

THERMODYNAMICS

→ Basic Terminologies:

- ① System → Part of universe under thermodynamic investigation
 - Open → Can exchange both energy and matter. (Coffee in open glass).
 - Close → Can exchange only energy (Coffee in close vessel).
 - Isolated → Cannot exchange matter and energy. (Coffee in thermoflask)
- ② Surrounding → Anything outside the system.
- ③ Universe = System + Surrounding
- ④ Boundary → Separate system and surrounding
 - Rigid → Immovable
 - Non-Rigid → Movable
 - Adiabatic → $q=0$
 - Diathermic → $q \neq 0$

Properties Of System

Extensive

Depend on amount substance in system, and size of system.

Volume, Gibbs, Internal energy, moles, enthalpy, surface-area, mass, entropy, force, heat capacity.

Intensive

Independent of amount of substance present in system and size of system.

Molar Volume, Density, Refractive Index, Pressure, Temp., Surface tension, B.P., freezing point, Vapour pressure

Trick for Intensive Property →

- E → Electrode potential
 m → Melting point / Molar Heat Capacity
 R → —
 V → Vapour Pressure
 η → Viscosity
 T → Temperature
 D → Density
 F → Freezing point
 S → Surface tension
 s → Specific heat Capacity
 C → Concentration
 B → Boiling point
 P → Pressure

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→ $\frac{A}{B} \rightarrow \text{extensive} \therefore \frac{A}{B} = \text{Intensive}$

e.g. → $D = \frac{m}{V}$, $[C] = \frac{n}{V}$

State Function → Depend on initial and final state of system.

→ Do not depend on path followed by system.

e.g. → Enthalpy, Internal energy, entropy, Gibbs Energy, Pressure, Temp, Volume

Path Function → Depend on path followed by system.

e.g. → Heat, Work.

Heat → Mode of energy transfer between system and surrounding.

→ Heat flowing into the system / Heat absorb by system = $+q$

→ Heat flowing out of the system / Heat released by system = $-q$

Work → Mode of energy transfer between system and surrounding.

→ Non P-V Work - Change in Volume is not essential (e.g. - electric Work)

→ P-V Work - Change in Volume is essential.

Irreversible

Reversible

$W = -P_{\text{ext}} \Delta V$

$W = -\int P \cdot dV$

Work done by System → Expansion (-ve)

Work done on System → Compression (+ve)

Zeroth Law Of Thermodynamics →

Two thermodynamic system 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 universe remains constant.

→ $\Delta U = q + W$ (Internal energy = Heat + Given Work)

Enthalpy :- $H = U + PV$

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

$$\Delta H = \Delta U + P\Delta V \text{ (at constant pressure)}$$

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

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

$$\Delta H = q$$

∴ Change in enthalpy is equal to Heat transfer at constant Pressure.

Relation b/w ΔH and ΔU :-

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

$\Delta n_g = \text{gaseous product} - \text{reactant}$

$\Delta n_g > 0 : \Delta H > \Delta U$
 $\Delta n_g < 0 : \Delta H < \Delta U$
 $\Delta n_g = 0 : \Delta H = \Delta U$

Heat exchange at Constant pressure

$$q_p = \Delta H$$

$$\Delta H = C_p dT \text{ - Heat capacity}$$

$$\Delta H = n C_p dT \text{ - molar heat capacity}$$

$$\Delta H = m c_p dT \text{ - specific heat capacity}$$

Heat exchange at Constant Volume

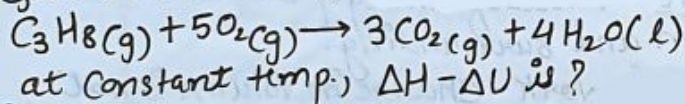
$$q_v = \Delta U$$

$$\Delta U = C_v dT$$

$$\Delta U = n C_v dT$$

$$\Delta U = m C_v dT$$

Que) For reaction,

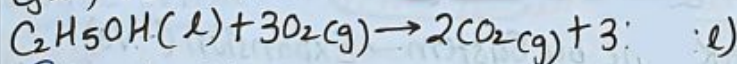


$$\Delta H - \Delta U = \Delta n_g RT$$

$$\Delta n_g = -3$$

$$= -3RT$$

Que) For reaction,



$$\Delta H = \Delta U - RT$$

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Que) Work done during isothermal expansion of one mole of an ideal gas from 10 atm \rightarrow 1 atm at 300K. is \rightarrow

Sol.ⁿ $\rightarrow n=1, P_1=10 \text{ atm}, P_2=1 \text{ atm}, T=300K$

$$W = -nRT \ln \frac{P_1}{P_2}$$

$$= -1 \times 2 \times 300 \ln 10$$

$$= -600 \times 2.303 \log 10$$

$$= 1381.8 \text{ Cal.}$$

Que) Max Work done in expanding 16 g oxygen at 300K and occupying volume of 5 dm³ isothermally until the volume becomes 25 dm³ is \rightarrow

Sol.ⁿ $\rightarrow n = \frac{1}{2}, T=300K, V_1=5 \text{ dm}^3, V_2=25 \text{ dm}^3$

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$W = -\frac{1}{2} \times 8.31 \times 300 \times \ln 5$$

$$= -4 \times 300 \times 2.303 \log 5$$

Que) Gas is allowed to expand in well insulated cylinder against constant external pressure of 2.5 atm from initial volume of 2.50 L to final volume of 4.50 L. Change in ΔU of gas in Joules will be? - (1 atm litre = 101 Joule)

Sol.ⁿ $P=2.5 \text{ atm}, V_1=2.50 \text{ L}, V_2=4.50 \text{ L}$

$$q=0 \rightarrow \Delta U = q + W \rightarrow \Delta U = W$$

$$W = -P_{\text{ext}} \Delta V$$

$$W = -2.5 (2) \text{ atmL}$$

$$= -5 \text{ atmL}$$

$$= -5 \times 101 \text{ J}$$

$$= -505 \text{ J}$$

Calculation of $q, W, \Delta U, \Delta H$ in various process for an ideal gas

Process	Work	Heat	ΔU	ΔH
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
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

Isobaric ($p = \text{const}$)	$W = -P(V_2 - V_1)$ $= -nR(T_2 - T_1)$	$q = \Delta H$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$
Isochoric ($V = \text{const.}$)	$W = 0$	$q = \Delta U$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$
Reversible Adiabatic. $PV^\gamma = K$ $TV^{\gamma-1} = K$ $TP^{\frac{1-\gamma}{\gamma}} = K$	$W = nC_v(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$
Irreversible Adiabatic	$W = nC_v(T_2 - T_1)$ $= -P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$	$q = 0$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$
Cyclic Process	Area Under PV-curve	$q = -W$	0	0

Que) Free expansion for ideal Gas under adiabatic condition?
 $\rightarrow q = 0, \Delta T = 0, W = 0$

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

Second Law Of Thermodynamics

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

Calculation of entropy change for an Ideal Gas: \rightarrow

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

$$\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Entropy for Different process: \rightarrow

Entropy \rightarrow Measure degree of randomness of the system.

Extensive property and state function.

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

Factors Affecting Entropy \rightarrow

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

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

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

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Unit of Entropy $\rightarrow \text{JK}^{-1}\text{mol}^{-1}$

Entropy Order: \rightarrow

Solid < Liquid < Gas

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

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

Entropy Change in phase transition: \rightarrow

① Fusion: $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)} : \Delta S = \frac{\Delta H_{\text{fusion}}}{T_f}$

② Vapourisation: $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)} : \Delta S = \frac{\Delta H_{\text{vap.}}}{T_{\text{vap.}}}$

③ Sublimation: $\text{X}_{(s)} \rightleftharpoons \text{X}_{(g)} : \Delta S = \frac{\Delta H_{\text{sub.}}}{T_{\text{sub.}}}$

Entropy Change in Chemical Rxn: \rightarrow

$$\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$$

Criteria for Spontaneity: \rightarrow

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

Que) At 27°C latent heat of fusion of a compound is 2930 J/mol .

Entropy Change: $\frac{2930}{300} = 9.77 \text{ J mol}^{-1} \text{ K}^{-1}$

Third Law Of Thermodynamics

\rightarrow Determine absolute entropy of substance.

\rightarrow At absolute temp (Zero Kelvin) entropy of perfectly crystalline substance is zero

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

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

$$\int ds = \int C_p \frac{dT}{T}$$

$$S_T - S_0^\circ = C_p \ln T$$



$$S_T = 2.303 C_p \log T \quad | \quad 2.303 C_v \log T$$

Gibb's Free Energy: \rightarrow

$$G = H - T \cdot S$$

$$\Delta G = \Delta H - T \Delta S \quad (\text{at const. Temp and pressure})$$

Change in
Gibbs
energy

Change in
enthalpy

Change in entropy

	ΔH	ΔS	ΔG	
①	-	+	-	Spontaneous at all temperature.
②	-	-	-	Spontaneous at low temperature.
③	-	-	+	Non-spontaneous at higher temperature
④	+	+	+	Non-spontaneous at low temp.
⑤	+	+	-	Spontaneous at higher temp.
⑥	+	-	+	Non-spontaneous at all temp

Que) If $\Delta G_{\text{system}} = 0$ system attained equilibrium.

Que) Enthalpy and Entropy change for reaction $\text{Br}_2(l) + \text{Cl}_2(g) \rightarrow 2\text{BrCl}(g)$ are 30 KJ mol^{-1} and $105 \text{ JK}^{-1} \text{ mol}^{-1}$. Temp at which rxn will be in equilibrium.

Sol. $\rightarrow \Delta H = T \Delta S$

$$\frac{\Delta H}{\Delta S} = T \rightarrow \frac{30 \times 10^3}{105} = 285.7$$

Que) Standard Enthalpy and Entropy changes for oxidation of ammonia at 298 K are $-382.64 \text{ KJ mol}^{-1}$ and $-145.6 \text{ J mol}^{-1}$. Standard Gibbs energy change, for same reaction at 298 K .

Sol. $\rightarrow \Delta G = \Delta H - T \Delta S$

$$\Delta G = -382.64 - 298 \times \frac{-145.6}{1000}$$
$$= -339.3 \text{ KJ mol}^{-1}$$

Relationship between Standard Gibb's free energy and equilibrium Constant \rightarrow

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \left\{ \begin{array}{l} \text{at equilibrium} \\ \Delta G = 0, Q = K \end{array} \right.$$

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

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

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