THERMODYANAMICS SHORT NOTES

Thermodyanamics

Reactant ⟶ 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 seperates 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.

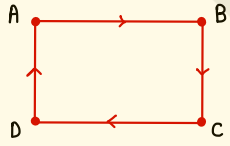
Intensive properties - which are independent of mass
Density, temperature, pressure, specific heat, molar specific Heat, Boiling point, melting point, Vapour pressure and viscosity.

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.



Change in state Function = 0

$\Delta E = 0$ $\Delta S = 0$

$\Delta H = 0$ $\Delta G_1 = 0$

Work - Area under P-V graph

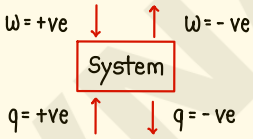
$W = -\int P dV$ $W = -P\Delta V$ $\Delta V = V_2 - V_1$

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

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

Reversible process	Irreversible process
Changes can be reversed.	Changes cannot be reversed.
Driving force should be infinite simally greater than opposing force.	Driving force is much greater than opposing force.
Place in very small steps and takes infinite time to complete the process.	takes finite time and usually a single step process.
Ideal process	All natural process.
System is in virtual equilibrium at any state.	System is in equilibrium only at initial and final state
P_{ext} is variable	P_{ext} is constant.

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



Units :

1 cal = 4·2 Joule 1 J = 10^7 erg

1 L atm = 101·3 Joule

1 L Bar = 100 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.

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

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

Note : Gravitational energy is not part of internal energy.

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

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

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

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

$w = 0$ $\Delta U = q_v$

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

NITESH DEVNANI

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Cyclic process: $\Delta U = 0 \quad \therefore q = -w$.
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 $\Delta H = \Delta U + V\Delta P$

$\Delta H = \Delta U + P\Delta V$ — $\Delta n_g = 0$ — $\Delta H = \Delta U$
$\Delta H = \Delta U + \Delta n_g RT$ — $\Delta n_g > 0$ — $\Delta H > \Delta U$
$q_p = q_v + \Delta n_g RT$ — $\Delta n_g < 0$ — $\Delta H < \Delta U$

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

Meyer's ratio: $C_p - C_v = R$ for 1 mole
$C_p - C_v = nR$ for n moles

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

Gas	C_v	C_p	$\gamma = C_p/C_v$
Monoatomic (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 $w = -\int P dV$
- P-V work - Area under P-V graph

a) Irreversible process P → constant.
$w_{irr} = -P\Delta V$

b) Reversible process P → 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 vaccum $w = 0$.

Reversible adiabatic process:
Work $\Delta U = w$ $\quad w = nC_v(T_2 - T_1)$

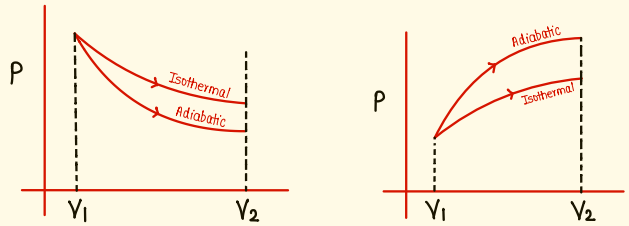
$$w = \frac{nR(T_2 - T_1)}{\gamma - 1} \qquad w = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

- Some important points:

a) Reversible adiabatic process:

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

b) Graphs: More slope More steep - Adiabatic.



Expansion

Limitations of First law:
Does not explain feasibility of a process under given conditions.
Reactants ⟶ 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.

NITESH DEVNANI

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Criteria for a process to be spontaneous.

a) Energy decrease.
b) Entropy increase.

Entropy : (S)

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

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

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

$\Delta S_{universe}$ or ΔS_{total} = ΔS_{system} + $\Delta S_{surrounding}$

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

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

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

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

Case I : Reversible isothermal

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

Case II - Isochoric process

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

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

More is the gaseous atom = more is entropy

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

$\Delta ng > 0$ $\Delta S = +ve$
$\Delta ng < 0$ $\Delta S = -ve$
$\Delta ng = 0$ $\Delta S = 0$

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

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

a) **Entropy of fusion** (solid → liquid) Melting point.

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

b) **Entropy of vapourisation** (liquid → Gas) Boiling point

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

c) **Entropy of sublimation** (Solid → Gas)

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

Some important points about entropy change :

1) Entropy of graphite > Graphite of Diamond
2) Rusting of iron , entropy increases.
3) On boiling of egg , denaturation of protien occurs. entropy increases.
4) Streching of rubber - entropy decreases.

Entropy change in reversible process

$\Delta S_{universe} = 0$
$\Delta S_{system} + \Delta S_{surrounding} = 0$
$\Delta S_{system} = - \Delta S_{surrounding}$

Entropy change in irreversible process

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

Second law of thermodyanamics

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

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

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

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

Gibbs free energy (G)

Capacity of system to do useful work.
Predict spontaneity of a process.
Extensive property
State Function.

Work → Expansion work (Not useful) PV - work
Work → Non - expansion work. (Useful work) ΔG

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

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

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

$\Delta S_{total} = 0$ - $\Delta G_{sys} = 0$ - 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 thermodyanamics :

At 0 K , Randomness = 0
Exception - NO, N_2O, CO, CO_2 Mixture of isotopes ice.

NITESH DEVNANI