

THERMODYNAMICS SHORT NOTES

Thermodynamics

Reactant $\longrightarrow$ Product energy changes.

Bond Breaking - Endothermic **Bond formation** - Exothermic

Some important terms:

System - specific part of universe which is under observation.

Surrounding - Rest part of universe excluding the system.

Boundary - Anything which separates system and surrounding.

Types of system:

- 1) **Open system** - which can exchange energy as well as matter
- 2) **Closed system** - can exchange energy but not matter.
- 3) **Isolated system** - cannot exchange energy and matter.

State of system - properties which define state of any system

Pressure, temperature, volume etc.

State Function - Variable which depend upon initial and final state.

Pressure, Volume, temperature, Internal energy, Entropy,

Gibbs free energy.

Path Function - Variable which depends on the path followed by system. Work and Heat.

Intensive properties - which are independent of mass

Density, temperature, pressure, specific heat, molar specific Heat, Boiling point, melting point, Vapour pressure and viscosity.

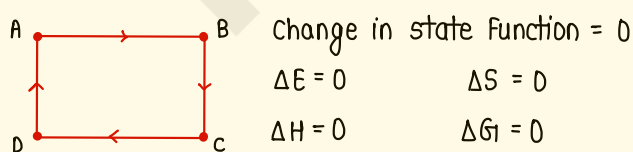
Extensive properties - which are dependent of mass.

Mass, Volume, moles, entropy, Gibbs free energy, enthalpy, Internal energy, Heat capacity.

Types of processes:

- a) **Isothermal** - T is constant - $\Delta T = 0$
- b) **Isobaric** - P is constant - $\Delta P = 0$
- c) **Isochoric** - V is constant - $\Delta V = 0$
- d) **Adiabatic** - Heat exchange is zero - $q = 0$

Cyclic process - Initial state = Final state.



Work - Area under P-V graph

$$W = - \int P dV \quad W = -P\Delta V \quad \Delta V = V_2 - V_1$$

Expansion $V_2 > V_1$ $W = -ve$ - work done by system

Compression $V_2 < V_1$ $W = +ve$ - Work done on system.

Reversible process

Changes can be reversed.

Driving force should be infinitesimally greater than opposing force.

Place in very small steps and takes infinite time to complete the process.

Ideal process

System is in virtual equilibrium at any state.

P_{ext} is variable

Irreversible process

Changes cannot be reversed.

Driving force is much greater than opposing force.

takes finite time and usually a single step process.

All natural process.

System is in equilibrium only at initial and final state

P_{ext} is constant.

Heat (q): Energy flow due to temperature different.

$W = +ve$ $\downarrow$ $\uparrow$ $W = -ve$

System

$q = +ve$ $\uparrow$ $\downarrow$ $q = -ve$

Units:

$1 \text{ cal} = 4.2 \text{ Joule}$ $1 \text{ J} = 10^7 \text{ erg}$

$1 \text{ L atm} = 101.3 \text{ Joule}$

$1 \text{ L Bar} = 100 \text{ Joule}$

Internal energy: (E or U)

Sum of different energies associated with its atoms and molecules like P.E, K.E, electronic energy, nuclear energy

Extensive property

State Function

We cannot find the absolute value of internal energy.

$$\Delta E = E_f - E_i \quad \Delta E = +ve \quad E_f > E_i$$

$$\Delta E = -ve \quad E_f < E_i$$

Note: Gravitational energy is not part of internal energy.

First law of thermodynamics: $\Delta U = q + w$

Based on conservation of energy

Energy neither be created nor be destroyed but can transformed from one form to another.

Total energy of universe is always constant.

Isothermal process - T is constant $\Delta T = 0$

For ideal gas, internal energy depends only on T

$$\Delta U = 0 \quad q = -w$$

Isochoric process: V is constant $\Delta V = 0$

$$W = 0 \quad \Delta U = q_v$$

Change in internal energy is equal to heat released or absorbed at const. volume.



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Cyclic process: $\Delta U = 0 \therefore q = -w$

Initial state = Final state

Change in state function = 0

Adiabatic process: $q = 0 \quad \Delta U = w$

Isobaric process: P is constant $\Delta P = 0$

Change in enthalpy is heat released or absorbed at constant pressure. $\Delta H = q_p$

Enthalpy:

$$H = U + PV \quad \Delta H = \Delta U + \Delta(PV)$$

If P is constant $\Delta H = \Delta U + P\Delta V$

If V is constant $\Delta H = \Delta U + V\Delta P$

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta n g = 0 \rightarrow \Delta H = \Delta U$$

$$\Delta H = \Delta U + \Delta n g RT$$

$$\Delta n g > 0 \rightarrow \Delta H > \Delta U$$

$$q_p = q_v + \Delta n g RT$$

$$\Delta n g < 0 \rightarrow \Delta H < \Delta U$$

$\Delta n g$ = Sum of the gaseous moles of product -
Sum of the gaseous moles of reactant.

Heat capacity (c) $c = \frac{q}{\Delta T}$

Specific Heat capacity (s) $s = \frac{q}{m\Delta T}$

Molar Heat capacity (C_m) $C_m = \frac{q}{n\Delta T}$

C_m
 Constant P — $C_p = \frac{q_p}{n\Delta T} \rightarrow \Delta H = q_p = nC_p\Delta T$
 Constant V — $C_v = \frac{q_v}{n\Delta T} \rightarrow \Delta U = q_v = nC_v\Delta T$

Meyer's ratio:

Poisson's Ratio (γ) $= \frac{C_p}{C_v}$

$C_p - C_v = R$ for 1 mole

$C_p - C_v = nR$ for n moles

Gas	C_v	C_p	$\gamma = C_p / C_v$
Monatomic (He, Ne)	$\frac{3R}{2}$	$\frac{5R}{2}$	$\frac{5}{3} = 1.67$
Diatomic (O ₂ , N ₂)	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5} = 1.4$
Triatomic (Linear, CO ₂)	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5} = 1.4$
Triatomic (Non-linear, SO ₂)	$3R$	$4R$	$\frac{4}{3} = 1.33$

Work $w = -\int PdV$

- P - V work - Area under P - V graph

a) Irreversible process $P \rightarrow$ constant.

$$w_{irr} = -P\Delta V$$

b) Reversible process $P \rightarrow$ Variable.

$$w = -nRT \ln \frac{V_2}{V_1} = -2.303 nRT \log \frac{V_2}{V_1}$$

$$w = -nRT \ln \frac{P_1}{P_2} = -2.303 nRT \log \frac{P_1}{P_2}$$

- Work done in vacuum $w = 0$.

Reversible adiabatic process:

$$w_{work} \quad \Delta U = w \quad w = nC_v (T_2 - T_1)$$

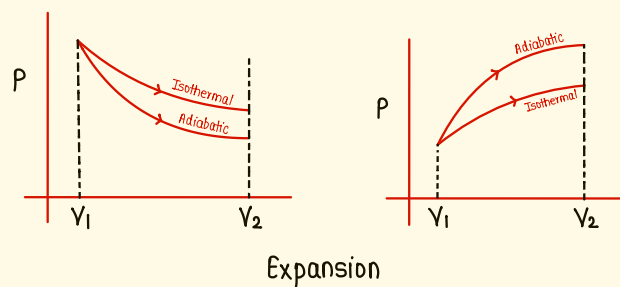
$$w = \frac{nR (T_2 - T_1)}{\gamma - 1} \quad w = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

- Some important points:

a) Reversible adiabatic process:

$$PV^\gamma = \text{Constant} \quad TV^{\gamma-1} = K \quad T^\gamma P^{1-\gamma} = K$$

b) Graphs: More slope More steep - Adiabatic.



Limitations of First law:

Does not explain feasibility of a process under given conditions.

Reactants $\rightarrow$ products.

Spontaneous process

Natural tendency to occur.

All natural processes are irreversible and spontaneous
Example - Flow of water from High level to low level. Flow of Heat from Hot Body to cold Body.

Non-spontaneous process:

Process which do not occur on its own.

When energy from some external source is applied. Example - Burning of Fuel.



THERMODYNAMICS SHORT NOTES

Criteria for a process to be spontaneous.

- Energy decrease.
- Entropy increase.

Entropy change in reversible process

$$\Delta S_{\text{universe}} = 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$$

$$\Delta S_{\text{system}} = -\Delta S_{\text{surrounding}}$$

Entropy change in irreversible process

$$\Delta S_{\text{universe}} > 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

Entropy: (S)

Degree of randomness or disorderness of the system
More the randomness = more is entropy

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{total}}$$

$$\Delta S = +ve - S_{\text{final}} > S_{\text{initial}}$$

$$\Delta S = -ve - S_{\text{final}} < S_{\text{initial}}$$

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Case I: Reversible isothermal Case II: Isochoric process

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

$$S_{\text{gas}} > S_{\text{liq}} > S_{\text{solid}}$$

More is the gaseous atom = more is entropy

Δn_g = Sum of the gaseous moles of product -
Sum of the gaseous moles of reactant.

$$\Delta n_g > 0 \quad \Delta S = +ve$$

$$\Delta n_g < 0 \quad \Delta S = -ve$$

$$\Delta n_g = 0 \quad \Delta S = 0$$

Reversible adiabatic: $q=0$ $\Delta S=0$ Isoentropic process.

Entropy change during phase transition: $\Delta S = \frac{q_{\text{rev}}}{T}$

a) Entropy of fusion (solid $\rightarrow$ liquid) **Melting point.**

$$\Delta S = \frac{\Delta H_{\text{fusion}}}{T_{\text{MP}}}$$

b) Entropy of vapourisation (liquid $\rightarrow$ Gas) **Boiling point**

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T_{\text{BP}}}$$

c) Entropy of sublimation (Solid $\rightarrow$ Gas)

$$\Delta S = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}}}$$

Some important points about entropy change:

- Entropy of graphite > Graphite of Diamond
- Rusting of iron, entropy increases.
- On boiling of egg, denaturation of protein occurs. entropy increases.
- Stretching of rubber - entropy decreases.

Second law of thermodynamics

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{total}} > 0 - \text{spontaneous}$$

$$\Delta S_{\text{total}} < 0 - \text{non-spontaneous}$$

$$\Delta S_{\text{total}} = 0 - \text{Equilibrium}$$

Gibbs free energy (G)

Capacity of system to do useful work.

Predict spontaneity of a process.

Extensive property

State Function.

Work $\rightarrow$ Expansion work (Not useful) PV-work
 $\rightarrow$ Non-expansion work. (Useful work) ΔG

$$\Delta G = \Delta H - T\Delta S \quad \Delta G_{\text{system}} = -T\Delta S_{\text{total}}$$

$$\Delta S_{\text{total}} > 0 - \Delta G_{\text{sys}} < 0 - \text{spontaneous}$$

$$\Delta S_{\text{total}} < 0 - \Delta G_{\text{sys}} > 0 - \text{non-spontaneous}$$

$$\Delta S_{\text{total}} = 0 - \Delta G_{\text{sys}} = 0 - \text{Equilibrium}$$

	ΔH	ΔS	ΔG	
Case I	-ve	+ve	< 0	always spontaneous
Case II	+ve	-ve	> 0	always non spontaneous
Case III	-ve	-ve	< 0	spontaneous at low T
Case IV	+ve	+ve	< 0	spontaneous at High T

Third law of thermodynamics

At 0 K, Randomness = 0

Exception - NO, N₂O, CO, CO₂ Mixture of isotopes ice.

