

THERMODYNAMICS

• Energy and its transformation in various forms in different physical & chemical process called thermodynamics.

• Thermo - Related to temp. or energy
Dynamics - study of change due to driving forces.

• system: part of universe under thermodynamic investigation

- open :- can exchange both energy & matter - coffee in open glass
- close: can exchange only energy - coffee in close vessel
- Isolated: can not exchange matter & energy: coffee in thermoflask

• surrounding: Anything outside the system

• universe: system + surrounding

• Boundary: separate system & surrounding

- Rigid — immovable
- Non Rigid — movable
- Adiabatic — $q=0$
- Diathermic — $q \neq 0$

• Properties of system:

Extensive



Intensive

• Depend on the amount of substance in the system & size of the system

• volume, Gibbs, Internal energy, moles, Enthalpy, surface Area, mass, Entropy, Force, Heat capacity

• Independent of the amount of substance present in the system and size of system

• molar volume, Density, Refraction index, Pressure, temperature, surface tension, B.P. freezing point, vapour pres.

• $\frac{A}{B} \leftarrow \begin{matrix} \text{Extensive} \\ \text{Extensive} \end{matrix}$ therefore $\frac{A}{B} = \text{Intensive}$: $D = \frac{M}{V}$, $[C] = \frac{n}{V}$

State function: Depend on the initial & final state of system, do not depend on Path follow by system.

ex:- Enthalpy, Internal Energy, Entropy, Gibbs energy, P, T, V,

Path function: Depend on the path follow by system: Heat, work

Reversible process:
 - very always slow process
 - system & surrounding always in equilibrium
 - do not go for completion

Irreversible process: very fast,
 complet in very short time

Heat: mode of energy transfer between system and surrounding
 Heat flowing into the system or Heat absorb by system $\leftarrow +q$
 Heat flowing out of the system or Heat released by system $\leftarrow -q$

Work: Mode of energy transfer between system and surrounding

→ Non P-V work: change in volume is not essential, ex electric work

→ **P-V work:** change in volume is essential

irreversible $W = -P_{ext} \Delta V$ Reversible $W = -\int P \cdot dV$

Work done by system i.e Expansion: $\ominus ve$

Work done on system i.e compression: $\oplus ve$

Internal Energy

In the absence of external field (no P.E.) when system is at rest (no K.E) the Energy is called internal energy

$$E_T = K.E. + P.E. + U$$

$$E_T = U = \sum U_{\text{translation}} + U_{\text{rotation}} + U_{\text{vibration}} + U_{\text{other}}$$

Zeroth law of thermodynamics: Two thermodynamic systems are in thermal equilibrium with third system then they are in thermal equilibrium with each other

$$A \rightleftharpoons B, B \rightleftharpoons C \text{ therefore } A \rightleftharpoons C$$

First law of thermodynamics:

- Based on energy conservation principle
- Total energy of the universe remain constant
- $\Delta U = q + w$

Enthalpy :- $H = U + PV$

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

$$\Delta H = \Delta U + P\Delta V \quad \because \text{at constant pressure}$$

$$\Delta H = q + w + P\Delta V$$

$$= q + (-P\Delta V) + P\Delta V$$

$$\boxed{\Delta H = q} \quad \because \text{change in enthalpy is equal to Heat transfer at const } P$$

Relation b/w ΔH & ΔU :

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\left\{ \begin{array}{l} \Delta n_g > 0 : \Delta H > \Delta U \\ \Delta n_g < 0 : \Delta H < \Delta U \\ \Delta n_g = 0 : \Delta H = \Delta U \end{array} \right.$$

Heat exchange at constant P

$$q_p = \Delta H$$

- $\Delta H = c_p dT$
- $\Delta H = n c_p dT$
- $\Delta H = m c_p dT$

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Heat exchange at constant volume

$$q_v = \Delta U$$

- $\Delta H = c_v dT$
- $\Delta U = m c_v dT$
- $\Delta U = n c_v dT$

calculation of $q, w, \Delta U, \Delta H$ in various processes for an ideal gas:

Process	Work	Heat	ΔU	ΔH
1. Reversible Isothermal	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \frac{V_2}{V_1}$ $= nRT \ln \frac{P_1}{P_2}$	0	0
2. Irreversible Isothermal	$w = -P_{\text{ext}} (V_2 - V_1)$ $= -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$q = P_{\text{ext}} (V_2 - V_1)$ $= P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	0	0
3. Isobaric	$w = -P (V_2 - V_1)$ $= -nR (T_2 - T_1)$	$q = \Delta H$	$\Delta U = nC_V \Delta T$	$\Delta H = nC_P \Delta T$
4. Isochoric	$w = 0$	$q = \Delta U$	$\Delta U = nC_V \Delta T$	$\Delta H = nC_P \Delta T$
5. Reversible Adiabatic $PV^\gamma = K$ $TV^{\gamma-1} = K$ $TP^{\frac{1-\gamma}{\gamma}} = K$	$w = nC_V (T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$	$\Delta U = nC_V \Delta T$	$\Delta H = nC_P \Delta T$
6. Irreversible adiabatic	$w = nC_V (T_2 - T_1)$ $= -P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$	$q = 0$	$\Delta U = nC_V \Delta T$	$\Delta H = nC_P \Delta T$
7. cyclic Process	Area Under in PV-curve	$q = -w$	0	0

Second Law of Thermodynamics:

- States about the direction of flow of heat
- All natural process in universe are irreversible process & spontaneous
- Due to spontaneous process entropy of universe increasing continuously.

Spontaneous process :-

- Process which occur in particular direction itself.
- Flow of heat from hotter body to colder body
- Flow of air from High Pressure to low pressure.

Non Spontaneous process

- Process which occurs in particular direction in presence of external Agency.
- Flow of heat from colder body to Hotter Body.

Entropy :- Measure degree of randomness of the system

Extensive property and state function

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

Factor affecting entropy:

$\Delta n_g > 0$	\leftarrow	$\Delta S > 0$
$\Delta n_g < 0$	\leftarrow	$\Delta S < 0$
$\Delta n_g = 0$	\leftarrow	$\Delta S = 0$

Entropy :- solid < liquid < gas
order

$$\Delta S \propto \frac{T}{P}$$

Mixture: $\left. \begin{matrix} s+s \\ l+l \\ g+g \end{matrix} \right\} \downarrow$ then $s \uparrow$

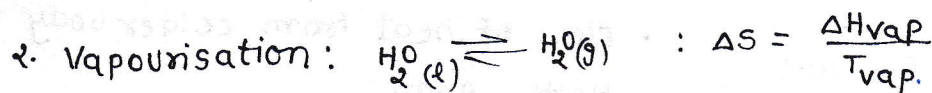
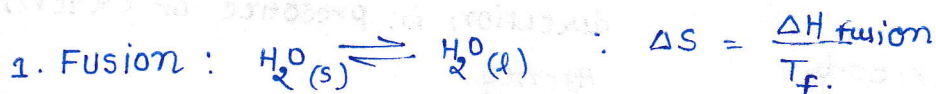
calculation of entropy change for an ideal gas: $\Delta S = n c_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$

$$\Delta S = n c_p \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}$$

Entropy for different process:

Isothermal	Isobaric	Isochoric	Reversible adiabatic
$\Delta S = nR \ln \frac{V_2/V_1}{P_1/P_2}$	$nC_p \ln T_2/T_1$	$nC_v \ln T_2/T_1$	$\Delta S = \frac{q_{rev}}{T}$ $= 0$

Entropy change in phase transition



Entropy change in chemical Rx: $\Delta S = \sum S_{product} - \sum S_{reactant}$

Third Law of Thermodynamics

- Determine absolute entropy of substance
- At absolute temp (zero kelvin) the entropy of perfectly crystalline substance is zero

$$\Delta S = \frac{\Delta H}{T}$$

$$ds = c_p \frac{dT}{T}$$

$$S ds = \int c_p dT$$

$$S_T - S_0 = c_p \ln T$$

$$S_T = 2.303 c_p \log T \quad \text{or} \quad 2.303 c_v \log T$$

Gibbs Energy: $G = H - T.S$

$\Delta G = \Delta H - T\Delta S$: at constant T & P

$\Delta G =$ change in gibbs energy
 $\Delta H =$ change in enthalpy
 $\Delta S =$ change in entropy

	ΔH	ΔS	ΔG	
①	-	+	-	∴ spontaneous at all temperature
②	-	-	-	∴ spontaneous at Low Temp.
③	-	-	+	∴ Non-spontaneous at higher temp.
④	+	+	+	∴ Non-spontaneous at Low temp.
⑤	+	+	-	∴ spontaneous at higher temp.
⑥	+	-	+	∴ Non-spontaneous at all temp.

Relationship Between standard gibbs free energy and equilibrium constant

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = -RT \ln K \quad \left\{ \begin{array}{l} \text{∴ at equilibrium } \Delta G = 0 \\ Q = K \end{array} \right.$$

$$\Delta G^\circ = -RT \ln K = -2.303 RT \log K$$