

# RIZVI COLLEGE ARTS SCIENCE AND COMMERCE

## CHEMICAL THERMODYNAMICS CLASS : SYJC (SCI)



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The image features a central white circle with a thick green border. Inside this circle, the word "THERMODYNAMICS" is written in a bold, white, sans-serif font. To the left of the circle, there are two white zigzag lines. To the right, there is a small orange circle with a white outline, a set of four parallel white diagonal lines, and a large solid orange circle in the bottom right corner. The background is solid black.

# THERMODYNAMICS

**SYSTEM : A selected part of the universe under thermodynamic investigation**

**SURROUNDING : All other parts of the universe outside the system**

**UNIVERSE : System + Surrounding**

## **Types of System**

<b>Open System</b>	<b>Closed System</b>	<b>Isolated System</b>
<b>Exchange Energy &amp; Matter</b>	<b>Only Exchange Energy</b>	<b>Neither Exchange Energy nor Matter</b>
<b>Hot Tea in open cup</b>	<b>Hot Tea in closed cup</b>	<b>Hot Tea in Thermos flask</b>

<b>PROPERTIES</b>	<b>EXTENSIVE PROPERTIES</b>	<b>INTENSIVE PROPERTIES</b>	<b>STATE FUNCTION</b>	<b>PATH FUNCTION</b>
<b>DEFINITION</b>	<b>Depends on the amount of matter present in the system</b>	<b>Independs on the amount of matter present in the system</b>	<b>Independs on the path, depends on the state of a system</b>	<b>Depends on the path</b>
<b>EXAMPLES</b>	<b>Mass, Volume, Internal energy, Heat capacity, No. of moles</b>	<b>Pressure, Temperature, Surface tension, Viscosity, Melting Point, Boiling Point, specific heat</b>	<b>Enthalpy</b>	<b>Work, Heat</b>

SR. NO	Types of Processes	Definitions	Symbols
1	Isothermal Process	Temperature Constant Internal Energy Constant	$\Delta T = 0,$ $\Delta U = 0$
2	Adiabatic Process	Heat does not exchange with the surroundings Temperature changes	$q = 0$
3	Isobaric Process	Pressure Constant	$\Delta P = 0$
4	Isochoric Process	Volume Constant	$\Delta V = 0$
5	Reversible Process	Driving & Opposing Forces differ by an infinitesimal amount	

# Sign Conventions

SR.NO	Symbols	Sign	Meanings
1	Q	(+) ve	Heat Absorbed
2	Q	(-) ve	Heat Evolved
3	W	(+) ve	Work done by the surrounding
4	W	(-) ve	Work done by the System
5	$\Delta H$	(+) ve	Endothermic
6	$\Delta H$	(-) ve	Exothermic
7	$\Delta S$	(+) ve	Spontaneous
8	$\Delta S$	(-) ve	Non-Spontaneous
9	$\Delta S$	0	Equilibrium
10	$\Delta G$	(+) ve	Non-Spontaneous
11	$\Delta G$	(-) ve	Spontaneous
12	$\Delta G$	0	Equilibrium

# Law of Thermodynamics

SR. NO.	LAW	STATEMENT
1	1 <sup>st</sup> Law of Thermodynamics	<p>Energy of the Universe remains constant</p> <p>Total Internal Energy of an isolated system constant</p> <p>Energy neither created nor destroyed and only be converted from one form to another</p> <p><math>\Delta U = Q+W</math></p> <p>Isothermal process, i.e <math>\Delta U =0</math> hence <math>W = -Q</math>,</p> <p>Adiabatic Process, i.e <math>q=0</math> hence <math>\Delta U = W</math>,</p> <p>Isochoric process, i.e <math>\Delta V=0, W=0</math> hence <math>\Delta U = Q</math></p>

SR. NO.	Law	Statement
2	2 <sup>nd</sup> Law of Thermodynamics	Total Entropy of a system and its surroundings increases in a spontaneous process $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Law	Statement
Hess's Law	<p>The law states that Overall Enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction</p> <p>Or</p> <p>Enthalpy is a state function (<math>\Delta H</math> depends only on initial &amp; final steps not on the path followed by reaction.)</p>

TERMS	Definitions
<b>Work [W]</b>	<p><b>Work is defined as The energy by which body is displaced through distance d with an application of force.</b></p> <p><b><math>W = f \cdot d</math></b></p>
<b>Internal Energy [U]</b>	<p><b>Every Substance is associated with a definite amount of energy, this stored energy in a substance is called as internal Energy.</b></p> <p><b>Internal Energy = Potential Energy + Kinetic energy</b></p>
<b>Enthalpy [H]</b>	<p><b>Enthalpy of a system is sum of Internal Energy of a system and the energy equivalent to PV work</b></p> <p><b><math>H = U + PV</math></b></p>
<b>Entropy [S]</b>	<p><b>Entropy is a measure of molecular disorder or randomness.</b></p> <p><b><math>\Delta S = Q_{rev} / T</math></b></p>
<b>Gibbs Free Energy [G]</b>	<p><b>The Gibbs energy is defined as <math>G = H - TS</math></b></p>

<b>Terms</b>	<b>DEFINITIONS-</b> Enthalpy change when
Enthalpy of Fusion	One mole of Solid converted into Liquid <b>at constant Temp &amp; Pressure</b>
Enthalpy of Vaporization	One mole of Liquid converted into Gas (vaporized) <b>at constant Temp &amp; Pressure</b>
Enthalpy of Sublimation	One mole of Solid converted into Gas <b>at constant Temp &amp; Pressure</b>
Enthalpy of Ionization	One mole of gaseous atom removes electron
Enthalpy of Atomization	One mole of gaseous atom dissociates into atoms
Enthalpy of solution	One mole of a substance is dissolved in a specific amount of solvent

Terms	DEFINITIONS- Enthalpy change when
Standard Enthalpy of formation	One mole of pure compound formed in its std state from its elements in their std states
Enthalpy of Combustion	One mole of the substance in its standard state is completely oxidised
Bond Enthalpy	Break particular covalent bond in One mole of gaseous molecule to produce gaseous atoms/ radicals
Enthalpy of Chemical Reaction	$\Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}}$
Enthalpy of Chemical Reaction [If Bond Enthalpy given]	$\Delta H = \sum H_{\text{reactants}} - \sum H_{\text{products}}$

Derive an expression for Pressure-Volume (PV) work or

Derive  $w = -P\Delta V$

Consider certain amount of gas enclosed in a cylinder fitted with frictionless, rigid movable piston of area 'A' at constant pressure 'P'.

$V_1$  = Initial volume

On expansion of gas, piston moves in a upward direction, a distance 'd'

The force exerted by gas 'F' = Area of piston  $\times$  External pressure

$$\therefore F = -P_{\text{ext}} \times A \quad \text{--- (i)} \quad [\text{c-ve sign that opposes movement}]$$

where  $P_{\text{ext}}$  = External atmospheric pressure

Amount of work done by the gas = force  $\times$  distance

$$\therefore w = F \times d \quad \text{--- (ii)}$$

On substitution eq<sup>n</sup> (i) in (ii) gives

$$w = -P_{\text{ext}} \times A \times d \quad \text{--- (iii)}$$

But  $A \times d = \Delta V$  i.e. volume change in the system

$$\therefore \boxed{w = -P_{\text{ext}} \times \Delta V} \quad \text{or}$$

$$\boxed{w = -P_{\text{ext}} \times (V_2 - V_1)}$$

Derive an expression for the maximum work done isothermally & reversibly. or

$$\text{Derive } \therefore W_{\max} = -2.303 nRT \log_{10} V_2/V_1 \text{ or}$$
$$W_{\max} = -2.303 nRT \log_{10} P_1/P_2$$

• Consider 'n' moles of an ideal gas enclosed in a cylinder fitted with frictionless, movable piston. Gas expands isothermally & reversibly from initial volume ( $V_1$ ) to final volume ( $V_2$ ).

• As the expansion is reversible, 'P' is greater by a very small quantity  $dP$  than  $P_{\text{ext}}$ . Thus,

$$P - P_{\text{ext}} = dP \therefore P_{\text{ext}} = P - dP \text{ ——— (i)}$$

Volume of a gas increases by an infinitesimal amount  $dv$   $\therefore V_2 = V_1 + dv$   $\therefore \left[ \begin{array}{l} \Delta V = V_2 - V_1 \\ = V_1 + dv - V_1 \end{array} \right]$

$$\Delta V = dv \text{ ——— (ii)}$$

The small quantity of work done,

$$dw = -P_{\text{ext}} \Delta V \text{ ——— (iii)}$$

Combining eq<sup>n</sup> (i) & (iii), gives

$$dw = -(P - dP) dv$$

$$dw = -Pdv + dP \cdot dv$$

Neglecting the product  $dP \cdot dv$  (very small)

$$\therefore \boxed{dw = -Pdv} \text{ ——— (iv)}$$

The total maximum work done is obtained by integration of eq<sup>n</sup> no. (iv) between the limits of initial and final states.

$$\int_{\text{initial}}^{\text{final}} dw = - \int_{V_1}^{V_2} Pdv \text{ ——— (v)}$$

$$\text{Hence, } W_{\max} = - \int_{V_1}^{V_2} Pdv$$

By using ideal gas equation,  $PV = nRT$

$$\therefore P = \frac{nRT}{V}$$

$$W_{\max} = - \int_{V_1}^{V_2} \frac{nRT}{V} dv$$

$$= -nRT \int_{V_1}^{V_2} \frac{dv}{V} \quad T = \text{Constant}$$

$$= -nRT [\ln V]_{V_1}^{V_2}$$

$$= -nRT \ln V_2 - \ln V_1$$

$$= -nRT \ln V_2/V_1$$

$$\boxed{W_{\max} = -2.303 nRT \log_{10} V_2/V_1}$$

Boyles law, At constant Temperature,

$$P_1 V_1 = P_2 V_2 \text{ or } V_2/V_1 = P_1/P_2$$

$$\therefore \boxed{W_{\max} = -2.303 nRT \log_{10} P_1/P_2}$$

# Derive relation between $\Delta H$ & $\Delta U$

$$H = U + PV$$

U = Internal Energy

P = Pressure,

V = Volume

$$H_1 = U_1 + P_1V_1$$

H<sub>1</sub> = Initial Enthalpy

$$H_2 = U_2 + P_2V_2$$

H<sub>2</sub> = Final Enthalpy

$$\Delta H = H_2 - H_1$$

$$\Delta H = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$\Delta H = (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

At constant Pressure,  $P = P_1 = P_2$

$$\Delta H = \Delta U + (PV_2 - PV_1)$$

$$\Delta H = \Delta U + P(V_2 - V_1)$$

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

Assume reactants & products behaves Ideally,

Applying Ideal Gas Equation,  $PV = nRT$

$$P_1V_1 = n_1RT \quad , \quad P_2V_2 = n_2RT$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

$$\Delta H = \Delta U + (n_2RT - n_1RT)$$

$$\Delta H = \Delta U + (n_2 - n_1)RT$$

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

$\Delta n_g$  = no. of moles of gaseous products – no of moles of gaseous reactants