Thermodynamics

Roughly, heat means "energy in transit" (i.e. the energy which crosses the system boundaries. Whereas Enthalpy refers to total heat content in a system) and dynamics relates to "movement"; thus, in essence thermodynamics studies the movement of energy and how energy instills movement.

Temperature

Temperature is a physical property of a system that underlies the common notions of hot and cold. On the macroscopic scale, temperature is the unique physical property that determines the direction of heat flow between two objects placed in thermal contact.

The basic unit of temperature (symbol: T) in the International System of Units (SI) is the kelvin (Symbol: K). For a system, where entropy S may be a function $S(E)$ of its energy E, the temperature T is given by:

$$\frac{1}{T} = \frac{dS}{dE}$$

ie. the reciprocal of the temperature is the rate of increase of entropy with respect to energy.

Zeroth law of thermodynamics

The *zeroth law of thermodynamics* is a generalized statement about bodies in contact at thermal equilibrium and is the basis for the concept of temperature. The most common enunciation of the zeroth law of thermodynamics is: "*If two thermodynamic systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other.*

Thermometer

A thermometer is a device that measures temperature or temperature gradient, using a variety of different principles. The word thermometer is derived from: *thermo* from the Greek for heat and *meter* also from Greek, meaning to measure. A thermometer has two important elements, the temperature sensor (e.g. the bulb on a mercury thermometer) in which some physical change occurs with temperature, plus some means of converting this physical change into a value (e.g. the scale on a mercury thermometer).

Platinum Resistance Thermometer

The Platinum Resistance Thermometer is based on the principle of change of resistance with change in temperature.

A platinum resistance thermometer consists of a pure pltinum wire wound in a double spiral to avoid inductive effects. The wire is wound in a mica plate. The two ends of the platinum wire are connected to thick copper leads and connected to the binding terminals *B1* and *B2*. For higher temperatures the leads are of Platinum. *C1* and *C2* are the compensating leads exactly similar and of the same resistance as the leads used with the Platinum wire. The platinum wire and the compensating leads are enclosed in a glazed porcelin tube. The tube is sealed and the binding terminals are provided at the top. The leads pass through mica discs which offer the best insulation and also prevent convection currents.

The resistance of a wire at $t^0C = R_t$ and $0^0C = R_0$. These resistances are connected by the relation

$$R_t = R_0(1 + \alpha t + \beta t^2) \qquad \text{.......(i)}$$

Here α and β are constants. The values of α and β depend on the nature of the material used. To find the values of α and β, the resistance of the platinum wire is determined at three fixed points (i) melting point ice, (ii) boiling point of water, (iii) boiling point of sulpher 444.6 ^{0}C for high temperature measurement. And (iv) boiling point of oxygen -182.5^{0}C for low temperature measurement.

From (i) $\qquad\qquad R_t = R_0 [1 + \alpha t + \beta t^2]$

Neglecting βt^2 (because β is very small)

$$R_t = R_0 [1 + \alpha t] \qquad \text{.......(ii)}$$

And $\qquad R_{100} = R_0[1 + \alpha 100]$

Therefore $\qquad R_t - R_0 = R_0 \alpha t \qquad\qquad\qquad \text{........(iii)}$
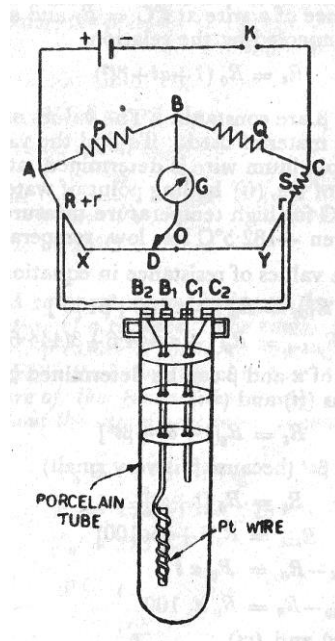
$$R_{100} - R_0 = R_0 \alpha 100 \qquad \text{.........(iv)}$$

Dividing (iii) by (iv)

$$\frac{R_t - R_0}{R_{100} - R_0} = \frac{t}{100}$$

$$t = \left(\frac{R_t - R_o}{R_{100} - R_0} \right) \times 100 \qquad \text{.........(v)}$$

Hence *t* can be calculated. The resistance of the platinum wire is found accurately using Callender and Griffiths' bridge.

Thermocouple

Thermocouples are a widely used type of temperature sensor which can convert thermal potential difference into electric potential difference. In 1821, the German–Estonian physicist Thomas Johann Seebeck discovered that when any conductor is subjected to a thermal gradient, it will generate a voltage. This is now known as the thermoelectric effect or Seebeck effect.

The relationship between the temperature difference and the output voltage of a thermocouple is nonlinear and is approximated by polynomial.

$$\Delta T = \sum_{n=0}^{N} a_n v^n$$

Thermocouples are most suitable for measuring over a large temperature range, up to 1800 °C. Thermocouples measure the temperature difference between two points, not absolute temperature.

A thermodynamic system is nothing but a region in space with well-defined boundaries and thus has a volume associated with it. Now when two systems are brought in contact or are allowed to interact with each other, they may exchange energy. This energy interaction can be in the form of work or heat or both. Both heat and work are forms of energy. Thus, heat is simply energy in

transit. During this interaction, the systems undergo a process and their states change. The system is said to have undergone a change if at least one of its properties change. Properties define the state of the system in state-space. Basically they act as co-ordinates. E.g. pressure (p), volume (v), temperature (T). The reason that they define the state of a system is because they are point functions i.e. their values depend only on the initial and final states of the system after it has undergone a process. One such property is the "Internal Energy, U".

First law of thermodynamics

In thermodynamics, the **first law of thermodynamics** is an expression of the law of the conservation of energy. The first law of thermodynamics states:

The amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done.

The first law can be stated mathematically as:

$$\delta H = dU + \delta W$$

where dU is a small increase in the internal energy of the system, δH is a small amount of heat added to the system, and δW is a small amount of work done by the system.

For a cyclic process, the change in internal energy of the system is zero because the system is brought back to the orginal condition. Therefore for a cyclic process

$$\oint dU = 0$$

And

$$\oint \delta H = \oint \delta W$$

This equation represents Joule's law

Heat capacity

Heat capacity is mathematically defined as the ratio of a small amount of heat δH added to the body, to the corresponding small increase in its temperature dT.

$$C = \frac{\delta H}{dT}$$

Specific heat

Specific heat is the quantity of the heat energy required to increase the temperature of a unit quantity of mass of a substance through one degree.

- The equation relating heat energy to specific heat capacity, where the unit quantity is in terms of mass is:

$$\Delta H = mc\Delta\theta \Rightarrow c = \frac{\Delta H}{m\Delta\theta}$$

  where ΔH is the heat energy put into or taken out of the substance, m is the mass of the substance, c is the specific heat and $\Delta\theta$ is the temperature differential.

Two specific heats of a gas

Consider a gas of mass m at a pressure P and volume V. If the gas is compressed, there is rise in temperature. In this case, no heat has been supplied to the gas to raise it's temperature and $c = 0$. On the other hand heat is supplied to the gas and the gas is allowed to expand such that there is no rise in temperature, the $c = \infty$. Thus, the specific heat of a gas varies from *zero* to *infinity*.

In order to fix the value of specific heat of a gas, the pressure or volume has to be kept constant. Consequently a gas has two specific heats.

Specific heat at constant volume c_V, which is defined as the quantity of heat required to raise the temperature of one gram of gas through 1^0C at constant volume.

Specific heat at constant pressure c_P, which is defined as the quantity of heat required to raise the temperature of one gram of gas through 1^0C at constant pressure.

Isothermal & adiabatic process

Isothermal is any process that takes place at constant temperature. In such a process heat is supplied or removed from the system at just the right rate to maintain constant temperature.

Adiabatic process is any process that occurs without heat entering or leaving a system. In general, an adiabatic change involves a fall or rise in temperature of the system. The mathematical equation for adiabatic process is

$$PV^{\gamma} = \text{constant}$$

where P is pressure, V is volume, and

$$\gamma = \frac{C_P}{C_V} = \frac{\alpha + 1}{\alpha},$$

C_P being the specific heat for constant pressure, C_V being the specific heat for constant volume and γ is the adiabatic index. α is the number of degrees of freedom divided by 2 (3/2 for monatomic gas, 5/2 for diatomic gas).

For reversible adiabatic processes, it is also true that

$$P^{\gamma-1}T^{-\gamma} = \text{constant}$$

Where T is an absolute temperature. This can also be written as

$$TV^{\gamma-1} = \text{constant}$$

kinetic theory of gases:

kinetic theory of gases posits that pressure is due not to static repulsion between molecules, as was Isaac Newton's conjecture, but due to collisions between molecules moving at different velocities. Kinetic theory is also known as the **kinetic-molecular theory** or the **collision theory**.

The theory for ideal gases makes the following assumptions:

- The gas consists of very small particles.
- The number of molecules is large such that statistical treatment can be applied.
- These molecules are in constant, random motion.
- The collisions of gas particles with the walls of the container holding them are perfectly elastic.
- The interactions among molecules are negligible.
- The total volume of the individual gas molecules added up is negligible compared to the volume of the container.
- The molecules are perfectly spherical in shape, and elastic in nature .
- The average kinetic energy of the gas particles depends only on the temperature of the system.
- The time during collision of molecule with the container's wall is negligible as comparable to the time between successive collisions.

Equipartition theorem

The equipartition theorem is also known as the **law of equipartition**, **equipartition of energy**, or simply **equipartition**. The original idea of equipartition was that, *in thermal equilibrium, energy is shared equally among its various forms; for example, the average kinetic energy in the translational motion of a molecule should equal the average kinetic energy in its rotational motion.*

■ The name "equipartition" means "share and share alike".

(a)　　　(b)　　　(c)
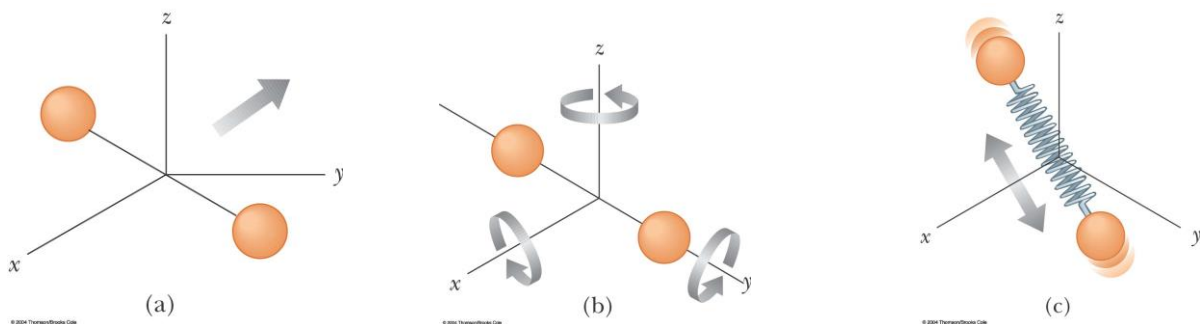
Degrees of freedom mean the number of independent variables that must be known to describe the state or the position of the body completely. A monoatomic gas molecule has three degrees of freedom. A diatomic gas molecule has three degrees of freedom of translation and two degrees of freedom of rotation. It has in all five degrees of freedom.

According to the kinetic theory of gases, the mean kinetic energy of a molecule at a temperature *T* is given by

$$\frac{1}{2}mC^2 = \frac{3}{2}kT \qquad\qquad \ldots\ldots\ldots\ldots(i)$$

But　　　　　　　　$C^2 = u^2 + v^2 + w^2$

As *x, y* and *z* are all equivalent, mean square velocities along the three axes are equal.

Therefore,　　　　　$u^2 = v^2 = w^2$

Or　　　　　　$\frac{1}{2}m(u^2) = \frac{1}{2}m(v^2) = \frac{1}{2}m(w^2)$

Therefore,
$$\frac{1}{2}mC^2 = 3[\frac{1}{2}m(u^2)] = 3[\frac{1}{2}m(v^2)] = 3[\frac{1}{2}m(w^2)]$$
$$= \frac{3}{2}kT$$

Therefore,
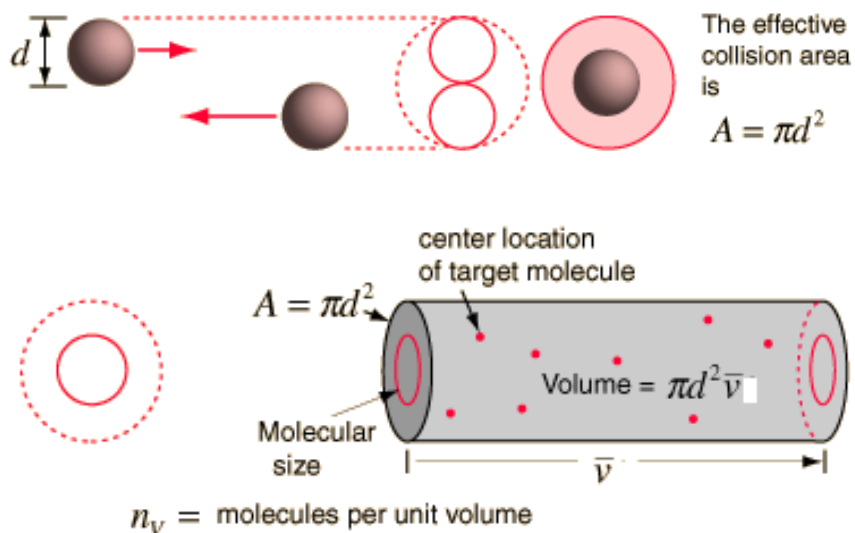$$\frac{1}{2}mu^2 = \frac{1}{2}kT$$
$$\frac{1}{2}mv^2 = \frac{1}{2}kT$$
$$\frac{1}{2}mw^2 = \frac{1}{2}kT$$

Therefore, **the average kinetic energy associated with each degree of freedom = $\frac{1}{2}kT$. This represents the theorem of equipartion of energy.**

Mean free path

In physics the **mean free path of a particle, is the average distance covered by a particle (photon, atom or molecule) between subsequent impacts.** The direction of the molecule is changed after every collision. After a number of collisions, the total path apears to be zig-zag and the free path is not constant. Therefore a term mean free path is used to indicate the mean distance travelled by a molecule between two collisions. If the total distance travelled after N collisions is S, then the mean free path λ is given by

$$\lambda = \frac{S}{N} \qquad\qquad\text{..........(i)}$$

The effective collision area is

$A = \pi d^2$

center location of target molecule

$A = \pi d^2$

Volume $= \pi d^2 \bar{v}$

Molecular size

$n_V =$ molecules per unit volume

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Let the molecules be assumed to be spheres of diameter **d**. A collision between two molecules will take place if the distance between the centres of the molecule is d. Collision will also occur if the colliding molecule has a diameter *2d* and the other molecule is simply a geometrical point. Thus all other molecules to be geometrical points and the colliding molecule of diameter *2d*, this molecule will cover a volume $\pi d^2 v$ in one second. This corresponds to the volume of a cylinder of diameter *2d* and length *v*.

Let *n* be the number of molecules per cc. The number of the molecules present in a volume $\pi d^2 v$

$$= \pi d^2 v \times n$$

This value also represents the number of collisions made by the molecule in one second. The distance moved in one second is *v* and the number of collisions in one second is $\pi d^2 v \times n$.

Therefore Mean free path $\qquad \lambda = \dfrac{v}{\pi d^2 vn} = \dfrac{1}{\pi d^2 n}$,

This equation was deduced by Clausias

Therefore, $\qquad\qquad\qquad \lambda \propto \dfrac{1}{d^2}$,

The mean free path is inversely proportional to the square of the diameter of the molecules. Let *m* be the mass of each molecule.

$\qquad$ Then $\qquad\qquad\qquad\qquad m \times n = \rho$

$$\lambda = \frac{m}{\pi d^2 \rho}$$

The mean free path is inversely proportional to the density of the gas.

The expression for the mean free path according to Boltzmann is
$$\lambda = \frac{3}{4\pi d^2 n}$$

He assumed that all molecules have same average speed.

Maxwell derived the expression,
$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$$
He calculated the value of λ on the basis of the law of distribution of velocities.

Van der Waals equation

While deriving the perfect gas equation PV = RT on the basis of kinetic theory, it was assumed that (i) the size of the molecules of the gas is negligible and (ii) the forces of the intermolecular attraction are absent. But in actual practice, at high pressure, the size of the molecules of the gas becomes significant and cannot be neglected in comparision with the volume of the gas. Also at high pressure, the molecules comes closer and the forces of intermolecular attraction are appreciable. Therefore correction should be applied to the gas equation.

(i) **Correction for pressure:** A molecule in the interior of the gas experiences forces of attraction in all directions and the resultant cohesive force is zero. A molecule near the walls of the container experiences the resultant force inwards. Due to this reason the observed pressure of the gas is less than the actual pressure. The correction for pressure p depends upon (i) the number of the molecules striking unit area of the walls of the container per second and (ii) the number of the molecules present in a given volume. Both these factors depend on the density of the gas.

Therefore corection for pressure $\quad p \propto \rho^2 \propto \dfrac{1}{V^2} \qquad \Rightarrow p = \dfrac{a}{V^2}$

Here a is a constant and V is the volume of the gas.

Hence correct pressure $= (P + p) = (P + \dfrac{a}{V^2})$, Where P is the observed pressure.

(ii) **Correction for Volume:** The fact that the molecules have finite size shows that the actual space for the movement of the molecules is less than the volume of the vessel. The molecules have the sphere of influence around them and due to this factor, the correction for volume is b where b is approximately four times the actual volume of the molecules. Therefore the corrected volume of the gas = *(V-b).*
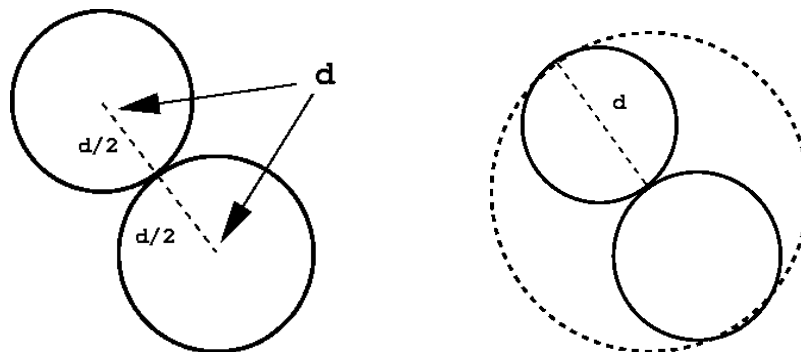
Let the radius of the molecule be *r.*

The volume of the molecule $= x = \dfrac{4}{3}\pi r^3$

The centre of any two molecules can approach each other only by a minimum distance of *2r* i.e., the diameter of each molecule,

$$S = \frac{4}{3}\pi(2r)^3 = 8x$$

Consider a container of volume *V*. If the molecules are allowed to enter one by one,

The volume available for the first molecule $= V$

The volume available for the second molecule $= V\text{-}S$

The volume available for the third molecule $= V - 2S$

$$\ldots\ldots\ldots\ldots\ldots\ldots.$$
$$\ldots\ldots\ldots\ldots\ldots..$$

The volume available for the n-th molecule $= V - (n\text{-}1)S$

Average space available for each molecule

$$= \frac{V + (V - S) + (V - 2S) + \ldots\ldots\{V - (n-1)S\}}{n}$$

$$= V - \frac{S}{n}\{1 + 2 + 3 + \ldots\ldots(n-1)\}$$

$$= V - \frac{S}{n} \cdot \frac{(n-1)n}{2} \qquad = V - \frac{nS}{2} + \frac{S}{2}$$

As the number of the molecules is very large $\frac{S}{2}$ can be neglected.

Average space available for each molecule $= V - \dfrac{nS}{2}$ (But $S = 8x$)

$$= V - \frac{n(8x)}{2}$$

$$= V\text{-} 4(nx) = V\text{-}b$$

Therefore, $b = 4(nx) =$ four times the actual volume of the molecules.

Thus the Van der Walls equation of state for a gas is

$$(P + \frac{a}{V^2})(V - b) = RT$$

Where *a* and *b* are Van der Walls constant.

Second law of thermodynamics

There are many ways of stating the second law of thermodynamics, but all are equivalent in the sense that each form of the second law logically implies every other form (Fermi, 1936).

The formulation of the second law that refers to entropy directly is due to Rudolf Clausius:

In an isolated system, a process can occur only if it increases the total entropy of the system.

Also due to Clausius is the simplest formulation of the second law, the heat formulation:

Heat cannot spontaneously flow from a material at lower temperature to a material at higher temperature.

A third formulation of the second law, the heat engine formulation, by Lord Kelvin, is:

It is impossible to convert heat completely into work.

In terms of time variation, the mathematical statement of the second law for a closed system undergoing an adiabatic transformation is:
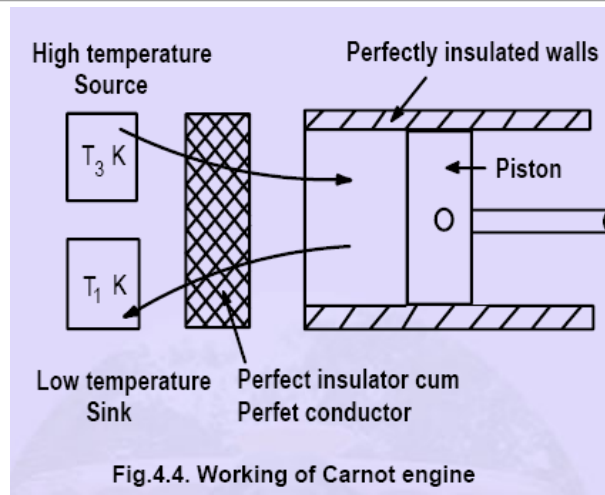
$$\frac{dS}{dt} \geq 0$$

where, S is the entropy and t is time.

This statement is the best-known phrasing of the second law i.e"The entropy of the universe tends to a maximum"

Reversible process & Irreversible process

In thermodynamics, a ***reversible process, or reversible cycle is the cyclic process i.e. a process that can be "reversed" by means of infinitesimal changes in some property of the system without loss or dissipation of energy.***

A process that is not reversible is termed irreversible.

High temperature Source

Perfectly insulated walls

T_3 K

← Piston

O

T_1 K

Low temperature Sink

Perfect insulator cum Perfet conductor

Fig.4.4. Working of Carnot engine

Carnot cycle

The Carnot cycle is a particular thermodynamic cycle, modeled on the hypothetical Carnot heat engine, proposed by Nicolas Léonard Sadi Carnot in 1824

A thermodynamic cycle occurs when a system is taken through a series of different states, and finally returned to its initial state. In the process of going through this cycle, the system may perform work on its surroundings, thereby acting as a heat engine. The system may be worked upon by an external force, and in the process, it can transfer thermal energy from a cooler system to a warmer one, thereby acting as a Heat Pump rather than a heat engine. The **Carnot cycle** when acting as a heat engine consists of the following steps:

1. **Reversible isothermal expansion of the gas at the "hot" temperature, T_H (isothermal heat addition).** During this step (A to B on Figure 1) the expanding gas causes the piston to do work on the surroundings. The gas expansion is propelled by absorption of heat from the high temperature reservoir.
2. **Isentropic (Reversible adiabatic) expansion of the gas.** For this step (B to C on Figure 1) we assume the piston and cylinder are thermally insulated, so that no heat is gained or lost. The gas continues to expand, doing work on the surroundings. The gas expansion causes it to cool to the "cold" temperature, T_C.
3. **Reversible isothermal compression of the gas at the "cold" temperature, T_C. (isothermal heat rejection)** (C to D on Figure 1) Now the surroundings do work on the gas, causing heat to flow out of the gas to the low temperature reservoir.
4. **Isentropic compression of the gas.** (D to A on Figure 1) Once again we assume the piston and cylinder are thermally insulated. During this step, the surroundings do work on the gas, compressing it and causing the temperature to rise to T_H. At this point the gas is in the same state as at the start of step 1.
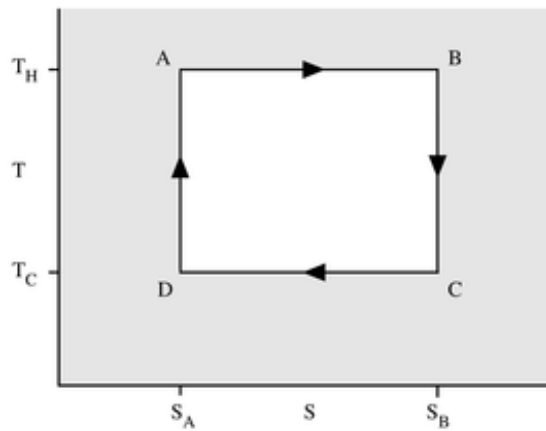
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Figure 1: A Carnot cycle acting as a heat engine, illustrated on a temperature-entropy diagram.

1. ($a \rightarrow b$) Isothermal expansion at thermodynamic temperature T_1 with heat Q_1 taken in. Heat energy is absorbed from a high-temperature source at constant temperature. The volume increases while the pressure drops somewhat.

2. ($b \rightarrow c$) Adiabatic expansion with a fall of temperature to T_2. While the working fluid is thermally isolated (so that there is no heat transfer between it and its surroundings), the volume further increases while the temperature drops.

3. ($c \rightarrow d$) Isothermal compression at temperature T_2 with heat Q_2 given out. Heat energy is given up to a cool heat sink during compression at constant temperature.

4. ($d \rightarrow a$) Adiabatic compression at temperature back to T_1. The fluid is compressed to its original state without transfer of heat to or from its surroundings.

The net result is that of the heat abstracted from the hot source, some, represented by the area *abcd*, is converted into mechanical (or electrical) work, the rest being rejected to the sink. According to the Carnot principle, the efficiency of any reversible heat engine depends only on the temperature range through which it works, rather than the properties of the working substances. It's important to recognize that what Carnot describes is an idealized heat engine.
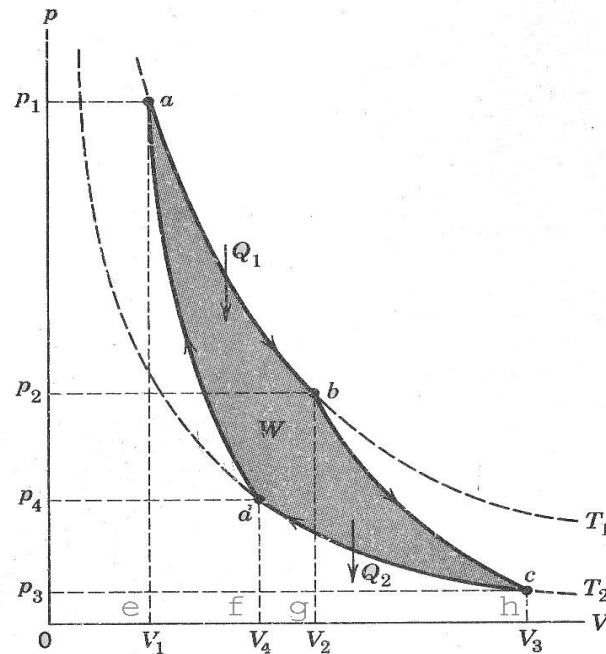
Efficiency of the Carnot cycle

Let us consider one gram molecule of the working substance. Work done from **a** to **b** (isothermal process)

$$W_1 = \int_{V_1}^{V_2} P.dV = RT_1 \log\frac{V_2}{V_1} = area \text{ abge} \qquad \text{............ (1)}$$

Work done from **b** to **c** (adiabatic process)

$$W_2 = \int_{V_2}^{V_3} P.dV = \frac{1}{\gamma-1}\left[RT_1 - RT_2\right] = area \text{ bc}hg \qquad \text{............ (2)}$$

Work done from **c** to **d** (isothermal process)

$$W_3 = \int_{V_3}^{V_4} P.dV = -RT_2 \log\frac{V_3}{V_4} = area \text{ chfd} \qquad \text{............ (3)}$$

The – ve sign indicates that work is done on the working substance.

Work done from **d** to **a** (adiabatic process)

$$W_4 = \int_{V_4}^{V_1} P.dV = -\frac{1}{\gamma - 1}[RT_1 - RT_2] = area \text{ dfea} \qquad \ldots\ldots\ldots (4)$$

W_2 and W_4 are equal and opposite and cancel each other. The net work done by the working substance in one complete cycle

$$= \text{Area abge + Area bchg} - \text{Area chfd} - \text{Area dfea}$$

$$= \text{Area abcd}$$

The net amount of heat absorved by the working substance $= H_1 - H_2$

Net work $= W_1 + W_2 + W_3 + W_4$

$$= RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \qquad \ldots\ldots\ldots (5)$$

The points **a** and **d** are on the same adiabatic

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \ldots\ldots\ldots (6)$$

The points **b** and **c** are on the same adiabatic

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \ldots\ldots\ldots (7)$$

From (6) and (7)

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

Or

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

From equation (5)

$$W = R\left[\log\frac{V_2}{V_1}\right][T_1 - T_2] = H_1 - H_2$$

Efficiency

$$\eta = \frac{\text{Useful output}}{\text{Input}} = \frac{W}{H_1}$$

Heat is supplied from the source from **a** to **b** only

$$H_1 = RT_1 \log\frac{V_2}{V_1}$$

$$\eta = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1}$$

$$= \frac{R[T_1 - T_2]\log\left(\dfrac{V_2}{V_1}\right)}{RT_1 \log\left(\dfrac{V_2}{V_1}\right)}$$

Or

$$\eta = 1 - \frac{H_2}{H_1}$$

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

The Carnot's engine is perfectly reversible. It can be operated in the reverse direction also. Then it works as a refrigerator. The isothermal process will take place only when the piston moves very slowly to give enough time for the heat transfer to take place. The adiabatic process will take place when the piston moves extremely fast to avoid heat transfer. Any practical engine cannot satisfy these conditions.

Carnot's theorem

Carnot's theorem is a formal statement of this fact: *No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between those same reservoirs.*

A corollary to Carnot's theorem states that: *All reversible engines operating between the same heat reservoirs are equally efficient.* maximum efficiency is achieved if and only if no new entropy is created in the cycle.

Entropy

In thermodynamics, entropy is a measure of the unavailability of a system's energy to do work. It is a measure of the randomness of molecules in a system. Spontaneous changes tend to smooth out differences in temperature, pressure, density, and chemical potential that may exist in a system, and entropy is thus a measure of how far this smoothing-out process has progressed.

Derivation of Maxwell's equation

We know that

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y$$

$$= \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \quad \ldots(i)$$

Here x and y can be any two variables out of P, V, T and S.

(1) Taking T and V as independent variables and

$$x = T$$

and

$$y = V$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (i)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

But

$$dS = \frac{\partial H}{T}$$

$$\therefore \quad \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

(2) Taking T and P as independent variables and

$$x = T$$

and

$$y = P$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

or

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$$

(3) Taking S and V as independent variables and

$$x = S$$

and

$$y = V$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial H}\right)_V$$

(4) Taking S and P as independent variables and

$$x = S$$

and

$$y = P$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

or

$$\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial H}\right)_P$$

(5) Taking P and V as independent variables and

$$x = P \quad \text{and} \quad y = V$$

$$\frac{\partial P}{\partial x} = 1, \frac{\partial V}{\partial y} = 1, \frac{\partial P}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1$$

(6) Taking T and S as independent variables and

$$x = T \quad \text{and} \quad y = S$$

$$\frac{\partial T}{\partial x} = 1, \ \frac{\partial S}{\partial y} = 1, \ \frac{\partial T}{\partial y} = 0, \ \frac{\partial S}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \qquad \dots(xiv)$$

These are the important thermodynamical relations. While solving a particular problem, the suitable equation is used.

Thermodynamic Functions

6·53 Helmholtz Function

Helmholtz function F, is the property of a system and is given by the equation

$$F = U - TS \qquad \dots(i)$$

In practice, the primary function of heat engines and other devices is to perform mechanical work. From the first law of thermo-dynamics, for a system working between two equilibrium states,

$$\delta H = dU + \delta W \qquad \dots(ii)$$

or

$$\delta W = \delta H - dU \qquad \dots(iii)$$

It means that the energy converted into work is provided partly by the heat reservoir with which the system is in contact and which gives up a quantity of heat δH and partly by the system whose internal energy decreases by $(-dU)$.

When a system undergoes a process between two equilibrium states, how much maximum work can be done by it ? This can be derived by assuming that the system exchanges heat energy only with a single heat reservoir at a temperature T_o.

Gibbs free energy

Gibbs free energy is a measure of the amount of energy available to do work in an isothermal and isobaric (constant temperature and pressure) thermodynamic system. This is where the term "free" comes from; it refers to the amount of energy in a system that is easily available for usage.

Its mathematical definition: $G = H - TS$

The Gibbs energy is thus the enthalpy (essentially the total energy of the system) minus the entropy times the temperature (a measure of the amount of energy that is unavailable). While there are many uses for Gibbs free energy, its most well-known application is in determining the spontaneity of a chemical process. If a process results in a negative change in the amount of Gibbs free energy, then it is said to occur spontaneously.

Enthalpy

A thermodynamic quantity equivalent to the total heat content of a system. It is equal to the internal energy (which is the energy required to create a system, and the amount of energy required to make room for it by displacing its environment and establishing its volume and pressure) of the system plus the product of pressure and volume.

The total enthalpy, H, of a system cannot be measured directly. Only a change or difference in energy carries physical meaning. The enthalpy of a homogeneous system is defined as

$$H = U + p\,V$$

Where H is the enthalpy of the system, U is the internal energy of the system, p is the pressure of the system, V is the volume of the system.

The Clausius-Clapeyron Equation

The vaporization curves of most liquids have similar shape. The relationship between the temperature of a liquid and its vapor pressure is not a straight line. The vapor pressure of water, for example, increases significantly more rapidly than the temperature of the system. This behavior can be explained with the Clausius-Clapeyron equation.

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

According to this equation, the rate at which the natural logarithm of the vapor pressure of a liquid changes with temperature is determined by the molar enthalpy of vaporization of the liquid, the ideal gas constant, and the temperature of the system. If we assume that Hvap does not depend on the temperature of the system, the Clausius-Clapeyron equation can be written in the following integrated form where C is a constant.

$$\ln P = \frac{RT}{\Delta H_{vap}} + C$$

The Clausius-Clapeyron equation allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

The Gibbs Phase Rule

The Gibbs Phase Rule describes the possible number of degrees of freedom **f** in a closed system at equilibrium, in terms of the maximum number of stable phases **M** and the number of system components **N**:

$$f = N - M + 2$$

In other words, the number of degrees of freedom for a system at equilibrium is the number of intensive variables (often taken as the pressure, temperature, and composition fraction) that may be arbitrarily specified without changing the number of phases. In a region with **M** stable phases, the values of N-M+2 state variables can be changed independently and preserving the same set of stable phases.

If the number of degrees of freedom is equal to zero, then an invariant equilibrium is defined (i.e., equilibrium can be attained only for a single set of values of all the state variables). If the number of degrees of freedom is equal to one, then a univariant equilibrium is defined (i.e., the set of stable phases depends on the value of one stable variable only).

Third law of thermodynamics

The 3rd law was developed by the chemist Walther Nernst during the years 1906–12, and is therefore often referred to as Nernst's theorem or Nernst's postulate. The third law of thermodynamics states that the entropy of a system at absolute zero is a well-defined constant. In 1912 Nernst stated the law thus: "It is impossible for any procedure to lead to the isotherm $T = 0$ in a finite number of steps."

Siabal Mitra, a professor of physics at Missouri State University, provides another implication of this law. "One version of the Third Law states that it would require an infinite number of steps to reach absolute zero, which means you will never get there. If you could get to absolute zero, it would violate the Second Law, because if you had a heat sink at absolute zero, then you could build a machine that was 100 percent efficient."

The third law of thermodynamics is sometimes stated as follows, regarding the properties of systems in equilibrium at absolute zero temperature:

"The entropy of a perfect crystal at absolute zero is exactly equal to zero."