

9 Important Applications

- A. Heat engines and biological systems
- B. Phase transformations
- C. Probabilities at a constant temperature
- D. Summary

The thermodynamic principles summarized in the preceding chapter lead to a wide range of practical applications. Some of these, discussed in the next sections, deal with the following kind of questions: To what extent is it possible to convert the internal energy, contained in oil or other substances, so as to build engines doing the work needed to move cars or heavy machinery? How is it possible for highly structured living organisms to be created out of disorganized assemblies of molecules? Why do solids melt or liquids vaporize? Why do some molecules in a gas move with much higher speeds than others — and can one quantitatively predict what fraction of the molecules move with any specified speed?

A. Heat engines and biological systems

Creating order out of randomness

Entropy of an isolated system. Any isolated system tends to approach a more probable situation which is more random and thus characterized by larger entropy. Indeed, the entropy principle (the second law of thermodynamics) asserts that the entropy S of any isolated system tends to increase, i.e., the change ΔS of entropy of any such system is such that

$$\text{for any isolated system,} \quad \Delta S \geq 0. \quad (\text{A-1})$$

How then is it possible to create systems which are more orderly, i.e., less random? For example, one may want to produce well-ordered large-scale motions of vehicles or of pistons in machinery. How can such well-ordered motion be produced from the random motions of the molecules contained in steam or gasoline? In other words, how is it possible to build all the many machines prevalent in our modern industrial society?

Coupled systems. In order to make a system X more orderly, its entropy S must decrease so that $\Delta S \leq 0$. According to (A-1), this is certainly *not* possible if the system is isolated. On the other hand, suppose that the system is not isolated, but interacts with another system X' (as schematically indicated in Fig. A-1). Then the entropy S^* of the entire isolated system X^* , consisting of X and X' , must increase so that

$$\Delta S^* = \Delta S + \Delta S' \geq 0. \quad (\text{A-2})$$

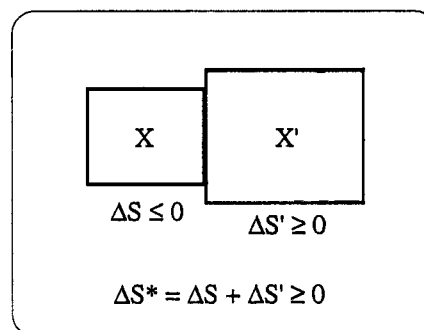


Fig. A-1. Increasing order of a system X interacting with another system X' .

But this requirement can be satisfied even if the entropy S of the system X decreases — provided that the entropy S' of the other system increases at least by a compensating amount.

The preceding considerations lead to the following general conclusion:

A system can be made less random provided that it interacts with another system whose randomness increases at least by a compensating amount.

(A-3)

Engines

An engine is a device which extracts energy from some system (e.g., from gasoline or coal) and converts it into macroscopic work done on some other system (e.g., into large-scale work to move pistons or other devices). The engine itself should not be permanently changed in this process. Thus the engine works in cycles, repeatedly returning to the same macroscopic state (so that its entropy remains unchanged).

Unrealizable ideal engine. Fig. A-2 illustrates a simple engine that one might ideally wish to construct. This engine absorbs an amount of heat q from some heat reservoir (at an absolute temperature T) and uses it to do some macroscopic work w done on some outside system. In this process, the internal energy of the heat reservoir decreases as it gives off the heat q absorbed by the engine. The energy law applied to the engine (whose own energy remains unchanged) then implies that

$$-w + q = 0 \quad \text{or} \quad w = q, \quad (\text{A-4})$$

i.e., the entire heat absorbed by the engine has simply been converted into an equivalent amount of work.

Such an ideally desirable engine can, however, *not* be constructed. Indeed, it would merely transform some of the random internal energy of the heat reservoir into orderly macroscopic work — and would thus reduce the entropy of the universe. To be specific the entropy change ΔS^* of the universe would be negative and equal to

$$\Delta S^* = \frac{-q}{T} \quad (\text{A-5})$$

since the only entropy change is that of the heat reservoir which absorbs an amount of heat $-q$.

Realizable engine. To construct a possible engine, one needs to follow the guideline (A-3) and let the engine of Fig. A-2 interact with another system whose entropy can increase by a compensating amount. Fig. A-3 illustrates such an engine which absorbs an amount of heat q from a heat reservoir (at the absolute temperature T) and gives off an amount of heat q' to another heat reservoir (at the absolute temperature T'). The heat absorbed by this second reservoir must then increase its entropy sufficiently so that the entropy the entire universe increases.

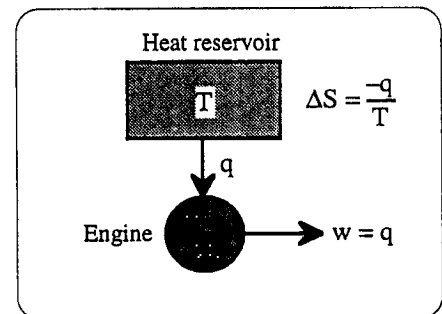


Fig. A-2. An unrealizable ideal engine. The lower-case letters q and w are here used to denote *positive* quantities of heat and work.

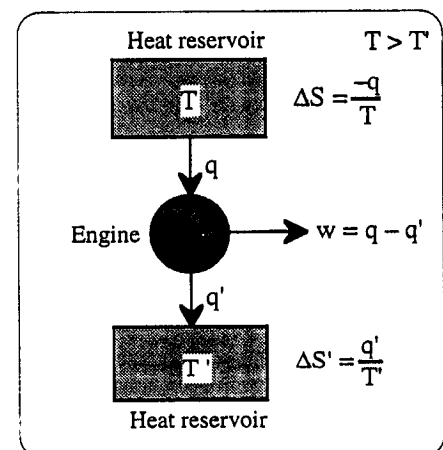


Fig. A-3. A realizable engine

The energy law applied to this engine implies that

$$0 = -w + q - q'$$

or $w = q - q'$. (A-6)

Thus the work obtained from this engine is smaller than that obtained from the unrealizable engine of Fig. A-2.

If the engine in Fig. A-3 is to do positive work, the heat q' given off to the second reservoir must be smaller than the heat q absorbed from the first reservoir. Yet, this smaller heat q' must increase the entropy of the second reservoir by a larger amount than the entropy decrease of the first reservoir. This is only possible if the absolute temperature T' of the second reservoir is sufficiently smaller than the absolute temperature of the first reservoir. The entropy change of the universe, as a result of the entropy changes of the two reservoirs, is then equal to

$$\Delta S^* = \frac{-q}{T} + \frac{q'}{T'} \geq 0. \quad (\text{A-7})$$

As indicated above, this total entropy change must be positive.

Efficiency of a engine. The heat q' given off to the second reservoir is, by (A-6), equal to

$$q' = q - w.$$

By substituting this into entropy condition (A-7), one then obtains

$$\Delta S^* = \frac{-q}{T} + \frac{q-w}{T'} \geq 0.$$

Hence
$$\frac{w}{T} \leq q \left(\frac{1}{T'} - \frac{1}{T} \right)$$

or
$$\frac{w}{q} \leq 1 - \frac{T'}{T} = \frac{T - T'}{T}. \quad (\text{A-8})$$

This ratio w/q compares the work done by the engine to the heat put into it. The ratio is called the engine's *efficiency* and is denoted by the letter η (the Greek letter *eta*). Because some heat q' is given off to the second reservoir, this efficiency is less than 1 (the efficiency of the unrealizable engine of Fig. A-2). The relation (A-8) thus implies that

$\text{engine efficiency: } \eta = \frac{q - q'}{q} \leq \frac{T - T'}{T}.$	(A-9)
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The *maximum* possible efficiency of an engine, operating between two heat reservoirs at the absolute temperatures T and T' , is thus equal to $(T' - T)/T$. The maximum possible efficiency is, therefore, larger if the temperature difference between the heat reservoirs is larger.

The maximum possible efficiency, corresponding to the equals sign in (A-9), could only be achieved if the entropy of the combined systems remains unchanged. For example, it might be achieved if the engine operated quasi-statically so that the systems would essentially always remain in equilibrium.

Example: Steam engine

Suppose that a steam engine operates between the temperature of boiling water at atmospheric pressure (100°C or 373 K) and a condenser at room temperature (20°C or 293 K). According to (A-9), the maximum possible efficiency of such a steam engine would thus be

$$\eta_{\max} = \frac{T - T'}{T} = \frac{373 - 293}{373} = \frac{80}{373} = 0.21.$$

Real steam engines have efficiencies smaller than this because of frictional effects and other factors preventing the conversion of heat into useful available work. However, the attainable efficiency can be increased by increasing the temperature difference, e.g., by using superheated steam at temperatures above 100°C.

Biological systems

Biological systems grow by becoming more orderly and thus decreasing their entropy. According to (A-3), this is only possible because they increase the entropy of their environment by more than a compensating amount.

An isolated biological organism could not survive. For example, a baby put into a completely isolated box would soon die and decompose into simpler chemical compounds. In this process, a well-organized biological organism would become transformed into more disordered substances. The entropy of the isolated system (consisting of the box and its contents) would then correspondingly increase.

Of course, one would never want to treat a baby like this. On the other hand, suppose that one puts the baby in a box which also contains milk, carrots, and other foods. The baby itself is then *not* an isolated system. Thus the baby could grow, forming highly organized biological organs of increasing size and thus decreasing its entropy. On the other hand, the carrots and other foods in its environment would be transformed into feces and other much less well-organized chemicals, i.e., their entropy would increase by more than a compensating amount. Thus the baby could grow while the entropy of the entire isolated system (consisting of the box and its contents) again increases.

Similar considerations apply on a molecular biochemical scale. For example, the formation of proteins involves the ordered assembly of simple molecules into well-ordered polymer chains. This is clearly a process which involves increasing order, i.e., decreasing randomness or decreasing entropy. Such processes must, therefore, always involve coupled chemical reactions in which other chemical compounds are transformed into less ordered form — so that their entropy increases by more than a compensating amount.

Problems

[A-1] Work obtainable from a steam turbine

A steam turbine is operated with an intake temperature of 400°C and an exhaust temperature of 150°C . Suppose that an amount of heat Q is supplied to the turbine at its intake.

- What is the minimum amount of heat which leaves the turbine exhaust?
- What is the maximum work which the turbine can do? $\langle h-9 \rangle \langle a-7 \rangle$

[A-2] Refrigerators

A refrigerator is a device which extracts heat from some system X and then gives off this system to an environment X' at a higher absolute temperature. In particular, consider the situation where the system X is a heat reservoir at a constant absolute temperature T and the environment X' is a heat reservoir at a higher absolute temperature T' . (The refrigerator itself merely goes through some cyclic process so that there is no net change in its entropy or other properties.)

- Fig. A-4 illustrates such a refrigerator designed to extract an amount of heat q from the system X and to give off this heat to the environment X' . What then would be the entropy change of the total system consisting of X and X' ? Is this entropy change positive or negative? Could such a refrigerator be constructed?
- Fig. A-5 illustrates a more realistic refrigerator where some positive work w is done on the refrigerator to extract some heat q from the system at the lower temperature. Some amount of heat q' is then given off to the reservoir at the higher temperature. How is the heat q' related to the heat q and the work w ?
- Use entropy considerations to show that the heats q and q' must be related to that $q/q' \leq T/T'$.
- The *coefficient of performance* of a refrigerator is the ratio q/w of the heat q , extracted from the system at the lower temperature, compared to the work w which needs to be done to extract it. What then is the maximum possible value of the coefficient of performance of the refrigerator in Fig. A-5? Express your answer in terms of the absolute temperatures T and T' of the reservoirs. $\langle a-6 \rangle$

Note that the refrigerator in Fig. A-5 is similar to the engine in Fig. A-3 but is running backwards (i.e., work is done to extract heat instead of heat being absorbed to do work).

[A-3] Heat pump used for heating a house

To heat a house in the winter, some electric work w can be done on an electric heater so as to supply to the house an amount of heat $q = w$. Alternatively one may do this electric work to run a special refrigerator (called a "heat pump") which supplies the heat q to the house by extracting some heat q_0 from the colder outside surroundings of the house.

Assume that the inside of the house is to be kept at the constant absolute temperature T while the outside surroundings of the house are at a lower constant absolute temperature T_0 .

- It is useful to compare the heat q supplied to the house by the heat pump with the work w that needs to be done on this pump. Use entropy considerations to determine the maximum value of the ratio q/w . Express your answer in terms of the absolute temperatures T and T_0 .
- What is the maximum value of the ratio q/w if the inside of the house is to be maintained at a temperature of 25°C and the outside surroundings of the house are at a temperature of 0°C ? Which requires a lower cost of needed electricity, the heat pump or an electric heater? $\langle a-12 \rangle$

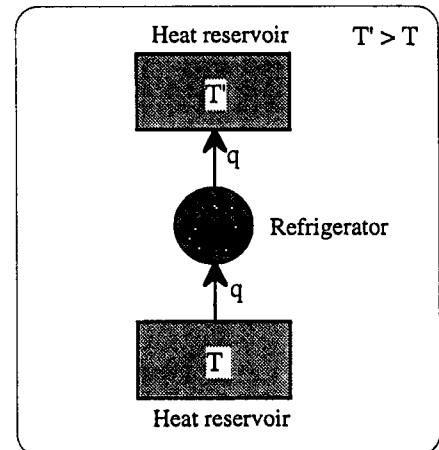


Fig. A-4. A hypothetical refrigerator.

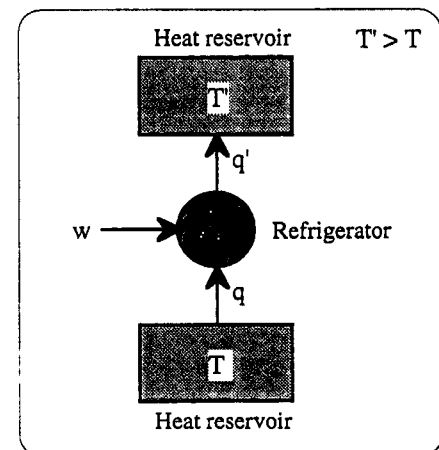


Fig. A-5. A realizable refrigerator.

B. Phase transformations

A system may often exist in several different forms. Thus, a substance may exist in the form of different *phases* corresponding to different arrangements of its molecules. (For example, the substance may exist in the form of a solid, a liquid, or a gas). A system may also consist of the same atoms combined into different kinds of molecules. (For example, the system might be a gas mixture consisting of CO, CO₂, and O₂ molecules in chemical equilibrium.) In all such cases, one may want to know in what form the system exists at different temperatures or pressures.

System interacting with a large environment

To examine this question, consider such a system X in contact with its environment X' (e.g., the system in contact with the surrounding atmosphere). If this environment X' is much larger than the system X, its temperature does not change significantly irrespective of any amount of energy transferred to the much smaller system, nor does its pressure p' change significantly irrespective of any volume change of the much smaller system. The absolute temperature T' and pressure p' of the environment can thus be clearly specified. Correspondingly, one can examine the properties of the system X when it is in equilibrium with its environment at any such temperature T' and pressure p'.

If the system X can exist in two different forms A and B, in which form is it more likely to be? To answer this question, consider the entropy S* of the total isolated system X* consisting of X and its environment X'. Then we know that this isolated system is more likely to be in equilibrium in the situation corresponding to a larger value of its entropy S*.

Suppose that the entropy of the total system is S_A* when the system X is in form A, and that the entropy of the total system is S_B* when the system is in form B. These entropies can be compared by considering the change

$$\Delta S^* = S_B - S_A \quad (\text{B-1})$$

of the total entropy when X changes from the form A to the form B. Then we can conclude the following:

- If S_B* > S_A (so that ΔS* > 0), then the system X is much more likely to be in form B.
- If S_B* < S_A (so that ΔS* < 0), then the system X is much more likely to be in form A.
- If S_B* = S_A (so that ΔS* = 0), then the system X can exist in equilibrium in any mixture of forms A and B.

The total isolated system X* is schematically illustrated in Fig. B-1. Its entropy change (B-1) is equal to

$$\Delta S^* = \Delta S + \Delta S' \quad (\text{B-3})$$

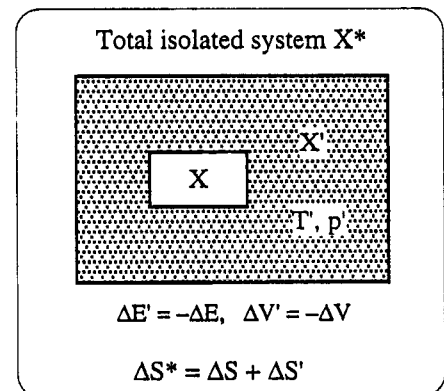


Fig. B-1. A system X interacting with a large environment X'.

where $\Delta S = S_B - S_A$ is the entropy change of the system X and $\Delta S' = S'_B - S'_A$ is the corresponding entropy change of its environment. But since the temperature T' and pressure p' of the environment remain constant, the entropy change of the environment is simply related to the heat Q' absorbed by it. Thus

$$\Delta S' = \frac{Q'}{T'} = \frac{\Delta E' + p' \Delta V'}{T'}. \quad (\text{B-4})$$

Here we have used the thermodynamic energy law to write

$$Q' = \Delta E' - W' = \Delta E' + p' \Delta V' \quad (\text{B-5})$$

where $\Delta E'$ is the energy change of the environment and where $W' = -p' \Delta V'$ is the work done on it when its volume change by an amount $\Delta V'$.

But since the energy and volume of the total isolated system remain constant,

$$\Delta E' = -\Delta E \quad \text{and} \quad \Delta V' = -\Delta V.$$

Hence the heat absorbed by the environment is simply related to the quantities describing the system X itself, i.e.,

$$Q' = -\Delta E - p' \Delta V = -Q \quad (\text{B-6})$$

where Q is the heat absorbed by the system X when it changes from form A to form B. Thus the entropy change (B-3) of the total system is equal to

$$\Delta S^* = \Delta S - \frac{Q}{T'} = \Delta S - \left(\frac{\Delta E + p' \Delta V}{T'} \right). \quad (\text{B-7})$$

Phases existing in equilibrium

Consider then the specific case where a substance can exist in two different phases A and B. For example, phase A might be the solid form of the substance and phase B might be the liquid form. Or phase A might be the liquid form and phase B might be the gaseous form. Or phase A might be the solid form and phase B might be the gaseous form.

Entropies and internal energies of different phases. In all these cases, the entropy of phase B is larger than that of phase A. For example, the entropy of the liquid is larger than that of the solid since the molecules in the liquid can move randomly about instead of being confined to remain near their fixed positions in the solid. Similarly, the entropy of the gas is larger than that of the liquid since the molecules can then move randomly throughout the entire volume of the confining container instead of being constrained to remain near each other by the attractive forces due to neighboring molecules.

In all these cases, the internal energy of phase B is also larger than that of phase A. For example, the internal energy of the liquid is larger than that of the solid since the molecules in the liquid can move about much more freely and thus have much larger kinetic energy. Similarly the internal energy of the gas is

larger than that of the liquid since the molecules are then much farther apart so that their potential energy of interaction is small (i.e., larger than the negative potential energy due to the attractive intermolecular forces in the liquid).

The entropies and internal energies of the phases A and B are thus related so that

$$S_B > S_A \quad \text{and} \quad E_B > E_A. \quad (\text{B-8})$$

Phases existing at different temperatures

At a particular temperature T' of the environment, is it more likely that the substance will exist in the form of phase A or in the form of phase B?

According to (B-2), we can answer this question by considering the entropy change ΔS^* of the total isolated system when the substance changes from phase A to phase B. When this happens, the entropy S of the substance increases. But since the substance absorbs some positive heat Q from the environment, the entropy S' of the environment decreases. The resultant effect on the total entropy change ΔS^* , specified in (B-7), depends then on the relative magnitudes of these entropy changes.

If the absolute temperature T' is sufficiently high, the entropy change $\Delta S' = -Q/T'$ of the environment has a smaller magnitude than the entropy change ΔS of the substance. The entropy change ΔS^* of the total system is, therefore, positive. Hence the total system can attain a larger entropy if the substance changes to the higher-entropy form B. At sufficiently high temperatures the substance will, therefore, exist in its high-entropy form. (This is why, at sufficiently high temperatures, solids change into liquids and liquids change into gases.)

But if the absolute temperature T' is sufficiently low, the entropy change $\Delta S' = -Q/T'$ of the environment has a *larger* magnitude than the entropy change ΔS of the substance. The entropy change ΔS^* of the total system is, therefore, negative. Hence the total system can attain a larger entropy if the substance changes to the lower-entropy form A because the entropy of the environment increases by more than a compensating amount. At sufficiently low temperatures the substance will, therefore, exist in its low-entropy form. (This is why, at sufficiently low temperatures, gases change into liquids and liquids change into solids.)

Lastly, there exists the special situation where the entropy change of the total system is zero (because the entropy increase of the substance is exactly compensated by a corresponding entropy decrease of its environment). According to (B-7), this special situation corresponds to one where the absolute temperature T' is such that

$$\Delta S^* = \Delta S - \frac{Q}{T'} = \Delta S - \left(\frac{\Delta E + p' \Delta V}{T'} \right) = 0$$

so that

$$T' = \frac{Q}{\Delta S} = \frac{\Delta E + p' \Delta V}{\Delta S}. \quad (\text{B-9})$$

At this special temperature, any amounts of the two phases of the substance can, therefore, coexist in equilibrium. (For example, at the temperature of 0°C any amounts of ice and water can coexist in equilibrium.)

Fig. B-2 summarizes the preceding conclusions by indicating in which temperature regions the substance will exist in phase A or in phase B.

Phases existing at different pressures

The preceding paragraphs examined the effects of the temperature when the substance is maintained at a fixed pressure p' of its environment. But this pressure too has an effect. Indeed, the heat Q absorbed by the system in a phase change depends on the pressure since the environment can do work on the substance if its volume changes. Hence the entropy change $\Delta S' = -Q/T$ of the environment is correspondingly affected.

The result (B-9) indicates explicitly how the pressure affects the temperature at which the phases A and B can coexist in equilibrium.

If the volume of the substance does not change in changing from phase A to phase B, then $\Delta V = 0$ so that $p'\Delta V = 0$. Hence (B-9) indicates that the coexistence temperature T' is then unaffected by pressure.

If the volume of the substance *increases* in changing from phase A to phase B, then $\Delta V > 0$ so that $p'\Delta V > 0$. Hence (B-9) indicates that the coexistence temperature T' is *larger* if the pressure p' is larger. [For example, most substances increase their volume when they melt so as to change from their solid to liquid forms. Thus (B-9) predicts that an increase in atmospheric pressure should raise the temperature at which such a substance melts.]

If the volume of the substance *decreases* in changing from phase A to phase B, then $\Delta V < 0$ so that $p'\Delta V < 0$. Hence (B-9) indicates that the coexistence temperature T' is *smaller* if the pressure p' is larger. [For example, a substance like water is exceptional in that its volume *decreases* when it melts when changing from ice into liquid water. Thus (B-9) predicts that an increase in atmospheric pressure should *lower* the temperature at which ice melts.]

Phase diagrams

All the preceding conclusions can be summarized in a *phase diagram* for any particular substance. Such a typical phase diagram, illustrated in Fig. B-3, indicates in what phase the substance is found in equilibrium at any particular temperature T' and pressure p' . The curves indicate the temperatures and corresponding pressures at which two phases can coexist in equilibrium. (In particular, the *melting curve* indicates when the solid and liquid can coexist, the *sublimation curve* indicates where the solid and gas can coexist, and the *vaporization curve* indicates where the liquid and gas can coexist.) The regions

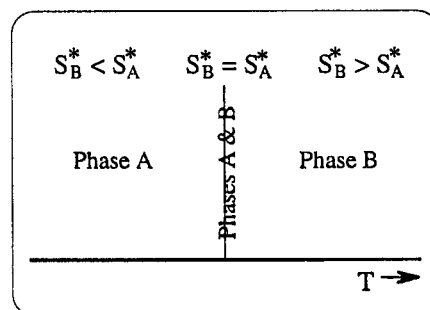


Fig. B-2. Phases existing at different temperatures.

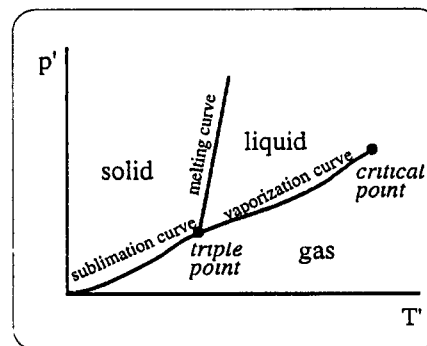


Fig. B-3. Phase diagram for a typical substance.

between these curves indicates ranges of temperature and pressure at which only one particular phase of the substance can exist in equilibrium.

All three coexistence curves meet at a single point called the *triple point*. This point indicates the unique temperature and pressure at which all *three* phases of the substance can coexist in equilibrium. (The temperature at which this is possible for a particular substance is thus very well specified. This is why the triple point of water has been chosen as a standard for defining the Kelvin temperature scale.)

As the pressure is increased, a gas becomes increasingly dense and becomes ultimately indistinguishable from a liquid. This is why the vaporization curve ultimately ends at a point called the *critical point*. At pressures below that corresponding to this point there is a well-observable phase transformation between the liquid and the gas. But at pressures higher than that, there is no distinct phase transformation, but merely a continuous transformation of liquid into dense gas.

The phase diagrams of some substances can be considerably more complicated. For example, there exist many different solid phases of water (i.e., of ice), corresponding to different crystal structures — with corresponding possible phase transformations between all of these.

Problems

[B-1] Phase changes with increasing temperature

Consider a substance whose phase diagram is shown in Fig. B-4. Suppose that one starts with this substance in its solid form at some low temperature and gradually increases its temperature. If one does this at each of the following pressures, what phase transformations occur and what phases of the substance will be successively observed?

- At a fairly low pressure like p_1 .
- At a moderate pressure like p_2 .
- At a high pressure like p_3 . <a-16>

[B-2] Phase changes with increasing pressure

Consider a substance whose phase diagram is shown in Fig. B-5. Suppose that one starts with this substance in its gaseous form at some very low pressure and gradually increases its pressure. If one does this at each of the following temperatures, what phase transformations occur and what phases of the substance will be successively observed?

- At a fairly low temperature like T_1 .
- At a moderate temperature like T_2 .
- At a high temperature like T_3 . <a-3>

[B-3] Phase diagrams for different kinds of substances

Fig. B-3 illustrates the phase diagram of a particular substance.

- When this substance melts, so as to change from its solid to its liquid form, does its volume increase, decrease, or remain the same?
- The fact that ice floats on the surface of a lake indicates that the volume of ice is larger than the volume of the same amount of liquid water. In what way would the phase diagram for water differ from that shown in Fig. B-3? Sketch this phase diagram. <h-9> <a-13>

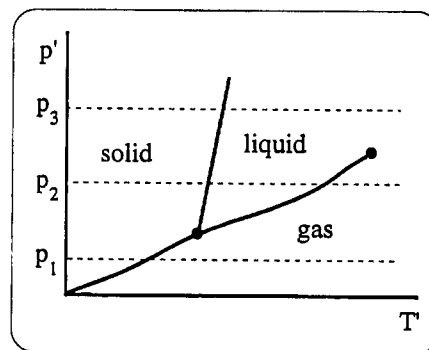


Fig. B-4. Phase diagram viewed at different pressures.

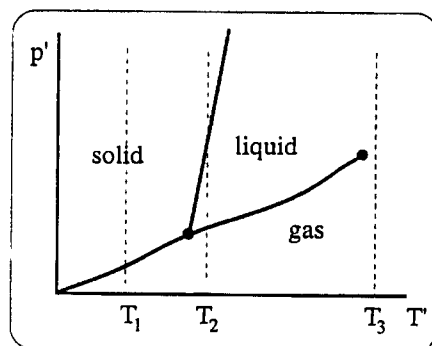


Fig. B-5. Phase diagram viewed at different temperatures.

C. Probabilities at a constant temperature

Isolated system. If a system X is isolated, its total energy has some constant value. According to the basic statistical postulate (3B-2), such a system in equilibrium is then equally likely to be in any one of its basic states consistent with this total energy.

System interacting with a large environment. However, it is much more common that a system X is *not* isolated, but interacts with a much larger environment X' whose temperature T' remains essentially constant (because it is nearly unaffected by any heat absorbed from the much smaller system.). For example, a glass of water sitting in a room interacts with the air and walls of the room whose temperature remains essentially constant. Similarly, any one molecule in a gas interacts with all the molecules in the rest of the gas whose temperature remains essentially constant.

Under these conditions, it is only the total energy E* of the entire system X* (consisting of X and X') which remains constant. Hence the system X can have different possible energies. Furthermore, it is only the entire isolated system X* which is equally likely to be found in any one of its basic states.

Probability of being in any basic state

Consider such a system X in equilibrium while interacting with its environment X' at an absolute temperature T'. What then is the probability P_r that this system is found in any one of its basic states r where its energy is E_r?

This probability is proportional to the number Ω* of basic states available to the entire isolated system X* under these conditions. But, when the system X is in the *one* particular state r, the number Ω* of basic states available to the entire system is just the number of basic states Ω' available to its environment X'. Thus

$$P_r \propto \Omega' \propto e^{S'/k} \tag{C-1}$$

where S' = k lnΩ' is the entropy of the environment.

Qualitative considerations. Suppose that the system X is in a particular state r where its energy E_r is small. (See Fig. C-1.) Since

$$E_r + E' = E^* = \text{constant}$$

or
$$E' = E^* - E_r, \tag{C-2}$$

the energy E' of the environment X' must then be correspondingly large. Accordingly, the number of basic states available to the environment is also large. Hence (C-1) implies that the probability of this situation (where X is found in a state of small energy) is relatively large.

Suppose, however, that the system X is in a particular state r where its energy E_r is larger than before. Then the energy of the environment X' must be correspondingly smaller. Accordingly, the number of basic states available to

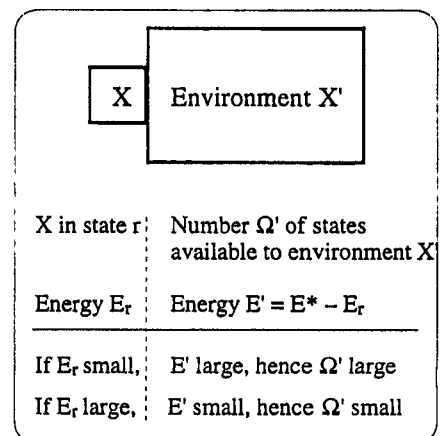


Fig. C-1. A system X in equilibrium with a much larger environment X'.

the environment is also smaller. Hence (C-1) implies that the probability of this situation (where X is found in a state of larger energy) is correspondingly smaller.

In short, it is more probable that the system X is found in a state of low energy than in a state of high energy (because the number of basic states available to its environment is then larger).

Quantitative description. The preceding qualitative considerations can easily be made quantitative. The entropy S' of the environment X' depends on its energy E' . As is apparent from (C-1), this energy differs from the energy E^* of the entire system only by the much smaller energy E_r of the system X. Correspondingly, the entropy S' of the environment differs only slightly from the entropy S'_0 which it would have if it had the energy E^* of the entire isolated system. This difference can, therefore, be written as

$$S' - S'_0 = \frac{dS'}{dE'} (-E_r) \quad (\text{C-3})$$

where the rate of change dS'/dE' indicates how rapidly the environment's entropy S' varies with its energy E' . But this rate of change is simply related to the absolute temperature T of the environment. Indeed, by the definition (§) of absolute temperature, (C-3) is simply

$$S' - S'_0 = \left(\frac{1}{kT} \right) (-E_r)$$

so that
$$S' = S'_0 - \frac{E_r}{kT} \quad (\text{C-4})$$

The probability (C-1) is thus simply equal to

$$P_r \propto e^{S'_0 - (E_r/kT)} = e^{S'_0} e^{-(E_r/kT)}$$

or
$$\boxed{P_r \propto e^{-(E_r/kT)}} \quad (\text{C-5})$$

since $e^{S'_0}$ is merely a constant factor.

The result (C-5), which is very widely useful, agrees with our previous qualitative conclusions. Indeed, it shows explicitly that a state r with a larger energy E_r is less probable than one with a smaller energy. It also indicates that the difference between these probabilities is more pronounced if the absolute temperature T is lower.

The result (C-5) is called the "canonical distribution". The exponential factor in (C-5) is also known as the "Boltzmann factor".

Molecular velocities in a gas

Probable velocity of a molecule. The preceding result can be immediately applied to predict the probable velocities of a molecule in a gas at an absolute temperature T . Any molecule in such a gas interacts with an environment consisting of all the other molecules at an absolute temperature T . This molecule can be in any basic state specified by the molecule's position and

velocity. The energy of the molecule in any such state r , where its velocity is \vec{v} , is merely its kinetic energy

$$E_r = \frac{1}{2} m v^2 \tag{C-6}$$

if we neglect the molecule's gravitational potential energy which is much smaller than its kinetic energy. According to (C-5), the probability P_r that the molecule is in this particular state is then

$$P_r \propto e^{-m v^2 / 2 k T} \tag{C-7}$$

Probable speeds of a molecule. The result (C-7) specifies the probability that a molecule is in a particular basic state where corresponding to one of its possible velocities \vec{v} . What then is the probability P_v that the molecule has a some speed in the range between v and some slightly larger speed $v + dv$?

The molecule can have many possible velocities, with different directions, corresponding to speeds in this range. The points in Fig. C-2 indicate the possible discretely described values of the molecule's velocities (corresponding to the possible discrete values of its velocity components v_x , v_y , and v_z). The possible values of the molecule's velocities, corresponding to speeds in the range between v and $v + dv$, are then indicated in Fig. C-2 by all those points which lie in the shaded spherical shell of radius v and thickness dv . The number of such points is proportional to the volume of this spherical shell (a volume equal to the area $4\pi v^2$ of the shell multiplied by its thickness dv). The probability P_v that a molecule has a speed in the range between v and $v + dv$ is then obtained by multiplying the probability (C-7) that the molecule has any particular velocity in this range by the total number of possible velocities in this range. Thus

$$P_v \propto (4\pi v^2 dv) e^{-m v^2 / 2 k T} \tag{C-8}$$

(This result is known as the "Maxwell speed distribution".)

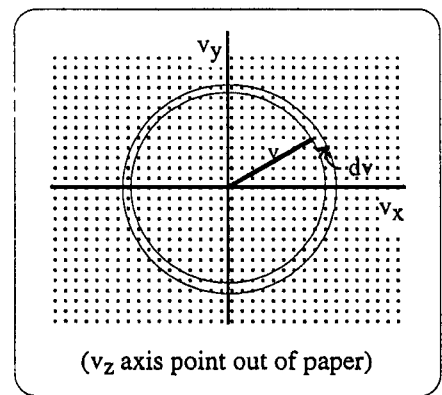


Fig. C-2. Range of molecular speeds between v and $v + dv$. (The points indicate possible discrete velocities of a molecule.)

The Scottish physicist James Clerk Maxwell (1831-1879), who is best known for his fundamental contributions to electromagnetic theory, derived this result in the year 1860.

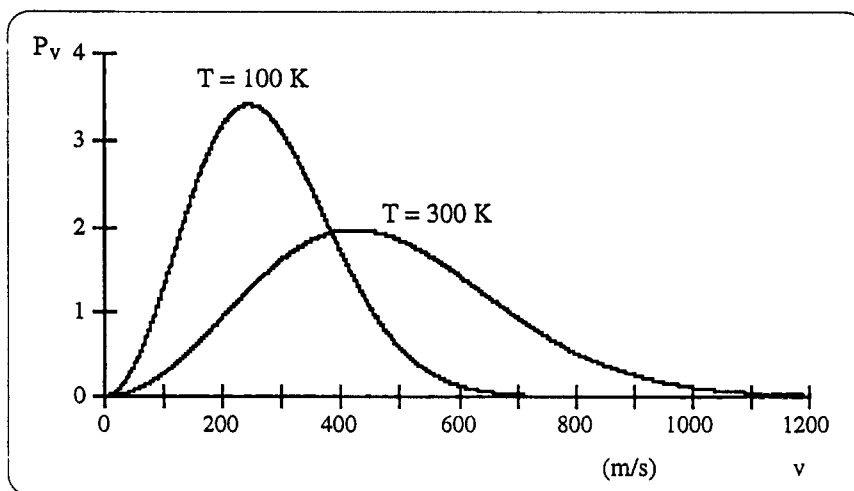


Fig. C-3. Probability P_v that a molecule in nitrogen gas has a speed in the range between v and $v + dv$.

Fig. C-3 illustrates graphically the probabilities of various molecular speeds at some absolute temperature of the gas. Note that there is a speed which is most probable; speeds much larger than that are much less probable. If the absolute temperature is larger, the most probable speed is correspondingly larger and the range of appreciably probable speeds is also larger.

Experimental verification. Experimental information about the speeds of the molecules in a gas can be obtained by making a very small hole in the vessel containing the gas. Some of the molecules then escape through this hole into a surrounding vacuum. The speeds of these escaping molecules can then be readily measured and are closely related to the speeds of the molecules inside the gas.

For example, such a measurement can be made with an arrangement like that indicated in Fig. C-4. Here the first shutter is momentarily opened, letting a bunch of molecules pass through. Some time t later, the second shutter is momentarily opened. If the distance between the shutters is L , only those molecules traveling with a speed $v = L/t$ pass through both shutters. In this way one can measure how many molecules have any particular speed.

Such experimental measurements have well confirmed the theoretically predicted probabilities of molecular speeds.

Problems

[C-1] Height dependence of molecules in a gas

A gas of molecules, each having a mass m , is located near the surface of the earth where the gravitational acceleration has a magnitude g . The following questions examine the effect of the gravitational interactions on the gas when it is in equilibrium at an absolute temperature T .

- What is the gravitational potential energy of a gas molecule located at a height h above the surface of the earth?
- Such a molecule (having any particular velocity) has a probability P of being located within a small range of heights near the height h . How does this probability depend on the height h ?
- What is the ratio P'/P of the probabilities that such a molecule is found near the height h' rather than near the height h ?
- Suppose that the gas is nitrogen gas, at a temperature of 25°C , contained in a 4-meter high room. What then is the ratio P'/P of the probability P' that a nitrogen molecule (whose molecular weight is 28) is found near the ceiling of the room compared to the probability P that it is found near the floor? Is this ratio significantly different from 1, or are the molecules nearly uniformly distributed throughout the entire room?
- How large would the difference ($h' - h$) of heights have to be so that the ratio $P'/P = 0.90$? <a-18>

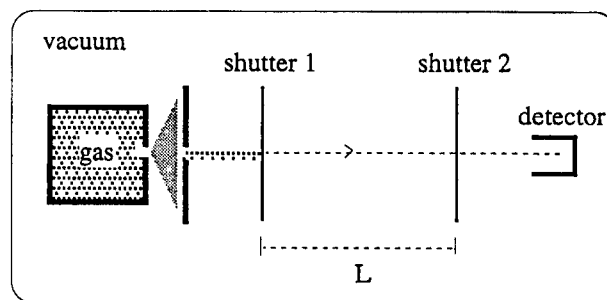


Fig. C-4. Measurement of the speeds of molecules escaping through a small hole of a gas-filled container.

A convenient shutter can be made by rotating a solid wheel with a slot in it.

D. Summary

Important knowledge

System interacting with its environment:

Relation between entropies: $\Delta S + \Delta S' \geq 0$

(A system's entropy can be decreased if the entropy of its environment is increased by at least a compensating amount)

Application to heat engines: Efficiency $\eta \leq (T - T')/T$.

Phase transformations:

Total entropy change in a transformation: $\Delta S^* = \Delta S - Q/T'$

(where ΔS is entropy change and Q heat absorbed in transformation).

Phases are in equilibrium if $\Delta S^* = 0$, i.e., at temperature $T' = Q/\Delta S$.

Application to phase diagrams. (See Fig. B-3.)

Probabilities at a constant temperature:

Probability of being in any one basic state r : $P_r \propto e^{-(E_r/kT)}$.

Application to molecular speeds in a gas. (See Fig. C-3.)

New abilities

You should now be able to do the following:

- (1) Use entropy arguments in order to discuss the possible functioning of heat engines or refrigerators.
- (2) Use phase diagrams to determine which phases of a substance will exist at particular temperatures or pressures.
- (3) Compare the probabilities that a system, maintained at a constant temperature, is in any two of its basis states.

Problems

[D-1] *Temperature inside a refrigerator*

A refrigerator is designed to maintain a constant temperature of its contents while removing from them an amount of heat q . The heat extracted from the refrigerator is given off to the surrounding room maintained at a higher constant absolute temperature T_0 . An amount of work w is done on the compressor used to operate this refrigerator.

- (a) Use entropy considerations to determine the minimum absolute temperature which can be maintained inside the refrigerator under these conditions. Express your answer in terms of T_0 , q , and w .
- (b) Suppose that the heat to be removed from the refrigerator is that due to a 100-watt light bulb used to illuminate its inside, and that the power available to run the compressor is also 100 watt. What then is the minimum temperature which can be maintained inside the refrigerator if the temperature of the room is 300 K? <a-2>

[D-2] *Work needed to freeze water*

An electric freezer is designed to take water at 25°C and cool it down so as to produce ice at 0°C. The heat extracted in this process is rejected to the room

whose temperature remains nearly constant at 25°C. The heat capacity of one gram of water is 4.19 J/K and the heat liberated when one gram of water freezes at 0°C is 333 J.

- How much heat must be extracted from one gram of water at 25°C to transform it into ice at 0°C?
- What is the entropy change of the water in this process?
- What is the entropy change of the room in this process if some amount w of electrical work is done to operate the freezer?
- What is the minimum amount of such electrical work which must be done? <a-14>

[D-3] Work obtainable by extracting heat from two identical systems

Each of two identical systems has a temperature-independent heat capacity C . Suppose that a heat engine is operated by extracting heat from one of these systems, initially at an absolute temperature T_1 , and rejecting heat to the other system, initially at a lower absolute temperature T_2 . After the engine has done a total amount of work w on its environment, the two systems then reach a common final absolute temperature T_f .

- What is the total amount work w done by the engine? Express your answer in terms of the heat capacity C and the temperatures T_1 , T_2 , and T_f . <h-7>
- Use entropy considerations to derive an inequality relating the final temperature T_f to the initial temperatures T_1 and T_2 .
- What is the maximum total work which can be done by this engine if the systems are initially at the absolute temperatures T_1 and T_2 ? <a-10>

[D-4] Cooling one object at the expense of another

Two identical objects, each of which has a temperature-independent heat capacity C , are initially at the same absolute temperature T . It is desired to cool one of these objects to a lower absolute temperature T_1 by using a refrigerator which extracts heat from this object and gives all heat off to the other object.

- What then is the minimum absolute temperature attained by the other object? <h-10>
- What is the minimum work which must be done on the refrigerator to accomplish this task? <a-1>

[D-5] Time needed to freeze water

What is the shortest possible time needed to freeze 2.0 kg water at 0°C if a 50-watt motor is available to run the freezer which rejects heat to its surroundings at the constant temperature of 27°C? (The heat needed to melt 1.0 kg of ice is 3.33×10^5 J.) <h-12> <a-5>

[D-6] Free energy of a system in contact with a large environment

Suppose that a system X is in contact with an environment X' which is so large that its absolute temperature T' and pressure p' remain essentially constant (irrespective of any energy or volume change of the system). The total entropy of $S + S'$ of the total isolated system consisting of X and X' then tends to increase and to approach a maximum value.

Show that the quantity

$$G = E - T'S + p'V$$

(where E is the energy of the system, S is its entropy, and V is its volume) then tends to decrease and to approach a minimum value. (The quantity G is called the "Gibbs free energy" of the system.) <h-4>

[D-7] Engine process described by temperature and entropy

A heat engine operates quasi-statically by going through the successive states $ABCD$ of the cyclic process indicated in Fig. D-1. The graph in this figure shows how the entropy S of the engine varies with its absolute temperature T . Answer the following questions without making any special assumptions about the nature of the engine.

- What is the numerical value of the heat absorbed by the engine in the process AB during which the engine does some work while its temperature is kept at the constant value $T_2 = 400\text{K}$?
- What is the numerical value of the heat absorbed by the engine in the process CD during which the engine does some work while its temperature is kept at the constant value $T_1 = 300\text{K}$?
- What is the numerical value of the work done by the engine in one cycle?
- What is the efficiency of the engine? $\langle h-1 \rangle \langle a-8 \rangle$

[D-8]† Carnot engine

In 1824 Carnot analyzed a particular idealized engine which can convert some of the internal energy of two heat reservoirs into usable macroscopic work. This engine operates with ν moles of any ideal gas and goes quasi-statically through the cyclic process $ABCD$ illustrated in Fig. D-2. The gas has, at constant volume, a temperature-independent specific heat c .

- In the process AB , the gas is maintained at the constant temperature T of the warmer reservoir while its volume is changed from V_A to V_B . In this process, what is the heat Q_{AB} absorbed by the gas from this reservoir? Is this heat positive or negative? Express your answer in terms of ν , R , T , and the volumes V_A and V_B . $\langle h-3 \rangle$
- In the process CD , the gas is maintained at the constant temperature T' of the colder reservoir while its volume is changed from V_C to V_D . In this process, what is the heat Q_{CD} by the gas to this reservoir? Is this heat positive or negative? Express your answer in terms of ν , R , T' , and the volumes V_C and V_D .
- In the adiabatic process BC the volume of the gas changes while its temperature changes from T to T' . What then is the ratio V_C/V_B of the volumes of the gas? Express your answer in terms of T and T' .
- In the adiabatic process DA the volume of the gas changes while its temperature changes from T' to T . What then is the ratio V_A/V_D of the volumes of the gas? Express your answer in terms of T and T' .
- By combining the results found in parts a and b with the results found in parts c and d , find the ratio Q_{AB}/Q_{CD} of the heats absorbed by the gas from the two reservoirs. Express your answer solely in terms of the temperatures T and T' of these reservoirs.
- What is the total work w done by the gas on its surroundings during the complete cycle $ABCD$? Express your answer in terms of the heats absorbed from the two reservoirs. $\langle h-6 \rangle$
- Use the preceding results to calculate the efficiency w/Q_{AB} of the engine. Express your answer solely in terms of the temperatures T and T' of the two heat reservoirs. Does the efficiency calculated for this particular engine agree with the general result (A-9) which specifies the efficiency of any engine operating quasi-statically between two heat reservoirs? $\langle a-4 \rangle$

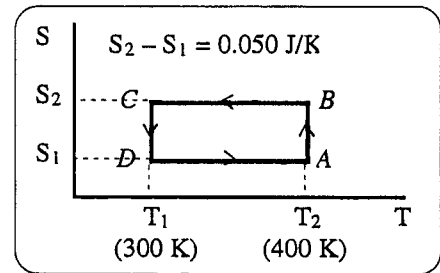


Fig. D-1. Engine process described by temperature and entropy.

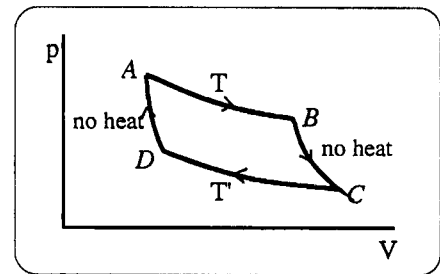


Fig. D-2. Cyclic process of a Carnot engine.

[D-9]‡ Gasoline engine

A gasoline engine operates by letting a gas, consisting of air with a small amount of gasoline, enter a cylinder closed by a movable piston. The gas then goes through a cyclic process *approximately* described by the graph in Fig. D-3 which shows how the pressure p of the gas varies with its volume V . Here AB represents the adiabatic compression of the air-gasoline mixture; BC represents the rise in pressure due to the explosion of the gas mixture at constant volume (since the explosion occurs so rapidly that the piston has no time to move); CD represents the adiabatic expansion of the gas mixture while it does useful work by moving the piston; and DA represents the final cooling of the gas at constant volume during the exhaust phase of the cycle.

An approximate analysis of this engine can be achieved by assuming that the previous cycle is carried out quasi-statically with a fixed amount of ideal gas having a temperature-independent molar specific heat c at constant volume.

- What is the heat Q_{BC} absorbed by the gas during the step BC of the cycle? Is this heat positive or negative? Express your answer in terms of c , R , V_1 , and the pressures p_B and p_C .
- What is the heat Q_{DA} absorbed by the gas during the step DA of the cycle? Is this heat positive or negative? Express your answer in terms of c , R , V_2 , and the pressures p_D and p_A .
- How is the work w , done *by* the gas on the piston during the entire cycle, related to the preceding heats? What then is the efficiency w/Q_{BC} of the engine? Express your answer in terms of V_1 , V_2 , and all the preceding pressures.
- By relating the initial and final pressures in each of the adiabatic processes AB and CD , express the efficiency solely in terms of c , R , and the volumes V_1 and V_2 .
- Assume that the gas used in the engine is air which is a diatomic gas (consisting of nitrogen and oxygen) whose heat capacity $c = (5/2)R$. What then would be the numerical value of the efficiency of this engine if the compression ratio $V_1/V_2 = 0.5$? What would be the value of this efficiency if this ratio is 0.1? <a-9>

[D-10]† Most probable speed of molecules in a gas

Use the Maxwell speed distribution (C-8) to find the most probable speed of a molecule in a gas (i.e., the speed corresponding to the maximum of one of the graphs in Fig. C-3).

- Express your answer in terms of the mass m of a molecule, the absolute temperature T of the gas, and Boltzmann's constant k . <h-2>
- What is the numerical value of the most probable speed of a molecule of nitrogen gas at a room temperature of 25°C ? (The molecular weight of a nitrogen molecule is 28.) <a-11>

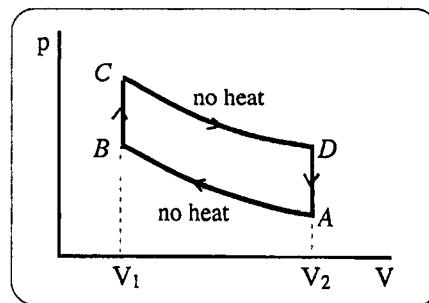


Fig. D-3. Cyclic process of a gasoline engine.