## CHAPTERS 6

## THE SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics. Consider the following three processes. (1) Two blocks at different temperatures are brought in contact with each other but are thermally insulated from their surroundings. The two blocks eventually come to the same temperature and the heat flowing out of the warmer block equals that flowing into the colder. (2) A rotating flywheel is brought to rest by friction in its bearings. The temperature of the wheel and bearings rises and the increase in their internal energy is equal to the original kinetic energy of the flywheel.(3) An ideal gas performs a free expansion through a stopcock into an evacuated vessel. The temperature remains constant. But the final pressure is less than the original pressure and the final volume is greater. In each of these processes, according to the first law or the principle of conservation of energy, the total energy of the system involved remains constant. Also, given the initial conditions, we know that the processes will take place as de-scribed above.

Now suppose we start with the three systems in the end states of the above processes, and imagine the processes to take place in reversed order. In the first example, one of the blocks would spontaneously become cooler and the other warmer until their original temperatures were restored. In the second, the wheel and bearings would cool down and the flywheel would start rotating with its original kinetic energy. In the third, the gas would rush back through the stopcock and compress itself into its original container. Everyone realizes that these reversed processes do not happen. But why not? The total energy of each system would remain constant in the reversed process as it did in the original, and there would be no violation of the first law. There must therefore be some other natural principle, in addition to the first law and not derivable from it, which determines the direction in which a process can take place in an isolated system. This principle is the second law of thermodynamics. Like the first, it is a generalization from experience and is a statement that certain processes such as those above, which would be entirely consistent with the first law, nevertheless do not happen.

These three impossible processes were selected as illustrations because they appear at first sight to differ widely from one another. The first is characterized by a spontaneous flow of heat from one body to another at a higher temperature. In the second, heat flows out of an object and an equivalent amount of kinetic energy appears. In the third, the volume of an isolated sample of gas decreases and its pressure increases while it's temperature remains constant. Many other illustrations
could be given. In the field of chemistry, for example, oxygen and hydrogen gas in the proper proportions can be enclosed in a vessel and a chemical reaction can be initiated by a spark. If the enclosure has rigid nonheat-conducting walls the internal energy of the system remains constant. After the reaction has taken place the system consists of water vapor at a high Temperature and pressure, but the water vapor will not spontaneously dissociate into hydrogen and oxygen at a lower temperature and pressure.

Can we find some feature which all of these dissimilar impossible processes have in common? Given two states of an isolated system, in both of which the internal energy is the same, can we find a criterion that determines which is a possible initial state and which a possible final state of a process taking place in the system? What are the conditions under which no process at all can occur, i.e., when a system is in equilibrium? These questions could be answered if there existed some property of the system, that is, some function of the state of the system, which had a different value at the beginning and at the end of a. possible process. This function cannot be the internal energy, since this is constant in an isolated system. A function having the desired property can be found, however. It was first devised by Claudius and is called the entropy of the system. Like the internal energy, it is a function of the state of the system only and, as we shall prove, it either increases or remains constant in any possible process taking place in an isolated system. In terms of entropy, the second law may be stated:

Processes in which the entropy of an isolated system would decrease do not occur, or, in every process taking place in an isolated system the entropy of the system either increases or remains constant.

Furthermore, if an isolated system is in such a state that its entropy is a maximum, any change from that state would necessarily involve a decrease in entropy and hence will not happen. Therefore the necessary condition for the equilibrium of an isolated system is that its entropy shall he a maximum.

Notice carefully that the statements above apply to isolated systems only. It is quite possible for the entropy of a no isolated system to de-crease in an actual process but it will always be found that the entropy of other systems with which the first interacts increases by at least an equal amount.

To understand why the entropy function exists and what its properties are, we first state the second law in more familiar terms. Many different statements can be made, all of them to the effect that some specified process is impossible. All such statements can be shown to be equivalent. Two useful formulations are the following:

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Clausius
( a)

$\longdiv { T _ { 1 } }$

Kelvin
(b)

FIG. 1. Schematic diagrams of the impossible processes referred to in (a) the Clausius and (b) the Kelvin statement of the Second Law.
I. No process is possible whose sole result is the removal of heat from reservoir at one temperature and the absorption of an equal quantity $\backslash$ of heat by a reservoir at a higher temperature.
II. II. No process is possible whose sole result is the abstraction of heat from a single reservoir and the performance of an equivalent amount of work.

The former is known as the Claudius statement of the second law, and the latter as the Kelvin (or Kelvin-Planck) statement. The impossible processes are shown diagrammatically in Fig. 1(a) and (b).

That the Kelvin and Claudius statements of the second law are equivalent may be shown a's follows. The proof consists of showing that if it were possible to violate one statement of the law, the other would or could be violated also. Suppose we have a cyclic heat engine that violates the Kelvin statement, that is, it takes in heat from a single reservoir at constant temperature and converts it completely to mechanical work. We could use the work output of this engine, represented by the rectangle in Fig. 2(a), to drive a refrigerator (not necessarily a Carnet refrigerator) as illustrated in the figure. The latter, if it is a refrigerator at all, takes in less heat from its low temperature reservoir than it delivers to its high temperature reservoir. A part of the heat it delivers to the high temperature reservoir can be diverted as shown to furnish the heat input to the engine, while there remains an outstanding flow of heat from a low to a high temperature reservoir. The device would operate continuously, with the
engine providing just enough work to run the refrigerator, but would violate th6 Claudius statement of the second law.

On the other hand, suppose we had a continuous flow of heat from a low to a high temperature reservoir, in violation of the Claudius statement, as illustrated by the left pipe line in Fig. 2(b). We could then operate an engine (any heat engine) between the two heat reservoirs. Whatever its efficiency, this engine takes in more heat than it rejects. Let it reject heat at the same rate at which heat flows upward from the low to the high temperature reservoir,, and take in enough additional heat from the high temperature reservoir to provide for its output of mechanical work. This system will also operate continuously, and it will be seen that its sole outstanding result is to withdraw heat from a single reservoir and convert it completely into mechanical work, in violation of the Kelvin statement. Therefore the two statements are equivalent.

A cyclic device which would continuously abstract heat from a single reservoir and convert the heat completely to mechanical work is called a perpetual motion machine of the second kind. Such a machine would not violate the first law (the principle of conservation of energy) since it would not create energy, but economically it would be just as valuable as if it did so, because of the existence of heat reservoirs, such as the oceans or the earth's atmosphere, from which heat could be abstracted continuously at no cost. Hence the sécond law is sometimes stated: "A perpetual motion niacin of the second kind is impossible."

(a)


FIG. 2. Proof of equivalence of Claudius and Kelvin statements of Second Law.

Efficiencies of reversible engines. We next derive two important consequences of the second law:
(a) No heat engine operating in cycles between two reservoirs at constant temperatures can have a greater efficiency than a reversible engage operating between the same two reservoirs.
(b) All reversible engines operating between two reservoirs at constant temperatures have the same efficiency.


FIG. 3. No engine can be more efficient than a reversible engine operating between the same two temperatures.

Note that a reversible engine which absorbs heat at a single temperature and rejects heat at a single (different) temperature is necessarily a Carnot engine and its cycle is bounded by two isothermals and two adiabatic.

The method of proving the statements above is to show that if they were not true, either the Kelvin or the Claudius statement of the second law would be violated.

In Fig. 3(a), the circle represents a reversible engine operating between two reservoirs at temperatures $T_{2}$ and $T_{1}$, taking in heat $Q_{2}$ from the reservoir at temperature $T_{2}$, rejecting heat $Q_{1}$ to the reservoir at temperature $T_{1}$, and doing work $W=Q_{2}-Q_{1}$. (We are considering both $Q_{2}$ and $Q_{1}$ as positive quantities.) The efficiency of this engine as shown is about $50 \%$. The rectangle at the right of the diagram represents an assumed engine having ahigher efficiency than the reversible engine (about $75 \%$ ). We assume that the engines are built or operated so that each delivers the same mechanical work. (This could be the work per cycle or the work in some whole number of cycles.) Since the engine-at the right is assumed to have a higher efficiency than the reversible engine, it takes in less heat from the high temperature reservoir and rejects less to the low temperature reservoir.

Now since the reversible engine is reversible, it can be reversed in the thermodynamic as well as the mechanical sense. That is, it can be operated as a refrigerator with no changes in the magnitudes of $Q_{2}, Q_{1}$, and $W$. Let us therefore couple the assumed high/efficiency engine to the other engine operated in reverse as a refrigerator, as in Fig.-3(b). It should be evident from the diagram that the device will run itself and will result in a transfer of heat from a lower to a higher temperature, in violation of the Claudius statement of the second law. Therefore the efficiency of the assumed engine cannot be greater than that of the reversible engine.

Now suppose that two engines, both reversible, have different efficiencies when operated between two given temperatures. Let the one with the higher efficiency, operated as an engine; drive the one with lower efficiency as a refrigerator. The diagram is the same as Fig. 3(b) and the second law is violated. Hence neither engine can have a higher efficiency than the other, which means that their efficiencies are equal.

Notice carefully that we have not proved that the efficiency of an irreversible engine is lower than that of a reversible engine but only that no engine, reversible or not, can have a higher efficiency than a reversible engine. We shall show, however, that the efficiency of an irreversible engine actually is lower than that of a reversible one operating between the same two temperatures.

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The Kelvin temperature scale. The conclusions drawn in the preceding section regarding the efficiencies of reversible engines were used by Kelvin to define a temperature scale that is independent of the properties of any particular thermometric material.

We showed in chapter-5 that when a Carnot engine using an ideal gas as the working substance is operated between two reservoirs at different temperatures, and when the temperatures of these reservoirs are measured by a gas thermometer using an ideal gas, the ratio of the heat absorbed to the heat rejected is equal to the ratios of the temperatures.

$$
\begin{equation*}
\frac{Q_{2}}{Q_{1}}=\frac{T_{2}}{T_{1}} \tag{1}
\end{equation*}
$$

We have shown before that even if the working substance is not an ideal gas, the efficiencies of all Carnot engines operating between the same two temperatures are the same. That is, whatever the nature of the fluid in the cylinder in Fig. 5-, if heat $Q_{2}$, is taken in at the higher temperature, the same amount of heat $Q_{1}$ will be rejected at the lower temperature. The ratio $\frac{Q_{2}}{Q_{2}}$ is therefore independent of the nature of the working substance. The same is not true of the temperature ratio $\frac{T_{2}}{T_{1}}$, if temperatures are measured by thermometers utilizing different materials. A constant volume helium thermometer, for example, filled to a finite pressure $P_{i}$ at the ice point, will give a different value for the ratio $\frac{T_{2}}{T_{1}}$ than will a constant volume hydrogen thermometer and neither ratio will equal the ratio of the heat absorbed to the heat liberated by a Carnot engine.

Kelvin proposed that we use a Carnot engine as a thermometer and define the ratio of two temperatures as the ratio of the heat absorbed by the engine to the heat rejected, when the engine is operated between reservoirs at these temperatures. Then the equality
$\frac{Q_{2}}{Q_{1}}=\frac{T_{2}}{T_{1}}$
becomes a matter of definition, and the fundamental problem of thermometry, that of establishing a temperature scale, reduces to a problem in calorimetric. That is, the experimental quantities that are measured in determining an unknown temperature are quantities of heat rather than pressures, volumes, lengths, etc. Temperatures defined in this way are called Kelvin temperatures: Since Eq. (2) has been shown to be satisfied if temperatures are measured by an ideal gas thermometer, it follows that the ideal gas temperature scale and the Kelvin scale are identical.

A definition of the ratio of two temperatures alone does not completely define the temperatures. They can be completely defined by assigning an arbitrary value to the difference between any two temperatures. We therefore say arbitrarily that the difference between the Kelvin- temperatures of the steam and ice points shall be exactly 100 degrees, and the Kelvin scale, as the term is ordinarily used, should properly be called the Kelvin centigrade scale. In engineering work, a difference of $180^{\circ}$ is assigned to the steam point-ice point interval, with the same definition of the ratio of two temperatures, and the scale is called the Rankin scale. The size of the Rankin degree is the same as on the Fahrenheit scale.

As an example, suppose we wish to determine the temperature of a tank of water, using a Carnot engine as the only thermometer As auxiliary equipment we require a heat reservoir at the steam point (of course, no thermometer is needed to ensure that it is at. the steam point), a heat reservoir at the ice point (again no thermometer is required), and a calorimeter for measuring heats absorbed and liberated by the Carnot engine. Even the calorimeter does not require the use of a thermometer. For example, the heat withdrawn from the reservoir at the steam point can be measured by measuring the input of electrical energy to a heating coil that keeps the reservoir at the steam point as heat is withdrawn. Let $T_{S}, T_{i}$, and $T$ represent, on the Kelvin scale, the steam point temperature, ice point temperature, and the temperature of the tank of water. All of these, including steam point and ice point, are unknown at the start of the experiment.

We first carry out a Carnot cycle between the reservoirs at the steam point and the ice point. Let $Q_{S}$, and $Q_{i}$ represent the quantities of heat absorbed and rejected. Then carry out a second cycle between the reservoir at the steam point and the tank of water (we could equally well use the tank of water and the reservoir at the ice point) and for simplicity let us take in the same amount of heat $Q_{S}$, at the steam point. Let $Q$ be the heat rejected at the unknown temperature $T$. We then have the following equations:

$$
\frac{Q_{S}}{Q_{i}}=\frac{T_{S}}{T_{i}}, \quad \frac{Q_{S}}{Q}=\frac{T_{S}}{T}, \quad T_{S}-T_{i}=100 \text { deg rees }
$$

The quantities $Q_{S}, Q_{i}$, and $Q$ are known from experiment and we have three equations from which to determine the three unknowns $T_{S}, T_{i}$, and $T$.

No one has ever measured a temperature in the manner described above. The Kelvin temperature scale is established by correcting the readings of a gas 'thermometer to what they would be if the gas were ideal, or by equivalent procedures for temperatures above and below the range accessible to gas thermometry. (By "establishing" the scale is meant that a large number of fixed temperatures such as the steam point, ice point, freezing point of gold, etc., are carefully measured once and for all.) This correction can be made from certain equations derived from the second law, and the experiments involved in ascertaining the magnitudes of the corrections require the measurement of quantities of heat. Hence the measurements reduce essentially to problems in calorimetric, as stated above, although the calorimetric is less direct than in our idealized experiment.

A Carnot engine operated in reverse becomes a. Carnot refrigerator. Since all processes are reversible, the ratio of the heat $Q_{1}$ absorbed from the reservoir at the lower temperature $T_{1}$, to the heat $Q_{2}$ rejected to the reservoir at the higher temperature $T_{2}$, is equal to the ratio of the temperatures,

$$
\frac{Q_{1}}{T_{1}}=\frac{Q_{2}}{T_{2}}
$$

The work $W$ required to operate the refrigerator, from the first law, is

$$
W=Q_{2}-Q_{1}
$$

and the coefficient of performance is

$$
E=\frac{Q_{1}}{W}=\frac{Q_{1}}{Q_{2}-Q_{1}}=\frac{T_{1}}{T_{2}-T_{1}}
$$

The coefficient of performance is independent of the nature of the working substance.
It is left as a problem to show by the method used before that no refrigerator operating between two given temperatures can have a greater coefficient of performance than a Carnot refrigerator.

Absolute zero. It follows from the definition of temperature on the Kelvin scale that Kelvin temperatures of zero degrees or less cannot exist. Consider a Carnot engine operated between a reservoir at a fixed temperature $T_{2}$ and a second reservoir at a lower temperature $T_{1}$. Let
The engine takes in heat $Q_{2}$ from the reservoir at temperature $T_{2}$. The mechanical work $W$ done by the engine, from the first law, is

$$
W=Q_{2}-Q_{1}
$$

And from the definition of Kelvin temperature,


$$
\begin{aligned}
& Q_{1}=Q_{2} \frac{T_{1}}{T_{2}}, \quad \text { Hence } \quad W=Q_{2}-Q_{2} \frac{T_{1}}{T_{2}}, \text { and } \\
& T_{1}=T_{2}\left(1-\frac{W}{Q_{2}}\right) \quad
\end{aligned}
$$

The larger the work $W$, the lower the temperature $T_{1}$. But from the second law.

$$
W<Q_{2}
$$

Since the engine cannot convert to work all of the heat supplied to it. Therefore the term in parentheses in Eq. (3) is always greater than zero. and hence the lowest attainable temperature is greater than zero. In other words, a temperature of absolute zero or less is unattainable.

The Clausius-Clapeyron equation. To state the fact that all Carnot engines operated between two given temperatures have the same efficiency is one way of stating the second law of thermodynamics. We shall put this law in a more useful analytical form in a later section, but many of its consequences can be deduced directly from the statement above.

A Carnot cycle is any reversible cycle bounded by two isotherms and two adiabatic. The working substance need not be an ideal gas. It may be a real gas, a liquid, a solid, or changes in phase may take place during the cycle. By considering a Carnot engine operated between two reservoirs differing infinitesimally in temperature, and by letting the

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FIG. 4. Infinitesimal reversible cycle used to derive Clausius-Clapeyron equation.

Working substance undergo a change in phase, we can derive an important relation known as the Clausius-Clapeyron equation, giving the slope of the) equilibrium lines in a pressure-temperature diagram.

We shall describe a cycle in which the phases in equilibrium are liquid and vapor, but the same argument can be applied to the solid-vapor or solid-liquid equilibrium. The cycle is indicated by shading in Fig. 4(a) and the Carnot engine is shown in Fig. 4(c). The initial state of the system is represented by point a in Fig. 4(a) and by part (a) of Fig. -4(c). The cylinder of the Carnot engine contains a liquid and vapor in equilibrium at temperature $T$ and pressure $p_{23}$. The specific volumes of
the liquid and vapor phases are respectively $v^{\prime \prime}$ and $v^{\prime \prime}$.We first carry out an isothermal expansion at temperature $T$ until an arbitrary mass $m$ has been vaporized, at which time the state of the system is represented by point b in Fig. 4(a) and by part (b) of Fig. 4(c). The pressure remains constant in this part of the cycle. The mass $m$, while in the liquid phase, occupied a volume $m v^{\prime \prime}$ and in the vapor phase it occupies a volume $m v^{\prime \prime \prime}$. The increase in volume of the system is therefore $m\left(v^{\prime \prime}-v^{\prime \prime}\right)$. The heat $Q$ absorbed by the system in this part of the cycle is the product of the mass $m$ and the latent heat of vaporization $l_{23}$.

In the next stage of the cycle, the cylinder at temperature $T$ and pressure $p_{23}$ is transferred to an insulating stand, and a very smalf adiabatic expansion is carried out. The work done is negligible and, of course, no heat ís absorbed, but the temperature drops to $(T-d T)$ and the pressure to $\left(p_{23}-d p_{23}\right)$. The state of the system is now represented by point $\boldsymbol{c}$ in Fig. 4(a).

The cylinder is next moved to a heat reservoir at temperature $(T-d T)$ and an isothermal and isobaric compression is carried out, taking the system to point $\boldsymbol{d}$ in Fig. 4(a). A final adiabatic compression returns the system to point a.

We have shown that the efficiency of any Carnot cycle is

$$
\frac{W}{Q_{2}}=\frac{Q_{2}-Q_{1}}{Q_{2}}=\frac{T_{2}-T_{1}}{T_{2}}
$$

In the present infinitesimal cycle, this becomes

$$
\frac{d^{\prime} W}{Q}=\frac{d T}{T}
$$

where $Q$ is the heat absorbed at the higher temperature and is given by

$$
Q=m l_{23}
$$

If the small volume changes in the adiabatic processes are neglected, the net work $d^{\prime} W$ done in the cycle is the area of the shaded "rectangle" in Fig. 4(a), whose base is $m\left(v^{\prime \prime}-v^{\prime \prime}\right)$ and whose height is $d p_{23}$

$$
\begin{align*}
d^{\prime} W & =m\left(v^{\prime \prime \prime}-v^{\prime \prime}\right) d p_{23} \\
\text { Then } \frac{d^{\prime} W}{Q} & =\frac{m\left(v^{\prime \prime \prime}-v^{\prime \prime}\right) d p_{23}}{m l_{23}}=\frac{d T}{T}, \\
\text { and } \frac{d p_{23}}{d T} & =\frac{l_{23}}{T\left(v^{\prime \prime \prime}-v^{\prime \prime}\right)} \tag{4}
\end{align*}
$$

This is one form of the Clausius-Clapeyron equation. It expresses the slope of the vapor pressure curve at any temperature in terms of the temperature, the latent heat of vaporization at that temperature, and the specific volumes of vapor and liquid. When the same reasoning is applied to the solid and vapor or solid and liquid phases, one obtains the corresponding equations:

$$
\frac{d p_{13}}{d T}=\frac{l_{13}}{T\left(v^{\prime \prime \prime}-v^{\prime}\right)}, \quad \frac{d p_{12}}{d T}=\frac{l_{12}}{T\left(v^{\prime \prime}-v^{\prime}\right)}
$$

Although the latent heat of any transformation varies with temperature, it is always positive, as is the temperature $T$. Also, the specific volume of the vapor phase is always greater than that of both the liquid or solid phase and the quantities $\left(v^{\prime \prime \prime}-v^{\prime \prime}\right)$ and $\left(v^{\prime \prime \prime}-v^{\prime}\right)$ are always positive. The slopes of the vapor pressure curves and sublimation pressure curves are therefore always positive. The specific volume of the solid phase however, may be greater or less than that of the liquid phase, and so the slope of the solid-liquid equilibrium line may be either positive or negative. We can now understand more fully why the $p-v-T$ surface for a substance like water, which expands on freezing, differs from that for a substance which contracts on freezing. The term $\left(v^{\prime \prime}-v^{\prime}\right)$ is negative for a substance that expands on freezing and is positive for a substance that contracts on freezing. Therefore the solid-liquid equilibrium surface, or its projection as a line in the $p-T$ plane, slopes upward to the left for a substance like water that expands and up-ward to the right for .a substance that contracts. Projections of the liquid-vapor and solid-vapor surfaces always have positive slopes.

For changes in temperature and pressure that are not too great, the latent heats of transformation and the specific volumes can be considered constant, and the slope
of an equilibrium line can be approximated by the ratio of the finite pressure and temperature changes, $\frac{\Delta p}{\Delta T}$. Thus the latent heat at any temperature can be found approximately from measurements of equilibrium pressures at two nearby temperatures, if the corresponding specific volumes are known. Conversely, if the equilibrium pressure and the latent heat are known at any one temperature, the pressure at a nearby temperature can be calculated. In calculations of this sort we usually assume that the vapor behaves like an ideal gas.

To integrate the Clausius-Clapeyron equation and obtain an expression for the pressure itself as .a function of temperature, the heats of trans-formation and the specific volumes must be known as functions of temperature. This is an important problem in physical chemistry but we shall not pursue it further here except to mention that if variations in latent heat can be neglected, and if one of the phases is a vapor, and if the vapor is assumed to be an ideal gas, and if the specific volume of the liquid or solid is neglected in comparison with that of the vapor, the integration can be readily carried out. The resulting expression is

$$
\begin{aligned}
& \frac{d p}{d T}=\frac{l}{T \frac{R T}{p}}, \quad \frac{d p}{d p}=\frac{l}{R} \frac{d T}{T^{2}} \\
& \ln p=-\frac{l}{R T}+\ln C \\
& p=C e^{-\frac{l}{R T}}
\end{aligned}
$$

In ch. 8 we shall give a more formal derivation of the Clausius-Clapeyron equation. The derivation above was given at this point, to show how an important consequence of the second (and first) law can be deduced in a very simple way.

Derivation of Stefan's law. As another example of the second law, we use it to derive Stefan's law for an ideal radiator. This law as ; usually given in elementary texts states that the total rate of emission of radiant energy by an ideal radiator or blackbody is proportional to the 4th power of the Kelvin temperature. It can be shown from this that the radiant energy density, or radiant energy per unit volume, within an en-closure whose walls are at a uniform temperature, is also
proportional to the 4th power of the Kelvin temperature, provided there is in the enclosure at least a speck of perfectly absorbing material, so that the frequency distribution of the radiant energy is always that given by Planck's law. tinder these conditions the energy density is a function of the temperature only, and the internal energy can be identified with the radiant energy.

Both the classical and quantum theories of radiation predict that when homogeneous isotropic radiant energy falls on a perfectly reflecting surface it exerts on the surface a pressure equal to $1 / 3$ of the energy density. Imagine an evacuated cylinder whose walls are perfectly reflecting thermal insulators, containing a "batch" of radiant energy which can be expanded or compressed like a gas. Provision is made for a flow of heat into or out of the cylinder, and a speck of perfectly absorbing material is included.

Let the radiant energy in the cylinder be carried through the Carnot cycle in Fig. 5. Process $\boldsymbol{a} \boldsymbol{b}$ is an isothermal expansion at the temperature $\boldsymbol{T}, \boldsymbol{b} \boldsymbol{c}$ is an infinitesimal adiabatic expansion in which the temperature drops to $T-d T, \boldsymbol{c d}$ is an isothermal compression, and $d \boldsymbol{a}$ is an adiabatic compression. Let $\boldsymbol{e}$ represent the energy density, so that


FIG. 5

$$
\begin{equation*}
p=\frac{1}{3} e \tag{6}
\end{equation*}
$$

The work $W$ done by the system in the isothermal process $\boldsymbol{a b}$ is

$$
W=p\left(V_{2}-V_{1}\right)=\frac{1}{3} e\left(V_{2}-V_{1}\right)
$$

Since the energy density is a function of the temperature only, it remains constant in this process and the change in internal energy is

$$
U_{2}-U_{1}=e\left(V_{2}-V_{1}\right)
$$

From the first law, the heat $Q$ flowing into the system is

$$
Q=\left(U_{2}-U_{1}\right)+W=\frac{4}{3} e\left(V_{2}-V_{1}\right)
$$

The net work $d^{\prime} W$ done in the cycle is the shaded area in Fig. 5, or

$$
d^{\prime} W=d p\left(V_{2}-V_{1}\right)
$$

From Eq. (.6),

$$
p=\frac{1}{3} e \quad \text { So. } \quad d^{\prime} W=\frac{1}{3} d e\left(V_{2}-V_{1}\right)
$$

From the second law, the efficiency of the cycle, $\frac{d^{\prime} W}{Q}$, is equal to $\frac{d T}{T}$, or

$$
\frac{\frac{1}{3} d e\left(V_{2}-V_{1}\right)}{\frac{4}{3} e\left(V_{2}-V_{1}\right)}=\frac{d T}{T}, \quad \frac{d e}{e}=4 \frac{d T}{T}
$$

Hence

$$
\begin{gathered}
\ln e=4 \ln T+\text { const. }, \\
e=\text { const } . \times T^{4}
\end{gathered}
$$

The energy density is therefore proportional to the 4th power of the Kelvin temperature.

## Questions

Q.(1) A Carnot engine absorbs heat from a reservoir at a temperature of $\mathbf{1 0 0} \mathbf{}{ }^{\mathbf{c}}$ and reject heat to a reservoir at a temperature of $\mathbf{0}^{\circ} \mathbf{c}$. If the engine absorbs $\mathbf{1 0 0 0}^{\circ}$ Joules from the high temperature reservoir, find : 1-the work done 2 - The heat rejected 3- The efficiency.
Q.(2) Which is the more effective way to increase The efficiency of a Carnot engine, to increase the temperature $T_{2}$, keeping $T_{1}$ fixed ${ }_{A}$ or to decrease the temperature $\mathrm{T}_{1}$, keeping $\mathrm{T}_{2}$ fixed?
Q.(3) A refrigerator having a coefficient of performance one -half as great as that of a Carnot refrigerator is operated between reservoirs at temperatures of $\mathbf{2 0 0} \mathbf{k}$ and $\mathbf{4 0 0 k}$, and it absorbs $\mathbf{6 0 0}$ joules from the low temperature reservoir. How much heat is rejected to the high temperature reservoir?
Q.(4) A Carnot refrigerator or heat pump is operated between reservoirs at $\mathbf{0}^{\circ} \mathbf{c}$ and $\mathbf{1 0 0}^{\mathbf{c}} \mathbf{c}$. a// If $\mathbf{1 0 0 0}$ joules are absorbed from the low temperature reservoir, how many joules are rejected to the high temperature reservoir? b// What is the coefficient of performance?
Q.(5) The temperature in a house hold refrigerator is $\mathbf{0}^{\circ} \mathbf{c}$ and the temperature of the room in which it is located is $\mathbf{2 5}^{\circ} \mathbf{c}$. The heat flowing in to the refrigerator from the warmer room every $\mathbf{2 4}$ hours is $\mathbf{8}^{* 10}$ joules (enough to melt about 50Ib of ice) and this heat must be pumped out again if the refrigerator is to be kept cold. If a Carnot refrigerator were available, operating between the temperature of $\mathbf{0}^{\circ} \mathbf{c}$ and $\mathbf{2 5}^{\circ} \mathbf{c}$, how much mechanical power in watts would be required to operate it? Compare the daily cost, at 2 cents per kwh, With the cost of 50 Ib of ice (about 40 cents in Cambridge) .

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Q.(6) One mole of a monatomic ideal gas $c_{v}=\frac{3}{2} R$ is carried around the closed cycle abc in Fig.. Process $\mathbf{b c}$ is a reversible adiabatic expansion. Given that $\mathbf{P}_{\mathbf{b}}=\mathbf{1 0}$ $\operatorname{atm}$., $V_{b}=\mathbf{2} \mathrm{m}^{3}$, and $V_{c}=\mathbf{4} \mathbf{m}^{\mathbf{3}}$,
$\mathbf{a} / /$ Compute the heat input to the gas, the heat output, and the efficiency of the cycle. $\mathrm{b} / /$ What is the maximum efficiency of an engine operating between the extremes of temperature of the cycle?

Q.(7) Taking the normal boiling point of water as $\mathbf{1 0 0}^{\mathbf{\circ}} \mathbf{c}$ and normal latent heat of vaporization 540calories, calculate the elevation of the boiling point for an increase of pressure of one atmosphere. One gram of system occupies a volume of $1677 \mathbf{c m}^{3}$.
Q.(8) The normal melting point of ice is $\mathbf{0}^{\circ} \mathbf{c}$ and the latent heat of fussion $\mathbf{8 0}$ calories. If $\mathbf{1 c m}^{3}$ of water on solidification has a volume $1.091 \mathbf{c m}^{3}$, calculate the depression of the freezing point for an increase of pressure of one atmosphere.
Q.(9) Calculate the radiant energy (energy density) emitted by a black body at a temperature of
a// $200 \mathrm{k}, \quad \mathrm{b} / / 4000 \mathrm{k}$. Stefan's constant $\mathrm{C}=5.67 * \mathbf{1 0}^{-8}$ M.K.S.units.
Q.(10) Luminosity of Rigel Star in Orion constellation is 1700 times that of our sun. If the surface temperature of the sun is 6000 k , Calculate the temperature of the star.
Q.(11) A metallic ball having a surface area of $\mathbf{2 0 0} \mathbf{c m}^{\mathbf{3}}$ and at a temperature of $\mathbf{5 2 7}^{\mathbf{o}} \mathbf{c}$ is placed in an enclosure at $\mathbf{2 7 ^ { \mathbf { o } } \mathbf { c } . \text { If the surface emissivity of the metal is } \mathbf { 0 . 4 } , ~}$ Find the rate at which heat is lost by the ball $\mathbf{C}=5.67 * 10^{-5} \mathrm{ergs} . \mathrm{cm}^{-2} \mathrm{sec}^{-1} \cdot \mathrm{c}^{-4}$
Q.(12) How watts of energy are required to keep a black body in the from of a cube with $\mathbf{1 c m}$, side at $\mathbf{a} / / 500^{\circ} \mathbf{k}$ and $\mathbf{b} / \mathbf{2 0 0 0} \mathbf{}{ }^{\circ} \mathbf{k}$. Assume that the surrounding walls are at temperature of $\mathbf{3 0 0}^{\circ} \mathbf{k}$, Stefan's constant $\sigma=5.67 * \mathbf{1 0}^{-\mathbf{8}} \mathbf{~ e r g} / \mathrm{cm}^{2} / \mathrm{sec} / \mathrm{deg}^{4}$.

