8 General Thermodynamic Interaction

The last several chapters have discussed systems that interact by absorbing or giving off heat, but without doing any large-scale work. The present chapter extends this discussion to considering the general case where interactions may involve both heat and work. It thereby leads to theoretical knowledge that can deal with all interactions between large-scale systems and that permits a wide range of practical applications.

A. Entropy change in a quasi-static process

Entropy change when no heat is absorbed

The preceding chapters considered systems on which no large-scale work is done, but which may absorb heat and thereby incur changes in their entropy. Let us now consider the opposite extreme case of systems which absorb *no* heat, but on which work may be done. What is the entropy change of such a system?

Entropy change of a moving object. Suppose that some solid object is slowly moved from one place to another. Large-scale work may then be done on this object (e.g., if the object moves downward by some distance, work is done on it by the gravitational force due to the earth). But the random internal motions of the atomic particles in the object are thereby unaffected, i.e., the entropy of the object remains thereby unchanged.

Entropy change of any system in a quasi-static process. Consider now a more complex system on which work can be done because its volume can change. For example, Fig. A-1 indicates such a system X (a gas or liquid) inside a cylinder closed by a movable piston X'. Work can then be done on this system as the piston moves (although we assume that negligible heat is absorbed by the system from the piston).

A very simple situation occurs when the volume V of the system changes quasi-statically, i.e., when the piston moves so slowly that the system remains always extremely close to an equilibrium situation. At any volume, the entire isolated system (consisting of the system X and the piston X') must then always be in its most probable situation, i.e., its entropy S* is always maximum. For any infinitesimal quasi-static volume change, this entropy thus neither increases nor decreases, i.e.,
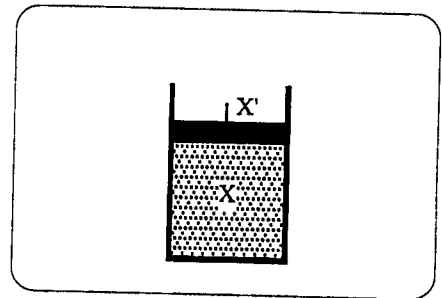

Fig. A-1. A system X (e.g., a gas in a cylinder) interacting with a piston X'

$$dS^* = 0. \tag{A-1}$$

Here $S^* = S + S'$, i.e., the entropy S^* of the entire system is equal to the sum of the entropies S of the system and S' of the piston. Thus (A-1) implies that

$$dS + dS' = 0.$$

But $dS' = 0$ since the entropy of the piston remains unchanged. Thus we arrive at the following conclusion:

in a quasi-static adiabatic process, $\quad dS = 0.$ \hfill (A-2)

In other words, *the entropy of a system remains unchanged in any infinitesimal quasi-static process in which no heat is absorbed.*

Entropy change in a general quasi-static process

Infinitesimal quasi-static process. Consider now any infinitesimal quasi-static process in which some small work d'W may be done on the system in changing its volume and in which the system may also absorb some small heat d'Q. Then one can imagine this process carried out by means of the following two successive quasi-static subprocesses:

(1) A first subprocess in which work may be done on the system in changing its volume by the specified amount, but in which no heat is absorbed. According to (A-2), the entropy of the system remain then unchanged.

(2) A second subprocess in which the volume of the system remains fixed so that no work is done, but in which the system absorbs the heat d'Q. According to (4F-8), the entropy of the system changes then by an amount $dS = $ d'Q/T if its absolute temperature is T.

The total entropy change of the system in this entire infinitesimal quasi-static process is thus due solely to the *heat* absorbed by the system in this process. Hence we arrive at the following general conclusion:

> ***Entropy-heat relation:***
>
> *In any quasi-static infinitesimal process,* $\quad dS = \dfrac{d'Q}{T}$.

\hfill (A-3)

Entropy change between any two macrostates. The result (A-3) allows one to find the entropy change between *any* two macrostates A and B of a system. Indeed, consider *any* quasi-static process leading from A to B. Then (A-3) implies that the corresponding entropy change is just the sum of all the successive infinitesimal entropy changes in this process. Thus,

$$\text{for a quasi-static process,} \quad S_B - S_A = \int_A^B \frac{d'Q}{T} \tag{A-4}$$

where d'Q is the infinitesimal amount of heat absorbed by the system when its absolute temperature is T.

In particular, (A-4) implies that *the entropy of a system remains unchanged in any quasi-static process in which no heat is absorbed.*

Importance of the quasi-static condition. It is crucially important to note that all the preceding results are valid only if a process is *quasi-static* (i.e., if it is carried out so slowly that the system remains always extremely close to an equilibrium situation). The following examples illustrates the distinction between rapid and quasi-static processes.

Example: Sudden expansion of a gas

Fig. A-2 shows a gas in a thermally insulated cylinder. The gas is initially in equilibrium (as indicated in Fig. A-2a) and the piston is then very suddenly pulled out. Immediately afterwards the gas is then still in its previously occupied region of the cylinder (as indicated in Fig. A-2b) and no work has been done on the gas by the piston which has lost contact with the gas. Then the gas quickly spreads out throughout the entire larger volume now available to it (to attain the final situation indicated in Fig. 2a-c). During this process the piston remains at rest so that no work is done on the gas.

During the entire process, the internal energy E of the gas remains then constant (since the gas absorbs no heat and no work is done on it). However, the entropy S of the gas has increased (since the gas now occupies a larger volume so that more possible positions have become available to its molecules).

Fig. A-2. Sudden expansion of a gas. (a) Initial situation. (b) Situation immediately after the piston has been moved. (c) Final situation.

Example: Quasi-static expansion of a gas

Consider the same gas, in the same thermally insulated cylinder, which is again in the same initial equilibrium situation illustrated in Fig. A-3a. However, now the piston is very slowly moved outward until one reaches the situation, illustrated in Fig. A-3c, where the volume of the gas is the same as it was in Fig. A-2c.

In this case, the volume of the gas has again increased. But, since this increase has occurred against the opposing fore exerted by the piston, negative work has been done on the gas by the piston. Hence the internal energy E of the gas has decreased. The increased volume of the gas causes its entropy to *increase* (since there are more possible positions available to the gas molecules). However, the decreased internal energy of the gas causes its entropy to *decrease* (since there are fewer possible velocities available to the molecules). There are then two compensating effects affecting the entropy. The net result is thus consistent with the conclusion (A-4) that the entropy of the gas remains *unchanged* in this quasi-static process where not heat is absorbed.
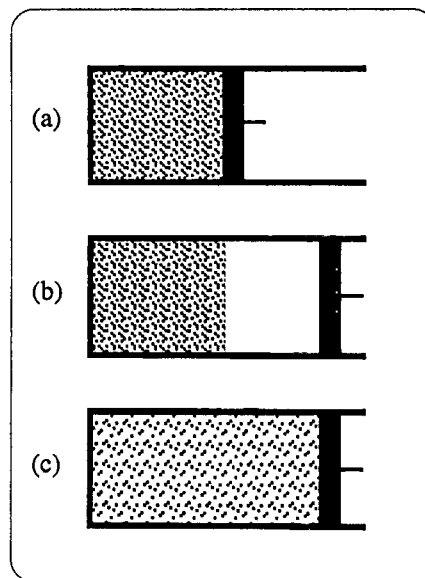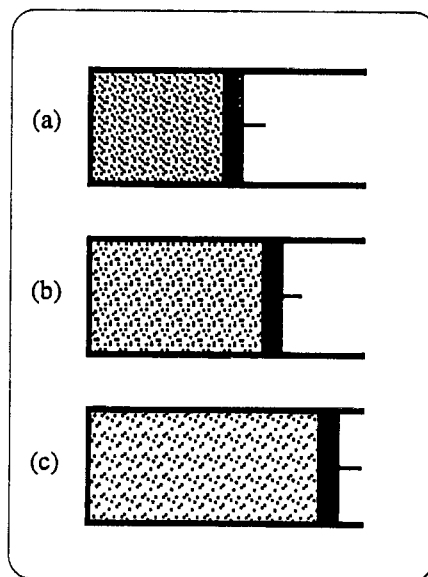

Fig. A-3. Quasi-static expansion of a gas. (a) Initial situation. (b) Intermediate situation. (c) Final situation.

Problems

[A-1] *Entropy changes under various conditions*

A system has a constant heat capacity C_V when the system is maintained at constant volume, and has a constant heat capacity C_p when it is maintained at constant pressure.

(a) Suppose that the system's absolute temperature is slowly changed from T_A to T_B while its *volume* is kept constant. Does the system's pressure then change? Is non-zero work done on the system? What is the entropy change of the system?

(b) Suppose that the system's absolute temperature is slowly changed from T_A to T_B while its *pressure* is kept constant. Does the system's volume then change? Is non-zero work done on the system? What is the entropy change of the system? <a-5>

B. Implications of the entropy-heat relation

The relation (A-3) indicates how the entropy change dS is related to the heat d'Q absorbed by the system. But this heat can be related to the system's change dE of internal energy. Indeed, by the thermodynamic energy law

$$dE = d'W + d'Q$$

or

$$d'Q = dE - d'W = dE + pdV. \qquad (B-1)$$

Thus the relation (A-3) implies that

$$\boxed{dS = \frac{dE + p\,dV}{T}.} \qquad (B-2)$$

This thermodynamic relation has many applications. In particular, one may use it to obtain knowledge about many important properties of a system if one knows how the system's entropy depends on its energy E and volume V.

Properties of the internal energy. Suppose that the volume V of a system is kept constant so that dV = 0. Then (B-2) implies that dS = dE/T or that

$$\left(\frac{dS}{dE}\right)_V = \frac{1}{T}. \qquad (B-3)$$

Remember that the subscript indicates the quantity which is kept constant (i.e., the volume V in this case).

If one knows how the entropy S depends on E and V, this relation can then be used to determine how the energy E of the system depends on its absolute temperature T and volume V.

Properties of the pressure. Suppose that the energy E of a system is kept constant so that dE = 0. Then (B-2) implies that dS = (p/T) dV or that

$$\left(\frac{dS}{dV}\right)_E = \frac{p}{T}. \qquad (B-4)$$

If one knows how the entropy S depends on E and V, this relation can then be used to determine how the energy p of the system depends on its absolute temperature T and volume V.

Applications to the properties of an ideal gas

Entropy of an ideal gas. Consider an ideal gas consisting of N molecules in a container of volume V and having a total energy E. As discussed in Section 4E, the number Ω_V of basic states, available to the gas molecules because of all their possible positions, is

$$\Omega_V = c \, V^N \qquad \text{(B-5)}$$

where c is some constant of proportionality.

The number Ω_E of basic states, available to the gas molecules because of all their possible velocities, depends on their total energy E. However, it does not depend on the volume of the gas since the potential energy of intermolecular interaction of an ideal gas is negligible and hence unaffected by any change in the average distance between molecules. Thus

$$\Omega_E \text{ depends only on E (but not on V).} \qquad \text{(B-6)}$$

In particular, as discussed in Section 4E,

for a monatomic ideal gas, $\qquad \Omega_E = c' \, E^{3N/2} \qquad \text{(B-7)}$

where c' is another constant of proportionality.

The total number Ω of basic states available to an ideal gas is the product of the number of states due to possible molecule positions and the number of states due to possible molecule velocities. Thus

$$\Omega = \Omega_V \, \Omega_E = c \, V^N \, \Omega_E. \qquad \text{(B-8)}$$

Hence the entropy of the ideal gas is

$$\boxed{S = k \ln\Omega = k \, (\ln c) + k \, N \, \ln V + k \, \ln\Omega_E.} \qquad \text{(B-9)}$$

Energy of an ideal gas. The properties of the energy of the ideal gas can now be obtained from (B-3). By applying this general relation to the entropy (B-9), we find that

$$k \left(\frac{d(\ln\Omega_E)}{dE} \right) = \frac{1}{T}. \qquad \text{(B-10)}$$

Here the left side involves only the energy E of the gas, but not its volume. Hence (B-10) shows that the energy E of the gas is related to its absolute temperature T, but does not depend on its volume. Hence we reach the following general conclusion:

$$\boxed{\textit{For any ideal gas, } \text{E depends on T (but not on V).}} \qquad \text{(B-11)}$$

Energy of a monatomic ideal gas. In the special case of a monatomic ideal gas, (B-7) implies that

$$\ln\Omega_E = \ln c' + (3N/2) \ln E \qquad \text{(B-12)}$$

Here (B-10) then yields the more specific result

$$k \, (3N/2) \frac{1}{E} = \frac{1}{T}$$

so that $\qquad\qquad\qquad E = \frac{3}{2} NkT. \qquad\qquad\qquad \text{(B-13)}$

Pressure of an ideal gas. The properties of the pressure of an ideal gas can now be obtained from (B-4). By applying this general relation to the entropy (B-9), we find that

$$k \left(\frac{N}{V} \right) = \frac{p}{T}$$

so that

$$\boxed{pV = N\,kT.}$$
(B-14)

This is the ideal-gas law which we obtained in Chapter 6 by much more complex arguments requiring a detailed analysis of molecular collisions with a wall.

Simplicity and generality of entropy considerations. Note that we have now been able to use much simpler arguments to obtain the ideal-gas law as well as the result (B-11) about the independence of internal energy on volume. Furthermore, these arguments have been more general -- showing immediately that these results are applicable to *any* ideal gas, even if it is not monatomic.

Problems

[B-1] *Entropy of a monatomic gas*

Consider a monatomic ideal gas of N molecules. Starting with the relations (B-9) and (B-12), answer the following questions.

(a) Write a relation indicating how the entropy S of this gas depends on its volume V and internal energy E. (Your relation may involve some undetermined additive constant independent of V and E.)

(b) Write a relation indicating how the entropy S of this gas depends on its volume V and absolute temperature T. (Your relation may involve some undetermined additive constant independent of V and T.)

(c) The principle (A-4) asserts that the entropy of the adiabatically insulated gas should remain constant if the volume of the gas is quasi-statically changed. Use this principle, and the result obtained in part *b*, to determine how the absolute temperature T of the gas depends on its volume V during such an adiabatic process. Is your answer consistent with that previously obtained in Problem E-2 of Chapter 7? *<a-9>*

[B-2] *Adiabatic temperature change of an ideal gas*

Consider any ideal gas (whether monatomic or more complex).

(a) Suppose that the volume of this gas is kept fixed. If the absolute temperature of the gas is larger, is the entropy of the gas then larger, smaller, or the same?

(b) Suppose that the temperature of this gas is kept fixed. If the volume of the gas is larger, is the entropy of the gas then larger, smaller, or the same?

(c) If the volume of the gas is quasi-statically increased while the gas is adiabatically insulated, the entropy of the gas must remain unchanged. *If* the temperature of the gas remained unchanged despite the increase of its volume, would its entropy increase, decrease, or remain unchanged? What then must actually happen to the temperature of the gas so as to keep its entropy unchanged?

(d) According to the preceding reasoning, should an adiabatic *expansion* of a gas increase or decrease its absolute temperature? Conversely, should an adiabatic *compression* of a gas increase or decrease its absolute temperature? *<a-2>*

[B-3] *Adiabatic temperature change of a rubber band*

Consider a partially stretched rubber band

(a) Suppose that the length of this rubber band is kept fixed. If the absolute temperature of the band is larger, is the entropy of the band larger, smaller, or the same?

(b) Suppose that the temperature of this rubber band is kept fixed. If the length of the band is made larger, does its entropy become larger, smaller, or remain the same? (A rubber band consists of chains of polymer molecules which are randomly coiled when the band is unstretched and which become more nearly aligned when the band is stretched.) <*h-3*>

(c) If the length of the rubber band is quasi-statically increased while the band is adiabatically insulated, the entropy of the band must remain unchanged. *If* the temperature of the band remained unchanged despite the increase of its length, would its entropy increase, decrease, or remain unchanged? What then must actually happen to the temperature of the band so as to keep its entropy unchanged?

(d) According to the preceding reasoning, should an adiabatic lengthening of a rubber band increase or decrease its absolute temperature? Conversely, should an adiabatic shortening of a rubber band increase or decrease its absolute temperature? <*a-7*>

To verify this prediction, hold a stretched rubber band against your lips and quickly reduce its length. Your lips are sufficiently sensitive that they should then be able to detect the temperature change of the band. (If you change the length quickly enough, the band is approximately adiabatic since there is not enough time for much heat transfer to occur between the band and its surroundings. On the other hand, the process is slow enough that the molecules in the band are at any instant nearly in internal equilibrium at a well-defined temperature.)

C. Principles of statistical thermodynamics

We have now obtained essentially all the basic principles of the science of statistical thermodynamics. Let us then review the basic hypotheses from which these principles are derived and then explicitly summarize these principles for future use.

Basic hypotheses

All our considerations of large-scale systems have been based on the following two basic hypotheses:

> *Atomic structure of matter.* Any large-scale system consists of atomic particles described by the laws of mechanics.   (C-1)

The second basic hypothesis is the statistical postulate introduced in Sec. 3B.

> *Statistical equilibrium postulate.* The probabilities of finding an isolated macroscopic system in its possible basic states change with time until they reach an unchanging equilibrium situation where they are equal.   (C-2)

Principles of macroscopic thermodynamics

Starting from the preceding basic hypotheses, we have been able to infer the following general principles. These are completely independent of the nature of the atomic particles constituting the large-scale systems of interest. Hence these principles can be applied to make inferences about the macroscopic properties of

Indeed, in the 19th century most of these principles were inferred from large-scale observations long before there was significant knowledge about atoms or molecules. Theses principles formed the laws of "classical thermodynamics".

systems *without* requiring any specific knowledge about the atoms or molecules in these systems.

Thermal equilibrium. One very simple principle follows from the following conclusion obtained in (4A-11):

Mutual thermal equilibrium *(zeroth law of thermodynamics).* If two systems are each in thermal equilibrium with a third system, they will be in thermal equilibrium with each other.

(C-3)

This principle is called the "zeroth law of thermodynamics" because its importance was historically realized only after the other laws of classical thermodynamics has already been formulated.

This principle allows one to use thermometers to determine whether two systems will be in thermal equilibrium or not.

Energy law. A very important principle is the energy principle expressed in (2B-6) so as to recognize the distinction between work and heat.

Thermodynamic energy law (first law of thermodynamics): $$\Delta E = W + Q.$$

(C-4)

This law asserts that any large-scale system can be characterized by a quantity E, its internal energy, which remains unchanged when the system is isolated. However, when this system changes by interacting with other systems, the change of its energy between any two macrostates is due to the large-scale work done on the system and to the heat absorbed by the system (i.e., to purely atomic-scale work done on it).

Entropy and absolute temperature. The next central principle specifies the properties of the entropy and consists of two parts:

Entropy law (second law of thermodynamics): In any small quasi-static process, $dS = d'Q/T.$ (a) For any isolated system, $\Delta S \geq 0$ (b)

(C-5)

Part *a* of this law is just the statement (A-3) previously obtained in the present chapter for any infinitesimal quasi-static process. This statement allows one to determine changes of entropy and relates these to the absolute temperature T.

By contrast, part *b* of the entropy law applies to any process of an *isolated* system. In that case, the system always tends to approach a much more probable macrostate so that its entropy increases (i.e., so that the change ΔS of its entropy is positive). The exception occurs when the system remains in equilibrium or when a process is performed so slowly that the system remains always extremely close to equilibrium. In that case the entropy of the system remains unchanged (i.e., the change ΔS of its entropy is zero).

The preceding statement also indicates that a process in which the entropy of an isolated system increases is irreversible since reversal of the process would require the entropy to decrease [something which, according to (C-4b), is

impossible (or unrealistically improbable).] On the other hand, a process in which the entropy remains unchanged (e.g., a quasi-static process) is reversible.

Statistical significance of the entropy. According to (4A-2), the probability P of finding an isolated system in a particular macrostate is proportional to the number Ω of possible basic states available to the system in this situation, i.e.,

$$P \propto \Omega \qquad \text{(C-6)}$$

But the definition $S = k \ln\Omega$ of the entropy implies that $\Omega = e^{S/k}$. Hence (C-6) leads to the following principle relating the entropy to probabilities:

> ***Probability and entropy.*** The probability P of finding any isolated system in a macrostate of entropy S is given by
> $$P \propto e^{S/k}$$

(C-7)

This principle was not a part of classical thermodynamics. However, it too is totally independent of the nature of the atomic particles in the system.

For example, suppose that the system's entropy in a macrostate A is S_A and its entropy in a macrostate B is S_B. Then the ratio of the probabilities of finding the system in these two states can be found from the difference of the entropies in these two states, i.e.,

$$\frac{P_A}{P_B} = \frac{e^{S_A/k}}{e^{S_B/k}} = e^{(S_A - S_B)/k} . \qquad \text{(C-8)}$$

Entropy and basic atomic states

According to its definition (4E-6), the entropy S of a system is related to the number Ω of possible basic states available to the system when it is described on an atomic scale. This definition provides a relation between the entropy, whose macroscopic properties are specified by (C-5), and the atomic properties of a system.

> ***Atomic specification of entropy.***
> $$S = k \ln\Omega.$$

(C-7)

If the atomic properties of a system are sufficiently well known, it is then possible to calculate its entropy and thereby to infer many of its macroscopic properties. (For example, in Section B we did this in the case of an ideal gas which is such a simple system that its entropy could be readily calculated.)

Historical notes.

The suggestion that heat is a form of energy was first advanced in 1798 by the American-British physicist Benjamin Thompson (better known as Count Rumford, 1753-1814). Around 1847 this suggestion was put on a firm experimental basis by the English physicist James Prescott Joule (1818-1889). The thermodynamic energy law was formulated around 1842 by the German physicist Julius Robert Mayer (1814-1878) and better established around 1847 by the German physiologist and physicist Hermann L. F. Helmholtz (1821-1894).

In 1824 (even before the recognition of heat as a form of energy) the young French engineer Nicolas L. S. Carnot (1796-1832) published pioneering work analyzing how heat engines convert heat into work. Around 1850 this work led to the formulation of the second law of thermodynamics by the German physicist Rudolf J. E. Clausius (1822-1888) and the Scottish physicist William Thomson (also known as Lord Kelvin, 1824-1907). In particular, they used purely macroscopic considerations to introduce the concepts of entropy and absolute temperature. In this way, they established "classical thermodynamics" as a macroscopic science based on the three thermodynamic laws (C-3), (C-4), and (C-5).

The motion of atoms in gases was theoretically examined around 1860 by the Scottish physicist James Clerk Maxwell (1831-1979). An atomic theory of gases, based on statistical considerations, was then fully developed in the 1870s by the Austrian physicist Ludwig Boltzmann (1844-1906). He thereby founded the science of "statistical mechanics" for dealing with macroscopic systems from an atomic point of view. In this process, he also introduced the atomic specification of the entropy, i.e., the relation $S = k \ln\Omega$.

In the 1870s the American physicist Josiah Willard Gibbs (1839-1903) expressed classical thermodynamics in a powerful mathematical form and applied it to a wide range of physical and chemical problems. Later he also formulated statistical mechanics in a more general form and showed its connection to classical thermodynamics. He thereby established a unified theory of "statistical thermodynamics". His work, done in isolation in the United States, only came to be well recognized in Europe in the 1890s. Despite later modifications by quantum mechanics, his theoretical framework still provides the basis of present-day scientific work dealing with macroscopic systems.

D. Summary and Review

Definitions

Entropy: $S = k \ln\Omega$

(where Ω = number of basic states available to atomic particles)

Important knowledge (independent of nature of atomic particles):

Thermodynamic energy law (first law of thermodynamics):

    Change of internal energy: $\Delta E = W + Q$

    (where W = work, Q = heat).

Entropy law (second law of thermodynamics):

    In any small quasi-static process, $dS = d'Q/T.$

    For any isolated system, $\Delta S \geq 0.$

Probability and entropy:

    For an isolated system $P \propto \Omega \propto e^{S/k}.$

New abilities

You should now be able to do the following:

(1) Calculate entropy changes for any quasi-static process.

(2) Apply all the principles of statistical thermodynamics jointly to solve problems like those included in this chapter.

Problems

[D-1] *Possible temperature changes of a system*

If any of the following processes is possible, give a specific example illustrating this possibility. Otherwise, prove that the process is impossible.

(a) Can the absolute temperature of a system change even if no heat is absorbed or given off by the system?

(b) Can the absolute temperature of a system change even if its internal energy remains unchanged?

(c) Can the absolute temperature of a system change even if its entropy remains unchanged? <a-6>

[D-2] *Different expansions of an ideal gas*

An ideal gas is contained in a cylinder closed by a piston. The volume of the gas can be increased under the following conditions listed in Fig. D-1: (1) By moving the piston slowly while keeping the gas in thermal contact with a heat reservoir so that its temperature remains constant. (2) By moving the piston slowly while the gas is adiabatically isolated. (3) By moving the piston extremely rapidly while the gas is adiabatically isolated.

For each of these three processes, the absolute temperature of the gas changes by an amount ΔT, its pressure changes by an amount Δp, its internal energy changes by an amount ΔE, and its entropy changes by an amount ΔS. In the table of Fig. D-1, indicate whether each of these changes is positive, negative, or zero. (Use a + sign to indicate that the change is positive, a − sign to indicate that it is negative, and 0 to indicate that it is zero.) <a-12>

	ΔT	Δp	ΔE	ΔS
slow, isothermal				
slow, adiabatic				
fast, adiabatic				

Fig. D-1. Changes resulting from expanding a gas under various conditions.

[D-3] *Entropy and volume change of an ideal gas*

One mole of an ideal gas is maintained at a constant absolute temperature T since it is in thermal contact with a heat reservoir at that temperature. The volume of the gas is then slowly changed from V_A to V_B.

(a) What is the work done on the gas in this process?

(b) What is the change of internal energy of the gas in this process?

(c) What is the heat absorbed by the gas in this process?

(d) Use the knowledge of this heat to find the change of entropy of the gas in this process.

(e) Use the general result (B-9) to calculate the change of the entropy of the gas in this process. Does your answer agree with that obtained in part *d*? <a-4>

[D-4] *Entropy change in an isothermal expansion of a gas*

One mole of an ideal gas, contained in the cylinder illustrated in Fig. D-2, is maintained in contact with a heat reservoir so that it remains at a constant absolute temperature T. The piston is now slowly moved so as to double the volume of the gas.

(a) What is the work done on the gas in this process?

(b) What is the change of internal energy of the gas in this process?

(c) What is the heat absorbed by the gas in this process?

(d) What is the resulting change of the entropy of the gas in this process?

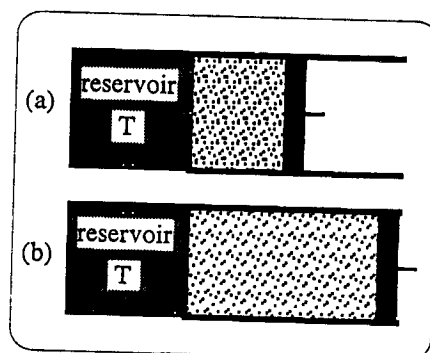(e) What is the change of the entropy of the heat reservoir in this process?

Fig. D-2. Isothermal quasi-static expansion of an ideal gas. (a) Initial state. (b) Final state.

(f) What is the change of entropy of the universe as a result of this process?

(g) Is this process reversible or irreversible? *<a-10>*

[D-5] *Entropy change in a free expansion of a gas*

One mole of an ideal gas, at an absolute temperature T, is confined by a partition within the left half of the adiabatically isolated container illustrated in Fig. D-3. When the partition is removed, the gas spreads throughout the entire container so that its volume is doubled.

(a) What is the work done on the gas in this process?

(b) What is the change of internal energy of the gas in this process?

(c) What is the heat absorbed by the gas in this process?

(d) What is the resulting change of the entropy of the gas in this process? Is this change of entropy larger than, smaller than, or the same as the change of entropy of the isothermally expanded gas in the preceding problem? *<h-2>*

(e) What is the change of entropy of the universe as a result of this process?

(f) Is this process reversible or irreversible? *<a-1>*

[D-6]† *Temperature-entropy diagram of a cyclic process*

The macroscopic state of a system may be specified by its entropy S and absolute temperature T. The graph in Fig. D-4 indicates a cyclic process *ABCA* of a system specified in this way. Express the answers to the following questions in terms of the absolute temperatures T_A and T_B of the system and in terms of its entropies S_A and S_C.

(a) What is the heat absorbed by the system in the process *AB* during which the absolute temperature of the system changes from T_A to T_B while its entropy S_A remains constant?

(b) What is the heat absorbed by the system in the process *BC* during which the entropy of the system changes from S_A to S_C while its absolute temperature T_B remains constant?

(c) What is the heat absorbed by the system in the process *CA* represented by the straight line *CA* in the graph of Fig. D-§? *<h-1>*

(d) Is the total heat absorbed by the system during the entire process *ABCA* positive, negative, or zero? Is the total work done on the system during this entire process positive, negative, or zero?

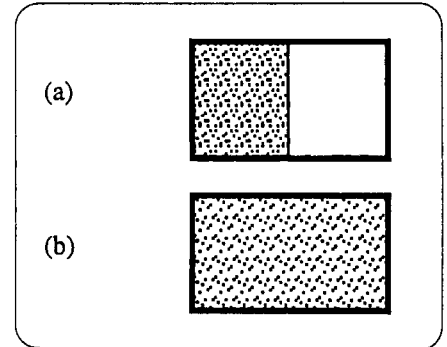(e) What is the work done on the system during this entire process? *<a-3>*

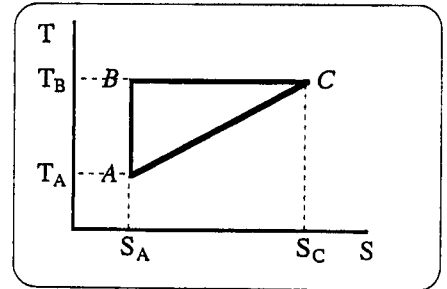**Fig. D-3.** Adiabatic free expansion of an ideal gas. (a) Initial state. (b) Final state.

Fig. D-4. Temperature entropy diagram of a cyclic process.