# B.Sc. Chemistry SEM III CHE3B03-PHYSICAL CHEMISTRY

## MODULE  II
## CHEMICAL THERMODYNAMICS-I
## Part 1

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# The First Law of Thermodynamics

- The **First Law of Thermodynamics** states that energy cannot be created nor be destroyed. It can only change from or be transferred from one object to another.

- It deals with the total amount of energy in the universe, and in particular, it states that this total amount does not change.

Examples
- Light bulbs transform electrical energy into light energy (radiant energy).
- One pool ball hits another, transferring kinetic energy and making the second ball move.
- Plants convert the energy of sunlight (radiant energy) into chemical energy stored in organic molecules.

It says that the change in the internal energy of a system **is equal to the sum of the heat gained or lost by the system and the work done by or on the system.**

- $\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$

$$\Delta U = q + w$$



Energy transformations

Chemical energy     Light energy

Kinetic energy     Chemical energy
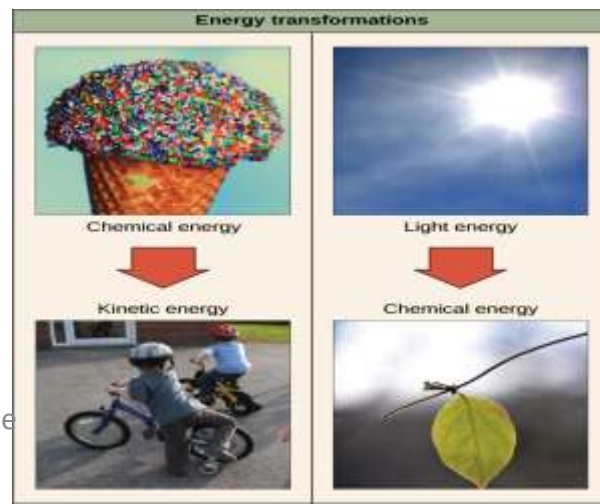
- **Energy**

The capacity to do work or to transfer heat

**Modes** of transfer of energy,

1.**Work-** Energy transfer at the **molecular level** between system and surroundings making use of **organized motion** of atoms or molecules.

2.**Heat** - Energy transfer at the **molecular level** between system and surroundings making use of disorderly molecular motion (**Thermal motion**)

Both are **Path functions**

Both are **Qualitatively equivalent**

- **Work**

Work is one means of transferring energy from our system to the surroundings or vice versa. Work is given the symbol $w$ in equations.

By the latest SI conventions,

Work done **on** the system,**+ve** (Increases its energy)

Work done **by** the system,**-ve** (decreases its energy)

- **Heat**

Heat is the Energy transfered between the system and the surroundings as a result of a temperature differential. This is the only kind of energy transfer that does not involve doing work. Heat is given the symbol $q$ in equations.

For **endothermic** process, q is **+ve**

For **exothermic** process, q is **-ve**

# work

- One of the most common definitions for work is,

when a force $f$ displaces an object by a distance $\Delta x$ does work $w = f \times \Delta x$. (also known as $w = f \times d$). This is a mechanical work and serves as the basis for our definition of $PV$ work.

- Work can also be done by pushing back the atmosphere (piston in a cylinder). In this case, one pushes back against the atmospheric pressure $P_{atm}$ and moves the piston a distance $\Delta x$.
- The force needed to push back the atmosphere is actually $P_{atm} \times A$. where, $A$ is the area of the piston. Hence, we can calculate the magnitude of the work done as

$|w| = P_{atm} \times A \times \Delta x = P_{atm} \times \Delta V$.

- Since the system increased in volume

and hence, did the work of pushing back the atmosphere
(positive value for $\Delta V$),
it has used up energy
so we can now write down
a more complete definition for PV work as:

$$w = -P_{atm} \times \Delta V$$

$\Delta V = Ad$

$F = PA$

$V$

$F$

$A$

$Q_{in}$

$W_{out} = Fd = PAd = P \Delta V$
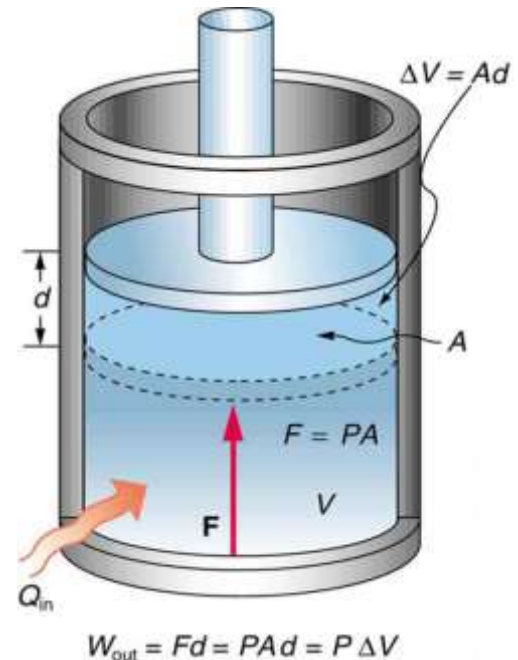
# UNITS

- **SI units of energy (work or heat):**

Let's start with work: *w* has dimension of force times distance.
The SI units are N m = $kg\ m^2\ s^{-2}$ = Joules (J). These are the same units used for heat transfer.

- In **CGS system**,

$$1J = 10^7\ ergs$$

**1 cal = 4.184  J**

**Energy and Work are Equivalent**

# Total Work done under different conditions

$w = -P_{atm} \times \Delta V$
Or
$W = -P_{ext}. \Delta V$

1.At Costant pressure , $W = -P_{ext}. \Delta V$

2.At Free Expansion, $W = 0$

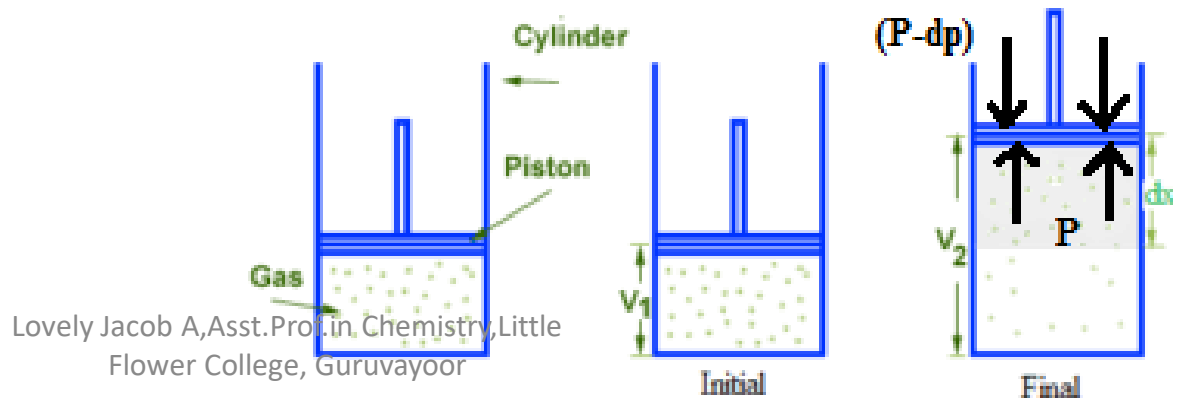3.At Reversible Expansion ($P_{ext} = P_{gas}$ ), $W = - P_{gas}. \Delta V$

### Resversibility & Maxi.Work

The **work** done by a system during a **reversible** process is the **maximum work** we can get.
The **work** done on a system in a **reversible** process is the minimum **work** we need to do to achieve that state change.

- ## $W_{rev} = w_{max}$

# Reversible & Irreversible

| Reversible process | Irreversible process |
|---|---|
| It is a slow process going through a series of smaller stages with each stage maintaining equilibrium between the system and surroundings. | In this process the system attains final state from the initial state with a measurable speed. During the transformation, there is no equilibrium maintained between the system and surroundings. |
| A reversible process can be made to proceed in forward or backward direction. | Irreversible process can take place in one direction only. |
| The driving force for the reversible process is small since the process proceeds in smaller steps. | There is a definite driving force required for the progress of the irreversible process. |
| Work done in a reversible process is greater than the corresponding work done in irreversible process. | Work done in a irreversible process is always lower than the same kind of work done in a reversible process. |
| A reversible process can be brought back to the initial state without making an change in the adjacent surroundings. | An irreversible process cannot be brought back to its initial state without making a change in the surroundings. |

**Reversible - Idealized concept,Nonspontaneous**
**Irreversible - Real Concept,Spontaneous,Natural Process**

# Internal energy

- $E_{total} = V+K+U$
- V = P.E of the system
- K = K.E. of the system

- **U** = Sum total of the kinetic energies associated with the translational, rotational, vibrational, electronic and nuclear motions at the **molecular level**, the relativistic rest mass energy of the electrons and nuclei, and the potential energy of interaction between the constituent particles of the molecules.

In short,
- U = kinetic and potential energies of the molecules.
- $\Delta U = U_2 - U_1$
- U ----- **State function**
- U -- **Total energy of system excluding the macroscopic K.E and P.E**
- U--- **Extensive Property**

- In Thermodynamics,

We consider the Total energy as the Internal Energy,U.

ie, in eqn

$E_{total} = V+K+U$

V,K are Zero

Therefore, the Mathematical expression for 1st Law of Thermodynamics is,

ΔU = q+w

Two conditions

- **For a Pressure-Volume work, ΔU = q - P. $\Delta V$**
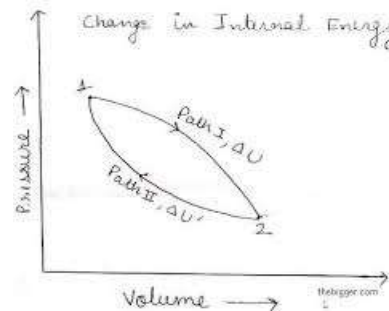- **At costant V, ΔU = q**

# Consequences of the 1$^{st}$ law

- **Path independence of Internal Energy Change-Exact differentials**

U is a state function (it does not depend on how the system got from the initial to the final state)

$$\Delta U = U_A - U_B$$

$$\Delta U = \int_A^B dU$$



- **Path dependence of Work and Heat- Inexact Differentials**
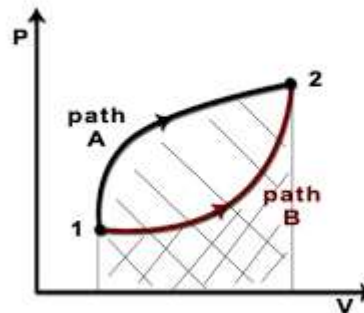
**Path dependence** implies that the amount of **work** or **heat** needed to make the change depends on how the process was performed, not just what state the material started in and ended in.

$$W = \int_{A,path}^B dw$$

$$q = \int_{A,path}^B dq$$



- Cannot write,   $w_B-w_A$
   $q_B-q_A$

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# ENTHALPY

- **Enthalpy**, the sum of the internal energy and the product of the pressure and volume of a thermodynamic system.

- *$H = U + PV$*

- Enthalpy is an energy-like property

- It has the dimensions of energy. (measured in units of joules or ergs)

- State function    $\Delta H = H_2 - H_1$

- For Exothermic process, **$\Delta H$ is +ve**

- For endothermic process , **$\Delta H$ is –ve**

# Relationship between ΔH & ΔU

- $\Delta H = \Delta U + P\Delta V$ (at Constant P)
- $\Delta U = q + w$

  $q = \Delta U - w$

- We considering **P-V work,**

  **Then,**           $w = - P\,\Delta V$

Therefore,

$$q_p = \Delta U + P\,\Delta V$$

$$\Delta H = q_p$$

*ie, For a process involving other than expansion work, the enthalpy change is equal to the heat added to the system*
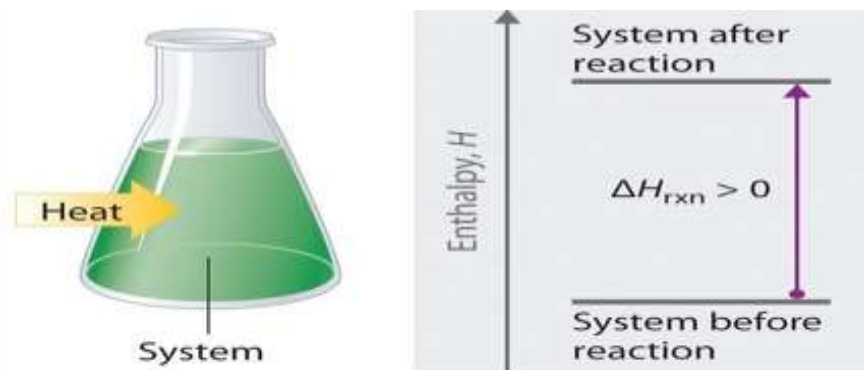
*If*   $\Delta U = q_v$

$$q_p = q_v + P\,\Delta V$$

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# Enthalpy of Reaction

$$\Delta H = \sum_p H_p - \sum_r H_r$$

- ## Reaction Type　　q　　　　　　ΔH$_{rxn}$

- **Exothermic**　　　　　　　　**< 0**　　　　**< 0  (heat flows from a system to its surroundings)**

- **Endothermic**　　　　　　　　**> 0**　　　　**> 0  (heat flows from the surroundings to a system**)
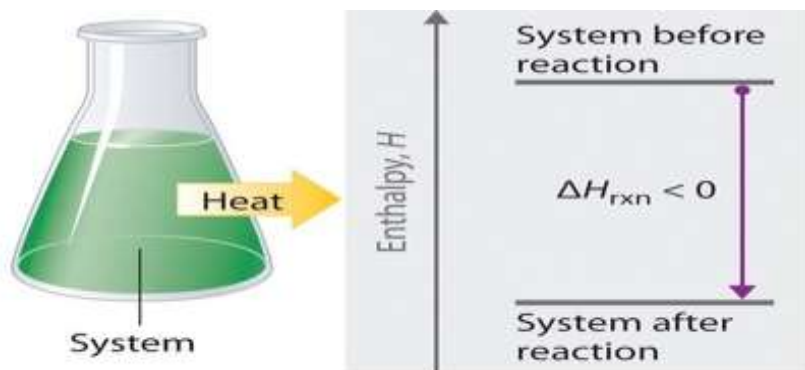


**(a) Exothermic reaction**　　　　　　　　**(b) Endothermic reaction**

Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, $\Delta H_{rxn}$ is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, $\Delta H_{rxn}$ is positive, and the reaction is endothermic; it is energetically uphill.

# Enthalpy Change in a reaction

$C_3H_8(g) + 5\ O_2(g)$ $\longrightarrow$ $3\ CO_2(g) + 4\ H_2O(g)$

6 mol gas $\longrightarrow$ 7 mol gas ( increase in volume at const. P)
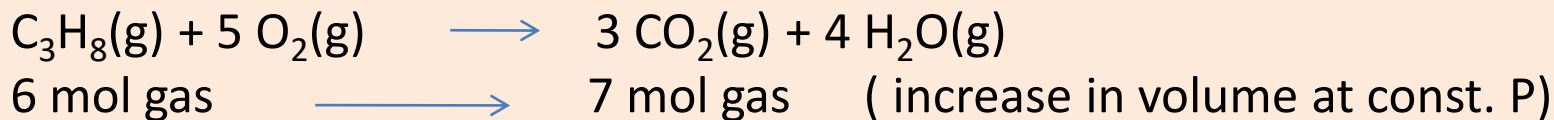
- $w = - P_{surr}\,\Delta V$ (gas expanding against an external pressure $P_{surr}$.)

- $\Delta U = q + w = q - P_{surr}\,\Delta V$

Or, $q_p = \Delta U + P_{surr}\,\Delta V$

- in this case, we can use the ideal gas law to get a more useful equation as long as the gas molecules all behave ideally.

- $q_p = \Delta U + \Delta n_g RT.$ *which is also written as* $\Delta H = \Delta U + \Delta n_g RT.$

- In a closed container (no volume change) there would be no work.
So, $\Delta V = 0$

So,

$\Delta U = q_v.$

# Heat Capacity

- Heat Capacity
- Amount of heat to raise an object or a given amount of substance by 1°C (1K).
- Molar Heat Capacity
- Amount of heat to raise one mole of a substance by 1°C (1K). (units $J\ K^{-1}mol^{-1}$).
  (water has molar heat capacity of 75.4 $J\ K^{-1}\ mol^{-1}$ .
- Specific Heat
- Amount of heat required to raise one gram by 1°C (1K). (units $J\ K^{-1}g^{-1}$)
  (water has specific heat of 1 cal $K^{-1}\ g^{-1}$ or 4.18 $J\ K^{-1}\ g^{-1}$
- Calorimeter
- Device used in Calorimetry to measure heat processes (normally thermally insulated from the surroundings)

$$C = \frac{q}{\Delta T}$$

$$C = \frac{q}{\Delta T}$$

It is not completely correct to talk of heat capacity in terms of $q$ since $q$ is not a state function. We are better off using the state functions $\Delta H$ rather than $q$.
We assume that no electrical or mechanical work $w'$ is being done.
At constant pressure, we measure heat as $\Delta H = q_p$, and hence the heat capacity we need to use is $C_p$, where we define

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

Thus, we can write (at constant $P$)
$\Delta H = C_p \Delta T$
The units of $C_p$ are J/K or J/°C (remember that $\Delta T$ is the same whether its measured in °C or in K).
Sometimes, we tabulate heat capacities in per mole or per gram values.
In these cases, we can think of modifying our equation for enthalpy to be
$\Delta H = nC_p \Delta T$ *(for molar heat capacity values)*
*OR*
$\Delta H = mC_p \Delta T$ *(for specific heat values).*

(Obviously, these equations hold $C_p$ to be independent of temperature.  In reality, while that's a reasonable estimate for our purposes, it is not strictly correct. The heat capacity of any substance changes slightly with changes in temperature.)

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

- At constant pressure, we measure heat as $\Delta H = q_p$,

and hence the heat capacity we need to use is $C_p$,

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

- At constant volume, the heat change we measure is $\Delta U = q_v$ and the heat capacity $C_v$,

$$C_V = \frac{\Delta U}{\Delta T}$$

# For Ideal Gas

- In many substances, the two heat capacities differ considerably.

- Consider one mole of ideal gas. We have

- $\Delta H - \Delta U = \Delta(PV) = R\Delta T$

$$\frac{\Delta H}{\Delta T} - \frac{\Delta U}{\Delta T} = R$$

Therefore

**$C_p - C_v = R$** for one mole of ideal gas

For water, $\quad C_p - C_v = 0.075R$
For benzene $\quad C_p - C_v = 5.1R$

- Let's do an example where we look at the *PV* work done.

- **When 2.00 mol of $SO_2(g)$ react completely with 1.00 mol $O_2(g)$ to form 2.00 mol of $SO_3(g)$ at 25ºC and constant pressure of 1.00 atm, 198 kJ of energy is released as heat. Calculate ΔU and ΔH for this reaction.**

   **2 $SO_2$(g) + 1 $O_2$(g)  $\longrightarrow$  2 $SO_3$(g)**

The heat released is $|q_p|$ since it was measured under constant pressure conditions. so we can say,

ΔH = -198 kJ (negative sign since the heat is released, *i.e.*, exothermic)

ΔU = ΔH - PΔV

ΔU = ΔH - $Δn_g$RT

or

ΔH = ΔU + $Δn_g$RT

Δn = (#moles product gas - #moles reactant gas) per mole of equation

 Δn = 2 - 3 = -1.

ΔU = -198 kJ/mol + -(-1 × 8.31451 J $K^{-1}mol^{-1}$ × 298 K)

   = -198 kJ/mol + 2.48 kJ/mol

   = -196 kJ/mol

# Expansion of Ideal Gas and Changes in Thermodynamic Properties

## I.    Isothermal Expansion of an Ideal Gas

### A) Reversible isothermal Expansion

i) **Work Done in Reversible Isothermal Expansion($w_{rev}$)**

ii) **Heat Transferred in Isothermal reversible expansion($q_{rev}$)**

### B) Irreversible isothermal Expansion

i) **Work Done in irreversible Isothermal Expansion** ($w_{irrev}$)

A)Expansion against *Constant P (Intermediate Expansion)*

B)For *Free Expansion*

## II) Adiabatic Expansion of an Ideal Gas

### i) Reversible  Adiabatic Expansion

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# Expansion of Ideal Gas and Changes in Thermodynamic Properties

## I. Isothermal Expansion of an Ideal Gas

For an iso thermal Expansion or compression,

$$\Delta U = 0$$

$\Delta H = \Delta U + n_g R \Delta T$

For an iso thermal Process, $\Delta U = 0$ & $\Delta T = 0$

$$\Delta H = 0$$

$\Delta U = q + w$

Since, $\Delta U = 0$

$$w = -q$$

# A) Reversible isothermal Expansion
## i) Work Done in Reversible Isothermal Expansion($w_{rev}$)

$$w = -\int_{V_1}^{V_2} P\,dV \quad \text{---------- (i)}$$

By ideal gas equation

$$PV = nRT$$

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

Substitute in (i), we get.

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV$$

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w = -nRT\,[\ln V]_{V_1}^{V_2} \quad \left[\because \int \frac{dx}{x} = \ln x\right]$$

$$w = -nRT\,[\ln V_2 - \ln V_1]$$

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

$$\boxed{w = -2.303\,nRT \log \frac{V_2}{V_1}} \qquad [\ln x = 2.303 \log x]$$

Since $P_1V_1 = P_2V_2$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

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

# A) Reversible isothermal Expansion
## ii) Heat Transferred in Isothermal reversible expansion($q_{rev}$)

$q_{rev}$   =  - $w_{rev}$

$q_{rev}$  = nRT ln $\dfrac{V2}{V1}$

$q_{rev}$ =2.303nRT log $\dfrac{V2}{V1}$

$q_{rev}$ =2.303nRT log $\dfrac{p2}{p1}$

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# B) Irreversible isothermal Expansion
## i) **Work Done in Reversible Isothermal Expansion($w_{irrev}$)**

- $w_{irrev} = \int_{V1}^{V2} - P_{ext}.\,dV$

**A)** Expansion against *Constant P (Intermediate Expansion)*

$$w = -P_{ext}.\,\Delta V$$

**B)** For *Free Expansion*

$$w = 0$$

# II) Adiabatic Expansion of an Ideal Gas

**Adiabatic Expansion-** No heat enters or leaves the system

$q = 0$

$\Delta U = q + w$

$\Delta U = w$

and, as a result, $\Delta U$ is negative, *i.e.*, internal energy decreases. In an adiabatic expansion, work is done at the expense of the internal energy of the system and consequently, the temperature of the system drops. (In an adiabatic compression the result would just be the opposite.)

We know that for 1 mole of a gas,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

For an *ideal gas*, $U$ is independent of the volume and hence it is permissible to write

$$C_V = \frac{dU}{dT}$$

Or

$$dU = C_V \, dT$$

For a finite change, we may write:

$$\Delta U = \int_{T_1}^{T_2} C_V \, dT \quad \text{for 1 mole of an ideal gas}$$

*i.e.,*

$$\Delta U = C_V(T_2 - T_1) \quad \text{for 1 mole of an ideal gas} \quad \text{----(3)}$$

For $n$ moles of an ideal gas,

$$\Delta U = nC_V(T_2 - T_1) \quad \text{----(4)}$$

From (2) and (5),

$$\Delta U = w = nC_V(T_2 - T_1) \quad \text{----(5)}$$

We know:

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

For 1 mole of an ideal gas,

$$\Delta H = \Delta U + \Delta(RT) \quad [\because PV = RT]$$
$$= \Delta U + R \, \Delta T$$
$$= C_V \Delta T + R \, \Delta T \quad [\because \Delta U = C_V \Delta T]$$
$$= (C_V + R) \, \Delta T$$
$$= C_P \Delta T \quad [\because C_P = C_V + R] \quad \text{----(6)}$$
$$= C_P(T_2 - T_1) \quad \text{----(7)}$$

For $n$ moles of an ideal gas,

$$\Delta H = nC_P(T_2 - T_1) \quad \text{----(8)}$$

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To sum up, for any adiabatic process, reversible or irreversible,

$$q = 0$$
$$w = \Delta U = nC_v \Delta T = nC_v(T_2 - T_1)$$
$$\Delta H = nC_p \Delta T = nC_p(T_2 - T_1)$$

It is seen that the same expression can be used to calculate the work done in a reversible and irreversible adiabatic expansion. But it should be understood that the final temperature ($T_2$), and hence $\Delta T$, depends upon the manner in which the process is carried out, *i.e.* whether reversible or irreversible. *Maximum work will be performed when the expansion is carried out under reversible conditions.* So, the decrease in temperature in a reversible adiabatic expansion will be greater than that in the irreversible process. *i.e.*, $T_2(rev) < T_2(irrev)$, so that $\Delta T$ (*i.e.*, $T_2 - T_1$) will be more negative for the reversible process than for the corresponding irreversible process. So, if the process is reversible, we can replace '$w$' with '$w_{max}$'.

## Reversible adiabatic expansion of an ideal gas

Expressions that show the $T$-$V$, $P$-$V$ and $T$-$P$ relationships in a reversible adiabatic expansion of an ideal gas can be derived in the following manner.

### (a) Relation between temperature and volume

Consider the reversible adiabatic expansion of 1 mol of an ideal gas. We know that for 1 mole of a gas,

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

For an *ideal gas*, $U$ is independent of the volume and hence it is permissible to write:

$$C_v = \frac{dU}{dT}$$

Or
$$dU = C_v\, dT \qquad ----(1)$$

From the first law of thermodynamics, for reversible adiabatic expansion,

$$dU = dw \qquad [\because dq = 0]$$
$$= -P\, dV \qquad [\because dw = -P\, dV] \qquad ----(2)$$

From eqns. (1) and (2), we get:

$$C_v\, dT = -PdV$$

Since for 1 mole of an ideal gas, $P = RT/V$, we get :

$$C_V \, dT = -RT \frac{dV}{V}$$

$$\cdots \text{-(3)}$$

Or

$$C_V \frac{dT}{T} = -R \frac{dV}{V}$$

Assuming $C_V$ to be independent of temperature,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

i.e.,

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\cdots \text{-(4)}$$

Or

$$C_V \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}$$

Since $C_P - C_V = R$ for 1 mole of an ideal gas, we may write:

$$C_V \ln \frac{T_2}{T_1} = (C_P - C_V) \ln \frac{V_1}{V_2}$$

Or

$$\ln \frac{T_2}{T_1} = \frac{C_P - C_V}{C_V} \ln \frac{V_1}{V_2}$$

Or

$$\ln \frac{T_2}{T_1} = \left(\frac{C_P}{C_V} - 1\right) \ln \frac{V_1}{V_2}$$

Putting $C_P/C_V = \gamma$, we get:

$$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{V_2}$$

Or

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Or

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\cdots \text{-(5)}$$

Or

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad \text{where } \gamma = C_P/C_V$$

$$\cdots \text{-(6)}$$

Or

$$TV^{\gamma-1} = \text{constant}$$

Since $\gamma > 1$ and also since $V_2 > V_1$ in an expansion, it is obvious from Eqn. (6) that $T_2 < T_1$. In other words, adiabatic expansion of a gas causes a drop in its temperature (*i.e.*, the gas cools).

**(b) Relation between volume and pressure** $PV$

For an ideal gas

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{V_1}{V_2} \times \frac{T_2}{T_1} = \frac{P_2}{P_1}$$

Since $(T_2/T_1) = (V_1/V_2)^{\gamma-1}$, we can write:

$$\frac{V_1}{V_2} \times \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{P_2}{P_1}$$

Or

$$\left(\frac{V_1}{V_2}\right)^{\gamma} = \frac{P_2}{P_1} \quad\quad\quad ----(7)$$

Or

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \quad \text{where } \gamma = C_p/C_V. \quad ----(8)$$

Or

$$PV^{\gamma} = \text{constant}$$

**(c) Relation between temperature and pressure** $TP$

From eqn. (7) or (8), we get:

$$\frac{V_1}{V_2} = \left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}} \quad\quad ----(9)$$

Let us take the $(\gamma-1)^{th}$ power of both sides. Then

$$\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \quad ---(10)$$

From eqn. (10) in eqn. (5), we get

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \quad \text{where } \gamma = C_p/C_V \quad ---(11)$$

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Another way of writing the above relationship is:

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}} \qquad \text{---(12)}$$

Or

$$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma} \qquad \text{---(13)}$$

Or

$$T P^{(1-\gamma)/\gamma} = \text{constant}$$

**Work done in a reversible adiabatic expansion of an ideal gas**

We have already shown that the work done in an adiabatic expansion is given by:

$$w = \Delta U = nC_V(T_2 - T_1)$$

Another convenient expression for reversible adiabatic expansion can be derived from the above equation.

$$w = nC_V(T_2 - T_1) \qquad \text{---(14)}$$

Dividing numerator and denominator by $(C_P - C_V)$ and rearranging:

$$w = \frac{n(C_P - C_V)(T_2 - T_1)}{(C_P - C_V)/C_V}$$

$$= -\frac{n(C_P - C_V)(T_2 - T_1)}{(C_V - C_P)/C_V}$$

$$= -\frac{n(C_P - C_V)(T_2 - T_1)}{1 - (C_P/C_V)}$$

Putting $C_P - C_V = R$, and $C_P/C_V = \gamma$, we get

$$w = -\frac{nR(T_2 - T_1)}{1 - \gamma} \qquad \text{---(15)}$$

Whenever the process is considered under reversible conditions, we may replace 'w' with '$w_{max}$'.

# Reversible Isothermal expansion of **Real gas**

✓ Reversible isothermal expansion of a real gas — Expressions for $w$, $\Delta U$, $\Delta H$ and $q$ for a van der Waals gas

(i) Expression for work of expansion ($w_{rev}$)

The general equation for the reversible work of expansion is:

$$w_{rev} = -\int_{V_1}^{V_2} P\,dV$$

# Joule Thomson Effect

## Joule-Thomson effect

Consider the expansion of an *ideal gas* into a vacuum (*i.e.*, free expansion) under adiabatic conditions. Obviously, no heat is absorbed or evolved, *i.e.*, $q = 0$. Further, since the external pressure $(P_{ext}) = 0$, it follows that $w = -P_{ext} \Delta V = 0$, *i.e.*, no work is done. Then, from the first law, for an adiabatic free expansion of an ideal gas,

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

*i.e.*, No internal energy change occurs. Consequently, the temperature of the system remains the same before and after expansion.

This is, however, not the case with real gases.

*When a gas under high pressure is allowed to expand under adiabatic conditions through a porous plug into a region of low pressure, there occurs a change in its temperature. This phenomenon is termed Joule-Thomson effect.* The difference in temperature observed is proportional to the pressure difference maintained. [The phenomenon is so named because it was first observed by Joule and Thomson (Lord Kelvin) in the middle of the 19th century.]

# Thank you

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