Chapter 11
Thermodynamics

Thermodynamics

Thermodynamics is a branch of physics which deals with the study of heat, temperature and their inter conversion of heat energy into other forms of energy.

Thermodynamic System

A thermodynamic system is a certain quantity of matter which is separated from its surroundings by a real or imaginary boundary. This system may be in solid , liquid or gaseous state.

Surroundings

Everything outside a thermodynamic system is its surrounding.

Boundary

The real or imaginary surface that separates the system from its surroundings is called boundary.

Boundary can be of two types: Adiabatic , Diathermic

Adiabatic wall (boundary)

An insulating wall that does not allow flow of energy (heat) from one system to another is called an adiabatic wall.

Diathermic wall

A conducting wall that allows energy flow (heat) from one system to another is called a diathermic wall.

Thermodynamic State Variables

Every equilibrium state of a thermodynamic system is completely described by specific values of some macroscopic variables. These are called thermodynamic state variables.

Eg: pressure, volume, temperature, mass , composition,Entropy, Enthalpy

Thermodynamic Equilibrium

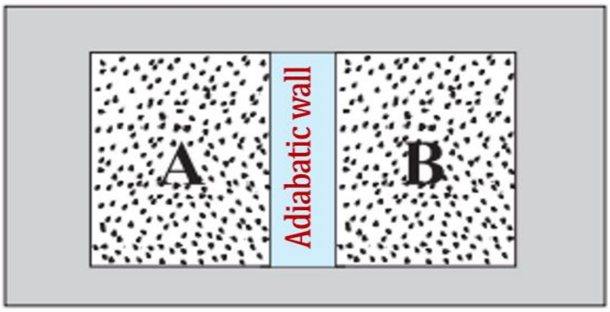
The state of a thermodynamic system is in equilibrium , if the macroscopic variables that characterise the system do not change in time.

Eg: A gas inside a closed rigid container, completely insulated from its surroundings, with fixed values of pressure, volume, temperature, mass and composition that do not change with time, is in a state of thermodynamic equilibrium.

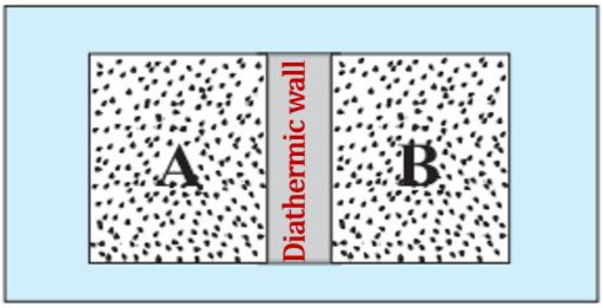
Thermal equilibrium

A system is said to be in thermal equilibrium with itself if the temperature of the system remains constant.
Two systems are said to be in thermal equilibrium, when there is no flow of thermal energy between them ,when they are connected by a diathermic wall. In thermal equilibrium, the temperatures of the two systems are equal.

If systems A and B (two gases) are separated by an adiabatic wall that does not allow flow of heat, system A will be in its own thermal equilibrium, and system B also will be in its own thermal equilibrium. But systems A and B will not be in thermal equilibrium with each other.

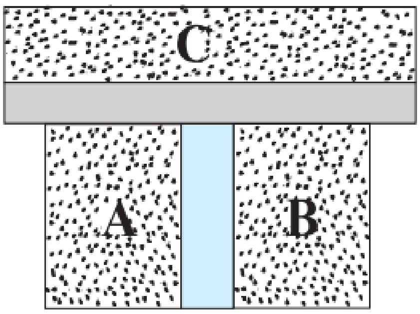


If the same systems A and B separated by a diathermic wall that allows heat to flow from one to another, thermal equilibrium is attained between the two systems in due course. In this case the temperature of the two systems become equal.



Zeroth Law of Thermodynamics

R.H. Fowler formulated this law in 1931 long after the first and second Laws of thermodynamics were stated and so numbered.



Systems A and B are separated by an adiabatic wall, while each is in contact with a third system C via a conducting wall. In this case A will be in thermal equilibrium with B.

Zeroth Law of Thermodynamics states that '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, $T_A = T_C$ and $T_B = T_C$. This implies that $T_A = T_B$ i.e. the systems A and B are also in thermal equilibrium.

i. e, If $T_A = T_C$ and $T_B = T_C$ then $T_A = T_B$

The concept of temperature from Zeroth Law

The thermodynamic variable whose value is equal for two systems in thermal equilibrium is called temperature (T).

Heat, Internal Energy and Work

**Heat and work are two modes of energy transfer to the system . (or)
Heat and work are two modes to change the internal energy of a system.
Heat and work are not thermodynamic state variables, but internal energy is a thermodynamic state variable.**

Internal Energy(U)

Internal energy of a system is the sum of kinetic energies and potential energies of the molecular constituents of the system.
It does not include the over-all kinetic energy of the system.

Internal energy U of a system is an example of a thermodynamic 'state variable' – its value depends only on the given state of the system, not on the 'path' taken to arrive at that state.

Heat(Q)

Heat is energy transfer due to temperature difference between two systems.
Heat is certainly energy, but it is the energy in transit.

Heat is not a thermodynamic state variable. its value depends on the 'path' taken to arrive a particular state.

Work (W)

Work is energy transfer brought about by means that do not involve such a temperature difference(e.g. moving the piston by raising or lowering some weight connected to it)

Work is not a thermodynamic state variable. its value depends on the 'path' taken to arrive a particular state.

First Law of Thermodynamics

The heat supplied supplied to the system is partly used to increase the internal energy of the system and the rest is used to do work on the environment .

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

ΔQ = Heat supplied to the system by the surroundings

ΔW = Work done by the system on the surroundings

ΔU = Change in internal energy of the system

- If work is done by the system against a constant pressure P ,then

$$\Delta W = P\,\Delta V \qquad (\Delta W = F\,\Delta x = PA\,\Delta x = P\,\Delta V)$$

$$\Delta Q = \Delta U + P\,\Delta V$$

- If a system is taken through a process in which $\Delta U = 0$

$$\Delta Q = \Delta W$$

Heat supplied to the system is used up entirely by the system in doing work on the environment.

Eg: Isothermal expansion of an ideal gas

- From the First Law of Thermodynamics,

$$\Delta Q - \Delta W = \Delta U$$

As ΔU is path independent ($\Delta Q - \Delta W$)should also be path independent.

i.e., eventhough ΔQ and ΔW are path dependent, their combination $\Delta Q - \Delta W$, is path independent.

Specific Heat Capacities of Gases

As gas is compressible, heat transfer can be achieved by keeping either pressure or volume constant. So gases have two types of molar specific heat capacities.

Molar specific heat capacity at constant pressure C_p

$$\mathbf{C_p = \frac{1}{\mu} \left(\frac{\Delta Q}{\Delta T}\right)_p}$$

Molar specific heat capacity at constant volume C_v

$$\mathbf{C_v = \frac{1}{\mu} \left(\frac{\Delta Q}{\Delta T}\right)_v}$$

Relation connecting C_p and C_v – Mayer's relation

First law of thermodynamics , $\Delta Q = \Delta U + P\,\Delta V$

If ΔQ is absorbed at constant volume, $\Delta V = 0$

$$\Delta Q = \Delta U$$

$$C_v = \left(\frac{\Delta Q}{\Delta T}\right)_v \qquad \text{(for 1 mole)}$$

$$C_v = \left(\frac{\Delta U}{\Delta T}\right)_v$$

(U depends only on T .So subscript V can be omitted)

$$\mathbf{C_v = \frac{\Delta U}{\Delta T} \text{ ---------(1)}}$$

If, on the other hand, ΔQ is absorbed at constant pressure,

$$\Delta Q = \Delta U + P\,\Delta V$$

$$C_p = \left(\frac{\Delta Q}{\Delta T}\right)_p$$

$$C_p = \left(\frac{\Delta U}{\Delta T}\right)_p + \left(P\frac{\Delta V}{\Delta T}\right)_p$$

(U depends only on T .So subscript P can be omitted)

$$\mathbf{C_p = \frac{\Delta U}{\Delta T} + \left(P\frac{\Delta V}{\Delta T}\right)_p \text{ ------------(2)}}$$

Now, for a mole of an ideal gas

$$PV = RT$$

$$P\left(\frac{\Delta V}{\Delta T}\right)_p = R\left(\frac{\Delta T}{\Delta T}\right)$$

$$P\left(\frac{\Delta V}{\Delta T}\right)_p = R$$

$$C_p = \frac{\Delta U}{\Delta T} + R$$

Substituting from eq(1) $\quad C_p = C_v + R$

$$\mathbf{C_p - C_v = R}$$

This is called Mayer's relation.

C_p is always greater than C_v . Why

From eqns (1) and (2)
$$C_v = \frac{\Delta U}{\Delta T}$$
$$C_p = \frac{\Delta U}{\Delta T} + \left(P\frac{\Delta V}{\Delta T}\right)_p$$

When gas is heated at constant volume, the entire heat is used to increase the internal energy of the gas. But when the gas is heated at constant pressure, the heat is used to increase the internal energy and also to do external work during expansion. $\frac{\Delta U}{\Delta T}$ is the same in both cases. Hence C_p is greater than C_v.

Thermodynamic State Variables and Equation of State

Every equilibrium state of a thermodynamic system is completely described by specific values of some macroscopic variables, also called **state variables.**

For example, an equilibrium state of a gas is completely specified by the values of pressure, volume, temperature, and mass (and composition if there is a mixture of gases).

Equation of state

The connection between the state variables is called the equation of state.

Eg: For an ideal gas, the equation of state is the ideal gas relation

$$PV = \mu RT$$

Extensive and Intensive Variables

The thermodynamic state variables are of two kinds:

Extensive and Intensive.

Extensive Variables

Extensive variables indicate the ‘size’ of the system.

(If we imagine ,to divide a system in equilibrium into two equal parts, the variables whose values get halved in each part are extensive.)

Eg:Internal energy, Volume , Mass

Intensive Variables

Intensive variables do not indicate the ‘size’ of the system.

(If we imagine, to divide a system in equilibrium into two equal parts, the variables that remain unchanged for each part are intensive.)

Eg: Pressure, Temperature , Density

Thermodynamic Process

A thermodynamic process is *defined* as a change from one equilibrium state to another.

Quasi-static process

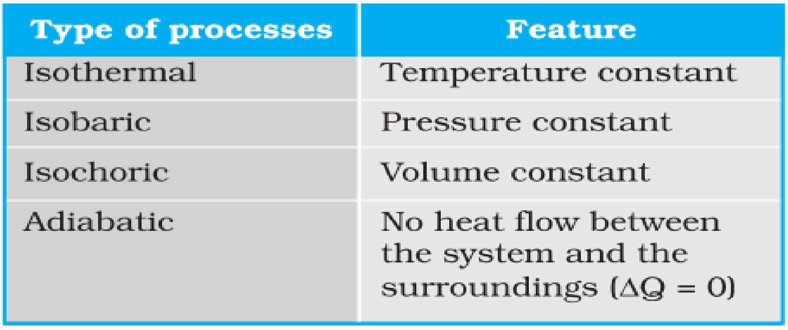
The name quasi-static means nearly static.

A quasi-static process is an infinitely slow process such that the system remains in thermal and mechanical equilibrium with the surroundings throughout.

In a quasi-static process, the pressure and temperature of the environment can differ from those of the system only infinitesimally.

Eg: Processes that are sufficiently slow and do not involve accelerated motion of the piston, large temperature gradient, etc. are reasonably approximation to an ideal quasi-static process.

Some special thermodynamic processes



Type of processes	Feature
Isothermal	Temperature constant
Isobaric	Pressure constant
Isochoric	Volume constant
Adiabatic	No heat flow between the system and the surroundings ($\Delta Q = 0$)

Isothermal process.

A process in which the temperature of the system is kept fixed throughout is called an isothermal process.

For isothermal process **$T = \text{constant}$** .

So internal energy does not change, **$\Delta U = 0$**

- Eg: Change of state (Melting, fusion, vaporistion..)
- The expansion of a gas in a metallic cylinder placed in a large reservoir of fixed temperature is an example of an isothermal process.

Equation of state for an isothermal process

For an ideal gas, $P V = \mu R T$

If an ideal gas goes isothermally from its initial state to the final state , its temperature remains constant

$$PV = \text{constant}$$

This is the equation of state for an isothermal process.

Work done by an ideal gas during an isothermal process

Consider an ideal gas undergoes a change in its state isothermally (at temperature T) from (P_1, V_1) to the final state (P_2, V_2).

$\Delta W = P\,\Delta V$

In the limit $\Delta V \rightarrow 0$

$dW = P\,dV$

$$W = \int_{V_1}^{V_2} P\,dV$$

$$P\,V = \mu R T \quad \text{(for 1 mole)}$$

$$P = \frac{\mu R T}{V}$$

$$W = \int_{V_1}^{V_2} \frac{\mu R T}{V}\,dV$$

$$W = \mu R T \int_{V_1}^{V_2} \frac{1}{V}\,dV$$

$$W = \mu R T\,[\ln V]_{V_1}^{V_2}$$

$$W = \mu R T\,[\ln V_2 - \ln V_1]$$

$$\mathbf{W = \mu RT \ln \left[\frac{V_2}{V_1}\right]}$$

Isothermal expansion,

For Isothermal expansion, $V_2 > V_1$ and hence $W > 0$ (workdone is positive)

That is, in an isothermal expansion, the gas absorbs heat and work is done by the gas on the environment.

Isothermal compression

In isothermal compression $V_2 < V_1$ and hence $W < 0$ (workdone is negative)

That is, In an isothermal compression, work is done on the gas by the environment and heat is released.

The First Law of Thermodynamics for an isothermal change

For isothermal process $\mathbf{\Delta U = 0}$

First Law of Thermodynamics $\Delta Q = \Delta U + \Delta W$

$$\Delta Q = \Delta W$$

The heat absorbed by the gas is entirely used to do the work on the environment.

Adiabatic process

In an adiabatic process, the system is insulated from the surroundings and heat absorbed or released is zero.

$$\Delta Q = 0$$

Equation of state for an adiabatic process

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

$$\text{Or} \quad T\,V^{\gamma-1} = \text{constant}$$

where γ is the ratio of specific heats (ordinary or molar) at constant pressure and at constant volume. $\gamma = \frac{C_p}{C_v}$

Workdone by an Ideal gas during an Adiabatic Process

Consider an ideal gas undergoes a change in its state adiabatically from (P_1, V_1) to the final state (P_2, V_2).

$$W = \int_{V_1}^{V_2} P\,dV$$

$$PV^{\gamma} = k$$

$$P = \frac{k}{V^{\gamma}}$$

$$P = k\,V^{-\gamma}$$

$$W = k\int_{V_1}^{V_2} V^{-\gamma}\,dV$$

$$W = k\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$W = \frac{k}{1-\gamma}\left[V_2^{-\gamma+1} - V_1^{-\gamma+1}\right]$$

$$W = \frac{1}{1-\gamma}\left[\frac{k}{V_2^{\gamma-1}} - \frac{k}{V_1^{\gamma-1}}\right]$$

$$PV^{\gamma} = k$$

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = k$$

$$W = \frac{1}{1-\gamma}\left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}}\right]$$

$$W = \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]$$

$$PV = \mu R T$$

$$W = \frac{1}{1-\gamma}\left[\mu R T_2 - \mu R T_1\right]$$

$$W = \frac{\mu R}{1-\gamma}\left[T_2 - T_1\right]$$

Or

$$W = \frac{\mu R}{\gamma-1}\left[T_1 - T_2\right]$$

Adiabatic expansion

In adiabatic expansion, the work is done by the gas ($W > 0$), we get $T_2 < T_1$ i.e., the temperature of the gas lowers.

Adiabatic compression

In Adiabatic compression, work is done on the gas ($W < 0$), we get $T_2 > T_1$. i.e., the temperature of the gas rises.

First law of thermodynamics for an adiabatic process

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

For adiabatic process, $\Delta Q = 0$

$$\Delta W = -\Delta U$$

i.e., Workdone = - change in internal energy

Isochoric process

In an isochoric process, V is constant.

Workdone in an isochoric process

$$\Delta W = P\,\Delta V$$

For isochoric process, $\Delta V = 0$

$$\Delta W = 0$$

In an isochoric process no work is done on or by the gas.

First law of thermodynamics for an isochoric process

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

For isochoric process, $\Delta W = 0$

$$\Delta Q = \Delta U$$

The heat absorbed by the gas goes entirely to change its internal energy and thereby its temperature.

Isobaric Process

In an isobaric process, P is constant.

Work done by the gas in an Isobaric process

Work done by the gas is

$$\Delta W = P\,\Delta V$$

$$W = P\,(V_2 - V_1)$$

$$W = \mu R\,(T_2 - T_1)$$

First Law of Thermodynamics for an Isobaric Process

Since temperature changes, internal energy also changes. The heat absorbed goes partly to increase internal energy and partly to do work.

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

Cyclic Process

In a cyclic process, the system returns to its initial state.

Since internal energy is a state variable, $\Delta U = 0$ for a cyclic process

First Law of Thermodynamics for Cyclic Process

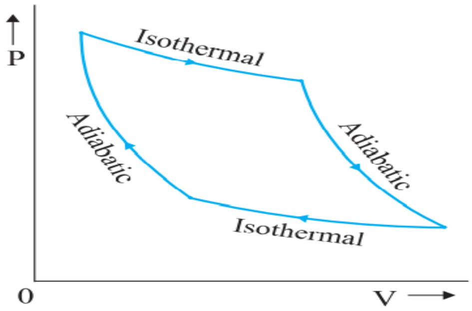
$$\Delta Q = \Delta U + \Delta W$$

$$\Delta U = 0$$

$$\Delta Q = \Delta W$$

The total heat absorbed equals the work done by the system.

P-V curves for isothermal and adiabatic processes of an ideal gas.



Second Law of Thermodynamics

Kelvin-Planck statement

No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

Clausius statement

No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

The two statements above are completely equivalent

Reversible and Irreversible Processes

Reversible Processes

A thermodynamic process is reversible if the process can be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe.

Eg: A quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is a reversible process.

A process is reversible only if:

1) It is quasi-static i.e., the system in equilibrium with the surroundings at every stage.
2) There are no dissipative factors such as friction, viscosity, etc.

Irreversible Processes

A thermodynamic process is irreversible if the process cannot be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe.

The spontaneous processes of nature are irreversible.

- Eg:The free expansion of a gas
- The combustion reaction of a mixture of petrol and air ignited by a spark .
- Cooking gas leaking from a gas cylinder in the kitchen diffuses to the entire room. The diffusion process will not spontaneously reverse and bring the gas back to the cylinder.

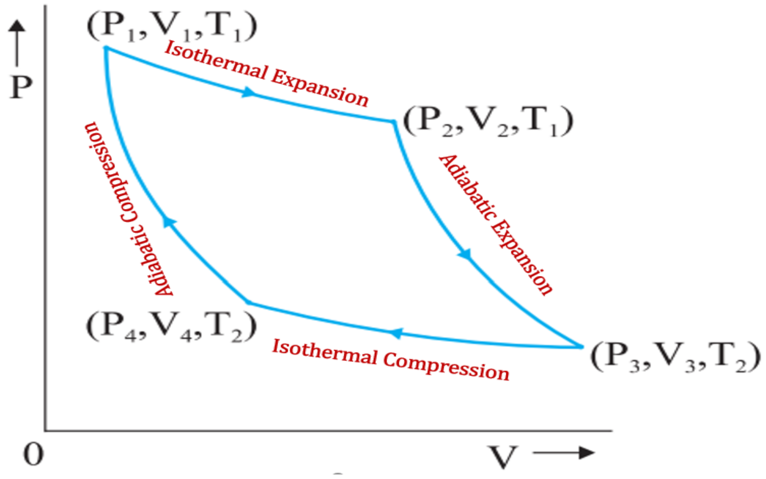
Irreversibility of a process arises due to:

1) Many processes take the system to non-equilibrium states.
2) Most processes involve friction, viscosity and other dissipative effects.

Carnot Engine

Sadi Carnot, a French engineer, developed Carnot engine. Carnot engine is a reversible engine operating between two temperatures T_1 (source) and T_2 (sink). **The working substance of the Carnot engine is an ideal gas.**

Carnot cycle



The four processes involved in carnot cycle are

1.Isothermal Expansion
2. Adiabatic Expansion
3. Isothermal Compression
4. Adiabatic Compression

Workdone in a Carnot cycle

(a)Step 1 →2 Isothermal expansion of the gas from (P_1, V_1, T_1) to (P_2, V_2, T_1).

Since the process is isothermal

The workdone $(W_{1\rightarrow 2})$ =Heat absorbed (Q_1)

Work done by the gas,

$$\mathbf{W_{1\rightarrow 2} = Q_1 = \mu\, RT_1 \ln \left|\frac{V_2}{V_1}\right|} \text{------------(1)}$$

(b) Step 2 → 3 Adiabatic expansion of the gas from (P_2, V_2, T_1) to (P_3, V_3, T_2).

Work done by the gas,

$$W_{2\to3} = \frac{\mu R}{\gamma-1}[\,T_1 - T_2\,] \text{ ------------------}(2)$$

(c)Step 3→4 Isothermal compression of the gas from (P_3, V_3, T_2) to (P_4, V_4, T_2).

The workdone $(W_{3\to4})$ =Heat released (Q_2)

Work done on the gas,

$$W_{3\to4} = Q_2 = \mu RT_2 \ln\left[\frac{V_4}{V_3}\right]$$

$$W_{3\to4} = Q_2 = -\,\mu RT_2 \ln\left[\frac{V_3}{V_4}\right] \text{ -----------}(3)$$

(d) Step 4 → 1 Adiabatic compression of the gas from (P_4, V_4, T_2) to (P_1, V_1, T_1)

Work done on the gas is,

$$W_{4\to1} = \frac{\mu R}{\gamma-1}[T_2 - T_1]$$

$$W_{4\to1} = -\frac{\mu R}{\gamma-1}[T_1 - T_2] \text{ -----------------}(4)$$

Total work done by the gas in one complete cycle is

$$W = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

$$W = \mu RT_1 \ln\left[\frac{V_2}{V_1}\right] + \frac{\mu R}{\gamma-1}[\,T_1 - T_2\,] - \mu RT_2 \ln\left[\frac{V_3}{V_4}\right] - \frac{\mu R}{\gamma-1}[\,T_1 - T_2\,]$$

$$W = \mu RT_1 \ln\left[\frac{V_2}{V_1}\right] - \mu RT_2 \ln\left[\frac{V_3}{V_4}\right] \text{ -------------}(5)$$

Efficiency of Carnot Engine

$$\eta = 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{\mu RT_2 \ln\left[\frac{V_3}{V_4}\right]}{\mu RT_1 \ln\left[\frac{V_2}{V_1}\right]}$$

As the two processes involved are adiabatic ,we get $\frac{V_3}{V_4} = \frac{V_2}{V_1}$

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

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

Carnot's theorem

(a) working between two given temperatures T_1 and T_2 of the hot and cold reservoirs respectively, no engine can have efficiency more than that of the Carnot engine

(b) the efficiency of the Carnot engine is independent of the nature of the working substance.

Example

Calculate the efficiency of a heat engine working between steam point and ice point. Can you design an engine of 100% efficiency.

Steam point , $T_1 = 100^0\mathrm{C} = 100 + 273 = 373\mathrm{K}$

Ice point , $T_2 = 0^0\mathrm{C} = 0 + 273 = 273\mathrm{K}$

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

$$\eta = \frac{373 - 273}{373} = 0.268$$

$$\boldsymbol{\eta = 26.8\%}$$

An ideal engine with $\eta = 1$ or (100%) efficiency is never possible, even if we can eliminate various kinds of losses associated with actual heat engines.