341.46 \text{ kcal}\end{aligned}$$

#

Table 1.5a Enthalpy Differences [$H(T) - H(T_r)$] (kcal/mol) for Various Substances^a

T (K)	O _{2(g)}	H _{2(g)}	N _{2(g)}	O _(g)	H _(g)	H _(g) ⁺	N _(g)	C _(graphite)
0	-2.075	-2.024	-2.072	-1.607	-1.481	-1.481	-1.481	-0.251
100	-1.381	-1.307	-1.379	-1.080	-0.984	-0.984	-0.984	-0.237
200	-0.685	-0.663	-0.618	-0.522	-0.488	-0.488	-0.488	-0.159
298.15	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
300	0.013	0.013	0.013	0.010	0.009	0.009	0.009	0.004
400	0.723	0.707	0.710	0.527	0.506	0.506	0.506	0.248
500	1.454	1.406	1.413	1.038	1.003	1.003	1.003	0.565
600	2.209	2.106	2.126	1.544	1.500	1.500	1.500	0.942
700	2.987	2.808	2.853	2.048	1.996	1.996	1.996	1.366
800	3.785	3.514	3.596	2.550	2.493	2.493	2.493	1.825
900	4.599	4.225	4.355	3.051	2.990	2.990	2.990	2.312
1000	5.426	4.943	5.130	3.552	3.487	3.487	3.487	2.819
1100	6.265	5.669	5.918	4.051	3.984	3.984	3.984	3.343
1200	7.113	6.405	6.718	4.550	4.480	4.480	4.480	3.881
1300	7.969	7.151	7.529	5.049	4.977	4.977	4.977	4.431
1400	8.833	7.907	8.350	5.548	5.474	5.474	5.474	4.990
1500	9.703	8.674	9.179	6.046	5.971	5.971	5.971	5.558
1600	10.580	9.451	10.015	6.544	6.467	6.467	6.467	6.132
1700	11.462	10.238	10.858	7.042	6.964	6.964	6.964	6.714
1800	12.350	11.035	11.706	7.540	7.461	7.461	7.461	7.301
1900	13.244	11.841	12.559	8.038	7.958	7.958	7.958	7.893
2000	14.143	12.656	13.417	8.536	8.455	8.455	8.455	8.491
2200	15.958	14.311	15.144	9.531	9.448	9.448	9.449	9.699
2400	17.795	15.996	16.883	10.527	10.442	10.442	10.443	10.924
2600	19.652	17.709	18.634	11.524	11.435	11.435	11.439	12.163
2800	21.529	19.448	20.393	12.522	12.429	12.429	12.436	13.416
3000	23.426	21.209	22.159	13.522	13.423	13.423	13.436	14.681
3500	28.242	25.706	26.603	16.032	15.907	15.907	15.958	17.899
4000	33.151	30.324	31.077	18.565	18.391	18.391	18.531	21.187
4500	38.139	35.053	35.576	21.125	20.875	20.875	21.179	24.542
5000	43.200	39.884	40.096	23.715	23.359	23.359	23.927	27.963
5500	48.343	44.805	44.637	26.335	25.843	25.843	26.791	31.448
6000	53.587	49.795	49.199	28.983	28.327	28.327	29.778	34.995

^aCompiled and converted from the JANAF Thermochemical Tables.²⁰

When the heat of reaction is negative, heat is evolved and the process is called an *exothermic process*. When the heat of reaction is positive, heat must be absorbed by the system during the chemical reaction and the process is called an *endothermic process*.

The *heating value* of a fuel is a term commonly used in discussing combustion. The heating value is a positive number that is equal to the enthalpy of combustion

Table 1.5b Enthalpy Differences [$H(T) - H(T_r)$] (kcal/mol) for Various Substances^a

T (K)	C _(g)	CO _(g)	NO _(g)	OH _(g)	H ₂ O _(g)	CO _{2(g)}	S _(g)	CH _{4(g)}
0	-1.562	-2.072	-2.197	-2.192	-2.367	-2.238	-1.591	-2.396
100	-0.992	-1.379	-1.451	-1.467	-1.581	-1.543	-1.092	-1.601
200	-0.489	-0.683	-0.705	-0.711	-0.784	-0.816	-0.554	-0.805
298.15	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
300	0.009	0.013	0.013	0.013	0.015	0.016	0.011	0.016
400	0.507	0.711	0.727	0.725	0.825	0.957	0.571	0.923
500	1.004	1.418	1.448	1.432	1.655	1.985	1.121	1.960
600	1.501	2.137	2.185	2.137	2.510	3.085	1.659	3.138
700	1.999	2.874	2.941	2.845	3.392	4.243	2.189	4.454
800	2.495	3.627	3.716	3.556	4.303	5.451	2.713	5.897
900	2.992	4.398	4.507	4.275	5.243	6.699	3.232	7.458
1000	3.489	5.184	5.313	5.004	6.214	7.982	3.747	9.125
1100	3.986	5.984	6.131	5.742	7.216	9.293	4.259	10.886
1200	4.483	6.795	6.960	6.491	8.247	10.629	4.769	12.732
1300	4.980	7.617	7.798	7.252	9.307	11.986	5.278	14.652
1400	5.477	8.447	8.643	8.023	10.395	13.359	5.785	16.637
1500	5.975	9.285	9.495	8.805	11.508	14.748	6.292	18.679
1600	6.472	10.130	10.353	9.596	12.645	16.147	6.798	20.772
1700	6.970	10.981	11.216	10.397	13.804	17.562	7.304	22.909
1800	7.469	11.837	12.083	11.207	14.984	18.984	7.811	25.086
1900	7.968	12.697	12.954	12.024	16.182	20.416	8.318	27.297
2000	8.469	13.562	13.829	12.849	17.397	21.854	8.826	29.539
2200	9.473	15.301	15.586	14.520	19.874	24.752	9.845	34.102
2400	10.482	17.047	17.353	16.214	22.405	27.672	10.871	38.753
2600	11.497	18.803	19.129	17.929	24.981	30.610	11.903	43.473
2800	12.519	20.572	20.911	19.662	27.597	33.564	12.943	48.252
3000	13.549	22.348	22.699	21.411	30.246	36.533	13.991	53.077
3500	16.157	26.813	27.189	25.841	36.990	44.003	16.643	65.300
4000	18.809	31.307	31.709	30.339	43.870	51.535	19.335	77.688
4500	21.499	35.826	36.248	34.893	50.852	59.119	22.058	90.188
5000	24.220	40.366	40.805	39.495	57.914	66.750	24.801	102.768
5500	26.965	44.923	45.379	44.141	65.047	74.430	27.557	115.408
6000	29.728	49.500	49.969	48.831	72.250	82.165	30.320	128.093

^aCompiled and converted from the JANAF Thermochemical Tables.²⁰

but has the opposite sign. There are many possible heating values for a fuel, depending on the phase of the water formed in the products (liquid or gas), the phase of the fuel (liquid or gas), and the conditions under which the combustion is carried out (e.g., constant pressure or constant volume).

The heat of combustion may be considered a special case of the heat of reaction. The *heat of combustion* of a substance is the heat liberated when a fuel (usually a hydrocarbon) reacts with oxygen to yield H₂O and CO₂.

Table 1.5c Enthalpy Differences $[H(T) - H(T_r)]$ (kcal/mol) for Various Substances^a

T (K)	$C_2H_{2(g)}$	$C_2H_{4(g)}$	$Cl_{2(g)}$	$Br_{2(g)}$	$I_{2(g)}$	$Cl_{(g)}$	$Br_{(g)}$	$I_{(g)}$
0	-2.393	-2.514	-2.194	-2.324	-2.418	-1.499	-1.481	-1.481
100	-1.698	-1.719	-1.498	-1.619	-1.692	-1.002	-0.984	-0.984
200	-0.938	-0.909	-0.772	-0.831	-0.857	-0.503	-0.488	-0.488
298.15	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
300	0.020	0.019	0.015	0.016	0.016	0.010	0.726	0.009
400	1.155	1.167	0.844	0.887	0.903	0.540	0.506	0.506
500	2.416	2.550	1.698	1.769	1.796	1.081	1.003	1.003
600	3.769	4.143	2.566	2.658	2.693	1.625	1.500	1.500
700	5.197	5.918	3.444	3.552	3.594	2.169	1.999	1.996
800	6.690	7.851	4.328	4.448	4.497	2.710	2.500	2.493
900	8.243	9.920	5.217	5.348	5.403	3.247	3.005	2.990
1000	9.849	12.109	6.110	6.250	6.311	3.780	3.513	3.487
1100	11.505	14.404	7.006	7.154	7.223	4.310	4.026	3.984
1200	13.206	16.791	7.906	8.060	8.139	4.836	4.543	4.482
1300	14.947	19.258	8.807	8.969	9.061	5.359	5.066	4.980
1400	16.727	21.796	9.711	9.879	9.990	5.880	5.592	5.478
1500	18.540	24.396	10.617	10.792	10.929	6.399	6.122	5.978
1600	20.384	27.051	11.525	11.707	11.879	6.915	6.656	6.479
1700	22.255	29.753	12.435	12.625	12.844	7.430	7.192	6.982
1800	24.152	32.497	13.348	13.546	13.824	7.943	7.731	7.486
1900	26.072	35.279	14.263	14.471	14.821	8.455	8.272	7.992
2000	28.012	38.093	15.180	15.400	15.834	8.966	8.814	8.500
2200	31.949	43.806	17.022	17.271	17.908	9.984	9.901	9.523
2400	35.950	49.613	18.878	19.162	20.034	10.998	10.990	10.555
2600	40.006	55.495	20.748	21.075	22.193	12.010	12.079	11.596
2800	44.109	61.438	22.636	23.009	24.361	13.020	13.167	12.646
3000	48.254	67.432	24.543	24.962	26.519	14.027	14.252	13.703
3500	58.768	82.588	29.386	29.903	31.763	16.540	16.950	16.374
4000	69.466	97.918	34.305	34.865	36.687	19.046	19.626	19.074
4500	80.315	113.370	39.232	39.778	41.263	21.548	22.280	21.790
5000	91.294	128.908	44.093	44.591	45.522	24.046	24.914	24.513
5500	102.391	144.509	48.831	49.281	49.512	26.542	27.530	27.235
6000	113.600	160.158	53.407	53.841	53.283	29.036	30.131	29.951

^aCompiled and converted from the JANAF Thermochemical Tables.²⁰

The heat of reaction of a certain reaction can be determined using Hess's law to sum the related reactions for which the heats of reaction are known. Bond energies and resonance energies can also be used for evaluating the heat of reaction or heat of combustion of a reaction, as illustrated in Example 1.11.

Example 1.11. Evaluate the heat of combustion of benzoic acid, $C_6H_5COOH_{(g)}$.

Solution: The reaction is

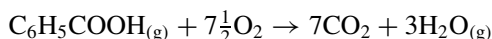
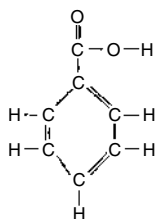


Table 1.5d Enthalpy Differences $[H(T) - H(T_r)]$ (kcal/mol) for Various Substances^a

T (K)	HCl _(g)	HBr _(g)	HI _(g)	F _{2(g)}	F _(g)	HF _(g)	(HF) _{2(g)}
0	-2.065	-2.067	-2.069	-2.109	-1.558	-2.055	-2.684
100	-1.379	-1.379	-1.380	-1.414	-1.060	-1.380	-1.882
200	-0.683	-0.683	-0.684	-0.714	-0.534	-0.683	-0.993
298.15	0.000	0.000	0.000	0.000	0.000	0.000	0.000
300	0.013	0.013	0.013	0.014	0.010	0.013	0.020
400	0.710	0.710	0.711	0.783	0.550	0.709	1.153
500	1.408	1.411	1.417	1.588	1.082	1.406	2.388
600	2.112	2.120	2.135	2.418	1.607	2.104	3.705
700	2.823	2.840	2.868	3.267	2.126	2.804	5.086
800	3.546	3.575	3.620	4.129	2.641	3.508	6.520
900	4.281	4.324	4.388	5.003	3.153	4.217	8.000
1000	5.030	5.089	5.172	5.885	3.663	4.934	9.521
1100	5.793	5.869	5.971	6.774	4.170	5.660	11.080
1200	6.568	6.662	6.783	7.669	4.676	6.395	12.673
1300	7.356	7.466	7.606	8.570	5.180	7.140	14.298
1400	8.155	8.282	8.439	9.476	5.684	7.896	15.951
1500	8.965	9.107	9.281	10.387	6.187	8.661	17.631
1600	9.783	9.941	10.130	11.302	6.689	9.437	19.336
1700	10.610	10.782	10.987	12.221	7.190	10.221	21.062
1800	11.445	11.631	11.850	13.143	7.691	11.015	22.808
1900	12.286	12.485	12.718	14.069	8.192	11.816	24.572
2000	13.134	13.346	13.591	14.996	8.692	12.626	26.352
2200	14.847	15.082	15.350	16.855	9.692	14.267	29.956
2400	16.579	16.834	17.124	18.712	10.691	15.933	33.609
2600	18.327	18.602	18.911	20.562	11.689	17.621	37.302
2800	20.089	20.382	20.709	22.396	12.686	19.329	41.029
3000	21.864	22.173	22.517	24.209	13.683	21.054	44.784
3500	26.345	26.691	27.074	28.624	16.174	25.429	54.270
4000	30.880	31.258	31.676	32.843	18.663	29.877	63.859
4500	35.458	35.865	36.318	36.861	21.151	34.383	73.519
5000	40.073	40.508	40.995	40.690	23.638	38.937	83.231
5500	44.722	45.185	45.705	44.354	26.124	43.533	92.983
6000	49.401	49.891	50.446	47.874	28.610	48.166	102.763

^aCompiled and converted from the JANAF Thermochemical Tables.²⁰

The molecular structure of benzoic acid is given below:



Benzoic acid

For the reactants, the bond and resonance energies are

$$4(\text{C}-\text{C}) + 3(\text{C}=\text{C}) + 5(\text{C}-\text{H}) + 1(\text{C}=\text{O}) \\ + 1(\text{C}-\text{O}) + 1(\text{O}-\text{H}) + 7\frac{1}{2}(\text{O}=\text{O}) \\ + 1(\text{C}_6\text{H}_6, \text{benzene-ring resonance}) + 1(-\text{COOH, carboxyl})$$

Inserting numerical values from Table 1.3, the total bond and resonance energy of the reactants is

$$4 \times 85 + 3 \times 145 + 5 \times 98.1 + 173 + 86 + 109 + 7.5 \times 119.1 + 48.9 + 28 \\ = 2603.7 \text{ kcal}$$

For the products, recognizing that CO_2 is formed with two double bonds, the bond and resonance energies are

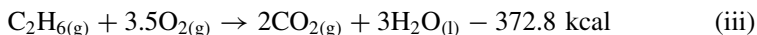
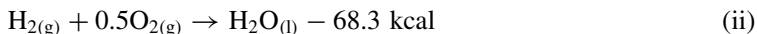
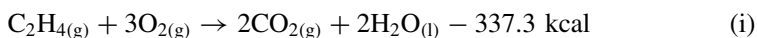
$$14(\text{C}=\text{O}) + 6(\text{O}-\text{H}) + 7(\text{CO}_2 \text{ resonance}) = 14 \times 173 + 6 \times 109 + 7 \times 33 = 3307 \text{ kcal}$$

Thus, the estimated heat of combustion of benzoic acid is

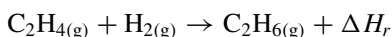
$$2603.7 - 3307 = -703.3 \text{ kcal}$$

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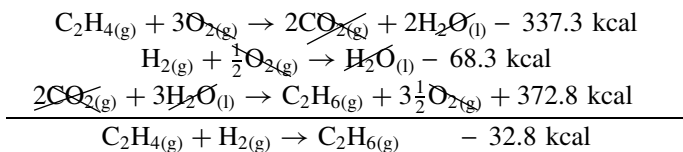
Example 1.12. Given the following three reactions at 298.15 K,



determine the heat of reaction for



Solution: The result is obtained simply by adding (i) and (ii) and subtracting (iii), or by using Lavoisier and Laplace's law on (iii) to reverse it first and add it to both (i) and (ii):



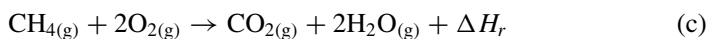
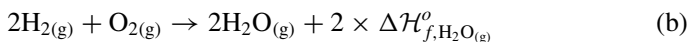
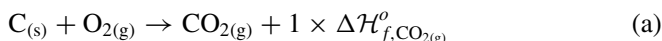
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Heat of reactions may also be manipulated by Hess's law to arrive at heats of formation for substances. The heat of combustion of CH_4 is about 10 times

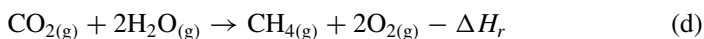
larger than the heat of formation of CH_4 . Some tabulated heats of formation of compounds are deduced from heats of combustion, which can be measured experimentally in the laboratory. The heat of formation of CH_4 can be deduced from the heats of formation of CO_2 and H_2O and the heat of reaction of $\text{CH}_4 + 2\text{O}_2$.

Example 1.13. Deduce the heat of formation of CH_4 from those of CO_2 and H_2O and the ΔH_r of the methane–oxygen reaction.

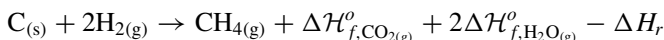
Solution: Consider the following reactions,



Using Lavoisier and Laplace's law, the last equation becomes



Summing Eqs. (a), (b), and (d) gives



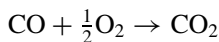
Therefore,

$$\Delta \mathcal{H}_{f, \text{CH}_{4(\text{g})}}^o = \Delta \mathcal{H}_{f, \text{CO}_{2(\text{g})}}^o + 2\Delta \mathcal{H}_{f, \text{H}_2\text{O}_{(\text{g})}}^o - \Delta H_r$$

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12.2 Constant-Volume Combustion

Let us consider the following simple reaction in a constant-volume situation:



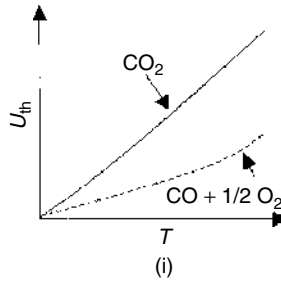
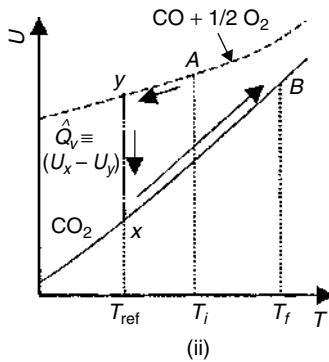
or

Reactants at state A \rightarrow product at state B

The sensible portion of the internal energy (without the chemical energy) of the reactants or products can be defined as

$$U_{\text{th}} \equiv \sum \int_{T_{\text{ref}}}^T n_i C_{v_i} dT$$

The U_{th} values of the reactants and products can be plotted versus temperature, as in Figure 1.9. If the chemical energy is added to both reactant and product curves, we have two new positions for these curves, as shown in Figure 1.10.


Figure 1.9 U_{th} values versus T .

Figure 1.10 Addition of chemical energy to Figure 1.9.

The internal energy difference between the product at thermodynamic state B and the reactants at state A is

$$\begin{aligned} \Delta U &= U_B - U_A = (U_B - U_x) + (U_x - U_y) + (U_y - U_A) \\ &= \int_{T_{ref}}^{T_f} n_{CO_2} C_{v,CO_2} dT + \hat{Q}_v - \int_{T_{ref}}^{T_i} \sum_{\text{reactants}} n_i C_{v,i} dT \end{aligned} \quad (1-147)$$

where the heat of reaction at constant volume is defined as

$$\hat{Q}_v \equiv \Delta U_r = (U_x - U_y)_{T_{ref}}$$

For an exothermic reaction, \hat{Q}_v is a negative quantity. Under the adiabatic condition, ΔU of Eq. (1-147) is zero; therefore $U_B = U_A$ and state B is at the same level as state A. If there is any heat loss from the system, $U_B < U_A$, then $\Delta U < 0$.

The temperature-reaction path of the above reaction is shown in Figure 1.11.

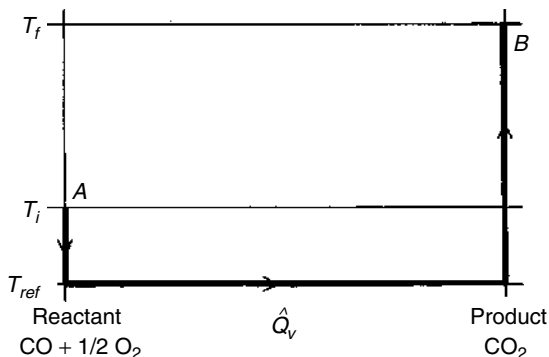


Figure 1.11 Temperature-reaction path.

The energy balance gives essentially the same equation as Eq. (1-147).

$$\Delta U = \int_{T_i}^{T_{ref}} \sum_{\text{reactants}} n_i C_{v_i} dT + \hat{Q}_v + \int_{T_{ref}}^{T_i} \sum_{\text{product}} n_i C_{v_j} dT \quad (1-147a)$$

where ΔU is equal to zero if the system is adiabatic. The value of \hat{Q}_v is related to \hat{Q}_p by

$$\hat{Q}_v = \hat{Q}_p - R_u T \Delta n \quad (1-148)$$

where Δn is defined by Eq. (1-139).

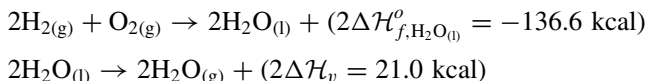
13 ENERGY BALANCE CONSIDERATIONS FOR FLAME TEMPERATURE CALCULATIONS

Consider a combustion process that takes place adiabatically in a closed system with negligible changes in kinetic and potential energies. For such a process, the temperature of the products is referred to as the *adiabatic flame temperature*. It is the maximum temperature that can be achieved for the given reactants, because any heat transfer from the reacting substances and any incomplete combustion would tend to lower the temperature of the products. The adiabatic temperature T_f can be controlled with an excess amount of air or diluent. In gas turbines, where the maximum permissible temperature is defined by metallurgical considerations in the turbine, close control of the temperature of the products is essential.

A few examples are given here to illustrate some of the steps used to calculate the adiabatic flame temperature.

Example 1.14. Calculate the adiabatic flame temperature of water vapor based on the reaction of gaseous H_2 and O_2 .

Solution: The overall reaction may be broken down as



where $\Delta\mathcal{H}_v$ represents the heat of vaporization. Adding these two equations, we have



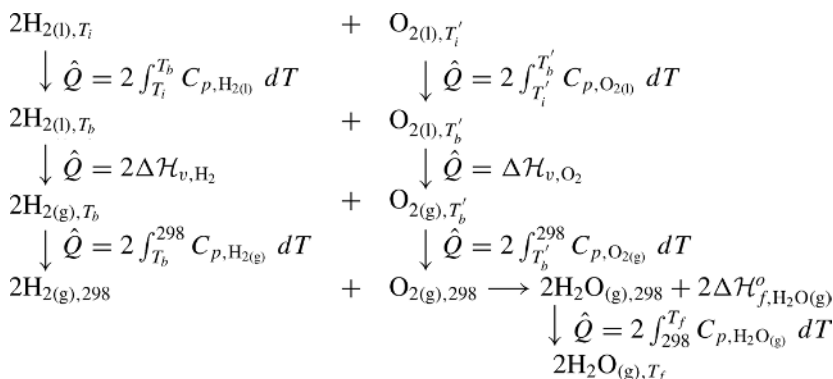
Therefore, the heat generated by the reaction is 115.6 kcal. If all of the heat is used to heat up the steam adiabatically under the assumption of no dissociation, then

$$115.6 \text{ kcal} = 2 \int_{298}^{T_f} C_{p,\text{H}_2\text{O}(\text{g})} dT \quad \text{or} \quad 57.8 \text{ kcal} = \mathcal{H}_{\text{H}_2\text{O},T_f} - \mathcal{H}_{\text{H}_2\text{O},298 \text{ K}}$$

Using Table 1.5*b*, the approximate value of T_f is found to be around 5000 K in order to balance the above equation. At such a high temperature, dissociation of steam must occur and the actual combustion products become unknown; therefore, to obtain a realistic value of the adiabatic flame temperature, we must include the effect of dissociation and equilibrium reactions among the product species. These complications will be discussed later. The adiabatic flame temperature for nondissociating products is normally called the adiabatic frozen-flame temperature.

#

To demonstrate the usefulness of the adiabatic assumption in calculating the adiabatic frozen-flame temperature, consider a more detailed example of the combustion of liquid H_2 with liquid O_2 . Let T_b represent the boiling temperature of $\text{H}_{2(\text{l})}$, T'_b the boiling temperature of $\text{O}_{2(\text{l})}$, and T_i the initial temperature of both reactants under cryogenic conditions. (The critical temperatures and pressures of H_2 and O_2 are 33.3 and 154.4 K and 1.3 and 5.04 MPa, respectively.) Considering the energy required for each step, we have



Since the system is assumed to be adiabatic,

$$\sum \hat{Q} = 0$$

Thus,

$$\begin{aligned} & 2 \int_{T_i}^{T_b} C_{p, \text{H}_2(\text{l})} dT + \int_{T'_i}^{T'_b} C_{p, \text{O}_2(\text{l})} dT + 2\Delta\mathcal{H}_{v, \text{H}_2} + \Delta\mathcal{H}_{v, \text{O}_2} \\ & + 2 \int_{T_b}^{298} C_{p, \text{H}_2(\text{g})} dT + \int_{T'_b}^{298} C_{p, \text{O}_2(\text{g})} dT \\ & + 2\Delta\mathcal{H}_{f, \text{H}_2\text{O}(\text{g})}^o + 2 \int_{298}^{T_f} C_{p, \text{H}_2\text{O}(\text{g})} dT = 0 \end{aligned} \quad (1-149)$$

The above equation can be written as

$$2\mathcal{H}_{\text{H}_2} \Big|_{T_i}^{298} + \mathcal{H}_{\text{O}_2} \Big|_{T'_i}^{298} + \Delta H_f^o + 2\mathcal{H}_{\text{H}_2\text{O}(\text{g})} \Big|_{298}^{T_f} = 0 \quad (1-150)$$

Either Eq. (1-149) or Eq. (1-150) can be utilized for T_f calculation.

Corresponding to the generalized chemical reaction,

$$\sum_{i=1}^N v'_i M_i \rightarrow \sum_{i=1}^N v''_i M_i \quad (1-151)$$

flame-temperature calculations can be conducted using the following enthalpy balance equation for either frozen or equilibrium processes:

$$\begin{aligned} & \overbrace{\sum_{i=1}^N v''_i \Delta\mathcal{H}_{f, M_i}^o - \sum_{i=1}^N v'_i \Delta\mathcal{H}_{f, M_i}^o}^{\Delta H_f} \\ & - \sum_{i=1}^N v'_i (\mathcal{H}_{M_i, T_i} - \mathcal{H}_{M_i, 298}) + \sum_{i=1}^N v''_i (\mathcal{H}_{M_i, T_f} - \mathcal{H}_{M_i, 298}) = \Delta H \end{aligned} \quad (1-152)$$

Note that in case a change of state takes place for a given species during the combustion process, different phases are considered as different species in this equation. For an adiabatic process, the heat addition from the surroundings to the system (ΔH) is zero. The above energy balance equation allows the calculation of the adiabatic frozen-flame temperature (where ΔH is positive for heat addition).

In general, the reactants may not be at the standard-state temperature T_0 , but rather at T_i , where T_i may be higher or lower than T_0 . During the combustion,

a part of the heat evolved is used to heat the product to a temperature T_2 . The energy-balance equation can also be written as

$$\Delta H = \sum_{\substack{j=1 \\ \text{products}}}^N v''_j \left\{ (\mathcal{H}_{T_f}^o - \mathcal{H}_{T_0}^o) + (\Delta \mathcal{H}_f^o)_{T_0} \right\}_j - \sum_{\substack{j=1 \\ \text{reactants}}}^N v'_j \left\{ (\mathcal{H}_{T_i}^o - \mathcal{H}_{T_0}^o) + (\Delta \mathcal{H}_f^o)_{T_0} \right\}_j \tag{1-153}$$

This equation says that under adiabatic condition ($\Delta H = 0$), the sum of sensible enthalpy and chemical enthalpy of product species is the same as that of the reactant species. The above energy balance can also be seen easily from the temperature-reaction path diagram in Fig. 1.12.

Let us define A , B , and C as

$$A = - \sum_{j=1}^N v'_j [(\mathcal{H}_{T_i}^o - \mathcal{H}_{T_0}^o)]_j$$

$$B = \sum_{j=1}^N v''_j (\Delta \mathcal{H}_f^o)_{T_0,j} - \sum_{j=1}^N v'_j (\Delta \mathcal{H}_f^o)_{T_0,j}$$

$$C = \sum_{j=1}^N v''_j [(\mathcal{H}_{T_f}^o - \mathcal{H}_{T_0}^o)]_j$$

Figure 1.12 indicates that

$$\Delta H = A + B + C$$

If $T_i < T_0$, then

$$\Delta H = A' + B + C$$

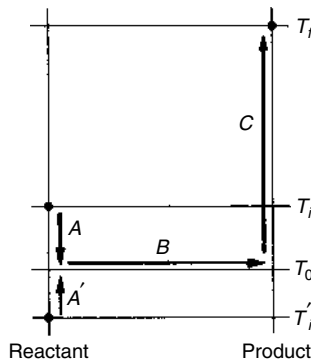
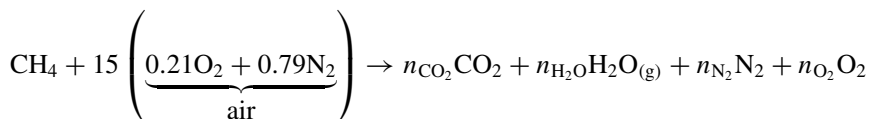


Figure 1.12 Temperature-reaction paths, showing the effect of initial reactant temperature.

Example 1.15. Assuming no dissociation of product species, determine the adiabatic flame temperature and product concentrations for the following chemical reaction at $T_i = 298$ K:



Solution: The four equations for conservation of atomic species are

$$\begin{aligned} \text{C:} & & 1 &= n_{\text{CO}_2} \\ \text{O:} & & 15 \times (0.21 \times 2) &= 2n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + 2n_{\text{O}_2} \\ \text{N:} & & 15 \times (0.79 \times 2) &= 2n_{\text{N}_2} \\ \text{H:} & & 4 &= 2n_{\text{H}_2\text{O}} \end{aligned}$$

Using the above equations, the values of n_{CO_2} , $n_{\text{H}_2\text{O}}$, n_{N_2} , and n_{O_2} are determined as 1.0, 2.0, 11.85, and 1.15, respectively. The adiabatic flame temperature T_f can then be calculated by letting $\Delta H = 0$ in Eq. (1-152), i.e.,

$$\begin{aligned} & \left[1\Delta\mathcal{H}_f^{\circ}\text{CO}_2 + 2\Delta\mathcal{H}_f^{\circ}\text{H}_2\text{O}_{(\text{g})} \right] - \left[1\Delta\mathcal{H}_f^{\circ}\text{CH}_4(\text{g}) \right] \\ & + \{ 1(\mathcal{H}_{T_f} - \mathcal{H}_{298})_{\text{CO}_2} + 2(\mathcal{H}_{T_f} - \mathcal{H}_{298})_{\text{H}_2\text{O}_{(\text{g})}} \\ & + 11.85(\mathcal{H}_{T_f} - \mathcal{H}_{298})_{\text{N}_2} + 1.15(\mathcal{H}_{T_f} - \mathcal{H}_{298})_{\text{O}_2} \} = 0 \end{aligned}$$

Using the values of $\Delta\mathcal{H}_f^{\circ}$ in Table 1.2, we have

$$\Delta H_r = [(-94.054) + 2(-57.798)] - (-17.895) = -191.755 \text{ kcal}$$

Assuming a flame temperature of 2000 K and using Table 1.5, the thermal energy change is

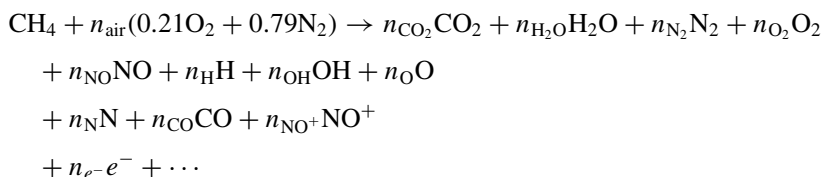
$$\begin{aligned} & 1(21.854)_{\text{CO}_2} + 2(17.397)_{\text{H}_2\text{O}} + 11.85(13.417)_{\text{N}_2} + 1.15(14.143)_{\text{O}_2} \\ & = 231.904 \text{ kcal} \end{aligned}$$

Assume a flame temperature of 1700 K, the thermal-energy change is

$$\begin{aligned} & 1(17.562)_{\text{CO}_2} + 2(13.804)_{\text{H}_2\text{O}} + 11.85(10.858)_{\text{N}_2} + 1.15(11.462)_{\text{O}_2} \\ & = 187.019 \text{ kcal} \end{aligned}$$

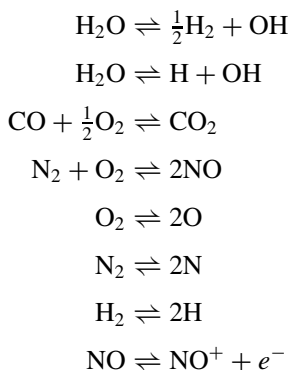
Interpolating for a value of 191.755 kcal, we arrive at $T_f = 1732$ K.

The above example shows that under the assumption of no product dissociation, there are five equations to be solved for five unknowns. It is important to note that the above method of calculation is appropriate only if T_f is low ($T_f < 1200$ K). At higher temperatures, the products dissociate and many other compounds are formed. The above chemical reaction could change into

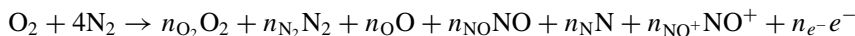


Because we still have only four equations from the conservation of atomic species, there are more unknowns than equations, and the adiabatic flame temperature cannot be calculated as in the simplified reaction.

If the products are in a condition of chemical equilibrium, we can obtain more relations between the mole fractions of the product constituents at equilibrium. Some equilibrium reactions are listed below.



The equilibrium constants (to be discussed in the next section) for each pair of equilibrium reactions will give us further information on the determination of the adiabatic flame temperature. We note here that for air at high temperatures, the reaction between O_2 and N_2 can produce many species. For example,



14 EQUILIBRIUM CONSTANTS

From previous discussion of Gibbs free energy, we have

$$G \equiv H - TS = U + pV - TS \quad (1-154)$$

Differentiating $U \equiv H - pV$ and utilizing the first law of thermodynamics, we have

$$dU = dH - p dV - V dp = T dS - p dV \quad (1-155)$$

where $p dV$ is the work done by the system. The differential form of Eq. (1-154) is

$$dG = dU + p dV + V dp - T dS - S dT \quad (1-156)$$

Then, substituting Eq. (1-155) into Eq. (1-156) gives

$$dG = V dp - S dT \quad (1-157)$$

Assuming the perfect-gas relation, for an isothermal process,

$$dG = V dp = \frac{nR_u T}{p} dp = nR_u T d(\ln p) \quad (1-158)$$

Integrating from p^o to p , Eq. (1-158) becomes

$$G - G^o = nR_u T (\ln p - \ln p^o) \quad (1-159)$$

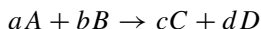
where p is given in the unit of bar and $p^o = 1$ bar. After combining the last two terms and rearranging, we have

$$G = G^o + nR_u T \ln(p/p^o) \quad (1-160)$$

Then, for species i in the system, we have

$$G_i = G_i^o + n_i R_u T \ln(p_i/p^o) \quad (1-161)$$

Let us now consider a reaction of A with B to produce C and D in a constant-temperature bath, i.e.,



Applying Eq. (1-161) to all four species flowing in and out of the Van't Hoff equilibrium box (see Fig. 1.13), we have

$$G_A = G_A^o + aR_u T \ln(p_A/p^o)$$

$$G_B = G_B^o + bR_u T \ln(p_B/p^o)$$

$$G_C = G_C^o + cR_u T \ln(p_C/p^o)$$

$$G_D = G_D^o + dR_u T \ln(p_D/p^o)$$

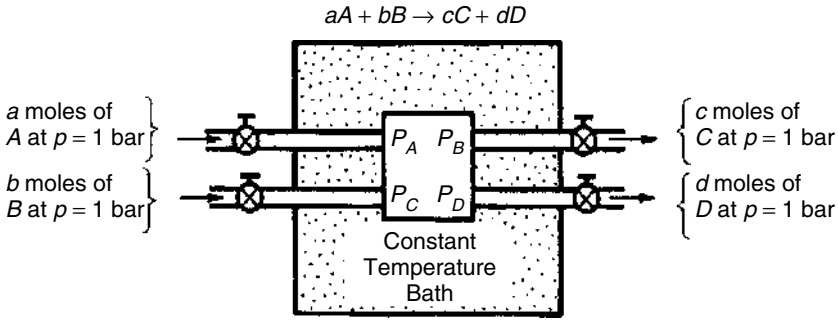


Figure 1.13 Van't Hoff equilibrium box.

Through the equilibrium box, we assume a moles of A and b moles of B are pumped into the box, the reaction occurs isothermally and equilibrium is reached, and then c moles of C and d moles of D are pumped out. From these considerations, the Gibbs free energy change can be written as

$$\begin{aligned}
 \Delta G &= G_{\text{product}} - G_{\text{reactant}} \\
 &= (G_C + G_D) - (G_A + G_B) \\
 &= [(G_C^\circ + G_D^\circ) - (G_A^\circ + G_B^\circ)] + R_u T \ln \left[\frac{p_C}{p^\circ} \right]^c \left[\frac{p_D}{p^\circ} \right]^d \\
 &\quad - R_u T \ln \left[\frac{p_A}{p^\circ} \right]^a \left[\frac{p_B}{p^\circ} \right]^b \\
 &= \Delta G^\circ + R_u T \ln \frac{[p_C/p^\circ]^c [p_D/p^\circ]^d}{[p_A/p^\circ]^a [p_B/p^\circ]^b} \tag{1-162}
 \end{aligned}$$

Since we have assumed the system to be at equilibrium,

$$\Delta G = 0$$

and

$$-\Delta G^\circ = R_u T \ln \frac{[p_C/p^\circ]^c [p_D/p^\circ]^d}{[p_A/p^\circ]^a [p_B/p^\circ]^b} \tag{1-163}$$

We can define

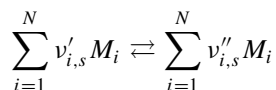
$$K_p \equiv \frac{[p_C/p^\circ]^c [p_D/p^\circ]^d}{[p_A/p^\circ]^a [p_B/p^\circ]^b} \tag{1-164}$$

$$\boxed{\Delta G^\circ = -R_u T \ln K_p} \tag{1-165}$$

Equation (1-165) shows the relation between the standard-free-energy change and the equilibrium constant at any arbitrary pressure and temperature. The value of K_p can be deduced from Eq. (1-165), if ΔG^o is known.

It is important to note that a large negative ΔG^o corresponds to a large equilibrium constant. Large K_p means that once reaction starts, the conversion of the reactants to products in their standard states will be quite complete at equilibrium with product concentrations much higher than those of reactants. Also, for any negative ΔG^o , K_p must be greater than unity.

The equilibrium constant can be put into a more general form by considering the general chemical reaction

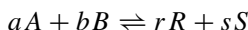


where v'_i and v''_i represent, respectively, the stoichiometric coefficients of reactants and products for the chemical species M_i , and N is the total number of chemical species involved. Then,

$$K_p = \prod_{i=1}^N \left[\frac{p_{i,e}}{p^o} \right]^{(v''_{i,s} - v'_{i,s})} \quad (1-166)$$

where in this product sum, the partial pressure of species i in the equilibrium mixture is raised to the power of $(v''_{i,s} - v'_{i,s})$ and the subscript s identifies the coefficients as the stoichiometric coefficients for the individual chemical equilibrium reactions. The subscript p in K_p means that the equilibrium constant is written in terms of partial pressures.

The same expression for the equilibrium constant can be obtained from thermodynamic considerations instead of from the Van't Hoff equilibrium box concept. Consider the hypothetical reaction between ideal gases



We shall now develop an expression for the free-energy change, which occurs when the reactants at partial pressures p_A and p_B are converted into products at partial pressures p_R and p_S . From earlier discussion,

$$G(p, T) = H(T) - TS(p, T) \quad (1-167)$$

Since we define the standard state at $p^o = 1$ bar, the Gibbs free energy at temperature T is

$$G^o(p^o, T) = H^o(T) - TS^o(p^o, T) \quad (1-168)$$

Subtracting Eq. (1-168) from (1-167) and noting that (since H is independent of pressure for a perfect gas) $H - H^o = 0$, we have

$$G - G^o = -T(S - S^o) \quad (1-169)$$

From the perfect-gas law, for an isothermal process

$$S - S^o = -nR_u \ln \left(\frac{p}{p^o} \right) \quad (1-170)$$

To see this, note that

$$\delta \hat{Q} = dE + \delta \hat{W}$$

For an isothermal process, $dE = 0$ and

$$\delta \hat{Q} = \delta \hat{W} = p dV \quad (1-171)$$

but

$$\begin{aligned} d_e S &= \frac{\delta \hat{Q}}{T} = \frac{p}{T} dV = \frac{nR_u}{V} dV = nR_u d(\ln V) \\ &= nR_u d \left[\ln \left(\frac{nR_u T}{p} \right) \right] \end{aligned} \quad (1-172)$$

Since we have made the isothermal assumption,

$$d_e S = -nR_u d(\ln p) \quad (1-173)$$

By integrating the above equation from p^o to p , we can obtain the same equation as Eq. (1-170). Substituting Eq. (1-170) into Eq. (1-169) gives

$$G(T, p) = G^o + nR_u T \ln \left(\frac{p}{p^o} \right) \quad (1-174)$$

For the mixture, then,

$$G(T, p) = \sum_{i=1}^N n_i \left\{ g_i^o + R_u T \ln \left(\frac{p_i}{p^o} \right) \right\} \quad (1-175)$$

where g_i is the molar Gibbs free energy of the i th species with units of cal/mol and p_i is the partial pressure as previously defined. At equilibrium,

$$(dG)_{T,p} = 0 \quad (1-176)$$

If we take the differential of Eq. (1-175), we get

$$0 = \sum_{i=1}^N g_i^o dn_i + R_u T \sum_{i=1}^N \left[\ln \left(\frac{p_i}{p^o} \right) \right] dn_i + R_u T \sum_{i=1}^N n_i \frac{dp_i}{p_i} \quad (1-177)$$

The last term of Eq. (1-177) vanishes because

$$\begin{aligned} \sum_{i=1}^N n_i \frac{dp_i}{p_i} &= \sum_{i=1}^N \left(\frac{n_{\text{total}}}{p} \right) dp_i = \frac{1}{p} \left(\sum_{i=1}^N n_i \right) \left(\sum_{i=1}^N dp_i \right) \\ &= \frac{1}{p} \left(\sum_{i=1}^N n_i \right) d \left(\sum_{i=1}^N p_i \right) = 0 \end{aligned} \quad (1-178)$$

since at equilibrium the system pressure is constant. The first term of Eq. (1-177) can be expressed as

$$\sum_{i=1}^N g_i^o dn_i = g_A^o dn_A + g_B^o dn_B + \cdots + g_R^o dn_R + g_S^o dn_S + \cdots \quad (1-179)$$

where

$$\begin{aligned} dn_A &= -a, & dn_B &= -b \\ dn_R &= r, & dn_S &= s \end{aligned}$$

Therefore,

$$\sum_{i=1}^N g_i^o dn_i \equiv \Delta G^o = G_{\text{products}}^o - G_{\text{reactants}}^o \quad (1-180)$$

Eq. (1-177) then becomes

$$\Delta G^o = -R_u T \ln K_p \quad (1-181)$$

where

$$K_p = \frac{(p_R/p^o)^r (p_S/p^o)^s}{(p_A/p^o)^a (p_B/p^o)^b}, \quad p^o = 1 \text{ bar} \quad (1-182)$$

and r , s , a , and b are the stoichiometric coefficients. We have thus arrived at the same result of Eq. (1-181) using two different methods.

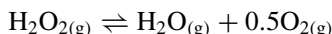
It should be noted that K_p is independent of system pressure, since K_p is related to ΔG^o and T by Eq. (1-165). Both G^o and ΔG^o are functions of T only, as can be seen from Eq. (1-168). The equilibrium constant K_p can therefore be tabulated as a unique function of temperature.

In the preceding discussion, the molar form of the free energy was introduced. We may also note that the molar standard free energy of formation $\Delta g_{f,i}^o$ is known for many compounds, allowing ΔG^o to be calculated for any reaction as

$$\Delta G^o = \sum_{i=1}^N v_i'' \Delta g_{f,i}^o - \sum_{i=1}^N v_i' \Delta g_{f,i}^o \quad (1-183)$$

where ΔG° depends only on the nature of the reactants and products. The values of Δg_f° for some selected species are given in Table 1.6. It is important to note that the value of Δg_f° for every element in its standard state is equal to zero.

Example 1.16. The decomposition of gaseous hydrogen peroxide occurs according to the reaction



What is the value of the equilibrium constant of this reaction at 298.15 K?

Solution: The value of ΔG° for this equilibrium reaction can be calculated using Table 1.6 and Eq. (1-183) as shown below:

$$\begin{aligned} \Delta G^\circ &= \sum_{i=1}^N v_i'' \Delta g_{f,i}^\circ - \sum_{i=1}^N v_i' \Delta g_{f,i}^\circ \\ &= \left[1\Delta g_{f,\text{H}_2\text{O}_{(\text{g})}}^\circ + \frac{1}{2}\Delta g_{f,\text{O}_{2(\text{g})}}^\circ + 0\Delta g_{f,\text{H}_2\text{O}_{2(\text{g})}}^\circ \right] \\ &\quad - [0\Delta g_{f,\text{H}_2\text{O}_{(\text{g})}}^\circ + 0\Delta g_{f,\text{O}_{2(\text{g})}}^\circ + 1\Delta g_{f,\text{H}_2\text{O}_{2(\text{g})}}^\circ] \\ &= [1(-54.63) + 0.5(0) + 0] - [0 + 0 + 1(-25.2)] = -29.43 \text{ kcal} \end{aligned}$$

ΔG° is related to K_p by Eq. (1-181). Considering the decomposition of 1 g-mol of H_2O_2 , we must use 29.43 kcal/g-mol for ΔG° . After rearrangement, we have

$$\begin{aligned} K_p &= \exp\left(-\frac{\Delta G^\circ}{R_u T}\right) = \exp\left(\frac{29.43 \times 10^3 \text{ cal/g-mole}}{(1.9872 \text{ cal/g-mole K})(298.15 \text{ K})}\right) \\ &= 3.736 \times 10^{21} \end{aligned}$$

#

Let us consider the equilibrium constants for the formation reactions of H_2O , H, and OH species. Their equilibrium constants can be written in terms of the partial pressures shown below:

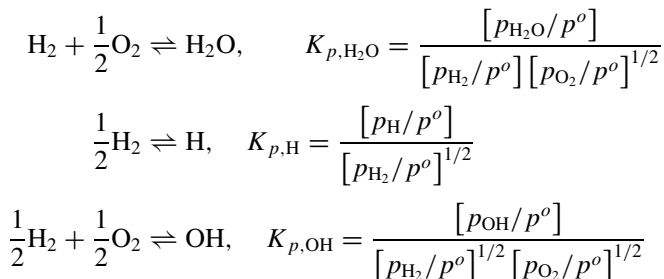
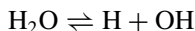


Table 1.6 Free Energy of Formation^a ΔG_f° (kcal/mol) at 298.15 K

<i>Gases</i>		<i>Solids</i>	
H ₂ O	-54.63	AgCl	-26.24
H ₂ O ₂	-25.20	AgBr	-23.2
O ₃	39.00	AgI	-15.81
HC1	-22.78	BaO	-124.37
HBr	-12.79	BaSO ₄	-325.6
HI	0.37	BaCO ₃	-271.1
SO ₂	-71.73	CaO	-144.24
SO ₃	-88.67	CaCO ₃	-269.9
H ₂ S	-7.97	Ca(OH) ₂	-214.73
N ₂ O	24.90	SiO ₂	-204.69
NO	20.70	Fe ₂ O ₃	-177.71
NO ₂	12.25	Al ₂ O ₃ (α crystal)	-378.17
NH ₃	-3.91	CuO	-31.00
CO	-32.78	Cu ₂ O	-34.89
CO ₂	-94.26	ZnO	-76.60
<i>Organic Compounds</i>			
GASES			
Methane, CH ₄	-12.13	Ethylene, C ₂ H ₄	16.35
Ethane, C ₂ H ₆	-7.65	Acetylene, C ₂ H ₂	59.31
Propane, C ₃ H ₈	-5.59	1-Butene, C ₄ H ₈	17.09
<i>n</i> -Butane, C ₄ H ₁₀	-3.75	<i>cis</i> -2-Butene, C ₄ H ₈	15.74
Isobutane, C ₄ H ₁₀	-4.3	<i>trans</i> -2-Butene, C ₄ H ₈	15.05
<i>n</i> -Pentane, C ₅ H ₁₂	-2.0	Isobutene, C ₄ H ₈	13.88
Isopentane, C ₅ H ₁₂	-3.5	1,3-Butadiene, C ₄ H ₆	36.01
Neopentane, C ₅ H ₁₂	-3.6	Methyl chloride, CH ₃ Cl	-14.0
LIQUIDS			
Methanol, CH ₃ OH	-39.82	Benzene, C ₆ H ₆	29.76
Ethanol, C ₂ H ₅ OH	-41.78	Chloroform, CHCl ₃	-17.6
Acetic acid, CH ₃ COOH	-93.19	Carbon tetrachloride, CCl ₄	-16.4
Water, H ₂ O	-56.68		
<i>Aqueous Ions</i>			
H ⁺	0.0	OH ⁻	-37.59
Na ⁺	-62.59	Cl ⁻	-31.35
K ⁺	-67.47	Br ⁻	-24.57
Ag ⁺	18.13	I ⁻	-12.35
Ba ²⁺	-134.0	HS ⁻	3.01
Ca ²⁺	-132.48	S ²⁻	20.0
Cu ²⁺	15.53	SO ₄ ²⁻	-177.34
Zn ²⁺	-35.18	SO ₃ ²⁻	-126.2
<i>Gaseous Atoms</i>			
H	48.58	I	16.7
F	14.9	C	160.43
Cl	25.17	N	108.87
Br	19.69	O	55.38
C ₂	186.83	S	56.52

^aCompiled and converted from the JANAF Table,²⁰ 79th edition of *Handbook of Chemistry and Physics*,¹⁶ and Mahan.⁴

We now consider an equilibrium reaction involving all three species H_2O , H , and OH :

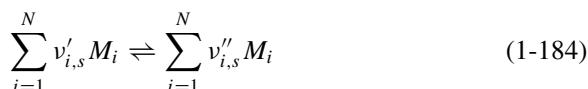


The equilibrium constant of this reaction is not tabulated as a function of T but can be evaluated from the following equation, where the last term contains the three $K_{p,i}$ which are tabulated with temperature for the formation reactions.

$$K_p = \frac{p_{\text{H}} p_{\text{OH}}}{p_{\text{H}_2\text{O}}} \frac{p_{\text{H}_2}^{1/2} p_{\text{O}_2}^{1/2}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} = \frac{(p_{\text{H}}/p_{\text{H}_2}^{1/2})(p_{\text{OH}}/p_{\text{H}_2}^{1/2} p_{\text{O}_2}^{1/2})}{(p_{\text{H}_2\text{O}}/p_{\text{H}_2} p_{\text{O}_2}^{1/2})} = \frac{K_{p,\text{H}} K_{p,\text{OH}}}{K_{p,\text{H}_2\text{O}}}$$

Note that p° is set to 1 bar for the above equation. In general, K_p of any elementary reaction can be calculated from the $K_{p,i}$ of the formation reactions of the species involved in the reaction.

Consider the following general equilibrium chemical reaction with $v'_{i,s}$ and $v''_{i,s}$ representing the stoichiometric coefficients of reactants and products for the chemical species M_i ; N is the total number of chemical species involved.



The equilibrium constant K_p expressed in terms of ratios of equilibrium partial pressures is given earlier in Eq. (1-166) as

$$K_p = K_p(T) = \prod_{i=1}^N (p_{i,e})^{(v''_{i,s} - v'_{i,s})} \quad (1-185a)$$

Other forms of the equilibrium constant are given by Eqs. (1-185b) through (1-185e)

$$K_n \equiv \prod_{i=1}^N (n_{i,e})^{(v''_{i,s} - v'_{i,s})} \quad (1-185b)$$

$$K_C \equiv \prod_{i=1}^N (C_{i,e})^{(v''_{i,s} - v'_{i,s})} \quad (1-185c)$$

$$K_X \equiv \prod_{i=1}^N (X_{i,e})^{(v''_{i,s} - v'_{i,s})} \quad (1-185d)$$

$$K_Y \equiv \prod_{i=1}^N (Y_{i,e})^{(v''_{i,s} - v'_{i,s})} \quad (1-185e)$$

For an ideal gas, we have

$$C_i = (\text{concentration of species } i) = \frac{p_i}{R_u T} \quad (1-186)$$

$$n_i \text{ (actual number of moles of species } i) = \frac{p_i V}{R_u T} = \frac{p_i}{p} n_T \quad (1-187)$$

$$X_i = (\text{mole fraction of species } i) = \frac{p_i}{p} = \frac{n_i}{n_T} \quad (1-188)$$

$$Y_i = (\text{mass fraction of species } i) = \frac{Mw_i p_i}{\rho T R_u} = \frac{Mw_i C_i}{\rho} = \frac{\rho_i}{\rho} \quad (1-189)$$

where

$$n_T = n = (\text{total number of moles in the mixture}) = \sum_{i=1}^N n_i$$

$$p = (\text{total mixture pressure}) = \sum_{i=1}^N p_i$$

$$\rho = \text{mixture density} = \sum_{i=1}^N \rho_i$$

Recall that we have defined

$$\Delta n = \sum_{i=1}^N v_i'' - \sum_{i=1}^N v_i' \quad (1-190)$$

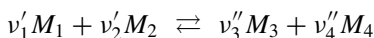
Various equilibrium constants are then related according to

$$K_p = K_C (R_u T)^{\Delta n} = K_n \left(\frac{R_u T}{V} \right)^{\Delta n} = K_n \left(\frac{p}{n_T} \right)^{\Delta n} \quad (1-191)$$

$$K_p = K_X \left(\frac{p}{p^o} \right)^{\Delta n} = K_Y \left(\frac{R_u T \rho}{p^o} \right)^{\Delta n} \prod_{i=1}^N Mw_i^{(v_i' - v_i'')} \quad (1-192)$$

When $\Delta n \neq 0$, unlike all other forms of equilibrium constants, K_p is a function of temperature only.

Now let us consider the following reaction involving only ideal gases:



Let $n^o(M_1)$, $n^o(M_2)$, $n^o(M_3)$, and $n^o(M_4)$ represent, respectively, the initial numbers of moles of M_1 , M_2 , M_3 , and M_4 before equilibrium has been reached

at a given temperature T . After equilibrium is reached, the following number of moles for each component are present in the mixture:

$$\begin{aligned} n_e(M_1) &= n^o(M_1) - v'_1x & n_e(M_2) &= n^o(M_2) - v'_2x \\ n_e(M_3) &= n^o(M_3) + v''_3x & n_e(M_4) &= n^o(M_4) + v''_4x \end{aligned}$$

They are given in the above form because for every v''_3x moles of M_3 formed, v''_4x moles of M_4 are formed, v'_1x moles of M_1 disappear, and simultaneously v'_2x moles of M_2 disappear. From the definitions of K_n and K_p , it now follows that

$$K_n = \frac{[n^o(M_3) + v''_3x]^{v''_3} [n^o(M_4) + v''_4x]^{v''_4}}{[n^o(M_1) - v'_1x]^{v'_1} [n^o(M_2) - v'_2x]^{v'_2}}$$

and

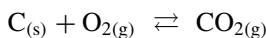
$$K_p = K_n \left(\frac{p}{n_T} \right)^{(v''_3 + v''_4 - v'_1 - v'_2)}$$

where the total number of moles in the final equilibrium mixture is

$$n_T = n^o(M_1) + n^o(M_2) + n^o(M_3) + n^o(M_4) + x(v''_3 + v''_4 - v'_1 - v'_2)$$

It is evident that for given values of K_n or K_p , the value of x can be calculated readily for given initial concentrations of the various reactants. Once the x value is known, the final equilibrium mixture composition is known.

Values of K_p for a number of formation reactions, compiled from the JANAF Thermochemical Tables,²⁰ are presented in terms of $\log_{10} K_p$ in Tables 1.7a through 1.7d. Note that the tabulated equilibrium constants are written for the formation of 1 mole of substances from their elements, for example,



When any elements are in the condensed phases, the equilibrium constants are written as in a script κ_p , that is, $\kappa_{p,CO_2} = p_{CO_2}/p_{O_2}p_{C(s)}$ for the above equilibrium reaction. Since $p_{C(s)}$ is very small, κ_p can be very large. Replacing $p_{C(s)}$ by the vapor pressure of graphite $p_{vp,C}$, which is a known function of temperature, and rearranging the equation, we have

$$K_{p,CO_2} \equiv \kappa_{p,CO_2} p_{vp,C} = \frac{p_{CO_2}}{p_{O_2}}$$

Values of K_{p,CO_2} defined by the above equation or those defined by Eq. (1-185a) are tabulated in Tables 1.7a through 1.7d. It is useful to note that K_p usually increases with increasing temperature for endothermic reactions and decreases for exothermic reactions.

Example 1.17. Consider the chemical reaction between methane and oxygen gas under a fuel-rich condition. The thermochemical reaction can be written as

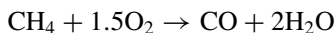


Table 1.7a Equilibrium Constants with Respect to the Elements in Their Standard States

T (K)	$\text{Log}_{10}K_{p1}$	$\text{Log}_{10}K_{p2}$	$\text{Log}_{10}K_{p3}$	$\text{Log}_{10}K_{p4}$	$\text{Log}_{10}K_{p5}$
0	∞	∞	∞	∞	∞
100	-126.729	-110.972	-19.438	123.579	-243.611
200	-61.986	-54.325	-9.351	60.792	-120.419
298.15	-40.599	-35.613	-6.005	40.047	-79.809
300	-40.330	-35.378	-5.963	39.785	-79.298
400	-29.469	-25.876	-4.265	29.238	-58.710
500	-22.936	-20.158	-3.246	22.884	-46.341
600	-18.570	-16.335	-2.568	18.631	-38.084
700	-15.446	-13.597	-2.085	15.582	-32.180
800	-13.098	-11.538	-1.724	13.287	-27.746
900	-11.269	-9.932	-1.444	11.496	-24.294
1000	-9.803	-8.644	-1.222	10.060	-21.530
1100	-8.603	-7.587	-1.041	8.881	-19.266
1200	-7.601	-6.705	-0.891	7.897	-17.377
1300	-6.752	-5.956	-0.764	7.063	-15.778
1400	-6.024	-5.313	-0.656	6.346	-14.407
1500	-5.392	-4.754	-0.563	5.724	-13.217
1600	-4.839	-4.264	-0.482	5.179	-12.175
1700	-4.350	-3.831	-0.410	4.698	-11.256
1800	-3.915	-3.446	-0.347	4.269	-10.437
1900	-3.525	-3.100	-0.291	3.885	-9.705
2000	-3.175	-2.788	-0.240	3.540	-9.045
2200	-2.568	-2.249	-0.153	2.942	-7.905
2400	-2.062	-1.798	-0.082	2.443	-6.954
2600	-1.633	-1.415	-0.021	2.021	-6.148
2800	-1.265	-1.087	0.030	1.658	-5.457
3000	-0.946	-0.801	0.074	1.344	-4.857
3500	-0.307	-0.228	0.160	0.713	-3.655
4000	0.173	0.203	0.223	0.239	-2.751
4500	0.547	0.539	0.270	-0.131	-2.046
5000	0.846	0.809	0.307	-0.428	-1.480
5500	1.092	1.029	0.335	-0.672	-1.015
6000	1.296	1.213	0.357	-0.877	-0.625

By permission, from the JANAF Thermochemical Tables.²⁰ The equilibrium constants are defined as follows: $K_{p1} = p_{\text{O}}/p_{\text{O}_2}^{1/2}$, $K_{p2} = p_{\text{H}}/p_{\text{H}_2}^{1/2}$, $K_{p3} = p_{\text{OH}}/p_{\text{O}_2}^{1/2}p_{\text{H}_2}^{1/2}$, $K_{p4} = p_{\text{H}_2\text{O}}/p_{\text{H}_2}p_{\text{O}_2}^{1/2}$, $K_{p5} = p_{\text{N}}/p_{\text{N}_2}^{1/2}$. The partial pressures are those of the (ideal) gas, unless the contrary is indicated explicitly.

Let us assume that the following water–gas equilibrium reactions occur within the product species,

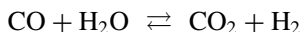


Table 1.7b Equilibrium Constants with Respect to the Elements in Their Standard States

T (K)	$\text{Log}_{10} K_{p6}$	$\text{Log}_{10} K_{p7}$	$\text{Log}_{10} K_{p8}$	$\text{Log}_{10} K_{p9}$	$\text{Log}_{10} K_{p10}$
0	∞	∞	∞	∞	∞
100	-46.460	-137.427	-365.689	62.807	205.639
200	-22.931	-65.238	-179.152	33.568	102.924
298.15	-15.172	-41.434	-117.599	24.030	69.095
300	-15.074	-41.135	-116.825	23.911	68.670
400	-11.143	-29.089	-85.606	19.110	51.539
500	-8.784	-21.932	-66.851	16.236	41.259
600	-7.210	-17.188	-54.336	14.320	34.404
700	-6.086	-13.815	-45.392	12.948	29.505
800	-5.243	-11.295	-38.681	11.916	25.829
900	-4.587	-9.405	-33.461	11.109	22.969
1000	-4.063	-8.154	-29.286	10.461	20.679
1100	-3.633	-7.128	-25.869	9.928	18.805
1200	-3.275	-6.272	-23.023	9.481	17.242
1300	-2.972	-5.548	-20.615	9.101	15.919
1400	-2.712	-4.926	-18.552	8.774	14.784
1500	-2.487	-4.386	-16.765	8.488	13.800
1600	-2.290	-3.914	-15.202	8.236	12.939
1700	-2.116	-3.497	-13.823	8.013	12.178
1800	-1.962	-3.126	-12.598	7.813	11.502
1900	-1.824	-2.793	-11.503	7.633	10.896
2000	-1.699	-2.494	-10.517	7.470	10.351
2200	-1.484	-1.977	-8.817	7.186	9.408
2400	-1.306	-1.546	-7.402	6.946	8.622
2600	-1.154	-1.180	-6.206	6.741	7.955
2800	-1.025	-0.867	-5.182	6.562	7.383
3000	-0.913	-0.595	-4.296	6.404	6.886
3500	-0.690	-0.050	-2.528	6.082	5.888
4000	-0.524	0.360	-1.207	5.830	5.134
4500	-0.396	0.680	-0.183	5.627	4.544
5000	-0.295	0.937	0.632	5.457	4.068
5500	-0.213	1.147	1.296	5.313	3.675
6000	-0.146	1.323	1.847	5.188	3.344

By permission, from the JANAF Thermochemical Tables.²⁰ The equilibrium constants are defined as follows: $K_{p6} = p_{\text{NO}}/p_{\text{N}_2}^{1/2} p_{\text{O}_2}^{1/2}$, $K_{p7} = p_{\text{S(g)}}/p_{\text{S(c)}}$, $K_{p8} = p_{\text{C(g)}}$ and $\kappa_{p8} = p_{\text{C(g)}}/p_{\text{C(c, graphite)}}$, $K_{p9} = p_{\text{CO}}/p_{\text{O}_2}^{1/2}$, and $\kappa_{p9} = p_{\text{CO}}/p_{\text{C(c, graphite)}} p_{\text{O}_2}^{1/2}$, $K_{p10} = p_{\text{CO}_2}/p_{\text{O}_2}$, $\kappa_{p10} = p_{\text{CO}_2}/p_{\text{C(c, graphite)}} p_{\text{O}_2}$.

Namely, a portion of the combustion product undergoes a further reaction and forms CO_2 and H_2 ; the equilibrium mixture can be assumed to consist of

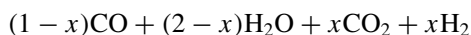


Table 1.7c Equilibrium Constants with Respect to the Elements in Their Standard States

T (K)	$\text{Log}_{10}K_{p11}$	$\text{Log}_{10}K_{p12}$	$\text{Log}_{10}K_{p13}$	$\text{Log}_{10}K_{p14}$	$\text{Log}_{10}K_{p15}$
0	∞	∞	∞	∞	∞
100	33.615	-123.562	-38.124	-60.319	-55.400
200	15.190	-63.116	-17.703	-28.855	-24.453
298.15	8.894	-43.477	-10.913	-18.449	-14.431
300	8.813	-43.232	-10.827	-18.318	-14.310
400	5.492	-33.426	-7.358	-13.028	-9.851
500	3.420	-27.626	-5.260	-9.841	-7.323
600	1.993	-23.816	-3.853	-7.709	-5.634
700	0.943	-21.138	-2.842	-6.180	-4.425
800	0.138	-19.162	-2.081	-5.029	-3.516
900	-0.500	-17.650	-1.486	-4.131	-2.808
1000	-1.018	-16.461	-1.009	-3.410	-2.239
1100	-1.447	-15.506	-0.617	-2.819	-1.773
1200	-1.807	-14.723	-0.290	-2.325	-1.384
1300	-2.115	-14.073	-0.012	-1.906	-1.054
1400	-2.379	-13.526	0.227	-1.546	-0.769
1500	-2.609	-13.061	0.435	-1.233	-0.522
1600	-2.810	-12.661	0.617	-0.959	-0.306
1700	-2.989	-12.316	0.778	-0.717	-0.114
1800	-3.147	-12.015	0.921	-0.501	0.057
1900	-3.289	-11.752	1.050	-0.307	0.211
2000	-3.416	-11.520	1.166	-0.133	0.350
2200	-3.636	-11.132	1.366	0.169	0.590
2400	-3.819	-10.823	1.534	0.422	0.792
2600	-3.973	-10.575	1.677	0.636	0.964
2800	-4.105	-10.374	1.799	0.820	1.112
3000	-4.219	-10.209	1.906	0.980	1.241
3500	-4.447	-9.914	2.121	1.301	1.500
4000	-4.619	-9.732	2.285	1.542	1.696
4500	-4.753	-9.622	2.415	1.729	1.850
5000	-4.863	-9.561	2.522	1.880	1.974
5500	-4.955	-9.533	2.612	2.003	2.076
6000	-5.034	-9.529	2.689	2.106	2.163

By permission, from the JANAF Thermochemical Tables.²⁰ The equilibrium constants are defined as follows: $K_{p11} = p_{\text{CH}_4}/p_{\text{H}_2}^2$ and $\kappa_{p11} = p_{\text{CH}_4}/p_{\text{H}_2}^2 p_{(\text{c, graphite})}$, $K_{p12} = p_{\text{C}_2\text{H}_2}/p_{\text{H}_2}$ and $\kappa_{p12} = p_{\text{C}_2\text{H}_2}/p_{\text{C}_{(\text{c, graphite})}} p_{\text{H}_2}$, $K_{p13} = p_{\text{F}}/p_{\text{F}_2}^{1/2}$, $K_{p14} = p_{\text{Cl}}/p_{\text{Cl}_2}^{1/2}$, and $K_{p15} = p_{\text{Br}}/p_{\text{Br}_2}^{1/2}$.

Table 1.7d Equilibrium Constants with Respect to the Elements in Their Standard States

T (K)	$\text{Log}_{10}K_{p16}$	$\text{Log}_{10}K_{p17}$	$\text{Log}_{10}K_{p18}$	$\text{Log}_{10}K_{p19}$	$\text{Log}_{10}K_{p20}$
0	∞	∞	∞	∞	∞
100	-49.601	142.739	48.702	19.630	-9.927
200	-21.502	71.548	24.625	12.076	-2.596
298.15	-12.294	48.117	16.696	9.375	-0.273
300	-12.179	47.822	16.596	9.336	-0.245
400	-7.582	35.956	12.573	7.327	0.839
500	-5.245	28.831	10.151	5.957	1.054
600	-3.920	24.077	8.530	5.038	0.953
700	-2.971	20.678	7.369	4.377	0.877
800	-2.258	18.125	6.494	3.878	0.818
900	-1.702	16.137	5.812	3.489	0.770
1000	-1.256	14.544	5.265	3.176	0.732
1100	-0.890	13.240	4.817	2.919	0.699
1200	-0.584	12.151	4.442	2.704	0.672
1300	-0.325	11.229	4.124	2.522	0.649
1400	-0.103	10.438	3.852	2.366	0.629
1500	0.090	9.751	3.615	2.231	0.612
1600	0.259	9.150	3.408	2.112	0.596
1700	0.409	8.619	3.225	2.007	0.583
1800	0.542	8.146	3.062	1.914	0.570
1900	0.661	7.723	2.916	1.830	0.559
2000	0.768	7.341	2.785	1.755	0.549
2200	0.953	6.682	2.558	1.625	0.530
2400	1.107	6.131	2.368	1.516	0.514
2600	1.237	5.665	2.207	1.424	0.499
2800	1.349	5.264	2.069	1.345	0.485
3000	1.445	4.917	1.950	1.275	0.473
3500	1.638	4.221	1.709	1.136	0.445
4000	1.783	3.699	1.526	1.030	0.422
4500	1.898	3.294	1.383	0.945	0.404
5000	1.993	2.970	1.267	0.877	0.390
5500	2.073	2.707	1.171	0.821	0.379
6000	2.143	2.488	1.091	0.774	0.371

By permission, from the JANAF Thermochemical Tables.²⁰ The equilibrium constants are defined as follows: $K_{p16} = p_1/p_{\text{I}_2}^{1/2}$, $K_{p17} = p_{\text{HF}}/p_{\text{H}_2}^{1/2}p_{\text{F}_2}^{1/2}$, $K_{p18} = p_{\text{HCl}}/p_{\text{H}_2}^{1/2}p_{\text{Cl}_2}^{1/2}$, $K_{p19} = p_{\text{HBr}}/p_{\text{H}_2}^{1/2}p_{\text{Br}_2}^{1/2}$, and $K_{p20} = p_{\text{HI}}/p_{\text{H}_2}^{1/2}p_{\text{I}_2}^{1/2}$.

Write the necessary mathematical relationships required for solving the equilibrium composition and adiabatic flame temperature.

Solution: The total number of moles of product species can be calculated as

$$n_T = \sum_{i=1}^N n_i = (1 - x) + (2 - x) + x + x = 3$$

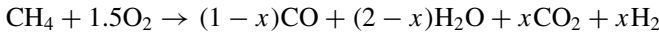
The mole fractions and partial pressures of product species are

$$\begin{aligned} X_{\text{CO}} &= \frac{1-x}{3}, & X_{\text{H}_2\text{O}} &= \frac{2-x}{3}, & X_{\text{CO}_2} &= X_{\text{H}_2} = \frac{x}{3} \\ p_{\text{CO}} &= \frac{1-x}{3}p, & p_{\text{H}_2\text{O}} &= \frac{2-x}{3}p, & p_{\text{CO}_2} &= p_{\text{H}_2} = \frac{x}{3}p \end{aligned}$$

For water-gas reaction, the equilibrium constant with $p^o = 1$ bar can be written as

$$K_p = \frac{p_{\text{CO}_2} p_{\text{H}_2}}{p_{\text{CO}} p_{\text{H}_2\text{O}}} = \frac{\left(\frac{x}{3}\right)^2 p^2}{\left(\frac{1-x}{3}\right) p \left(\frac{2-x}{3}\right) p} = \frac{x^2}{(1-x)(2-x)} \quad (\text{a})$$

For the chemical reaction



the general enthalpy balance equation for an adiabatic system can be written as

$$\Delta H = \sum_{i=1}^N v_i'' (\Delta \mathcal{H}_f^o)_i - \sum_{i=1}^N v_i' (\Delta \mathcal{H}_f^o)_i + \sum_{i=1}^N v_i'' \mathcal{H}_i \Big|_{298}^{T_f} + \sum_{i=1}^N v_i' \mathcal{H}_i \Big|_{T_i}^{298} = 0$$

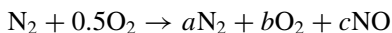
In terms of individual species, we have

$$\begin{aligned} &(1-x)\Delta \mathcal{H}_{f,\text{CO}}^o + (2-x)\Delta \mathcal{H}_{f,\text{H}_2\text{O}}^o + x\Delta \mathcal{H}_{f,\text{CO}_2}^o - \Delta \mathcal{H}_{f,\text{CH}_4}^o + [\mathcal{H}_{298} - \mathcal{H}_{T_i}]_{\text{CH}_4} \\ &+ 1.5[\mathcal{H}_{298} - \mathcal{H}_{T_i}]_{\text{O}_2} + (1-x)[\mathcal{H}_{T_f} - \mathcal{H}_{298}]_{\text{CO}} + (2-x)[\mathcal{H}_{T_f} - \mathcal{H}_{298}]_{\text{H}_2\text{O}} \\ &+ x[\mathcal{H}_{T_f} - \mathcal{H}_{298}]_{\text{CO}_2} + x[\mathcal{H}_{T_f} - \mathcal{H}_{298}]_{\text{H}_2} = 0 \end{aligned} \quad (\text{b})$$

Assuming a value of T_f , the equilibrium constant $K_p(T_f)$ can be determined from the equilibrium constants of the formation reactions of CO_2 , CO , and H_2O . Knowing K_p , the value of x can be solved from equation (a). Substitute the x value together with heats of formation and enthalpy changes into the left-hand side of equation (b) to see whether the sum is equal to zero. If not balanced, reassume a flame temperature and repeat the above process. Finally, the converged values of adiabatic flame temperature T_f and x can be determined through iteration, using equations (a) and (b). It is also possible to speed up the converging process using Newton-Raphson's descent method²³ for solving corrections to the initial estimated values of T_f .

Example 1.18. A mixture of 1 mole of N_2 and 0.5 mole of O_2 is heated to 4000 K at 1 atm pressure, resulting in an equilibrium mixture of N_2 , O_2 , and NO only. If the O_2 and N_2 were initially at 298.15 K and were heated steadily, how much heat was required to bring the final mixture to 4000 K on the basis of 1 initial mole of N_2 ?

Solution: The reaction is written as



The law of conservation of atomic species requires

$$N: 2 = 2a + c$$

$$O: 1 = 2b + c$$

This implies that

$$a = 0.5(2 - c) = 1 - \frac{c}{2}$$

$$b = 0.5(1 - c) = 0.5 - \frac{c}{2}$$

Letting $x = c$, the reaction equation can then be written as



Considering the equilibrium reaction $0.5N_2 + 0.5O_2 \rightleftharpoons NO$ at $T_f = 4000$ K, we can obtain $\log_{10} K_p = -0.524$ from Table 1.7b or $K_p = 0.2992 \approx 0.3$; therefore,

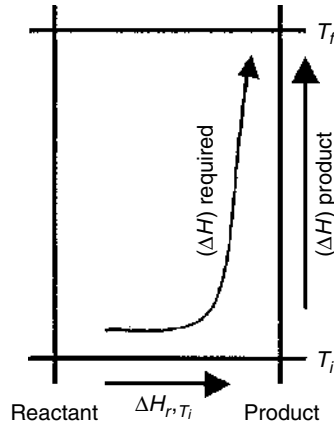
$$K_p = 0.3 = \frac{p_{NO}}{p_{N_2}^{1/2} p_{O_2}^{1/2}} = \frac{x}{(1 - x/2)^{1/2} (0.5 - x/2)^{1/2}} \left(\frac{p}{\sum n} \right)^{1-1/2-1/2}$$

Thus, $0.09 = 4x^2/[2(2 - x)(1 - x)]$, or $43.5x^2 + 3x - 2 = 0$, so that

$$x = \frac{-3 \pm \sqrt{9 + 8 \times 43.5}}{2 \times 43.5} = \frac{-3 \pm 18.89}{87} = 0.1825$$

Note that the negative root of $x = -0.2516$ has no physical meaning and therefore is ignored. The final mixture is then $0.90875N_2 + 0.40875O_2 + 0.1825NO$.

The heat of formation of NO can be found from Table 1.2, i.e., $(\Delta \mathcal{H}_{f,T_0}^o)_{NO} = 21.58$ kcal/mol.



The temperature-reaction path showing
 $(\Delta H)_{required} = \Delta H_{r, T_i} + (\Delta H)_{product}$

$$\begin{aligned}
 (\Delta H)_{required} &= \underbrace{\left(\sum_{i=1}^N v_i''(\Delta \mathcal{H}_f^o)_i - \sum_{i=1}^N v_i'(\Delta \mathcal{H}_f^o)_i \right)}_{\Delta H_{r, T_i}} + (\Delta H)_{product} \\
 &= 0.1825 \times 21.58 + 0.90875(\mathcal{H}_{4000}^o - \mathcal{H}_{298.15}^o)_{N_2} \\
 &\quad + 0.40875(\mathcal{H}_{4000}^o - \mathcal{H}_{298.15}^o)_{O_2} + 0.1825(\mathcal{H}_{4000}^o - \mathcal{H}_{298.15}^o)_{NO} \\
 &= 0.1825 \times 21.58 + 0.90875 \times 31.077 + 0.40875 \times 33.151 \\
 &\quad + 0.1825 \times 31.709 \\
 &= 51.52 \text{ kcal}
 \end{aligned}$$

#

More-complicated reactions (including dissociation) will be discussed following the introduction of the concepts of fugacity and activity.

15 REAL-GAS EQUATIONS OF STATE AND FUGACITY CALCULATION

In many combustion problems, when the system pressure is at an elevated level, the ideal gas law can no longer be applied. Section 1.2 of Appendix A gives various forms of real-gas equations of state for high-pressure considerations. Section 1.3 of the same appendix describes the mixing rules for gaseous mixtures. In addition to these real-gas equations of state, it is useful to consider a thermodynamic parameter called fugacity and its usage at high pressures.

G. N. Lewis in 1901 introduced the concept of *fugacity*, which has proved of great value in representing the actual behavior of real gases, especially at high pressures. For ideal gases at a constant temperature [see Eq. (1-158)],

$$(dG)_T = nR_uT d(\ln p)_T \quad (1-193)$$

For a gas that does not behave ideally, the above equation will not hold, but a function f , known as the fugacity, may be defined in such a manner that the relationship

$$(dG)_T \equiv nR_uT d(\ln f)_T \quad (1-194)$$

is always satisfied, irrespective of whether the gas is ideal or not. Integrating Eq. (1-194) from thermodynamic state 1 to state 2, we have

$$G_2 - G_1 = nR_uT \ln \frac{f_2}{f_1} \quad (1-195)$$

Fugacity of the i th species may be considered to be the corrected partial pressure for that species:

$$\frac{f_i}{p_i} = \Gamma \text{ (proportionality factor)} \quad (1-196)$$

where Γ is a function of many parameters, such as the temperature and pressure. For an ideal gas,

$$\frac{f}{p} = 1 \quad (1-197)$$

As the pressure of the real gas is decreased, however, the behavior approaches that for an ideal gas. Therefore, the gas at very low pressure is chosen as the reference state, and it is postulated that the ratio f/p then approaches unity. Thus,

$$\lim_{p \rightarrow 0} \frac{f}{p} = 1 \quad (1-198)$$

where f has the units of pressure.

In terms of specific quantities, Eq. (1-194) can be written as

$$(dg)_T = RT (d \ln f)_T \quad (1-194a)$$

For a real gas, the equation of the state could be given as $pv = ZRT$, then

$$(dg)_T = ZRT(d \ln p)_T \quad (1-194b)$$

where Z represents the compressibility factor of the real gas. For an isothermal process at temperature T , the fugacity can be determined from the compressibility factor Z and the pressure p by the following relationship:

$$Z d(\ln p)_T = d(\ln f)_T \quad (1-199)$$

Integrating along an isothermal line from $p = 0$ to a finite pressure, we have

$$\ln \frac{f}{p} = \int_0^{P_r} (Z - 1) d(\ln P_r)_T \quad (1-200)$$

The reduced temperature (T_r) and reduced pressure (P_r) of a gas are defined as the ratios of temperature and pressure to their critical values, respectively. The critical temperatures (T_c) and pressures (P_c) of selected gases are shown in Table 1.8. A generalized compressibility chart for some selected gases is shown in Fig. 1.14 from Ref. 28 based on the original results of Su.²⁹

At any temperature, the right-hand side of this equation can be integrated graphically, using the generalized compressibility chart to find Z at each reduced pressure P_r ($\equiv p/p_c$). The value of f is therefore determined. The use of fugacity at high pressures is given in later chapters (e.g., Chapter 6).

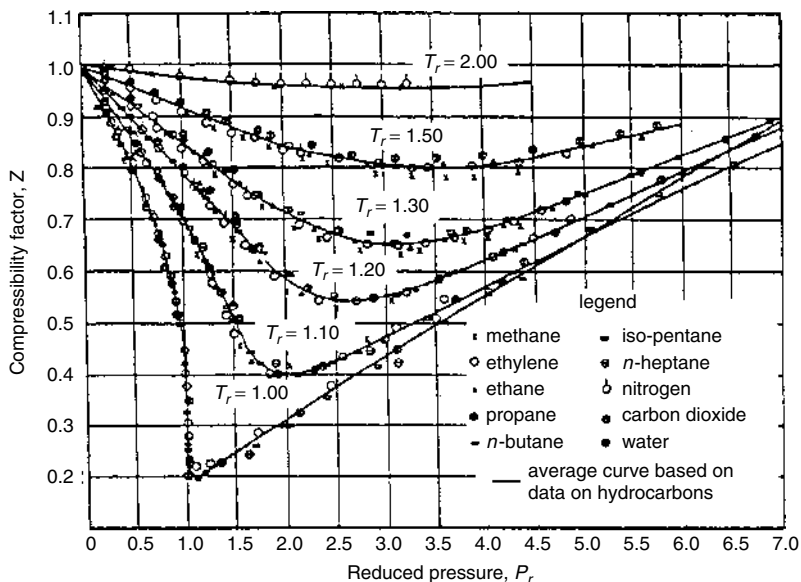


Figure 1.14 Generalized compressibility chart for selected gases.²⁸ (Gouq-Fen Su Modified Law of Corresponding States for Real Gases.²⁹ Reprinted from *Ind. and Eng., Chemistry*, vol. 38, p. 804, August, 1946. Copyright 1946 by the American Chemical Society and reprinted by permission of the copyright owner.)

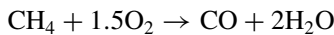
Table 1.8 Critical Temperatures and Pressures of Selected Gases^a

Gas	Formula	T_C (K)	P_C (MPa)
Air	—	132.5	3.766
Methane	CH ₄	190.56	4.592
Acetylene	C ₂ H ₂	308.3	6.138
Ethylene	C ₂ H ₄	282.34	5.041
Ethane	C ₂ H ₆	305.32	4.872
Propane	C ₃ H ₈	369.83	4.248
<i>n</i> -Butane	C ₄ H ₁₀	425.12	3.796
Isopentane	C ₅ H ₁₂	460.45	3.38
<i>n</i> -Heptane	C ₇ H ₁₆	474.8	1.62
Chlorine	Cl ₂	416.9	7.991
Carbon dioxide	CO ₂	304.13	7.375
Carbon monoxide	CO	132.91	3.499
Fluorine	F ₂	144.13	5.172
Helium	He	5.19	0.227
Hydrogen	H ₂	32.97	1.293
Neon	Ne	44.40	2.760
Nitrogen	N ₂	126.20	3.390
Hydrazine	N ₂ H ₄	653.0	14.7
Nitric oxide	NO	180.0	6.48
Nitrogen dioxide	NO ₂	430.95	10.132
Nitrous oxide	N ₂ O	309.57	7.255
Oxygen	O ₂	154.58	5.043
Ozone	O ₃	261.1	5.57
Water	H ₂ O	646.99	22.064
Xenon	Xe	289.73	5.840

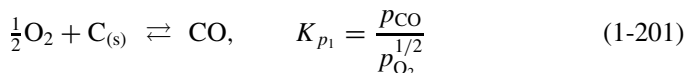
^aExcerpted (with units converted) from the 79th edition of *CRC Handbook of Chemistry and Physics*.¹⁶

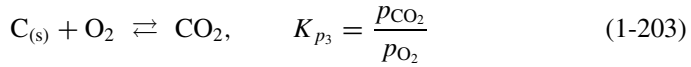
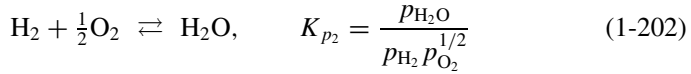
16 MORE-COMPLICATED DISSOCIATION IN THE COMBUSTION OF HYDROCARBONS

The frozen reaction process in the combustion of methane under fuel-rich conditions can be represented by

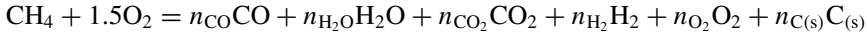


However, in reality there are more chemical product species to consider. In equilibrium, the following three equilibrium reactions should be considered:





The seven unknown quantities are the flame temperature and the partial pressures of the species $\text{C}_{(s)}$, CO , CO_2 , H_2 , H_2O , and O_2 , and the reaction equation can be written as



The conservation of atomic species equations for the three elements are

$$\text{C: } 1 = n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{C}_{(s)}}$$

$$\text{O: } 3 = n_{\text{CO}} + n_{\text{H}_2\text{O}} + 2n_{\text{CO}_2} + 2n_{\text{O}_2}$$

$$\text{H: } 4 = 2n_{\text{H}_2\text{O}} + 2n_{\text{H}_2}$$

Recall that

$$\frac{n_i}{n_T} = \frac{p_i}{p} \quad (1-204)$$

Although n_T is unknown, it does not generally differ significantly from the stoichiometric value; the value of n_T for $\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$ can be assumed to be 3 for the initial computation. With p known, we can substitute Eq. (1-204) into the atomic species conservation equations to get

$$\frac{p}{n_T} = p_{\text{CO}} + p_{\text{CO}_2} + p_{\text{C}} \quad (1-205)$$

$$3\frac{p}{n_T} = p_{\text{CO}} + p_{\text{H}_2\text{O}} + 2p_{\text{CO}_2} + 2p_{\text{O}_2} \quad (1-206)$$

$$4\frac{p}{n_T} = 2p_{\text{H}_2\text{O}} + 2p_{\text{H}_2} \quad (1-207)$$

Assuming $T_f = T_{f(1)}$, we can find from tables the values for $K_{p_1}(T_{f(1)})$, $K_{p_2}(T_{f(1)})$, and $K_{p_3}(T_{f(1)})$. The values of p_{C} , p_{CO} , p_{CO_2} , $p_{\text{H}_2\text{O}}$, p_{H_2} , and p_{O_2} can be obtained by solving the six simultaneous equations (1-201), (1-202), (1-203), (1-205), (1-206), and (1-207). n_{C} , n_{CO} , n_{CO_2} , $n_{\text{H}_2\text{O}}$, n_{H_2} , and n_{O_2} can be obtained from Eq. (1-204). The n_i values or v_i'' values are therefore known, and the enthalpy balance equation can be used for determination of T_f :

$$\sum_{i=1}^N v_i'' \Delta \mathcal{H}_{f,M_i}^o - \sum_{i=1}^N v_i' \Delta \mathcal{H}_{f,M_i}^o + \sum_{i=1}^N v_i'' \mathcal{H}_i \Big|_{298}^{T_f} - \sum_{i=1}^N v_i' \mathcal{H}_i \Big|_{298}^{T_i} = 0 \quad (1-208)$$

If Eq. (1-208) is not satisfied, we compute $n_T = \sum_{i=1}^N n_i$, reassume a value for T_f , and solve the six simultaneous equations again. This procedure is repeated until the enthalpy balance equation is satisfied. This is a general way of calculating the flame temperature and equilibrium compositions, when the combustion system is not extremely complicated. One disadvantage of this solution method is that as the partial pressure of a particular species becomes very small, errors can be introduced through very low values of partial pressure, which appears in the denominator of certain K_p expressions. Again, Newton-Raphson's descent method²³ can be used to speed up the converging process for obtaining corrections to the estimated values of T_f .

If a certain substance in an equilibrium mixture has two phases, an additional unknown is introduced. For example, if liquid water and water vapor coexist in one system, it is necessary to break $n_{\text{H}_2\text{O}_{\text{total}}}$ into $n_{\text{H}_2\text{O}_{(\text{g})}}$ and $n_{\text{H}_2\text{O}_{(\text{l})}}$, i.e.,

$$n_{\text{H}_2\text{O}_{\text{total}}} = n_{\text{H}_2\text{O}_{(\text{g})}} + n_{\text{H}_2\text{O}_{(\text{l})}}$$

and the fugacity of water vapor at relatively low pressures can be approximated by

$$f_{\text{H}_2\text{O}_{(\text{g})}} \approx p_{\text{H}_2\text{O}_{(\text{g})}} = \text{Known function of temperature, } T$$

Note that the vapor pressure of water is known at a certain temperature. The equilibrium constant for phase equilibrium of H_2O is known as a function of temperature:

$$K_p = \frac{P_{\text{H}_2\text{O}_{(\text{g})}}}{P_{\text{H}_2\text{O}_{(\text{l})}}}$$

For $\frac{1}{2}\text{O}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O}$, the equilibrium constant is

$$K_p = \frac{P_{\text{H}_2\text{O}_{(\text{g})}}}{P_{\text{O}_2}^{1/2} P_{\text{H}_2}}$$

The vapor pressure in the numerator is a known quantity. Therefore, p_{O_2} can be expressed as a function of p_{H_2} or $n_{\text{O}_2} = F(n_{\text{H}_2})$.

The conservation equations of atomic species then become

$$\text{O:} \quad [\text{O}] = 2n_{\text{O}_2} + n_{\text{H}_2\text{O}_{\text{total}}} + \dots = 2F(n_{\text{H}_2}) + n_{\text{H}_2\text{O}_{\text{total}}} + \dots$$

$$\text{H:} \quad [\text{H}] = 2n_{\text{H}_2} + 2n_{\text{H}_2\text{O}_{\text{total}}}$$

In general, when a change in phase of certain species occurs, the adiabatic flame temperature versus F/O has a flat region. (See Fig. 1.15.) For some problems in which $\text{H}_2\text{O}_{(\text{l})}$ is present in appreciable amounts, CO_2 may dissolve in the H_2O , resulting in the fugacity of the solution being different from that of pure $\text{H}_2\text{O}_{(\text{l})}$. This phenomenon further complicates the problem of finding equilibrium composition and flame temperature.

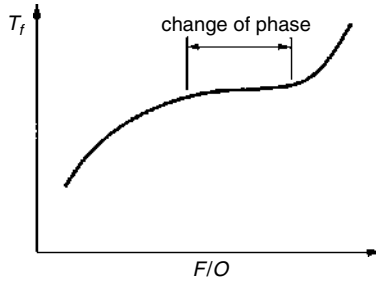
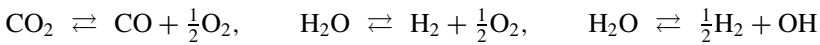


Figure 1.15 Exaggerated effect of phase change on the dependence of adiabatic flame temperature on fuel–oxidant ratio.

Some dissociation reactions are highly endothermic. This implies that T_f and equilibrium composition can be affected greatly by dissociation reactions. In general, for a C, H, O, N system, we should consider the following species in the equilibrium mixture: CO_2 , H_2O , CO , H_2 , O_2 , OH , H , O , O_3 , $\text{C}_{(s)}$, CH_4 , N_2 , N , NO , NH_3 , NO^+ , and e^- . For low-pressure combustion systems (with $p \sim 1$ atm and $T_f > 2200$ K) or intermediate pressure systems (with $p \sim 20$ atm and $T_f > 2500$ K), the dissociation of CO_2 and H_2O by following equilibrium reactions must be considered.



The degree of dissociation will be at least 1%.

17 THE CLAUSIUS–CLAPEYRON EQUATION FOR PHASE EQUILIBRIUM

Consider any system consisting of two phases, for example, liquid and vapor. As long as both phases are present, a finite amount of vaporization of the liquid phase (represented by B) into gas phase (represented by A) will not disturb the equilibrium at constant temperature and pressure conditions, i.e.,

$$[(G_A + \Delta G_A) + (G_B - \Delta G_B)] - [G_A + G_B] = 0$$

or

$$\Delta G = 0$$

Under phase equilibrium, there is no work done other than that of expansion. Therefore, based on Eq. (1-99), dG_A and dG_B can be written as

$$dG_A = V_A dp - S_A dT \tag{1-209}$$

$$dG_B = V_B dp - S_B dT \tag{1-210}$$

where, because $\Delta G = 0$,

$$dG_A = dG_B \quad \text{and} \quad V_A dp - S_A dT = V_B dp - S_B dT \quad (1-211)$$

Therefore,

$$\frac{dp}{dT} = \frac{S_A - S_B}{V_A - V_B} = \frac{\Delta S}{\Delta V} \quad (1-212)$$

The change of entropy ΔS is related to heat of vaporization by

$$\Delta S = \frac{\Delta H_v}{T}$$

Using the molar heat of vaporization and molar volume, Eq. (1-212) becomes

$$\frac{dp}{dT} = \frac{\Delta \mathcal{H}_v}{T \Delta v} \quad (1-213)$$

where Δv is the difference in the molar volumes of the two phases. Therefore, for liquid–vapor equilibrium, Eq. (1-213) becomes

$$\boxed{\frac{dp}{dT} = \frac{\Delta \mathcal{H}_v}{T(v_g - v_l)}} \quad (1-214)$$

This is the so-called Clausius–Clapeyron equation for phase equilibrium; it effectively relates the change in vapor pressure of a substance to a very small change in temperature. If the variation of vapor pressure with temperature is known, it is possible to calculate the heat of vaporization from Eq. (1-214). If the temperature is not too near the critical point of the substance, then

$$v_g \gg v_l \quad \text{or} \quad v_g - v_l \simeq v_g$$

Equation (1-214) then becomes

$$\frac{dp}{dT} \approx \frac{\Delta \mathcal{H}_v}{T v_g} \quad (1-215)$$

Furthermore, in regions well below the critical point, the vapor pressure is relatively small, and the ideal-gas law may be assumed to be applicable, that is, $p v_g = R_u T$ where v_g is the molar volume of the vapor. Thus,

$$\frac{dp}{dT} = \frac{p \Delta \mathcal{H}_v}{R_u T^2}$$

Therefore, the Clausius–Clapeyron equation may be written as

$$\boxed{\frac{d(\ln p)}{dT} = \frac{\Delta \mathcal{H}_v}{R_u T^2}} \quad (1-216)$$

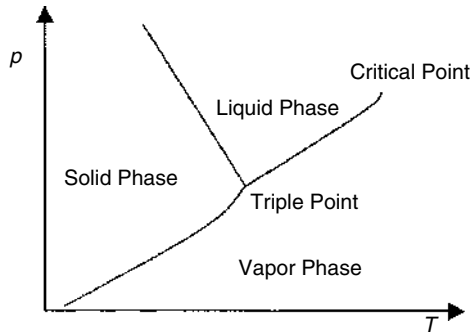


Figure 1.16 Phase diagram in terms of pressure and temperature, showing the abrupt change in slope at the triple point from solid–vapor interface to liquid–vapor interface.

If $\Delta\mathcal{H}_v$ is a constant, after integration, the algebraic form of the Clausius–Clapeyron equation is

$$\ln \frac{p_2}{p_1} \approx -\frac{\Delta\mathcal{H}_v}{R_u} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1-217)$$

This equation implies that the vapor pressure p_2 at T_2 can be calculated if the vapor pressure p_1 at T_1 is known. However, it should be noted that when a change of state is involved between T_1 and T_2 , the vapor-pressure-versus-temperature curve may have significant changes in slope, as shown by Fig. 1.16. If $\Delta\mathcal{H}_v$ is a function of T , then we have to integrate it analytically or numerically from Eq. (1-216).

Table 1.9 gives thermodynamic data for phase changes of many substances. These data are compiled from Ref. 16 and should be very useful in the consideration of phase-change computations.

18 CALCULATION OF EQUILIBRIUM COMPOSITIONS WITH NASA'S CEA COMPUTER PROGRAM

In various design and analysis applications to mechanical systems involving reactive mixtures, it is highly beneficial to be able to determine the chemical equilibrium compositions of the reacting media. Mechanical systems include aircraft combustors, rocket motors, gas turbines, shock tubes, heat exchangers, automobile engines, chemical processing equipment, nozzles, gun propulsion systems, and so on.

For more than four decades, Gordon,^{1,21} McBride,^{2,25} Zeleznik,²⁴ and Svehla²⁵ of NASA Lewis Research Center have made great efforts in developing methods and computer programs for calculating complex chemical equilibrium compositions, as well as thermodynamic and transport properties of the mixtures.

Table 1.9 Thermodynamic Data for Phase Changes^{a,b}

Substance	Process	Pressure (Torr)	Temperature (K)	ΔH (kcal/mol)	ΔS (cal/mol-K)	ΔC_p (cal/mol-K)
C ₂ H ₄ O	<i>c</i> → <i>l</i>	760	160.71	1.236	7.69	3.45
(ethylene oxide)	<i>l</i> → <i>g</i>		293.8	6.104	21.50	-9.7
C ₂ H ₆ O	<i>c</i> → <i>l</i>		131.66	1.180	8.96	6.8
(dimethylether)	<i>l</i> → <i>g</i>		248.4	5.141	20.70	-10.6
C ₂ H ₅ OH	<i>c</i> → <i>l</i>		158.9	1.200	7.57	5.70
(ethanol)	<i>l</i> → <i>g</i>	760	351.45	9.216	26.22	
CO(NH ₂) ₂	<i>c</i> → <i>l</i>		405.8	3.60	8.9	
(urea)						
CH ₃ NO ₂	<i>c</i> → <i>l</i>		244.78	2.319	9.47	
(nitromethane)	<i>l</i> → <i>g</i>	760	374.35	8.123		
CH ₃ ONO	<i>l</i> → <i>g</i>	760	255	5.0	19.7	
(methyl nitrite)						
CH ₃ NO ₃	<i>l</i> → <i>g</i>	760	339.7	7.8	23.0	
(methyl nitrate)						
C ₂ H ₅ NO ₂	<i>c</i> → <i>l</i>		18			
(nitroethane)	<i>l</i> → <i>g</i>	17	293	9.1	31	
C ₂ H ₅ ONO	<i>l</i> → <i>g</i>	760	290.1	6.64	22.9	
(ethyl nitrite)						
C ₂ H ₅ NO ₃	<i>c</i> → <i>l</i>		171			
(ethyl nitrate)	<i>l</i> → <i>g</i>	760	361.9			
C ₂ H ₄ (NO ₃) ₂	<i>c</i> → <i>l</i>		250.9	4.5	18	
(glycol dinitrate)	<i>l</i> → <i>g</i>	19	378			
C(NO ₂) ₄	<i>c</i> → <i>l</i>		286			
(tetranitromethane)	<i>l</i> → <i>g</i>	760	398.9	9.2	23	
CO	<i>l</i> → <i>g</i>	760	81.7	1.44	17.68	
CO ₂	<i>l</i> → <i>g</i>	760	194.68	6.031	30.98	
Cl ₂	<i>c</i> → <i>l</i>		171.5	1.530	8.892	2.75
	<i>l</i> → <i>g</i>	760	238.96	4.878	20.4	-8.76
ClF	<i>l</i> → <i>g</i>	760	172.9	5.34	30.88	
Cl ₂ O ₇	<i>l</i> → <i>g</i>	760	354.7	7.88	22.2	
F ₂	<i>c</i> → <i>l</i>		53.6	0.122	6.74	1.86
	<i>l</i> → <i>g</i>	760	85.04	1.58	17.7	4.27
F ₂ O	<i>l</i> → <i>g</i>	760	128.41	2.651	20.7	
H ₂	<i>c</i> → <i>l</i>	54.0	13.9	0.029	2.0	1.9
	<i>l</i> → <i>g</i>	760	20.29	0.22	10.6	
HBr	<i>c</i> → <i>l</i>		186.30	0.5751	3.087	1.64
	<i>l</i> → <i>g</i>	760	206.44	4.210	20.39	-7.37
HCl	<i>c, l</i> → <i>l</i>		158.97	0.4760	2.994	2.10
	<i>l</i> → <i>g</i>	760	188.13	3.86	20.5	-7.14
HCN	<i>l</i> → <i>g</i>	760	298.86	6.027	20.17	
HF	<i>c</i> → <i>l</i>		190.09	1.094	15.756	2.55
	<i>l</i> → <i>g</i>	760	293.1	1.8	6.1	10.9
HI	<i>c</i> → <i>l</i>					
	<i>c</i> → <i>g</i>	0.31	298.16	14.88	49.91	
	<i>c</i> → <i>l</i>		222.37	0.6863	3.086	1.10
HNO ₃	<i>c</i> → <i>l</i>		231.6	2.510	10.808	10.55
	<i>l</i> → <i>g</i>	48	293	9.43	32.17	

(continued overleaf)

Table 1.9 (continued)

Substance	Process	Pressure (Torr)	Temperature (K)	ΔH (kcal/mol)	ΔS (cal/mol-K)	ΔC_p (cal/mol-K)
H ₂ O	<i>c</i> → <i>l</i>	760	273.16	1.436	5.2581	8.911
	<i>l</i> → <i>g</i>	4.58	273.16	10.767	39.416	-10.184
	<i>l</i> → <i>g</i>	23.75	298.16	10.514	35.263	9.971
	<i>l</i> → <i>g</i>	760	373.16	9.716	26.040	10.021
H ₂ O ₂	<i>c</i> → <i>l</i>		272.73	2.99	9.29	
	<i>l</i> → <i>g</i>	2.1	298.16	13.01	43.64	
I ₂	<i>c</i> → <i>l</i>		386.9	3.709	9.67	
IF ₇	<i>c</i> → <i>l</i>	760	276.6	7.37	26.64	
N ₂	<i>c, I</i> → <i>l</i>	94	63.16	0.17	2.709	
	<i>l</i> → <i>g</i>	760	77.36	1.33	17.231	
NH ₃	<i>c</i> → <i>l</i>	45.57	195.42	1.35	6.9133	
	<i>l</i> → <i>g</i>	760	239.76	5.581	23.277	
N ₂ H ₄	<i>c</i> → <i>l</i>		274.6	3.01		
	<i>l</i> → <i>g</i>	764	386.71	9.99	25.9	
NH ₄ N ₃	<i>c</i> → <i>g</i>	760	407	15.1	37.11	
NH ₄ NO ₃	<i>c, V</i> →					
	<i>c, IV</i>	760	255	0.13	0.511	
	<i>c, IV</i> →					
	<i>c, III</i>	760	305.3	0.38	1.23	
	<i>c, III</i>					
	<i>c, II</i>	6.32 × 10 ⁵	336.5	0.20	0.594	
	<i>c, II</i> → <i>c, I</i>	760	398.4	1.01	2.535	
	<i>c, I</i> → <i>l</i>	760	442.8	1.3	12.94	
	<i>c, I</i> → <i>l</i>					
N ₂ H ₁ · HNO ₂	<i>c, I</i> → <i>l</i>		316			
N ₂ H ₄ NO ₃	<i>c, I</i> → <i>l</i>		343.9			
N ₂ H ₄ · H ₂ O	<i>c</i> → <i>l</i>		233			
	<i>l</i> → <i>g</i>		118.5	391.7		
NH ₂ OH	<i>c</i> → <i>l</i>		306.3			
	<i>l</i> → <i>g</i>		331			
NO	<i>c</i> → <i>l</i>	164.4	109.6	0.550	5.016	6.0
	<i>l</i> → <i>g</i>	760	121.42	3.305	27.113	11.8
N ₂ O	<i>c</i> → <i>l</i>	658.9	182.4	1.56	8.5719	4.67
	<i>l</i> → <i>g</i>	760	184.68	3.951	21.421	
N ₂ O ₃	<i>c</i> → <i>l</i>		162			
	<i>l</i> → <i>g</i>	760	275	9.4	34.2	
N ₂ O ₄	<i>c</i> → <i>l</i>	139.78	263.9	3.501	13.368	6.12
	<i>l</i> → <i>g</i>	760	294.31	9.111	30.954	
N ₂ O ₅	<i>c</i> → <i>g</i>	760	305.6	13.6	44.50	
NO ₂ F	<i>c</i> → <i>l</i>		107.2			
	<i>l</i> → <i>g</i>	760	200.8	4.314	21.46	
NO ₃ F	<i>c</i> → <i>l</i>		92			
	<i>l</i> → <i>g</i>	103	193			
O ₂	<i>c, I</i> → <i>l</i>	1.1	54.5	0.11	1.95	1.74
	<i>l</i> → <i>g</i>	760	90.21	1.63	18.07	-6.00
O ₃	<i>l</i> → <i>g</i>	760	162.65	2.59	15.92	
Br ₂	<i>c</i> → <i>l</i>	760	266.0	2.526	9.48	0.9
	<i>l</i> → <i>g</i>	214	332.0	7.16	24.6	
C	<i>c</i> → <i>g</i>	760	4765	28.0		

Table 1.9 (continued)

Substance	Process	Pressure (Torr)	Temperature (K)	ΔH (kcal/mol)	ΔS (cal/mol-K)	ΔC_p (cal/mol-K)
CH ₄	c → l	87.7	90.8	0.225	2.48	
	l → g	760	111.68	1.96	17.51	
C ₂ H ₂ (ethyne, acetylene)	c → l	900	191.7	0.9	5	
	l → g	900	191.7	4.2	22	
C ₂ H ₄ (ethane, ethylene)	c → l	0.9	104	0.801	7.702	
	l → g	760	169.39	3.234	19.10	
C ₂ H ₆ (ethane)	c → l	0.006	90.4	0.684	7.597	
	l → g	760	184.6	3.511	19.06	-11.5
CHF ₃ (trifluoromethane)	c → l		113			
	l → g	760	189.0	4.4	2.3	
CH ₃ NH ₂ (methylamine)	c → l		150.0	1.41	8.16	
	l → g	760	266.84	6.17	23.1	
(CH ₃) ₂ NH (dimethylamine)	c → l		181.0	1.42	7.85	9.81
	l → g	760	280.0	6.33	22.6	17.1
C ₂ H ₈ N ₂ (2-dimethyl hydrazine)	l → g	760	354			
CH ₂ O (formaldehyde)	c → l		154.9			
	l → g	760	253.9	5.85	23.0	
CH ₃ OH (methanol)	c, l → l		175.48	0.760	4.32	4.2
	l → g	760	337.8	8.415	24.95	
CH ₄ O ₂ (methyl hydrogen peroxide)	l → g	34	298	7.9	26.5	

^aBy permission, compiled and converted from *Selected Values of Chemical Thermodynamic Properties*³⁶ and 79th ed. of *CRC Handbook of Chemistry and Physics*.¹⁶

^bc denotes the solid phase or the condensed-phase material.

Many versions of their programs have been adopted broadly for research studies, development work, and chemical equilibrium computer (CEC) programs, including Zeleznik and Gordon's earlier version of 1962, Svehla and McBride's CEC73, Gordon and McBride's CEC76, Gordon, McBride, and Zeleznik's TRAN84 with calculations of transport properties, and the latest version called CEA (Chemical Equilibrium and Application) by McBride and Gordon¹ in 1996 and 2000. More information about the code can be obtained from the following web site: <http://www.lerc.nasa.gov/www/ceaweb/>.

18.1 Assumptions and Capabilities

The CEA program^{1,2} is designed to provide both thermodynamic and transport properties for a wide range of scientific and engineering applications and for a wide range of independent variables. Thermodynamic data for more than 2000 chemical species (including gases, solids, and ions) are provided with the program for a temperature range of 300 to 5000 K. Transport and relaxation data

are provided for many common species; transport data are also provided for interactions between unlike species. In contrast with the thermodynamic data, the temperature range of the transport data is not the same for all interactions.

The range of applicability of the thermodynamic calculations is approximately described by the limits of applicability of the ideal-gas law. The lower limit for temperature in the transport calculations occurs when ternary and higher-order molecular collisions become important. This also defines the upper pressure limit for the transport property calculations. The upper limit for temperature occurs when ionization becomes appreciable. Incipient ionization can be included in the calculations. For increasing ionization, however, higher approximations are needed in the transport calculations. The lower limit is given by the onset of free-molecular-flow regime, which occurs when the mean free path is of the same order of magnitude as the dimensions of the container. Under these conditions, the equations for the transport properties are no longer applicable.

Thermodynamic data contained in the CEA data file is obtained from the JANAF Thermochemical Tables²⁰ and from data generated at NASA Lewis Research Center (now called NASA Glenn Research Center). Standard-state pressure of 1 bar and temperature of 298.15 K are used as the reference conditions for computations. Heats of transition are included in the thermodynamic data, and the program automatically checks for the condensation of species. Thus, without any special instructions, the proper concentrations of gaseous, liquid, and solid phases of all species included in the THERMO library are calculated.

The usual equations for the conservation of mass, momentum, and energy are used along with the ideal-gas assumption. Composition and properties are calculated for equilibrium conditions and, in some situations, for frozen conditions (sometimes called nonreacting). The effects of chemical kinetics—that is, of finite reaction rates—are not included.

The program is capable of calculating several types of problems:

1. Equilibrium compositions for assigned thermodynamic states
2. Theoretical rocket performance
3. Chapman–Jouguet detonations
4. Shock-tube parameter calculations for both incident and reflected shocks

In the first type of problem, it can calculate the equilibrium composition of a mixture for assigned thermodynamic states. The thermodynamic states are assigned by specifying two thermodynamic state functions (code names are given in parentheses):

1. Temperature and pressure (*tp*)
2. Enthalpy and pressure (*hp*)
3. Entropy and pressure (*sp*)
4. Temperature and volume or density (*tv*)
5. Internal energy and volume or density (*uv*)
6. Entropy and volume or density (*sv*)

The *hp* problem provides constant-pressure combustion properties, and the *uv* problem gives constant-volume combustion properties. As mentioned, the ideal-gas law is taken for the equation of state for the mixture. The analysis assumes that interactions between phases are negligible. In the event that condensed species are present, it is assumed that they occupy negligible volume and exert negligible pressure compared with the gaseous species.

18.2 Equations Describing Chemical Equilibrium

Prior to 1958, all equilibrium computations were carried out using the equilibrium constant formulation of the governing equations. In 1958, White, Johnson, and Dantzig²⁶ suggested that equilibrium compositions be calculated by free-energy minimization. Their procedure soon captured the fancy of some of the researchers making thermodynamic calculations, and the world of equilibrium computations was then divided into two camps, the free-energy minimizers and the traditional equilibrium-constant formulators. Most present-day multipurpose chemical-equilibrium computer programs use the free-energy minimization procedure; however, in some special-purpose computer programs, the equilibrium-constant formulation technique is used. The two formulations reduce to the same number of nonlinear iterative equations.

There are several disadvantages of the equilibrium-constant method, which limit the versatility of a multipurpose program. Briefly, these disadvantages are more bookkeeping, numerical difficulties with the use of components, more difficulty in testing for the presence of condensed species, and more difficulties in extending the method to include the effects of nonideal equations of state. Furthermore, with the minimization-of-free-energy method, each species can be treated independently without specifying a set of reactions a priori, as is required with equilibrium constants. For these reasons, the free-energy minimization formulation was used in the CEA program. A very brief discussion of the development of the nonlinear iterative equations is presented in the following section. For a more complete thermodynamic and mathematical treatise, the reader is referred to Refs. 1 and 2.

18.2.1 Thermodynamic Equations As discussed earlier, it is assumed that all gases are ideal and that interactions among phases may be neglected. The equation of state for the mixture is

$$Pv = n^* R_u T \quad (1-218)$$

or

$$\frac{P}{\rho} = n^* R_u T \quad (1-218a)$$

where n^* represents the number of moles per unit mass of mixture (kg-mole/kg), and the units for the variables are those of the International System (SI). Equation (1-218) is assumed to be correct even when small amounts of condensed

species (up to several percent by weight) are present. The specific volume v and number of moles n^* refer to the gases only, while the mass in the system is for the entire mixture including condensed-phase species. The word *mixture* is used to designate the burned (reacted) mixture of species at equilibrium, to distinguish it from the mixture of unburned reactants, which is referred to as *total reactants*. The molecular weight Mw of the mixture (including condensed species) is then defined to be

$$Mw = \frac{\sum_{j=1}^N n_j^* Mw_j}{\sum_{j=1}^{N_g} n_j^*} = \frac{1}{\sum_{j=1}^{N_g} n_j^*} = \frac{1}{n^*} \quad (1-219)$$

where n^* is the number of kilogram-moles of species j per kilogram of mixture, and Mw_j is the molecular weight of species j . Among the N possible species considered, gases are indexed from 1 to N_g and condensed species from $N_g + 1$ to N .

It should be noted that the molecular weight of a multicomponent mixture is conventionally defined as

$$Mw_{\text{conv}} \equiv \frac{\sum_{j=1}^N n_j^* Mw_j}{\sum_{j=1}^N n_j^*} \quad (1-219a)$$

CEA code gives Mw instead of Mw_{conv} as the output. Mw_{conv} can be calculated from Mw by means of

$$Mw_{\text{conv}} = Mw \left(1 - \sum_{j=N_g+1}^N X_j \right) \quad (1-219b)$$

18.2.2 Minimization of Gibbs Free Energy The condition for equilibrium may be stated in terms of any of several thermodynamic functions, for example, the minimization of the Gibbs free energy or Helmholtz free energy, or the maximization of the entropy. If one wishes to use temperature and pressure to characterize a thermodynamic state, the Gibbs free energy is most easily minimized, inasmuch as temperature and pressure are its natural variables. Similarly, the Helmholtz free energy is most easily minimized if the thermodynamic state is characterized by temperature and volume (or density). In the following equations, the nonlinear iterative procedure for minimization of the Gibbs free energy is presented. A parallel development for minimization of the Helmholtz free energy can be found in Ref. 1, if the thermodynamic state is characterized by temperature and volume.

For a mixture of N species, the Gibbs free energy (g) per kilogram of mixture is given by

$$g = \sum_{j=1}^N \mu_j n_j^* \quad (1-220)$$

where the chemical potential per kilogram-mole of species j is defined to be

$$\mu_j = \left[\frac{\partial g}{\partial n_j^*} \right]_{T, P, n_{i \neq j}^*} \quad (1-221)$$

The condition for chemical equilibrium is the minimization of free energy. This minimization is usually subject to certain constraints, such as the following mass-balance constraints:

$$\sum_{j=1}^N a_{ij} n_j^* - b_i^o = 0, \quad i = 1, 2, \dots, l \quad (1-222)$$

or

$$b_i - b_i^o = 0, \quad i = 1, 2, \dots, l \quad (1-222a)$$

where the coefficient a_{ij} is the number of kilogram-atoms of element i per kilogram-mole of species j , b_i^o is the assigned number of kilogram-atoms of element i per kilogram of total reactants (fuel and oxidant), and l is the number of chemical elements. If ions are considered, l is equal to the number of elements plus 1. Comparing Eq. (1-222) with Eq. (1-222a), we have

$$b_i = \sum_{j=1}^N a_{ij} n_j^*, \quad i = 1, \dots, l \quad (1-223)$$

where b_i is the number of kilogram-atoms of element i per kilogram of mixture.

To minimize G , we shall follow the well-known Lagrange method²⁷ developed by the great eighteenth-century mathematician J. L. Lagrange. Let us define

$$\tilde{G} \equiv g + \sum_{i=1}^l \lambda_i (b_i - b_i^o) \quad (1-224)$$

where λ_i are Lagrange multipliers that incorporate the l constraints in Eq. (1-222a). Treating the variations δn_j^* and $\delta \lambda_i$ as independent gives

$$\begin{aligned} \delta g &= \sum_{j=1}^N \mu_j \delta n_j^* \\ \delta \sum_{i=1}^l \lambda_i (b_i - b_i^o) &= \delta \sum_{i=1}^l \lambda_i \left(\sum_{j=1}^N a_{ij} n_j^* - b_i^o \right) = \sum_{j=1}^N \sum_{i=1}^l \lambda_i a_{ij} \delta n_j^* \\ &\quad + \sum_{i=1}^l \left(\sum_{j=1}^N a_{ij} n_j^* \right) \delta \lambda_i - \sum_{i=1}^l b_i^o \delta \lambda_i \end{aligned}$$

$$\delta \sum_{i=1}^l \lambda_i (b_i - b_i^o) = \sum_{j=1}^N \sum_{i=1}^l \lambda_i a_{ij} \delta n_j^* + \sum_{i=1}^l b_i \delta \lambda_i - \sum_{i=1}^l b_i^o \delta \lambda_i$$

$$\delta \tilde{G} = \sum_{j=1}^N \left(\mu_j + \sum_{i=1}^l \lambda_i a_{ij} \right) \delta n_j^* + \sum_{i=1}^l (b_i - b_i^o) \delta \lambda_i$$

Then, the condition for equilibrium becomes

$$\delta \tilde{G} = \sum_{j=1}^N \left(\mu_j + \sum_{i=1}^l \lambda_i a_{ij} \right) \delta n_j^* + \sum_{i=1}^l (b_i - b_i^o) \delta \lambda_i = 0 \quad (1-225)$$

$$\mu_j + \sum_{i=1}^l \lambda_i a_{ij} = 0 \quad j = 1, \dots, N \quad (1-226)$$

and the mass-balance equation (1-222a).

Based on the assumption of an ideal gas, the chemical potential may be written

$$\mu_j = \begin{cases} \mu_j^o + R_u T \ln \left(\frac{n_j^*}{n^*} \right) + R_u T \ln p \text{ (bar)} & (j = 1, \dots, N_g) \\ \mu_j^o & (j = N_g + 1, \dots, N) \end{cases} \quad (1-227)$$

where μ_j^o represents the chemical potential at the standard state for gases with $j = 1$ to N_g and for condensed phases with $j > N_g$. The numerical values of μ_j^o are generally found in JANAF Thermochemical Tables.²⁰ The pressure p in Eq. (1-227) must be in bars. Equations (1-226) and (1-222a) permit the determination of equilibrium compositions for thermodynamic states specified by an assigned temperature T_0 and pressure p_0 .

The equations required to obtain equilibrium composition are not all linear in the composition variables, and therefore an iteration procedure is generally required. Detailed iteration procedures are described in Ref. 1. Briefly speaking, the CEA program follows a widely used steepest-descent Newton-Raphson method to solve for corrections to initial estimates of compositions n_j^* , Lagrange multipliers λ_i , mole number n , and (when required) temperature T . This method involves a Taylor series expansion of the appropriate equations with all terms containing derivatives higher than the first order omitted. The correction variables used are $\Delta \ln n_j^*$ (for $j = 1, \dots, N_g$), Δn_j^* (for $j = N_g + 1, \dots, N$), $\Delta \ln n$, $\pi_i = -(\lambda_i/R_u T)$, and $\Delta \ln T$. As pointed out in Refs. 22 and 1, there is no restriction in starting iteration with an estimate of the Lagrange multipliers equal to zero, inasmuch as they appear linearly in Eq. (1-226).

For chemical systems containing many species, it would be necessary to solve a large number of simultaneous equations. They can be reduced quite simply to a much smaller number by algebraic substitution, eliminating $\Delta \ln n_j^*$

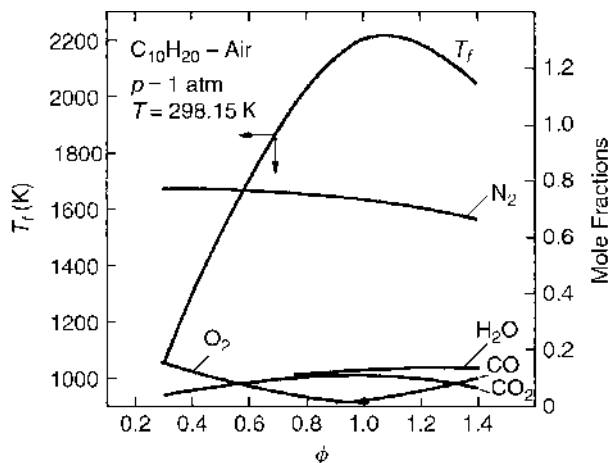


Figure 1.17 Calculated adiabatic flame temperature and equilibrium composition of products from combustion of kerosene in air.

terms for gaseous species. The resulting equations are solved through continuous iteration until the corrections become smaller than the specified tolerance. Convergence of the Newton–Raphson iterative equations with 35 iterations is permitted by the program.¹ For most problems, a typical number of iterations is 8 to 12.

A typical output for the combustion of kerosene ($C_{10}H_{20}$) in air at initial temperature of 298.15 K and at constant pressure of 1 atm is shown in Fig. 1.17. The calculated equilibrium compositions and the flame temperature of the combustion product are plotted against equivalence ratio. As we can see from this figure, the adiabatic flame temperature reaches a peak very close to the stoichiometric condition ($\phi = 1.0$) on the slightly fuel-rich side. This is due to the fact that when the system is slightly under-oxidized, the specific heat of the products is reduced and thus the flame temperature is increased. Dissociation of combustion products also contributes to this shifting effect.

19 OTHER WELL-ESTABLISHED CHEMICAL EQUILIBRIUM CODES

In addition to NASA CEA code, there are number of chemical equilibrium codes developed in the combustion and propulsion fields. These programs include, for example, BLAKE Code,³⁰ developed by Freedman of the U.S. Army Ballistic Research Lab, based on the initial development of the TIGER Code³¹ of the Stanford Research Institute; the PEP Code³² of the U.S. Navy by Cruise; the STANJAN Code³³ of Reynolds of Stanford University; and the Cheetah Code³⁴ of the Lawrence Livermore National Laboratory by Fried, Howard, and Souers. In view of limited space, no extensive discussions are given to these codes. Also, some of these codes have license requirements.

Depending on the user's application, certain codes may have some limitations based on the assumptions made in the analysis. For example, the broadly used NASA CEA code is limited to cases with system pressure below 200 bars, due to its assumption of ideal-gas law. For people interested in gun interior ballistics, the high-pressure effects become significant and the real-gas behavior must be taken into account in the analysis. In this case, the BLAKE code would be more adequate than CEA code, since it considers the real-gas effect. In general, the BLAKE code was developed for gas pressures up to 700 MPa and temperatures up to 4000 K. It uses four different equations of states (EOS), including (1) ideal-gas law; (2) truncated virial EOS; (3) Becker-Kistiakowsky-Wilson (BKW) EOS; and (4) NBS EOS proposed by Powell, Wilmot, Haar, and Klein.³⁵ Among these four different EOS, the truncated virial EOS is best suited for calculations of thermochemical equilibrium under gun environments. BLAKE code contains enthalpies of formation for 349 different ingredients most often found in military propellants. The equilibrium calculations are performed using the method based on equilibrium constants. Similar to CEA code, the BLAKE code can be executed for various combinations of thermodynamic variables, including pv , ps , vt , ve , and vs problems.

To demonstrate the differences in the computed results at high pressures, BLAKE and NASA CEA were used by the author to calculate the adiabatic flame temperature and chamber pressure of a closed bomb loaded with solid propellants at various loading densities. (This is not a fair test for CEA, since the code was not designed for extremely high pressures. It is used only as a demonstration to prove a point.) Departure in calculated chamber pressure started at the propellant loading density of 0.14 gm/cm³, and the difference becomes very large (47% lower) at the propellant loading density of 0.6 gm/cm³. The calculated adiabatic flame temperature from CEA code is higher than that of the BLAKE code by about 6.5% at the propellant loading density of 0.1 to 0.4 gm/cm³. In general, one should know how to select the suitable code to perform the specific task in question. For example, for propellant burning in a very high-pressure environment such as a closed bomb or gun chamber, BLAKE code, or other high-pressure application codes should be used.

Recently, a commercial code called Cequel™ has become available for computation of equilibrium products and other propulsion related problems. Cequel™ stands for "Chemical EQUilibrium in excEL", and was developed by Software & Engineering Associates, Inc. It is based on CCET™ (Compressible Chemical Equilibrium and Transport properties) code developed as an extension of the NASA Lewis's Gordon-McBride CEA (Chemical Equilibrium with Applications) code. Cequel™ code considers Lennard-Jones Parameters (LJP) in the equation of state to treat the nonideal gas behavior. The results of the Cequel™ code are written directly in Microsoft Excel. This eliminates the need to cut and paste from external thermodynamics codes' output files into Excel and provides the additional power of allowing the parametric calculations. This allows the user to quickly evaluate many different scenarios as well as to utilize Excel's built-in solvers and optimization routines.

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HOMework

1. A mixture of 1 mole of gaseous ethane (C_2H_4) and 3 moles of oxygen at 298 K react in a constant-volume bomb. Assume the combustion products are CO_2 and $H_2O_{(g)}$ and there is insignificant amount of dissociation products. Heat is transferred out of the bomb until the products are cooled to 600 K. Determine the amount of heat transferred in cal/g-mole of the fuel.

2. Show that the rate equation of the first law for a control volume (c.v.) can be expressed as

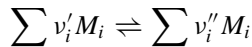
$$\dot{Q}_{\text{c.v.}} + \sum \dot{m}_i \left(h_i + \frac{|\mathbf{v}_i|^2}{2g_c} + z_i \frac{g}{g_c} \right) = \frac{dE_{\text{c.v.}}}{dt} + \sum \dot{m}_e \left(h_e + \frac{|\mathbf{v}_e|^2}{2g_c} + z_e \frac{g}{g_c} \right) + \dot{W}_{\text{c.v.}}$$

where h represents specific enthalpy ($h = u + p/\rho$) and subscripts i and e designate the inlet and exit conditions, respectively. Give the physical meaning of each term.

3. Air flows steadily through an air heater at the rate of 125 g/s. It enters at 290 K and 1.2 atm with a velocity of 15 m/s and leaves at 325 K and 1 atm with a velocity of 18 m/s. There is no shaft work done on or by the air, and the centerlines of the inlet and discharge ducts are in the same horizontal plane. The heating is accomplished with steam coils. What is the rate of heat input to the air in J/s? ($C_{p,\text{air}} = 0.24$ cal/g K.)

ANSWER: $\dot{Q}_{\text{in}} = 4401.3$ J/s

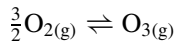
4. Consider a general chemical equilibrium reaction



established in a heterogeneous mixture containing N chemical components. Some of the components have multiple phases in phase equilibrium. Show that

$$\mu_{j(\text{g})} = \mu_{j(\text{l})} = \mu_{j(\text{s})} \quad \text{for any component } j$$

5. Suppose gaseous ozone, $\text{O}_{3(\text{g})}$, is formed from molecular oxygen, $\text{O}_{2(\text{g})}$, by the following reaction:



What is the value of the standard-free-energy change, ΔG° , of this reaction? What is the equilibrium constant of this reaction at 298 K? If the value of K_p is very small, what does that imply?

ANSWER: $\Delta G^\circ = 39.06$ kcal, $K_p = 2.261 \times 10^{-29}$

6. A combustible mixture of air and carbon monoxide that is 10% rich [air/fuel = $\frac{100}{110}$ (air/fuel)_{st}] is compressed to a pressure of 8.28 bar and a temperature of 555 K. The mixture is ignited, and combustion occurs adiabatically at constant volume. When the maximum temperature is attained, analysis shows 0.228 moles of CO present for each mole of CO supplied. Show that the

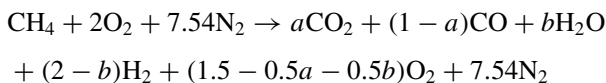
maximum temperature reached is 2950 K. If the pressure at this temperature is now doubled, calculate the amount of CO present.

ANSWER: $n_{\text{CO}} = 0.194$ when the pressure is doubled.

7. Using bond energies, determine the heat of formation of gaseous normal butane (C_4H_{10}).

ANSWER: $\Delta\mathcal{H}_{f,\text{C}_4\text{H}_{10}}^\circ = -32.94$ kcal/mole

8. Methane supplied at 1 atm and 25°C is burned adiabatically in a steady-flow burner with the stoichiometric amount of air supplied at the same conditions. Assume the reaction equation is



Determine the temperature of the products.

ANSWER: $T_f = 2244.3$ K

9. Show that the fugacity of a real gas is related to the pressure p and compressibility factor Z by

$$\ln \frac{f}{p} = \int_0^{P_r} (Z - 1) d(\ln P_r)_T$$

where P_r is the reduced pressure ($P_r = p/p_{\text{critical}}$). Discuss the use of this equation. Hint: Integrate Eq. (1-199) from $p = 0$ to a finite pressure.

10. Consider the combustion of kerosene ($\text{C}_{10}\text{H}_{20}$) in air at initial temperature 298.15 K and at constant pressure 1 atm. Use the NASA Lewis computer program (CEA) to carry out the thermochemical calculations for the equilibrium compositions and flame temperature for equivalence ratios of 0.3 to 1.4 ($\Delta\phi = 0.1$ increment). Plot T_f and the mole fractions of CO_2 , H_2O , N_2 , O_2 , CO , NO , OH , O , H , H_2 , and NO_2 versus ϕ ($\Delta\mathcal{H}_{f,\text{C}_{10}\text{H}_{20}}^\circ = -59$ kcal/mol).

ANSWER: For $\phi = 1$, $T_f = 2280$ K, $X_{\text{CO}} = 0.01455$, $X_{\text{CO}_2} = 0.1160$, $X_{\text{H}_2\text{O}} = 0.12584$, $X_{\text{N}_2} = 0.72753$, and $X_{\text{O}_2} = 0.00653$.

11. Methane is burned with 80% of stoichiometric air in a steady-flow process at 1 atm. Methane and air are both supplied at 298 K, and the products leave at 1666 K. Assuming that no CH_4 , OH , NO , or free oxygen appears in the products, determine the amount of heat transferred per kilogram of methane.

ANSWER: $Q = -2291$ kcal/(kg of CH_4)

12. Consider the combustion of a homogeneous propellant in a closed bomb. The ingredients of this propellant together with their chemical formulas, weight fractions, and heats of formation are listed below:

Ingredients	Chemical Formula	Heats of Formation (kcal/g-mol)	Weight Fraction
NC nitrocellulose (13.25% N)	$C_6H_{7.329}O_5(NO_2)_{2.671}$	-163.81	0.75
NG, nitroglycerin	$C_3H_5O_3(NO_2)_3$	-88.6	0.15
DBP, dibutylphthalate	$C_{16}H_{22}O_4$	-201.4	0.09
DPA, diphenylamine	$C_{12}NH_{11}$	31.07	0.01

Use the computer program NASA CEA to compute the adiabatic flame temperature, chamber pressure, and product concentrations for loading densities of 0.05, 0.25, and 0.4 g/cm³.

ANSWER: For loading density = 0.25 g/cm³, $T_f = 2773$ K, $p = 2480$ atm, $X_{CO} = 0.47251$, $X_{H_2O} = 0.17751$, $X_{H_2} = 0.17099$, $X_{N_2} = 0.10436$, and $X_{CO_2} = 0.07276$.

13. Consider the two-stream mixing and combustion system shown in the sketch below. Let us assume that both the fuel-rich stream and the oxidizer-rich stream are contaminated by a portion of combustion products and inert diluents. There is a small amount of oxidizer in the fuel stream and vice versa. Sketch the burned and unburned planes of mass fractions of fuel (F), oxidant (O), diluent (D), and combustion products (P) versus mixture fraction f , defined by the following equation.



$$f = \frac{[Y_F - (F/O)_{st}Y_{O|}]_M - [Y_F - (F/O)_{st}Y_{O|}]_A}{[Y_F - (F/O)_{st}Y_{O|}]_F - [Y_F - (F/O)_{st}Y_{O|}]_A}$$

14. The vapor pressure of liquid chlorine, in centimeters of mercury, can be represented by the expression

$$\log_{10} p = -1414.8T^{-1} + 9.91635 - 1.206 \times 10^{-2}T + 1.34 \times 10^{-5}T^2$$

The specific volume of chlorine gas at its boiling point is 269.1 cm³/g and that of the liquid is approximately 0.7 cm³/g. Calculate the heat of vaporization of liquid chlorine in cal/g at its boiling point, 239.05 K.

Note:
$$\frac{d(\log_{10} p)}{dT} = \frac{1}{2.303} \frac{d(\ln p)}{dT}$$

ANSWER: $\Delta \mathcal{H}_v = 68.3$ cal/g

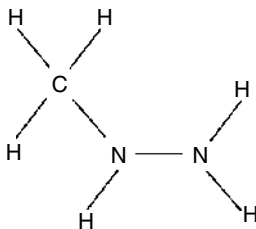
15. Imagine that a fuel is burned in a large excess of each of these various oxygen mixtures:

- (a) $0.21\text{O}_2 + 0.79\text{N}_2$
- (b) $0.21\text{O}_2 + 0.79\text{Ar}$
- (c) $0.21\text{O}_2 + 0.79\text{CO}_2$
- (d) pure O_2

Order the mixtures according to the adiabatic flame temperatures that you would expect, by noting the highest first, the next highest second, etc. If you believe all will give the same temperature, state so and explain. The fuel is arbitrary, of course.

16. Calculate the adiabatic flame temperature, T_f , and the equilibrium composition of the decomposition flame of pure liquid hydrazine, $\text{N}_2\text{H}_4(\text{l})$. The initial temperature of the pure $\text{N}_2\text{H}_4(\text{l})$ is 273 K. Total pressure on the system is 1 atm. Products to be considered are $\text{NH}_3(\text{g})$, N_2 , and H_2 .

17. Find the heat of formation of gaseous monomethylhydrazine (MMH) from its bond energies. The molecular structure of MMH is shown below. Its chemical formula is $\text{CH}_3\text{NHNH}_2(\text{g})$.



Note that the heat of formation of $\text{N}_{(\text{g})}$ is 112.97 kcal/mol. The average bond energy of the N–N bond is 60 kcal/mol. The average bond energy for the N–H bond is 88 kcal/mol. Please compare your estimated result with some reported values of heat of formation of MMH as 20.41 kcal/mol, or 22.55 kcal/mol.

PROJECTS

1.1 Octane vapor (C_8H_{18}) at 1 atm and 298.15 K is burned adiabatically at constant pressure with 100% excess air at the same conditions. Determine the flame temperature of the products, assuming CO_2 , H_2O , O_2 , and N_2 are produced in the reaction. Verify that the dissociation products CO , H_2 , and NO will not appear in substantial quantities.

- 1.2** Propane (C_3H_8) gas supplied at 1 atm and 298.15 K is burned adiabatically in a steady-flow burner with air ($O_2 + 3.762N_2$) supplied at the same pressure and temperature. Assume that the air in the combustible mixture is 10% richer (by volume) than the stoichiometric condition. Do the following:
- Write the chemical reaction equation to express the full utilization of fuel and air in the generation of combustion products under the assumption of no product dissociation.
 - If the combustion product contains CO_2 , H_2O , CO , H_2 , O_2 , and N_2 , rewrite the chemical reaction equation to reflect the dissociation of CO_2 and water vapor. Also, express the relationships between the moles of product species.
 - Calculate the fuel–oxidant mass ratio.
 - Calculate the adiabatic flame temperature and the equilibrium composition of case (b).