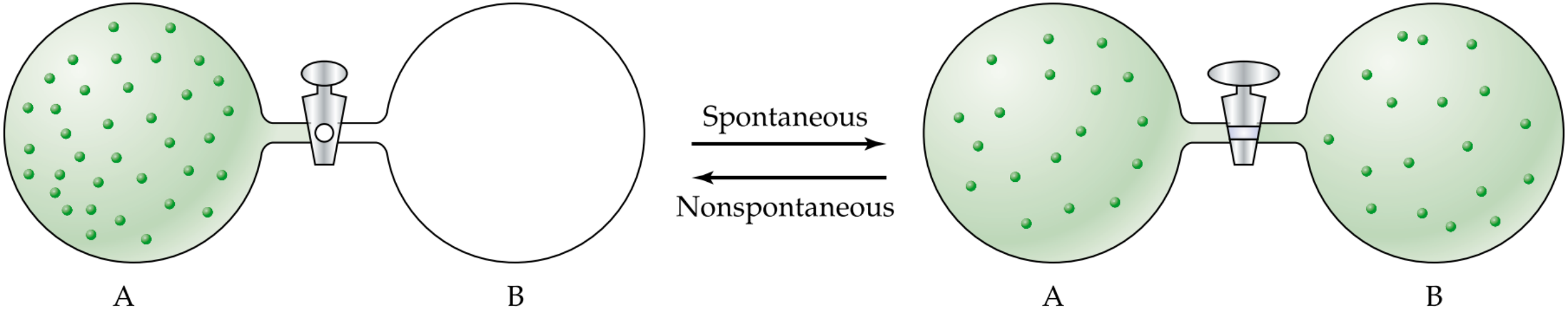
Spontaneous Processes

We have defined a spontaneous process as one that proceeds on its own without any external influence. The reverse of a spontaneous process is always nonspontaneous and takes place only in the presence of some continuous external influence. Consider, for example, the expansion of a gas into a vacuum. When the stopcock in the apparatus shown in Figure is opened, the gas in bulb A expands spontaneously into the evacuated bulb B until the gas pressure in the two bulbs is the same. The reverse process, migration of all the gas molecules into one bulb, does not occur spontaneously. To compress a gas from a larger to a smaller volume, we would have to push on the gas with a piston.



When the stopcock is opened, the gas in bulb A expands spontaneously into evacuated bulb B to fill all the available volume. The reverse process, compression of the gas, is nonspontaneous.

Spontaneous Processes

As a second example, consider the combination of hydrogen and oxygen in the presence of a platinum catalyst:

$$2\,H_2(g) + O_2(g) \xrightarrow{\text{Catalyst}} 2\,H_2O(l)$$

The forward reaction occurs spontaneously, but the reverse reaction, decomposition of water into its elements, does not occur no matter how long we wait. We'll see that we can force the reverse reaction to occur by electrolysis, but that reverse process is nonspontaneous and requires a continuous input of electrical energy.

In general, whether the forward or reverse reaction is spontaneous depends on the temperature, pressure, and composition of the reaction mixture. Consider the Haber synthesis of ammonia:

$$N_2(g) + 3\,H_2(g) \xrightarrow{\text{Catalyst}} 2\,NH_3(g)$$

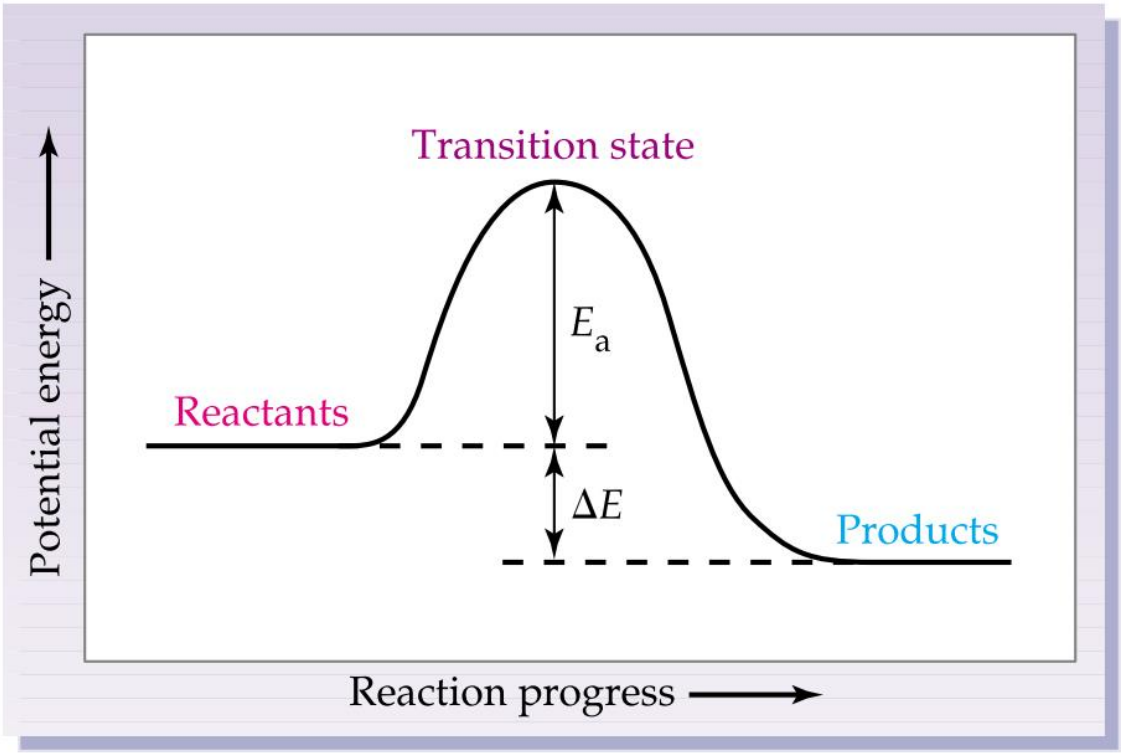
Spontaneous Processes

A mixture of gaseous N_2, H_2, and NH_3, each at a partial pressure of 1 atm, reacts spontaneously at 300 K to convert some of the N_2 and H_2 to NH_3. We can predict the direction of spontaneous reaction from the relative values of the equilibrium constant K and the reaction quotient Q Since $K_p = 4.4 \times 10^5$ at 300 K and $Q_p = 1$ for partial pressures of 1 atm, the reaction will proceed in the forward direction because Q_p is less than K_p. Under these conditions, the reverse reaction is nonspontaneous. At 700 K, however, $K_p = 8.8 \times 10^{-5}$, and the reverse reaction is spontaneous because Q_p is greater than K_p.

A spontaneous reaction always moves a reaction mixture toward equilibrium. By contrast, a nonspontaneous reaction moves the composition of a mixture away from the equilibrium composition. Remember, though, that the word "spontaneous" doesn't mean the same thing as "fast." A spontaneous reaction can be either fast or slow—for example, the gradual rusting of iron metal is a slow spontaneous reaction. Thermodynamics tells us where a reaction is headed, but it says

Spontaneous Processes

nothing about how long it takes to get there. As discussed in Section 12.10, the rate at which equilibrium is achieved depends on kinetics, especially on the height of the activation energy barrier between the reactants and products (Figure 17.2).



Criteria for spontaneity

Enthalpy

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H^\circ = -890.3\ \text{kJ}$$

Because spontaneous reactions so often give off heat, the nineteenth-century French scientist Marcellin Berthelot proposed that spontaneous chemical or physical changes are *always* exothermic. But Berthelot's proposal can't be correct. Ice, for example, spontaneously absorbs heat and melts at temperatures above 0°C. Similarly, liquid water absorbs heat and spontaneously boils at temperatures above 100°C. As further examples, gaseous N_2O_4 absorbs heat when it decomposes to NO_2 at 400 K, and table salt absorbs heat when it dissolves in water at room temperature:

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H_{\text{fusion}} = +6.01\ \text{kJ}$$

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H_{\text{vap}} = +40.7\ \text{kJ}$$

$$N_2O_4(g) \longrightarrow 2\,NO_2(g) \qquad \Delta H^\circ = +57.1\ \text{kJ}$$

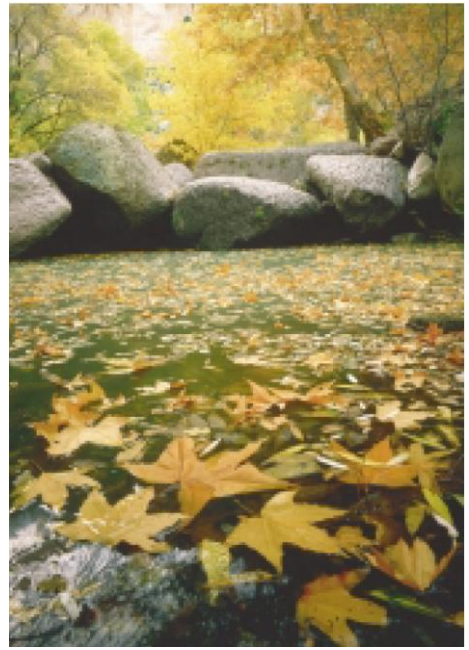
$$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq) \qquad \Delta H^\circ = +3.88\ \text{kJ}$$

All these processes are endothermic, yet all are spontaneous. In all cases, the system moves spontaneously to a state of *higher* potential energy by absorbing heat from the surroundings.

Criteria for spontaneity

Entropy

Since some spontaneous reactions are exothermic and others are endothermic, enthalpy alone can't account for the direction of spontaneous change; a second factor must be involved. This second thermodynamic driving force is nature's tendency to move to a condition of maximum randomness or disorder

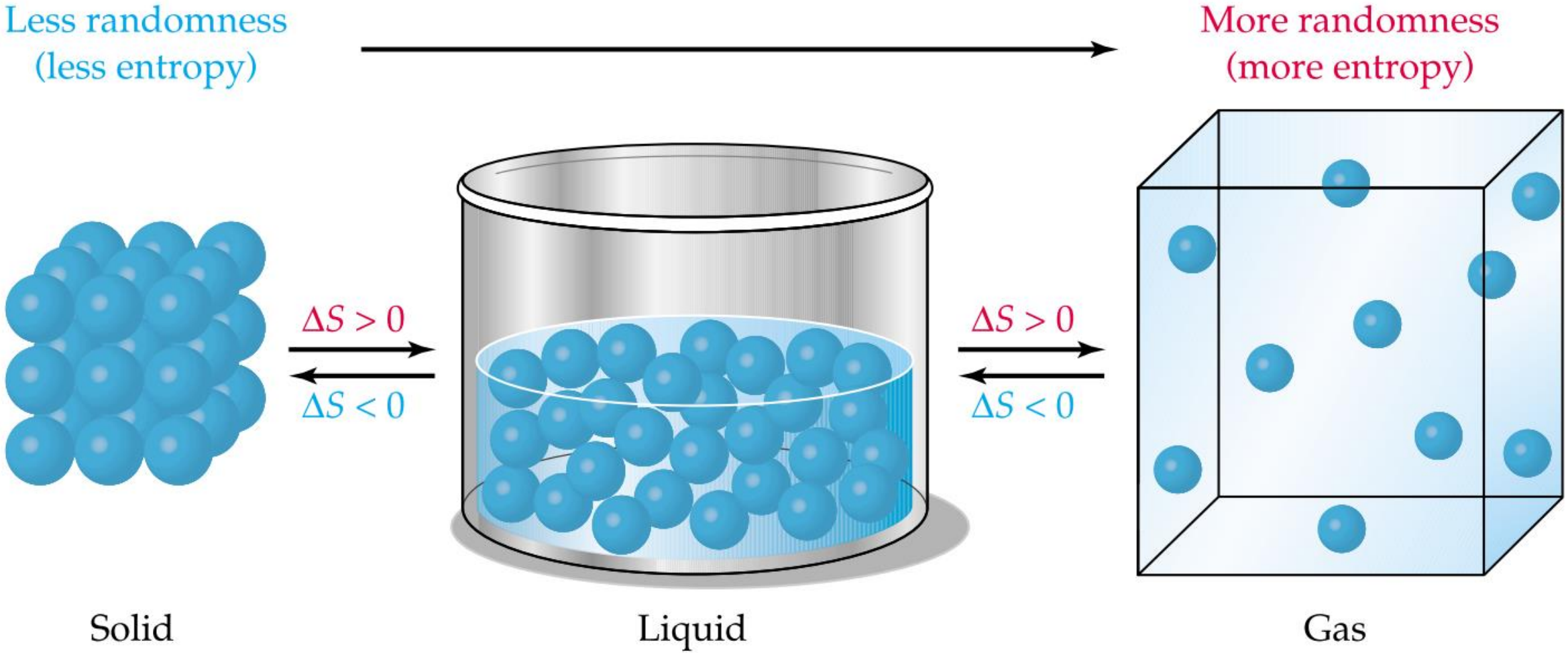


The tendency of things to get "messed up" is common in everyday life. You may rake the leaves on your lawn into an orderly pile, but after a few windy days the leaves are again scattered randomly. The reverse process is nonspontaneous; the wind never blows the randomly disordered leaves into a neatly arranged pile. Molecular systems behave similarly: *Molecular systems tend to move spontaneously to a state of maximum randomness or disorder*.

Molecular randomness, or disorder, is called **entropy** and is denoted by the symbol S. Entropy is a state function and the entropy change ΔS for a process thus depends only on the initial and final states of the system:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

When the randomness or disorder of a system increases, ΔS has a positive value; when randomness decreases, ΔS is negative.


Less randomness
(less entropy)
More randomness
(more entropy)
ΔS > 0
ΔS < 0
ΔS > 0
ΔS < 0
Solid
Liquid
Gas

The dispersal of energy

The signpost of spontaneous change: we look for the direction of change that leads to dispersal of the total energy of the isolated system. This principle accounts for the direction of change of the bouncing ball, because its energy is spread out as thermal motion of the atoms of the floor. The reverse process is not spontaneous because it is highly improbable that energy will become localized, leading to uniform motion of the ball's atoms.

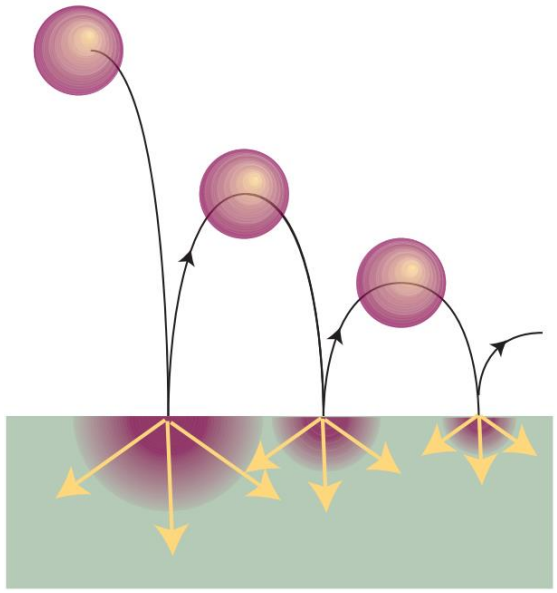


Fig. The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

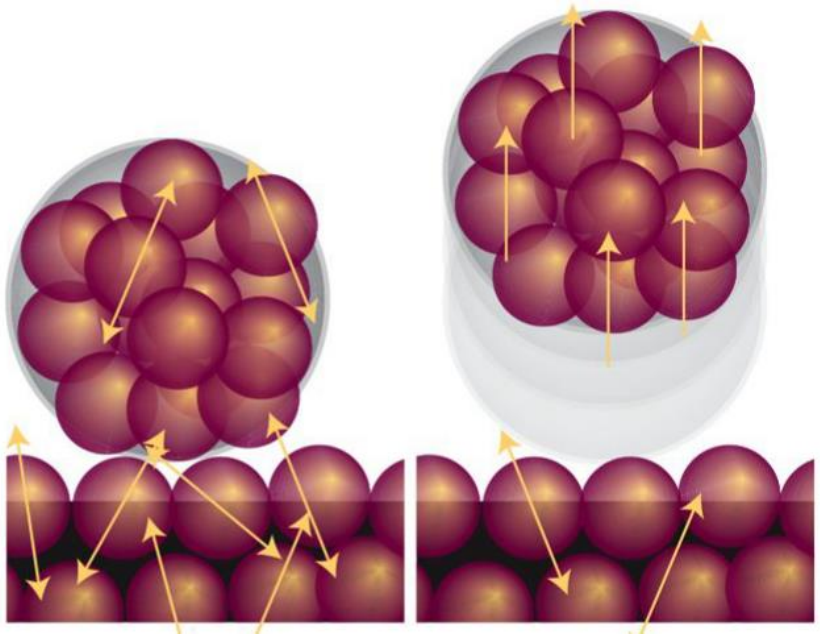


Fig. The molecular interpretation of the irreversibility expressed by the Second Law. (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows. (b) For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is highly improbable.

Entropy and Probability

The Austrian physicist Ludwig Boltzmann proposed in 1896 that the entropy of a particular state is related to the number of ways that the state can be achieved, according to the formula

$$S = k \ln W$$

where S is the entropy of the state, $\ln W$ is the natural logarithm of the number of ways that the state can be achieved, and k, now known as *Boltzmann's constant*, is a universal constant equal to the gas constant R divided by Avogadro's number ($k = R/N_A = 1.38 \times 10^{-23}$ J/K). Because a logarithm is dimensionless, you can see from the Boltzmann equation that entropy has the same units as the constant k, namely, joules per kelvin.

Now let's apply Boltzmann's formula to our hypothetical crystal containing 20 CO molecules. Because the perfectly ordered state can be achieved in only one way ($W = 1$ in the Boltzmann equation) and because $\ln 1 = 0$, the entropy of the perfectly ordered state is zero:

$$\begin{aligned} S &= k \ln W = k \ln 1 \\ &= 0 \end{aligned}$$

The more probable totally disordered state, however, can be achieved in 2^{20} ways and thus has a higher entropy:

$$\begin{aligned} S &= k \ln W = k \ln 2^{20} \\ &= (1.38 \times 10^{-23}\,\text{J/K})\,(20)\,(\ln 2) \\ &= 1.91 \times 10^{-22}\,\text{J/K} \end{aligned}$$

where we have made use of the relation $\ln x^a = a \ln x$

If our crystal contained 1 mol of CO molecules, the entropy of the perfectly ordered state (6.02×10^{23} C atoms up) would still be zero, but the entropy of the totally disordered state would be much higher because Avogadro's number of molecules can be arranged randomly in a huge number of ways ($W = 2^{N_A} = 2^{6.02\times10^{23}}$). According to Boltzmann's formula, the entropy of the disordered state is

$$S = k \ln W = k \ln 2^{N_A} = kN_A \ln 2$$

Because $k = R/N_A$,

$$\begin{aligned} S &= R \ln 2 = (8.314\,\text{J/K})\,(0.693) \\ &= 5.76\,\text{J/K near 0 K} \end{aligned}$$

Boltzmann's formula also explains why a gas expands into a vacuum.

In general, when the volume of one mole of an ideal gas changes from V_{initial} to V_{final} at constant temperature, the entropy of the gas changes by an amount

$$\Delta S = R \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$$

Because the pressure and volume of an ideal gas are related inversely ($P = nRT/V$), we can also write

$$\Delta S = R \ln \frac{P_{\text{initial}}}{P_{\text{final}}}$$

Thus, the entropy of a gas *increases* when its pressure *decreases* at constant temperature, and the entropy *decreases* when pressure *increases*. Common sense tells us that the more we squeeze the gas, the less space the gas molecules have and so the more ordered they will be.

The thermodynamic definition of entropy

The thermodynamic definition of entropy concentrates on the change in entropy, dS, that occurs as a result of a physical or chemical change (in general, as a result of a 'process'). The definition is motivated by the idea that a change in the extent to which energy is dispersed depends on how much energy is transferred as heat. As we have remarked, heat stimulates random motion in the surroundings. On the other hand, work stimulates uniform motion of atoms in the surroundings and so does not change their entropy.

The thermodynamic definition of entropy is based on the expression

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

Definition of entropy change

where q_{rev} is the heat supplied reversibly. For a measurable change between two states i and f this expression integrates to

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

Entropy and the Second Law of Thermodynamics

Limitations of the first law of thermodynamics

1. It puts no restriction on the direction of flow of heat
2. Gives no idea about the spontaneity (feasibility of a process)
3. The First law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work.

Entropy and the Second Law of Thermodynamics

The First Law of thermodynamics led to the introduction of the internal energy, U. The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant. The law that is used to identify the signpost of spontaneous change, the Second Law of thermodynamics, uses the entropy to identify the *spontaneous changes* among those permissible changes.

The Second Law of thermodynamics can be expressed in terms of the entropy:

The entropy of an isolated system increases in the course of a spontaneous change:

$$\Delta S_{\text{tot}} > 0$$

where S_{tot} is the total entropy of the system and its surroundings. Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy.

Carnot cycle

Cyclic Process. When a system, after completing a series of changes, returns to original state, it is said to have completed a **cycle.** The entire process is known as a **cyclic process.** Since the internal energy of a system depends only upon its state, it follows that in a cyclic process, the net change of internal energy is zero, *i.e.*, $\Delta U=0$. Therefore, according to the First law,

$$\Delta U = 0 = q + w \qquad \text{or} \qquad q = -w$$

If the series of changes in a cycle are conducted at constant temperature, the cycle is said to be an **isothermal cycle.** If the changes are carried out reversibly, the cycle is said to be a **reversible cycle.**

Although the reversible cyclic processes are merely theoretical and imaginary, the concept is highly useful in deriving certain important relationships. The most well known cyclic process is the **Carnot cycle.**

Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work. The system consists of one mole of an ideal gas which is subjected to a series of four successive operations, commonly termed as **four strokes,** as given below.

I. Stroke 1. Isothermal Expansion. The gas is allowed to expand reversibly and isothermally at the temperature T_2 so that the volume increases from V_1, represented by the point A, to V_2 represented by the point B (Fig. 1.). Since in the isothermal expansion of an ideal gas $\Delta U=0$, it follows from the First law equation (*viz.*, $\Delta U=q+w$) that $q=-w$, *i.e.*, the heat absorbed is equal to the work done by the system on the surroundings. Let q_2 be the heat absorbed by the system at the temperature T_2 and w_1 be the work done by the system on the surroundings. Then

$$q_2 = -w_1 = RT_2 \ln (V_2/V_1) \qquad \ldots(1)$$

II. Stroke 2. Adiabatic Expansion. The gas is then allowed to expand reversibly and adiabtically from the volume V_2 to V_3, *i.e.*, from the point B to C.

Since work is done by the system adiabatically, it is not in a position to absorb heat. The temperature of the system, therefore, falls from T_2 to say, T_1. As q is equal to

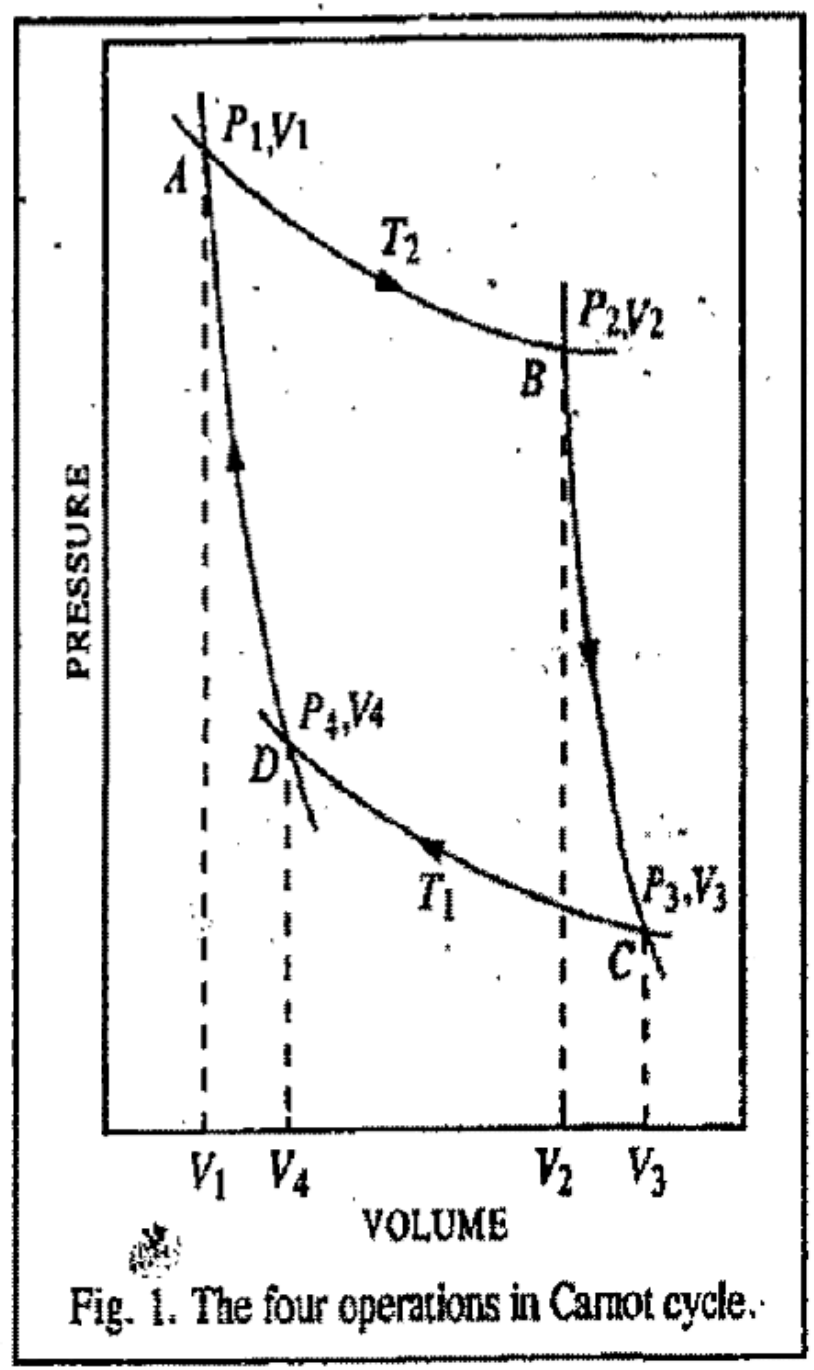


Fig. 1. The four operations in Carnot cycle.

zero in this case, it follows from the First law equation (*viz.*, $\Delta U = q + w$) that $\Delta U = w$. Since the process involves expansion of the gas, therefore, work is done by the system on the surroundings. Hence, by convention, w is negative so that $\Delta U = -w$.

Now, by definition, $C_v = (\partial U/\partial T)_v$ ...(2)

$\therefore$ $\Delta U = C_v \Delta T = C_v(T_1 - T_2) = -w$ ...(3)

(change in temperature, ΔT = final temperature – initial temperature)

or $-w = C_v(T_1 - T_2) = -C_v(T_2 - T_1)$ ...(4)

If the work done in this stage is denoted by w_2, then

$\therefore$ $-w_2 = -C_v(T_2 - T_1)$ ...(5)

III. Stroke 3. Isothermal Compression. After this, the gas is subjected to a reversible and isothermal compression at the lower temperature T_1 so that the volume decreases from V_3 to V_4 (*i.e.*, from the point C to D). In this case, evidently, work is done on the system. Hence, heat will be produced and *given up* to the surroundings. Since compression takes place isothermally and reversibly, $\Delta U = 0$. Therefore, if q_1 is the heat *given out* to the surroundings at the temperature T_1 and w_3 is the work done on the system in this process, then remembering signs of q and w,

$-q_1 = w_3 = RT_1 \ln (V_4/V_3)$ ...(6)

IV. Stroke 4. Adiabatic Compression. Finally, by an adiabatic and reversible compression, the gas is restored to its original volume V_1 and temperature T_2. Thus, the gas is compressed adiabatically from D to A. In this case, work is done on the system. Hence, w is positive. According to the First law, $\Delta U = q + w$. Since in adiabatic process, $q = 0$, hence,

$$\Delta U = w = C_v \Delta T = C_v(T_2 - T_1)$$

Let w_4 be the work done in this stage. Then,

$$w_4 = C_v(T_2 - T_1) \qquad \ldots(7)$$

where $T_2 - T_1$ is the increase in temperature produced by the adiabatic compression.

The net heat absorbed (q) by the ideal gas in the whole cycle is given by

$$q = q_2 + (-q_1) = RT_2 \ln (V_2/V_1) + RT_1 \ln (V_4/V_3)$$
$$= RT_2 \ln (V_2/V_1) - RT_1 \ln (V_3/V_4) \qquad \ldots(8)$$

In the light of adiabatic expansion of an ideal gas the following equations can be written :

$$C_v \ln (T_2/T_1) = R \ln (V_3/V_2) \quad \text{(For stage II)}$$
$$C_v \ln (T_2/T_1) = R \ln (V_4/V_1) \quad \text{(For stage IV)}$$

or $$V_3/V_2 = V_4/V_1 \text{ or } V_2/V_1 = V_3/V_4 \qquad \ldots(9)$$

Hence, the net **heat absorbed,** according to Eq. 8, may be put as

$$q = q_2 - q_1 = R\,(T_2 - T_1)\ln\,(V_2/V_1) \qquad ...(10)$$

Similarly, the **net work done** by the gas is given by

$$\begin{aligned} w &= -w_1 + (-w_2) + w_3 + w_4 \\ &= RT_2 \ln V_2/V_1 - C_v(T_2 - T_1) + RT_1 \ln (V_4/V_3) + C_v(T_2 - T_1) \\ &= RT_2 \ln (V_2/V_1) - RT_1 \ln (V_3/V_4) \qquad ...(11) \end{aligned}$$

Since $V_2/V_1 = V_3/V_4$

Hence, $w = R(T_2 - T_1) \ln (V_2/V_1)$ ...(12)

It follows from Eqs.10 and 12 that $q=w$. Thus, *the essential condition for a cyclic process that the net work done is equal to the net heat absorbed is fully satisfied.*

The relationship between w, the net work done by the system and q_2, the quantity of heat absorbed at the higher temperature T_2, in Carnot cycle, can be obtained from the following two equations :

$$w = R(T_2 - T_1) \ln (V_2/V_1) \qquad \text{(Eq. 12)}$$

and

$$q_2 = RT_2 \ln (V_2/V_1) \qquad \text{(Eq. 1)}$$

Hence, dividing Eq. 12 by Eq. 1,

$$w = q_2 (T_2 - T_1)/T_2 \qquad (13)$$

Since $(T_2 - T_1)/T_2 < 1$, it follows that $w < q_2$, *i.e.*, work done is less than the heat absorbed. This means that only a part of the heat absorbed by the system at the higher temperature T_2 is transformed into work. The rest of the heat q_1 is given out by the system to the surroundings which is at the lower temperature T_1.

Thus, Kelvin stated the **second law of thermodynamics** as follows :

It is impossible to use a cyclic process to extract heat from a reservoir and to convert it into work without transferring at the same time a certain amount of heat from a hotter to a colder part of the system.

Efficiency of a Heat Engine. *The fraction of the heat absorbed by an engine which it can convert into work gives the* **efficiency** (η) *of the engine.*

From Eq. 13, it is seen that

$$\text{Efficiency, } \eta = w/q_2 = (T_2 - T_1)/T_2 \qquad \ldots(14)$$

Since $(T_2 - T_1)/T_2$ is invariably less than 1, the efficiency of a heat engine is always less than 1. No heat engine has yet been constructed which has an efficiency equal to unity. Mathematically, however, if $T_1 = 0$, efficiency = 1.

It follows from Eq. 14 that the efficiency depends upon the difference between T_2 and T_1. Thus, the greater the difference between the temperature of the 'source' and the 'sink', the greater is the efficiency. This explains why superheated steam is used in a steam engine.

The net heat absorbed by the system, q, is equal to $q_2 - q_1$ and according to the First law of thermodynamics, this must be equivalent to the net work done by the system. Thus,

$$w = q_2 - q_1$$

Combining this with Eq. 14, we get

$$(q_2 - q_1)/q_2 = (T_2 - T_1)/T_2 \qquad (15)$$

Thus, $$\text{efficiency, } \eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad (16)$$

Eq. 16 has been arrived at by assuming that the series of changes in the cycle are brought about in a thermodynamically reversible manner so as to obtain maximum possible work. But, in actual practice, it is not possible to carry out the process infinitesimally slowly so that the efficiency is even less than that given by the above equation.

Carnot Theorem. According to Eq. 16, the efficiency of a machine working reversibly depends only on the temperature of the source and the sink. It is independent of the nature of the substance or substances used for operations. The same idea may be expressed by saying that *all periodic machines working reversibly between the same two temperatures have the same efficiency*. This statement is commonly known as the **Carnot theorem,** in honour of S. Carnot (1796-1832), the brilliant French physicist, known for important contributions to thermodynamics.

It may be noted that while the First law states that when one form of energy is transformed into another, the amount of energy that disappears is exactly equivalent to the amount of energy that is produced, it is silent about the extent to which such conversion can take place. The Second law of thermodynamics gives information about this point. It tells us that while all other forms of energy can be *completely* converted into heat, the complete conversion of heat into any other form of energy cannot take place without leaving some lasting change in the system. This has led to the following enunciation of the **Second law of thermodynamics :**

It is impossible to convert heat into work without compensation.

Calculation of Entropy Change of an Ideal Gas with Change in P, V and T. Since entropy of a system varies with the state of the system, its value for a pure gaseous substance will depend upon any two of the three variables T, P and V. Since T is taken generally as one of the variables, the second variable to be considered may be V or P. Thus, the two variables to be considered are either T and V or T and P.

When T and V are the two variables. The increase in entropy of the gas for an infinitesimally small change is given by the expression

$$dS = dq_{rev}/T$$

where dq_{rev} is the small amount of heat *absorbed* by the gas (system) *reversibly* from the surroundings at temperature T.

According to the equation of the First law of thermodynamics, *viz.*, $\Delta U = q + w$, we have

$$dq_{rev} = dU - dw$$

If the work involved is due to *expansion of the gas*, then, for an infinitesimal increase in volume dV against a pressure P,

$$-dw = PdV$$

Substituting the value of dU from $C_V = (\partial U/\partial T)_v$ and $-dw$

$$dq_{rev} = C_V\,dT + PdV$$

For one mole of an ideal gas,

$$dq_{rev} = C_V\,dT + RT\,dV/V$$

$$dq_{rev}/T = dS = C_V\,dT/T + R\,dV/V$$

For a finite change of state of a system, the entropy change (ΔS) is obtained by integrating the above equation between the limits of the initial state 1 and the final state 2. Assuming C_V to be constant within the temperature range T_1 and T_2, for one mole of the gas we have

$$\Delta S = S_2 - S_1 = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

Thus,

$$\Delta S = C_V \ln T_2/T_1 + R \ln V_2/V_1$$

For n moles of the ideal gas, the above equation may be written as

$$\Delta S = nC_V \ln (T_2/T_1) + nR \ln (V_2/V_1)$$

It is evident that the entropy change for the change of state of an ideal gas depends upon the initial and final volumes as well as on the initial and final temperatures.

When T and P are the two variables. If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then

$$P_1V_1 = RT_1 \text{ for one mole of the gas in the initial state}$$

$$P_2V_2 = RT_2 \text{ for one mole of the gas in the final state.}$$

$$\therefore \quad V_2/V_1 = P_1T_2/(P_2T_1)$$

Substituting in Eq. 42, for one mole of the gas, we have

$$\Delta S = C_V \ln T_2/T_1 + R \ln T_2/T_1 - R \ln P_2/P_1$$

Remembering that $C_P - C_V = R$

$$\Delta S = C_P \ln T_2/T_1 - R \ln P_2/P_1$$

For n moles of the ideal gas,

$$\Delta S = nC_P \ln (T_2/T_1) - nR \ln (P_2/P_1)$$

It is evident from the above equations that the entropy change for the change of state of an ideal gas depends on the initial and final pressure as well as on the initial and final temperature.

The Entropy of an Isolated System Increases as a Result of a Spontaneous Process

We all know that energy as heat will flow spontaneously from a region of high temperature to a region of low temperature. Let's investigate the role entropy plays in this process. Consider the two-compartment system shown in Figure where parts A and B are large one-component systems. Both systems are at equilibrium, but they are not at equilibrium with each other. Let the temperatures of these two systems be T_A and T_B. The two systems are separated from each other by a rigid, heat-conducting wall so that energy as heat can flow from one system to the other, but the two-compartment system itself is isolated. When we call a system *isolated*, we mean that the system is separated from its surroundings by rigid walls that do not allow matter or energy to pass through them. We may picture the walls as rigid, totally non-heat conducting, and impervious to matter. Consequently, the system can do no work nor can work be done on the system, nor can it exhange energy as heat with the surroundings. The two-compartment system is described by the equations

$$U_A + U_B = \text{constant}$$

$$V_A = \text{constant} \qquad V_B = \text{constant} \tag{20.13}$$

$$S = S_A + S_B$$

Because V_A and V_B are fixed, we have for each separate system

$$\begin{aligned} dU_A &= \delta q_{rev} + \delta w_{rev} = T_A dS_A \quad (dV_A = 0) \\ dU_B &= \delta q_{rev} + \delta w_{rev} = T_B dS_B \quad (dV_B = 0) \end{aligned} \tag{20.14}$$

The entropy change of the two-compartment system is given by

$$\begin{aligned} dS &= dS_A + dS_B \\ &= \frac{dU_A}{T_A} + \frac{dU_B}{T_B} \end{aligned} \tag{20.15}$$

But $dU_A = -dU_B$ because the two-compartment system is isolated, so we have

$$dS = dU_B \left(\frac{1}{T_B} - \frac{1}{T_A} \right) \tag{20.16}$$

Experimentally, we know that if $T_B > T_A$, then $dU_B < 0$ (energy as heat flows from system B to system A), in which case $dS > 0$. Similarly, $dS > 0$ if $T_B < T_A$

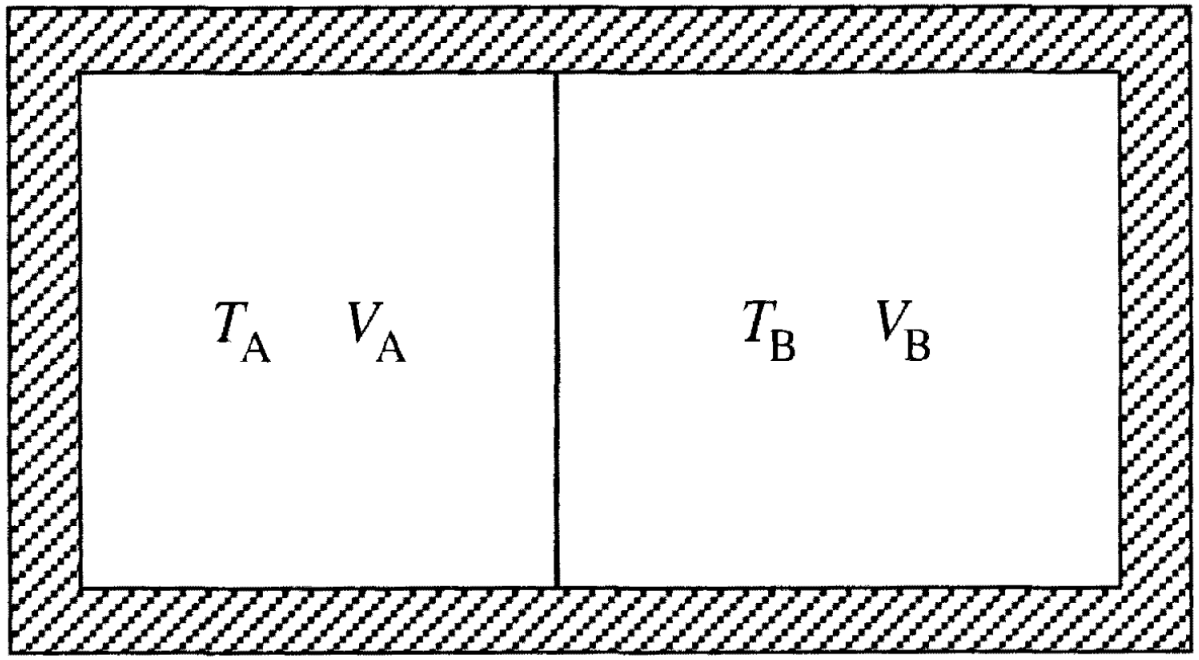
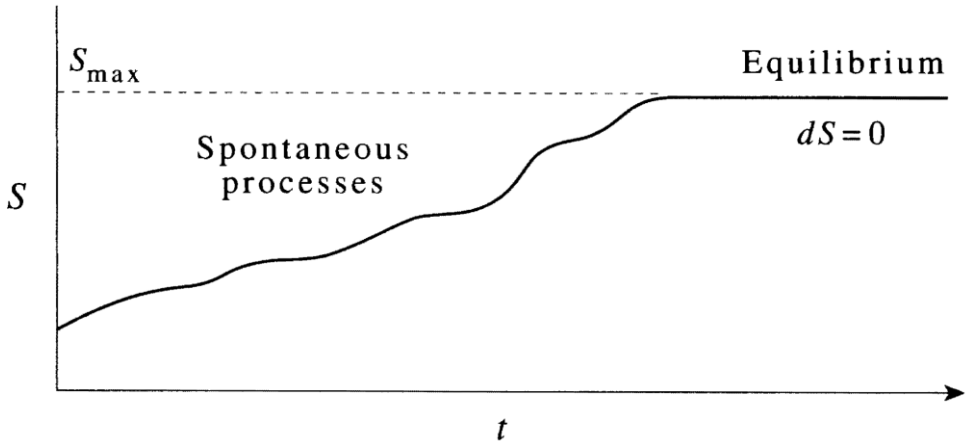


FIGURE
A two-compartment system in which A and B are large, one-component systems. Each system is at equilibrium, but they are not at equilibrium with each other. The two systems are separated from each other by a rigid, heat-conducting wall. The total two-compartment system itself is isolated.

because $dU_B > 0$ in this case (energy as heat flows from system A to system B). We may interpret this result by saying that the spontaneous flow of energy as heat from a body at a higher temperature to a body at a lower temperature is governed by the condition $dS > 0$. If $T_A = T_B$, then the two-compartment system is in equilibrium and $dS = 0$.

Unlike energy, entropy is not necessarily conserved; it increases whenever a spontaneous process takes place. In fact, the entropy of an isolated system will continue to increase until no more spontaneous processes occur, in which case the system will be in equilibrium (Figure). Thus, we conclude that the entropy of an isolated system is a maximum when the system is in equilibrium. Consequently, d S = 0 at equilibrium. Furthermore, not only is d S = 0 in an isolated system at equilibrium, but d S = 0 for any reversible process in an isolated system because, by definition, a reversible process is one in which the system remains essentially in equilibrium during the entire process.



A schematic plot of entropy versus time for an isolated system. The entropy increases (d S > 0) until no more spontaneous processes occur, in which case the system is in equilibrium, and dS = 0

To summarize our conclusions thus far, then, we write

$$\begin{aligned} dS &> 0 \quad \text{(spontaneous process in an isolated system)} \\ dS &= 0 \quad \text{(reversible process in an isolated system)} \end{aligned} \tag{20.17}$$

Because we have considered an isolated system, no energy as heat can flow in or out of the system. For other types of systems, however, energy as heat can flow in or out, and it is convenient to view dS in any spontaneous infinitesimal process as consisting of two parts. One part of dS is the entropy created by the irreversible process itself, and the other part is the entropy due to the energy as heat exchanged between the system and its surroundings. These two contributions account for the entire change in entropy. We will denote the part of dS that is created by the irreversible process by dS_{prod} because it is *produced* by the system. This quantity is always positive. We will denote the part of dS that is due to the exchange of energy as heat with the surroundings by dS_{exch} because it is due to *exchange*. This quantity is given by $\delta q/T$, and it can be positive, negative, or zero. Note that δq need not be δq_{rev}. The quantity δq will be δq_{rev} if the exchange is reversible and δq_{irr} if the exchange is irreversible. Thus, we write for *any* process

$$dS = dS_{\text{prod}} + dS_{\text{exch}}$$

$$= dS_{\text{prod}} + \frac{\delta q}{T} \tag{20.18}$$

For a reversible process, $\delta q = \delta q_{\text{rev}}$, $dS_{\text{prod}} = 0$, so

$$dS = \frac{\delta q_{\text{rev}}}{T} \tag{20.19}$$

in agreement with Equation 20.3. For an irreversible or spontaneous process, $dS_{\text{prod}} > 0$, $dS_{\text{exch}} = \delta q_{\text{irr}} / T$, and so

$dS = \frac{\delta q_{\text{rev}}}{T}$ (20.3)

$$dS > \frac{\delta q_{\text{irr}}}{T} \tag{20.20}$$

Equations 20.19 and 20.20 can be written as one equation,

$$dS \geq \frac{\delta q}{T} \tag{20.21}$$

or
$$\Delta S \geq \int \frac{\delta q}{T} \tag{20.22}$$

where the equality sign holds for a reversible process and the inequality sign holds for an irreversible process. Equation 20.22 is one of a number of ways of expressing the Second Law of Thermodynamics and is called the *Inequality of Clausius*.

A formal statement of the Second Law of Thermodynamics is as follows:

There is a thermodynamic state function of a system called the entropy, S, such that for any change in the thermodynamic state of the system,

$$dS \geq \frac{\delta q}{T}$$

where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.

Because the universe itself may be considered to be an isolated system and all naturally occurring processes are irreversible, one statement of the Second Law of Thermodynamics says that the entropy of the universe is constantly increasing. In fact, Clausius summarized the first two laws of thermodynamics by

The energy of the Universe is constant;

the entropy is tending to a maximum.

ENTROPY CHANGES FOR AN IDEAL GAS

According to the first law of thermodynamics, we have

$$\mathrm{d}q_{\mathrm{rev}} = \mathrm{d}U + p\ \mathrm{d}V$$

Dividing this by T, we have

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \frac{\mathrm{d}U}{T} + \frac{p}{T}\ \mathrm{d}V$$

Taking U to be a function of T and V and writing its differential, we have

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

Substituting this in the previous expression, we get

$$\mathrm{d}S = \frac{1}{T}\left\{\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V\right\} + \frac{p}{T}\ \mathrm{d}V$$

Now for an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \text{(Joule's law)}$$

and $$\frac{p}{T} = \frac{nR}{V}$$

With these, alongwith the fact that $(\partial U/\partial T)_V = C_V$, the previous expression becomes

$$dS = \frac{C_V}{T} dT + \frac{nR}{V} dV \tag{4.16.1}$$

For a finite change, we have

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{nR}{V} dV$$

Considering C_V to be independent of temperature, we have

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \tag{4.16.2}$$

or
$$\Delta S = n \left[C_{V,\mathrm{m}} \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \right] \tag{4.16.3}$$

This is the expression when both the volume and temperature of an ideal gas are changed. For an isothermal change in volume, the entropy change is given by the relation

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

where V_2 is the final volume and V_1 is the initial volume.

Next we proceed to calculate the change in total entropy for the following categories.

Reversible Change

If the expansion or compression is carried out reversibly, then

$$q_{rev} = -w = RT \ln \frac{V_2}{V_1} \quad \text{and} \quad \Delta S_{sys} = \frac{q_{rev}}{T} = R \ln \frac{V_2}{V_1}$$

If it is assumed that the heat q_{rev} is exchanged reversibly between the system and the surroundings at temperature T, it is obvious that

$$\Delta S_{surr} = -\frac{q_{rev}}{T}$$

Thus $$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 0 \qquad (4.20.1)$$

Irreversible Change

Two cases of expansion process may be considered:

Free expansion The gas expands into vacuum for this process, we have

$$w = 0 \qquad \text{and} \qquad q = 0$$

Since entropy is a state function, the entropy change of a system in going from volume V_1 to V_2 by any path will be same as that of a reversible change; therefore,

$$\Delta S_{sys} = R \ln \frac{V_2}{V_1}$$

Since no heat is supplied by the surroundings the entropy change of the latter would be zero, i.e.

$$\Delta S_{\text{surr}} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = R \ln \frac{V_2}{V_1} + 0 = R \ln \frac{V_2}{V_1} = \text{positive} \qquad (4.20.2)$$

Intermediate expansion Since ΔS_{sys} is the same as that of reversible change, therefore,

$$\Delta S_{\text{sys}} = R \ln \frac{V_2}{V_1} = \frac{q_{\text{rev}}}{T}$$

where q_{rev} is the amount of heat that the system would have absorbed had the process been carried out reversibly. In the present case the expansion is done against a constant pressure, thus

$$q_{\text{irr}} = -w = p_{\text{ext}} (V_2 - V_1)$$

The change in entropy of the surroundings will be given by

$$\Delta S_{\text{surr}} = -\frac{q_{\text{irr}}}{T} = -\frac{p_{\text{ext}}(V_2 - V_1)}{T}$$

Since the magnitude of work involved in the intermediate expansion is smaller than that involved in reversible expansion, it is obvious that $q_{\text{irr}} < q_{\text{rev}}$. With this, ΔS_{total} becomes

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{irr}}}{T} = \text{positive} \qquad (4.20.3)$$

Work and Free Energy Functions

We have seen earlier that the sum total of the entropy change of the system and the surroundings (*viz.*, $\Delta S_{sys} + \Delta S_{sur}$) serves as a criterion of spontaneity or feasibility of a process. If the total entropy change is positive, the process is feasible. If it is *zero*, the system remains in a state of *equilibrium*. However, in order to decide about the feasibility of a process, we shall have to know the entropy change of the system as well as that of the surroundings. This is not always convenient. We, therefore, consider entropy change in terms of other state functions which can be determined more conveniently Two such functions are the **work function** and the **free energy function** represented by A and G, respectively. These are defined by the equations

$$A = U - TS \qquad \ldots(66)$$

$$G = H - TS \qquad \ldots(67)$$

Since, U, H and S depend only upon the state of a system (the temperature is included in the state), it is evident that the functions A and G also depend upon the state of the system only. Let the three functions in Eq. 66. at constant T, be A_1, U_1 and S_1 so that

$$A_1 = U_1 - TS_1 \qquad \ldots(68)$$

Let an appreciable change take place at the same temperature T so that the three functions in another state of the system become A_2, U_2 and S_2. Then,

$$A_2 = U_2 - TS_2 \qquad \ldots(69)$$

Subtracting Eq. 68 from Eq. 69, we have

$$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1) \quad \text{or} \quad \Delta A = \Delta U - T\Delta S \qquad \ldots(70)$$

where ΔA is the change in the function A, ΔU is the corresponding change in internal energy and ΔS is the change in entropy of the system.

Suppose the change under reference is brought about reversibly at the constant temperature T and that the heat *absorbed* is equal to q_{rev}.

Since from Eq. 28, $\Delta S = q_{rev}/T$, hence, substituting in Eq. 70, we have

$$\Delta A = \Delta U - q_{rev} \qquad \ldots(71)$$

From the equation of the First law of thermodynamics, *viz.*, $\Delta U = q + w$, it follows that

$$w_{rev} = \Delta U - q_{rev} \qquad \ldots(72)$$

$$-w_{rev} = \Delta U - q_{rev} \quad \ldots(73)$$

Comparing Eq. 71 with Eq. 73,

$$-\Delta A = w_{rev} \quad \ldots(74)$$

Since the process is carried out reversibly, w represents the maximum work. It is thus clear that *decrease in the function A (i.e., $-\Delta A$) gives the maximum work that can be done by the system during the given change*.. The function A is, therefore, termed as the **work function.** This is also referred to as **Helmholtz free energy** or **Helmholtz function.**

The German physicist Hermann von Helmholtz (1821-1894) was a versatile scientist who made contributions to optics, thermodynamics, acoustics and physiology.

If G_1, H_1 and S_1 represent the thermodynamic functions in the initial state and G_2, H_2 and S_2 in the final state, the temperature remaining constant at T, we have from Eq. 67,

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \text{ or } \Delta G = \Delta H - T\Delta S \quad \ldots(75)$$

But, as already shown in Chapter 13, at constant pressure

$$\Delta H = \Delta U + P\Delta V$$

$$\therefore \quad \Delta G = \Delta U + P\Delta V - T\Delta S \quad \ldots(76)$$

Comparing with Eq. 70,

$$\Delta G = \Delta A + P\Delta V \quad \ldots(77)$$

Since ΔA is equal to $-w$ (Eq. 74), hence

$$\Delta G = -w + P\Delta V \text{ or } -\Delta G = w - P\Delta V \quad ...(78)$$

The quantity $P\Delta V$ is the work done by the gas on expansion against the constant external pressure P. Therefore, $-\Delta G$ gives the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure. The work other than that due to change of volume is called the **net work.** Thus,

$$\text{Net work} = w - P\Delta V = -\Delta G \quad ...(79)$$

Hence, $-\Delta G$ is a measure of the net work that can be obtained from a system at constant temperature and pressure. The quantity G is called the **Gibbs function** or **Gibbs free energy** or merely **free energy**. Thus, $-\Delta G$ is a measure of the decrease in free energy. The net work that it measures may be electrical work or chemical work. This quantity is of great importance in physical chemistry ; it is named in honour of the great American physicist, J.W. Gibbs (1839-1903).

Variation of Free Energy Change with Temperature and Pressure. The variation of free energy change with variation of temperature and pressure may now be considered. According to Eq. 67,

$$G = H - TS$$

Since $H = U + PV$, hence $G = U + PV - TS$ ...(80)

Upon differentiation, $dG = dU + PdV + VdP - TdS - SdT$ ... (81)

The First law equation for an infinitesimal change may be written as

$$dq = dU - dw \qquad ...(82)$$

If the work done is only due to expansion, then, $-dw = PdV$

$$\therefore \qquad dq = dU + PdV \qquad ...(83)$$

For a reversible process,

$$dS = dq/T \quad \text{or} \quad TdS = dq = dU + PdV \qquad ...(84)$$

Combining Eqs. 81 and 84, we have

$$dG = VdP - SdT \qquad ...(85)$$

This equation gives change of free energy when a system undergoes, reversibly, a change of pressure as well as change of temperature.

If pressure remains constant, *i.e.*, $dP=0$, then, from Eq. 85

$$dG = -SdT \quad \text{or} \quad (\partial G/\partial T)_P = -S \qquad ...(86)$$

On the other hand, if temperature remains constant, *i.e.*, $dT=0$, then, from Eq. 85,

$$dG = VdP \quad \text{or} \quad (\partial G/\partial P)_T = V \qquad ...(87)$$

Let the free energy of a system be G_1 in the initial state and G_2 in the final state when an appreciable change in pressure has taken place, at constant temperature. Then, integrating Eq. 87, the free energy change, ΔG, is given by

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} VdP \qquad ...(88)$$

where P_1 and P_2 are the initial and final pressures, respectively.

If one mole of an ideal gas is under consideration, then $PV = RT$.

$$\therefore \qquad \Delta G = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2} \qquad ...(89)$$

where V_1 and V_2 are the initial and final volumes, respectively.

For n moles of the gas,

$$\Delta G = nRT \ln (P_2/P_1) = nRT \ln (V_1/V_2) \qquad ...(90)$$

The Sign of the Helmholtz Energy Change Determines the Direction of a Spontaneous Process in a System at Constant Volume and Temperature

Let's consider a system with its volume and temperature held constant. The criterion that $dS \geq 0$ does not apply to a system at constant temperature and volume because the system is not isolated; a system must be in thermal contact with a thermal reservoir to be at constant temperature. If the criterion $dS \geq 0$ does not apply, then what is the criterion for a spontaneous process that we can use for a system at constant temperature and volume? Let's start with the expression of the First Law of Thermodynamics, Equation 19.9,

$$dU = \delta q + \delta w \tag{22.1}$$

Because $\delta w = -P_{\text{ext}} dV$ and $dV = 0$ (constant volume), then $\delta w = 0$. If we substitute Equation 20.3, $dS \geq \delta q / T$, and $\delta w = 0$ into Equation 22.1, we obtain

$$dU \leq T dS \qquad \text{(constant } V\text{)} \tag{22.2}$$

The equality holds for a reversible process and the inequality for an irreversible process. Note that if the system is isolated, then $dU = 0$ and we have $dS \geq 0$. We can write Equation 22.2 as

$$dU - T dS \leq 0$$

If T and V are held constant, we can write this expression as

$$d(U - TS) \leq 0 \qquad \text{(constant } T \text{ and } V\text{)} \tag{22.3}$$

Equation 22.3 prompts us to define a new thermodynamic state function by

$$A = U - TS \tag{22.4}$$

so Equation 22.3 becomes

$$dA \leq 0 \qquad \text{(constant } T \text{ and } V\text{)} \tag{22.5}$$

The quantity A is called the *Helmholtz energy*. In a system held at constant T and V, the Helmholtz energy will decrease until all the possible spontaneous processes have occurred, at which time the system will be in equilibrium and A will be a minimum. At equilibrium, $dA = 0$ (see Figure 22.1). Note that Equation 22.5 is the analog of the criterion that $dS \geq 0$ to occur in an isolated system (cf. Figures 20.5 and 22.1).

For an isothermal change from one state to another, Equation 22.4 gives

$$\Delta A = \Delta U - T\Delta S \tag{22.6}$$

Using Equation 22.5, we see that

$$\Delta A = \Delta U - T\Delta S \leq 0 \qquad \text{(constant } T \text{ and } V\text{)} \tag{22.7}$$

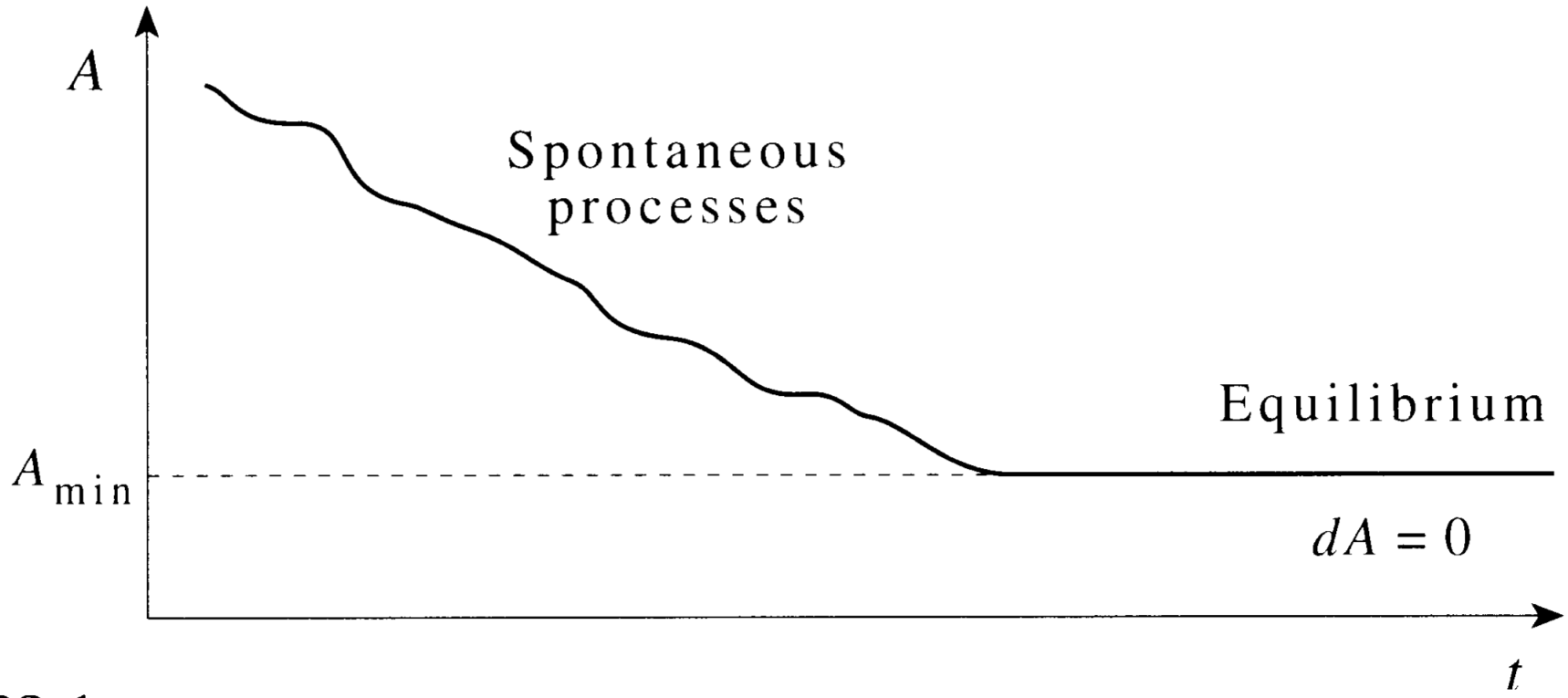


FIGURE 22.1
The Helmholtz energy, A, of a system will decrease during any spontaneous processes that occur at constant T and V and will achieve its minimum value at equilibrium.

In addition to serving as our criterion for spontaneity in a system at constant temperature and volume, the Helmholtz energy has an important physical interpretation. Let's start with Equation 22.6

$$\Delta A = \Delta U - T\Delta S \tag{22.8}$$

for a spontaneous (irreversible) process, so that $\Delta A < 0$. In this process, the initial and final states are well-defined equilibrium states, and there is no fundamental reason we have to follow an irreversible path to get from one state to the other. In fact, we can gain some considerable insight into the process if we look at any reversible path connecting these two states. For a reversible path we can replace ΔS by q_{rev}/T, giving

$$\Delta A = \Delta U - q_{\text{rev}}$$

But according to the first law, $\Delta U - q_{rev}$ is equal to w_{rev}, so we have

$$\Delta A = w_{rev} \qquad \text{(isothermal, reversible)} \tag{22.9}$$

If $\Delta A < 0$, the process will occur spontaneously and w_{rev} represents the work that can be done *by* the system if this change is carried out reversibly. This quantity is the maximum work that could be obtained. If any irreversible process such as friction occurs, then the quantity of work that can be obtained will be less than w_{rev}. If $\Delta A > 0$, the process will not occur spontaneously and w_{rev} represents the work that must be done *on* the system to produce the change in a reversible manner. If there is any irreversibility in the process, the quantity of work required will be even greater than w_{rev}.

The Gibbs Energy Determines the Direction of a Spontaneous Process for a System at Constant Pressure and Temperature

Most reactions occur at constant pressure rather than at constant volume because they are open to the atmosphere. Let's see what the criterion of spontaneity is for a system at constant temperature and pressure. Once again, we start with Equation 22.1, but now we substitute $dS \geq \delta q/T$ and $\delta w = -PdV$ to obtain

$$dU \leq TdS - PdV$$

or

$$dU - TdS + PdV \leq 0$$

Because both T and P are constant, we can write this expression as

$$d(U - TS + PV) \leq 0 \qquad \text{(constant } T \text{ and } P\text{)} \qquad (22.10)$$

We now define a new thermodynamic state function by

$$G = U - TS + PV \tag{22.11}$$

so Equation 22.10 becomes

$$dG \leq 0 \qquad \text{(constant } T \text{ and } P\text{)} \tag{22.12}$$

Note that Equation 22.11 is the analog of Equation 22.4.

The quantity G is called the *Gibbs energy*. In a system at constant T and P, the Gibbs energy will decrease as the result of any spontaneous processes until the system reaches equilibrium, where $dG = 0$. A plot of G versus time for a system at constant T and P would be similar to the plot of A versus time for a system at constant T and V (Figure 22.1). Thus, we see that the Gibbs energy, G, is the analog of the Helmoltz energy, A, for a process that takes place at constant temperature and pressure.

Equation 22.11 can also be written as

$$G = H - TS \tag{22.13}$$

where $H = U + PV$ is the enthalpy. Note that the enthalpy plays the same role in a constant T and P process that the energy U plays in a constant T and V process (cf. Equation 22.4). Note also that G can be written as

$$G = A + PV \tag{22.14}$$

thus relating the Gibbs energy and the Helmholtz energy in the same manner that H and U are related.

The analog of Equation 22.7 is

$$\Delta G = \Delta H - T\Delta S \leq 0 \qquad \text{(constant } T \text{ and } P\text{)} \qquad (22.15)$$

The equality holds for a reversible process, whereas the inequality holds for an irreversible (spontaneous) process. If $\Delta H < 0$ and $\Delta S > 0$ in Equation 22.15, both terms in Equation 22.15 contribute to ΔG being negative. But if ΔH and ΔS have the same sign, then $\Delta G = \Delta H - T\Delta S$ represents the compromise between the tendency of a system to decrease its enthalpy and to increase its entropy in a constant T and P process. Because of the factor of T multiplying ΔS in Equation 22.15, the ΔH term can dominate at low temperatures, whereas the $T\Delta S$ term can dominate at high temperatures. Of course if $\Delta H > 0$ and $\Delta S < 0$, then $\Delta G > 0$ at all temperatures and the process is never spontaneous.

Criteria for Reversible and Irreversible Processes. We have seen earlier that the net entropy change of a process determines whether the process would proceed irreversibly (*i.e.*, spontaneously) or not. If there is net increase in the entropy of the system and the surroundings taken together, the process would proceed irreversibly, *i.e.*, it would be thermodynamically feasible. If there is no net change in the entropy of the system and the surroundings put together, the process will be reversible, *i.e.*, the system will remain in a state of equilibrium.

We can express the criteria for reversibility and irreversibility in terms of entropy of the system (alone) as well as in terms of other fundamental thermodynamic properties, namely, U, H, A and G.

It was stated earlier that change of entropy for a given change of state is a definite quantity, independent of the fact whether the change is brought about reversibly or irreversibly. But, mathematically, it is given (for a small change) by the equation

$$dS = dq_{rev}/T = (dU + PdV)/T \qquad ...(103)$$

only if the change (involving expansion of an ideal gas) is brought about reversibly.

Suppose the small change of state is brought about *irreversibly*. Now the heat absorbed by the system will be *less* ($\because q_{irr} < q_{rev}$). But the entropy change dS will have the same value. Hence, for an *irreversible* process,

$$TdS > dq_{rev}$$

We may thus write $TdS = dU + PdV$ (For a reversible process)

$TdS > dU + PdV$ (For an irreversible process)

Combining the two, we have

$$TdS \geq dU + PdV \quad \ldots(104)$$

The 'equal to' sign refers to a reversible process while the 'greater than' sign refers to an irreversible process.

(i) Criterion in Terms of Change of Entropy. If U and V (internal energy and volume) remain constant, then, for an isothermal process (*i.e.*, T is constant),

$$dS \geq 0$$

The 'equal to' sign refers to reversible process while the 'greater than' sign refers to an irreversible process.

(ii) Criterion in Terms of Change of Internal Energy. If S and V (entropy and volume) are kept constant, then, for an isothermal process (*i.e.*, T is constant).

$$dU \leq 0$$

The 'equal to' sign refers to a reversible process while 'less than' sign refers to an irreversible process.

(iii) Criterion in Terms of Change of Enthalpy. If S and P are kept constant, the expression $TdS \geq dU + PdV$ may be written as

$$dU + PdV \leq 0$$

But $$dU + PdV = dH$$

$$\therefore \quad dH \leq 0$$

where the sign 'equal to' refers to a *reversible* process while the sign 'less than' refers to an irreversible process.

(iv) Criterion in Terms of Change of Work Function. Combining Eq.104, *viz.*, $TdS \geq dU + PdV$ with Eq. 70, *viz.*, $dA = dU - TdS$ for an infinitesimally small change, we have

$$dA \leq -PdV$$

At constant volume, therefore, $dA \leq 0$

where the sign 'equal to' refers to a reversible process while the sign 'less than' refers to an irreversible process.

(v) *Criterion in Terms of Change of Free Energy.* Substituting $TdS \geq dU + PdV$ in Eq. 85, we have

$$dG \leq VdP - SdT$$

$\therefore$ At constant temperature and pressure, $dG \leq 0$ ...(105)

where, as usual, the sign 'equal to' refers to a reversible process while the sign 'less than' refers to an irreversible process.

The criterion in terms of free energy change *viz.*, $(\partial G)_{T,P} \leq 0$, is the most useful criterion to decide between reversibility and irreversibility of a process. If free energy change of a process has a negative value, the process is irreversible, *i.e.*, it can take place spontaneously. If, on the other hand, the free energy change of a process is *zero*, then the process is reversible, *i.e.*, a state of equilibrium exists. Lastly, if the free energy change of process is positive, *i.e.*, there is likely to be an increase in the free energy change, then the process will not proceed.

The Gibbs-Helmholtz Equation

Let G_1 represent the free energy of a system in its initial state at temperature T. Suppose the temperature rises to $T+dT$ where dT is infinitesimally small. Let the free energy at the new temperature be G_1+dG_1.

Now suppose that when the system is in its final state, its free energy is given by G_2 at the temperature T and by G_2+dG_2 at the temperature $T+dT$. If the pressure remains constant all along, Eq. 86 is applicable, *i.e.*,

$$dG_1 = -S_1 dT \quad \ldots(106)$$

and

$$dG_2 = -S_2 dT \quad \ldots(107)$$

where S_1 and S_2 are the entropies of the system in the initial and final states of the system, respectively.

Subtracting Eq. 106, from Eq. 107, we have

$$d(G_2 - G_1) = -(S_2 - S_1)\, dT$$

$$d(\Delta G) = -\Delta S dT \quad \ldots(108)$$

As the pressure is constant, therefore,

$$(\partial(\Delta G)/\partial T)_P = -\Delta S \quad \ldots(109)$$

Also, since from Eq. 75, $-\Delta S = (\Delta G - \Delta H)/T$, hence, Eq. 109 becomes

$$(\Delta G - \Delta H)/T = (\partial(\Delta G)/\partial T)_P \quad \ldots(110)$$

or

$$\Delta G = \Delta H + T(\partial(\Delta G)/\partial T)_P \quad \ldots(111)$$

This equation is known as the **Gibbs-Helmholtz equation.** It is applicable to all processes occurring at constant pressure. It has been used for calculating the enthalpy change ΔH for a process or a reaction provided the values of free energy changes at two different temperatures are known.

For a reaction at constant volume, the corresponding equation will be

$$\Delta A = \Delta U + T(\partial(\Delta A)/\partial T)_V \quad \ldots(112)$$

The Third Law of thermodynamics

At $T = 0$, all energy of thermal motion has been quenched, and in a perfect crystal all the atoms or ions are in a regular, uniform array. The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy. This conclusion is consistent with the molecular interpretation of entropy, because $S = 0$ if there is only one way of arranging the molecules (all molecules occupy the ground state).

The Nernst heat theorem

The experimental observation that turns out to be consistent with the view that the entropy of a regular array of molecules is zero at $T = 0$ is summarized by the **Nernst heat theorem:**

> The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \to 0$ as $T \to 0$ provided all the substances involved are perfectly ordered.

Nernst heat theorem

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline compounds also have zero entropy at $T = 0$ (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero). This conclusion is summarized by the **Third Law of thermodynamics**:

The entropy of all perfect crystalline substances is zero at $T = 0$.

Third Law of thermodynamics

As far as thermodynamics is concerned, choosing this common value as zero is a matter of convenience. The molecular interpretation of entropy, however, justifies the value $S = 0$ at $T = 0$. According to the Boltzmann formula, the entropy is zero if there is only one accessible microstate ($W = 1$). In most cases, $W = 1$ at $T = 0$ because there is only one way of achieving the lowest total energy: put all the molecules into the same, lowest state.

Therefore, $S = 0$ at $T = 0$, in accord with the Third Law of thermodynamics. In certain cases, though, W may differ from 1 at $T = 0$. This is the case if there is no energy advantage in adopting a particular orientation even at absolute zero. For instance, for a diatomic molecule AB there may be almost no energy difference between the arrangements . . . AB AB AB . . . and . . . BA AB BA . . . , so $W > 1$ even at $T = 0$. If $S > 0$ at $T = 0$ we say that the substance has a **residual entropy**. Ice has a residual entropy of 3.4 J K^{-1} mol^{-1}. It stems from the arrangement of the hydrogen bonds between neighbouring water molecules: a given O atom has two short O–H bonds and two long O···H bonds to its neighbours, but there is a degree of randomness in which two bonds are short and which two are long.