THERMODYNAMICAL LAWS AND ENTROPY

UNIT – I

US05CPHY23

By

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Introduction and some Terminology

What is heat? Heat is a form of energy that can be transferred from one object to another or even created at the expense of the loss of other forms of energy.

What is Temperature? Temperature is a measure of the ability of a substance, or more generally of any physical system, to transfer heat energy to another physical system.

What is thermodynamics?

- The study of the relationship between work, heat, and energy.
- Deals with the conversion of energy from one form to another.
- Deals with the interaction of a system and it surroundings.

Or

- Thermodynamics, **is a science** of the relationship between heat, work, temperature and energy . In broad terms, thermodynamics deals with the transfer of energy from one place to another and from one form to another. The key concept is that heat is a form of energy corresponding to a definite amount of mechanical work.

Introduction and some Terminology

What is difference between Isothermal Process and adiabatic Process?

Isothermal process	Adiabatic process
Isothermal process is defined as one of the thermodynamic processes which occurs at a constant temperature	Adiabatic process is defined as one of the thermodynamic processes which occurs without any heat transfer between the system and the surrounding
Work done is due to the change in the net heat content in the system	Work done is due to the change in its internal energy
The temperature cannot be varied	The temperature can be varied
There is transfer of heat	There is no transfer of heat
$PV = nRT(\theta)$	$PV^{\gamma} = \text{Constant}$

Introduction and some Terminology

Zeroth Law of thermodynamics: *"if two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with one another"*

If $T_1=T_2$ and $T_2=T_3$ then $T_1=T_3$

First Law of thermodynamics: "the change in internal energy of a closed system is equal to the energy added to it as a result of heat plus the work that is done on the system"

$$\Delta E_{internal} = Q + W$$

Second Law of thermodynamics: Kelvin–Planck statement (or the Heat Engine **Statement**) *"it is impossible to devise a cyclically operating heat engine, the effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work".* $\Delta S = \Delta S_{system} + \Delta S_{surrounding}$

Third Law of thermodynamics: "It is impossible to reach absolute zero (0°K) in any number of finite process". $\eta = 1 - \frac{T_2}{T_1}$

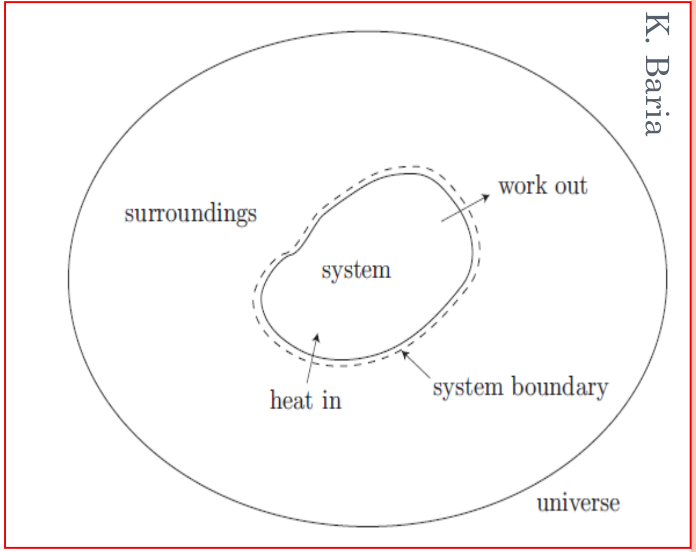
$\eta = 1 - \frac{T_2}{T_1}$ $if\ T_2 \rightarrow 0\ (absolute\ zero\ temperature), \eta = 100\%$ practically impossible

Introduction and some Terminology

0th Law	1st Law	2nd Law	3rd Law
Defines Temperature	Defines the Energy	Defines Flow of Energy & Concept of Entropy	Numerical Value of Entropy and absolute temperature

Thermodynamic system: a quantity of fixed mass under investigation,

- **Surroundings:** everything external to the system
- **System boundary**: interface separating system and surroundings
- **Universe**: combination of system and surroundings.



Property	Definition	Symbol	S.I.Unit
Volume	Volume of a substance	V	m^3
Internal Energy	The translational, rotational and vibrational kinetic energy of a substance	U	Joules (J)
Enthalpy	U + PV	H	Joules (J)
Entropy	The entropy is a measure of the lack of structure or the amount of disorder in a system	S	Joules/Kelvin (J / K)

Introduction and some Terminology

Systems can be classified as:

- **Open**: mass and energy can be transferred between system and surroundings
- **Closed**: energy can be transferred but not mass
- **Isolated**: Neither energy nor mass can be transferred between system and surroundings

A Closed system (a controlled mass) consists of a fixed amount of mass, and no mass can cross its boundary. That is, no mass enters or leave a closed system.

such as, Piston-cylinder device

An Open system (or a control volume) is a properly selected region in space. Both mass and energy can cross the boundary of a control volume.

such as, A Water heater, a turbine and a compressor, etc

Refrigerator, Clausius Statement of the Second Law:

- heat engine is a device through which a working substance is taken through a cycle in such a direction that some heat is absorbed while the temperature is high, a smaller amount is rejected at a lower temperature, and a net amount of work is done on the outside.
- If we imagine a cycle performed in a direction reverse to that of an engine, the net result would be the absorption of some heat at a low temperature, the rejection of a larger amount at a higher temperature, and a net amount of work done on the working substance.
- A device that perform a cycle in this direction is called a refrigerator, and the working substance is called a refrigerant.

Refrigerator, Clausius Statement of the Second Law:

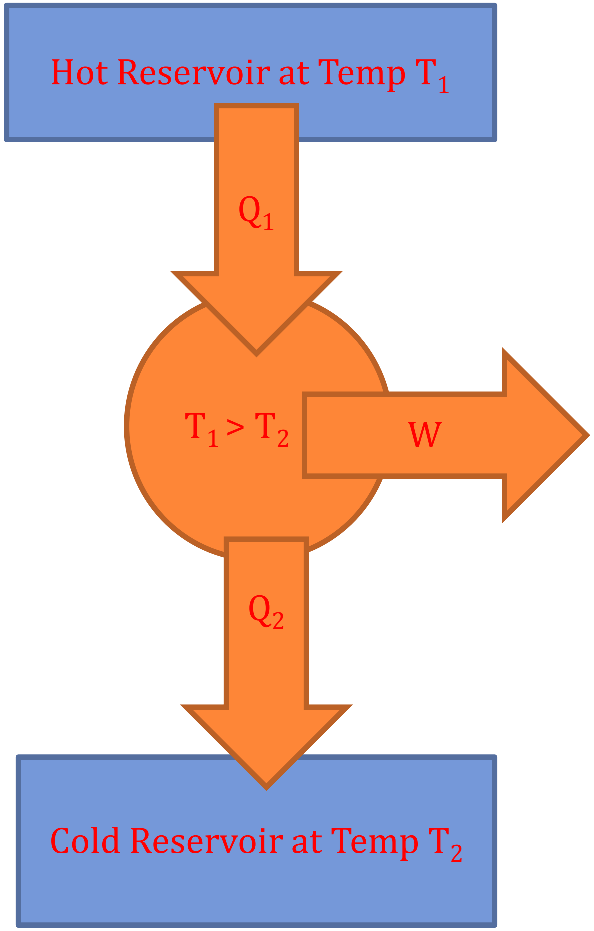


Fig. 1.1 (a) a heat engine and

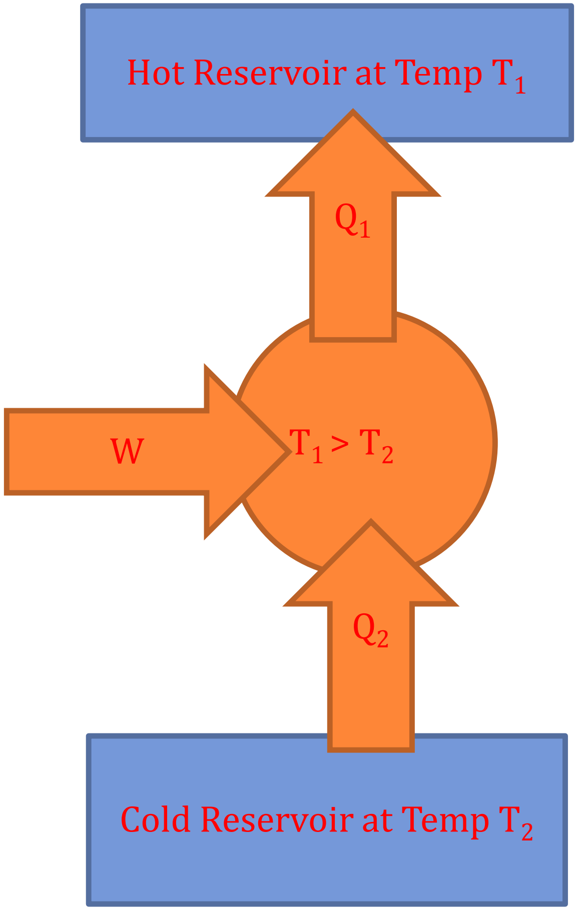


Fig. 1.1 (b) a refrigerator

Refrigerator, Clausius Statement of the Second Law:

Let the following notation (all positive quantities) refers to one complete cycle.

Q_1 = amount of heat rejected by the refrigerant.

Q_2 = amount of heat absorbed by the refrigerant.
W = Net work done on the refrigerant.

Since the refrigerant undergoes a cycle, there is no change in internal energy, and the first law becomes

$Q_2 - Q_1 = - W$

Hence,

$Q_1 = Q_2 + W$
Means the heat rejected to the hot reservoir is larger than the heat extracted from the cold reservoir by the amount of work done.

The purpose of a refrigerator is to extract as much heat Q_2 as possible from the cold reservoir with the expenditure of as little work W as possible. The quantity that expresses the ability of a refrigerator to do its job is therefore Q_2/W, which is known as the coefficient of performance. Hence, it is essential that work is always necessary to transfer heat from a cold to hot reservoir. It would be beneficiary to mankind if no external supply of the energy were needed, but it must certainly be admitted that experience indicates the contrary. This negative statement leads us to the Clausius statement of the second law.

"It is impossible to construct a device that, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body"

Carnot's Theorem and Corollary:

Carnot's Theorem: "No engine operating between two given reservoir can be more efficient than a Carnot engine operating between the same two reservoir"

Imagine a Carnot engine R and any other engine I working between the same two reservoir and adjusted so that they both deliver the same amount of work W.

Thus,

	Carnot engine R	Any Other engine I
1	Absorb heat Q_1 from the hot reservoir.	Absorb heat Q_1' from the hot reservoir.
2	Perform work W.	Perform work W.
3	Rejects heat Q_1-W to the cold reservoir.	Rejects heat Q_1'-W to the cold reservoir.
4	Efficiency $\eta_R = W/Q_1$	Efficiency $\eta_I = W/Q_1'$

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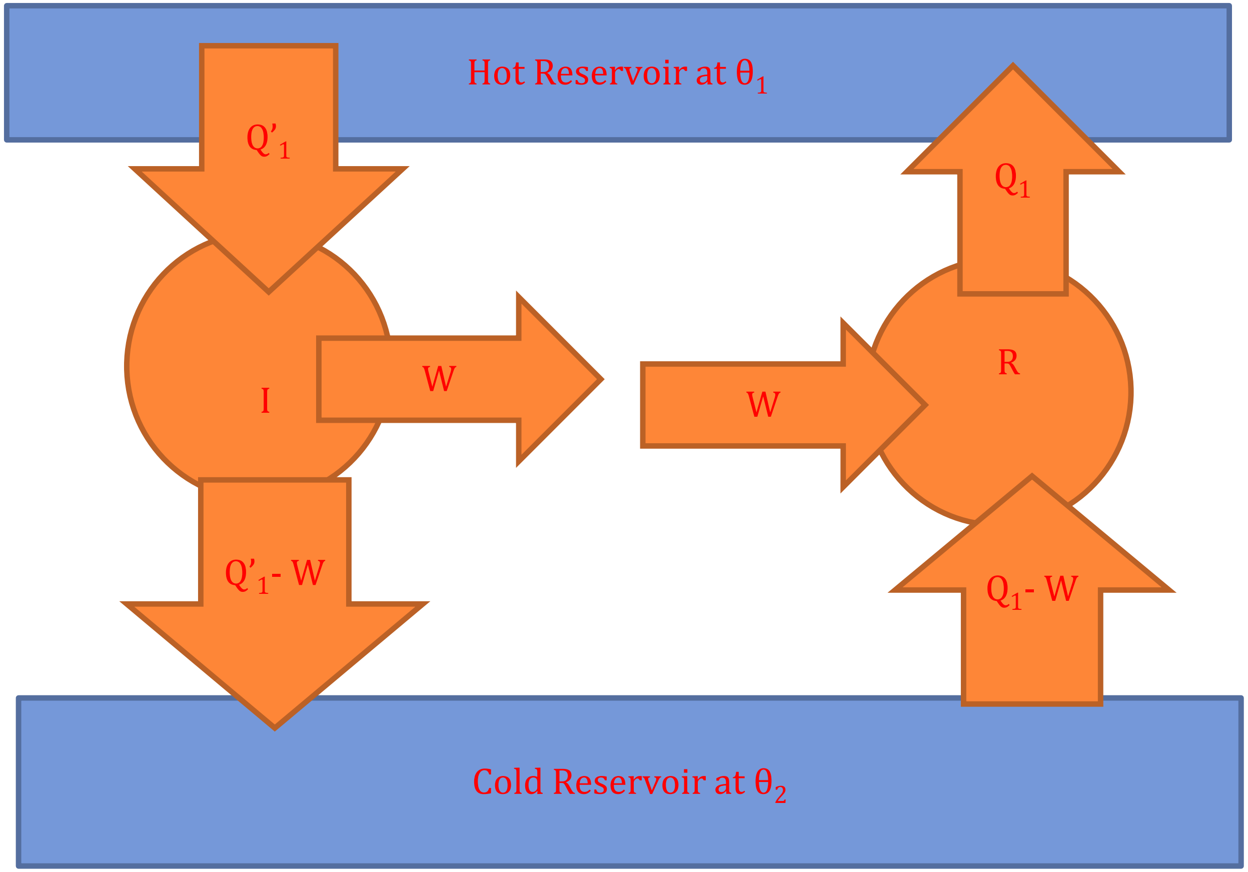
Carnot's Theorem and Corollary:

Let us assume that the efficiency of the engine I is greater than that of R. thus,

$\eta_I > \eta_R$

$\frac{W}{Q_1'} > \frac{W}{Q_1}$ Hence, $Q_1 > Q_1'$

Now let the engine I derive the Carnot engine R backward as a Carnot refrigerator. This is shown symbolically in fig. 1.2.



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Carnot's Theorem and Corollary:

The engine I and the refrigerator R coupled together in this way constitute a self-acting device, since all the work needed to operate the refrigerator is supplied by the engine. The net heat extracted from the cold reservoir is

$$Q_1 - W - (Q_1' - W) = Q_1 - Q_1'$$

Which is positive. The net heat delivered to the hot reservoir is also $Q_1 - Q_1'$. *The effect therefore, of this self-acting device is to transfer $Q_1 - Q_1'$ units of heat from a cold reservoir to the hot reservoir. Since this is a violation of the second law of thermodynamics (Clausius Statement) our original assumption that $\eta_I > \eta_R$ is false and Carnot's theorem is proved.*

We may express this result in symbols as $\eta_I \leq \eta_R$

The following corollary to Carnot's theorem may be easily proved:

"All Carnot engine operating between the same two reservoirs have the same efficiency"

Consider two Carnot engines R_1 and R_2, operating between the same two reservoirs. If we imagine R_1 driving R_2 backward. Then Carnot's theorem states that,

$$\eta_{R_1} \leq \eta_{R_2}$$

If R_2 drives R_1 backward then,

$$\eta_{R_2} \leq \eta_{R_1}$$

It therefore follows that

$$\eta_{R_1} = \eta_{R_2}$$

It is clear from the above result that the nature of the working substance which undergoing the Carnot cycle has no influence on the efficiency of the Carnot engine.

Kelvin Temperature Scale:

A Carnot engine absorbing Q_1 units of heat from hot reservoir at a temperature θ_1 and rejecting Q_2 units of heat to a cold reservoir at temperature θ_2 has an efficiency η_R that is independent of the nature of the working substance. The efficiency therefore depends only on the two temperatures, and we may write

$$\eta_R = 1 - \frac{Q_2}{Q_1} = \varphi\,(\theta_1, \theta_2)$$

Where φ is an unknown function. Rearranging the above equation, we have,

$$\frac{Q_2}{Q_1} = \frac{1}{1 - \varphi\,(\theta_1, \theta_2)} = f(\theta_1, \theta_2)$$

Were f is also an unknown function.

Imagine now a Carnot engine operating between reservoir at θ_2 and θ_3, absorbing Q_2 at θ_2 and rejecting Q_3 at θ_3. The same equation must hold as in the previous case; thus,

$$\frac{Q_2}{Q_3} = f(\theta_2, \theta_3)$$

Since the heat rejected by the first Carnot engine, Q_2, is absorbed by the second Carnot engine, both engines working together constitute a third Carnot engine, which absorbs heat Q_1 from a reservoir at θ_1 and rejects heat Q_3 to a reservoir at θ_3 where

$$\frac{Q_1}{Q_3} = f(\theta_1, \theta_3)$$

Kelvin Temperature Scale:

Since,

$$\frac{Q_1}{Q_2} = \frac{Q_1/Q_3}{Q_2/Q_3}$$

Therefore, $f(\theta_1, \theta_2) = \frac{f(\theta_1,\theta_3)}{f(\theta_2,\theta_3)}$

Now the temperature θ_3 is arbitrarily chosen; and since it does not appear in the left-hand side of the above equation, it must therefore dropout the ratio on the right. After it has been cancelled, the the numerator can be written $\psi(\theta_1)$ and the denominator $\psi(\theta_2)$ where ψ is another unknown function. Thus,

$$\frac{Q_1}{Q_2} = \frac{\psi(\theta_1)}{\psi(\theta_2)}$$

The ratio on the right is defined as the ratio of two Kelvin temperatures and is denoted by

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Thus, two temperatures on the Kelvin scale are to each other as the heats absorbed and rejected, respectively, by a Carnot engine operating between reservoirs at these temperatures. It is seen that the Kelvin temperature scale is independent of the peculiar characteristics of any particular substance.

Kelvin Temperature Scale:

At first thought it might seem that the ratio of two Kelvin temperature would be impossible to measure, since a Carnot engine is an ideal engine, quite impossible to construct. The situation, however, is not as bad as it seems. The ratio of two Kelvin temperatures is the ratio of two heats that are transferred during two isothermal processes bounded by the same two adiabatic. The two adiabatic boundaries may be located experimentally, and the heats transferred during two isothermal "nearly reversible" processes can be measured with considerable precision. As a matter of fact, this is one of the methods used in measuring temperature below 1^oK.

To complete the definition of the Kelvin scale we arbitrarily select the value of 273.16^o K to the temperature of the triple point of the water T_3. Tus,

$$T_3 = 273.16^o \text{K}$$

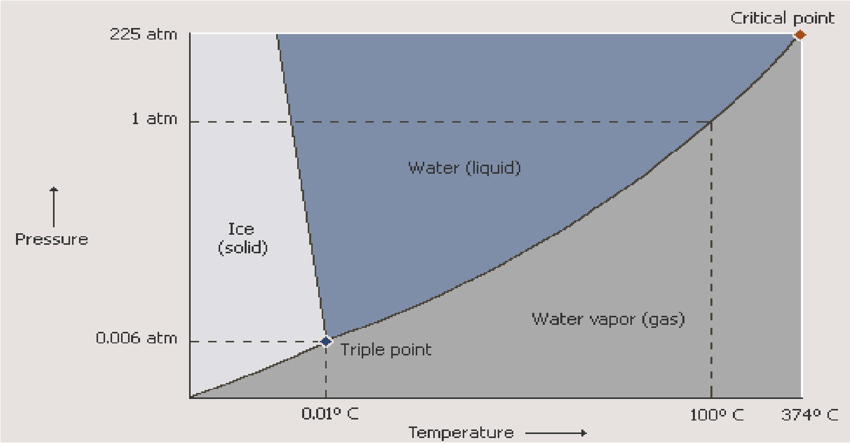
For a Carnot engine operating between reservoir at the temperatures T and T_3 we have,

$$\frac{Q}{Q_3} = \frac{T}{T_3}$$

$$T = 273.16^o K \frac{Q}{Q_3}$$

Kelvin Temperature Scale:

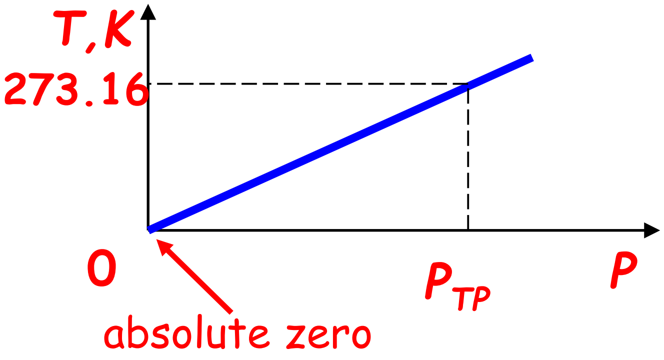
The absolute (Kelvin) temperature scale is based on fixing ***T*** of the triple point for water (a specific ***T* = 273.16 K** and ***P* = 611.73 Pa** where water can coexist in the solid, liquid, and gas phases in equilibrium).



for an ideal gas constant-volume thermoscope

$$T = 273.16^oK\,\frac{Q}{Q_3}$$

$$T = 273.16^oK\,\frac{T}{T_3}$$



P_{TP} – the pressure of the gas in a constant-volume gas thermoscope at T = 273.16 K

$$\boxed{T \equiv 273.16\,K\left(\frac{P}{P_{TP}}\right)}$$

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Absolute Zero:

It follows from the equation

$$T = 273.16^o K \, \frac{Q}{Q_3}$$

That the heat transferred isothermally between two given adiabatics decreases as the temperature decreases. Conversely the smaller the value of Q, the lower the corresponding T. the smallest possible value of Q is zero, and corresponding T is absolute zero. Thus, if a system undergoes a reversible isothermal process without transfer of heat, the temperature at which this process takes place is called absolute zero.

In other words, at absolute zero, an isotherm and adiabatic are identical.

A Carnot engine absorbing heat Q_1 from the hot reservoir at T_1 and rejecting heat Q_2 to a cooler reservoir at T_2 has efficiency, $\eta = 1 - \frac{Q_2}{Q_1}$ *and* $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

$$\eta = 1 - \frac{T_2}{T_1}$$

$$\eta = 1 - \frac{T_2}{T_1} \; if \; T_2 \rightarrow 0 \; (\, absolute\ zero\ temperature),$$

$\eta = 100\%$ practically impossible.

Carnot Cycle of an ideal Gas.

Equality of Ideal gas temperature and Kelvin Temperature:

A Carnot cycle of an ideal gas is shown in figure 1.3 the two isothermal processes b → c and d → a are represented by equilateral hyperbolas whose equations are, respectively

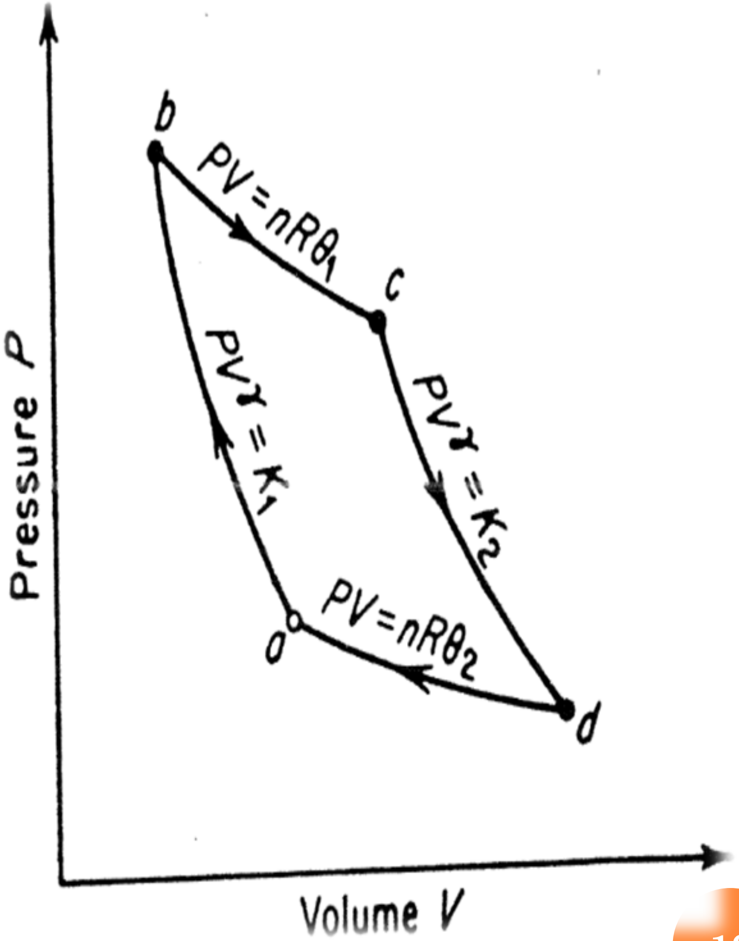
$$PV = \mathrm{nR}\theta_1$$

$$PV = \mathrm{nR}\theta_2$$

and

For any infinitesimal reversible process of an ideal gas, the first law of thermodynamic may be written as,

$$dQ = \mathrm{C}_V \mathrm{d}\theta + \mathrm{P\ dv}$$



Carnot Cycle of an ideal Gas.

Equality of Ideal gas temperature and Kelvin Temperature:

Applying this equation to the isothermal process b → c the heat absorbed is found to be

$$Q_1 = \int_{V_b}^{V_c} \mathrm{P\,dv} = \mathrm{nR}\,\theta_1\, ln\frac{V_c}{V_b}$$

Similarly, isothermal process d → a the heat rejected is found to be

$$Q_2 = \int_{V_d}^{V_a} \mathrm{P\,dv} = \mathrm{nR}\,\theta_1\, ln\frac{V_d}{V_a}$$

Therefore,

$$\frac{Q_1}{Q_2} = \frac{\theta_1\, ln\frac{V_c}{V_b}}{\theta_2\, ln\frac{V_d}{V_a}}$$

Since the process a → b is adiabatic, we may write for any infinitesimal portion

$$-\,C_V\, d\theta = \mathrm{P\,dV}$$

$$-\,C_V\, d\theta = \frac{n\,R\,\theta}{V}\mathrm{dV}$$

Integrating from a to b we get,

$$\frac{1}{n\,R}\int_{\theta_2}^{\theta_1} C_V\, d\theta = ln\frac{V_a}{V_b}$$

Carnot Cycle of an ideal Gas.

Equality of Ideal gas temperature and Kelvin Temperature:

Similarly for adiabatic process c → d,

$$\frac{1}{n\,R}\int_{\theta_2}^{\theta_1} C_V\,d\theta = ln\frac{V_d}{V_c}$$

Therefore, $ln\frac{V_a}{V_b} = \; ln\frac{V_d}{V_c} \;\Rightarrow\; ln\frac{V_c}{V_b} = \; ln\frac{V_d}{V_a}$

And finally we get,

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}$$

If θ and T refer to any temperature and, θ_3 and T_3 refer to the triple point of water, the preceding equation becomes,

$$\frac{\theta}{\theta_3} = \frac{T}{T_3}$$

Since $\theta_3 = T_3 = 273.16^oK$ it follows that $\theta = T$

The Kelvin temperature is therefore numerically equal to the ideal gas temperature and, in the proper range, may be measured with a gas thermometer.

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Clausius' Theorem

Let us consider a generalized work diagram in which generalized force y is plotted against corresponding generalized displacement X for general discussions.

Consider a reversible process represented by the smooth curve $i \rightarrow f$ on the generalized work diagram shown in figure 1.4. The nature of the system is immaterial. The dotted curves through i and f, respectively, represent portions of adiabatic processes. Let us draw a curve $a \rightarrow b$ representing an isothermal process in such a way that the area under the smooth curve *if* is equal to the area under the zigzag path *iabf*. Then the work done in traversing both paths is the same or

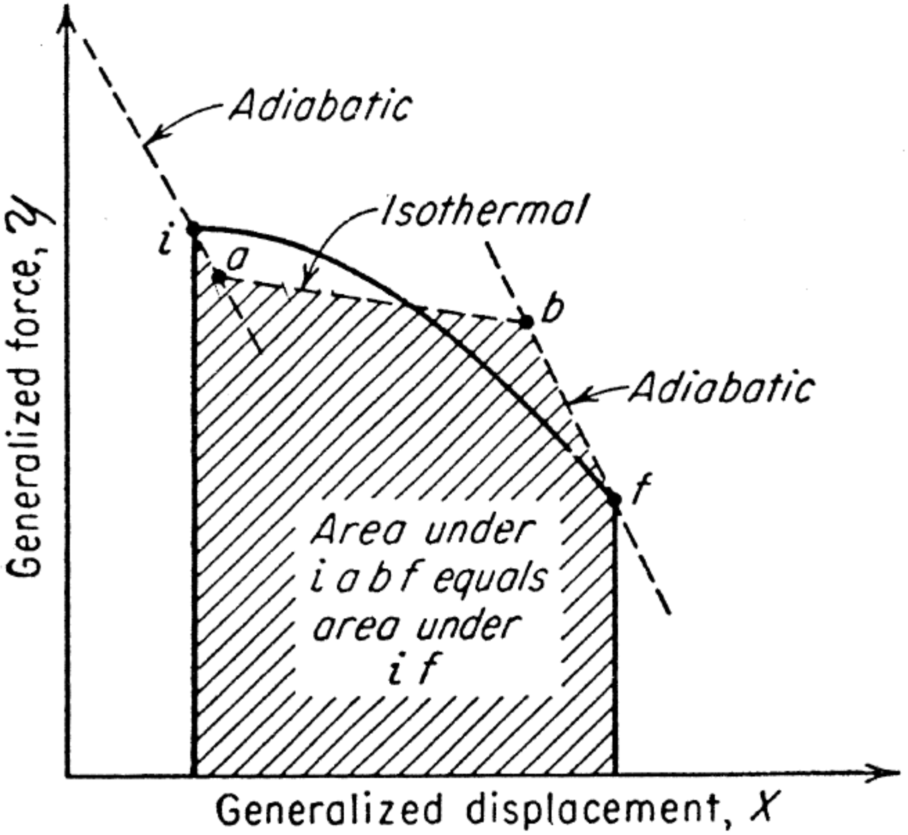

Fig. 1.4 Generalized work diagram (i → f, any reversible process; i → a, reversible adiabatic process, a → b, reversible isothermal process, b → f, reversible adiabatic process.)

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Clausius' Theorem

$W_{if} = W_{iabf}$

Now, $Q_{if} = U_f - U_i + W_{if}$, And $Q_{iabf} = U_f - U_i + W_{iabf}$

$Q_{if} = Q_{iabf}$

But since no heat is transferred in the two adiabatic processes *ia* and *bf*,

We have $Q_{if} = Q_{iabf}$

If we are given, therefore, a reversible process in which the temperature may change in any manner, it is always possible to find a reversible zigzag path between the same two states, consisting of an adiabatic followed by a isothermal followed by an adiabatic, such that the heat transferred during the isothermal portion is the same as that transferred during the original process.

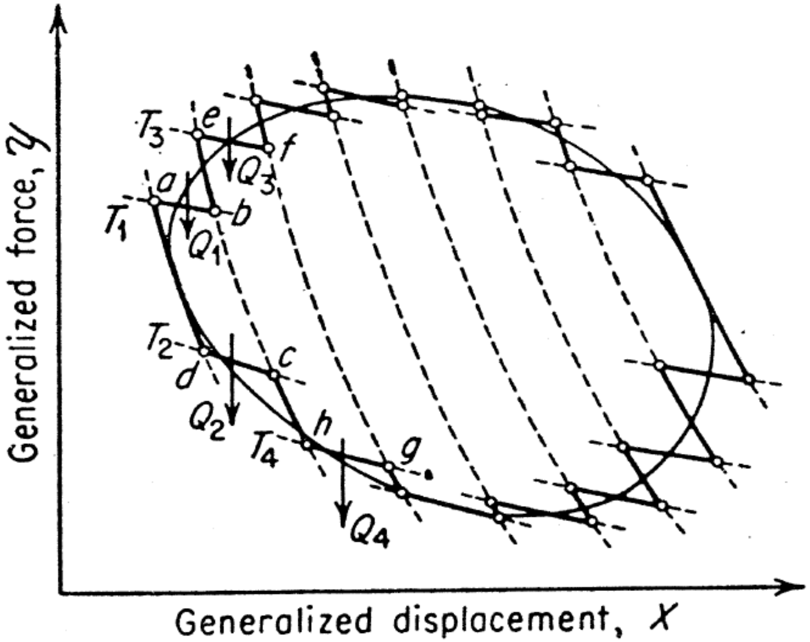

Fig. 1.5 *Generalized work diagram (Smooth closed curve = reversible cycle; zigzag closed path = alternate reversible isothermal and adiabatic processes.)*

Now consider the smooth closed curve representing a reversible cycle on the work diagram shown in fig. 1.5. Since no two adiabatic lines can intersect a number of adiabatic lines may be drawn, dividing the cycle into a number of adjacent strips. A zigzag closed path may now be drawn, consisting of alternate adiabatic and isothermal portions, such that the heat transferred during all the isothermal portions is equal to the heat transferred in the original cycle. Consider the two isothermal processes ab at the temperature T_1, during which heat Q_1 is absorbed, and *cd* at the temperature T_2, during which heat Q_2 is rejected. Since *ab* and *cd* are bounded by the same adiabatics, *abcd* is a Carnot cycle and we may write,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Clausius' Theorem

Ignoring the sign convention. Let us now adhere to the sign convention and regard any Q as an algebraic symbol, positive for heat absorbed and negative for head rejected. We may then write, $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$

Where, Q_1 stands for a positive number and Q_2 for a negative number. Since the isothermals *ef* and *gh* are bounded by the same two adiabatics *efgh* is also a Carnot cycle, and $\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$

If a similar equation is written for each pair of isothermals bounded by the same two adiabatics and if all the equations are added, the result is obtained that

$$\frac{Q_1}{T1} + \frac{Q_2}{T_2} + \frac{Q_3}{T3} + \frac{Q_4}{T4} + \cdots = 0$$

Since no heat is transferred during the adiabatic portions of the zigzag cycle, we may write. $\sum \frac{Q}{T} = 0$,

Where the summation is taken over the complete zigzag cycle.

Now imagine the cycle divided into a very large number of strips by drawing a large number of adiabatics close together. If we connect these adiabatics with small isothermals in the manner already described, a zigzag path may be traced that may be made to appropriate the original cycle as closely as we please. When these isothermal processes become infinitesimal, the ratio dQ/T for the infinitesimal piece of the original cycle bounded by the same two adiabatics. In the limit, therefore, we may write, for any reversible cycle.

$$\oint_R \frac{dQ}{T} = 0$$

The circle through the integral sign signifies that the integration takes place over the complete cycle and the letter R emphasizes the fact that the equation is true only for a reversible cycle. This result is known as Clausius theorem.

Entropy and the Mathematical Formulation of the Second Law

Let an initial equilibrium state of any thermo dynamic system be represented by the point *i* on any convenient diagram such as the generalized work diagram of Fig. 1.6.

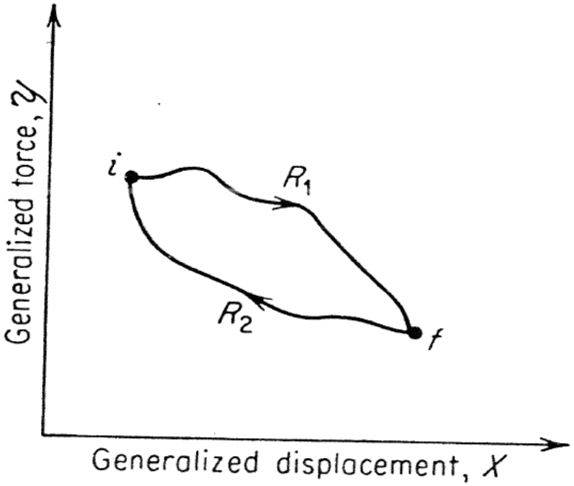

Fig. 1.6 *Two reversible paths joining two equilibrium state if a system.*

Denote a final equilibrium state by the point *f*. It is possible to take the system from *i* to *f* along any number of different reversible paths since *i* and *f* are equilibrium states. Suppose the system is taken from *i* to *f* along the reversible path R_1 and then back to *i* again along another reversible path R_2. The two paths obviously constitute a reversible cycle, and from Clausius' theorem, we may write.

$$\oint_{R_1R_2} \frac{dQ}{T} = 0$$

The above integral may be expressed as the sum of two integrals, one for the path R_1 and the other for the path R_2. We have them

$$\underset{R_1}{\oint_i^f} \frac{dQ}{T} + \underset{R_2}{\oint_f^i} \frac{dQ}{T} = 0$$

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Entropy and the Mathematical Formulation of the Second Law

${}_{R_1}\oint_i^f \frac{dQ}{T} = -\ {}_{R_2}\oint_f^i \frac{dQ}{T}$ Since R_2 is a reversible path. $-\ {}_{R_2}\oint_f^i \frac{dQ}{T} = {}_{R_2}\oint_i^f \frac{dQ}{T}$ And finally ${}_{R_1}\oint_i^f \frac{dQ}{T} = {}_{R_2}\oint_i^f \frac{dQ}{T}$,

Since R_1 and R_2 were chosen at random and represent any two reversible paths, the above equation expresses the important fact that ${}_{R}\oint_i^f \frac{dQ}{T}$ is independent of the reversible parth connecting i and f. It therefore follows that there exists a function of thermodynamic coordinates of a system whose value at the final state minus its value at the initial state equals the integral ${}_{R}\oint_i^f \frac{dQ}{T}$. This function is called the entropy and is denoted by S. If S_i is the entropy at the initial state and S_f that at the final state, then we have the result that ${}_{R}\oint_i^f \frac{dQ}{T} = S_f - S_i$,

Where the difference $S_f - S_i$ is the entropy change

Finally if the two equilibrium states i and f are infinitesimally near the integral sign may be eliminated and $S_f = S_i$ becomes dS. The equation then becomes

$$\frac{dQ_R}{T} = dS$$

Where dS is an exact differential, since it is the differential of an actual function. The subscript R written along with dQ indicates that the preceding equation is true only if dQ is transferred reversibly. This equation is the mathematical formulation of the second law.

Entropy of an Ideal Gas

If a system absorbs an infinitesimal amount of heat dQ_R during a reversible process, the entropy change of the system is equal to

$$dS = \frac{dQ_R}{T}$$

It is interesting to notice that, although dQ_R is an inexact differential, the ratio dQ_R/T is exact. The reciprocal of the Kelvin temperature is therefore the integrating factor of dQ_R. If dQ_R is expressed as a sum of differentials involving thermodynamic coordinates, then, upon dividing by T, the expression may be integrated and the entropy of the system obtained. As an example of this procedure, consider one of the expressions for dQ_R of an ideal gas, namely

$$dQ_R = C_P\, dT - V\, dP$$

Dividing by T, we get

$$\frac{dQ_R}{T} = C_P \frac{dT}{T} - \frac{V}{T}\, dP$$

$$dS = C_P \frac{dT}{T} - n\,R\,\frac{V}{T}\, dP$$

Entropy of an Ideal Gas

Let us now calculate the entropy change *ΔS* of the gas between an arbitrarily chosen standard state with coordinates T_S, P_s and any other state with coordinates *T*, *P*. Integrating between these two states, we get

$$\Delta S = \int_{T_S}^{T} C_p \frac{dT}{T} - n\, R \ln \frac{P}{P_s}$$

Suppose we ascribe to the standard state an entropy S_S and choose any arbitrary numerical value for this quantity. Then an entropy S may be associated with the other state where $S - S_S = \Delta S$. To make the discussion simpler, let C_P be constant. Then

$$S = C_P\, lnT - n\, R\, lnP + (S_S - C_P \ln T_S + n\, R \ln P_s)$$

Denoting the quality in parentheses by the constant S_0,

$$S = C_P\, lnT - n\, R\, lnP + S_0$$

Substituting for T and *P* thousands of different values, we may calculate thousands of corresponding values of *S* which, after tabulation, constitute an entropy table. Any one value from this table, taken alone, will have no meaning. The difference between two values, however, will be an actual entropy change.

Let us now return to the original differential equation

$$dS = C_F \frac{dT}{T} - nR \frac{dP}{P}$$

Again for simplicity, assuming C_F to be constant, we may take the indefinite integral and obtain $S = C_P\, lnT - n\, R\, lnP + S_0$

Where S_0 is the constant of integration.

Entropy of an Ideal Gas

Since this is precisely the equation obtained previously, we see that, in taking the indefinite integral of dS, we do not obtain an "absolute entropy," but merely an entropy referred to a nonspecified standard state whose coordinates are contained within the constant of integration. Thus, for an ideal gas

$$S = \int C_P \frac{dT}{T} - nR \ln P + S_0$$

To calculate the entropy of an ideal gas as a function of T and V, we

Use the other expression for dQ_R of an ideal gas. Thus,

$$\frac{dQ_R}{T} = C_V \frac{dT}{T} + \frac{P}{T} dV$$

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

Proceeding in the same way as before, we get for the entropy, referred to an unspecified standard state, the expression

$$S = \int C_V \frac{dT}{T} + nR \ln V + S_0$$

Which becomes, if C_V is constant

$$S = C_V \ln T - n R \ln V + S_0$$

T-S Diagram

For each infinitesimal amount of heat that enters a system during an infinitesimal portion of a reversible process there is an equation

$dQ_R = T\,dS$

It follows therefore that the total amount of heat transferred in a reversible process is given by

$Q_R = \int_i^f T\,dS$

This integral can be interpreted graphically as the area under a curve on a diagram in which T is plotted along the Y axis and S along the X axis. The nature of the curve on the T-S diagram is determined by the kind of reversible process that the system undergoes. Obviously an isothermal process is a horizontal line

In the case of a reversible adiabatic process, we have

$$dS = \frac{dQ_R}{T}$$

And $dQ_R = 0$

Hence, if T is not zero, dS=0

And S is constant.

T-S Diagram

Therefore during a reversible adiabatic process, the entropy of a system remains constant or, in other words, the system undergoes an *isentropic process*. An isentropic process on a T-S diagram is obviously a vertical line. It is therefore clear that the two isothermal and the two adiabatic processes which go to make up a Carnot cycle form a rectangle on a T-S diagram, no matter what the working substance is. Only reversible processes may be plotted on a T-S diagram since entropy has been defined only for equilibrium states.

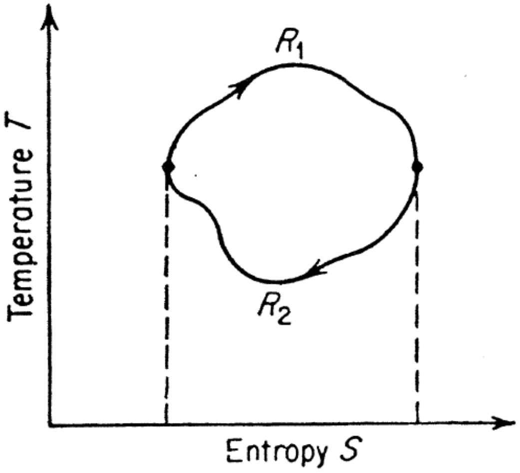


Fig. 1.7 Reversible cycle on a T-S diagram.

The T-S diagram is particularly convenient for representing reversible cycles. The closed curve shown in figure 1.7 consisting of an upper portion R_1 and a lower portion R_2 represents a reversible engine cycle. The area under R_1 (positive area) is equal to the heat absorbed Q_1 and the area under R_2 (negative area) to the heat rejected Q_2. The area inside the closed curve is therefore $Q_1 - Q_2$ or W. Since the efficiency of the engine is $1 - (Q_2/Q_1)$, it may be measured directly from the diagram.

Entropy and Reversibility

The fact that the area under a curve on a T-S diagram is equal to the heat transferred in a reversible process is of some importance to the mechanical engineer but of little interest to the theoretical physicist.

In order to understand the physical meaning of entropy and its significance in the world of science, it is necessary to study all the entropy changes that take place when a system undergoes a process.

If we calculate the entropy change of the system and add to this the entropy change of the local surroundings, we obtain a quantity that is the sum of all the entropy changes brought about by this particular process. We may call this the entropy change of the universe due to the process in question.

When a finites amount of heat is absorbed or rejected by a reservoir, extremely small changes in the coordinates take place in every unit of mass. The entropy change of a unit of mass is therefore very small. Since, however, the total mass of a reservoir is large; the total entropy change is finite. Suppose that a reservoir is in contact with a system and that heat Q is absorbed by the reservoir at the temperature T. The reservoir undergoes nondissipative changes determined entirely by the quantity of head absorbed. Exactly the same changes in the reservoir would take place if the same amount of heat Q were transferred reversibly. Hence the entropy change of the reservoir is Q/T. Therefore, whenever a reservoir absorbs head Q at the temperature T from any system during any kind of process, the entropy change of the reservoir is Q/T.

Entropy and Reversibility

Consider now the entropy change of the universe that is brought about by the performance of any reversible process. The process will in general, be accompanied by a flow of heat between a system and set of reservoirs ranging in temperature from T_i to T_f. During any infinitesimal portion of the process, an amount of heat dQ_R is transferred between the system and one of the reservoirs at the temperature T. Let dQs be a positive number, if dQ_R is absorbed by the system. Then

$$dS\ of\ the\ system = +\frac{dQ_R}{T}$$

$$dS\ of\ the\ reservoir = -\frac{dQ_R}{T}$$

And the entropy change of the universe is zero.

If dQ_R is rejected by the system then obviously

$$dS\ of\ the\ system = -\frac{dQ_R}{T}$$

$$dS\ of\ the\ reservoir = +\frac{dQ_R}{T}$$

And the entropy change the universe is again zero. If dQ_R is zero, then neither the system nor the reservoir will have an entropy change and the entropy change of the universe is still zero. Since this is true for any infinitesimal portion of the reversible process, it is true for all such portions, and therefore we may conclude that, *when a reversible process is performed the entropy of the universe remains unchanged.*

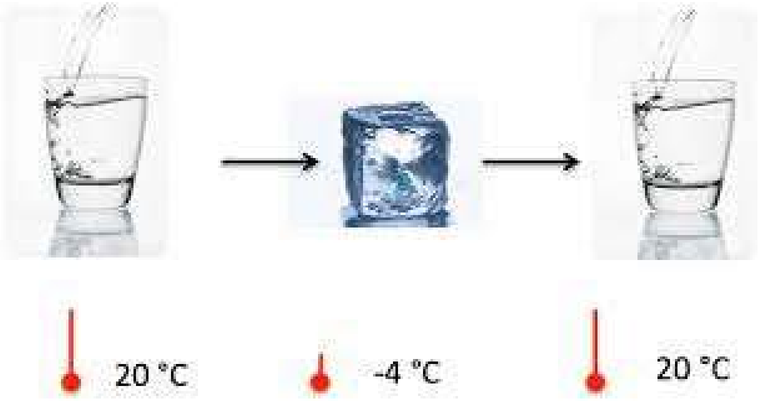
Reversible Vs Irreversible processes

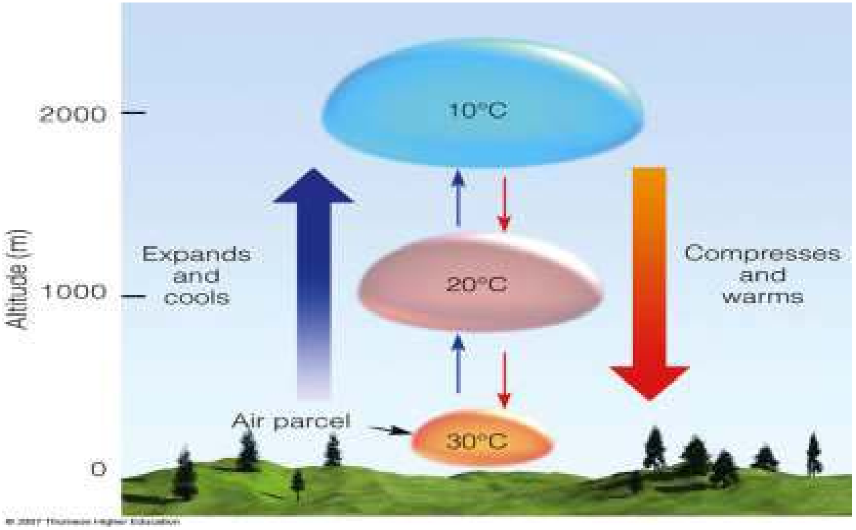
A reversible process is defined as:

“A reversible process is a process whose direction can be "reversed" by inducing infinitesimal changes to some property of the system via its surroundings, while not increasing entropy.”

Or

“A process that can be reversed without leaving any change on the surroundings.”





Reversible Vs Irreversible processes

"*A process that is not reversible is called an Irreversible Process*."

- In irreversible process, system passes through a series of non-equilibrium states.
- It is difficult to locate properties on property diagram as they don't have a unique value.
- When irreversible process is made to proceed in backward direction, it does not reach its original state.
- The system reaches a new state.
- Irreversible processes are usually represented by dotted lines.

The factors that cause a process to be Irreversible are :

1. Friction
2. Free Expansion
3. Mixing of two gases
4. Heat transfer between finite temperature difference
5. Electric resistance
6. Inelastic deformation
7. Chemical reactions

The presence of any of these effects makes a process irreversible.

Reversible Vs Irreversible processes

Clausius inequality conditions

$$dS = \oint \frac{dQ}{T} = 0, \mathit{the\ process\ is\ reversible}$$

$$dS = \oint \frac{dQ}{T} < 0, \mathit{the\ process\ is\ irreversible\ and\ possible}$$

$$dS = \oint \frac{dQ}{T} > 0, \mathit{the\ process\ is\ impossible}$$

For any irreversible process, $dS > \frac{dQ}{T}$

For any reversible process, $dS > \frac{(dQ)_{rev}}{T}$

Entropy and Irreversibility

When a system undergoes an irreversible process between an initial equilibrium state and a final equilibrium state, the entropy change of the system is equal to

$$S_f - Si = \;_R\int_i^f \frac{dQ}{T}$$

Where R indicates any reversible process arbitrarily chosen by which the system may be brought from the given initial state to the given final state. No integration is performed over the original irreversible path. The irreversible process is replaced by a reversible one. This can easily be done when the initial and the final state of the system are equilibrium states. When either the initial or the final state is a non-equilibrium state, special methods must be used. At first, we shall limit ourselves to irreversible processes all of which involve initial and final states of equilibrium.

Entropy and Irreversibility

Processes Exhibiting External Mechanical Irreversibility.

(a) Those involving the isothermal dissipation of work through a system (which remains unchanged) into internal energy of a reservoir, such as

1. Irregular stirring of a viscous liquid in contact with a reservoir.
2. Coming to rest of a rotating or vibrating liquid in contact with a reservoir.
3. Inelastic deformation of a solid in contact with a reservoir.
4. Transfer of electricity through a resistor in contact with a reservoir.
5. Magnetic hysteresis of a material in contact with a reservoir.

In the case of any process involving the isothermal transformation of work if through a system into internal energy of a reservoir, there is no entropy change of the system because the thermodynamic coordinates do not change. There is a flow of heat Q into the reservoir where Q = W. Since the reservoir absorbs Q units of heat at the temperature T, its entropy change is + Q/T or + W/T. The entropy change of the universe is therefore W/T, which is a positive quantity.

Entropy and Irreversibility

Processes Exhibiting External Mechanical Irreversibility.

(b) Those involving the adiabatic dissipation of work into internal energy of a system such.

1. Irregular stirring of a viscous thermally insulated liquid.
2. Coming to rest of a rotating or vibrating thermally insulated liquid.
3. Inelastic deformation of a thermally insulated sold.
4. Transfer of electricity through a thermally insulated resistor
5. Magnetic hysteresis of a thermally insulated material

In the case of any process involving the adiabatic transformation of work W into internal energy of a system whose temperature rises from T_i to T_f at constant pressure, there is no flow of heat to or from the surroundings and therefore the entropy change of the local surroundings is zero. To calculate the entropy change of the system, the original irreversible process must be replaced by a reversible one that will take the system from the given initial state (temperature T_i, pressure P) to the final state (temperature T_f, pressure P). Let us replace the irreversible performance of work by a reversible isobaric flow of heat from a series of reservoirs ranging in temperature from T_i to T_f. The entropy change of the system will then be $S_f - Si\ (System) = {}_R\int_{T_i}^{T_f} \frac{dQ}{T}$

For an isobaric process $dQ_R = C_P\, dT$, and $S_f - Si\ (system) \int_{T_i}^{T_f} C_P \frac{dT}{T}$

Finally, if C_P is assumed constant, $S_f - Si\ (system) C_P\ ln\ \frac{T_f}{T_i}$

and the entropy change of the universe is $C_P \ln (T_f / T_i)$ which is a positive quantity.

Entropy and Irreversibility

Process exhibiting internal mechanical irreversibility.

Those involving the transformation of internal energy of a system into mechanical energy and then back into internal energy again, such as

1. Ideal gas rushing into a vacuum (free expansion)
2. Gas seeping through a porous plug (throttling process)
3. Snapping of a stretched wire after it is cut.
4. Collapse of a soap film after it is pricked.

In the case of a free expansion of an ideal gas, the entropy change of the local surroundings is zero. To calculate the entropy change of the system, the free expansion must be replaced by a reversible process that will take the gas from its original state (volume V_i. temperature T) to the final state (volume V_f, temperature T). Evidently, the most convenient reversible process is a reversible isothermal expansion at the temperature T from a volume V_i. The entropy change of the system is then $S_f - Si\ (System)\ {}_R\int_{V_i}^{V_f} \frac{dQ}{T}$

For an isothermal process of an ideal gas And $dQ_R = P\ dV$ and $\frac{dQ_R}{T} = nR\ \frac{dV}{V}$,

Whence $S_f - Si\ (system) = n\ R\ \ ln\ \frac{V_f}{V_i}$

The entropy change of the universe is therefore, $n\ R\ \ ln\ \frac{V_f}{V_i}$, which is a positive number

Entropy and Irreversibility

Processes Exhibiting External Thermal Irreversibility.

Those involving a transfer of heat by virtue of a finite temperature difference, such as

1. Conduction or radiation of heat from a system to its cooler surroundings
2. Conduction or radiation of heat through a system (which remains unchanged) from a hot reservoir to a cooler one.

In the case of the conduction of Q units of heat through a system (which remains unchanged) from a hot reservoir at T_1 to a cooler reservoir at T_2, the following steps are obvious.

$$S_f - Si\ (system) = 0$$

$$S_f - Si\ (hot\ reservoir) = -\frac{Q}{T_1}$$

$$S_f - Si\ (cold\ reservoir) = +\frac{Q}{T_2}$$

$$S_f - Si\ (univers) = \frac{Q}{T_2} - \frac{Q}{T_1}$$

Entropy and Irreversibility

Processes Exhibiting Chemical Irreversibility.

Those involving a spontaneous change of internal structure, chemical composition, density, etc. such as

1. A chemical reaction
2. Diffusion of two dissimilar inert ideal gases
3. Mixing of alcohol and water
4. Freezing of super cooled liquid.
5. Condensation of a supersaturated vapor
6. Solution of a solid in water

Assuming the diffusion of two dissimilar inert gases to be equivalent to two separate free expansions, for one of which $S_f - Si\ (universe) = n\, R\, ln\, \frac{V_f}{V_i}$

And taking a mole of each gas with $V_i = \nu$, and $V_f = 2\nu$

we obtain $S_f - Si\ (universe) = 2\, R\, ln\, 2$

Which is a positive number.

Entropy and Irreversibility

Table 1.1. Entropy Change of the Universe Due to Natural Processes.

Type of irreversibility	Irreversible process	Entropy change of the system	Entropy change of the local surroundings	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work through a system into internal energy of a reservoir	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work into internal energy of a system	$C_P \ln \frac{T_f}{T_i}$	0	$C_P \ln \frac{T_f}{V_i}$
Internal mechanical irreversibility	Free expansion of an ideal gas	$nR \ln \frac{V_f}{V_i}$	0	$nR \ln \frac{V_f}{V_i}$
External thermal irreversibility	Transfer of heat through a medium from a hot to a cooler reservoir	0	$\frac{Q}{T_2} - \frac{Q}{T_1}$	$\frac{Q}{T_2} - \frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert ideal gases	$2\ R\ ln\ 2$	0	$2\ R\ ln\ 2$

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Entropy and Nonequilibrium States

Consider, the following process involving internal thermal irreversibility. A thermally conducting bar, brought to a no uniform temperature distribution by contact at one end with a hot reservoir and at the other end with a cold reservoir, is removed from the reservoirs and then thermally insulated and kept at constant pressure. An internal flow of heat will finally bring the bar to a uniform temperature, *but the transition will be from an initial nonequilibrium state to a final equilibrium state.*

It is obviously impossible to find one reversible process by which the system may be brought from the same initial to the same final state.

Let us consider the bar to be composed of an infinite number of infinitesimally thin sections, each of which has a different initial temperature but all of which have the same final temperature. Suppose we imagine all the sections to be insulated from one another and all kept at the same pressure and then each section to be put in contact successively with a series of reservoirs ranging in temperature from the initial temperature of the particular section to the common final temperature. This defines an infinite number of reversible isobaric processes, which may be used to take the system from its initial non equilibrium state to its final equilibrium state.

We shall now define the entropy change as the result of integrating dQ/T over all of these reversible processes. In other words, in the absence of one reversible process to take the system from i to f we conceive of an infinite number of reversible processes – one for each volume element.

Let us consider the uniform bar of length L shown in fig. 1.8 A typical volume element at x has a mass

$$dm = \rho A \, dx$$

Where ρ is the density and A the cross sectional area. The heat capacity of the section is

$$C_P \, dm = C_P \, \rho A \, dx$$

Entropy and Nonequilibrium States

Let us suppose that the initial temperature distribution is linear, so that the section at x has an initial temperature.

$$T = T_0 - \frac{T_0 - T_L}{L} x$$

If no heat is lost and if we assume for the sake of simplicity that the thermal conductivity, density and heat capacity of all sections remain constant, then the final temperature will be

$$T_f = \frac{T_0 + T_L}{2}$$

Integrating dQ/T over a reversible isobaric transfer of heat between the volume element and a series of reservoirs ranging in temperature from T_i to T_f we get for the entropy change of this one volume element.

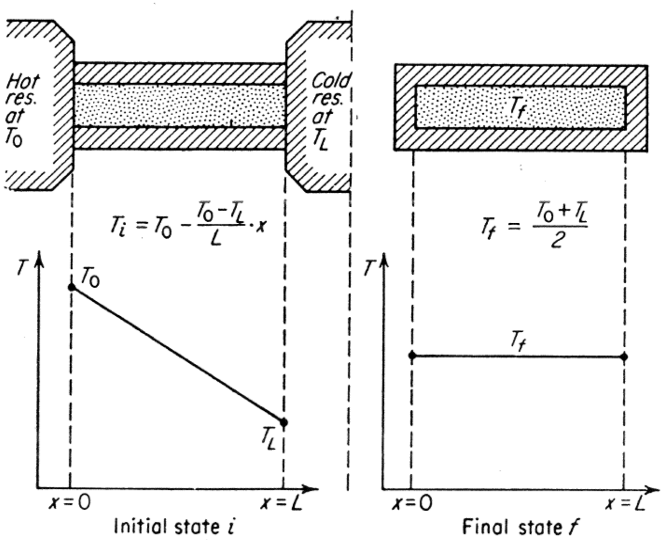

Figure 1.8. Process exhibiting internal thermal irreversibility.

$$C_P \, \rho \, A \, dx \int_{T_i}^{T_f} \frac{dT}{T} = C_P \, \rho \, A \, dx \ln \frac{T_f}{T_i}$$

$$= C_P \;\; \rho \, A \, dx \;\; \ln \frac{T_f}{T_0 - \frac{T_0 - T_L}{L} x}$$

$$= C_P \;\; \rho \, A \, dx \;\; \ln \left(\frac{T_0}{T_f} - \frac{T_0 - T_L}{L T_f} x \right)$$

Entropy and Nonequilibrium States

Upon integrating over the whole bar, the total entropy change is

$$s_f - s_i = -C_P\,\rho\,A \int_0^L \ln\left(\frac{T_0}{T_f} - \frac{T_0 - T_L}{LT_f}\,x\right) dx$$

Which after integration and simplification, becomes

$$S_f - S_i = -C_P\,l\left(1 + \ln T_f + \frac{T_L}{T_0 - T_L}\ln T_L - \frac{T_0}{T_0 - T_L}\ln T_0\right)$$

To show that the entropy change is positive,

let us take a convenient numerical case such as $T_0 = 400^0K$, $T_L = 200^0K$, whence $T_f = 300^0K$

then,

$$S_f - S_i = 2.30\ C_P\,l\left(\frac{1}{2.30} + 2.477 + 2.301 - 2x2.602\right) = 0.021\ C_P$$

The same method may be used to compute the entropy change of a system during a process from an initial non equilibrium state characterized by a nonuniform pressure distribution to a final equilibrium state where the pressure is uniform.

Principle of the Increase of Entropy

The entropy change of the universe associated with each of the irreversible processes treated up to now is positive. We are led to believe, therefore, that whenever an irreversible process takes place the entropy of the universe increases. To establish this we take adiabatic process only, since we have already seen that the entropy principle is true for all processes involving the irreversible transfer of heat. *We start the proof by considering the special case of an adiabatic irreversible process between two equilibrium states of a system.*

1. Let the initial state of the system be represented by the point *i* on the generalized work diagram of fig 1.9 and suppose that the system undergoes an *irreversible adiabatic process* to the state *f*. Then the entropy change is

$$\Delta S = S_i - S_f$$

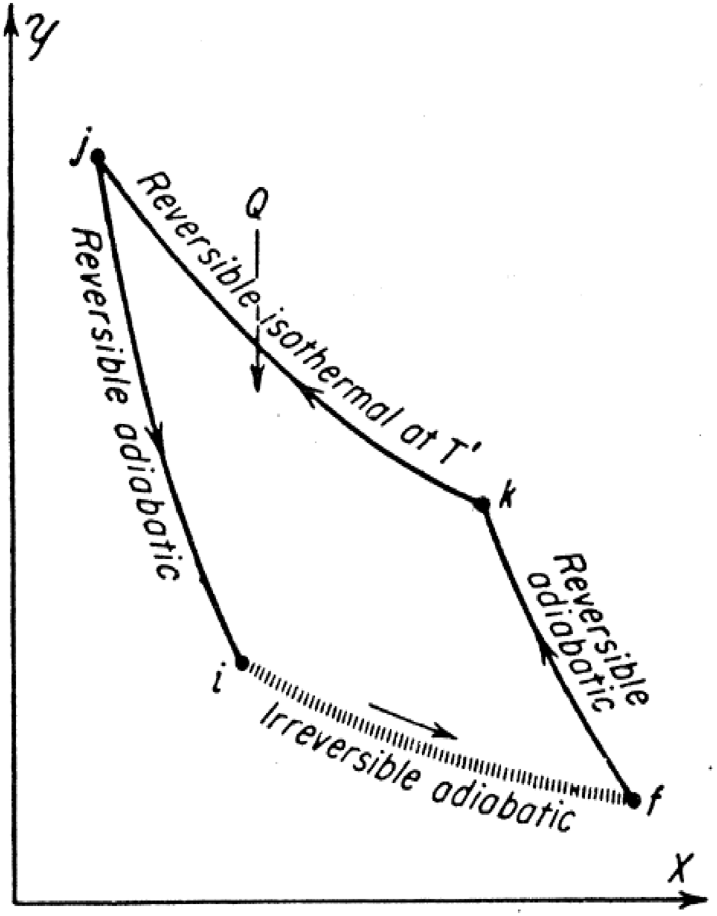

Figure 1.9. Cycle which contradicts the second law unless $S_f > S_i$

Principle of the Increase of Entropy

A temperature change may or may not have taken place. Whether or not, let us cause the system to undergo a reversible adiabatic process $f \rightarrow k$ in such a direction as to bring its temperature to that of any arbitrarily chosen reservoir, say, at T′, Then, since $S_f = S_k$

$$\Delta S = S_k - S_i$$

Now suppose that the system is brought into contact with the reservoir and caused to undergo a reversible isothermal process $k \rightarrow j$ until its entropy is the same as at the beginning. A final reversible adiabatic process $j \rightarrow i$ will now bring the system back to its initial state, and since $S_j = S_i$,

$$\Delta S = S_k - S_j$$

The only heat transfer Q that has taken place in the cycle is during the isothermal process k → j, where

$$Q = \mathrm{T}' \left(\mathrm{S}_j - \mathrm{S}_k\right)$$

A net amount of work W has been done in the cycle, where W = Q

It is clear from the second law of thermodynamics that the heat Q cannot be positive, for then we would have a cyclic process in which no effect has been produced other than the extraction of heat from a reservoir and the performance of an equivalent amount of work. Therefore $Q \leq 0$, and

$$\mathrm{T}' \left(\mathrm{S}_j - \mathrm{S}_k\right) \leq 0 \text{ , And finally } \Delta S \geq 0.$$

2. If we assume that the original irreversible adiabatic process took place without any change in entropy, then it would be possible to bring the system back to i by means of one reversible adiabatic process. Moreover, since the net heat transferred, in this cycle is zero, *the net work would also be zero.* Therefore, under these circumstances, the system and its surroundings would have been restored to their initial states without producing changes elsewhere, which implies that the original process was reversible. Since this is contrary to our original assertion, the entropy of the system cannot remain unchanged. Therefore

$$\Delta \mathrm{S} > 0.$$

Principle of the Increase of Entropy

3. Let us now suppose that the system is not *homogeneous* and not of uniform temperature and pressure and that it undergoes an irreversible adiabatic process in which mixing and chemical reaction may take place. If we assume that the system may be subdivided into parts (each one infinitesimal, if necessary) and that it is possible to ascribe a definite temperature, pressure, composition etc. to each part, so that each part shall have a definite entropy depending on its coordinates, then we may define the entropy of the whole system as the sum of the entropies of its parts. *If we now assume that it is possible to take each part back to its initial state by means of the reversible processes described in (1), using the same reservoir for each part, then it follows that ΔS of the whole system is positive.*

It should be emphasized that we have had to make two assumptions, namely, (1) that the entropy of a system may be defined by sub dividing the system into parts and summing the entropies of these parts and (2) that reversible processes may be found or imagined by which mixtures may be unmixed and reactions may be caused to proceed in the opposite direction.

The behavior of the entropy of the universe as a result of any kind process may now be represented in the following succinct manner.

$\Delta S \text{ (universe)} \geq 0$

Where the equality sign refers to reversible processes and the inequality sign to irreversible processes.

Application of the entropy principle

We have seen that whenever irreversible processes take place the entropy of the universe increases. In the actual operation of a device, such as an engine or a refrigerator, it is often possible to calculate the sum of all the entropy changes. The fact that this sum is positive enables us to draw useful conclusions concerning the behaviour of the device. An important example from the field of refrigeration engineering will illustrate the power and simplicity of the entropy principle. Suppose it is desired to freeze water or to liquefy air, i.e., to lower the temperature of a body of finite mass from the temperature T_1 of its surroundings to any desired temperature T_2. A refrigerator operating in a cycle between a reservoir at T_1 and the body itself is utilized and after a finite number of complete cycles has been traversed a quantity of heat Q has been removed from the body, a quantity of work W was been supplied to the refrigerator and a quantity of head $Q + W$ has been rejected to the reservoir as shown in fig. 1.10.

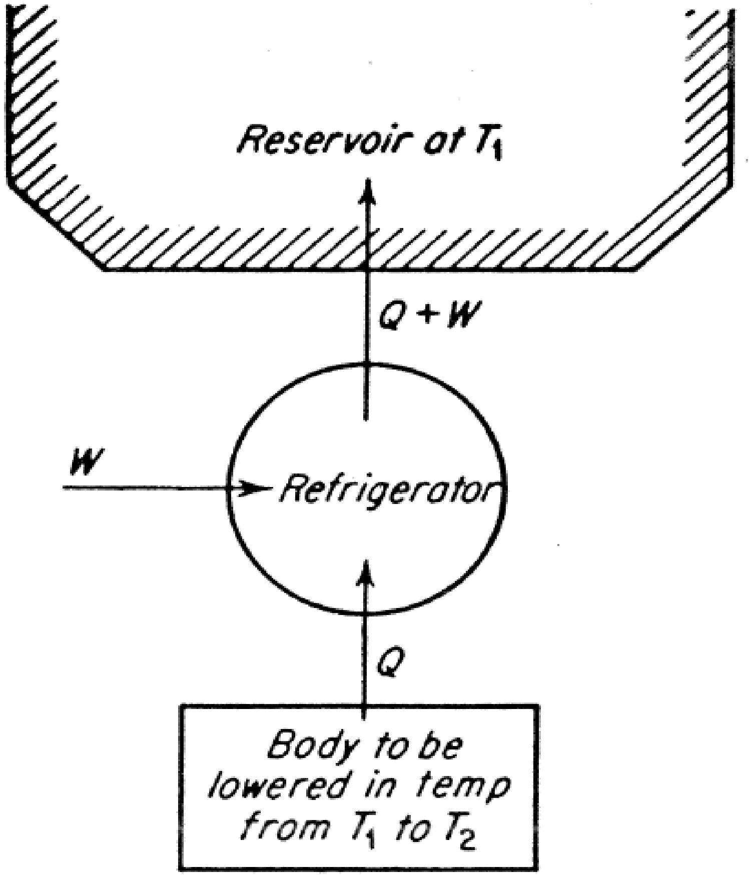

Figure 1.10 Operation of refrigerator in lowering the temperature of a body from that of its surrounding T_1 to any desired value T_2.

Application of the entropy principle

Listing the entropy changes, we have

ΔS of the body = $S_2 - S_1$

ΔS of the refrigerant = 0

$$\Delta S \; of \; the \; reservoir = \frac{Q+W}{T_1}$$

Applying the entropy principle

$$S_2 - S_1 + \frac{Q+W}{T_1} \geq 0$$

Multiplying by T_1 and rearranging we get

$$W \geq T_1 \left(S_2 - S_1\right) - Q$$

It follows that the smallest possible value for W is

$$W \; (min) = T_1 \left(S_2 - S_1\right) - Q$$

If tables of the thermodynamic properties of the material are available, a knowledge of the initial and final states is all that is needed to read from the tables the values of $S_1 - S_2$ and if the body undergoes an isobaric process of Q. *The calculated value of W (min) is used to provide an estimate of the minimum cost of operation of the refrigeration plant.*

Entropy and Unavailable Energy

Suppose that a quantity of head Q may be extracted from reservoir at the temperature T and that it is desired to convert as much as possible of this heat into work. If a colder reservoir is at the temperature T and that it is desired to convert as much as possible of this heat into work. If a colder reservoir is at the temperature T′. A Carnot engine may be used, to derive amount of work, where

$$W = Q\left(1 - \frac{T'}{T}\right)$$

The lower the temperature of the colder reservoir, the greater will be the output of work. If T_0 is the temperature of the coldest reservoir then,

$$W_{(\max)} = Q\left(1 - \frac{T_0}{T}\right)$$

Which represents the maximum amount of energy available for work when Q units of heat are extracted from a reservoir at T. *It is obvious therefore, that any energy which resides with the reservoir at T_0 and which may be extracted only in the form of heat is in a form in which it is completely unavailable for work.*

whenever an irreversible process takes place, the effect on the universe is the same as that which would be produced if a certain quantity of energy were converted from a form in which it was completely available for work into a form in which it is completely unavailable for work. This amount of energy E is T_0 times the entropy change of the universe brought about by the irreversible process.

Entropy and Unavailable Energy

Since the general proof of this is somewhat abstract, let us consider first a special case, namely, the irreversible conduction of heat under a finite temperature gradient. Suppose that heat Q is conducted along a bar from a region at temperature T_1 to a region at temperature T_2. After conduction has taken place, we have heat Q available at the lower temperature T_2, of which the following amount is available for work:

Maximum work after conduction = Q $\left(1 - \frac{T_0}{T_2}\right)$

If conduction had not taken place, heat Q would have been available at the higher temperature T_1, and the maximum amount of work that could have been obtained from this is

Maximum work before conduction = Q $\left(1 - \frac{T_0}{T_1}\right)$

Evidently the amount of energy E that has become unavailable for work is the difference.

$$E = Q\left(1 - \frac{T_0}{T_1}\right) - Q\left(1 - \frac{T_0}{T_2}\right) = T_0\left(\frac{Q}{T_2} - \frac{Q}{T_1}\right) = T_0 \,\Delta\, S\ (univers)$$

This is true for the special case of heat conduction. Since it is not possible to handle all irreversible processes in this simple manner, we shall have to adopt a more abstract point of view, in order to establish the proposition generally. Consider a mechanical device such as a suspended weight or a compressed spring capable of doing work on a system. Suppose the system is in contact with a reservoir at the temperature T. The mechanical device and the reservoir at T constitute the local surroundings of the system. Suppose an irreversible process takes place in which the mechanical device does work W on the system, the internal energy of the system changes U_i to U_f and heat Q is transferred between the system and the reservoir. Then the first law demands that

$$Q = U_f - U_i + W$$

And the second law that

$S_f - S_i$ (System and local surroundings) > 0.

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Entropy and Unavailable Energy

Now suppose that it is desired to produce exactly the same changes in the system and the local surroundings that resulted from the performance of the irreversible process, but by reversible processes only. This would require, in general, the services of Carnot engines and refrigerators, which in turn, would have to be operated in conjunction with an auxiliary mechanical device may be considered, as usual to be either a suspended weight or a compressed spring. For the auxiliary reservoir let us choose the one whose temperature is the lowest say, T_0, These constitute the auxiliary surroundings. With the aid suitable Carnot engines and refrigerators all operating in cycles in conjunction with the auxiliary surroundings, it is now possible to produce in the system and the local surroundings by reversible processes only, the same changes that were formerly brought about by the irreversible process. If this is done, the entropy change of the system and the local surroundings is the same as before since they have gone from the same initial states to the same final states. The auxiliary surroundings, however, must undergo an equal and opposite entropy change, because the net entropy change of the universe during reversible process is zero.

Since the entropy change of the system and local surroundings is positive, the entropy change of the auxiliary surroundings is negative. Therefore the reservoir at T_0 must have rejected a certain amount of heat, say E. since no extra energy has appeared in the system and local surroundings, the energy E must have been transformed into work on the auxiliary mechanical device. We have the result therefore that, *when the same changes which were formerly produced in a system and local surroundings by an irreversible process are brought about reversibly, an amount of energy E leaves an auxiliary reservoir at T_0 in the form of heat, and appears in the form of work on an auxiliary mechanical device.* In other words, energy E is converted from a form in which it was completely unavailable for work into a form in which it is completely available for work. Since the original process was not performed reversibly, the energy E was not converted into work, and therefore *E is the energy that is rendered unavailable for work* because of the performance of the irreversible process.

Entropy and Unavailable Energy

It is a simple matter to calculate the energy that becomes unavailable during an irreversible process. If the same changes are brought about reversibly, the entropy change of the system and local surroundings is the same as before, namely, $S_f - S_i$. The entropy change of the auxiliary surroundings is merely the entropy change of the auxiliary reservoir due to the rejection of E units of heat at the temperature T_0, that is $-E/T_0$. Since the sum of the entropy changes of the system, local surroundings, and auxiliary surroundings is zero, we have.

$$S_f - S_i - \frac{E}{T_0} = 0$$

Hence $E = T_0(S_f - S_i)$

Therefore, the energy that becomes unavailable for work during an irreversible process is T_0 times the entropy change of the universe that is brought about by the irreversible process. Since no energy becomes unavailable during a reversible process, it follows that the maximum amount of work is obtained when a process takes place reversibly.

Since irreversible processes are continually going on in nature, energy is continually becoming unavailable for work. This conclusion, known as the principle of the degradation of energy, was first developed by Kelvin and provides an important physical interpretation of that mysterious quantity, the entropy change of the universe. It must be understood that energy which becomes unavailable for work is not energy which is lost.

The first law is obeyed at all times. Energy is merely transformed from into another. In picturesque language, one may say that energy is "running downhill".

Entropy and Disorder

It has been emphasized that work, as it is used in thermodynamics, is a macroscopic concept. There must be changes that are describable by macroscopic coordinates. Haphazard motions of individual molecules against intermolecular forces do not constitute work.

Work involves order or orderly motion. Whenever work is dissipated into internal energy, the disorderly motion of molecules is increased. Thus, during either the isothermal or adiabatic dissipation of work into internal energy, the disorderly motion of the molecules of either a reservoir or a system is increased. Such processes therefore involve a transition from order to disorder.

Similarly two gases that are mixed represent a higher degree of disorder than when they are separated. It is possible to regard all natural processes from this point of view, and in all cases the result obtained is that there is a tendency on the part of nature to proceed toward a state of grater disorder.

The increase of entropy of the universe during natural processes is an expression of this transition. In other words, we may state roughly that the entropy of a system or of a reservoir is a measure of the degree of molecular disorder existing in the system or reservoir. To put these ideas on a firm foundation, the concept of disorder must be properly defied. It is shown in statistical mechanics that the disorder of a system may be calculated by the theory of probability and expressed by a quantity B known as the thermodynamic probability. The relation between entropy and disorder is then shown to be

$$S = (constant) \ln B$$

Entropy and Disorder

This means that a non-equilibrium state corresponds to a certain degree of disorder and therefore to a definite entropy.

According to this relation, when the entropy of an isolated system increases, the system is proceeding from a state of lower to a state of higher probability. That is the direction in which natural processes take place is governed by the laws of probability. *The second law of thermodynamics is therefore seen to be statistical law.*

The statistical character of the second law arises from the fact that the motions of individual molecules cannot be directed or controlled by any human agency. Suppose, for example that a vessel containing a gas were divided into two compartments by a partition in which there was a small trap door and that, standing by the trap door, there were a superhuman being called a Maxwell demon, since the idea was first propounded by James Clerk Maxwell. Suppose that the demon opened the trap door only when fast molecules approached, thus allowing the fast molecules to collect in one compartment and slow ones in the other. This would obviously result in a transition from disorder to order, thus constituting a violation of the second law. If the trap door were left open and unattended by a Maxwell demon, there would be a small probability of a separation of the fast from the slow molecules, but a much larger probability of an even distribution.

Imagine a telegraphic system in which the receiver may exist in a large number B_0 of possible states, all of them of the same probability. When information is received, the number of possible states is reduced to B_1. We take the logarithm of the ratio B_0/B_1 as a measure of the information I_1. Thus the equation

$$I_1 = (Const.)\ln\frac{B_0}{B_1}$$

Entropy and Disorder

When compared with the relation between entropy and thermodynamic probability.

$$S = (constant) \ln B,$$

and when the two constants are considered to be equal, yield the result that

$$S_1 = S_0 - I_1$$

Where, $S_0 = (constant) \ln B_0$ is the initial entropy, and $S_1 = (constant) \ln B_1$ is the final entropy with the information I_1. Thus, the information corresponds to a negative term in the final entropy of a physical system, or

Information = negentropy.

Entropy and Direction. Absolute Entropy

The second law of thermodynamics provides an answer to the question that is not contained within the scope of the first law, namely, “In what direction does a process take place?” The answer is that a process always taken place in such a direction as to cause an increase in the entropy of the universe. In the case of an isolated system it is the entropy of the system that tends to increase. To find out, therefore, the equilibrium state of an isolated system it is necessary merely to express the entropy as a function of certain coordinates and to apply the usual rules of calculus to render the function a maximum. When the system is not isolated but instead, let us say, is maintained at constant temperature and pressure, there are other entropy changes to be taken into account. It will be shown later, however, that there exists another function, known as the Gibbs function, referring to the system alone whose behavior determines equilibrium under these conditions.

In practical applications of thermodynamics one is interested only in the amount by which the entropy of a system changes in going from an initial to a final state. In cases where it is necessary to perform many such calculations with the minimum of effort, for example, in steam engineering, in problems in refrigeration and gas liquefaction, etc., it is found expedient to set up an entropy table in which the “entropy” of the system in thousands of different states is represented by appropriate numbers. This is done by assigning the value zero to the entropy of the system in an arbitrarily chosen standard state and calculating the entropy change from this standard state to all other states. *When this is done, it is understood that one value of what is listed as “the entropy” has no meaning, but that the difference between two values is actually the entropy change.*

Entropy and Direction. Absolute Entropy

It is a very interesting and also a very important question in physics as to whether there exists an absolute standard state of a system in which the entropy is really zero, so that the number obtained by calculating the entropy change from the zero state to any other represents the "absolute entropy" of the system. It was first suggested by Planck that the entropy of a single crystal of a pure element at the absolute zero of temperature should be taken to be zero. Zero entropy, however, has statistical implications implying in a rough way, the absence of all molecular, atomic, electronic and nuclear disorder. Before any meaning can be attached to the idea of zero entropy, one must know all the factors that contribute to the disorder of a system.

An adequate discussion requires the application of quantum ideas to statistical mechanics.

First order transition. Clapeyron's Equaton

In the familiar phase transition – melting, vaporization and sublimation as well as in some less familiar phase transitions such as from one crystal modification to another, the temperature and pressure remain constant while the entropy and volume change. Consider n_0 moles of material in phase *i* with molar entropy $s^{(i)}$ and molar volume $v^{(i)}$ cc. Both $s^{(i)}$ and $v^{(i)}$ are functions of T and P and hence remain constant during the phase transition which ends with the material in phase *f* with molar entropy $s^{(f)}$ and molar volume $v^{(i)}$. The different phases are indicated by superscripts in order to reserve subscripts to specify different states of the same phase or different substances. Let x equal the fraction of the initial phase which has been transformed into the final phase at any moment. Then the entropy and volume of the mixture at any moment, S and V, respectively are given by

$$S = n_0\,(1-x)\,s^{(i)} + n_0\,x\,s^{(f)}$$

$$V = n_0\,(1-x)\,s^{(i)} + n_0\,x\,s^{(f)}$$

And S and V are seen to be linear functions of x

If the phase transition takes place reversibly, the heat (commonly known as a latent heat) transferred per mole is given by

$$l = T\left(s^{(f)} - s^{(i)}\right)$$

First order transition. Clapeyron's Equaton

The existence of a latent heat, therefore, means that there is a change of entropy. Since

$$dg = -s\,dT + v\,dP$$

$$s = -\left(\frac{\partial g}{\partial T}\right)_P \quad \text{And} \quad v = -\left(\frac{\partial g}{\partial P}\right)_T$$

We may characterize the familiar phase transition by either of the following equivalent statements.

1. There are changes of entropy and volume
2. The first order derivatives of the Gibbs function Change discontinuosly.

Any phase change that satisfies these requirements is known as a phase change of the first order. First order transitions are represented crudely by the three graphs on the left hand side of fig. 1.11 The changes that take place according to the 3 graphs on the right hand side of Fig 1.11 are characteristics of a phase change of the second order, since as we shall see later, in such a phase change the second order derivatives of the Gibbs function change discontinuosly.

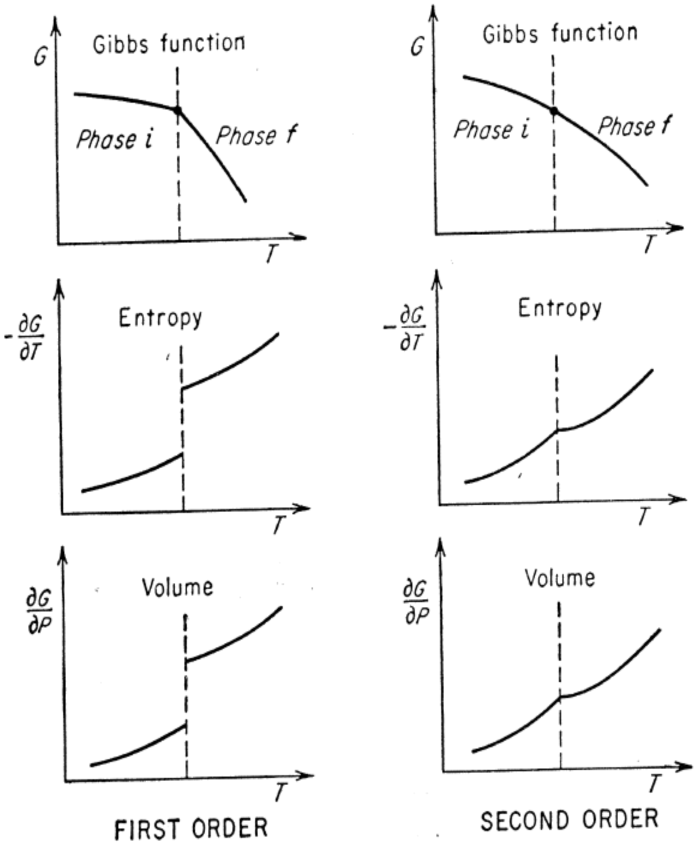

Figure 1.11. First order and second order phase transition.

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First order transition. Clapeyron's Equaton

In the case of a first order phase transition, consider the reversible isothermal isobaric change of 1 mole of substance from phase *i* to phase *f*. using the first T ds equation.

$$T\,ds = C_v\;dT + T\left(\frac{\partial P}{\partial T}\right)_V dv,$$

And integrating over the whole change of phase, remembering that $(\partial P/\partial T)_v$ is independent of v, we get.

$$T\left(s^{(f)} - s^{(i)}\right) = T\,\frac{dP}{dT}\left(v^{(f)} - v^{(i)}\right),$$

The lefthand side of this equation is latent heat per mole,

$$\therefore\ \frac{dP}{dT} = \frac{l}{T\,(v^{(f)} - v^{(i)})}$$

This equation is known as Clapeyron's equation, applies to any first-order change of phase transition that takes place at constant T and P.

First order transition. Clapeyron's Equaton

It is instructive to derive Clapeyron's equation in another way. We know that the Gibbs function remains constant during a reversible process taking place at constant temperature and pressure.

Hence for a change of phase at T and P.

$g^{(i)} = g^{(f)}$

and, for a phase change at $T + dT$ and $P + dP$.

$$g^{(i)} + dg^{(i)} = g^{(f)} + dg^{(f)}$$

Since, $g^{(i)} = g^{(f)}$, we get $dg^{(i)} = dg^{(f)}$;

$$-s^{(i)}\,dT + v^{(i)}\,dP = -s^{(f)}\,dT + v^{(f)}\,dP$$

Therefore $\frac{dP}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}}$

And, finally,

$$\therefore \frac{dP}{dT} = \frac{l}{T\,(v^{(f)} - v^{(i)})}$$

Second order Transition. Ehrenfest's Equations

- In fig. 1.11 (right hand side) a second order phase transition is seen to be one that takes place at constant temperature and pressure with no change of entropy or volume.
- The first order derivatives of the Gibbs function therefore change continuously as the substance passes from one phase to the other. There are only a few transitions that seem to satisfy these requirements, and even in these cases it is still somewhat doubtful as to whether, for example there is no latent heat or merely an extremely small latent heat.
- The following processes are among those which are generally regarded by most physicists as second order phase transitions:

1. A ferromagnetic material such as iron or nickel becomes para magnetic at the Curie point.
2. A superconducting metal becomes an ordinary conductor in the absence of a magnetic field at a definite transition temperature.
3. Certain alloys and chemical compounds undergo an "order-dis-order" transition at a definite temperature.
4. Liquid helium II become liquid helium I at various temperature and pressures, such as the λ point where $T = 2.19^0$K and P = 38.65 mm.

Second order Transition. Ehrenfest's Equations

In all these processes, one or more of the quantitiesC_P, k, and β show discontinuous changes during the phase transition. In some cases, the changes are very small, leading us to believe that a discontinuous change in all three quantities is a necessary property of a second order transition. Since,

$$\frac{C_P}{T} = \left(\frac{\partial s}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[-\left(\frac{\partial g}{\partial T}\right)_P\right]_P = -\frac{\partial^2 g}{\partial T^2}$$

$$kv = -\left(\frac{\partial v}{\partial P}\right)_T = -\frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_T = -\frac{\partial^2 g}{\partial P^2}$$

$$\beta v = \left(\frac{\partial v}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_P = \frac{\partial^2 g}{\partial T\,\partial P}$$

It follows that second order transition is characterized by discontinuous changes in the second order derivatives of the Gibbs function. We may find relations between the changes in these quantities and the pressure and temperature as follows: Indicating the two phases in question by the superscripts *i* and *f*, we have

$$s^{(i)} = s^{(f)} \qquad (\,at\ T, P)$$

$$s^{(i)} + ds^{(i)} = s^{(f)} + ds^{(f)} \qquad (at\ T + dT, P + dP)$$

$$\therefore\ Ts^{(i)} = Ts^{(f)}$$

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Second order Transition. Ehrenfest's Equations

Using the second T ds equation we get

$$c_p^{(i)}\, dT - T\, v\, \beta^{(i)}\, d\, P = c_p^{(f)}\, dT - Tv\, \beta^{(f)}\, dP$$

And, finally

$$\frac{dP}{dT} = \frac{C_P^{(f)} - C_p^{(i)}}{Tv\, (\beta^{(f)}) - \beta^{(i)}}$$

For the same phase transition we have also,

$$v^{(i)} = v^{(f)} \qquad (\, at\ T, P)$$

$$v^{(i)} + dv^{(i)} = v^{(f)} + dv^{(f)} \qquad (at\ T + dT, P + dP)$$

$$\therefore\ Tv^{(i)} = Tv^{(f)}$$

$$dv = (\partial v/\partial P)_P\, dT + (\partial v/\partial P)_T\, dP, we\ have$$

$$v\beta^{(i)} dT - vk^{(i)} dP = v\beta^{(f)}\, dT - v\, k^{(f)}\, dP$$

OR

$$\frac{dP}{dT} = \frac{\beta^{(f)} - \beta^{(i)}}{k^{(f)} - K^{(i)}}$$

These two equations are known as *Ehrenfest's equations*