

THERMODYNAMICS

The branch dealing with measurement of temperature is called thermometry and the devices used to measure temperature are called thermometers.

Heat

Heat is a form of energy called thermal energy which flows from a higher temperature body to a lower temperature body when they are placed in contact.

Heat or thermal energy of a body is the sum of kinetic energies of all its constituent particles, on account of translational, vibrational and rotational motion.

The SI unit of heat energy is joule (J).

The practical unit of heat energy is calorie.

$$1 \text{ cal} = 4.18 \text{ J}$$

1 calorie is the quantity of heat required to raise the temperature of 1 g of water by 1°C.

Mechanical energy or work (W) can be converted into heat (Q) by $1 \text{ W} = JQ$

where J = Joule's mechanical equivalent of heat.

J is a conversion factor (not a physical quantity) and its value is 4.186 J/cal.

Temperature

Temperature of a body is the degree of hotness or coldness of the body. A device which is used to measure the temperature, is called a thermometer.

Highest possible temperature achieved in laboratory is about 10⁸ while lowest possible temperature attained is 10⁻⁸ K.

Branch of Physics dealing with production and measurement temperature close to 0 K is known as cryogenics, while that dealing with the measurement of very high temperature is called pyrometry. Temperature of the core of the sun is 10⁷ K while that of its surface 6000 K.

NTP or STP implies 273.15 K (0°C = 32°F).

Different Scale of Temperature

1. **Celsius Scale** In this scale of temperature, the melting point ice is taken as 0°C and the boiling point of water as 100°C and space between these two points is divided into 100 equal parts
2. **Fahrenheit Scale** In this scale of temperature, the melt point of ice is taken as 32°F and the boiling point of water as 211 and the space between these two points is divided into 180 equal parts.
3. **Kelvin Scale** In this scale of temperature, the melting point ice is taken as 273 K and the boiling point of water as 373 K the space between these two points is divided into 100 equal parts

Relation between Different Scales of Temperatures

$$\frac{C}{100} = \frac{F - 32}{180} = \frac{K - 273}{100} = \frac{R}{80}$$

Thermometric Property

The property of an object which changes with temperature, is called thermometric property. Different thermometric properties thermometers have been given below

(i) Pressure of a Gas at Constant Volume

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

and

$$P_t = P_0 \left(1 + \frac{t}{273} \right)$$

$$t = \left(\frac{P_t - P_0}{P_{100} - P_0} \times 100 \right)^{\circ}\text{C}$$

where p , p_{100} , and p_t , are pressure of a gas at constant volume 0°C , 100°C and $t^{\circ}\text{C}$.

A constant volume gas thermometer can measure temperature from -200°C to 500°C .

(ii) Electrical Resistance of Metals

$$R_t = R_0(1 + \alpha t + \beta t^2)$$

where α and β are constants for a metal.

As β is too small therefore we can take

$$R_t = R_0(1 + \alpha t)$$

where, α = temperature coefficient of resistance and R_0 and R_t , are electrical resistances at 0°C and $t^\circ\text{C}$.

$$\alpha = \frac{R_2 - R_1}{R_1 t_2 - R_2 t_1}$$

where R_1 and R_2 are electrical resistances at temperatures t_1 and t_2 .

$$t = \frac{R_t - R_0}{R_{100} - R_0} \times 100^\circ\text{C}$$

where R_{100} is the resistance at 100°C .

Platinum resistance thermometer can measure temperature from -200°C to 1200°C .

(iii) Length of Mercury Column in a Capillary Tube

$$l_t = l_0(1 + \alpha t)$$

where α = coefficient of linear expansion and l_0 , l_t are lengths of mercury column at 0°C and $t^\circ\text{C}$.

Thermo Electro Motive Force

When two junctions of a thermocouple are kept at different temperatures, then a thermo-emf is produced between the junctions, which changes with temperature difference between the junctions. Thermo-emf

$$E = at + bt^2$$

where a and b are constants for the pair of metals.

Unknown temperature of hot junction when cold junction is at 0°C .

$$t = \left(\frac{E_t}{E_{100}} \times 100 \right)^\circ\text{C}$$

Where E_{100} is the thermo-emf when hot junction is at 100°C .

A thermo-couple thermometer can measure temperature from -200°C to 1600°C .

Thermal Equilibrium

When there is no transfer of heat between two bodies in contact, the the bodies are called in thermal equilibrium.

Zeroth Law of Thermodynamics

If two bodies A and B are separately in thermal equilibrium with third body C, then bodies A and B will be in thermal equilibrium with each other.

Triple Point of Water

The values of pressure and temperature at which water coexists in equilibrium in all three states of matter, i.e., ice, water and vapour called triple point of water.

Triple point of water is 273 K temperature and 0.46 cm of mercury pressure.

Specific Heat

The amount of heat required to raise the temperature of unit mass of the substance through 1°C is called its specific heat.

It is denoted by c or s .

Its SI unit is joule/kilogram-°C (J/kg-°C). Its dimensions are $[L^2T^{-2}\theta^{-1}]$.

The specific heat of water is 4200 J kg⁻¹°C⁻¹ or 1 cal g⁻¹ °C⁻¹, which is high compared with most other substances.

Gases have two types of specific heat

1. The specific heat capacity at constant volume (C_v).
2. The specific heat capacity at constant pressure (C_p).

Specific heat at constant pressure (C_p) is greater than specific heat at constant volume (C_v), i.e., $C_p > C_v$.

For molar specific heats $C_p - C_v = R$
where R = gas constant and this relation is called Mayer's formula.

The ratio of two principal specific heats of a gas is represented by γ .

$$\gamma = \frac{C_p}{C_v}$$

The value of γ depends on atomicity of the gas.

Amount of heat energy required to change the temperature of any substance is given by

$$Q = mc\Delta t$$

- where, m = mass of the substance,
- c = specific heat of the substance and
- Δt = change in temperature.

Thermal (Heat) Capacity

Heat capacity of any body is equal to the amount of heat energy required to increase its temperature through 1°C .

$$\text{Heat capacity} = mc$$

where c = specific heat of the substance of the body and m = mass of the body.

Its SI unit is joule/kelvin (J/K).

Water Equivalent

It is the quantity of water whose thermal capacity is same as the heat capacity of the body. It is denoted by W .

$$W = ms = \text{heat capacity of the body.}$$

Latent Heat

The heat energy absorbed or released at constant temperature per unit mass for change of state is called latent heat.

Heat energy absorbed or released during change of state is given by

$$Q = mL$$

where m = mass of the substance and L = latent heat.

Its unit is cal/g or J/kg and its dimension is $[L^2T^{-2}]$.

For water at its normal boiling point or condensation temperature (100°C), the latent heat of vaporisation is

$$\begin{aligned} L &= 540 \text{ cal/g} \\ &= 40.8 \text{ kJ/mol} \\ &= 2260 \text{ kJ/kg} \end{aligned}$$

For water at its normal freezing temperature or melting point (0°C), the latent heat of fusion is

$$\begin{aligned} L &= 80 \text{ cal/g} = 60 \text{ kJ/mol} \\ &= 336 \text{ kJ/kg} \end{aligned}$$

It is more painful to get burnt by steam rather than by boiling water. When 100°C water gets converted to steam at 100°C , then it gives out 536 heat. So, it is clear that steam at 100°C has more heat than water at 100°C (i.e., boiling of water).

After snow falls, the temperature of the atmosphere becomes very low. This is because the snow absorbs the heat from the atmosphere to melt. So, in the mountains, when snow falls, one does not feel too hot but when ice melts, he feels too cold.

There is more shivering effect of ice cream on teeth as compared to that of water (obtained from ice). This is because when ice cream melts, it absorbs large amount of heat from teeth.

Melting

Conversion of solid into liquid state at constant temperature is melting.

Evaporation

Conversion of liquid into vapour at all temperatures (even below boiling point) is called evaporation.

Boiling

When a liquid is heated gradually, at a particular temperature saturated vapour pressure of the liquid becomes equal to atmospheric pressure, now bubbles of vapour rise to the surface of the liquid. This process is called boiling of the liquid.

The temperature at which a liquid boils, is called boiling point. The boiling point of water increases with increase in pressure and decreases with decrease in pressure.

Sublimation

The conversion of a solid into vapour state is called sublimation.

Hoar Frost

The conversion of vapours into solid state is called hoar frost.

Calorimetry

This is the branch of heat transfer that deals with the measurement of heat. The heat is usually measured in calories or kilocalories.

Principle of Calorimetry

When a hot body is mixed with a cold body, then heat lost by hot body is equal to the heat gained by cold body.

Heat lost = Heat gain

Thermal Expansion

Increase in size on heating is called thermal expansion. There are three types of thermal expansion.

1. Expansion of solids
2. Expansion of liquids
3. Expansion of gases

Expansion of Solids

Three types of expansion -takes place in solid.

Linear Expansion Expansion in length on heating is called linear expansion.

Increase in length

$$l_2 = l_1(1 + \alpha \Delta t)$$

where, l_1 and l_2 are initial and final lengths, Δt = change in temperature and α = coefficient of linear expansion.

Coefficient of linear expansion

$$\alpha = (\Delta l / l * \Delta t)$$

where l = real length and Δl = change in length and

Δt = change in temperature.

Superficial Expansion Expansion in area on heating is called superficial expansion.

Increase in area $A_2 = A_1(1 + \beta \Delta t)$

where, A_1 and A_2 are initial and final areas and β is a coefficient of superficial expansion.

Coefficient of superficial expansion

$$\beta = (\Delta A / A * \Delta t)$$

where. A = area, ΔA = change in area and Δt = change in temperature.

Cubical Expansion Expansion in volume on heating is called cubical expansion.

Increase in volume $V_2 = V_1(1 + \gamma \Delta t)$

where V_1 and V_2 are initial and final volumes and γ is a coefficient of cubical expansion.

Coefficient of cubical expansion

$$\gamma = \frac{\Delta V}{V \times \Delta t}$$

where V = real volume, ΔV = change in volume and Δt = change in temperature.

Relation between coefficients of linear, superficial and cubical expansions

$$\beta = 2\alpha \text{ and } \gamma = 3\alpha$$

$$\text{Or } \alpha:\beta:\gamma = 1:2:3$$

2. Expansion of Liquids

In liquids only expansion in volume takes place on heating.

(i) Apparent Expansion of Liquids When expansion of the container containing liquid, on heating is not taken into account then observed expansion is called apparent expansion of liquids.

Coefficient of apparent expansion of a liquid

$$(\gamma_a) = \frac{\text{apparent increase in volume}}{\text{original volume} \times \text{rise in temperature}}$$

(ii) Real Expansion of Liquids When expansion of the container, containing liquid, on heating is also taken into account, then observed expansion is called real expansion of liquids.

Coefficient of real expansion of a liquid

$$(\gamma_r) = \frac{\text{real increase in volume}}{\text{original volume} \times \text{rise in temperature}}$$

Both, γ_r , and γ_a are measured in $^{\circ}\text{C}^{-1}$.

We can show that $\gamma_r = \gamma_a + \gamma_g$

where, γ_r , and γ_a are coefficient of real and apparent expansion of liquids and γ_g is coefficient of cubical expansion of the container.

Anomalous Expansion of Water

When temperature of water is increased from 0°C , then its vol decreases upto 4°C , becomes minimum at 4°C and then increases. behaviour of water around 4°C is called, anomalous expansion water.

3. Expansion of Gases

There are two types of coefficient of expansion in gases

(i) Volume Coefficient (γ_v) At constant pressure, the change in volume per unit volume per degree celsius is called volume coefficient.

$$\gamma_V = \frac{V_2 - V_1}{V_0 (t_2 - t_1)}$$

where V_0 , V_1 , and V_2 are volumes of the gas at 0°C , $t_1^\circ\text{C}$ and $t_2^\circ\text{C}$.

(ii) Pressure Coefficient (γ_p) At constant volume, the change in pressure per unit pressure per degree celsius is called pressure coefficient.

$$\gamma_P = \frac{P_2 - P_1}{P_0 (t_2 - t_1)}$$

where p_0 , p_1 and p_2 are pressure of the gas at 0°C , $t_1^\circ\text{C}$ and $t_2^\circ\text{C}$.

Practical Applications of Expansion

1. When rails are laid down on the ground, space is left between the end of two rails.
2. The transmission cables are not tightly fixed to the poles.
3. The iron rim to be put on a cart wheel is always of slightly smaller diameter than that of wheel.
4. A glass stopper jammed in the neck of a glass bottle can be taken out by warming the neck of the bottles.

Important Points

- Due to increment in its time period a pendulum clock becomes slow in summer and will lose time.
- Loss of time in a time period $\Delta T = (1/2)\alpha \Delta\theta T$
 \therefore Loss of time in any given time interval t can be given by $\Delta T = (1/2)\alpha \Delta\theta t$
- At some higher temperature a scale will expand and scale reading will be lesser than true values, so that
true value = scale reading $(1 + \alpha \Delta t)$
Here, Δt is the temperature difference.
- However, at lower temperature scale reading will be more or true value will be less.

The branch of physics which deals with the study of transformation of heat energy into other forms of energy and vice-versa.

A thermodynamical system is said to be in thermal equilibrium when macroscopic variables

(like pressure, volume, temperature, mass, composition etc) that characterise the system do not change with time.

Thermodynamical System

An assembly of an extremely large number of particles whose state can be expressed in terms of pressure, volume and temperature, is called thermodynamic system.

Thermodynamic system is classified into the following three systems

- (i) **Open System** It exchange both energy and matter with surrounding.
- (ii) **Closed System** It exchanges only energy (not matter) with surroundings.
- (iii) **Isolated System** It exchanges neither energy nor matter with the surrounding.

A thermodynamic system is not always in equilibrium. For example, a gas allowed to expand freely against vacuum. Similarly, a mixture of petrol vapour and air, when ignited by a spark is not an equilibrium state. Equilibrium is acquired eventually with time.

Thermodynamic Parameters or Coordinates or Variables

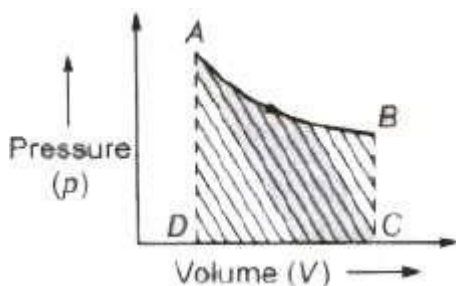
The state of thermodynamic system can be described by specifying pressure, volume, temperature, internal energy and number of moles, etc. These are called thermodynamic parameters or coordinates or variables.

Work done by a thermodynamic system is given by

$$W = p * \Delta V$$

where p = pressure and ΔV = change in volume.

Work done by a thermodynamic system is equal to the area enclosed between the p - V curve and the volume axis



Work done in process A-B = area ABCDA

Work done by a thermodynamic system depends not only upon the initial and final states of the system but also depend upon the path followed in the process.

Work done by the Thermodynamic System is taken as

Positive \rightarrow ΔV as volume increases.

Negative \rightarrow ΔV as volume decreases.

Internal Energy (U)

The total energy possessed by any system due to molecular motion and molecular configuration, is called its internal energy.

Internal energy of a thermodynamic system depends on temperature. It is the characteristic property of the state of the system.

Zeroth Law of Thermodynamics

According to this law, two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other. Thus, if A and B are separately in equilibrium with C, that is if $T_A = T_C$ and $T_B = T_C$, then this implies that $T_A = T_B$ i.e., the systems A and B are also in thermal equilibrium.

First Law of Thermodynamics

Heat given to a thermodynamic system (ΔQ) is partially utilized in doing work (ΔW) against the surrounding and the remaining part increases the internal energy (ΔU) of the system.

Therefore, $\Delta Q = \Delta U + \Delta W$

First law of thermodynamics is a restatement of the principle conservation of energy.

In isothermal process, change in internal energy is zero ($\Delta U = 0$).

Therefore, $\Delta Q = \Delta W$

In adiabatic process, no exchange of heat takes place, i.e., $\Delta \theta = 0$.

Therefore, $\Delta U = -\Delta W$

In adiabatic process, if gas expands, its internal energy and hence, temperature decreases and vice-versa.

In isochoric process, work done is zero, i.e., $\Delta W = 0$, therefore

$$\Delta Q = \Delta U$$

Thermodynamic Processes

A thermodynamical process is said to take place when some changes occur in the state of a thermodynamic system i.e., the thermodynamic parameters of the system change with time.

(i) Isothermal Process A process taking place in a thermodynamic system at constant temperature is called an isothermal process.

Isothermal processes are very slow processes.

These process follows Boyle's law, according to which

$$pV = \text{constant}$$

From $dU = nC_v dT$ as $dT = 0$ so $dU = 0$, i.e., internal energy is constant.

From first law of thermodynamic $dQ = dW$, i.e., heat given to the system is equal to the work done by system surroundings.

$$\text{Work done } W = 2.3026\mu RT \log_{10}(V_f / V_i) = 2.3026\mu RT \log_{10}(p_i / p_f)$$

where, μ = number of moles, R = ideal gas constant, T = absolute temperature and V_i V_f and P_i , P_f are initial volumes and pressures.

After differentiating $P V = \text{constant}$, we have

$$\frac{dp}{dV} = -\frac{p}{V} \text{ and } -\frac{dp}{dV} = \frac{p}{V}$$

i.e., bulk modulus of gas in isothermal process, $\beta = p$.

$P - V$ curve for this process is a rectangular hyperbola

Examples

(a) Melting process is an isothermal change, because temperature of a substance remains constant during melting.

(b) Boiling process is also an isothermal operation.

(ii) **Adiabatic Process** A process taking place in a thermodynamic system for which there is no exchange of heat between the system and its surroundings.

Adiabatic processes are very fast processes.

These process follows Poisson's law, according to which

$$pV^\gamma = TV^{\gamma-1} = \frac{T^\gamma}{p^{\gamma-1}} = \text{constant}$$

From $dQ = nCdT$, $C_{\text{adi}} = 0$ as $dQ = 0$, i.e., molar heat capacity for adiabatic process is zero.

From first law, $dU = -dW$, i.e., work done by the system is equal to decrease in internal energy. When a system expands adiabatically, work done is positive and hence internal energy decrease, i.e., the system cools down and vice-versa.

Work done in an adiabatic process is

$$W = \frac{nR(T_i - T_f)}{\gamma - 1} = \frac{p_i V_i - p_f V_f}{\gamma - 1}$$

where T_i and T_f are initial and final temperatures. Examples

(a) Sudden compression or expansion of a gas in a container with perfectly non-conducting wall.

(b) Sudden bursting of the tube of a bicycle tyre.

(c) Propagation of sound waves in air and other gases.

(iii) **Isobaric Process** A process taking place in a thermodynamic system at constant pressure is called an isobaric process.

Molar heat capacity of the process is C_p and $dQ = nC_p dT$.

Internal energy $dU = nC_v dT$

From the first law of thermodynamics

$$dQ = dU + dW$$

$$dW = pdV = nRdT$$

Process equation is $V / T = \text{constant}$.

p- V curve is a straight line parallel to volume axis.

(iv) **Isochoric Process** A process taking place in a thermodynamic system at constant volume is called an isochoric process.

$dQ = nC_v dT$, molar heat capacity for isochoric process is C_v .

Volume is constant, so $dW = 0$,

Process equation is $p / T = \text{constant}$

p- V curve is a straight line parallel to pressure axis.

(v) **Cyclic Process** When a thermodynamic system returns to its initial state after passing through several states, then it is called cyclic process.

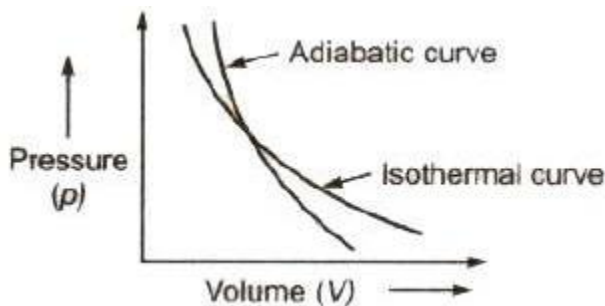
Efficiency of the cycle is given by

$$\eta = \frac{\text{Work done}}{\text{Heat supplied}}$$

Work done by the cycle can be computed from area enclosed cycle on p- V curve.

Isothermal and Adiabatic Curves

The graph drawn between the pressure p and the volume V of a given mass of a gas for an isothermal process is called **isothermal curve** and for an adiabatic process it is called **adiabatic curve**.



The slope of the adiabatic curve

$= \gamma \times \text{the slope of the isothermal curve}$

Volume Elasticities of Gases

There are two types of volume elasticities of gases

(i) Isothermal modulus of elasticity $E_s = p$

(ii) Adiabatic modulus of elasticity $E_T = \gamma p$

Ratio between isothermal and adiabatic modulus

$$E_S / E_T = \gamma = C_p / C_v$$

where C_p and C_v are specific heats of gas at constant pressure and at constant volume.

For an isothermal process $\Delta t = 0$, therefore specific heat,

$$c = \Delta \theta / m \Delta t = \infty;$$

For an adiabatic process $\Delta \theta = 0$, therefore specific heat,

$$c = 0 / m \Delta t = 0$$

Second Law of Thermodynamics

The second law of thermodynamics gives a fundamental limitation to the efficiency of a heat engine and the coefficient of performance of a refrigerator. It says that efficiency of a heat engine can never be unity (or 100%). This implies that heat released to the cold reservoir can never be made zero.

Kelvin's Statement

It is impossible to obtain a continuous supply of work from a body by cooling it to a temperature below the coldest of its surroundings.

Clausius' Statement

It is impossible to transfer heat from a lower temperature body to a higher temperature body without use of an external agency.

Planck's Statement

It is impossible to construct a heat engine that will convert heat completely into work.

All these statements are equivalent as one can be obtained from the other.

Entropy

Entropy is a physical quantity that remains constant during a reversible adiabatic change.

Change in entropy is given by $dS = \delta Q / T$

Where, δQ = heat supplied to the system

and T = absolute temperature.

Entropy of a system never decreases, i.e., $dS \geq 0$.

Entropy of a system increases in an irreversible process

Heat Engine

A heat energy engine is a device which converts heat energy into mechanical energy.

A heat engine consists of three parts

- (i) Source of heat at higher temperature
- (ii) Working substance
- (iii) Sink of heat at lower temperature

Thermal efficiency of a heat engine is given by

$$\eta = \frac{\text{Work done / cycle}}{\text{Total amount of heat absorbed / cycle}}$$
$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

where Q_1 is heat absorbed from the source,

Q_2 is heat rejected to the sink and T_1 and T_2 are temperatures of source and sink.

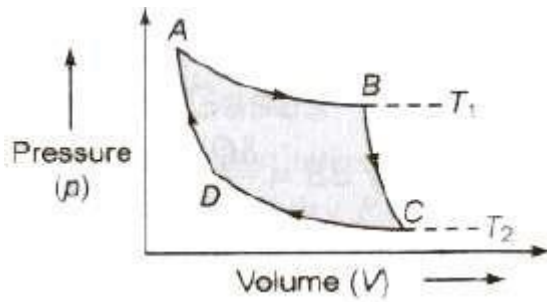
Heat engine are of two types

(i) **External Combustion Engine** In this engine fuel is burnt a chamber outside the main body of the engine. e.g., steam engine. In practical life thermal efficiency of a steam engine varies from 12% to 16%.

(ii) **Internal Combustion Engine** In this engine. fuel is burnt inside the main body of the engine. e.g., petrol and diesel engine. In practical life thermal efficiency of a petrol engine is 26% and a diesel engine is 40%.

Carnot's Cycle

Carnot devised an ideal cycle of operation for a heat engine, called Carnot's cycle.



A Carnot's cycle contains the following four processes

- (i) Isothermal expansion (AB)
- (ii) Adiabatic expansion (BC)
- (iii) Isothermal compression (CD)
- (iv) Adiabatic compression (DA)

The net work done per cycle by the engine is numerically equal to the area of the loop representing the Carnot's cycle .

After doing the calculations for different processes we can show that

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

Therefore, efficiency of the cycle is

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

[Efficiency of Carnot engine is maximum (not 1000/0) for given temperatures T_1 and T_2 . But still Carnot engine is not a practical engine because many ideal situations have been assumed while designing this engine which can practically not be obtained.]

Refrigerator or Heat Pump

A refrigerator or heat pump is a device used for cooling things. It absorb heat from sink at lower temperature and reject a larger amount of heat to source at higher temperature.

Coefficient of performance of refrigerator is given by

$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

where Q_2 is heat absorbed from the sink, Q_1 is heat rejected to source and T_1 and T_2 are temperatures of source and sink.

Relation between efficiency (η) and coefficient of performance (β)

$$\beta = \frac{1 - \eta}{\eta}$$