02 Thermodynamics-I

Introduction:

Thermodynamics is the branch of science which deals with the energy changes taking place in all physical and chemical processes.

Thermodynamics	≡	Thermo + dynamics
Thermo	≡	Thermal which is related to temperature or energy.
Dynamics	≡	Study of change due to a driving force

Advantages of thermodynamics:

(i) It gives information about various **thermodynamic laws**.

(ii) It gives information about various **energy changes**.

(iii) It helps us to predict whether a given **chemical reaction will take place** or not under the given set of conditions.

(iv) It helps to calculate efficiency of the process.

Limitations of thermodynamics :

(i) Thermodynamics deals with the properties like temperature, pressure, volume etc of matter in bulk but doesn't tell us anything about the individual properties of atoms or molecules.

or

Thermodynamics deals with **macroscopic** models but not with **microscopic models.**

(ii) It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the **rate of reaction.**

Some basic definitions (Thermodynamic terms):

System :

The macroscopic part of the universe under study is called a **system**. Rest of the universe outside the system is called **surroundings**. The actual or imaginary surface that separates the system from the surroundings is called the **boundary**.

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

Types of boundary :

(i) Real or imaginary

(ii) Rigid (fixed) or movable (flexible)

(iii) Permeable (allow mass transfer) or impermeable (does not allow mass transfer).

(iv) Diathermal (allow heat transfer) or Adiabatic (does not allow heat transfer).

Golden Key Point :

- Exchange of energy and matter between system and surroundings occurs through boundary.
- Heat and work appear at system boundary.

Types of systems :

(i) Open system : A system is said to be open if it can exchange matter and energy.

Eg.1 A thermos flask or a steel flask if not closed.

Eg.2 Coffee in open glass.

Eg.3 All living systems. human being, plants, animals.

Eg.4 Reaction in open container.

(ii) Closed system : A system is said to be closed if it can exchange energy but not matter.

Eg.1 Coffee in a closed stainless-steel flask.

Eg.2 Glowing bulb, tube light.

Eg.3 Reaction in closed container.

(iii) Isolated system : A system is said to be isolated if it cannot exchange both matter and energy with the surroundings.

Eg. coffee in a thermos flask.

Note : A perfectly isolated system is only a theoretical system.

(iv) State of system :

- A system is called in a particular state where all the macroscopic properties of the system have definite value.
- The state of the system is defined by its measurable properties like temperature, pressure, volume etc.
- If any of these properties change, state of the system is said to be changed.

(v) Properties of system : The state of a system is defined by a particular set of its measurable quantities called properties. They can be categorised into extensive and intensive properties.

Intensive property is one whose value is independent of the size (or mass) of the system. An extensive property is one whose value depends on the size (or mass) of the system.

Special Points :

* Extensive properties are additive but intensive properties are non-additive.

* Ratio of two extensive property gives an intensive property.

Eg. Mass per unit volume = density; $d = \frac{M}{V}$

Extensive Properties	Intensive Properties
Volume	Molar volume
Number of moles	Density
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy (S)	Viscosity
Enthalpy (H)	Free energy per mole
Internal energy (E & U)	Specific heat

Heat capacity	Pressure
	Temperature
	Boiling point, freezing point etc

State function or state variable :

- Variables like P, V, T are State Functions or State Variables because their values depend only on the present state of a system and not on how the state was reached
- State functions are denoted by capital letters.
- State functions are not absolute in nature. So, we talk about change in state function like ΔE, ΔH, ΔS, ΔG etc.
  Ex. E, H, S, G, T etc.

Condition for a function to be a state function :

(i) If ϕ is state function, $\int_A^B d\phi = \phi_B - \phi_A$

(ii) If ϕ is a state function, $\oint d\phi = 0$

Path function : Function which depends on the path, i.e. how the process is carried out
E.g. work (w) & heat (q).

- Path functions are denoted by small letters.

Thermodynamic process : A thermodynamic process involves change of a system from one state to another state.
Thermodynamic processes may be in form of expansion or compression.

Illustration 1:

Which of the following are extensive and which are intensive properties ?
Temperature, boiling point, melting point, pressure, density, viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, Mass, Volume, number of moles, Heat capacity, internal energy, enthalpy, entropy, ΔG, concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.

Solution:

Intensive property : Temperature, (boiling point, melting point), pressure, density, viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.
Extensive property : Mass, Volume, number of moles, Heat capacity, internal energy, enthalpy, entropy

Illustration 2:

Which of the following are state function & path function ?
Pressure, Volume, Enthalpy, Work, Heat, Gibbs energy, temperature, Internal energy, Entropy,

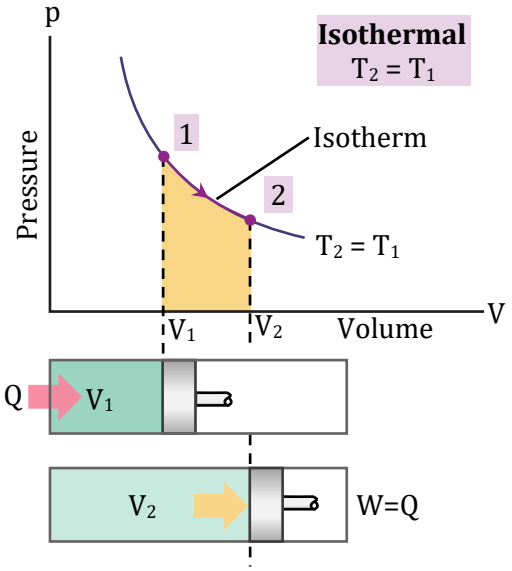
Solution:

State function : Pressure, volume, enthalpy, Gibbs energy, temperature, Internal energy, Entropy,
Path function : Work, Heat

Types of thermodynamic process :

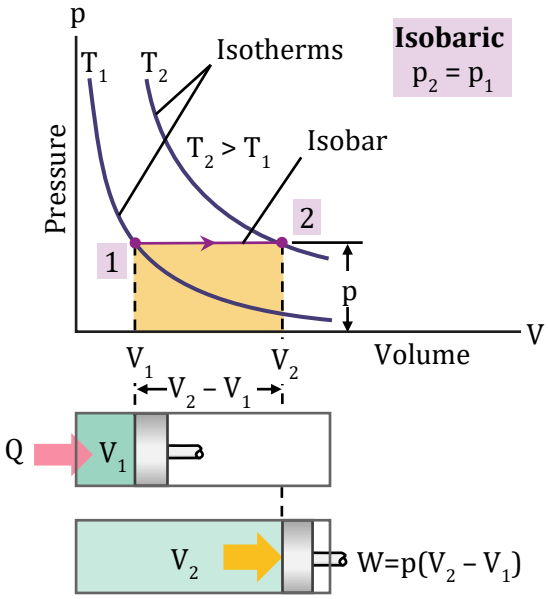
(i) Isothermal process :

- A process in which temperature of the system remains constant is called isothermal process.
- T - constant; $dT = 0$ & $\Delta T = 0$
- Heat is exchanged with surroundings ($q \neq 0$)
- System is placed at a constant temperature.
- Conducting (or diathermic boundary)



(ii) Isobaric process :

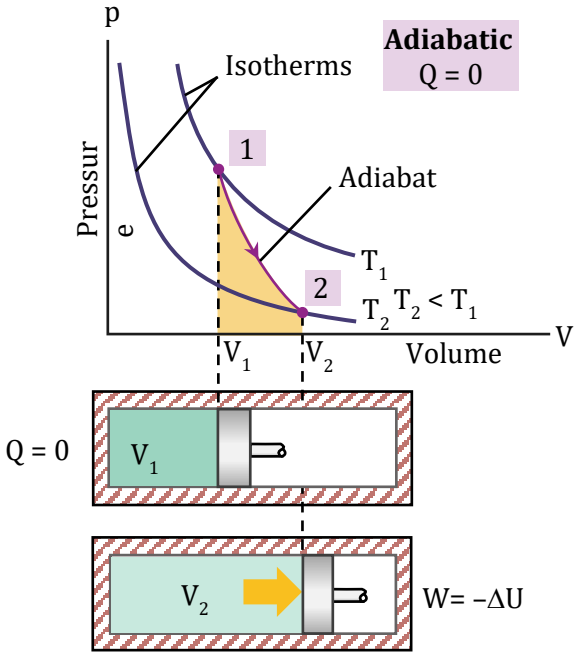
- A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.
- P = constant; $dP = 0$ & $\Delta P = 0$
- Process in open system is isobaric in nature.



Ex. All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

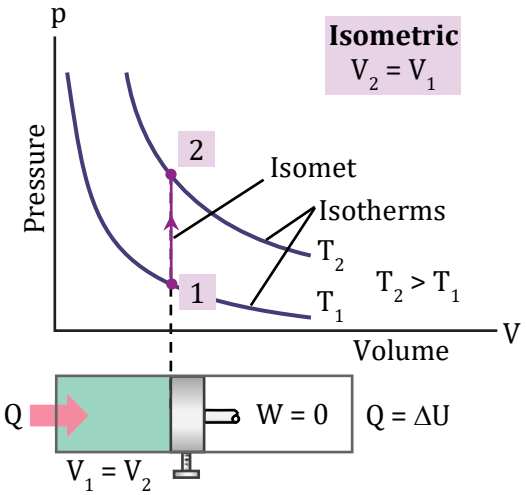
(iii) Adiabatic process :

- A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in systems with insulated walls.
- No exchange of heat takes place i.e. q = 0
- The temperature of the system varies. ($\Delta T \neq 0$)
- The system is thermally insulated (by keeping the system in an insulated container).



(iv) Isochoric process :

- The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed or rigid vessel.
- Volume remains constant i.e. dV = 0 & $\Delta V = 0$
- Pressure and Temperature are variable
- Process in closed rigid system is isochoric.



(v) Cyclic process : It is combination of two or more process in which the final state of system, becomes identical to the initial.

In cyclic process change in all state functions will be zero.

$\Delta T = \Delta P = \Delta V = \Delta H = \Delta S = \Delta G..... = 0$

However, Q_{net} or W_{net} may or may not be zero.

(vi) Reversible or Irreversible process :

- If the initial state may be received just by reversing the direction of process at any state, process is called reversible. In irreversible process the initial state can never be achieved just by reversing the direction of process.
- In the reversible process, the driving force is only infinitesimally greater than the opposing force. In the irreversible process, they differ largely.
- A perfectly reversible process is a theoretical process because it takes infinite time but reversible processes are important because it results maximum efficiency in any machine. The actual process occurring in the machine is quasi static which may tend to reversible or irreversible process.
- During irreversible process, one of the equations of state like PV = nRT, is valid. Such equation is valid only at initial & final state. However, during reversible process such equation are valid throughout the process.
- A reversible process is bidirectional whereas irreversible process is unidirectional.
- Reversible process never goes 100% completion but irreversible process goes upto 100% completion.
- During reversible process state variable do not change but during irreversible process it is changed.
- A process is reversible when the system throughout remains in thermodynamic equilibrium with the surrounding.
- A system is said in thermodynamic equilibrium when it simultaneously satisfies the following equilibria.
  (a) Thermal equilibrium: Same temperature throughout (No heat transfer within the system)
  (b) Mechanical equilibrium : Same pressure or force throughout the system (No work should be performed by one part on the other)
  (c) Material equilibrium : No change in the composition of system with time. No mass transfer within the system.
- If a system is in thermodynamic equilibrium there is no net energy or mass transfer within the system.

Work (w):

Thermodynamically, work may be defined as the form of energy which appears only when, there is some change in the boundary of the system. Such work is called mechanical or PV work.

Work may also be non-mechanical like electric work.

Presently, we will discuss only mechanical work.

(i) It is not thermodynamic property of system.

(ii) It depends on the quantity of system.

(iii) Sign convention :- **As work done by the references positive.**

In physics, references is gas (or internal agent) but in chemistry external agent is reference. Therefore, in physics work done by the system is positive.

And in chemistry work done by the external agent is positive.

In physics, work is calculate from the force applied by system, but in chemistry due to external force.

Derivation of Work :

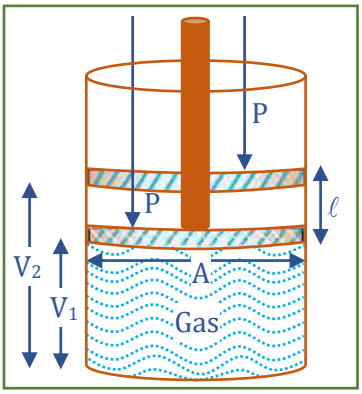
Work (W) = force (F) × displacement (ℓ)

Consider a gas enclosed in a cylinder fitted with a frictionless piston.

Suppose area of cross section of cylinder = A and pressure on the piston = P,

Initial volume of the gas = V_1 and final volume of the gas = V_2

(By expansion) displacement of piston = ℓ



work done by the gas (in expansion) = W = F.ℓ

$\because$ $P = \frac{F}{A}$ $\therefore$ $F = P \times A$

$W = P \times A \times \ell$ [change in volume = $A \times \ell = (V_2 - V_1)$]

$W = P \times (V_2 - V_1)$

$$W = \int_{V_1}^{V_2} P \cdot dV = -\int_{V_1}^{V_2} P_{ext} dV$$

Physics Chemistry

Heat (q):

Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the system and its surrounding.

According to IUPAC convention

heat lost by system is expressed with –ive sign

heat given to system is expressed with +ive sign

* $q_v = nC_{v,m}dT$
* $q_p = nC_{p,m}dT$
* $C_{p,m} - C_{v,m} = R$ (for ideal gas)
* C_v & C_p depends on temperature even for an ideal gas. ($C = a + bT + cT^2$.....)

General values of C_V & C_P for an ideal gas can be taken as follows.

Atomicity		n_{tr}	n_{Rot}	n_{vib}	C_V		C_P		γ	
					Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono		3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di		3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non linear	3	3	3	3R	6R	4R	7R	$\frac{4}{3}$	$\frac{7}{6}$

Units of heat & work :

Calorie : It is defined as the quantity of heat required to raise the temperature of 1 g of water by 1°C or 1K (14.5 to 15.5°C)

1 Nm = 1J = 10^7 erg = 0.239 Cal

1 Cal = 4.184 J = 4.2 J

1 L-atm = 101.3 J = 24.206 Cal = 101.3 × 10^7 erg

1 L-atm > Cal > J > erg

Golden Key Points :

- In cyclic process change in all state functions will be equal to zero.
  $\Delta E = 0$; $\Delta H = 0$ $\Delta P = 0$, $\Delta T = 0$ etc.
- All natural process are irreversible in nature.
- Reversible process are quasistatic so ideal in nature.
- Both q and w are (+) **to** system.
- Both q and w are (–) **by** the system.
- $P_{ext} = 0$ in vacuum
- Work done in free expansion is zero for an ideal gas.

Internal energy (E & U):

- Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.
- We can **never find out the absolute value** of internal energy (E) of the system.
- We can only calculate the change in internal energy of the system (ΔE) by using an instrument which is called as Bomb calorimeter. In Bomb calorimeter reactions are carried out at constant volume.
- For real gas internal energy depends on temperature and pressure.
- For ideal gas internal energy depends only on temperature.

$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{nuclear} + ...$

U is a state function & is an extensive property.

$\Delta U = U_{final} - U_{initial}$

ΔU is + ve if $U_f > U_i$

ΔU is – ve if $U_f < U_i$

For a given closed system

$U = f(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Enthalpy (H):

- Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** (H) as.

  $H = U + PV$

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

  at constant pressure

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

  combining with first law.

  $\Delta H = q_p$
- Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

Relationship between ΔH & ΔU:

The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids)

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

If substance is not undergoing chemical reaction or phase change.

$\Delta H = \Delta U + nR\Delta T$

In case of chemical reaction

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

For chemical reactions	**For ideal gas (in a process)**
T = constant	n_g = constant
n_g = can vary	T = can vary
$\boxed{\Delta H = \Delta U + \Delta n_g RT}$	$\boxed{\Delta H = \Delta U + n_g R\Delta T}$

$\because$ heat at constant volume = $q_V = \Delta E$

and heat at constant pressure = $q_P = \Delta H$

$\therefore$ $\boxed{q_p = q_v + \Delta n_g RT}$ $\boxed{q_p = q_v + n_g R\Delta T}$

Golden KeyPoint :

- If, $\Delta n_g = 0 \rightarrow$ $\boxed{\Delta H = \Delta E}$ eg. $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- If, $\Delta n_g > 0 \rightarrow$ $\boxed{\Delta H > \Delta E}$ eg. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
- If, $\Delta n_g < 0 \rightarrow$ $\boxed{\Delta H < \Delta E}$ eg. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Zeroth law of thermodynamics:

Two system in thermal equilibrium with a third system are also in thermal equilibrium with each other. It introduces temperature as a state function.

i.e. if A and B are in thermal equilibrium with C then A and B are must be in thermal equilibrium.

First law of thermodynamics:

"Total energy of universe remains constant." It is law of conservation of energy.

Let us consider a system whose internal energy is U_1. If the system is supplied with heat q, the internal energy of the system increases to $U_1 + q$. If work (w) is done on the system, the internal energy in the final state of the system, U_2 is given by

$U_2 = U_1 + q + w$

or $U_2 - U_1 = q + w$

$\Delta U = q + w$

According to IUPAC, heat added to the system and work done on the system are assigned positive values as both these modes increase the internal energy of the system.

Illustration 3:

Represent the following observations in terms of proper IUPAC symbol?

(a) Heat absorbed by a system is 20 Joule.

(b) Work done by a system is 40 Joule.

(c) Work done on a system is 5 Joule.

(d) Heat given out by system is 50 Joule.

Solution:

It is standard practice to represent both types of heat and work (in/out or on/by) by single symbols q and w-

(a) q = +20 Joule. **(b)** w = –40 Joule. **(c)** w = +5 Joule. **(d)** q = –50 Joule.

Illustration 4:

For certain processes the heat and work exchanged between system and surrounding is given in standard format. Describe the physical interpretation of each observation.

(a) q = +10 kJ **(b)** w = –20 kJ

Solution:

(a) q = + 10 kJ :

Since numerical value of q is positive, this shows heat is absorbed by the system from surrounding resulting in gain of energy by system.

(b) w = – 20 kJ :

Since numerical value of work is negative, this shows work is done by the system on surrounding resulting in loss of energy of system.

Illustration 5:

Explain why variation of enthalpy for a process involving an ideal gas is given by $dH = nC_P dT$, irrespective of process ?

Solution:

Because

$H_{ideal\ gas} = f(T)$, independent of pressure or volume

Illustration 6:

The heat capacity of a molecule depends upon complexity of the molecule. Explain ?

Solution:

The heat capacity can be defined as energy needed to raise the temperature of a body by 1°C. The molecule which have large number of degrees of freedom requires larger quantity of heat to raise the temperature by 1°C. This is because energy supplied is distributed in each degree of freedom equally.

Illustration 7:

A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :-
(R = 8.314 J/mol K) (ln 7.5 = 2.01)

(A) q = + 208 J, w = – 208 J (B) q = – 208 J, w = – 208 J
(C) q = – 208 J, w = + 208 J (D) q = + 208 J, w = + 208 J

Ans. (A)

Solution:

q = + 208 Joule

for isothermal process

$\Delta U = 0$

$\because$ from I^{st} law of thermodynamics

$\Delta U = q + w$

$0 = q + w$

$\Rightarrow$ w = – q = – 208 Joule

Calculation of q, w, ΔU & ΔH in various process:

Isothermal expansion or compression of ideal gas :

For isothermal process : $\Delta T = 0$

$\therefore \quad \Delta U = n.C_{p,m}.\Delta T = 0$

$\Delta H = n.C_{p,m}.\Delta T = 0$

and $q = \Delta U - w = -w$

Now, w depends on path (reversible or irreversible).

Reversible process :

$$w_{rev.} = -\int_{V_1}^{V_2} P_{ext} \cdot dV = -\int_{V_1}^{V_2} (P \pm dP) \cdot dV = -\int_{V_1}^{V_2} P \cdot dV = -\int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$\therefore \quad w_{rev.} = -nRT \cdot \ln \frac{V_2}{V_1} = -nRT \cdot \ln \frac{P_1}{P_2}$$

$$\boxed{W_{rev.} = -2.303nRT \log_{10}\left(\frac{V_2}{V_1}\right)}$$ according to Boyle's law at constant temperature $P \propto \frac{1}{V}$

$$\boxed{W_{rev.} = -2.303nRT \log\left(\frac{P_1}{P_2}\right)}$$

Irreversible process, against a constant external pressure :

$$w_{irr.} = -P_{ext} \int_{V_1}^{V_2} dV = -P_{ext}(V_2 - V_1)$$

Free expansion (or expansion in vacuum) :

$P_{ext} = 0$ but dV = finite, Hence, w = 0

Comparison of magnitude of work :

In expansion, magnitude of work = $-w_{exp}$

In compression, magnitude of work = w_{comp}

Now, $w_{rev} - w_{irr} = (-P.dV) - (-P_{ext}.dV) = (P_{ext} - P).dV$

= –ve, always

In expansion, $P_{ext} < P$ and dV = +ve

In compression, $P_{ext} > P$ and dV = –ve

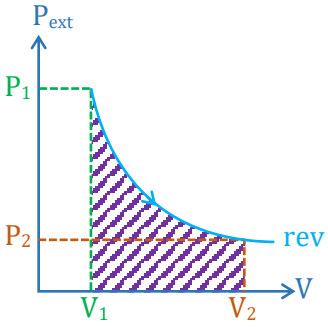
Hence, $w_{rev} < w_{irr}$ (Always, with proper sign).

Now, as magnitude of work in expansion is $-w_{exp}$, hence, $(-w_{rev, exp}) > (-w_{irr, exp})$, i.e., magnitude of work is greater when expansion is reversible.

And, as magnitude of work in compression is w_{comp}, hence, $(w_{rev, comp}) < (w_{irr, comp})$, i.e., magnitude of work is greater when compression is irreversible.

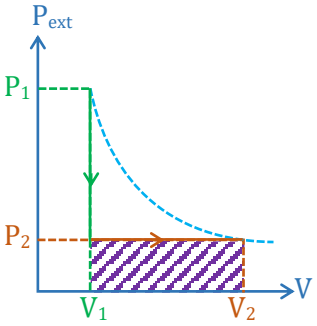
Graphical comparison :

(a) Expansion :

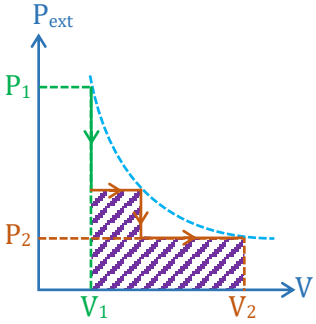


($P \approx P_{ext}$)

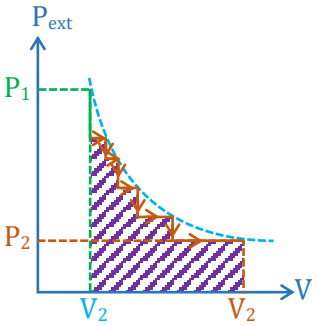
(Reversible)



(Single step irreversible)



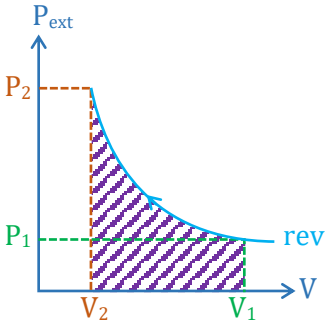
(Two step irreversible)



(n step irreversible)

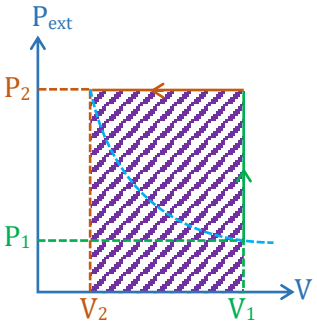
($-w_{exp}$) : Rev > n step >..... > 2 step > single step

(b) Compression :

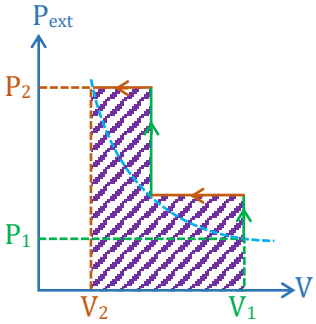


($P \approx P_{ext}$)

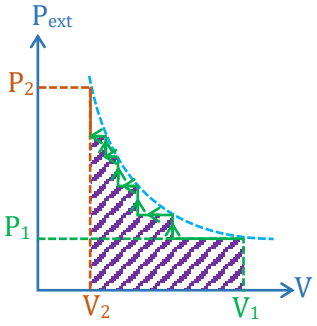
(Reversible)



(Single step irreversible)



(Two step irreversible)



(n step irreversible)

(w_{comp}) : Rev < n step <..... < 2 step < single step

Illustration 8:

Two moles of an ideal gas undergoes isothermal expansion from 4L to 20L at 27°C. Calculate q, w, ΔU and ΔH, if the process is performed.

(i) reversibly

(ii) irreversibly, against a constant external pressure of 1atm.

(iii) as free expansion

Solution:

For isothermal process, ΔT = 0. Hence,

$\Delta U = n.C_{v,m}.\Delta T = 0$

$\Delta H = n.C_{p,m}.\Delta T = 0$

(i) $w = -nRT\cdot\ln\frac{V_2}{V_1} = -2\times8.314\times300\times\ln\frac{20}{4} = -8028.52J$

and $q = -w = 8028.52$ J

(ii) $w = -P_{ext}.(V_2 - V_1) = -1$ atm$(20L - 4L) = -16$L-atm

$= -16 \times 101.3J = -1620.8J$

$q = -w = 1620.8J$

(iii) $w = 0$ and $q = 0$

Adiabatic expansion or compression of ideal gas:

$q = 0$

$\therefore\ \Delta U = w = n.C_{v,m}.(T_2 - T_1)$

and $\Delta H = n.C_{p,m}.(T_2 - T_1)$

The change in temperature may be calculated as

$$n\cdot\int_{T_1}^{T_2} C_{v,m}\cdot dT = -\int_{V_1}^{V_2} P_{ext}\cdot dV$$

(a) If $C_{v,m}$ is temperature independent and the process is reversible, then

$T.V^{\gamma-1}$ = constant

or, $P.V^{\gamma}$ = constant

or, $T^{\gamma}P^{1-\gamma}$ = constant

(b) If $C_{v,m}$ is temperature independent and the process is irreversible, then

$n.C_{v,m}.(T_2 - T_1) = -P_{ext}.(V_2 - V_1)$

$$\boxed{W = nC_V(T_2 - T_1)} \qquad ...(1)$$

$\because\ C_P - C_V = R$

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\gamma - 1 = \frac{R}{C_V} \qquad \left(\because \gamma = \frac{C_P}{C_V}\right)$$

$$\Rightarrow\ C_V = \frac{R}{\gamma - 1} \qquad ...(2)$$

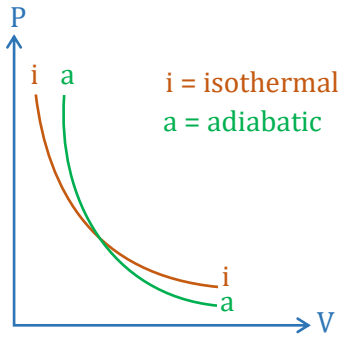
From equation (1) and (2) $\boxed{W = \frac{nR}{\gamma-1}(T_2 - T_1)} = \boxed{W = \frac{P_2V_2 - P_1V_1}{(\gamma-1)}}$

(i) The temperature of ideal gas decreases in adiabatic expansion (except free expansion, which is isothermal too) and the temperature of ideal gas increases in adiabatic compression.

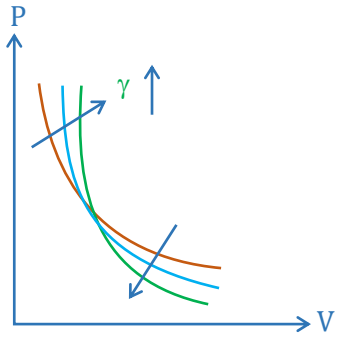
(ii) The final temperature of gas is always higher in irreversible process (expansion or compression) relative to reversible process, for the same change in volume.

(iii) Just like isothermal process, the magnitude of work is maximum when expansion is reversible and compression is irreversible (single step).

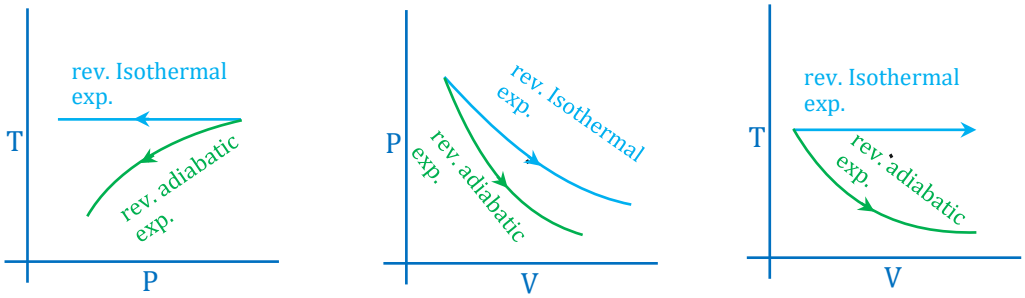
(iv) Work in reversible isothermal and adiabatic processes may be compared graphically.



(v) Work in reversible adiabatic process may be compared graphically.



(vi)



Comparison of reversible adiabatic expansion and reversible isothermal expansion on TP, PV and TV diagram

Illustration 9:

Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5L, 127°C to 40L. Calculate q, ΔU, w and ΔH, if the process is performed.

(i) reversibly

(ii) irreversibly, against a constant external pressure of 0.1atm.

(iii) as free expansion

Solution:

For adiabatic process, q = 0

(i) $T \cdot V^{\gamma-1} = \text{constant} \Rightarrow T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1}$

$\therefore\ T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 400\times\left(\frac{5}{40}\right)^{\frac{5}{3}-1} = 100K$

Now, $w = \Delta U = nC_v\Delta T = -7482.6\ J$

$\Delta H = \gamma\Delta U = -12471\ J$

(ii) $\Delta U = w = -P_{ext}.(V_2 - V_1) = -0.1 \times (40 - 5) \times 101.3 = -354.55J$

and $\Delta H = \frac{5}{3}\cdot\Delta U = -590.92J$

(iii) $\Delta U = w = 0$

and $\Delta H = 0$

Illustration 10:

Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm, against a constant external pressure of 1 atm. If the initial temperature of gas is 27°C, calculate the final temperature. Also calculate q, ΔU, w and ΔH.

Solution:

$q = 0$

$\Delta U = w$

or, $n.C_{v,m}.(T_2 - T_1) = -P_{ext}.(V_2 - V_1)$

or, $n.\frac{3}{2}R(T_2 - T_1) = -P_2\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$

or, $\frac{3}{2}(T_2 - 300) = -\left(T_2 - 300\times\frac{1}{12}\right) \Rightarrow T_2 = 190K$

or, $\Delta U = w = 5\times\frac{3}{2}R\times(190-300) = -6859.05J$

and $\Delta H = \gamma.\Delta U = -11431.75J$

Isobaric process for an ideal gas :

$q = \Delta H = n.C_{v,m}.\Delta T$

$\therefore\ \Delta U = n.C_{v,m}.\Delta T$

$w = -P.(V_2 - V_1) = -nR.\Delta T$

Illustration 11:

One mole of an ideal diatomic undergoes isobaric expansion from 27°C to 87°C. Calculate q, ΔU, w and ΔH.

Solution:

$q = \Delta H = n.C_{v,m}.\Delta T = 1 \times \frac{7}{2}R \times 60 = 1745.94\ J$

$\Delta U = \frac{\Delta H}{\gamma} = 1247.1J$

and $w = -nR.\Delta T = -1 \times 8.314 \times 60 = -498.84J$

Isochoric process for an ideal gas:

$w = 0$

$q = \Delta U = n.C_{v,m}.\Delta T$

$\therefore \quad \Delta U = n.C_{v,m}.\Delta T$

Illustration 12:

Ten moles of an ideal gas ($\gamma = 1.2$) is heated from 27°C to 47°C at constant volume. Calculate q, ΔU, w and ΔH.

Solution:

$w = 0$

$$q = \Delta U = n.C_{v,m}.\Delta T = 2 \times \frac{R}{1.2-1} \times 20 = 200\ R$$

$\Delta H = \gamma.\Delta U = 240R$

Polytropic process for an ideal gas :

$\Delta U = n.C_{v,m}.\Delta T$

$\therefore \quad \Delta H = n.C_{p,m}.\Delta T$

For ideal gas is reversible polytropic process and $C_{v,m}$ temperature independent,

$P.V^x = \text{constant}$

or, $T.V^{x-1} = \text{constant}$

where x = polytropic index

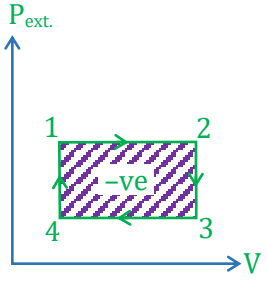
$$w_{rev} = \frac{P_2V_2 - P_1V_1}{1-x} = -\frac{nR(T_2 - T_1)}{1-x} \qquad (x \neq 1)$$

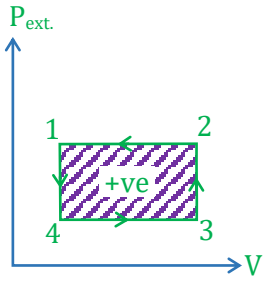
$$= -nRT \cdot \ln\frac{V_2}{V_1} \qquad (x = 1)$$

and $q = n.C_m.\Delta T$

The molar heat capacity, $C_m = C_{v,m} + \frac{P \cdot dV}{n \cdot dT} = C_{v,m} + \frac{R}{1-x}$

Cyclic process :





Change in physical sate :

Solid $\rightleftharpoons$ liquid

Liquid $\rightleftharpoons$ Gas

Solid $\rightleftharpoons$ Gas

Changes in physical state occurs at constant pressure and temperature conditions.

$\Delta U = q + w$

$q = \Delta H = m.L$

and $w = -P(V_{\text{final state}} - V_{\text{initial state}})$

Illustration 13:

90 gm water is completely converted into steam at 100°C and 1 atm. Calculate q, ΔU, w and ΔH. Latent heat of vaporisation of water at 100°C is 540 cal/gm.

Solution:

$\Delta H = m.L = 90 \times 540 = 48600$ cal

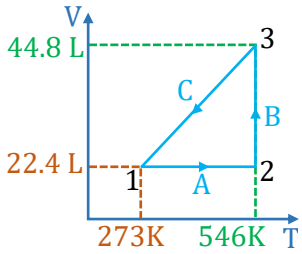
$w = -P(V_{vap} - V_{water}) = -P.V_{vap} = -nRT = -\frac{90}{18} \times 2 \times 373 = -3730$ cal

$\Delta U = q + w = 48600 + (-3430) = 44870$cal

Illustration 14:

One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

Table-1			
State	**P**	**V**	**T**
1			
2			
3			



Step	Name of process	q	w	ΔE	ΔH
A					
B					
C					
overall					

Solution:

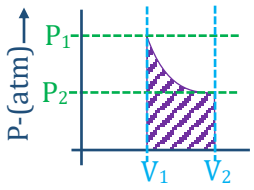
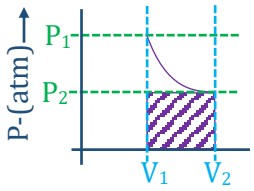
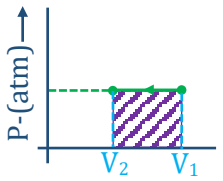
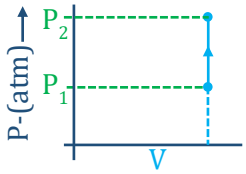
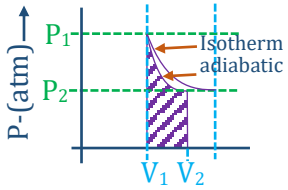
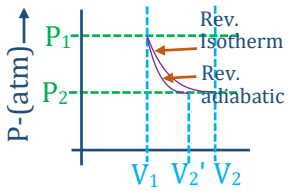
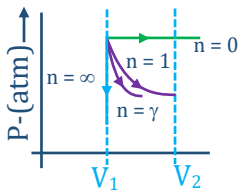
Table-1			
State	**P**	**V**	**T**
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Step	Name of process	q	w	ΔE	ΔH
A	Isochoric	3/2 R (273)	0	3/2 R (273)	5/2 R(273)
B	Isothermal	546 R ln 2	–546 Rln2	0	0
C	Isobaric	–5/2 R(273)	R(273)	–3/2 R (273)	–5/2 R(273)

Limitation of first law:

It can predict the change in energy as a result of change in state or vice-versa, but cannot predict the natural direction of change (whether a change can happen on its own or not).

Summary:

Process	Expression for w	Expression for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal	$w = -nRT\ln\frac{V_2}{V_1}$ $= -nRT\ln\frac{P_1}{P_2}$	$q = nRT\ln\left(\frac{V_2}{V_1}\right)$ $q = nRT\ln\left(\frac{P_1}{P_2}\right)$	0 process	0	
Irreversible isothermal	$w = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$	$q = P_{ext}(V_2 - V_1)$	0	0	
Isobaric Process	$w = -P_{ext}(V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_P\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_V\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Reversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $PV^{\gamma} = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Irreversible adiabatic process	$w = nC_V(T_2 - T_1)$ $= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$	$q = 0$ $nC_V(T_2 - T_1)$ $= -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Polytropic	$w = \frac{P_2V_2 - P_1V_1}{n-1}$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$q = \int_{T_1}^{T_2} C_V dT$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_P\Delta T$	
Cyclic process	Area enclosed in PV-diagram For clockwise negative For anticlockwise positive	$q = -w$	0	0