Thermodynamics.

It is the branch of science that deals with the concepts of heat and temperature and the inter-conversion of heat and other forms of energy.

Thermodynamic system.

An assembly of a very large number of particles having a certain value of pressure, volume and temperature is called a thermodynamic system.

Surroundings.

Everything outside the system which can have a direct effect on the system is called its surroundings.

Thermodynamic variables.

The quantities like:

Pressure(P), volume(V) and temperature(T) which help us to study the behaviour of a thermodynamic system are called thermodynamic variables.

Equation of state.

The mathematical relation between the pressure, volume and temperature of a thermodynamic system is called its equation of state. For example, the equation of state of n moles of an ideal gas can be written as

$$\boldsymbol{PV = nRT}.$$

Thermal equilibrium.

Two systems are in thermal equilibrium with each other if they have the same temperature. Heat is the flow of energy from a high temperature to a low temperature. When these temperatures balance out, heat stops flowing, then the system (or set of systems) is said to be in thermal equilibrium. Thermal equilibrium also implies that there's no matter flowing into or out of the system.

Thermodynamic equilibrium.

A system is said to be in a state of thermodynamic equilibrium if the macroscopic variables describing the thermodynamic state of the system do

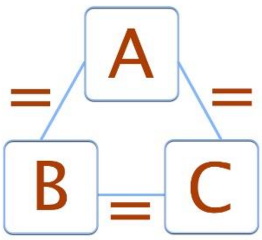
not change with time. A system in a state of thermodynamic equilibrium possesses mechanical, thermal and chemical equilibria simultaneously.

State variables.

The macroscopic quantities which are used to describe the equilibrium state of a thermodynamic system are called state variables. The value of a state variable depends only on the particular state, not on the path used to attain that state. Pressure(P), volume(V), temperature(T) and mass (m) are state variables. Heat (Q) and work(W) are not state variables.

Zeroth law of thermodynamics.

If two systems A and B are in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other. According to this law, temperature is a physical quantity which has the same value for all systems which are in thermal equilibrium with each other.



Internal energy.

The internal energy of a system is the sum of molecular kinetic and potential energies in the frame of reference relative to which the centre of mass of the system is at rest. It does not include the over-all kinetic energy of the system. It is a state variable denoted by U.

Quasi-static process.

A quasi-static process is an infinitely slow process such that system remains in thermal and mechanical equilibrium with the surroundings throughout. In such a process, the pressure and temperature of the surroundings can differ from those of the system only infinitesimally.

Isothermal process.

A process in which temperature remains constant is called an isothermal process. For such a process,

$$PV = constant \qquad or \qquad P_1V_1 = P_2V_2$$

Adiabatic process.

A process in which thermally insulated system neither loses nor gains heat from the surroundings is called adiabatic process.

Equations of state for adiabatic processes are:

(i) $PV^\gamma = constant \quad or \quad P_1V_1^\gamma = P_2V_2^\gamma$

(ii) $TV^{\gamma-1} = constant \quad or \quad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

(iii) $\frac{P^{\gamma-1}}{T^\gamma} = constant \qquad or \quad \frac{P_1^{\gamma-1}}{T_1^\gamma} = \frac{P_2^{\gamma-1}}{T_2^\gamma}$

where $\gamma = C_p/C_v$.

Isobaric process.

A process in which pressure remains constant is called isobaric process. For such a process

$$\frac{V}{T} = constant \qquad or \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Isochoric process.

A process in which volume remains constant is called isochoric process. For such a process,

$$\frac{P}{T} = constant \qquad or \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Indicator diagram.

A graphical representation of the state of a system with the help of two thermodynamical variables is called indicator diagram of the system. The graph between pressure P and Volume V is called P-V diagram.

Work done during the expansion of a gas.

When the volume of a gas changes from V_1 to V_2, the work done is

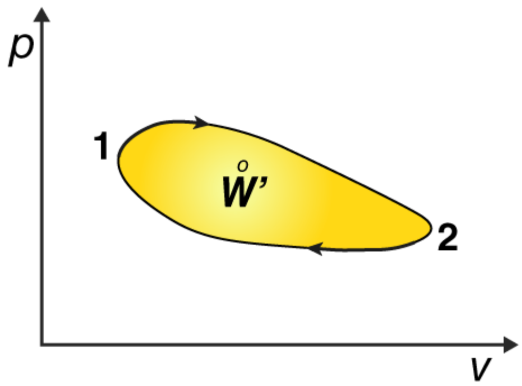
$$W = \int_{V_1}^{V_2} P\, dV$$

$$= \textit{area enclosed between the } P - V \textit{ curve and the volume axis}.$$

Work done during a cyclic process.

From the P-V diagram,

Work done per cycle = area of the loop representing the cycle



(i) If the loop is traced clockwise, the work done is positive and work is done by the system.

(ii) If the loop is traced anticlockwise, the work done is negative and work is done on the system.

First law of thermodynamics.

It states that If heat dQ is given to a system, a part of it is used in increasing the internal energy by an amount dU and the remaining energy is used in doing the external work dW. It is just a restatement of the law of conservation of energy. Thus,

$$dQ = dU + dW \qquad or \qquad dQ = dU + PdV.$$

Sign conventions used

(i) Heat absorbed by a system is positive and heat given out by a system is negative.

(ii) Increase in internal energy of a system is positive and decrease in internal energy of a system is negative.

(iii) Work done by a system is positive and work done on a system is negative.

Work done in an isothermal process.

Work done when 1 mole of a gas expands isothermally,

$$W_{iso} = 2.303\ RT \log \frac{V_2}{V_1} = 2.303\ RT \log \frac{P_1}{P_2}.$$

Work done in an adiabatic process.

Work done when 1 mole of a gas expands adiabatically and its temperature falls from T_1 to T_2,

$$W_{adia} = \frac{R}{\gamma - 1}[T_1 - T_2] = \frac{1}{\gamma - 1}[P_1 V_1 - P_2 V_2]$$

Molar specific heat of a gas at constant volume (C_v).

It is defined as the amount of heat required to raise the temperature of 1 mole of the gas through 1℃ at constant volume.

If c_v is specific heat of gas for 1g at constant volume and M is its molecular weight, then molar specific heat at constant volume,

$$C_v = Mc_v$$

Molar specific heat of a gas at constant pressure (C_p).

It is defined as the amount of heat required to raise the temperature of 1 mole of the gas through 1℃ at constant pressure. Thus,

$$C_p = Mc_p$$

Relation between two specific heats of a gas.

Specific heat of a gas at constant pressure is greater than the specific heat at constant volume.

For one mole of a gas:

(i) $C_p - C_v = R\ (when\ C_p, C_v\ are\ in\ units\ of\ work)$

(ii) $C_p - C_v = \frac{R}{J}\ (when\ C_p, C_v\ are\ in\ units\ of\ heat)$

Where R is universal gas constant for 1 mole of a gas.

For 1g of a gas:

(i) $c_p - c_v = r$ (when c_p, c_v $are\ in\ units\ of\ work$)

(ii) $c_p - c_v = \frac{r}{J}$ (when c_p, c_v $are\ in\ units\ of\ heat$)

Where $r = \frac{R}{M}$ = gas constant for 1g of a gas.

Clearly, heat lost or gained by n moles of a gas,

(i) $Q = nC_p\Delta T$ (at constant pressure)

(ii) $Q = nC_v\Delta T$ (at constant volume)

Where n = number of moles of gas = mass of gas/ molecular mass.

Heat engine.

It is a device which converts continuously heat energy into mechanical energy in a cyclic process. It essentially consists of (i) a source of heat (ii) a sink of heat and (iii) a working substance.

Efficiency of a heat engine.

It is the ratio of useful work done (W) by the engine per cycle to the heat energy (Q_1) absorbed from the source per cycle.

$$\eta = \frac{work\ output}{heat\ input} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Where Q_2 is the heat rejected to the sink.

Second law of thermodynamics.

(i) Kelvin-Planck statement. It is impossible to construct an engine, which will produce no effect other than extracting heat from a reservoir and performing an equivalent amount of work.

(ii) Clausius statement. It is impossible for a self-acting machine, unaided by an external energy, to transfer heat from a body to another at higher temperature.

Reversible process.

A process which can be made to proceed in the reverse direction by variations in its conditions so that any change occurring in any part of the direct process is exactly reversed in the corresponding part of the reverse process is called a reversible process.

Irreversible process.

A process which cannot be made to proceed in the reverse direction is called an irreversible process.

Carnot engine.

It is an ideal heat engine which is based on Carnot's reversible cycle. Its working consists of four steps viz. Isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression. The efficiency of Carnot engine is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

Where T_1 and T_2 are the temperatures of source and sink respectively.

Carnot theorem.

It states that

(i) no engine working between two given temperatures can have efficiency greater than that of the Carnot engine working between the same two temperatures and

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

Refrigerator.

It is a heat engine working in the reverse direction. Here a working substance absorbs heat Q_2 from the sink at temperature T_2. An external agency does work W on the working substance. A larger amount of heat Q_1 is rejected to source at a higher temperature T_2.

$$Q_1 = \ Q_2 + W$$

Coefficient of performance.

It is defined as the ratio to the amount of heat (Q_2) removed per cycle from the contents of the refrigerator to the work done (W) by the external agency to remove it.

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