

3

Thermodynamics*

The First Law of Thermodynamics
Thermochemistry
The Second Law of Thermodynamics

The Third Law of Thermodynamics
Free Energy Functions and Applications

Thermodynamics is concerned with the quantitative relationships between heat and other forms of energy, including mechanical, chemical, electric, and radiant energy. A body is said to possess *kinetic energy* because of its motion or the motion of its parts (i.e., its molecules, atoms, and electrons), and to possess *potential energy* by virtue of its position or the configuration of its parts. It is not possible to know the absolute value of the energy of a system; it is sufficient to record the changes in energy that occur when a system undergoes some transformation. Mechanical energy changes are expressed in ergs or joules and heat changes in calories. Count Rumford in 1798 and James Joule in 1849 showed the relationship between mechanical work and heat. Today the calorie, as defined by the United States National Bureau of Standards, is equal to 4.1840×10^7 ergs of 4.1840 joules, so that work and heat can be expressed in the same units.

Energy can be considered as the product of an *intensity factor* and a *capacity factor*. Stated more explicitly, the various types of energy may be represented as a product of an intensive property independent of the quantity of material, and the differential of an extensive property that is proportional to the mass of the system. For example, the mechanical work done by a gas on its surroundings is PdV , and the work performed by the molecules in the surface of a liquid

against the surface tension is γdA . Some of the forms of energy, together with these factors and their accompanying units, are given in Table 3-1.

Thermodynamics is based on three "laws" or facts of experience that have never been proved in a direct way. Various conclusions, usually expressed in the form of mathematical equations, however, may be deduced from these three principles, and the results consistently agree with observation. Consequently, the laws of thermodynamics, from which these equations are obtained, are accepted as valid for systems involving large numbers of molecules.

THE FIRST LAW OF THERMODYNAMICS

The first law is a statement of the conservation of energy. It states that, although energy can be transformed from one kind into another, it cannot be created or destroyed. Put another way, the total energy of a system and its immediate surroundings (which together are often referred to as an *isolated system*) remains constant during any operation. This statement follows from the fact that the various forms of energy are equivalent, and when one kind is formed, an equal amount of another kind must disappear. The present relativistic picture of the universe, expressed by Einstein's equation,

$$\text{Energy} = (\text{mass change}) \times (\text{velocity of light})^2$$

suggests that matter can be considered as another form of energy, 1 gram being equal to 9×10^{20} erg. These enormous quantities of energy, while involved in nuclear transformations, are not important in ordinary chemical reactions.

According to the first law,

$$\Delta E = Q - W \quad (3-1)$$

*The student will find the subject of this chapter presented in a most readable form in the following books: G. Pimentel and R. Spratley, *Understanding Chemical Thermodynamics*, Holden-Day, San Francisco, 1969; B. H. Mahan, *Elementary Chemical Thermodynamics*, Benjamin/Cummings, Menlo Park, Calif., 1963; L. K. Nash, *Elements of Chemical Thermodynamics*, 2nd Edition, Addison-Wesley, Menlo Park, Calif., 1970; R. P. Bauman, *Introduction to Equilibrium Thermodynamics*, Prentice-Hall, Englewood Cliffs, N.J., 1966. Clear definitions of thermodynamic terms and discussions of concepts are found in A. M. James, *A Dictionary of Thermodynamics*, Wiley, New York, 1976.

TABLE 3-1. *Intensity and Capacity Factors of Energy*

Energy Form	Intensity or Potential Factor (Intensive Property)	Capacity or Quantity Factor (Extensive Property)	Energy Unit Commonly Used
Heat (thermal)	Temperature (deg)	Entropy change (cal/deg)	Calories
Expansion	Pressure (dyne/cm ²)	Volume change (cm ³)	Ergs
Surface	Surface tension (dyne/cm)	Area change (cm ²)	Ergs
Electric	Electromotive force or potential difference (volts)	Quantity of electricity (coulombs)	Joules
Chemical	Chemical potential (cal/mole)	Number of moles	Calories

in which ΔE is the increase in internal energy, Q the heat absorbed, and W the work done by the system. It should be noted that an input of heat is usually necessary before work can be done *by* a system. Conversely, work done *on* a system usually is accompanied by the evolution of heat. The convention followed in writing the first law is to give heat input as a positive quantity $+Q$ and work output as a negative quantity $-W$. The converse is to give heat output as a negative quantity $-Q$ and work input as a positive quantity $+W$. Internal energy results from the motions of the molecules, electrons, and nuclei in a system and depends on the *measurable properties*: pressure, volume, and temperature. Any two of these variables must be specified to define the internal energy. For an infinitesimal increase in the energy dE , equation (3-1) is written

$$dE = q - w \quad (3-2)$$

in which q is the heat absorbed and w is the work done during the small change of the system. Capital letters, Q and W , are used for heat and work in equation (3-1) to signify finite changes in these quantities. Lower case q and w in equation (3-2) signify infinitesimal changes.

Changes of internal energy, rather than a knowledge of the absolute energy value (which, incidentally, cannot be determined), is the concern of thermodynamics. The finite change of internal energy is written

$$\Delta E = E_2 - E_1 \quad (3-3)$$

in which E_2 is the energy of the system in its final state, say 1 g of water at 1 atm and 10° C, and E_1 is the energy of the system in its initial state, say 1 g of water at 5 atm and 150° C.

Exact and Inexact Differentials. dE is an exact differential and is written

$$dE = \left(\frac{\partial E}{\partial P}\right)_T dP + \left(\frac{\partial E}{\partial T}\right)_P dT \quad (3-4)$$

The internal energy depends only on the initial and final conditions of, say, pressure and temperature and not on the manner in which these factors are varied. This fact is stated as follows: The increase in energy, $\Delta E = E_2 - E_1$, is independent of the "path" followed in going from state 1 to state 2.

We will come back to a consideration of the term *path* in a later paragraph, but first let us clarify the word

state. The term *thermodynamic state* means the condition in which the measurable properties have a definite value. The state of 1 g of water at E_1 may be specified by the conditions of, say, 1 atm pressure and 10° C and the state E_2 by the conditions of 5 atm and 150° C. Hence, the states of most interest to the chemist ordinarily are defined by specifying any two of the three variables, temperature, pressure, and volume; however, additional independent variables sometimes are needed to specify the state of the system. Any equation relating the necessary variables—for example, $V = f(T, P)$ —is an *equation of state*. The ideal gas law and the van der Waals equation are equations of state. The variables of a thermodynamic state are known as *thermodynamic properties*. E , V , P , and T all belong to this class. In the study of interfacial phenomena, surface area also becomes one of the thermodynamic properties necessary to characterize the system completely. On the other hand, both the heat absorbed q and the work done w depend on the manner in which the change is conducted. Hence, q and w are not exact differentials, and heat and work are not, in these circumstances, thermodynamic properties.

To clarify the statement that the change in energy of a process does not depend on the path, whereas the heat absorbed and the work done vary with the means used to carry out the process, let us take the example of transporting a box of equipment from a camp in a valley to one at the top of the mountain. Here we are concerned with potential energy rather than internal energy of a system, but the principle is the same. We can haul the box to the top of the mountain by a block and tackle suspended from an overhanging cliff and produce little heat by this means. We can drag the box up a path, but more work is required and considerably more heat is produced owing to the frictional resistance. We can carry the box to the nearest airport, fly it over the spot, and drop it by parachute. It is readily seen that each of these methods involves a different amount of heat and work. The change in potential energy depends only on the difference in the height of the camp in the valley and the one at the top of the mountain, and it is independent of the path used to transport the box.

Although a number of variables, such as chemical composition, refractive index, and dielectric constant, can be specified, they are not all independent. In order

to fix the internal energy, we need specify only two of the independent variables, pressure, volume, and temperature, in a closed system.

A *closed system* is one that may exchange heat and work but not *matter* with its surroundings. An *open system*, on the other hand, involves a transfer of matter in addition to the exchange of heat and work. If two immiscible solvents, for example; water and carbon tetrachloride, are confined in a closed container and iodine is distributed between the two phases, each phase is an open system, yet the total system made up of the two phases is closed, for it does not exchange matter with its surroundings. The discussion here is first restricted to reversible changes occurring in closed systems. Open systems are considered in a later section.

Isothermal and Adiabatic Processes. When the temperature is kept constant during a process, the reaction is said to be conducted *isothermally*. An isothermal reaction may be carried out by placing the system in a large constant-temperature bath so that heat is drawn from or returned to it without affecting the temperature significantly. When heat is neither lost nor gained during a process, the reaction is said to occur *adiabatically*. A reaction carried on inside a sealed Dewar flask or "vacuum bottle" is adiabatic since the system is thermally insulated from its surroundings. In thermodynamic terms, it can be said that an adiabatic process is one in which $q = 0$, and the first law under adiabatic conditions reduces to

$$w = -dE \quad (3-5)$$

According to equation (3-5), when work is done by the system, the internal energy decreases, and since heat cannot be absorbed in an adiabatic process, the temperature must fall. Here, the work done becomes a thermodynamic property dependent only on the initial and final states of the system.

Reversible Processes. Imagine the hypothetical case of water at its boiling point contained in a cylinder fitted with a weightless and frictionless piston. The apparatus is immersed in a constant-temperature bath maintained at the same temperature as the water in the cylinder. By definition, the vapor pressure of water at its boiling point is equal to the atmospheric pressure, and if the pressure is 1 atm, the temperature is 100° C. The process is an isothermal one, that is, it is carried out at constant temperature. If the external pressure is decreased slightly, the volume of the system increases, and the vapor pressure falls. Water then evaporates to maintain the vapor pressure constant at its original value, and heat is extracted from the bath to keep the temperature constant and bring about the vaporization.

On the other hand, if the external pressure is increased slightly, the system is compressed and the vapor pressure rises. Some of the water condenses to reestablish the equilibrium vapor pressure, and the liberated heat is absorbed by the constant-temperature

bath. If the process could be conducted infinitely slowly so that no work is expended in supplying kinetic energy to the piston, and if the piston is considered to be frictionless so that no work is done against the force of friction, all the work is used to expand or compress the vapor. Then, since this process is always in a state of virtual thermodynamic equilibrium, being reversed by an infinitesimal change of pressure, it is said to be *reversible*. If the pressure on the system is increased or decreased rapidly, or if the temperature of the bath cannot adjust instantaneously to the change in the system, the isolated system is not in the same thermodynamic state at each moment, and the process cannot be reversible.

Although no real system can be made strictly reversible, some are nearly so. One of the best examples of reversibility is that involved in the measurement of the potential of an electrochemical cell using the potentiometric method (p. 193).

Maximum Work. The work done by a system in an isothermal process is at a maximum when it is done reversibly. This statement can be shown to be true by the following argument. No work is accomplished if an ideal gas expands freely into a vacuum, where $P = 0$, since any work accomplished depends on the external pressure. As the external pressure becomes greater more work is done by the system, and it rises to a maximum when the external pressure is infinitesimally less than the pressure of the gas, that is, when the process is reversible. Of course, if the external pressure is continually increased, the gas is compressed rather than expanded and work is done *on* the system rather than *by* the system in an isothermal reversible process.

Work of Expansion Against a Constant Pressure. Let us first discuss the work term, considering only that work resulting from an expansion or compression of a gas against a *constant* opposing pressure, P .

Imagine a vapor confined in a hypothetical cylinder fitted with a weightless, frictionless piston of area A , as shown in Figure 3-1. If a constant external pressure P is exerted on the piston, the total force is $P \times A$, since $P = \text{force/area}$. The vapor in the cylinder is now made

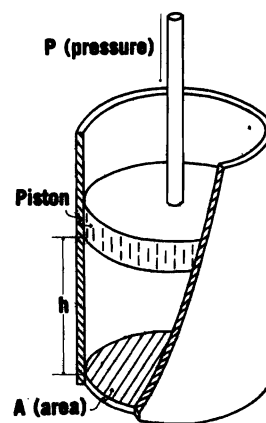


Fig. 3-1. Cylinder with weightless and frictionless piston.

to expand by increasing the temperature, and the piston moves a distance h . The work done against the opposing pressure is

$$W = \underbrace{P \times A \times h}_{\substack{\text{total} \\ \text{force}}} \quad (3-6)$$

Now $A \times h$ is the increase in volume, $\Delta V = V_2 - V_1$, so that, at constant pressure,

$$W = P \Delta V \quad (3-7)$$

$$W = P(V_2 - V_1) \quad (3-8)$$

Example 3-1. A gas expands by 0.5 liter against a constant pressure of 0.5 atm at 25° C. What is the work in ergs and in joules done by the system?

$$\begin{aligned} W &= P \Delta V \\ 1 \text{ atm} &= 1.013 \times 10^6 \text{ dyne/cm}^2 \\ W &= (0.507 \times 10^6 \text{ dyne/cm}^2) \times 500 \text{ cm}^3 \\ &= 2.53 \times 10^8 \text{ ergs} = 25.3 \text{ J} \end{aligned}$$

The following example demonstrates the kind of problem that can be solved by an application of the first law of thermodynamics.

Example 3-2. One mole of water in equilibrium with its vapor is converted into steam at 100° C and 1 atm. The heat absorbed in the process (i.e., the heat of vaporization of water at 100° C) is about 9720 cal/mole. What are the values of the three first-law terms, Q , W , and ΔE ?

The amount of heat absorbed is the heat of vaporization, given as 9720 cal/mole. Therefore,

$$Q = 9720 \text{ cal/mole}$$

The work W performed against the constant atmospheric pressure is obtained by using equation (3-8), $W = P(V_2 - V_1)$. Now V_1 is the volume of 1 mole of liquid water at 100° C, or about 0.018 liter. The volume V_2 of 1 mole of steam at 100° C and 1 atm is given by the gas law, assuming that the vapor behaves ideally:

$$V_2 = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.6 \text{ liters}$$

It is now possible to obtain the work,

$$W = P(V_2 - V_1) = 1 \times (30.6 - 0.018) = 30.6 \text{ liters atm/mole} = 741 \text{ cal/mole}$$

The internal energy change ΔE is obtained from the first-law expression

$$\Delta E = Q - W = 9720 - 741 = 8979 \text{ cal/mole}$$

Therefore, of the 9720 cal of heat absorbed by 1 mole of water, 741 cal are employed in doing work of expansion or " $P \Delta V$ work" against an external pressure of 1 atm. The remaining 8979 cal increase the internal energy of the system. This quantity of heat supplies potential energy to the vapor molecules, that is, it represents the work done against the intermolecular forces of attraction. Internal energy includes not only potential energy due to intermolecular forces, but also rotational, vibrational, and translational kinetic energy of the atoms and the energy of the electrons that constitute the molecules.

Ideal Gases and the First Law. An ideal gas has no internal pressure, and hence no work need be done to separate the molecules against their cohesive forces when the gas expands. We therefore can write

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad (3-9)$$

Equation (3-9) suggests that the internal energy of an ideal gas is a function of the temperature only, which is one of the conditions needed to define an ideal gas in thermodynamic terms.

It follows from this discussion that for an ideal gas involved in an isothermal process ($dT = 0$), dE is equal to zero, and the first law becomes

$$q = w \quad (3-10)$$

Thus the work done in the isothermal expansion of an ideal gas is equal to the heat absorbed by the gas.

Isothermal Work of Expansion Against a Variable Pressure. Since the external pressure is only infinitesimally less than the pressure of an ideal gas in an isothermal expansion, the external pressure can be replaced by the pressure of the gas $P = nRT/V$ in the equation

$$\begin{aligned} \int dW_{\max} &= nRT \int_{V_1}^{V_2} \frac{dV}{V} \\ W_{\max} &= nRT \ln \frac{V_2}{V_1} \\ &= 2.303nRT \log \frac{V_2}{V_1} \quad (3-11) \end{aligned}$$

Equation (3-11) gives the heat absorbed as well as the maximum work done in the expansion, because $Q = \Delta E + W$, and ΔE is equal to zero for an ideal gas in an isothermal process. The maximum work in an isothermal reversible expansion may also be expressed in terms of pressure, since, from Boyle's law, $V_2/V_1 = P_1/P_2$ at constant temperature. Therefore, equation (3-11) can be written

$$W_{\max} = 2.303nRT \log \frac{P_1}{P_2} \quad (3-12)$$

Example 3-3. What is the maximum work done in the isothermal reversible expansion of 2 moles of an ideal gas from 1 to 5 liters at 25° C?

$$W_{\max} = 2.303 \times 2 \times 1.987 \times 298.2 \times \log 5 = 1908 \text{ cal}$$

Expressing R as 8.3143 J° K⁻¹ mole⁻¹ we obtain the answer in SI units:

$$W_{\max} = 2.303 \times 2 \times 8.3143 \times 298.2 \times \log 5 = 7982 \text{ J}$$

Heat Content (Enthalpy). When work of expansion is done at constant pressure, $W = P \Delta V = P(V_2 - V_1)$ by equation (3-7), and under these conditions, the first law may be written

$$\Delta E = Q_P - P(V_2 - V_1) \quad (3-13)$$

in which Q_P is the heat absorbed at constant pressure. Rearranging,

$$Q_P = E_2 - E_1 + P(V_2 - V_1) \quad (3-14)$$

$$= (E_2 + PV_2) - (E_1 + PV_1) \quad (3-15)$$

The term $E + PV$ is called the *heat content* or *enthalpy* H . The increase in heat content ΔH is equal to the heat absorbed at constant pressure by the system. It is the heat required to increase the internal energy and to perform work of expansion as seen by substituting H in equation (3-15),

$$Q_P = H_2 - H_1 = \Delta H \quad (3-16)$$

and writing equation (3-13) as

$$\Delta H = \Delta E + P \Delta V \quad (3-17)$$

For an infinitesimal change, one can write

$$dQ_P = dH \quad (3-18)$$

The heat absorbed in a reaction carried out at atmospheric pressure is independent of the number of steps and the mechanism of the reaction. It depends only on the initial and final conditions. We will take advantage of this fact in the section on thermochemistry.

It should also be stressed that $\Delta H = Q_P$ only when nonatmospheric work (i.e., work other than that against the atmosphere) is ruled out. When electric work, work against surfaces, or centrifugal forces are considered, we must write

$$\Delta H = Q_P - W_{\text{nonatm}}$$

Heat Capacity. The *molar heat capacity* C of a system is defined as the heat q required to raise the temperature of 1 mole of a substance by 1 degree. Since C varies with temperature, it is better to define it for an infinitely small change of temperature

$$C = \frac{q}{dT} \quad (3-19)$$

A system at constant volume, for example, a gas confined in a calorimeter, does no PV work since $dV = 0$, and the first law becomes

$$dE = q_v \quad (3-20)$$

Thus, the molar heat capacity C_v at constant volume can be defined as

$$C_v = \frac{q_v}{dT} = \left(\frac{\partial E}{\partial T} \right)_v \quad (3-21)$$

which states that C_v is the ratio of the increase in energy content or the heat absorbed at constant volume to the increase of temperature. The partial notation is used because E is a function of volume as well as of temperature, and the volume is being held constant in this case.

When the pressure rather than the volume is held constant, as, for example, when a reaction proceeds in an open container in the laboratory at essentially constant atmospheric pressure, a heat capacity C_P at constant pressure is defined. Since $q = dH$ at constant

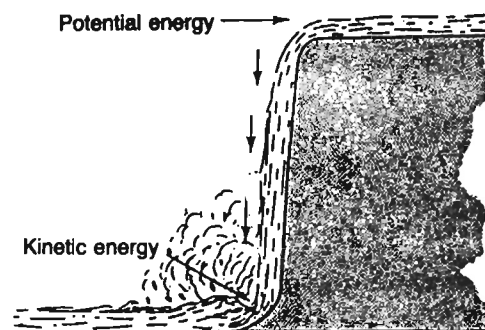


Fig. 3-2. Schematic of a waterfall showing its potential and kinetic energy. (Modified from H. E. White, *Modern College Physics*, 5th Ed., Van Nostrand, New York, 1966, p. 90, reproduced with permission of the copyright owner.)

pressure according to equation (3-18), the molar heat capacity C_P at constant pressure is written

$$C_P = \frac{q_P}{dT} = \left(\frac{\partial H}{\partial T} \right)_P \quad (3-22a)$$

and for a change in heat content between product and reactant,

$$\Delta H = H_{\text{product}} - H_{\text{reactants}}$$

equation (3-22a) may be written

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = \Delta C_P \quad (3-22b)$$

where $\Delta C_P = (C_P)_{\text{product}} - (C_P)_{\text{reactants}}$. Equation (3-22b) is known as the *Kirchhoff equation*.

Example 3-4.* A waterfall (Fig. 3-2) is often used in physics and thermodynamics as an example of a change from potential energy to kinetic energy or heat. At the top of a 200-ft (200 ft \times 30.48 cm/ft = 6096 cm) waterfall, 1 g of water possesses the potential energy

$$E = mgh$$

or

$$1 \text{ g} \times (981 \text{ cm sec}^{-2} \times 6096 \text{ cm}) = 0.598 \times 10^7 \text{ g cm}^2 \text{ sec}^{-2} \\ = 0.598 \times 10^7 \text{ erg} = 0.598 \text{ joule} = 0.143 \text{ cal}$$

The potential energy, mgh , at the top of the falls is converted completely into heat (kinetic) energy, $Q = mc\Delta T$, at the bottom, where c is the specific heat of the water. Specific heat is the heat Q required to raise the temperature of 1 g of a substance by 1° C. Thus we have a relationship between the top and bottom of the falls:

$$mgh = mc\Delta T$$

in which the masses cancel, leaving

$$\Delta T = gh/c \\ = \frac{981 \text{ cm sec}^{-2} \times 6096 \text{ cm}}{1 \text{ cal g}^{-1} \text{ deg}^{-1}} = \frac{0.598 \times 10^7 \text{ g cm}^2 \text{ sec}^{-2} \text{ (erg)}}{\text{cal deg}^{-1}} \\ = \frac{0.598 \text{ joule}}{\text{cal deg}^{-1}} = \frac{0.143 \text{ cal}}{\text{cal deg}^{-1}}$$

$$\Delta T = 0.143^\circ \text{ K} = 0.143^\circ \text{ C.}$$

*After J. W. Moncrief and W. H. Jones, *Elements of Physical Chemistry*, Addison-Wesley, Reading, Mass., 1977, p. 18.

TABLE 3-2. Modified First-Law Equations for Processes Occurring under Various Conditions

Specified Condition		Process	Common Means for Establishing the Condition	Modification of the First Law, $dE = q - w$, Under the Stated Condition	
(a) Constant heat	$q = 0$	Adiabatic	Insulated vessel, such as a Dewar flask	$dE = -w$	(a)
(b) Reversible process at constant temperature	$dT = 0$	Isothermal	Constant-temperature bath	$w = w_{\max}$	(b)
(c) Ideal gas at constant temperature	$(\partial E/\partial V)_T = 0$ $dT = 0$	Isothermal	Constant-temperature bath	$dE = 0$ $\therefore q = w$	(c)
(d) Constant volume	$dV = 0$	Isometric (isochoric)	Closed vessel of constant volume, such as a bomb calorimeter	$w = PdV = 0$ $\therefore dE = q_v$	(d)
(e) Constant pressure	$dP = 0$	Isobaric	Reaction occurring in an open container at constant (atmospheric) pressure	$dH = q_p$ $\therefore dE = dH - P dV$	(e)

Thus the potential energy of the water at the top of the waterfall has been converted completely into kinetic energy at the bottom, which is exhibited as an increase in temperature $\Delta T = 0.143^\circ \text{C}$. In *Modern College Physics*, Professor White states "All the available energy at the top of a waterfall is potential. At the bottom it is kinetic" (see Fig. 3-2).

In this process, no heat Q is exchanged with the surroundings and no work is done, so the net change in energy, by the first law, is zero:

$$\Delta E = Q - W = 0$$

William Thomson,* an important contributor to the development of thermodynamics (who later became Lord Kelvin) recalled how in the summer of 1847 he met Joule on a vacation in the Alps. James Joule, who had studied the relationship between work and heat and for whom the unit of energy was named, was on his honeymoon in the mountains. When Thomson met him, Joule had left his bride behind in the carriage and with a long and accurate thermometer in hand was attempting to measure the temperature at various heights of a waterfall. It is unlikely that Joule was successful in this crude attempt, particularly since we see in Example 3-4 that the temperature change is indeed small even for a very high waterfall. Joule would no doubt have done better to set aside his science experiments and pay more attention to his bride on their honeymoon in the beautiful Alps.

Summary. Some of the special restrictions that have been placed on the first law up to this point in the chapter, together with the resultant modifications of the law, are brought together in Table 3-2. A comparison of the entries in Table 3-2 with the material that has gone before will serve as a comprehensive review of the first law.

*D. Eisenberg and D. Crothers, *Physical Chemistry with Applications to the Life Sciences*, Benjamin/Cummings, Menlo Park, Calif., 1979, p. 93.

THERMOCHEMISTRY

Heat may be absorbed or evolved in physical and chemical processes, and the reactions are referred to as *endothermic* when heat is absorbed and *exothermic* when heat is evolved. Thermochemistry deals with the heat changes accompanying isothermal chemical reactions. These are usually carried out at atmospheric (essentially constant) pressure, and the heat absorbed is equal to the increase in heat content (i.e., $Q_p = \Delta H$). If the reaction is carried out at constant volume, then $Q_v = \Delta E$. In solution reactions, the $P \Delta V$ terms are not significant, so that $\Delta H \cong \Delta E$. This close approximation does not hold, however, for reactions involving gases.

In the reaction



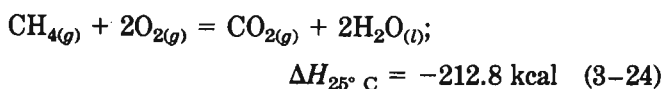
$$\Delta H^\circ_{25^\circ\text{C}} = -94,052 \text{ cal}$$

the subscripts represent the physical states, (s) standing for solid and (g) for gas. Additional symbols, (l) for liquid and (aq) for dilute aqueous solution, will be found in subsequent thermochemical equations. $\Delta H^\circ_{25^\circ\text{C}}$ is the *standard heat of reaction* for the process at 25°C . The negative sign accompanying the value for ΔH in equation (3-23) signifies that heat is evolved, that is, the reaction is exothermic. Equation (3-23) states that when 1 mole of solid carbon (graphite) reacts with 1 mole of gaseous oxygen to produce 1 mole of gaseous carbon dioxide at 25°C , 94,052 cal are liberated. This means that the reactants contain 94,052 cal in excess of the product, so that this quantity of heat is evolved during the reaction. If the reaction were reversed and CO_2 were converted to carbon and oxygen, the reaction would be endothermic. It would involve the absorption of 94,052 cal, and ΔH would have a positive value. When the pressure is not specifically stated, it is assumed, as it is in this case, that the reaction is carried out at 1 atm.

Heat of Formation. Equation (3-23) gives the *standard heat of formation* of carbon dioxide from its

elements. The heat content of 1 mole of carbon dioxide is 94,052 cal less than the heat content of its elements in the *standard* or *reference state* of 25° C and 1 atm pressure. The state of matter or allotropic form of the elements also must be specified in defining the standard state. The heat contents of all elements in their standard states are arbitrarily assigned values of zero. Consequently, the heat involved in the formation of a compound from its elements is the *heat of formation* of the compound. The heat of formation of carbon dioxide is -94,052 cal. The heats of formation of a number of compounds have been determined, and some of these are found in Table 3-3.

Heat of Combustion. The heat involved in the complete oxidation of 1 mole of a compound at 1 atm pressure is known as the *heat of combustion*. The compound is burned in the presence of oxygen in a sealed calorimeter to convert it completely to carbon dioxide and water. The combustion of methane is written



This result can also be obtained from the heats of formation of reactants and products, since

$$\Delta H_{\text{reaction}} = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}} \quad (3-25)$$

in which the terms on the right are the heats of formation of the products and reactants. According to the National Bureau of Standards data (Table 3-3), the heat of formation of $\text{CH}_{4(g)}$ (methane_[g]) is -17.889; $\text{CO}_{2(g)}$, -94.052; and $\text{H}_2\text{O}_{(l)}$, -68.317 kcal/mole at 25° C. Since oxygen $\text{O}_{2(g)}$ is an element, it has a heat of formation of zero.

Employing equation (3-25),

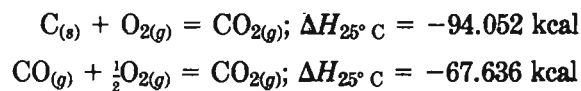
$$\Delta H_{25^\circ \text{C}} = [-94.052 + 2(-68.317)]$$

$$-(-17.889) = -212.797 \text{ kcal}$$

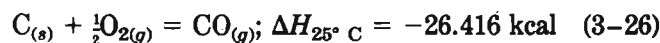
Note the 2 molecules of water, $2\text{H}_2\text{O}$, requiring that its standard heat of formation, -68.317, be multiplied by 2.

In the year 1840, Hess showed that since ΔH depends only on the initial and final states of a system, thermochemical equations for several steps in a reac-

tion can be added and subtracted to obtain the heat of the overall reaction. The principle is known as *Hess's law of constant heat summation* and is used to obtain the heats of reactions that are not easily measured directly. If one desires to obtain $\Delta H_{25^\circ \text{C}}$ for a reaction that cannot be carried out in a calorimeter, he or she may proceed as illustrated in the following example.



Subtracting the second equation and its heat of combustion from the first yields the desired result:



Differential and Integral Heats of Solution. When a mole of a solute is dissolved, the heat absorbed or liberated is not a constant quantity but varies with the concentration of the solution. Two kinds of heats of solution are recognized: differential or partial, and integral or total.

The *differential heat of solution* is the heat effect produced when 1 mole of a solute is dissolved in a large quantity of a solution of a definite concentration. No appreciable change in concentration results when the solute is added, and the heat change is thus obtained at the specified concentration. Differential heat of solution can be defined, in an equivalent way, as the heat change that occurs when an infinitely small amount of solute is dissolved in a definite quantity of solution. Since the amount of solute is infinitesimal, no change in concentration would result.

The *integral heat of solution* is the effect obtained when 1 mole of a solute is dissolved in a definite quantity of pure solvent, say 1000 g of water, to yield a solution.

Differential and integral heats of solution are not generally equal. In the case of differential heat, the process is conducted so that concentration does not change when the solute is added. The heat effects depends only on the conversion of the crystalline solute to the dissolved state, and the solvent is in essentially the same state before and after the dissolution of the solute. In integral heat, both the solute and the solvent are affected during the process.

Heats of hydration, mentioned on page 230, may be calculated from integral heats of solution. As seen in Figure 10-6, anhydrous sodium sulfate dissolves in water with the liberation of heat, because the heat of hydration is more than sufficient to disintegrate the crystal. The already hydrated $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, on the other hand, dissolves with the absorption of heat because no hydration energy is available to overcome the crystal energy. In the thermodynamic considerations of dissolution (solubility of a drug in a solvent, chapter 10) the heat term involved is a partial or differential heat of solution.

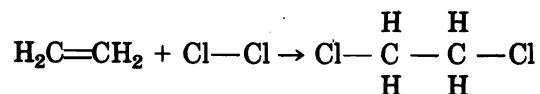
Heats of Reaction from Bond Energies. Heats of reaction may be estimated from covalent bond energies, found in

TABLE 3-3. *Standard Heats of Formation at 25° C**

Substance	ΔH° (kcal/mole)	Substance	ΔH° (kcal/mole)
$\text{H}_{2(g)}$	0	Methane _(g)	-17.889
$\text{H}_{(g)}$	52.09	Ethane _(g)	-20.236
$\text{O}_{2(g)}$	0	Ethylene _(g)	12.496
$\text{O}_{(g)}$	59.16	Benzene _(g)	19.820
$\text{I}_{2(g)}$	14.88	Benzene _(l)	11.718
$\text{H}_2\text{O}_{(g)}$	-57.798	Acetaldehyde _(g)	-39.76
$\text{H}_2\text{O}_{(l)}$	-68.317	Ethyl alcohol _(l)	-66.356
$\text{HCl}_{(g)}$	-22.063	Glycine _(g)	-126.33
$\text{HI}_{(g)}$	6.20	Acetic acid _(l)	-116.4
$\text{CO}_{2(g)}$	-94.052		

*From Rossini et al., *N.B.S. Circulars* No. C461 and 500.

books on thermodynamics listed in the footnote on the first page of this chapter. In the reaction



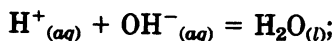
a C=C bond is broken (requiring 130 kcal), a Cl—Cl bond is broken (requiring 57 kcal), a C—C bond is formed (liberating 80 kcal), and two C—Cl bonds are formed (liberating 2×78 or 156 kcal). Thus the energy ΔH of the reaction is

$$\Delta H = 130 + 57 - 80 - 156 = -49 \text{ kcal}$$

Since 1 calorie = 4.184 joule, -49 kcal is expressed in SI units as 2.05×10^5 J.

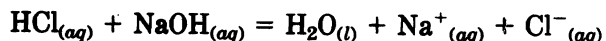
Additional Applications of Thermochemistry. Thermochemical data are important in many chemical calculations. Heat of mixing data can be used to determine whether a reaction such as precipitation is occurring during the mixing of two salt solutions. If no reaction takes place when dilute solutions of the salts are mixed, the heat of reaction is zero.

The constancy of the heats of neutralization, obtained experimentally when dilute aqueous solutions of various strong acids and strong bases are mixed, has shown that the reaction involves only



$$\Delta H_{25^\circ \text{C}} = -13.6 \text{ kcal} \quad (3-27)$$

No combination occurs between any of the other species in a reaction such as



since HCl, NaOH, and NaCl are completely ionized in water. In the neutralization of a weak electrolyte by a strong acid or base, however, the reaction involves ionization in addition to neutralization, and the heat of reaction is no longer constant at about -13.6 kcal/mole. Since some heat is absorbed in the ionization of the weak electrolyte, the heat evolved falls below the value for the neutralization of completely ionized species. Thus, a knowledge of ΔH of neutralization permits one to differentiate between strong and weak electrolytes.

Another important application of thermochemistry is the determination of the number of calories obtained from various foods. The subject is discussed in books on food and nutrition.

THE SECOND LAW OF THERMODYNAMICS

Heat flows spontaneously only from hotter to colder bodies, and a steam engine can do work only with a fall in temperature and a flow of heat to the lower temperature. No useful work can be obtained from heat at constant temperature. Gases expand naturally from

higher to lower pressures, and solute molecules diffuse from a region of higher to lower concentration. These spontaneous processes will not proceed in reverse without the intervention of some external agency. Although spontaneous processes are not thermodynamically reversible, they can be carried out in a nearly reversible manner by an outside agency. Maximum work is obtained by conducting a spontaneous process reversibly; however, the frictional losses and the necessity of carrying out the process at an infinitely slow rate preclude the possibility of complete reversibility in real processes.

The first law of thermodynamics simply observes that energy must be conserved when it is converted from one form to another. It has nothing to say about the probability that a process will occur. The second law refers to the probability of the occurrence of a process based on the observed tendency of a system to approach a state of energy equilibrium. The energy that may be freed for useful work in a gas, liquid, or solid, or any reaction mixture, is known as the *free energy* of the system. The free energy decreases as a physical or chemical reaction proceeds. In general, *spontaneous processes at constant temperature and pressure are accompanied by a loss in free energy*, and this decrease signifies the natural tendency for the transformation to occur.

When a substance melts, it passes from a condition of low heat content and a highly ordered arrangement to a condition of higher heat content and more randomness. This change from orderliness to randomness is said by the physical chemist to represent an increase in the *entropy* of the system. The energy that is used to increase the randomness or, as Gibbs, one of the founders of thermodynamics, once referred to it, the "mixed-upness" of a system is obviously not available for other purposes, such as useful work. All forms of energy are made up of two terms: an *intensity factor* and a *capacity factor*, as shown in Table 3-1. Temperature is the intensity factor and entropy change is the capacity factor of heat energy.

The Efficiency of a Heat Engine. An important consideration is that of the possibility of converting heat into work. Not only is heat isothermally unavailable for work; *it can never be converted completely into work.*

The spontaneous character of natural processes and the limitations on the conversion of heat into work constitute the second law of thermodynamics.

Falling water can be made to do work, owing to the difference in the potential energy at the two levels, and electric work can be done because of the difference in electric potential (emf). A heat engine (such as a steam engine) likewise can do useful work by using two heat reservoirs, a "source" and a "sink," at two different temperatures. Only part of the heat at the source is converted into work, however, the remainder being returned to the sink (which, in practical operations, is

often the surroundings) at the lower temperature. The fraction of the heat Q at the source converted into work W is known as the *efficiency* of the engine:

$$\text{efficiency} = \frac{W}{Q} \quad (3-28)$$

The efficiency of even a hypothetical heat engine operating without friction cannot be unity, for W is always less than Q in a continuous conversion of heat into work, according to the second law of thermodynamics.

Imagine a hypothetical steam engine operating reversibly between an upper temperature T_2 and a lower temperature T_1 . It absorbs heat Q_2 from the hot boiler or source, and by means of the working substance, steam, it converts the quantity W into work, and returns heat Q_1 to the cold reservoir or sink. Carnot (1824) proved that the efficiency of such an engine, operating reversibly at every stage and returning to its initial state (cyclic process), can be given by the expression

$$\frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} \quad (3-29)$$

We know that the heat flow in the operation of the engine follows the temperature gradient, so that the heat absorbed and rejected can be related directly to temperatures. Now, Lord Kelvin used the ratios of the two heat quantities Q_2 and Q_1 of the Carnot cycle to establish the Kelvin temperature scale

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \quad (3-30)$$

We can therefore write, by combining equations (3-28), (3-29), and (3-30),

$$\text{Efficiency} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \quad (3-31)$$

It is observed from equation (3-31) that the higher T_2 becomes and the lower T_1 becomes, the greater is the efficiency of the engine. When T_1 reaches absolute zero on the Kelvin scale, the reversible heat engine converts heat completely into work, and its theoretic efficiency becomes unity. This can be seen by setting $T_1 = 0$ in equation (3-31). Since absolute zero is considered unattainable, however, an efficiency of unity is impossible, and heat can never be completely converted to work. We can write this statement using the notation of limits as follows:

$$\lim_{T_1 \rightarrow 0} \frac{W}{Q} = 1 \quad (3-32)$$

If $T_2 = T_1$ in equation (3-31), the cycle is isothermal and the efficiency is zero, confirming the earlier statement that heat is isothermally unavailable for conversion into work.

Example 3-5. A steam engine operates between the temperatures of 373° and 298° K. (a) What is the theoretic efficiency of the engine? (b) If the engine is supplied with 1000 cal of heat Q_2 , what is the theoretic work in ergs?

(a)

$$\begin{aligned} \text{Efficiency} &= \frac{W}{Q_2} = \frac{373 - 298}{373} \\ &= 0.20 \text{ or } 20\% \end{aligned}$$

(b)

$$W = 1000 \times 0.20 = 200 \text{ cal}$$

$$200 \text{ cal} \times 4.184 \times 10^7 \text{ erg/cal} = 8.36 \times 10^9 \text{ ergs}$$

Entropy. When equation (3-31) is written as

$$\frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} \quad (3-33)$$

$$W = \frac{Q_2 T_2}{T_2} - \frac{Q_2 T_1}{T_2} \quad (3-34)$$

$$W = Q_2 - T_1 \frac{Q_2}{T_2} \quad (3-35)$$

it can be seen that only part of the heat Q_2 is converted to work in the engine. For example, suppose that the energy $T_1 Q_2 / T_2 = 800$ cal. This is the heat Q_1 that is returned to the sink at the lower temperature and is unavailable for work. One can easily show that Q_1 is equal to $T_1 Q_2 / T_2$ of equation (3-35). The term Q_2 / T_2 is known as the *entropy change* of the reversible process at T_2 , and Q_1 / T_1 is the entropy change at T_1 . When the entropy changes at the two temperatures are calculated, they are both found to equal 2.7 cal/deg. The entropy change ΔS_2 during the absorption of heat is positive, however, since Q_2 is positive. At the lower temperature where heat is expelled, Q_1 is negative and the entropy change ΔS_1 is negative. The total entropy change ΔS_{cycle} in the reversible cyclic process is thus zero.

$$\Delta S_2 = \frac{Q_{2\text{rev}}}{T_2} = \frac{1000 \text{ cal}}{373} = 2.7 \text{ cal/deg}$$

$$\Delta S_1 = -\frac{Q_{1\text{rev}}}{T_1} = -\frac{800}{298} = -2.7 \text{ cal/deg}$$

$$\therefore \Delta S_{\text{cycle}} = \Delta S_2 + \Delta S_1 = 0$$

We may also note that if Q_2 is the heat absorbed by an engine at T_2 , then $-Q_2$ must be the heat lost by the surroundings (the hot reservoir) at T_2 , and the entropy of the surroundings is

$$\Delta S_{\text{surr}} = -\frac{Q_2}{T_2}$$

Hence, for any system and its surroundings, or *universe*

$$\Delta S_{\text{total system}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \quad (3-36)$$

Thus we have two cases in which $\Delta S = 0$: (a) a system in a reversible cyclic process and (b) a system and its surroundings undergoing any reversible process.

Entropy S may be defined as the molar energy per degree of absolute temperature that is unavailable for work, and, as shown in Table 3-1, it is the capacity factor of thermal energy. For the absorption of heat in any step of a reversible process, the entropy change is written as

$$\Delta S = \frac{Q_{\text{rev}}}{T} \quad (3-37)$$

and for an infinitesimal change

$$dS = \frac{q_{\text{rev}}}{T} \quad (3-38)$$

In an *irreversible process*, the entropy change of the total system or universe (a system and its surroundings) is always positive, because ΔS_{surr} is always less than ΔS_{syst} in an irreversible process. Consider the heat being absorbed irreversibly by an ideal gas at T_2 in the example just given. The entropy of the system depends only on the initial and final states; thus, $\Delta S = 2.7$ cal/deg is the same for an irreversible process as it is for a reversible process. The work done in an irreversible process is less than the maximum work, however, and $\Delta S_{\text{surr}} = Q_{\text{surr}}/T_2$ is less than -2.7 cal/deg, say -2.5 cal/deg. For this irreversible process

$$\Delta S_{\text{total system}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} = 2.7 - 2.5 = 0.2$$

Therefore, in an irreversible process, the entropy of the system and its surroundings is increasing. In mathematical symbols, it is written,

$$\Delta S_{\text{total system}} > 0 \quad (3-39)$$

and this can serve as a criterion of spontaneity of a process.

Two examples of entropy calculations will now be given, first considering a reversible process and second an irreversible process.

Example 3-6. What is the entropy change accompanying the vaporization of 1 mole of water in equilibrium with its vapor at 25°C ? In this reversible isothermal process, the heat of vaporization ΔH_v required to convert the liquid to the vapor state is 10,500 cal/mole.

The process is carried out at a constant pressure so that $Q = \Delta H_v$, and since it is a reversible process, the entropy change can be written as

$$\Delta S = \frac{\Delta H_v}{T} = \frac{10,500}{298} = 35.2 \text{ cal/mole deg}$$

The entropy change involved as the temperature changes is often desired in thermodynamics; this relationship is needed for the next example. The heat absorbed at constant pressure is given by equation (3-22), $q_P = C_P dT$, and for a reversible process

$$\frac{C_P dT}{T} = \frac{q_{\text{rev}}}{T} = dS \quad (3-40)$$

Integrating between T_1 and T_2 yields

$$\Delta S = C_P \ln \frac{T_2}{T_1} = 2.303 C_P \log \frac{T_2}{T_1} \quad (3-41)$$

Example 3-7. Compute the entropy change in the (irreversible) transition of a mole of liquid water to crystalline water at -10°C at constant pressure. The entropy is obtained by calculating the entropy changes for several *reversible* steps.

We first reversibly convert supercooled liquid water at -10° to liquid water at 0°C , then change this to ice at 0°C , and finally cool the ice reversibly to -10°C . The sum of the entropy changes of these steps gives ΔS_{water} . To this we add the entropy change undergone by the surroundings so as to obtain the total entropy change. If the process is spontaneous, the result will be a positive value. If the system is at equilibrium, that is, if liquid water is in equilibrium with ice at -10°C , there is no tendency for the transition to occur, and the total entropy change will be zero. Finally, if the process is not spontaneous, the total entropy change will be negative.

The heat capacity of water is 18 cal/deg, and that of ice is 9 cal/deg within this temperature range.

The reversible change of water at -10°C to ice at -10°C is carried out as follows:

$$^* \text{H}_2\text{O}_{(l, -10^\circ)} \rightarrow \text{H}_2\text{O}_{(l, 0^\circ)}; \Delta S = C_P \ln \frac{T_{\text{final}}}{T_{\text{initial}}} = 0.67$$

$$\text{H}_2\text{O}_{(l, 0^\circ)} \rightarrow \text{H}_2\text{O}_{(s, 0^\circ)}; \Delta S = \frac{q_{\text{rev}}}{T} = \frac{-1437}{273.2} = -5.26$$

$$\text{H}_2\text{O}_{(s, 0^\circ)} \rightarrow \text{H}_2\text{O}_{(s, -10^\circ)}; \Delta S = C_P \ln \frac{T_{\text{final}}}{T_{\text{initial}}} = -0.37$$

$$\text{H}_2\text{O}_{(l, -10^\circ)} \rightarrow \text{H}_2\text{O}_{(s, -10^\circ)}; \Delta S_{\text{H}_2\text{O}} = -4.96 \text{ cal/mole deg}$$

The entropy of water decreases during the process since ΔS is negative, but we cannot judge the spontaneity of the process until we also calculate ΔS of the surroundings.

For the entropy change of the surroundings, we consider the water to be in equilibrium with a large bath at -10°C , and the heat liberated when the water freezes is absorbed by the bath without a significant temperature increase. Thus, the reversible absorption of heat by the bath is given by

$$\Delta S_{\text{bath}} = -\frac{q_{\text{rev}}}{T} = \frac{1343}{263.2} = 5.10 \text{ cal/mole deg}$$

where 1343 cal/mole is the heat of fusion of water at -10°C .

$$\begin{aligned} \therefore \Delta S_{\text{total system}} &= \Delta S_{\text{H}_2\text{O}} + \Delta S_{\text{bath}} \\ &= -4.91 + 5.10 \\ &= 0.19 \text{ cal/mole deg} \end{aligned}$$

The process in *Example 3-7* is spontaneous since $\Delta S > 0$. This criterion of spontaneity is not a convenient one, however, for it requires a calculation of the entropy change both in the system and the surroundings. The free energy functions, to be treated in a later section, do not demand information concerning the surroundings and are more suitable criteria of spontaneity.

Entropy and Disorder. The impossibility of converting all thermal energy into work results from the "disorderliness" of the molecules existing in the system. Every substance at room temperature possesses a certain amount of entropy owing to molecular motion. The large number of molecules of a gas confined in a cylinder (Fig. 3-3) are traveling in all directions, and some of these will not contribute to driving the piston.

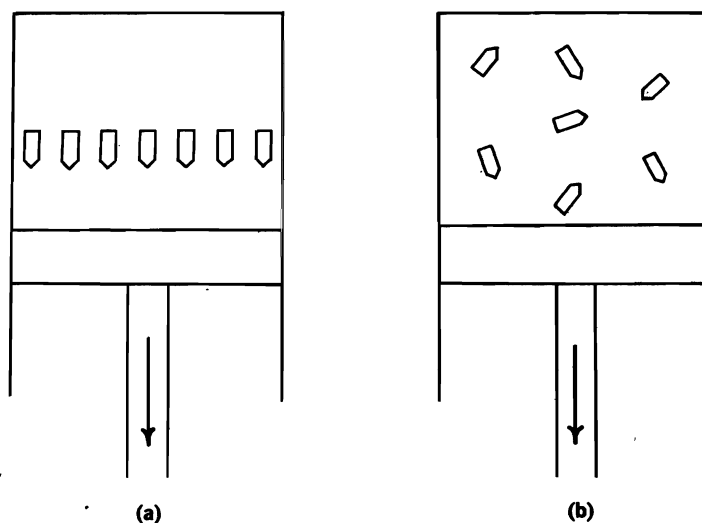


Fig. 3-3. Cylinders containing gas molecules showing (a) low entropy, or orderliness, and (b) high entropy, or disorderliness. The orderly motion of the molecules in (a) could be converted almost entirely into the work of driving the piston; however, nature knows no regimentation of this kind. An actual gas is composed of a large proportion of “wrong-way” molecules with a high degree of freedom or entropy as seen in (b). This randomness of motion results in a loss of work, but apparently molecules, like people, are willing to sacrifice some efficiency for greater freedom. (Modified from W. M. Latimer, *Chem. Eng. News*, 31, 3366, 1953.)

Latimer² states that the entropy of the gas is associated with these “wrong-way molecules,” which are manifesting their individual freedom to go in any direction they please. All systems tend to an increased freedom of motion, and the increase in randomness or disorderliness in a natural process is embodied in the second law of thermodynamics. The law may now be stated in the form: *a spontaneous reaction involving a system and its surroundings proceeds in the direction of increased entropy; when the system finally reaches equilibrium, the net entropy change undergone by the system and its surroundings is equal to zero.*

The idea of entropy may become clearer to the student when he or she understands the relationship of entropy and the number of configurations W that a system can assume, as shown by Boltzmann:

$$S = k \ln W \quad (3-42)^*$$

In this equation k is the Boltzmann constant (the gas constant R divided by Avogadro's number, $R/N = 1.38066 \times 10^{-16}$ erg deg⁻¹ molecule⁻¹). When a molecule can assume an increasing number of arrangements, W , as happens when a large flexible protein molecule passes from the solid into the liquid state, the entropy of the system increases, as expressed by equation (3-42). When the protein is bound into a limited number of configurations by the presence of, say, a zinc atom, the entropy of the protein-zinc complex decreases. Thus, the increase in entropy with increasing number of configurations of a molecule, and the de-

crease in entropy with restriction or ordering of the structure, is nicely described by Boltzmann's concept given in equation (3-42).

THE THIRD LAW OF THERMODYNAMICS

The third law of thermodynamics states that the entropy of a pure crystalline substance is zero at absolute zero because the crystal arrangement must show the greatest orderliness at this temperature. The third law cannot be applied to supercooled liquids because their entropy at 0° K is probably not zero.

As a consequence of the third law, it is possible to calculate the absolute entropies of pure substances. The absolute entropy of a perfect crystal at any temperature may be determined from a knowledge of the heat capacity, so long as there is no change of phase during the temperature rise. By integration of equation (3-40),

$$\Delta S = \int_0^T \frac{C_P}{T} dT = 2.303 \int_0^T C_P d \log T \quad (3-43)$$

from $T = 0^\circ$ where $S = 0$ to T where $S = S$. The integral of equation (3-43) is obtained by plotting C_P values against $\log T$ and determining the area under the curve by use of a planimeter.

FREE ENERGY FUNCTIONS AND APPLICATIONS

Two new thermodynamic properties, the *Gibbs free energy* G and the *Helmholtz free energy* or *work function* A are now introduced, and some applications of these important functions to chemistry and pharmacy

*His ingenious and renowned formula, $S = k \ln W$, is carved on Ludwig Boltzmann's tombstone in Vienna. As k is named the Boltzmann constant, it has been suggested that R be called the molar Boltzmann constant.

are considered. According to Roseveare,³ these functions may be related to the other thermodynamic quantities in the following way. Disregarding electric and other forms of energy, we consider PV work as the only useful work or *external energy* that a system can accomplish. The heat content or *total energy* of the system is then divided into *internal* and *external energy*:

$$\begin{array}{rcccl} H & = & E & + & PV & (3-44) \\ \text{Total} & & \text{Internal} & & \text{External} & \\ \text{energy} & & \text{energy} & & \text{energy} & \end{array}$$

By a second classification, the total heat may be divided into isothermally available or *free energy* G and isothermally unavailable energy, TS :

$$\begin{array}{rcccl} H & = & G & + & TS & (3-45) \\ \text{Total} & & \text{Isothermally} & & \text{Isothermally} & \\ \text{energy} & & \text{available} & & \text{unavailable} & \\ & & \text{energy} & & \text{energy} & \end{array}$$

Finally, the internal energy can be divided into isothermally available internal energy or work function A and isothermally unavailable energy TS . Thus, for an isothermal process

$$\begin{array}{rcccl} E & = & A & + & TS & (3-46) \\ \text{Internal} & & \text{Isothermally} & & \text{Isothermally} & \\ \text{energy} & & \text{available} & & \text{unavailable} & \\ & & \text{internal} & & \text{energy} & \\ & & \text{energy} & & & \end{array}$$

A number of relationships may be obtained by rearranging these quantities and placing various restrictions on the processes described. Thus, equation (3-45) is rearranged to

$$G = H - TS \quad (3-47)$$

and substituting $E + PV$ for H , we have

$$G = E + PV - TS \quad (3-48)$$

Since $A = E - TS$ from equation (3-46), equation (3-48) can be written as

$$G = A + PV \quad (3-49)$$

Pressure and Temperature Coefficients of Free Energy.

By differentiating equation (3-48), one obtains several useful relationships between free energy and the pressure and temperature. Applying the differential of a product, $d(uv) = u dv + V du$, to equation (3-48), we obtain the result:

$$dG = dE + P dV + V dP - T dS - S dT \quad (3-50)$$

Now, in a reversible process in which $q_{\text{rev}} = T dS$, the first law, restricted to expansion work (i.e., $dE = q_{\text{rev}} - P dV$), can be written

$$dE = T dS - P dV \quad (3-51)$$

and substituting dE of equation (3-51) into equation (3-50) gives

$$dG = T dS - P dV + P dV + V dP - T dS - S dT$$

or

$$dG = V dP - S dT \quad (3-52)$$

At constant temperature, the last term becomes zero, and equation (3-52) reduces to

$$dG = V dP \quad (3-53a)$$

or

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad (3-53b)$$

At constant pressure, the first term on the right side of equation (3-52) becomes zero, and

$$dG = -S dT \quad (3-54)$$

or

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (3-55)$$

To obtain the isothermal change of free energy, equation (3-53a) is integrated between states 1 and 2 at constant temperature

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dP \quad (3-56)$$

For an ideal gas, the volume V is equal to nRT/P , thus allowing the equation to be integrated:

$$\begin{aligned} \Delta G &= (G_2 - G_1) = nRT \int_{P_1}^{P_2} \frac{dP}{P} \\ \Delta G &= nRT \ln \frac{P_2}{P_1} = 2.303nRT \log \frac{P_2}{P_1} \end{aligned} \quad (3-57)$$

in which ΔG is the free energy change of an *ideal gas* undergoing an *isothermal* reversible or irreversible alteration.

Example 3-8. What is the free energy change when 1 mole of an ideal gas is compressed from 1 atm to 10 atm at 25° C?

$$\begin{aligned} \Delta G &= 2.303 \times 1.987 \times 298 \times \log \frac{10}{1} \\ \Delta G &= 1360 \text{ cal} \end{aligned}$$

The change in free energy of a solute when the concentration is altered is given by the equation

$$\Delta G = 2.303nRT \log \frac{a_2}{a_1} \quad (3-58)$$

in which n is the number of moles of solute and a_1 and a_2 are the initial and final activities of the solute (see pp. 69, 131 for a discussion of activities).

Example 3-9. Borsook and Winegarden⁴ roughly computed the free energy change when the kidneys transfer various chemical constituents at body temperature (37° C or 310.2° K) from the blood plasma to the more concentrated urine. The ratio of concentrations was assumed to be equal to the ratio of activities in equation (3-58).

The concentration of urea in the plasma is 0.00500 mole/liter; the concentration in the urine is 0.333 mole/liter. Calculate the free

energy change in transporting 0.100 mole of urea from the plasma to the urine.

$$\Delta G = 2.303 \times 0.100 \times 1.987 \times 310.2 \times \log \frac{0.333}{0.00500}$$

$$\Delta G = 259 \text{ cal}$$

This result means that 259 cal of work must be done on the system, or this amount of net work must be performed by the kidneys to bring about the transfer.

Maximum Net Work. The maximum work W_{\max} of a reversible process is not all available for accomplishing *useful work* since some must be used as PV work to bring about the expansion or contraction of the system. The net available work is thus $W_{\max} - P \Delta V$.

The maximum work W_{\max} can be expressed in terms of the work function A as follows. For an isothermal change, equation (3-46) can be written

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

or

$$\Delta A = \Delta E - T \Delta S \quad (3-59)$$

and from the definition of entropy, assuming the process is reversible, $T \Delta S$ is equal to Q , and

$$\Delta A = \Delta E - Q \quad (3-60)$$

or from the first law

$$-\Delta A = W_{\max} \quad (3-61)$$

The free energy G , like the work function, depends only on the initial and final states of the system so that dG is an exact differential, that is, $\Delta G = G_2 - G_1$. For a reaction involving change in free energy, equation (3-49) becomes

$$G_2 - G_1 = (A_2 + P_2V_2) - (A_1 + P_1V_1)$$

$$= (A_2 - A_1) + (P_2V_2 - P_1V_1)$$

and at constant pressure

$$\Delta G = \Delta A + P(V_2 - V_1)$$

$$\Delta G = \Delta A + P \Delta V \quad (3-62)$$

By substituting W_{\max} from equation (3-61) into equation (3-62), one obtains

$$-\Delta G = W_{\max} - P \Delta V \quad (3-63)$$

for an isothermal process at constant pressure. Equation (3-63) expresses the fact that the decrease in free energy is equal to the maximum work exclusive of expansion work, that is, the decrease in free energy at constant temperature and pressure equals ($W_{\max} - P \Delta V$), which is the *useful* or *maximum net work* that can be obtained from the process. Under those circumstances in which the $P \Delta V$ term is insignificant (in electrochemical cell and surface tension measurements, for example), the free energy decrease is approximately equal to the maximum work.

Criteria of Equilibrium. When net work can no longer be obtained from a process, G is at a minimum and

$\Delta G = 0$. This statement signifies that the system is at equilibrium. Let us prove this by considering a system that is at equilibrium (and hence reversible) at a constant temperature and pressure. Now, for a reversible process restricted to expansion work, we have seen in equation (3-52) that $dG = V dP - S dT$. When we specify that the temperature and pressure be fixed, equation (3-52) becomes

$$dG = 0 \quad (3-64)$$

or for a finite change in G ,

$$\Delta G = 0 \quad (3-65)$$

Therefore, the criterion for equilibrium at constant temperature and pressure is that ΔG be zero. A negative free energy change, $-\Delta G$, is written sometimes as $\Delta G < 0$, and it signifies that the process is a spontaneous one. If ΔG is positive ($\Delta G > 0$), it indicates that net work must be absorbed for the reaction to proceed, and accordingly it is not spontaneous.

When the process occurs isothermally at constant volume rather than constant pressure, ΔA serves as the criterion for spontaneity and equilibrium. It is negative for a spontaneous process and becomes zero at equilibrium.

These criteria, together with the entropy criterion of equilibrium, are listed in Table 3-4.

It was once thought that at constant pressure, a negative ΔH (evolution of heat) was itself proof of a spontaneous reaction. Many natural reactions do occur with an evolution of heat; the spontaneous melting of ice at 10° C, however, is accompanied by an absorption of heat, and a number of other examples can be cited to prove the error of this assumption. The reason ΔH often serves as a criterion of spontaneity can be seen from the familiar expression,

$$\Delta G = \Delta H - T \Delta S$$

If $T \Delta S$ is small compared with ΔH , a negative ΔH will occur when ΔG is negative (i.e., when the process is spontaneous). When $T \Delta S$ is large, however, ΔG may be negative, and the process may be spontaneous even though ΔH is positive.

The entropy of a system, as previously stated, is a measure of the natural "wrong-way" tendency or, as Gibbs has called it, the "mixed-upness" of molecules. All systems spontaneously tend toward randomness, according to the second law, so that *the more disordered a system becomes, the higher is its probability and the greater its entropy*. Hence, we can write the equation just given as

$$\Delta G = \left[\begin{array}{l} \text{difference in bond energies or} \\ \text{attractive energies between} \\ \text{products and reactants, } \Delta H \end{array} \right]$$

$$- \left[\begin{array}{l} \text{change in probability} \\ \text{during the process,} \\ T \Delta S \end{array} \right] \quad (3-66)$$

TABLE 3-4. Criteria for Spontaneity and Equilibrium

Function	Restrictions	Sign of Function		
		Spontaneous	Nonspontaneous	Equilibrium
ΔS	Total system, $\Delta E = 0, \Delta V = 0$	+ or > 0	- or < 0	0
ΔG	$\Delta T = 0, \Delta P = 0$	- or < 0	+ or > 0	0
ΔA	$\Delta T = 0, \Delta V = 0$	- or < 0	+ or > 0	0

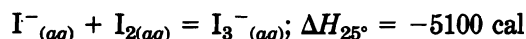
We can state that ΔG will become negative and the reaction will be spontaneous either when the heat content decreases or the probability of the system increases at the temperature of the reaction.

Thus, although the conversion of ice into water at 25° C requires an absorption of heat or 1650 cal/mole, the reaction leads to a more probable arrangement of the molecules; that is, an increased freedom of molecular movement. Hence, the entropy increases, and $\Delta S = 6$ cal/mole deg is sufficiently positive to make ΔG negative, despite the positive value of ΔH .

$$\Delta G = 1650 - (298 \times 6) = -138 \text{ cal/mole}$$

Many of the complexes of Chapter 11 form in solution with an absorption of heat, and the processes are spontaneous only because the entropy change is positive. The increase in randomness occurs for the following reason. The dissolution of solutes in water may be accompanied by a decrease in entropy, because both the water molecules and the solute molecules lose freedom of movement as hydration occurs. In complexation, this highly ordered arrangement is disrupted as the separate ions or molecules react through coordination, and the constituents thus exhibit more freedom in the final complex than they had in the hydrated condition. The increase in entropy associated with this increased randomness results in a spontaneous reaction as reflected in the negative value of ΔG .

Conversely, some association reactions are accompanied by a decrease in entropy, and they occur in spite of the negative ΔS only because the heat of reaction is sufficiently negative. For example, the Lewis acid-base reaction by which iodine is rendered soluble in aqueous solution,



is accompanied by a ΔS of -4 cal/mole deg. It is spontaneous because

$$\begin{aligned} \Delta G &= -5100 - [298 \times (-4)] \\ &= -5100 + 1192 = -3908 \text{ cal/mole} \end{aligned}$$

The reader should not be surprised to find a negative entropy associated with a spontaneous reaction. The ΔS values considered here are the changes in entropy of the *substance alone*, and not of the total system, that is, the substance and its immediate surroundings. When ΔS is used as a test of the spontaneity of a reaction, the

entropy change of the entire system must be considered. For reactions at constant temperature and pressure, which are the most common types, the change in free energy is ordinarily used as the criterion in place of ΔS . It is more convenient since we need not compute any changes in the surroundings.

By referring back to *Example 3-7*, it will be seen that ΔS was negative for the change from liquid to solid water at -10° C. This is to be expected since the molecules lose some of their freedom when they pass into the crystalline state. The entropy of water plus its surroundings increases during the transition, however; and it is a spontaneous process. The convenience of using ΔG instead of ΔS to obtain the same information is apparent from the following example, which may be compared with the more elaborate analysis required in *Example 3-7*.

Example 3-10. ΔH and ΔS for the transition from liquid water to ice at -10° C and at 1 atm pressure are -1343 cal/mole and -4.91 cal/mole deg, respectively. Compute ΔG for the phase change at this temperature (-10° C = 263.2° K) and indicate whether or not the process is spontaneous.

$$\Delta G = -1343 - [263.2 \times (-4.91)] = -51 \text{ cal/mole} = -213 \text{ J}$$

The process is spontaneous, as reflected in the negative value of ΔG .

Open Systems. The systems considered so far have been closed. They exchange heat and work with their surroundings, but the processes involve no transfer of matter, so that the amount of the components of the system remains constant.

The term *component* should be clarified before we proceed. A phase consisting of w_2 grams of NaCl dissolved in w_1 grams of water is said to contain two independently variable masses or two *components*. Although the phase contains the species Na^+ , Cl^- , $(\text{H}_2\text{O})_n$, H_3O^+ , OH^- , etc., they are not all independently variable. Because H_2O and its various species, H_3O^+ , OH^- , $(\text{H}_2\text{O})_n$, etc., are in equilibrium, the mass m of water alone is sufficient to specify these species. All forms can be derived from the simple species, H_2O . Similarly, all forms of sodium chloride can be represented by the single species NaCl, and the system therefore consists of just two components, H_2O and NaCl. As stated on p. 37, the *number of components* of a system is the smallest number of independently variable chemical substances that must be specified to describe the phases quantitatively.

In an open system in which the exchange of matter among phases also must be considered, any one of the

extensive properties such as volume or free energy becomes a function of temperature, pressure, and the number of moles of the various components.

Chemical Potential. For an infinitesimal reversible change of state, the free energy change in a two-component phase (binary system) is given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} dn_2 \quad (3-67)$$

According to Gibbs (who is credited with the development of a great part of chemical thermodynamics), the *chemical potential* of a component, say n_1 , is defined as

$$\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \mu_1 \quad (3-68)$$

and equation (3-67) is written more conveniently as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \mu_1 dn_1 + \mu_2 dn_2 \quad (3-69)$$

Now, from equations (3-55) and (3-53b), $(\partial G/\partial T)_P = -S$ and $(\partial G/\partial P)_T = V$ for a closed system. These relationships also apply to an open system, so that equation (3-69) can be written

$$dG = -S dT + V dP + \mu_1 dn_1 + \mu_2 dn_2 + \cdots \quad (3-70)$$

The chemical potential, also known as the *partial molar free energy*, can be defined in terms of other extensive properties, the definition given in equation (3-68), however, is the most useful. It states that, at constant temperature and pressure and with the amounts of the other components held constant, the chemical potential of a component i is equal to the change in the free energy brought about by an infinitesimal change in the number of moles n_i of the component. It may be considered as the change in free energy, for example, of an aqueous sodium chloride solution when 1 mole of NaCl is added to a large quantity of the solution, so that the composition does not undergo a measurable change.

At constant temperature and pressure, the first two right-hand terms of equation (3-70) become zero, and

$$dG_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 \quad (3-71)$$

or, in abbreviated notation,

$$dG_{T,P} = \sum \mu_i dn_i \quad (3-72)$$

which, upon integration, gives

$$G_{T,P,N} = \mu_1 n_1 + \mu_2 n_2 + \cdots \quad (3-73)$$

for a system of constant composition, $N = n_1 + n_2 + \cdots$. In equation (3-73), the sum of the right-hand terms equals the total free energy of the system at

constant pressure, temperature, and composition. Therefore, $\mu_1, \mu_2, \dots, \mu_n$ can be considered as the contributions per mole of each component to the total free energy. The chemical potential, like any other partial molar quantity, is an *intensive* property, in other words, it is independent of the number of moles of the components of the system.

For a closed system at equilibrium and constant temperature and pressure, the free energy change is zero, $dG_{T,P} = 0$, and equation (3-72) becomes

$$\mu_1 dn_1 + \mu_2 dn_2 + \cdots = 0 \quad (3-74)$$

for all the phases of the overall system, which is closed.

Equilibrium in a Heterogeneous system. We begin with an example suggested by Klotz.⁵ For a two-phase system consisting of, say, iodine distributed between water and an organic phase, the overall system is a closed one, whereas the separate aqueous and organic solutions of iodine are open. The chemical potential of iodine in the aqueous phase is written as μ_{Iw} , and in the organic phase, μ_{Io} . When the two phases are in equilibrium at constant temperature and pressure, the free energy changes dG_w and dG_o of the two phases must be equal since the free energy of the overall system is zero. Therefore, the chemical potentials of iodine in both phases are identical. This can be shown by allowing an infinitesimal amount of iodine to pass from the water to the organic phase in which, at equilibrium, according to equation (3-74),

$$\mu_{Iw} dn_{Iw} + \mu_{Io} dn_{Io} = 0 \quad (3-75)$$

Now, a decrease of iodine in the water is exactly equal to an increase of iodine in the organic phase:

$$-dn_{Iw} = dn_{Io} \quad (3-76)$$

Substituting (3-76) into (3-75) gives

$$\mu_{Iw} dn_{Iw} + \mu_{Io} (-dn_{Iw}) = 0 \quad (3-77)$$

and finally

$$\mu_{Iw} = \mu_{Io} \quad (3-78)$$

This conclusion may be generalized by stating that the chemical potential of a component is identical in all phases of a heterogeneous system when the phases are in equilibrium at a fixed temperature and pressure. Hence, we write

$$\mu_{i\alpha} = \mu_{i\beta} = \mu_{i\gamma} = \cdots \quad (3-79)$$

in which $\alpha, \beta, \gamma, \dots$ are various phases among which the substance i is distributed. For example, in a saturated aqueous solution of sulfadiazine, the chemical potential of the drug in the solid phase is the same as the chemical potential of sulfadiazine in the solution phase.

When two phases are not in equilibrium at constant temperature and pressure, the total free energy of the system tends to decrease, and the substance passes spontaneously from a phase of higher chemical potential to one of lower chemical potential until the potentials

are equal. Hence, the chemical potential of a substance can be used as a measure of the *escaping tendency* of the component from its phase. The concept of escaping tendency, defined on page 106, will be used in various chapters throughout the book. The analogy between chemical potential and electric or gravitational potential is evident, the flow in these cases always being from the higher to the lower potential and continuing until all parts of the system are at a uniform potential.

For a phase consisting of a *single pure substance*, the chemical potential is the free energy of the substance per mole. This can be seen by beginning with

$$dG = \left(\frac{\partial G}{\partial n}\right)_{T,P} dn = \mu dn \quad (3-80)$$

for a pure substance at constant pressure and temperature. By integrating equation (3-80), noting that $G = 0$ when $n = 0$, we obtain

$$G = \mu n$$

or

$$\mu = \frac{G}{n} \quad (3-81)$$

For a two-phase system of a single component, for example, liquid water and water vapor in equilibrium at constant temperature and pressure, the *molar free energy* G/n is identical in all phases. This statement can be verified by combining equations (3-79) and (3-81).

Clausius-Clapeyron Equation. If the temperature and pressure of a two-phase system of one component, for example, of liquid water (*l*) and water vapor (*v*) in equilibrium, are changed by a small amount, the molar free energy changes are equal and

$$dG_l - dG_v \quad (3-82)$$

In a phase change, the free energy changes for 1 mole of the liquid vapor are given by equation (3-52)

$$dG = V dP - S dT$$

From equations (3-82) and (3-52)

$$V_l dP - S_l dT = V_v dP - S_v dT$$

or

$$\frac{dP}{dT} = \frac{S_v - S_l}{V_v - V_l} = \frac{\Delta S}{\Delta V} \quad (3-83)$$

Now, at constant pressure, the heat absorbed in the reversible process (equilibrium condition) is equal to the molar latent heat of vaporization, and from the second law we have

$$\Delta S = \frac{\Delta H_v}{T} \quad (3-84)$$

Substituting (3-84) into (3-83) gives

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta V} \quad (3-85)$$

where $\Delta V = V_v - V_l$, the difference in the molar volumes in the two phases. This is the *Clapeyron equation*, which was introduced in one of its forms on page 31.

The vapor will obey the ideal gas law to a good approximation when the temperature is far enough away from the critical point so that V_v may be replaced by RT/P . Furthermore, V_l is insignificant compared with V_v . In the case of water at 100° C, for example, $V_v = 30.2$ liters and $V_l = 0.0188$ liters.

Under these restrictive circumstances, equation (3-85) becomes

$$\frac{dP}{dT} = \frac{P \Delta H_v}{RT^2} \quad (3-86)$$

which is known as the *Clausius-Clapeyron equation*. It can be integrated between the limits of the vapor pressures P_1 and P_2 and corresponding temperatures T_1 and T_2 , assuming ΔH_v is constant over the temperature range considered:

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} T^{-2} dT \quad (3-87)$$

$$[\ln P]_{P_1}^{P_2} = \frac{\Delta H_v}{R} \left[\left(-\frac{1}{T_2}\right) - \left(-\frac{1}{T_1}\right) \right] \quad (3-88)$$

$$\ln P_2 - \ln P_1 = \frac{\Delta H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (3-89)$$

and finally

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v(T_2 - T_1)}{RT_1 T_2},$$

or,

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v(T_2 - T_1)}{2.303RT_1 T_2} \quad (3-90)$$

This equation is used to calculate the mean heat of vaporization of a liquid if its vapor pressure at two temperatures is available. Conversely, if the mean heat of vaporization and the vapor pressure at one temperature are known, the vapor pressure at another temperature can be obtained.

The Clapeyron and Clausius-Clapeyron equations are important in the study of various phase transitions and in the development of the equations of some of the colligative properties.

Example 3-11. The average heat of vaporization of water can be taken as about 9800 cal/mole within the range of 20° to 100° C. What is the vapor pressure at 95° C? The vapor pressure P_2 at temperature $T_2 = 373^\circ \text{K}$ (100° C) is 78 cm Hg, and R is expressed as 1.987 cal/deg mole.

$$\log \frac{78.0}{P_1} = \frac{9800}{2.303 \times 1.987} \left(\frac{373 - 368}{368 \times 373} \right)$$

$$P_1 = 65 \text{ cm Hg}$$

Fugacity. Recall that for a reversible isothermal process restricted to PV work, $(\partial G/\partial P)_T = V$ (equation

[3-53b]). The analogous equation relating the change of chemical potential to pressure changes is

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, n_2, \dots} = \bar{V}_i \quad (3-91)$$

where \bar{V}_i is the partial molar volume of component i and is equal to RT/P_i for an ideal gas, or

$$\int d\mu_i = RT \int \frac{dP}{P_i}$$

$$\mu_i = RT \ln P_i + \mu^\circ \quad (3-92)$$

in which the integration constant μ° depends only on the temperature and the nature of the gas. It is the chemical potential of component i in the reference state where P_i is equal to 1. When a mixture of real gases does not behave ideally, a function known as the *fugacity* f can be introduced to replace pressure, just as activities are introduced to replace concentration in nonideal solutions. Equation (3-92) becomes

$$\mu_i = \mu^\circ + RT \ln f_i \quad (3-93)$$

Activities: Activity Coefficients. If the vapor above a solution can be considered to behave ideally, the chemical potential of the solvent in the vapor state in equilibrium with the solution can be written in the form of equation (3-92). If Raoult's law (pp. 106-107) is now introduced for the solvent $P_1 = P_1^\circ X_1$, equation (3-92) becomes

$$\mu_1 = \mu_1^\circ + RT \ln P_1^\circ + RT \ln X_1 \quad (3-94)$$

Combining the first and second right-hand terms into a single constant gives

$$\mu_1 = \mu^\circ + RT \ln X_1 \quad (3-95)$$

for an ideal solution. We see that the reference state μ° is equal to the chemical potential μ_1 of the pure solvent (i.e., $X_1 = 1$). For nonideal solutions, equation (3-95) is modified by introducing the "effective concentration" or *activity* of the solvent to replace the mole fraction (see pp. 131-134 for more on activities.):

$$\mu_1 = \mu^\circ + RT \ln a_1 \quad (3-96)$$

or where

$$a = \gamma X \quad (3-97)$$

and γ is referred to as the *activity coefficient*:

$$\mu_1 = \mu^\circ + RT \ln \gamma_1 X_1 \quad (3-98)$$

For the *solute* on the mole fraction scale

$$\mu_2 = \mu^\circ + RT \ln a_2 \quad (3-99)$$

$$\mu_2 = \mu^\circ + RT \ln \gamma_2 X_2 \quad (3-100)$$

Based on the practical (molal and molar) scales

$$\mu_2 = \mu^\circ + RT \ln \gamma_m m \quad (3-101)$$

$$\mu_2 = \mu^\circ + RT \ln \gamma_c c \quad (3-102)$$

Equations (3-96) and (3-99) are frequently used as definitions of activity.

Gibbs-Helmholtz Equation. For an isothermal process at constant pressure proceeding between the initial and final states 1 and 2, equation (3-47) yields

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T \Delta S \quad (3-103)$$

Now, equation (3-55) may be written as

$$-\Delta S = -(S_2 - S_1) = \left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P$$

or

$$-\Delta S = \left[\frac{\partial(G_2 - G_1)}{\partial T}\right]_P = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad (3-104)$$

Substituting equation (3-104) into (3-103) gives

$$\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad (3-105)$$

which is one form of the *Gibbs-Helmholtz equation*.

Standard Free Energy and the Equilibrium Constant. Many of the processes of pharmaceutical interest such as complexation, protein binding, the dissociation of a weak electrolyte, or the distribution of a drug between two immiscible phases are reactions at equilibrium and can be described by an equilibrium constant, K . The relationship between the equilibrium constant and the standard free energy change of the reaction, ΔG° , is one of the more important applications of thermodynamics used to solve equilibrium problems.

Consider a closed system at constant pressure and temperature, such as the chemical reaction



The free energy change of the reaction is

$$\Delta G = \sum \Delta G_{\text{products}} - \sum \Delta G_{\text{reactants}} \quad (3-107)$$

Equation (3-106) represents a closed system made up of several components. Therefore, at constant T and P the total free energy change of the products and reactants in equation (3-107) is given as the sum of the chemical potential μ of each component times the number of moles (p. 67). At equilibrium, ΔG is zero and equation (3-107) becomes

$$\Delta G = (a\mu_A + b\mu_B) - (c\mu_C + d\mu_D) = 0 \quad (3-108)$$

When the reactants and products are ideal gases the chemical potential of each component is expressed in terms of partial pressure (equation (3-92)). For nonideal gases, μ is written in terms of fugacities (equation (3-93)). The corresponding expressions for solutions are given by equations (3-96) to (3-102). Let us use the more general expression that relates the chemical potential to the activity (equation (3-96)). Substituting this equation for each component in equation (3-108) yields

$$c(\mu^{\circ}_C + RT \ln a_C) + d(\mu^{\circ}_D + RT \ln a_D) - a(\mu^{\circ}_A + RT \ln a_A) - b(\mu^{\circ}_B + RT \ln a_B) = 0 \quad (3-109)$$

Rearranging equation (3-109) gives

$$c \mu^{\circ}_C + d \mu^{\circ}_D - a \mu^{\circ}_A - b \mu^{\circ}_B + RT(\ln a_C^c + \ln a_D^d) - RT(\ln a_A^a + \ln a_B^b) = 0 \quad (3-110)$$

Since μ° is the partial molar free energy change or chemical potential under standard conditions and is multiplied by the number of moles in equation (3-110), the algebraic sum of the terms involving μ° represents the *total standard free energy change of the reaction*, and is called ΔG° :

$$\Delta G^{\circ} = c\mu^{\circ}_C + d\mu^{\circ}_D - a\mu^{\circ}_A - b\mu^{\circ}_B \quad (3-111)$$

or, in general,

$$\Delta G^{\circ} = \sum n\mu^{\circ}(\text{products}) - \sum n\mu^{\circ}(\text{reactants}) \quad (3-112)$$

Using the rules of logarithms, equation (3-110) is expressed as

$$\Delta G^{\circ} + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} = 0 \quad (3-113)$$

or, in general,

$$\Delta G^{\circ} = -RT \ln \frac{\sum a^n(\text{products})}{\sum a^n(\text{reactants})} \quad (3-114)$$

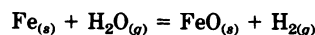
Since ΔG° is a constant at constants P and T , and RT is also constant, it follows that the logarithm of the ratio of activities must also be a constant. Equation (3-113) or (3-114) is then written as

$$\Delta G^{\circ} = -RT \ln K \quad (3-115)$$

Equation (3-115) is a very important expression that relates the standard free energy change of a reaction ΔG° to the equilibrium constant K . This expression allows one to compute K knowing ΔG° and vice versa.

The equilibrium constant has been expressed in terms of activities. Analogously, it can be given as the ratio of partial pressures, fugacities (for gases), and as the ratio of the different concentration expressions used in solutions (mole fraction, molarity, molality). The equilibrium constant is dimensionless, the ratio of activities or concentration canceling the units. However, the numerical value of K differs depending on the units used (activity, mole fraction, fugacity, etc.).

Example 3-12. Derive an expression for the free energies, ΔG and ΔG° , of the reaction



Since the chemical potential of a solid is constant (it does not depend on concentration), the equilibrium constant depends only on the pressures (or fugacities) of the gases. Using pressures

$$\Delta G = \mu^{\circ}_{\text{FeO}_{(s)}} + \mu^{\circ}_{\text{H}_{2(g)}} - \mu^{\circ}_{\text{Fe}_{(s)}} - \mu^{\circ}_{\text{H}_2\text{O}_{(g)}} + RT \ln P_{\text{H}_{2(g)}} - RT P_{\text{H}_2\text{O}_{(g)}} = 0$$

$$\Delta G = \Delta G^{\circ} + RT \ln P_{\text{H}_{2(g)}} - RT P_{\text{H}_2\text{O}_{(g)}} = 0$$

and

$$\Delta G^{\circ} = -RT \ln \frac{P_{\text{H}_{2(g)}}}{P_{\text{H}_2\text{O}_{(g)}}}$$

The magnitude and sign of ΔG° indicate whether the reaction is spontaneous but only under *standard conditions* (see pp. 67, 134). When the reaction is not at equilibrium, $\Delta G \neq 0$ and the free energy change is

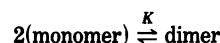
$$\Delta G = \Delta G^{\circ} + RT \ln \frac{\sum a^n(\text{products})}{\sum a^n(\text{reactants})} \neq 0 \quad (3-116)$$

or

$$\Delta G = \Delta G^{\circ} + RT \ln Q \quad (3-117)$$

where Q , like K , is the ratio of activities (equation [3-116]) fugacities, or concentration units of the products and reactants, but under different conditions than those of equilibrium. Q should not be confused with K (the ratio of activities, fugacities, and so on under *standard conditions at equilibrium* [see p. 134, for definitions of standard state]).

Example 3-13. Sodium cholate is a bile salt that plays an important role in the dissolution or dispersion of cholesterol and other lipids in the body. Sodium cholate may exist either as monomer or dimer (or higher n -mers) in aqueous solution. Let us consider the equilibrium monomer-dimer reaction⁶:



which states that two moles (or molecules) of monomer form one mole (or molecule) of dimer.

(a) If the molar concentration at 25°C of monomeric species is 4×10^{-3} mole/liter and the concentration of dimers is 3.52×10^{-5} mole/liter, what is the equilibrium constant and the standard free energy for the dimerization process?

$$K = \frac{[\text{dimer}]}{[\text{monomer}]^2} = \frac{3.52 \times 10^{-5}}{(4 \times 10^{-3})^2} = 2.20$$

$$\ln K = 0.788$$

$$\Delta G^{\circ} = -RT \ln K = -(1.9872 \times 298 \times 0.788) = -466.6 \text{ cal/mole}$$

The process is spontaneous under standard conditions.

(b) While keeping the concentration of monomer constant, suppose that one is able to remove part of the dimeric species by physical or chemical means so that its concentration is now four times less than the original dimer concentration. Compute the free energy change. What is the effect on the equilibrium?

The concentration of dimer is now

$$\frac{3.52 \times 10^{-5}}{4} = 8.8 \times 10^{-6} \text{ mole/liter}$$

Since the conditions are not at equilibrium, equation (3-117) should be used. First calculate Q :

$$Q = \frac{[\text{dimer}]}{[\text{monomer}]^2} = \frac{8.8 \times 10^{-6}}{(4 \times 10^{-3})^2} = 0.550; \ln Q = -0.598$$

and from equation (3-117),

$$\Delta G = -466.6 + [1.9872 \times 298 \times (-0.598)] = -820.7 \text{ cal/mole}$$

ΔG is negative, Q is less than K , and the reaction shifts to the right side of the equation with the formation of more dimer.

If we remove monomer from the solution, the reaction is shifted to the left side, forming monomer, and ΔG becomes positive. Suppose that [monomer] is now 1×10^{-3} mole/liter and [dimer] is 3.52×10^{-5} mole/liter:

$$Q = \frac{3.52 \times 10^{-5}}{(1 \times 10^{-3})^2} = 35.2; \ln Q = 3.561$$

$$\Delta G = -466.6 + (1.9872 \times 298 \times 3.561) = +1642 \text{ cal/mole}$$

The positive sign of ΔG indicates that the reaction does not proceed forward spontaneously.

The van't Hoff Equation. The effect of temperature on equilibrium constants is obtained by writing the equation

$$\ln K = -\frac{\Delta G^\circ}{RT} \quad (3-118)$$

and differentiating with respect to temperature to give

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta G^\circ/T)}{dT} \quad (3-119)$$

The Gibbs–Helmholtz equation may be written in the form (cf. one of the thermodynamics books given in the footnote on p. 53):

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2} \quad (3-120)$$

Expressing equation (3-120) in a form for the reactants and products in their standard states, in which ΔG becomes equal to ΔG° , and substituting into equation (3-119), yields

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (3-121)$$

in which ΔH° is the standard heat of reaction. Equation (3-121) is known as the *van't Hoff equation*. It may be integrated, assuming ΔH° to be constant over the temperature range considered; it thus becomes

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad (3-122)$$

Equation (3-122) allows one to compute the heat of a reaction if the equilibrium constants at T_1 and T_2 are available. Conversely, it can be used to supply the equilibrium constant at a definite temperature if it is known at another temperature. ΔH° varies with temperature, however, and equation (3-122) gives only an approximate answer; more elaborate equations are required to obtain accurate results. The solubility of a solid in an ideal solution is a special type of equilibrium, and it is not surprising that equation (10-11), p. 221, can be written as

$$\ln \frac{X_2}{X_1} = \frac{\Delta H_f}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad (3-123)$$

which closely resembles equation (3-122). These expressions will be encountered in later chapters.

Combining equations (3-103) and (3-118) yields yet another form of the van't Hoff equation, namely

$$\ln K = -(\Delta H^\circ/R)1/T + \Delta S^\circ/R \quad (3-124)$$

or

$$\log K = -[\Delta H^\circ/(2.303R)]1/T + \Delta S^\circ/(2.303R) \quad (3-125)$$

in which $\Delta S^\circ/R$ is the intercept on the $\ln K$ axis of a plot of $\ln K$ versus $1/T$.

Whereas equation (3-122) provides a value of ΔH° based on the use of two K values at their corresponding absolute temperatures, T_1 and T_2 , equations (3-124) and (3-125) give the values of ΔH° and ΔS° , and therefore the value of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. In the least-squares linear regression equations (3-124) and (3-125), one uses as many $\ln K$ and corresponding $1/T$ values as are available from experimentation.

Example 3-14. In a study of the transport of pilocarpine across the corneal membrane of the eye, Mitra and Mikkelsen⁷ presented a van't Hoff plot of the log of the ionization constant, $\log K_a$, of pilocarpine versus the reciprocal of the absolute temperature, $T^{-1} = 1/T$.

Using the data in Table 3-5, regress $\log K_a$ versus T^{-1} . With reference to the van't Hoff equation (equation 3-124), obtain the standard heat (enthalpy), ΔH° , of ionization for pilocarpine and the standard entropy for the ionization process. From ΔH° and ΔS° calculate ΔG° at 25° C. What is the significance of the signs and the magnitudes of ΔH° , ΔS° , and ΔG° ?

$$\begin{aligned} \text{Answers:} \quad \Delta H^\circ &= 9784 \text{ cal/mole} \\ &= 40.94 \text{ kJ/mole} \\ \Delta S^\circ &= 1.30 \text{ cal/mole deg} \\ \Delta G^\circ_{25} &= \Delta H^\circ - T\Delta S^\circ = 9397 \text{ cal/mole} \end{aligned}$$

These thermodynamic values have the following significance. ΔH° is a large positive value that indicates that the ionization of pilocarpine (as its conjugate acid) should increase as the temperature is elevated. The increasing values of K_a in the table show this to be a fact. The standard entropy increase, $\Delta S^\circ = 1.30$ entropy units, although small, provides a force for the reaction of the pilocarpinium ions to form pilocarpine (Fig. 3-4). The positively charged pilocarpine molecules, because of their ionic nature, are probably held in a more orderly arrangement than the predominantly nonionic pilocarpine in the aqueous environment. This increase in disorder in the dissociation process accounts

TABLE 3-5. Ionization Constants of Pilocarpine at Various Temperatures

Temperature				
(t)° C	T(° K)	1/T × 10 ³ *	K _a × 10 ⁷ *	log K _a
15	288	3.47	0.74	-7.13
20	293	3.41	1.07	-6.97
25	298	3.35	1.26	-6.90
30	303	3.30	1.58	-6.80
35	308	3.24	2.14	-6.67
40	313	3.19	2.95	-6.53
45	318	3.14	3.98	-6.40

*When a column is headed $1/T \times 10^3$ it means that the numbers in this column are 1000 (i.e., 10^3) times larger than the actual numbers. Thus the first entry in column 3 has the real value 3.47×10^{-3} or 0.00347. Likewise, in the next column $K_a \times 10^7$ signifies that the number 0.74 and the other entries in this column are to be accompanied by the exponential value 10^{-7} , not 10^{-7} . Thus, the first value in the fourth column should be read as 0.74×10^{-7} and the last value 3.98×10^{-7} . (From A. K. Mitra and T. J. Mikkelsen, *J. Pharm. Sci.* 77, 772, 1988, (reproduced with permission of the publishers.)

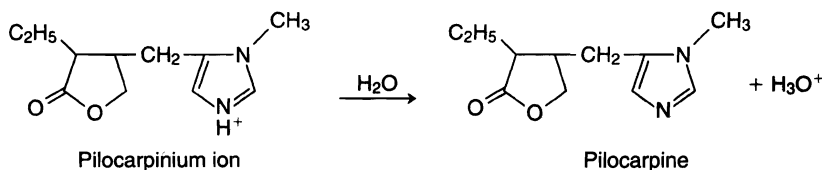
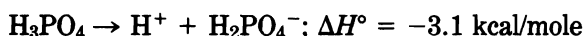
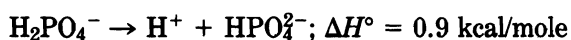


Fig. 3-4. Reaction of pilocarpinium ion to yield pilocarpine base.

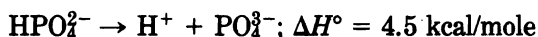
for the increased entropy, which, however, is a small value: $\Delta S^\circ = 1.30$ entropy units. Note that a positive ΔH° does not mean that the ionization will not occur; rather, it signifies that the equilibrium constant for the forward reaction (ionization) will be a small value, say $K_a \cong 1 \times 10^{-7}$, as observed in Table 3-5. A further explanation regarding the sign of ΔH° is helpful here. Mahan⁸ has pointed out that in the first stage of ionization of phosphoric acid (p. 149), for example,



the hydration reaction of the ions being bound to the water molecules is sufficiently exothermic to produce the necessary energy for ionization; that is, enough energy to remove the proton from the acid, H_3PO_4 . For this reason, ΔH° in the first stage of ionization is negative and $K_1 = 7.5 \times 10^{-3}$ at 25° C (see Table 7-1). In the second stage,



ΔH° is now positive, the reaction is *endothermic*, and $K_2 = 6.2 \times 10^{-8}$. Finally, in the third stage,



ΔH° is a relatively large positive value and $K_3 = 2.1 \times 10^{-13}$. These ΔH° and K_a values show that increasing energy is needed to remove the positively charged proton as the negative charge increases in the acid from the first to the third stage of ionization. Positive ΔH° (endothermic reaction) values do not signal nonionization of the acid—that is, that the process is nonspontaneous—but rather simply show that the forward reaction, represented by its ionization constant, becomes smaller and smaller.

References and Notes

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Problems*

3-1. Why is alcohol used in thermometers for measuring very low temperatures, whereas mercury is used for high temperatures? *Hint*: Look up in a handbook of chemistry and physics the melting points of alcohol and mercury.

3-2. Calculate the work to vaporize 1.73 moles of water at 0.68 atm pressure and a temperature of 373° K. Assume that the vapor behaves as an ideal gas. *Hint*: The volume may be calculated using the ideal gas equation and the work may be calculated using $W = P\Delta V$. ΔV is the difference in volume between liquid water at 373° K, i.e., 18.795 cm³/mole \times 1.73 mole, and its vapor at 373° K.

Answer: The work is 52.96 liter atm or 5366 J (1 liter atm = 101.328 J).

3-3. By the use of thermodynamic calculations, we can relate work done and heat produced in various processes regardless of how seemingly unrelated the processes might be. Consider the following: A 30-year-old man weighing 70 kg (154 lb) produces 3600 kcal of heat per 24 hours working 8 hours as a brick layer and bowling in the evenings. If this heat were used to raise the temperature of 200 kg of water (specific heat of water = 1 cal g⁻¹ deg⁻¹)† that was originally at 25° C, how hot would the water become?

*Problem 3-4 is modified from J. W. Moncrief and W. H. Jones, *Elements of Physical Chemistry*, Addison-Wesley, Reading, Mass., 1977, p. 15, example 7. Problem 3-5 is modified from Moncrief and Jones, *ibid.*, p. 28, example 12. Problem 3-14 is modified from Moncrief and Jones, *ibid.*, p. 96. Problem 3-15 is modified from Moncrief and Jones, *ibid.*, p. 64, example 17. Problem 3-20 is from Moncrief and Jones, *ibid.*, p. 123, problem 6.6. Problem 3-23 is from Moncrief and Jones, *ibid.*, p. 123, problem 6.8. Problem 3-27 is from A. L. Lehninger, *Bioenergetics*, 2nd Edition, Benjamin/Cummings, Menlo Park, Calif., 1971, pp 30, 31; I. M. Klotz, *Introduction to Biomolecular Energetics*, Academic Press, Orlando, Fl., p. 24.

†The term *heat capacity* is usually expressed in cal or joules mole⁻¹ deg⁻¹. When it is referred to as 1 gram or 1 kilogram of material rather than as 1 mole it is called *specific heat* rather than *heat capacity*.

Answer: The temperature of the mass of water would be raised $18^\circ\text{K} \equiv 18^\circ\text{C}$. The final temperature would be $25^\circ + 18^\circ = 43^\circ\text{C}$.

3-4. An athlete resting on his back on the floor lifts an 80-lb dumbbell 2 feet above his head. From physics we know that force = mass \times acceleration of gravity, and the force multiplied by the distance the mass is lifted yields the work done or energy used.

(a) How much work is done when the dumbbell is lifted 500 times?

(b) If we assume that the energy expended is obtained totally from burning body fat, how many pounds will the athlete lose in this exercise? Approximately 9.0 kilocalories of metabolic energy are obtained per gram of fat burned.

(c) How many lifts of the 80-lb weight would be required to lose 1 lb of fat?

(d) It is agreed that exercise such as weight-lifting is excellent to tone the muscles of the body. From your calculations do you find that it also contributes significantly to weight reduction as part of a diet regimen?

Answers: (a) $W = 1.09 \times 10^5\text{ J}$ or $2.6 \times 10^4\text{ cal} = 26\text{ kcal}$ (food calories). (b) The person loses 2.9 g or 0.006 lb. (c) More than 8000 lifts would be required to lose 1 lb of fat from the body (actually 8333 lifts).

3-5. An active adult woman generates about 3000 kcal of heat per day and it is lost through metabolism. If all the heat is lost by evaporation of moisture from the skin, how much water is lost in a 24-hour day? The heat of vaporization of water is $\Delta H_v \approx 10,000\text{ cal/mole}$ and the density is 0.997049 g/cm^3 at 25°C .

Answer: 5.4 liters or 5.7 quarts. Of course, water is also eliminated by way of the kidneys, lungs, and feces, and the water loss from these various routes with normal food intake should also be taken into account.

3-6. James Joule found a waterfall in Switzerland that was 920 ft (280.42 m) high. The potential energy of the water at the top of the falls is converted at the bottom into kinetic energy (heat) by friction, as observed in Figure 3-2, and Joule was interested in studying these energy changes. What is the difference in the temperature between the top and the bottom of the falls which Joules would have been expected to find if he had used a very accurate thermometer?

Use SI units in your calculations, then repeat using cgs units. Assume that the velocity of the water at the top of the falls is essentially zero so that we are considering only the potential energy of fall. The specific heat of water is $1\text{ cal/g }^\circ\text{K}$ in the cgs system.

Answer: 0.66°K , 0.66°C

3-7. As we learned on page 58, Joule had a bad day. He did not have the attention of his bride on their honeymoon nor was he successful in his study of the thermodynamics of waterfalls. According to Bent,⁹ Joule later did estimate—probably from the kind of calculations in *Example 3-4*—that the water at the base of Niagara Falls at the Canadian-U.S. border (Horseshoe Falls) should be approximately 0.2°F Fahrenheit warmer than the water at the top of the falls.

Using the calculation given in *Example 3-4*, estimate the height of Horseshoe Falls. Check the height you have calculated with the actual height given in an encyclopedia.

Answer: 154 feet or 46.9 meters

3-8. At the beginning of the nineteenth century, Dulong and Petit determined the heat capacity, C_p , of solid elements to be approximately $6\text{ cal mole}^{-1}\text{ }^\circ\text{K}^{-1}$.

A bar of iron, atomic weight = 55.847 g , falls accidentally from the top of a building 93 meters high. Taking the molar heat capacity C_p of iron as approximately $6\text{ cal mole}^{-1}\text{ }^\circ\text{K}^{-1}$, compute the increase in the temperature of the bar as it falls from the top of the building to the street. Use SI units in your calculations.

We actually desire the heat capacity per gram (i.e., the specific heat), or, since we are using SI units, we want the heat capacity per kilogram. To convert from calories/mole to calories/gram we divide the molar heat capacity of iron by its "molecular" or atomic weight, 55.847 g . Thus,

$$C_v = \frac{6\text{ cal mole}^{-1}\text{ }^\circ\text{K}^{-1}}{55.847\text{ g mole}^{-1}} = 0.1074\text{ cal/g }^\circ\text{K} = 107.4 \frac{\text{cal}}{\text{kg }^\circ\text{K}}$$

The calculations are analogous to those for the waterfall's temperature change, *Problem 3-6*. *Hint:* Express C_v in $\text{J}/(\text{kg }^\circ\text{K})$.

Answer: The increase in temperature of the iron bar as a result of falling 93 meters from the top of the building to the street below is $2.03^\circ\text{C} = 2.03^\circ\text{K}$.

3-9. The molar heat capacity at constant pressure, C_p , varies with temperature. The changes in the heat capacity, ΔC_p , for a reaction at a fixed temperature is given by the expression

$$\Delta C_p = \sum (nC_p)_{\text{products}} - \sum (nC_p)_{\text{reactants}}$$

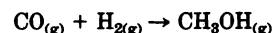
where Σ stands for "the sum of" and n is the number of moles of the compound.

C_p can be calculated at different temperatures using the empirical equation

$$C_p = \alpha + \beta T + \gamma T^2 + \dots$$

where α , β , and γ are constant coefficients. C_p and ΔC_p are given here in $\text{cal }^\circ\text{K}^{-1}\text{ mole}^{-1}$

Calculate C_p for $\text{CO}_{(g)}$, $\text{H}_{2(g)}$, and $\text{CH}_3\text{OH}_{(g)}$ at 25°C and compute the change in heat capacity, ΔC_p , for the reaction:



Data for *Problem 3-9**

	$\text{CO}_{(g)}$	$\text{H}_{2(g)}$	$\text{CH}_3\text{OH}_{(g)}$
α	6.342	6.947	4.398
$\beta \times 10^3$	1.836	-0.20	24.274
$\gamma \times 10^6$	-0.2801	0.4808	-6.855

*From S. Glasstone, *Thermodynamics for Chemists*, Van Nostrand, New York, 1947, pp. 53, 503.

Answer: $C_p(\text{CO}) = 6.864\text{ cal }^\circ\text{K}^{-1}\text{ mole}^{-1}$; $C_p(\text{H}_2) = 6.930\text{ cal }^\circ\text{K}^{-1}\text{ mole}^{-1}$; $C_p(\text{CH}_3\text{OH}) = 11.025\text{ cal }^\circ\text{K}^{-1}\text{ mole}^{-1}$. For the reaction at 25°C , $\Delta C_p = -9.699\text{ cal }^\circ\text{K}^{-1}\text{ mole}^{-1}$

3-10. Equation (3-22b) on page 57, the Kirchoff equation, demonstrates the effect of temperature on the heat of reaction. Integration of equation (3-22b) between T_1 and T_2 is shown as

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT$$

Over a small temperature range, ΔC_p may be considered constant, then the above integration simplifies to

$$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$$

Compute ΔH_2° for the synthesis of methanol at 35°C , using ΔH_1° at 25°C as -21.68 kcal per mole as obtained in *Problem 3-12*, and ΔC_p as the value, $-9.699\text{ cal}/(\text{deg mole})$, obtained in *Problem 3-9*, as the value at 25°C . Remember to write ΔC_p as $-9.699 \times 10^{-3}\text{ kcal}/(\text{deg mole})$ in order to obtain ΔH_2° in kcal/mole.

Answer: ΔH_2° (at 35°C) = -21.78 kcal/mole

3-11. The heat of reaction associated with the preparation of calcium hydroxide is represented as

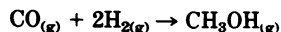


What is the standard heat of formation ΔH° of Ca(OH)_2 at 25°C ? The standard heat of formation of water $\Delta H^\circ(\text{H}_2\text{O}_{(lq)}) = -68.3\text{ kcal/mole}$ and the standard heat of formation of calcium oxide $\Delta H^\circ(\text{CaO}_{(s)}) = -151.9\text{ kcal/mole}$.

Answer: $\Delta H^\circ[\text{Ca(OH)}_{2(s)}] = -235.8\text{ kcal/mole}$

3-12. The synthesis of methanol involves the reaction of carbon monoxide and hydrogen gas. The reaction, together with values at 25°

C for S^0 cal deg $^{-1}$ mole $^{-1}$, ΔH_f^0 in kcal mole $^{-1}$, and ΔG^0 in kcal mole $^{-1}$, is given as follows¹⁰:



Data for Problem 3-12

	$\text{CO}_{(g)}$	$\text{H}_{2(g)}$	$\text{CH}_3\text{OH}_{(g)}$
S^0	47.219	31.208	56.63
ΔH_f^0	-26.416	0	-48.10
ΔG_f^0	-32.78	0	-38.90

(a) Calculate ΔH^0 for the synthesis of methanol under standard conditions. (b) Calculate ΔG^0 , using the above data. (c) From ΔG^0 and ΔH^0 , compute ΔS^0 at 25° C. Compare this value with ΔS^0 obtained directly from S^0 in the above table.

Answers: (a) $\Delta H^0 = -21.684$ kcal/mole; (b) $\Delta G^0 = -6.12$ kcal/mole; (c) ΔS^0 (from ΔG^0 and ΔH^0) = -52.20 cal/mole degree. ΔS^0 (from S^0 values in the table) = -53.01 cal/mole deg.

3-13. What is the theoretical efficiency of a steam engine operating between the boiler at 20 atm, where the boiling point of water T_2 is 209° C (482° K), and the low temperature reservoir or sink, where the temperature T_1 is 30° C (303° K).*

Answer: Efficiency = 0.37 or 37%

3-14. What is the minimum work in joules that must be done by a refrigerator to freeze 1 avoirdupois pound (453.6 grams) of water at 0° C with the surroundings at 23° C? How much heat is discharged into the room at room temperature (23° C)? The heat of fusion of ice is 1438 cal/mole or 1438/18.016 g/mole = 79.8 cal/g (in the range of 0° to 100°). Thus, 79.8 cal/g \times 453.6 g of heat must be removed from the water to form ice (from 0° or 273° K [T_1] to 296° K [T_2]).

The principle of a refrigerator (or air conditioner) is the opposite to that of a heat engine.* The refrigerator fluid takes up heat at the low temperature of the refrigerator and discharges it at the higher temperature of the surroundings (see p. 60 for an explanation of a heat engine).

Since heat is discharged in a refrigerator (or air conditioner) rather than taken up, as in a heat engine, the work has the opposite sign to that given in equation (3-29):

$$-\frac{W}{Q_1} = \frac{T_2 - T_1}{T_1}$$

$$-W = \left(\frac{T_2 - T_1}{T_1}\right) Q_1$$

What is the efficiency $(T_2 - T_1)/T_1$ or, as it is called, the *coefficient of performance* of this refrigerator?

Answer: The work required to remove the heat from 1 pound of water and form ice at 0° C is 1.28×10^4 J in a refrigerator in an environment at 23° C. The coefficient of performance of the refrigerator is 0.084 or 8.4%.

3-15. What is the entropy change involved in the fusion of 1 mole of ice at 0° C? What is the entropy change in the surroundings? The heat of fusion of ice is 79.67 cal/g.

Answer: $\Delta S_{\text{H}_2\text{O}} = 5.26$ cal/(mole deg); $\Delta S_{\text{surr.}} = -5.26$ cal/(mole deg)

3-16. A Thermos jug, insulated so that no heat enters or leaves the container (adiabatic), contains 2 moles of ice at -10° C and 8.75 moles of liquid water at 20° C. (See Examples 3-6 and 3-7 on p. 62.)

Calculate the change in entropy, ΔS , accompanying the melting of the ice and elevation of its temperature to 0.496° C in the form of liquid water. Also calculate ΔS for the lowering of the temperature of the water from 20° C to the final temperature of 0.496° C. The molar

heat of fusion of ice is 1437 cal/mole and C_p for ice is 9 cal/(deg mole); C_p for liquid water is 18 cal/(deg mole).

Obtain the total entropy change ΔS_T and state whether the process is spontaneous or not.

Answers (see Example 3-7): The heat needed to raise the temperature of the ice and melt it results from the cooling of the water in the insulated Thermos jug.

In heating 2 moles of ice from -10° C to 0° C, the entropy change in this reversible process at constant pressure is 0.671 cal/deg.

Melting of the 2 mole of ice reversibly at 0° C is accompanied by an entropy change of 10.52 cal/deg.

The 2 moles of ice that have now been melted to liquid water is heated to 0.496° C and this step involves an entropy change of 0.0653 cal/deg.

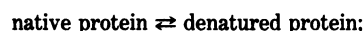
Finally, the 8.75 moles of liquid water added to the jug at 20° C is cooled reversibly to 0.496° C. The entropy change in this final step is -10.84 cal/deg.

The total entropy change is

$$\Delta S_T = 0.671 + 10.52 + 0.0653 - 10.84 = 0.42 \text{ cal } ^\circ\text{K}^{-1}$$

It is left for the student to calculate each of these above values and to state whether the process is spontaneous or not.

3-17. At 50° C, a certain protein denatures reversibly with a heat of reaction of 29,288 J mole $^{-1}$:



$$\Delta H_{50^\circ} = 29,288 \text{ J mole}^{-1}$$

The system is at equilibrium and $\Delta G = 0$. Compute the entropy change for the reaction.

Answer: $\Delta S = 90.6 \text{ J } ^\circ\text{K}^{-1} \text{ mole}^{-1}$

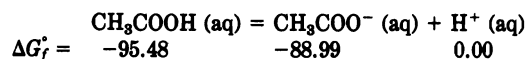
3-18. According to Hill,¹¹ the stomach excretes HCl in the concentration of 0.14 M from the blood where the concentration is 5.0×10^{-8} M. Calculate the work done by the body in the transport (excretion) of 1 mole of HCl at a temperature of 37° C.

Answer: 9150 cal/mole

3-19. Rework Example 3-11, page 68, first converting ΔH_V into the units of joules/mole and P_2 into Pascals ($\text{Pa} = \text{N m}^{-2} = \text{kg m}^{-1} \text{ s}^{-2}$). Calculate ΔH_V in J/mole and P_1 in units of Pascals.

Answer: $\Delta H_V = 41003$ J/mole; $P_1 = 86908$ Pa

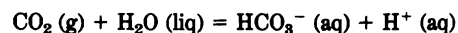
3-20. For the ionization of acetic acid in aqueous solution,



The standard free energies of formation G_f^0 at 25° C are given immediately under each species in kcal/mole. Calculate the standard free energy change ΔG^0 for this reaction; and from the thermodynamic equation giving the equilibrium constant (ionization constant), $\Delta G^0 = -RT \ln K$, calculate K for acetic acid. Compare your result with the value found in Table 7-1.

Answer: $\Delta G^0 = 6490$ cal/mole; $K = 1.75 \times 10^{-5}$

3-21. Given the standard free energy of formation, ΔG^0 , and the standard enthalpy of formation, ΔH^0 , calculate the standard entropy change ΔS^0 and the equilibrium constant K for the reaction



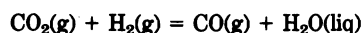
The values for ΔG^0 and ΔH^0 are obtained from tables of standard thermochemical data (Wagman et al.¹²) for 1 mole at 1 atm pressure and 25° C, where (aq) refers to a hypothetical ideal aqueous solution. The values of ΔG^0 and ΔH^0 for H^+ are taken as 0.00.

For the various species in solution, the values of ΔG^0 and ΔH^0 in kcal/mole are as follows:

	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{liq})$	$\text{HCO}_3^-(\text{aq})$	$\text{H}^+(\text{aq})$
ΔG^0 (kcal/mole)	-94.254	-56.687	-140.3	0.0
ΔH^0 (kcal/mole)	-94.051	-68.315	-164.8	0.0

Answer: $\Delta S^0 = -44$ e.u.; $K = 1.59 \times 10^{-8}$

3-22. For the reaction of carbon dioxide and molecular hydrogen to form carbon monoxide:

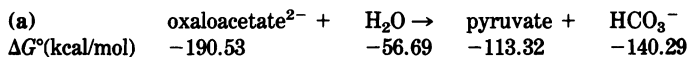


*From S. Glasstone, Thermodynamics for Chemists. Van Nostrand, New York, 1947, pp. 138, 139.

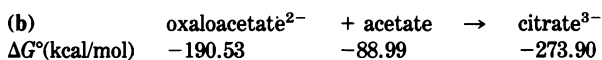
calculate the standard free energy of the process at 25° C and obtain the equilibrium constant K . The standard heat of formation for $\text{CO}_2(\text{g})$ is $\Delta H_f^\circ = -94.051$ kcal/mole and its standard entropy is $S^\circ = 51.06$ cal/deg mole. The standard heat of formation of $\text{CO}(\text{g})$ is $\Delta H_f^\circ = -26.416$ kcal/mole and its standard entropy is $S^\circ = 47.2$ cal/deg mole. The standard heat of formation of water (liq) is $\Delta H_f^\circ = -68.315$ kcal/mole and its standard entropy $S^\circ = 18.5$ cal/deg mole. Finally, the standard entropy of $\text{H}_2(\text{g})$ is $S^\circ = 31.208$ cal/deg mole. By convention its ΔH_f° is 0.0.

Answer: $\Delta G^\circ = 4260$ cal/mole; $K = 7.54 \times 10^{-4}$

3-23. For one of the steps in the citric acid (Krebs) cycle,¹³



and for another step in this complex series of chemical reactions required for energy production in the body,



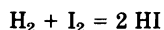
Calculate ΔG° and K at 37° C for these two reactions.

Answer: (a) $\Delta G^\circ = -6.39$ kcal/mole, $K = 3.2 \times 10^4$; (b) $\Delta G^\circ = 5.62$ kcal/mole, $K = 1.1 \times 10^{-4}$

3-24. Diluted hydriodic acid (HI) is a pharmaceutical product containing 10% of HI and about 0.8% of hypophosphorous acid (H_3PO_2) to prevent discoloration of the aqueous preparation in the presence of light and air.

Hydriodic acid is prepared on a large scale by several processes, principally by the interaction of I_2 and H_2S . Diluted hydriodic may be made into a syrup with dextrose and used for the therapeutic properties of the iodides and as a vehicle for expectorant drugs.

Taylor and Crist¹⁴ investigated the reaction of hydrogen and iodine to form hydrogen iodide at a temperature of 457.6° C (730.75° K),



They obtained the following results in which K is the equilibrium constant,

Data for Problem 3-24

$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$		
H_2 mole/liter	I_2 mole/liter	HI mole/liter
3.841×10^{-3}	1.524×10^{-3}	1.687×10^{-2}
1.696×10^{-3}	1.696×10^{-3}	1.181×10^{-2}
5.617×10^{-3}	0.5936×10^{-3}	1.270×10^{-2}

(a) Calculate the equilibrium constants for the three experiments shown above and obtain the average of these K values at 730.75° K.

(b) At 666.8° K the average equilibrium constant K_{av} for the reaction of I_2 and H_2 to form hydrogen iodide (hydriodic acid) is 60.80.¹⁵ Calculate the enthalpy change ΔH° for the reaction over the temperature range of 666.8 to 730.75° K.

(c) Does the constant, K , increase or decrease as the temperature is elevated? What does this say about an increased or decreased production of hydrogen iodide from its elements as the temperature is elevated? Do these results suggest that the reaction would be exothermic or endothermic? What quantitative result do you have to answer this last question? How does the van't Hoff equation (equation 3-122) help to answer this question?

Answers: (a) $K_{\text{av}} = 48.49$; (b) $\Delta H^\circ = -3425$ cal = -14330 J; (c) this series of questions is left for the student to assure himself or herself of an understanding of chemical equilibria.

3-25. Equation (3-115) allows the student to calculate the free energy change at the three separate temperatures for the reaction of hydrogen and iodine to yield hydrogen iodide. Given the experimentally determined K values and corresponding absolute temperatures,

Data for Problem 3-25

K	45.62	48.49	60.80
T (°K)	763.8	730.8	666.8

calculate the standard free energy change at these three temperatures.

Answer: ΔG° at 763.8° K = -5799 cal; ΔG° at 730.8° K = -5637 cal; ΔG° at 666.8° K = -5443 cal

3-26. A student cannot find the heat of vaporization, the heat of sublimation, or the heat of fusion of water in her handbook of chemical properties, but she is able to find a table of vapor pressures (in mm Hg) for liquid water in equilibrium with its vapor at temperatures from -15° C to $+20^\circ$ C, and for ice in equilibrium with its vapor from -50° C to 0° C.

For ice passing directly to water vapor (sublimation), and for the conversion of liquid water to vapor (vaporization), the following values are found (Table 3-6).

(a) Plot the sublimation and vaporization curves in the form of $\ln(\text{vapor pressure})$ vs. $1/T$ (°K⁻¹).

(b) Using the indefinite integrated form of the Clausius-Clapeyron equation,

$$\ln P - \frac{\Delta H}{R} \frac{1}{T} + \text{constant}$$

calculate the heat of vaporization and the heat of sublimation for water within the temperature ranges found in Table 3-6. ΔH is the heat of vaporization or the heat of sublimation. Linear regression on the data in Table 3-6, $\ln(\text{vapor pressure})$ vs. $1/T$, yields ($-\Delta H/R$) as the slope from which ΔH_v or ΔH_s is obtained. An estimate of the slope,

$$\frac{\ln P_2 - \ln P_1}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

may also be obtained from a plot of $\ln P$ versus $1/T$ on rectangular coordinate graph paper. Use least-squares linear regression, or the

TABLE 3-6. Vapor Pressures for the Sublimation and Vaporization of Water, for Problem 3-26

Ice \rightarrow vapor (sublimation)		liq. water \rightarrow vapor (vaporization)	
Vapor press. (mm Hg)	t (°C)	Vapor press. (mm Hg)	t (°C)
0.0296	-50	1.436	-15
0.0966	-40	1.691	-13
0.2859	-30	2.149	-10
0.476	-25	2.715	-7
0.776	-20	3.163	-5
1.241	-15	3.673	-3
1.950	-10	4.579	0
3.013	-5	6.593	5
4.579	0	9.209	10
—	—	12.788	15
—	—	17.535	20

slope of the line obtained from a plot of the data, to calculate ΔH_v and ΔH_s .

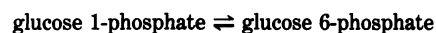
(c) For conversion of a solid to a vapor at constant temperature the process should be independent of the path: solid \rightarrow liquid \rightarrow vapor; therefore, $\Delta H_s = \Delta H_v + \Delta H_f$, where ΔH_f is the enthalpy change involved in the fusion (melting) process.

Compute ΔH_f (for the transition water \rightarrow ice) from ΔH_v and ΔH_s obtained in (b).

Answers: (b) For ice to water vapor (sublimation) the least-squares line is expressed by the equation $\ln P_s = -6146.5 \frac{1}{T} + 24.025$; $r^2 = 0.9999$; for sublimation, ice to vapor, $\Delta H_s = 12,214$ cal/mol within a range of -50 to 0° C. For liquid water to vapor (vaporization), $\ln P_v = -5409 \frac{1}{T} + 21.321$; $r^2 = 0.9999$; $\Delta H_v = 10,749$ cal/mol within a range of -15° to 20° C. (c) Finally, one calculates $\Delta H_f = 1465$ cal/mole. Experimentally, $\Delta H_f(\text{H}_2\text{O}) = 1440$ cal/mole.*

(*A satisfactory ΔH of sublimation is not always obtained by this procedure.)

3-27. In the breakdown (metabolism) of glycogen in the muscle of man to form lactate, glucose 1-phosphate is converted to glucose 6-phosphate in the presence of the enzyme phosphoglucomutase:



This biochemical reaction has been studied in some detail in a number of laboratories and the standard free energy change, ΔG° , is found to be about -1727 cal/mole. Calculate the equilibrium constant K at 25° C.

$$K = \frac{[\text{glucose 6-phosphate}]}{[\text{glucose 1-phosphate}]}$$

Hint: The application of equation (3-115) allows one to calculate the equilibrium constant.

Answer: $K = 18.45$