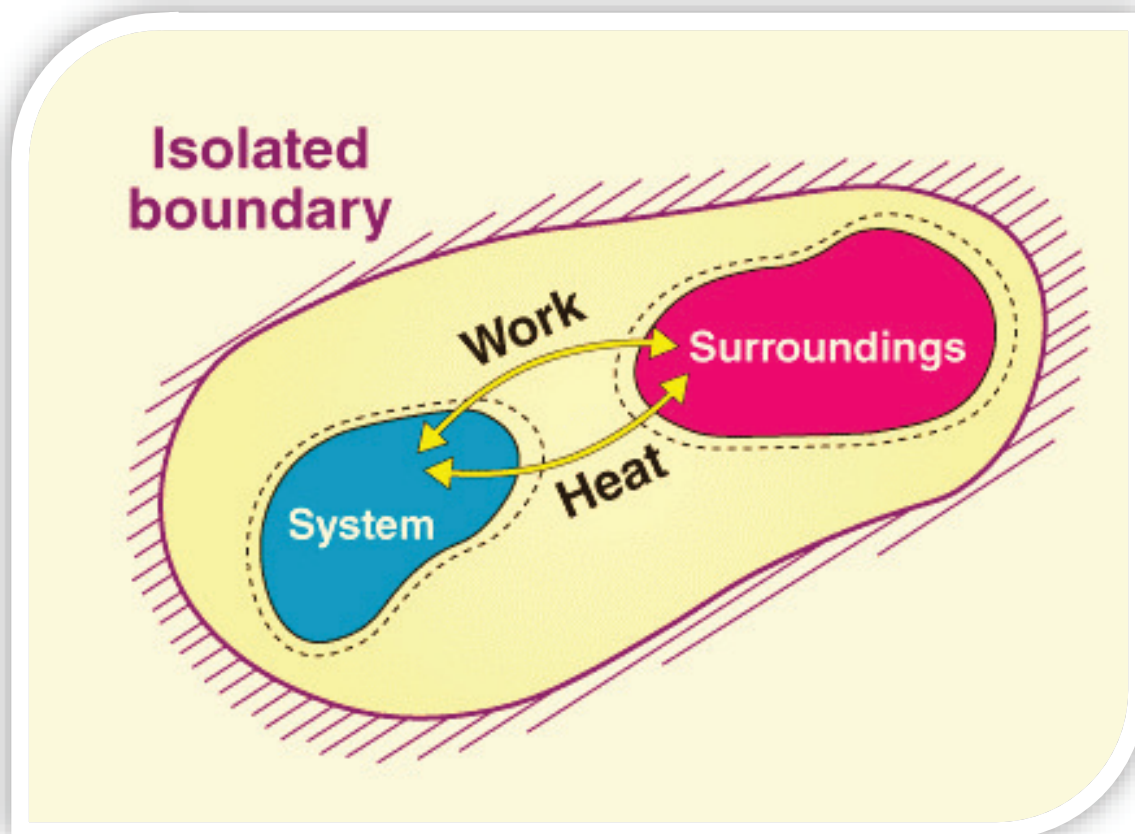


Thermodynamics



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Thermodynamics

Thermodynamics: It is the macroscopic description of the interaction of a system with its environment, i.e., the surroundings. By interaction we mean the transformation of heat to other forms of energy and vice versa.

A thermodynamic system: It is an assembly of extremely large number of particles (atoms or molecules) in solid, liquid, gaseous, or a combination of two or more phases.

Environment: It is anything outside a thermodynamic system that has a direct effect on the system.

Thermodynamic (or state) variables: They are the parameters used to describe the state or condition of a thermodynamic system. They are also referred to as thermodynamic coordinates. State variables are **path independent**, i.e., they depend on the initial and final states of a system, but not how the change is brought about.

Example: (i) Composition (ii) Temperature (iii) Volume (iv) Pressure (v) Internal energy (vi) Entropy

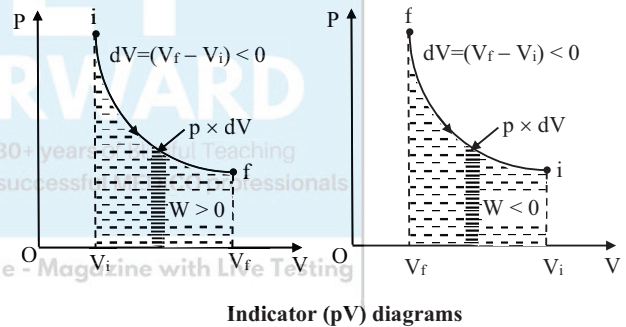
Thermodynamic process: Whenever the state of a system changes, it is said to undergo a thermodynamic process. Common thermodynamic processes are (i) isothermal, (ii) isochoric (iii) isobaric (iv) adiabatic (v) cyclic processes.

Quasi-static process is a process that occurs so slowly that the system proceeds through a series of equilibrium states during the change. It can be represented by a curve on a p-V, or a p-T, or a V-T diagram. All real processes are being regarded as quasi-static. Rapidly or violently changing process is not quasi-static.

Work: It is the energy exchanged between a system and its environment by means independent of temperature difference between them.

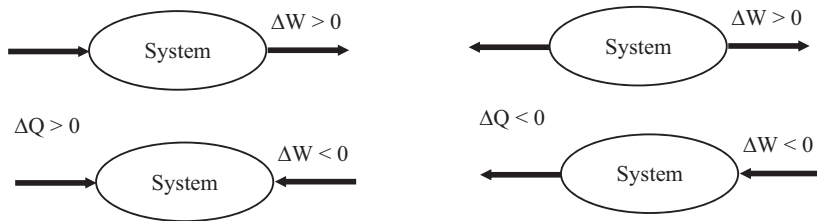
(a) Work done during a quasi-static process from initial state characterised by (V_i, p_i, T_i) to a final

state (V_f, p_f, T_f) is given by $W = \int_{V_i}^{V_f} p \times dV$



To evaluate the integral, we must know how pressure varies during the process. Area under p.V curve gives the work done, i.e., if $V_f \neq V_i$

(b) **Sign convention:** (i) Heat entering a system is considered positive, i.e., $\Delta Q > 0$, while that leaving it is negative, i.e., $\Delta Q < 0$.

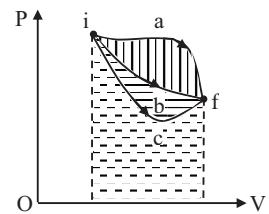


Symbolic representation of sign convention

(ii) Work done by a system, i.e., work leaving a system, is considered positive, i.e., $\Delta W > 0$, while that done on the system, i.e., work entering the system, is negative i.e., $\Delta W < 0$.

(c) **Dependence of work and heat on the process:** p-V diagram shows three processes a, b and c between states i and f of a system. It is obvious from the diagram that $Q_a \neq Q_b \neq Q_c$ and $W_a > W_b > W_c$

so, heat added and work done are path dependent.



(d) **Work done during various processes:**

(i) **Isochoric process (constant volume process):** No work is done since there is no change in volume.

$$W_v = 0 \text{ since } \Delta V = 0$$

(ii) **Isobaric process (constant pressure process):** $W_p = nR[T_f - T_i]$

$n \rightarrow$ number of moles of an ideal gas

$T_i \rightarrow$ temperature of the initial state (i)

$T_f \rightarrow$ temperature of the final state (f)

(iii) **Isothermal process (constant temperature process):**

$$W_T = nRT \ln\left(\frac{V_f}{V_i}\right) = nRT \ln\left(\frac{p_i}{p_f}\right)$$

$V_i, V_f \rightarrow$ initial and final volumes of a system

$p_i, p_f \rightarrow$ initial and final pressure of the system at temp. T

$W_T > 0$ if $V_f > V_i$

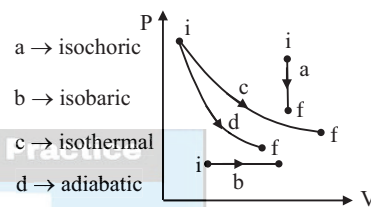
$W_T < 0$ if $V_i > V_f$

(iv) **Adiabatic process:**

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

$W_A < 0$ if $V_f < V_i$ (sudden compression)

$W_A > 0$ if $V_f > V_i$ (sudden expansion)



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The first law of thermodynamics

Experiments show that the quantity $(Q - W)$ is a constant for all processes for the given states. The quantity $(Q - W)$ must represent some intrinsic property of the system, called its internal energy. This experimental fact leads to the first law of thermodynamics.

The first law of thermodynamics states that the net energy transferred equals the change in the internal energy of a system undergoing a process.

$$\Delta E_{int} = E_{f_{int}} - E_{i_{int}} = Q - W$$

where i indicates for initial state and f final state of the system.

When the energy transfers are small, $\Delta E_{int} = \Delta Q - \Delta W$



- The first law of thermodynamics is an extension of the principle of conservation energy to systems that are not isolated. In such cases, energy may be transferred into or out of the system as either work or heat.
- Internal energy** is the sum of the molecular kinetic energy, molecular potential energy and other kinds of molecular energy viewed from a reference frame at rest with respect to the system.

- Internal energy is associated with the random translational, rotational and vibrational motion of the particles that make up the system.
- Internal energy also includes other kinds of energy like intermolecular potential energy together with nuclear, atomic and molecular binding energy.
- Internal energy does not include kinetic energy of the molecules due to translation, rotation, or vibration of the whole or part of the system, and potential energy due to interactions of the molecules of the system with something outside the system.
- Internal energy of a monatomic gas is associated with the translational kinetic energy of its atoms. $E_{int} = 3nRT / 2$
- For diatomic and polyatomic molecules, internal energy includes other forms of energy as well.

Application of the first law of thermodynamics

(a) **Isochoric process (constant volume process → change in volume $\Delta V = 0$):** $W = 0$; since $\Delta V = 0$, $\Delta E_{int} = Q$. So, heat transferred to a system at constant volume goes to increase the internal energy (and temperature) of the system.

(b) **Isobaric process (constant pressure process):** Boiling of water at atmospheric pressure is an example. Phase change occurs at constant temperature and pressure from liquid to vapour.

$W = p(V_f - V_i)$; $Q = mL_v$; $\Delta E_{int} = Q - W = mL_v - p(V_f - V_i)$

$m \rightarrow$ mass of water, $L_v \rightarrow$ latent heat of vapourisation.

(c) **Isothermal process:** $\Delta E_{int} = 0$ since $\Delta T = 0$; $W = Q$

Heat transferred to a system at constant temperature appears as work against the surroundings.

(d) **Adiabatic process:** $\Delta E_{int} = -W$ since $Q = 0$

Work is done at the expense of internal energy. When a system undergoes an adiabatic expansion $W > 0$. When the system undergoes an adiabatic compression, $W < 0$.

(e) **Melting process:** The change of phase occurs at constant temperature and pressure. Slight change in volume can be neglected.

$W = 0$ since $\Delta V \approx 0$; $\Delta E_{int} = Q = mL_f$

$m \rightarrow$ mass of the solid, $L_f \rightarrow$ latent heat of fusion of the solid. So, the **internal energy increases**, but the **temperature does not**. It implies that the internal potential energy increases, not the internal kinetic energy.

(f) **Cyclic process:** It is a process in which a system returns to its initial state after a certain interchange of heat and work. No intrinsic property (including its internal energy) can possibly change.

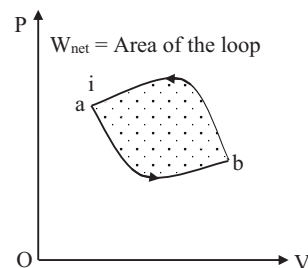
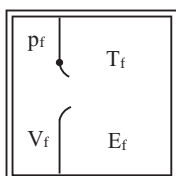
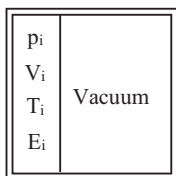
$Q = W$ since $\Delta E_{int} = 0$

Thus, the net work during cyclic process equals the net heat transferred.

(g) **Free expansion:** Consider an ideal gas in a two chambered container having an adiabatic membrane separating the chambers. The other chamber is evacuated. If

the membrane breaks spontaneously, the gas expands freely to occupy the entire container. Such a process is called free expansion. In free expansion, $Q = 0$ and $W = 0$ because no heat is transferred and no work is done since the gas rushes into a vacuum.

$\therefore \Delta E_{int} = 0$





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