

# **THERMODYNAMICS**

Thermodynamics deals with the study of the flow of heat and its consequence. It is concerned with the relationship between heat and work. Thermodynamics helps us to predict the direction of the process or chemical change would proceed and to what extent?

Thermodynamics is based on the four simple laws. These are as,

- (i) Zeroth law of thermodynamics
- (ii) First law of thermodynamics
- (iii) Second law of thermodynamics
- (iv) Third law of thermodynamics

These laws are not derived, rather these are deduced from our long experience with energy. Thermodynamics does not make any hypothesis as to the structure of matter. It deals with the macroscopic observable properties of matter without assumptions of its atomic nature.

The approach of thermodynamics is entirely different from the kinetic theory. For example, pressure in kinetic theory can be treated as the measurement of impact of the molecules at the wall per second, whereas in thermodynamics pressure is the property of the state of system.

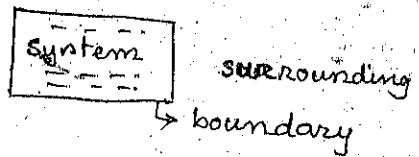
Before going to the laws of thermodynamics, it is necessary to know about the most commonly used term which would be needed in our discussion.

## **I. Thermodynamic System**

In thermodynamics, a system is defined as an object or a quantity of matter, i.e., a part of the universe chosen, for observation, which is separated from the rest of the universe.

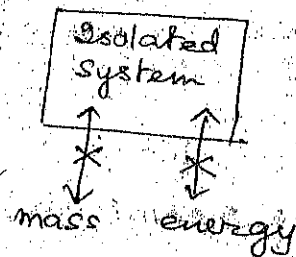
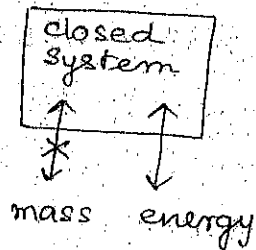
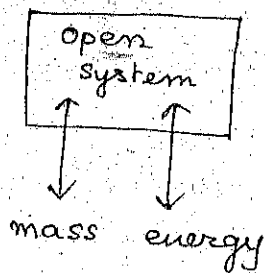
A system is enclosed by a boundary which separates the system from the universe. All the others, outside of the system are called surrounding. Therefore,

$$\text{Universe} = \text{System} + \text{Surrounding}$$



Depending upon the mass and energy exchange phenomena of a system, the systems are divided into three classes,

- ① Open system: There is a transfer of both mass and energy across the boundary.
- ② Closed system: energy exchange is only possible but no exchange of mass across the boundary.
- ③ Isolated system: No exchange of mass and energy both across the boundary.



Another more, two types of systems are also defined.

- ① Homogeneous system: When two or more components in a system mixed together forming a single phase and the properties are same at all part in the system, then the system is called homogeneous system.

- ② Heterogeneous system: When two or more components in a system remain with a different phases and the properties are not found same at all parts in the system, then it is called heterogeneous system.

i. Properties of the system : The physical characteristics which are experimentally measurable and which can also represent a system are called thermodynamical parameters or properties of the system such as pressure (P), temperature (T), volume (V), viscosity ( $\eta$ ), surface tension ( $\gamma$ ), refractive index ( $n$ ), dipole moment, - - - etc.

out of all properties of the system some are mass dependent and some are mass independent. Mass dependent properties are called extensive properties, such as energy, volume, surface area, - - - etc. Mass independent properties are called intensive properties such as temp., pressure, viscosity, density - - - etc. molar volume, energy, enthalpy, entropy, free energy are all intensive.

The state of a system can be represented by using at least three thermodynamical parameters, out of which one should be extensive and other two should be intensive.

### ii. Equilibrium and Steady State :

When there is no unidirectional flow of thermodynamical parameters, then the system is said to be an equilibrium.

Mechanical Equilibrium :

There is no unidirectional flow of mass.

Thermal Equilibrium :

There is no unidirectional flow of temperature.

Chemical Equilibrium :

There is no unidirectional flow of chemical composition.

If all the three equilibriums are present ~~simultaneously~~, then we can say the system is in thermodynamic equilibrium. There is no unidirectional force between different parts of the system or between the system and surrounding.

An equilibrium state is one where the properties are not changing with time. This definition is not sufficient for non isolated systems. For non isolated systems, a system is in an equilibrium when (i) the properties do not change with time, and (ii) the removal of the system from contact with the surroundings causes no change of properties. If the condition (i) is satisfied and condition (ii) is not satisfied, then the system is in a steady state.

#### IV. Zeroth Law of Thermodynamics :

Two systems that are both thermal equilibrium with a third system are in thermal equilibrium with each other.

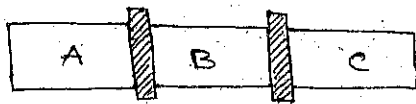


fig-(a)

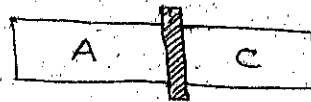


fig-(b)

consider three systems are arranged as in fig-(a). system A & B are thermally contact and systems B and C are thermally contact each other.

V. Process : Any change in a system is called process. There are mainly five types of processes as,

- (i) Isothermal process (ii) Adiabatic process (iii) Reversible process,
- (iv) Irreversible process (v) cyclic process.

#### VI. A Few Mathematical Expression ; Perfect differential and State function.

Partial differential ; Suppose a quantity  $z$  is a function of two independent quantities  $x$  and  $y$ , i.e.  $x$  and  $y$  are the independent variables of  $z$ .

$$\therefore z = f(x, y)$$

Differentiate partially, we can write,

$$\Delta z = \left( \frac{\partial z}{\partial x} \right)_y \Delta x + \left( \frac{\partial z}{\partial y} \right)_x \Delta y$$

Here  $\left(\frac{\partial z}{\partial x}\right)_y$  be the rate of change of  $z$  w.r. to  $x$  at const.  $y$  and  $\left(\frac{\partial z}{\partial y}\right)_x$  be the rate of change of  $z$  w.r. to  $y$  at const.  $x$ .

Now suppose, the independent quantities  $x, y$  and  $z$  are related as,

$$f(x, y, z) = 0 \text{ and also}$$

$$x = f(y, z) \text{ and } y = \phi(z, x)$$

$$\therefore \Delta x = \left(\frac{\partial x}{\partial y}\right)_z \Delta y + \left(\frac{\partial x}{\partial z}\right)_y \Delta z \quad \text{--- (1)}$$

$$\Delta y = \left(\frac{\partial y}{\partial z}\right)_x \Delta z + \left(\frac{\partial y}{\partial x}\right)_z \Delta x \quad \text{--- (2)}$$

Substituting (2) in (1), we have,

$$\begin{aligned} \Delta x &= \left(\frac{\partial x}{\partial y}\right)_z \left\{ \left(\frac{\partial y}{\partial z}\right)_x \Delta z + \left(\frac{\partial y}{\partial x}\right)_z \Delta x \right\} + \left(\frac{\partial x}{\partial z}\right)_y \Delta z \\ &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z \Delta x + \left[ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right] \Delta z \end{aligned}$$

This equation is valid for all values of  $x, y$  and  $z$ . (3)

(a) Suppose,  $\Delta z = 0$  and  $\Delta x \neq 0$

$$\text{Then, } \Delta x = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z \Delta x$$

$$\therefore \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \quad \therefore \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

(b) Suppose,  $\Delta x = 0$  and  $\Delta z \neq 0$ .

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0$$

$$\therefore \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = - \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

$$\therefore \boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

So, if  $f(P, V, T) = 0$ , and  $V = f_1(P, T)$  and  $T = f_2(P, V)$

So, we can have,  $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$

This is cyclic rule.

## Perfect differential and State function :

If  $Z$  represents a single valued function of a system, the magnitude of which depends upon the state of the system and let  $x$  &  $y$  be the two state parameters, then we can write,

$$Z = f(x, y)$$

If any change in the value of  $Z$ , i.e.,  $dZ$  solely depends upon the final and initial state of the system, not depends upon the path of the system, then  $dZ$  will be called perfect differential.

Now,  $Z = f(x, y)$

~~Differentiating~~ Differentiating partially,

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$$
$$= M \cdot dx + N \cdot dy$$

If  $\left(\frac{dM}{dy}\right)_x = \left(\frac{dN}{dx}\right)_y$  or  $\frac{\partial^2 Z}{\partial x \cdot \partial y} = \frac{\partial^2 Z}{\partial y \cdot \partial x}$ , then  $dZ$  will be called a perfect differential and ' $Z$ ' be called as a state function. where  $M = \left(\frac{\partial Z}{\partial x}\right)_y$  and  $N = \left(\frac{\partial Z}{\partial y}\right)_x$ .

State Function: State function is a single valued thermodynamic function or property of a system, the magnitude of which depends only on the state of system. It is such a function that any change of it will depend upon the change of state of the system and not upon the manner of change of state. The state function can be written as,

$$Z = f(x, y)$$

parameters.

where  $x$  and  $y$  are the state

Internal energy ( $E$  or  $U$ ), enthalpy ( $H$ ), entropy ( $S$ ), free energy ( $G$ ), ..... are all state functions. These functions can be represented as the function of  $(P, V)$ ,  $(V, T)$  or  $(P, T)$ . They are all perfect differentials.

Criteria of a state function:

- ① It is a single valued function.
- ② It is continuous function.
- ③ For a complete cyclic process, it is zero, i.e.,  $\oint dz = 0$

④ The change of it does not depend upon the manner of change but it does depend upon the final and initial state of the system only.

⊗ For an ideal gas, we can write that  $T = f(P, V)$  and  $PV = RT$ .

so,  $\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R}$  and  $\frac{\partial^2 T}{\partial P \partial V} = \frac{1}{R}$

and again  $\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R}$  and  $\frac{\partial^2 T}{\partial V \partial P} = \frac{1}{R}$

Hence  $\frac{\partial^2 T}{\partial P \partial V} = \frac{\partial^2 T}{\partial V \partial P}$  so,  $dT$  is a perfect differential and  $T$  is a state function.

## VI. Heat, Work and Energy:

When a force  $F$ , is applied on a point, and if the point is displaced from original position, the work is said to be done.

$$W = F \times \Delta l$$

$W \rightarrow$  obtainable work  
 $\Delta l \rightarrow$  displacement of the point.

If a quantity of electricity ( $Q$ ) be transported under a electromotive force ( $E$ ), then electrical work is  $E Q$ .

In this note I have taken a convention, the work obtained from the system is regarded as negative and the work done on the system is regarded as positive.

This is IUPAC convention

## Non IUPAC convention of work

work done on the system is negative  
 work done by the system or work obtained from the system is positive.

→ **\*\*** If the volume of the system is increased against pressure then work is done by the system on the surrounding, and by IUPAC convention it is negative. If the volume of the system is decreased, then work is done on the system and it is positive.



Heat, obviously, is another form of energy since it can yield work or can be produced from work. Heat is defined as, "that which is transferred between a body and its surroundings by virtue of temperature difference only." or we can say that the agent that causes a change in temp. is termed as heat.

All forms of energy can be completely transformed into work but heat can not completely converted into work.

[\*] convention: The heat taken up by a system leads to the increase in internal energy of the system is taken +ve, The heat released by the system ~~increases~~ leads to the decrease in internal energy of the system is taken -ve.

ENERGY: The term energy may be defined as "the capacity of the system to do the work" or any property which may be generated from or be converted into work.

Many forms of energy are known to exist, eg, thermal energy, mechanical energy. which may be further subdivided into K.E and P.E, electrical energy, radiant energy--- etc. All these forms of energy can be converted into heat and also ~~one~~ into one another. Therefore energy can also be defined as the anything that can be converted into heat.

The energy proposed by any system may be divided into two classes:

① Internal energy and ② External energy.

### Internal Energy

It is a characteristic property of the system and includes the translational energy of the moving molecules, the rotational and vibrational energy of the molecules and the atoms constituting the molecules, as well as the energy of electrons and nuclei of atoms. We are thus to believe that every system has within itself a quantity of energy. This energy is called internal energy. It is represented by  $E$  or  $U$ .

$$\therefore U = E_{\text{electronic}} + E_{\text{nuclei}} + E_{\text{trans.}} + E_{\text{rot.}} + E_{\text{vib.}}$$



It is denoted as  $E$  or  $U$ .

For a system, the internal energy ( $E$ ) depends upon the thermodynamic variables ( $P, V, T$ ) of the system.

Internal energy of the system can be represented as,

$$U = f(P, V) \quad \text{when } T \text{ is const.}$$

$$= f(V, T) \quad \text{when } P \text{ is const.}$$

$$= f(P, T) \quad \text{when } V \text{ is const.}$$

For isothermal change,  $(\Delta U)_T = 0$ . (for ideal gases mainly).

The internal energy of the system is a state function, that means the change ( $dU$ ) of it depends only on the initial and final state of the system. So,  $dE$  is also called a perfect differential.

$$dU = U_f - U_i$$

It is also an extensive property of the system. In thermodynamical cyclic process, the change of it be zero, i.e.,  $\oint dU = 0$ . For isothermal process of ideal gas,  $\Delta U_T = 0$ .

External Energy: This is due to the position of the system in space and in a field of force such as magnetic, electric or gravitational as well as due to the motion of the system as whole.

Usually, all the forms of energy are represented as  $\text{mass} \times (\text{length}/\text{time})^2$ .

## VIII. FIRST LAW OF THERMODYNAMICS:

Scientist Joule suggested that, heat is a form of energy and heat and work are interchangeable. Depends on this idea, heat and work are interrelated as,

$$W \propto Q$$

$$W = J \cdot Q$$

$W \rightarrow$  obtainable work  
 $Q \rightarrow$  Heat absorbed by the system.  
 $J \rightarrow$  Mech. equivalent.

From his long experience Joule suggested that, "energy can neither be created nor destroyed though it may be converted one form to another".

No person could succeed in constructing a machine which may continue to operate with out any expenditure of fuel  $\rightarrow$

and may thus create energy out of nothing. This failure ~~led~~ led to the universal acceptance of law of conservation of energy which is considered as first law of thermodynamics.

There are various ways of defining the first law of thermodynamics, as,

- ① Energy may be converted from one form to another, but it can be neither created nor destroyed.
- ② Energy of an isolated system must remain constant, although it may be transformed one into another.
- ③ Whenever a quantity of one kind of heat or energy is produced, then an exactly equivalent amount of some other kind of energy must disappear.

Mathematical form: Now consider a closed system in a state 'A' having internal energy  $U_A$  undergoing a change into state 'B', having internal energy  $U_B$ . During this transformation, let  $\partial q$  amt. of heat is absorbed from the surrounding and  $\partial w$  be the work done on the system.

Now total internal energy  $U_A$  increases to  $U_A + \partial q + \partial w$

Therefore,  $U_B = U_A + \partial q + \partial w$

$$\therefore \boxed{\partial q = (U_B - U_A) - \partial w = du - \partial w}$$

This is the algebraic form of the first law of thermodynamics. Here  $\partial q$  and  $\partial w$  are not perfect differential but  $du$  is a perfect differential.

Now if the volume of a gas be increased against low pressure, then work is done by the system

$$\partial w = -P \cdot dv$$

so, 1st law of thermodynamics is as,

$$\boxed{\partial q = du - \partial w = du + P dv}$$

\* According to Non-IUPAC system the first law of thermodynamics is written as,

$$\boxed{\partial q = du + dw}$$

, where  $\partial w = + P \cdot dv$

Here work done by the system is +ve.

Therefore,

$$\boxed{\partial q = du + P \cdot dv}$$

## IX. ENTHALPY :

If a system be present under pressure  $P$  and volume  $V$ , then the product  $P \cdot V$  is a energy term, called mechanical work. So the total energy of the system is the sum of internal energy ( $u$ ) and mechanical work ( $P \cdot V$ ). This total energy or heat content is universally represented by  $H$ . Therefore,

$$\boxed{H = u + P \cdot V}$$

$$\text{OR, } dH = du + P \cdot dv + V \cdot dP$$

$$\boxed{dH = \partial q + V \cdot dP}$$

Like internal energy ( $E$ ), it is also a state function and extensive property of the system. It can also be represented as following,

$$H = f(P, V), \text{ when } T \text{ const.}$$

$$H = f(P, T), \quad " \quad V \quad "$$

$$H = f(V, T), \quad " \quad P \quad "$$

For isothermal process of ideal gas,  $\Delta H_T = 0$

The change of it, i.e.,  $dH$  is a perfect differential, because, the change of it does not depend upon the path of change, only depends upon the final and initial state of the system.

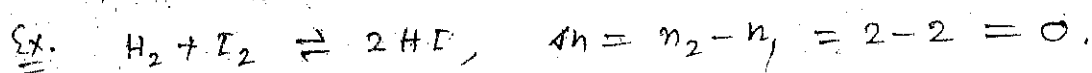
Now, at constant pressure,  $\boxed{dH_P = \partial q_P}$ , i.e., enthalpy change is equal with the heat absorbed.

$$\text{Again, } \Delta H = \Delta u + P \cdot \Delta V = \Delta u + P(V_2 - V_1) = \Delta u + RT(n_2 - n_1)$$

$$\boxed{\Delta H = \Delta u + \Delta n \cdot RT}$$

} For gaseous system and at const. pressure.

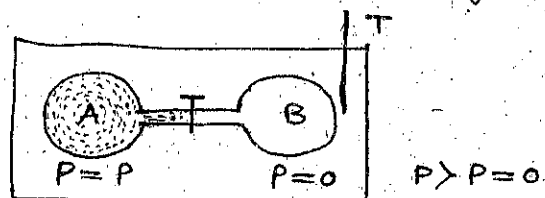
where  $n_1$  &  $n_2$  are the no. of moles of reactant and resultant respectively. When  $\Delta n = 0$ , then  $\Delta H = \Delta u$ .



X. For an ideal gas,  $\left(\frac{\partial u}{\partial v}\right)_T = 0$ ,  $\left(\frac{\partial u}{\partial p}\right)_T = 0$  and  $\left(\frac{\partial H}{\partial v}\right)_T = 0$  and  $\left(\frac{\partial H}{\partial p}\right)_T = 0$ , when the system performing no work under expansion of gas volume against zero pressure.

Let us consider an experiment for the expansion of ideal gas under zero pressure. Let two bulbs A and B connected by a stop cock at the middle of the connection between two bulbs.

The pressure of the bulb A is taken  $P$  atm. and the pressure of bulb B is taken  $p=0$  atm. And whole system



is surrounded by an adiabatic jacket.

In this case when stop cock is opened, then the ideal gas is expanded under pressure zero atm. So, no work is obtained, i.e.,  $dw = 0$ .

Again under constant temperature, as the gas performs no work, so the heat absorbed will also be zero.

Therefore,  $dq = 0$  and from the first law of thermodynamics

$$du = dq + dw = 0 \text{ ----- (I)}$$

Now, we know,  $u = f(v, T)$

$$\therefore du = \left(\frac{\partial u}{\partial v}\right)_T dv + \left(\frac{\partial u}{\partial T}\right)_T dT = 0$$

At constant temp.,  $dT = 0$ .

therefore,  $\left(\frac{\partial u}{\partial v}\right)_T dv = 0$

$$\therefore \boxed{\left(\frac{\partial u}{\partial v}\right)_T = 0}, \text{ when } dv \neq 0 \text{ ----- (II)}$$

We can also write,  $\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial u}{\partial p}\right)_T \left(\frac{\partial p}{\partial v}\right)_T = 0$

As,  $\left(\frac{\partial p}{\partial v}\right)_T \neq 0$ , so,  $\boxed{\left(\frac{\partial u}{\partial p}\right)_T = 0} \text{ ----- (III)}$

At constant temperature for an ideal gas, we know that,

$$\left\{ \frac{\partial (pV)}{\partial p} \right\}_T = 0 \text{ . We know } H = U + pV$$

$$\therefore \left(\frac{dH}{dp}\right)_T = \left(\frac{du}{dp}\right)_T + \left\{ \frac{\partial (pV)}{\partial p} \right\}_T$$

As,  $(du/dp)_T = 0$  and  $\left\{ \frac{\partial(PV)}{\partial P} \right\}_T = 0$ , therefore  $\boxed{\left( \frac{dH}{dP} \right)_T = 0}$  (iv)

$$\therefore \left( \frac{dH}{dP} \right)_T = \left( \frac{dH}{dv} \right)_T \cdot \left( \frac{dv}{dP} \right)_T = 0$$

$$\therefore \boxed{\left( \frac{dH}{dv} \right)_T = 0}, \text{ when } \left( \frac{dv}{dP} \right)_T \neq 0 \text{ ————— (v)}$$

XI. Heat capacity: The amount of heat required to raise the temperature of one gm. of substance by 1°K is called specific heat or heat capacity of that substance.

If  $\partial q$  amount of heat is required to increase the temp. about  $dT$  for one mole of the substance, then

$$c = \left( \frac{\partial q}{\partial T} \right).$$

In case of gases, there are two types of heat capacities — ① heat capacity under constant volume ( $c_v$ ) and ② heat capacity under constant pressure ( $c_p$ ).

$$\text{Now, } \partial q = du + P \cdot dv$$

$$\therefore \boxed{c_v = \left( \frac{\partial q}{\partial T} \right)_v = \left( \frac{du}{dT} \right)_v}$$

$$\text{and } c_p = \left( \frac{\partial q}{\partial T} \right)_p = \left\{ \frac{du + d(PV)}{dT} \right\}_p = \left( \frac{dH}{dT} \right)_p$$

$$\therefore c_p - c_v = \left( \frac{dH}{dT} \right)_p - \left( \frac{du}{dT} \right)_v$$

$$\therefore \boxed{c_p = \left( \frac{dH}{dT} \right)_p}$$

$$= \left( \frac{du}{dT} \right)_p + P \cdot \left( \frac{dv}{dT} \right)_p - \left( \frac{du}{dT} \right)_v \text{ ————— (1)}$$

Again, we know,  $U = f(V, T)$

$$\therefore du = \left( \frac{\partial u}{\partial v} \right)_T \cdot dv + \left( \frac{\partial u}{\partial T} \right)_v \cdot dT$$

$$\therefore \left( \frac{du}{dT} \right)_p = \left( \frac{\partial u}{\partial v} \right)_T \cdot \left( \frac{dv}{dT} \right)_p + \left( \frac{\partial u}{\partial T} \right)_v \text{ ————— (2)}$$

Substituting (2) in (1), we get,

$$\begin{aligned} c_p - c_v &= \left( \frac{\partial u}{\partial v} \right)_T \cdot \left( \frac{dv}{dT} \right)_p + \left( \frac{\partial u}{\partial T} \right)_v + P \cdot \left( \frac{dv}{dT} \right)_p - \left( \frac{du}{dT} \right)_v \\ &= \left( \frac{dv}{dT} \right)_p \left\{ \left( \frac{\partial u}{\partial v} \right)_T + P \right\} \end{aligned}$$

For ideal gases,  $\left(\frac{\partial u}{\partial v}\right)_T = 0$ , so, therefore  $C_p - C_v = p \left(\frac{dv}{dT}\right)_p$   
 $= p \cdot \frac{R}{p} = R$   
 $\therefore \boxed{C_p - C_v = R}$ , for ideal gases.

Usually, heat capacities  $C_p$  and  $C_v$  both increase with temp.  
 as,  $C_p = \alpha + \beta T + \gamma T^2 + \delta T^3 + \dots$

\* Question: Prove that  $C_p - C_v = R + \frac{2ap}{RT^2} = R \left(1 + \frac{2ap}{RT^2}\right)$  for a van der Waal gas.

Ans:

$$C_p - C_v = \left(\frac{dH}{dT}\right)_p - \left(\frac{dU}{dT}\right)_v$$

$$= \left(\frac{dU}{dT}\right)_p + p \left(\frac{dv}{dT}\right)_p - \left(\frac{dU}{dT}\right)_v \quad \text{--- (1)}$$

Now,  $U = f(v, T)$

$$\therefore dU = \left(\frac{\partial U}{\partial v}\right)_T dv + \left(\frac{\partial U}{\partial T}\right)_v dT$$

$$\therefore \left(\frac{dU}{dT}\right)_p = \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{dv}{dT}\right)_p + \left(\frac{\partial U}{\partial T}\right)_v \quad \text{--- (2)}$$

$$\therefore C_p - C_v = \left\{ p + \left(\frac{\partial U}{\partial v}\right)_T \right\} \cdot \left(\frac{dv}{dT}\right)_p$$

For real gases,  $\left(\frac{\partial U}{\partial v}\right)_T = a/v^2$  (এই প্রমাণ পাওয়া যায় অন্যভাবে)

$$\therefore C_p - C_v = \left(p + \frac{a}{v^2}\right) \cdot \left(\frac{dv}{dT}\right)_p$$

$$= \frac{RT}{(v-b)} \cdot \left(\frac{dv}{dT}\right)_p \quad \left[ \text{from van der Waal equation} \right] \quad \text{--- (3)}$$

$$\text{Now, } \left(p + \frac{a}{v^2}\right) \cdot (v-b) = RT$$

$$pV + \frac{a}{v} - pb = RT \quad (\text{Neglecting } ab/v^2, \text{ which is small})$$

$$\therefore p \cdot \left(\frac{dv}{dT}\right)_p - \frac{a}{v^2} \cdot \left(\frac{dv}{dT}\right)_p = R$$

$$\therefore \left(\frac{dv}{dT}\right)_p = \frac{R}{p - a/v^2} = \frac{R}{\left(p + \frac{a}{v^2}\right) - \frac{2a}{v^2}} = \frac{R}{\frac{RT}{v-b} - \frac{2a}{v^2}}$$

$$\left(\frac{dv}{dT}\right)_p = \frac{R}{\frac{RT}{v-b} \left(1 - \frac{2a(v-b)}{RTv^2}\right)}$$

$$\therefore \left(\frac{dv}{dT}\right)_p = \frac{R}{\frac{RT}{v-b} \left(1 - \frac{2a}{RTv}\right)} \quad \left\{ \begin{array}{l} \text{As, } b \text{ is very small,} \\ \text{so, } v-b \approx v \end{array} \right\}$$

(4)

$$\begin{aligned}
 C_p - C_v &= \frac{RT}{V-b} \cdot \frac{R}{\frac{RT}{(V-b)} \cdot \left(1 - \frac{2a}{RTV}\right)} \quad \left[ \text{By putting eqn}^n - (4) \text{ in equation } - (3) \right] \\
 &= \frac{R}{1 - \frac{2a}{RTV}} = R \left(1 - \frac{2a}{RTV}\right)^{-1} \\
 &= R \left(1 + \frac{2a}{RTV}\right)
 \end{aligned}$$

$$\boxed{C_p - C_v = R \left(1 + \frac{2aP}{R^2 T^2}\right)} \quad \text{Proved.}$$

⊗ Question: Prove that  $C_p - C_v = \frac{\alpha^2 TV}{\beta}$  using first law of thermodynamics.

Ans: we know, the coefficient of thermal expansion ( $\alpha$ ) of a gas is given by,

$\alpha = \frac{1}{V} \cdot \left(\frac{dV}{dT}\right)_P$  and coefficient of compressibility factor ( $\beta$ ) is given by,

$$\beta = -\frac{1}{V} \cdot \left(\frac{dV}{dP}\right)_T$$

For ideal gases, we know,  $C_p - C_v = P \cdot \left(\frac{dV}{dT}\right)_P$  — (1)

we know,  $dq = dU + P \cdot dV$  — (1st law of thermodynamics)

$$\begin{aligned}
 &= C_v \cdot dT + P \cdot dV \\
 \left(\frac{dq}{dT}\right)_P &= C_v + P \cdot \left(\frac{dV}{dT}\right)_P \\
 C_p &= C_v + P \cdot \left(\frac{dV}{dT}\right)_P
 \end{aligned}$$

$$\therefore C_p - C_v = P \cdot \left(\frac{dV}{dT}\right)_P$$

Now, we know,  $PV = RT$

$$\therefore \left(\frac{dP}{dT}\right)_V = \frac{R}{V} = \frac{P}{T} \quad \text{above}$$

$$\therefore P = T \cdot \left(\frac{dP}{dT}\right)_V \quad \text{--- (2)}$$

from (1) & (2), we can write,

$$C_p - C_v = T \cdot \left(\frac{dP}{dT}\right)_V \cdot \left(\frac{dV}{dT}\right)_P \quad \text{--- (3)}$$

Again,  $\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial T}{\partial V}\right)_P = -1$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P \cdot \left(\frac{\partial V}{\partial P}\right)_T} \quad \text{--- (4)}$$



Putting (4) in (3), we get,

$$C_p - C_v = -T \cdot \left( \frac{\partial v}{\partial T} \right)_P^2 \cdot \left( \frac{\partial P}{\partial v} \right)_T = \frac{T \cdot v \cdot \frac{1}{v^2} \cdot \left( \frac{dv}{dT} \right)_P^2}{-\frac{1}{v} \cdot \left( \frac{dv}{dP} \right)_T}$$

$C_p - C_v = \frac{\alpha^2 \cdot T \cdot v}{\beta}$

Proved.

## XII. Reversible process:

Reversible  
Thermodynamic

It is defined as "the process which can be reversed completely ~~and~~ by making an infinitesimal change in one of the variable, producing the change".

This process is usually carried out very slowly so that during its operation the system remains always in a state of virtual equilibrium. Again, when rate of forward process and rate of backward process having very very small difference, then the process is said to be a reversible process.

Criteria: To sum up the reversible process have the following criteria:

- ① In a reversible process the energy changes at each step of the system would be reversed in direction, the reverse direction on each step controlling by external factors.  
if driving force & opposing force (reverse)
- ② In a reversible process, system always proceeds under equilibrium condition. Thus a paradoxical idea, that a process and an equilibrium coexists, has been imaginary.
- ③ A reversible process proceeds infinitely slow. so that, infinite amount of time would be necessary for a finite change to occur.
- ④ work or energy evolved in a reversible process ~~is~~ is maximum. (Though rev. work of compression is min<sup>m</sup>).
- ⑤ Process is an ideal one to which actual process can approach only roughly.

### Isothermal reversible work (expansion)

Suppose  $n$  moles of an ideal gas is enclosed in a cylinder by a piston, which is more or less frictionless. Let  $P_1$  and  $V_1$  be the pressure and the volume of the gas respectively at the initial stage. Now external press. is made  $(P_1 - dp)$ , the gas expands to  $(V_1 + dv)$ . Again pressure is made  $(P_1 - 2dp)$ , the volume of the gas ~~could~~ be  $(V_1 + 2dv)$ . In this way when the external pressure will be  $P_2$ , the gas volume expands to  $V_2$ , then we can write, (Here work is done by system)

$$w_r = \int_0^w dw = -(P_1 - dp) dv - (P_1 - 2dp) \cdot dv + \dots$$

$$= - \int_{P_1, V_1}^{P_2, V_2} P \cdot dv + \int_{V_1, P_1}^{V_2, P_2} dp \cdot dv$$

Say  $P_1 = P_{ext}$

$$= - \int_{V_1}^{V_2} \frac{P}{P_{ext}} \cdot dv = - RT \cdot \int_{V_1}^{V_2} \frac{dv}{V}$$

[others are neglected because of  $dp \cdot dv$  is very small.]

Here max<sup>m</sup> amount of work is obtained.

$$W_{rev} = - nRT \ln \frac{V_2}{V_1} = - nRT \ln \frac{P_1}{P_2}$$

(work is done by system)

⊗ If the gas is compressed reversibly - isothermally, then minimum work will be done on gas.

$$W_{rev} = - nRT \ln \frac{V_2}{V_1}$$

( $V_2 < V_1$ ) After putting the values of  $V_1, V_2$ , then  $W$  will come automatically Positive

### XIII. Irreversible process :

In irreversible process is one which occurs suddenly or spontaneously without remaining any virtual equlm during transition. In this process, the system after undergoing a change will not have the tendency to return to initial stage by itself. It is an unidirectional change and where rate of forward process and the rate of backward process are unequal. driving force  $\gg$  oppo for criteria:

- ① All spontaneous processes are irreversible in nature.
- ② Irreversible process never yield the maximum work.
- ③ The process do not go for equilibrium except radioactive equilibrium.
- ④ It is generally faster except radioactive change.

10 pm

## Isothermal irreversible work :

Let  $P_1$  and  $V_1$  be the pressure and volume of gas at initial stage. Now the pressure is made  $P_2$  and where  $P_2 < P_1$ , an irreversible expansion of volume from  $V_1$  to  $V_2$  ~~can~~ be obtained.

So irreversible work  $= -P_{\text{ext.}}(V_2 - V_1)$   
 Now, say,  $P_{\text{ext}} = P_2$   

$$W_{\text{ir}} = -\frac{nRT(P_1 - P_2)}{P_1}$$

$$= -P_{\text{ext.}}(V_2 - V_1) = -P_{\text{ext.}}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$= -P_2\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right) = -\frac{nRT(P_1 - P_2)}{P_1}$$

Question: show that isothermal reversible work of expansion is always greater than irreversible work ( $W_{\text{ir}}$ ) of expansion.

Ans: we know from the isothermal reversible work of expansion,  $-W_R = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2}$

$$= RT \ln \left(1 + \frac{P_1 - P_2}{P_2}\right)$$

$$-W_R = RT \left(\frac{P_1 - P_2}{P_2}\right)$$

from the irreversible change,

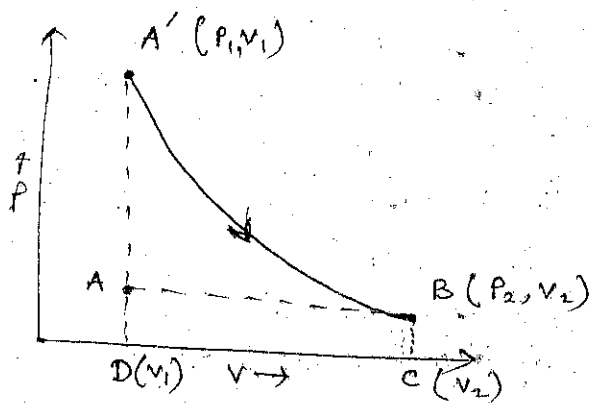
$$-W_{\text{ir}} = P_2(V_2 - V_1) = RT \frac{(P_1 - P_2)}{P_1}$$

$$\therefore |W_R - W_{\text{ir}}| = \frac{RT(P_1 - P_2)}{P_2} - \frac{RT(P_1 - P_2)}{P_1}$$

$$= \frac{RT(P_1 - P_2)^2}{P_1 P_2} = \text{Positive quantity.}$$

ie,  $|W_R - W_{\text{ir}}| > 0 \quad \therefore -W_R > -W_{\text{ir}}$

Graphically explanation:



If we look at the  $P$ - $V$  diagram, we see that irreversible expansion from  $(P_1, V_1)$  to  $(P_2, V_2)$  against  $P_2$ , where  $P_1 > P_2$

$$\therefore \text{work} = -P(V_2 - V_1) = \text{area } ABCD$$

However during reversible expansion from  $P_1, V_1$  to  $P_2, V_2$ , the work done  $= -\int_{V_1}^{V_2} P \cdot dV = \text{area } A'BED$

As the area  $A'BED > \text{area } ABCD$ , rev. work is greater than irrev. work.

#### XIV. Kirchhoff's Equation:

This equation gives the change of internal energy and enthalpy with the influence of temperature. Let  $U_i$  and  $H_i$  be the internal energy and enthalpy of the system at initial stage, and  $U_f$  and  $H_f$  be the internal energy and enthalpy of the system at final stage.

So, the change in internal energy,

$$\Delta U = U_f - U_i \quad \text{-----} \textcircled{1}$$

the change in enthalpy,

$$\Delta H = H_f - H_i \quad \text{-----} \textcircled{2}$$

Differentiating partially w.r. to temperature, we get, from ①,

$$\left\{ \frac{\partial(\Delta U)}{\partial T} \right\}_V = \left( \frac{\partial U_f}{\partial T} \right)_V - \left( \frac{\partial U_i}{\partial T} \right)_V = C_V^f - C_V^i = \Delta C_V \quad \text{-----} \textcircled{3}$$

From ②,

$$\left\{ \frac{\partial(\Delta H)}{\partial T} \right\}_P = \left( \frac{\partial H_f}{\partial T} \right)_P - \left( \frac{\partial H_i}{\partial T} \right)_P = C_P^f - C_P^i = \Delta C_P \quad \text{-----} \textcircled{4}$$

From ③ and ④, we can take,

$$\partial(\Delta U) = \Delta C_V \cdot \partial T \quad \text{-----} \textcircled{5}$$

$$\partial(\Delta H) = \Delta C_P \cdot \partial T \quad \text{-----} \textcircled{6}$$

Integrating ⑤ & ⑥ within the limit zero to a finite temp. (T),

$$\int_0^T d(\Delta H) = \int_0^T \Delta C_P \cdot dT$$

$$\therefore \boxed{\Delta H_T = \Delta H_0 + \int_0^T \Delta C_P \cdot dT} \quad \text{-----} \textcircled{7}$$

Again,  $\int_0^T d(\Delta U) = \int_0^T \Delta C_V \cdot dT$

$$\therefore \boxed{\Delta U_T = \Delta U_0 + \int_0^T \Delta C_V \cdot dT} \quad \text{-----} \textcircled{8}$$

Both the equations ⑦ and ⑧ are called Kirchhoff's equation.

Now we know that  $C_p$  and  $C_v$  both can change with temp as,

$$C_p^i = a_i + b_i T + c_i T^2 + d_i T^3 + \dots$$

$$C_p^f = a_f + b_f T + c_f T^2 + d_f T^3 + \dots$$

$$\Delta C_p = C_p^f - C_p^i = (a_f - a_i) + (b_f - b_i)T + (c_f - c_i)T^2 + \dots$$

$$\Delta C_p = \alpha + \beta T + \gamma T^2 + \delta T^3 + \dots$$

Therefore, Kirchhoff's equation can be taken as,

$$\Delta H_T = \Delta H_0 + \int_0^T (\alpha + \beta T + \gamma T^2 + \delta T^3 + \dots) \cdot dT$$

$$\Delta H_{T_1} - \Delta H_{T_2} = \alpha (T_1 - T_2) + \frac{\beta}{2} (T_1^2 - T_2^2) + \frac{\gamma}{3} (T_1^3 - T_2^3) + \dots$$

## XV. Adiabatic Process

In case of adiabatic change, the system does not allow any transfer of heat from surrounding, i.e.  $dq = 0$ . From first law of thermodynamics,

$$\partial q = dU - \partial w = 0$$

$$\therefore dU = \partial w = -P \cdot dv$$

$$C_v \cdot dT = -P \cdot dv$$

$$C_v \cdot \frac{dT}{T} = -R \cdot \frac{dv}{v}$$

Let one mole of an ideal gas expanding adiabatically and reversibly from  $T_1$  to  $T_2$  and volume  $V_1$  to  $V_2$ . We have,

$$\int_{T_1}^{T_2} C_v \cdot \frac{dT}{T} = -R \cdot \int_{V_1}^{V_2} \frac{dv}{v}$$

$$\therefore C_v \cdot \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}$$

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

$$\therefore \boxed{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}}$$

or

$$\boxed{T V^{\gamma-1} = \text{constant.}} \quad \text{--- (1)}$$

By putting,  $T = \frac{PV}{R}$  in the equation (1), we get,

$$\frac{PV}{R} \cdot V^{4-1} = \text{const} \quad \text{or} \quad \boxed{PV^4 = \text{const.}} \quad \text{--- (2)}$$

$$\text{So, } \boxed{P_1 V_1^4 = P_2 V_2^4}$$

Similarly, by putting  $v = \frac{RT}{P}$  in the equation (2)

$$P \cdot \left(\frac{RT}{P}\right)^4 = T^4 \cdot P^{1-4} = \text{const.}$$

$$\text{Hence, } \boxed{T_1^4 \cdot P_1^{1-4} = T_2^4 \cdot P_2^{1-4}} \quad \text{--- (3)}$$

All these equations are valid only for reversible process.

### Adiabatic Rev. work

We have,  $dw = du$

$$\text{or } \boxed{W = \Delta U = n C_v (T_2 - T_1)}$$

When  $T_2 > T_1$ ,  $w$  is positive, i.e., work is done on the system.

When  $T_2 < T_1$ ,  $w$  is negative, i.e., work is done by the system.

$$\begin{aligned} \text{Again, } w_{\text{ad.}}^{\text{rev.}} &= n C_v (T_2 - T_1) \\ &= n C_v \left\{ T_1 \cdot \left(\frac{V_1}{V_2}\right)^{4-1} - T_1 \right\} \end{aligned}$$

$$\begin{aligned} \text{Again, } w &= n C_v (T_2 - T_1) \\ &= n C_v \left\{ \frac{P_2 V_2}{R} - \frac{P_1 V_1}{R} \right\} = \frac{n C_v}{R} \{ P_2 V_2 - P_1 V_1 \} \\ &= \frac{n C_v}{R} \{ R T_2 - R T_1 \} \end{aligned}$$

$$\text{Adiabatic irrev. work: } \boxed{W = \frac{nR}{4-1} (T_2 - T_1)}$$

Here the work is done against const. pressure.

For expansion,  $dw = -P_{\text{ex}} dv$

If  $P_{\text{ex}} = P_2$ ,  $dw = -P_2 \cdot dv$

Here,

$$\Delta U = W = -P_2 (V_2 - V_1)$$

$$\therefore \boxed{W_{\text{ad}} = -P_2 (V_2 - V_1)}$$

calculation of final temperature for irrev. adiabatic

$$\Delta U = W$$

$$\boxed{n C_v (T_2 - T_1) = -P_2 (V_2 - V_1)}$$

For expansion  
of gas against  
low pressure, i.e.,  
work is -ve.

$$\begin{aligned} &= -P_2 \left\{ \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right\} \\ &= -nR \left\{ T_2 - T_1 \cdot \frac{P_2}{P_1} \right\} \end{aligned}$$

For irrev. compression, i.e.,  $w$  is +ve, so

$$\boxed{n C_v (T_2 - T_1) = P_2 (V_2 - V_1) = nR \left\{ T_2 - T_1 \cdot \frac{P_2}{P_1} \right\}}$$

For reversible adiabatic expansion of a real gas

$$\text{Now, } U = f(V, T)$$

$$\therefore du = \left( \frac{\partial u}{\partial T} \right)_V dT + \left( \frac{\partial u}{\partial V} \right)_T dV$$

$$du = C_v dT + \frac{a}{V^2} dV$$

$$\text{For } n\text{-mole, } du = n C_v dT + n^2 \frac{a}{V^2} dV$$

$$\therefore \Delta U = n C_v (T_2 - T_1) - a n^2 \left\{ \frac{1}{V_2} - \frac{1}{V_1} \right\} \quad \text{--- (1)}$$

$$\text{Now, } \left( P + \frac{a}{V^2} \right) (V - b) = RT$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Now, for expansion. (reversible), for one mole,

$$du = -P dV$$

$$C_v dT + \frac{a}{V^2} dV = - \left\{ \frac{RT}{V-b} - \frac{a}{V^2} \right\} dV$$

$$\therefore \frac{C_v}{R} \frac{dT}{T} = - \frac{dV}{V-b}$$

$$\text{Integrating, we get, } \frac{C_v}{R} \ln \frac{T_2}{T_1} = \ln \frac{V_1 - b}{V_2 - b}$$

$$\therefore \boxed{T_1 \cdot (V_1 - b)^{\gamma-1} = T_2 \cdot (V_2 - b)^{\gamma-1}}$$



Calculation of work and  $\Delta H$  :

$$dW_{ad} = du = n\tilde{C}_v \cdot dT + n\tilde{a} \cdot \frac{dv}{v^2}$$

$$W_{ad} = \Delta U = n\tilde{C}_v (T_2 - T_1) - n\tilde{a} \left\{ \frac{1}{v_2} - \frac{1}{v_1} \right\}$$

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

$$= \Delta U + \Delta \left\{ \frac{nRT}{v - nb} - \frac{n\tilde{a}}{v^2} \right\} \cdot v$$

$$= \Delta U + nR \left( \frac{v_2 T_2}{v_2 - nb} - \frac{v_1 T_1}{v_1 - nb} \right) - n\tilde{a} \left( \frac{1}{v_2} - \frac{1}{v_1} \right)$$

\* Free expansion of ideal gas is adiabatic and as well as isothermal. —

For free expansion,  $W=0$ , i.e., gas is expanded against zero external pressure.

For adiabatic process,

$$Q=0, \quad \text{Now, } Q = \Delta U - W = 0 \quad \text{Here work is done by the gas, } W \text{ is } -ve$$

$$\therefore \Delta U = W = 0$$

For isothermal process of ideal gas, we know that  $\Delta U_T = 0$ . So, free expansion of ideal gas is adiabatic and as well as isothermal.

\* Question:  $du = n\tilde{C}_v \cdot dT$  and  $dH = n\tilde{C}_p \cdot dT$ . Are these expressions correct — Justify.

$$U = f(v, T)$$

$$du = \left( \frac{\partial u}{\partial T} \right)_v \cdot dT + \left( \frac{\partial u}{\partial v} \right)_T \cdot dv$$

At const. volume,

$$du = \left( \frac{\partial u}{\partial T} \right)_v \cdot dT = n\tilde{C}_v \cdot dT$$

This expression is correct when system performs only mechanical work at const. volume.

$$H = f(P, T)$$

$$dH = \left( \frac{\partial H}{\partial P} \right)_T \cdot dP + \left( \frac{\partial H}{\partial T} \right)_P \cdot dT$$

At const. pressure,

$$dH = \left( \frac{\partial H}{\partial T} \right)_P \cdot dT = n\tilde{C}_p \cdot dT$$

This expression is correct when system performs mechanical work only at const. pressure.

$\square$  we know  $du = n C_v \cdot dT$   
 $\therefore \Delta U = U_2 - U_1 = \int_1^2 du = \int_{T_1}^{T_2} n C_v \cdot dT$ , when  $C_v$  is not const.,  
 $= n C_v (T_2 - T_1)$ ; when  $C_v$  is const.  
 similarly,  $dH = n C_p \cdot dT$   
 $\therefore \Delta H = \int_1^2 n C_p \cdot dT$ ; when  $C_p$  is not const.  
 $= n C_p (T_2 - T_1)$ ; when  $C_p$  is const.

Question:  $\partial q$  is path dependent func<sup>n</sup> - why?

we know,  $\partial q = du + P \cdot dv$   $u = f(T, v)$

$\therefore \partial q = \left(\frac{\partial u}{\partial T}\right)_v \cdot dT + \left(\frac{\partial u}{\partial v}\right)_T \cdot dv + P \cdot dv$   $du = \left(\frac{\partial u}{\partial T}\right)_v \cdot dT + \left(\frac{\partial u}{\partial v}\right)_T \cdot dv$   
 At const. volume,  $dv = 0$ . (I)

$\therefore \left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v$   $\therefore \frac{\partial^2 q}{\partial v \cdot \partial T} = \frac{\partial^2 u}{\partial v \cdot \partial T}$  (II)

Again at const. temp.,  $dT = 0$

$\left(\frac{\partial q}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T + P$   $\therefore \frac{\partial^2 q}{\partial T \cdot \partial v} = \frac{\partial^2 u}{\partial T \cdot \partial v} + \left(\frac{\partial P}{\partial T}\right)_v$  (III)

$\therefore$  eq<sup>n</sup> (II) & (III) are not same, so  $\frac{\partial^2 q}{\partial T \cdot \partial v} \neq \frac{\partial^2 q}{\partial v \cdot \partial T}$   
 Hence  $\partial q$  is not state func<sup>n</sup>

Question: Prove that isothermal curve is more dipper than adiabatic P-V curve.

The slope of the P-V curve is  $(dP/dv)$

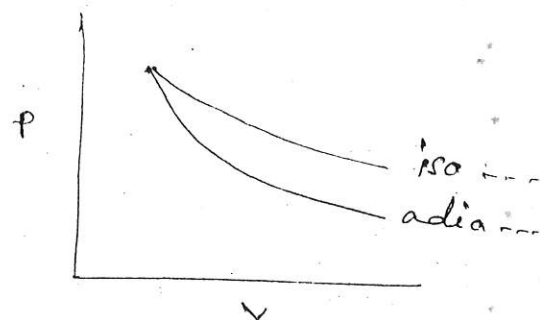
$\therefore$  For isothermal process,  
 $PV = RT$ ,

$\therefore \left(\frac{dP}{dv}\right)_T = -\frac{P}{v}$  (I)

For adiabatic process,  $PV^\gamma = \text{const.}$

$\left(\frac{dP}{dv}\right) = -\gamma \cdot \frac{P}{v}$

$\therefore \gamma > 1$ , so  $\left(\frac{dP}{dv}\right)_{\text{adia}} > \left(\frac{dP}{dv}\right)_{\text{iso}}$



Question: Compare the total work obtained by isothermal expansion and adiabatic expansion of gas for same amount of change.

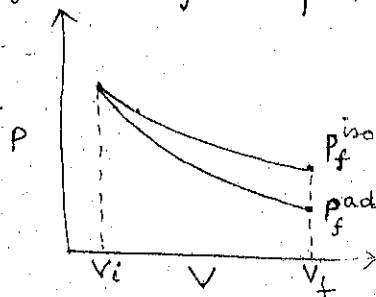
Ans: For both processes, let  $V_i$  be the initial volume and  $V_f$  be the final volume and  $P_i$  and  $P_f$  be the initial pressure & final pressure respectively.

Now, for isothermal process, work can be given as for expansion,

$$W^{iso} = -P_f (V_f - V_i)$$

Again we know,  $P_f V_f = P_i V_i$  or

$$\therefore W^{iso} = -P_i \left( \frac{V_i}{V_f} \right) (V_f - V_i)$$



For adiabatic change,

$$W^{ad} = -P_f (V_f - V_i) = -P_i \left( \frac{V_i}{V_f} \right)^{\gamma} (V_f - V_i)$$

As  $V_f > V_i$ , so,  $\left( \frac{V_i}{V_f} \right)^{\gamma} < \frac{V_i}{V_f}$ , when  $\gamma > 1.0$

therefore,  $-W^{iso} > -W^{adia}$

Question: Show that  $\left( \frac{\partial u}{\partial P} \right)_V = C_v \cdot \frac{\beta}{\alpha}$

$$\begin{aligned} \text{Ans: } \left( \frac{\partial u}{\partial P} \right)_V &= \left( \frac{\partial u}{\partial T} \right)_V \cdot \left( \frac{\partial T}{\partial P} \right)_V \\ &= C_v \cdot \left[ - \frac{1}{\left( \frac{\partial P}{\partial V} \right)_T \cdot \left( \frac{\partial V}{\partial T} \right)_P} \right] \\ &= C_v \cdot \left[ - \frac{\left( \frac{\partial V}{\partial P} \right)_T}{\left( \frac{\partial V}{\partial T} \right)_P} \right] = C_v \cdot \frac{-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T}{\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P} \end{aligned}$$

$u \rightarrow$  internal energy

$$\left( \frac{\partial u}{\partial P} \right)_V = C_v \cdot \frac{\beta}{\alpha}$$

Question: Find out the values of  $\left( \frac{\partial u}{\partial V} \right)_T$  for an ideal gas and for vander waal gas, and comment on your result.

Ans: From the first law of thermodynamics,  $\partial q_{rev} = du + P \cdot dv$

$$\therefore du = \partial q_{rev} - P \cdot dv = T \cdot ds - P \cdot dv \quad \left[ \text{from 2nd law, } ds = \frac{\partial q}{T} \right]$$

$$\left( \frac{\partial u}{\partial V} \right)_T = T \cdot \left( \frac{\partial s}{\partial V} \right)_T - P = T \cdot \left( \frac{\partial P}{\partial T} \right)_V - P \quad \left[ \text{From Maxwell relation, } \left( \frac{\partial s}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \right]$$

For ideal gases,  $P = \frac{RT}{V} \therefore \left( \frac{\partial P}{\partial T} \right)_V = \frac{P}{T}$

$$\therefore \left( \frac{\partial u}{\partial V} \right)_T = T \cdot \frac{P}{T} - P = 0.$$

For Vander waal gases,  $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{(V-b)}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{(V-b)} - P = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$

$$\therefore \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}} \text{ for vander waal gases}$$

For an ideal gases,  $\left(\frac{\partial U}{\partial V}\right)_T = 0$ . This is because in an ideal gas there is no intermolecular force of attraction between the gas molecules. Therefore the internal work is zero.

For real gases,  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$  using vander waal equation. This is because there is intermolecular force of attraction between the molecules. Therefore some internal work is to do to overcome the intermolecular force of attraction.

Question: What is quasistatic process?

Ans: It is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes can be considered as equilibrium state.

Question (\*) Calculate  $W$ ,  $\Delta U$  and  $\Delta H$  for a vander waal gas (i) when it is expanded reversibly and isothermally and (ii) when it is expanded adiabatically & reversibly.

Ans: (i) Work (W)

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

Now, we know,  $\left(P + \frac{n^2 a}{V^2}\right) (V - nb) = nRT$

$$\therefore P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\therefore W = - \int_{V_1}^{V_2} \frac{nRT}{V - nb} \cdot dV + \int_{V_1}^{V_2} \frac{n^2 a}{V^2} \cdot dV$$

$$\therefore -W = nRT \ln \frac{V_2 - nb}{V_1 - nb} + n^2 a \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

change in  
Internal energy ( $\Delta U$ )

$$\boxed{\Delta U = ?}$$

$$U = f(V, T)$$

At constant temp.,  $dU = \left( \frac{\partial U}{\partial V} \right)_T dV$

Here  $\left( \frac{\partial U}{\partial V} \right)_T$  is called internal pressure of the gas, which is the measure of attractive forces.

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{n^2 a}{V^2}$$

$$\therefore dU = \frac{n^2 a}{V^2} dV$$

$$\therefore \Delta U = U_2 - U_1 = n^2 a \left( \frac{1}{V_1} - \frac{1}{V_2} \right)$$

As,  $V_2 > V_1$   $\therefore \underline{\Delta U > 0}$

Again,  $Q = \Delta U - W$

change in  
Enthalpy ( $\Delta H$ ):

$$\boxed{\Delta H = ?}$$

$$H_1 = U_1 + P_1 V_1$$

$$H_2 = U_2 + P_2 V_2$$

$$\left. \begin{array}{l} H_1 = U_1 + P_1 V_1 \\ H_2 = U_2 + P_2 V_2 \end{array} \right\} \Delta H = H_2 - H_1 = \Delta U + (P_2 V_2 - P_1 V_1)$$

Now,  $PV = \frac{nRT \cdot V}{(V - nb)} - \frac{n^2 a}{V}$

$$\therefore P_2 V_2 - P_1 V_1 = nRT \left[ \frac{V_2}{V_2 - nb} - \frac{V_1}{V_1 - nb} \right] + n^2 a \left[ \frac{1}{V_1} - \frac{1}{V_2} \right]$$

$$\therefore \Delta H = \Delta U + P_2 V_2 - P_1 V_1$$

$$= 2n^2 a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) + nRT \left[ \frac{V_2}{V_2 - nb} - \frac{V_1}{V_1 - nb} \right]$$

$$\begin{aligned} Q = \Delta U - W &= n^2 a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) + nRT \ln \frac{V_2 - nb}{V_1 - nb} + n^2 a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \\ &= nRT \ln \frac{V_2 - nb}{V_1 - nb} \end{aligned}$$

(ii) Here,  $Q=0$   $\therefore W = -\Delta U$

$$U = f(V, T)$$

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

$$= nC_v dT + \frac{n^2 a}{V^2} dV$$

$$\therefore \Delta U = nC_v (T_2 - T_1) + n^2 a \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

Question: Prove that,

For expansion,

$$(W_{rev})_{ideal} > (W_{rev})_{real\ gas}$$

$$\text{For ideal gas: } -W_{rev} = 2.303 \cdot nRT \log \frac{V_2}{V_1}$$

$$\text{For real gas: } -W_{rev} = 2.303 \cdot nRT \log \frac{V_2 - nb}{V_1 - nb}$$

$$+ n^2 a \left\{ \frac{1}{V_2} - \frac{1}{V_1} \right\}$$

$\therefore$  when  $V_1, V_2 \gg nb$ ,  
then

$$\left| (W_{rev})_{ideal} \right| - \left| (W_{rev})_{real} \right| = n^2 a \left( \frac{1}{V_1} - \frac{1}{V_2} \right)$$

~~As~~ During expansion,  $V_2 > V_1$ ,

$$\therefore \left| (W_{rev})_{ideal} \right| > \left| (W_{rev})_{real} \right|$$

Question: Derive an expression for isothermal reversible work for a gas obeying  $P\bar{V} = RT + (bRT - a) \frac{1}{\bar{V}}$  equation,

$$\text{where } \bar{V} = \frac{V}{n}$$

Ans:

$$P\bar{V} = RT + (bRT - a) \frac{1}{\bar{V}}$$

$$= RT + RT \left( b - \frac{a}{RT} \right) \cdot \frac{1}{\bar{V}}$$

$$P = \frac{RT}{\bar{V}} + \frac{RT}{\bar{V}} \left( b - \frac{a}{RT} \right) \cdot \frac{1}{\bar{V}}$$

$$= \frac{nRT}{V} + \frac{nRT}{V^2} (b - \frac{a}{RT})$$

$$b - \frac{a}{RT} = B$$

This is 2nd virial coefficient

For expansion,

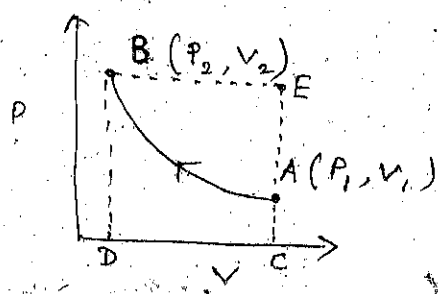
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Now,  $-dw = p \cdot dv$

$$-w = \int_{V_1}^{V_2} p \cdot dv = \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dv + \int_{V_1}^{V_2} \frac{nRT \cdot B}{V^2} \cdot dv$$

$$-w = nRT \ln \frac{V_2}{V_1} + nRTB \left( \frac{1}{V_1} - \frac{1}{V_2} \right)$$

Question: show graphically reversible work of compression is minimum.



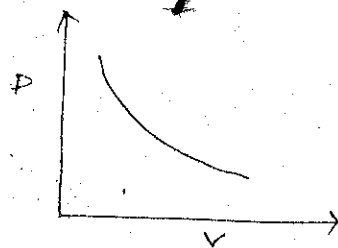
Here  $w_{rev} = - \int_{V_1}^{V_2} p \cdot dv = \text{area ABCD}$

$$w_{irr} = -P_2 (V_2 - V_1) = BD \times CD = EC \times CD = \text{area BECD}$$

As area BECD > area ABCD, So rev. work of compression is minimum.

Question: Draw 'P-V' diagram for a gas obeying  $PV = RT$  eqn for reversible and as well as irreversible also. Is there any difference between them?

P, V and T all are state functions. So these functions and their changes are also path independent. So P-V curve will be same for both reversible and irreversible processes.



Question: An alternative statement for 1st law can be taken as "In an isolated system work is a state function" - Justify.

Ans: For isolated system,  $\partial q = 0$ , so this is obviously the adiabatic process.

First law:  $\partial q = du + dw = 0$



$$dw = -du = nC_v dT$$

$$W = nC_v(T_2 - T_1)$$

So, here work depends upon only the final and initial state (temp.) of system.

Therefore, work is path-independent for isolated system.

Question: show that for water at 4°C,  $C_p = C_v$ .

Ans: we know,  $C_p - C_v = T \left( \frac{dp}{dT} \right)_v \left( \frac{dv}{dT} \right)_p$  [see page eqn - (3)]

Again,

$$PV = RT$$

$$\left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{V}$$

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

$$\frac{P}{RT} = \frac{1}{V} \quad \left( \frac{dv}{dT} \right)_p = 0$$

$$\left( \frac{dp}{dT} \right)_v = \frac{R}{V}$$

$P = T \left( \frac{\partial P}{\partial T} \right)_v$  As  $\rho$  is max<sup>m</sup> at 4°C, volume is minimum } so  $\left( \frac{dv}{dT} \right)_p = 0$

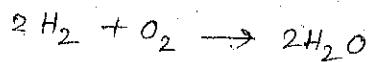
$$\left( \frac{dv}{dT} \right)_p = 0$$

$$C_p - C_v = 0$$

$$\therefore C_p = C_v$$

Question: In a thermally insulated closed vessel the following reaction takes place:  $2H_2 + O_2 \rightarrow 2H_2O$   
what should be the change in internal energy?

Ans:



$$\Delta H = -2 \times 285.8 \text{ kJ}$$

It is an exothermic reaction.

In laboratory, this reaction takes place at const. pressure.

we know,  $Q = Q_p = \Delta H$ .

Again as reaction is taken in closed vessel, so  $\Delta V = 0$

$$\therefore Q = \Delta U + P \Delta V$$

$$Q = Q_v = \Delta U$$

$$\therefore \Delta H = \Delta U = Q = -2 \times 285.8 \text{ kJ/mole}$$

Show that  $Q$  is not a state function

We know,  $dQ = du + PdV = C_v \cdot dT + PdV$  ——— ①

$\therefore Q = f(T, V)$

Now, from ①,  $\left(\frac{\partial Q}{\partial T}\right)_V = C_v$

and  $\frac{\partial^2 Q}{\partial V \cdot \partial T} = \left(\frac{\partial C_v}{\partial V}\right)_T$  ——— ②

Again from ①,  $\left(\frac{\partial Q}{\partial V}\right)_T = P \quad \therefore \frac{\partial^2 Q}{\partial T \cdot \partial V} = \left(\frac{\partial P}{\partial T}\right)_V$  ——— ③

From ② & ③,  $\frac{\partial^2 Q}{\partial V \cdot \partial T} \neq \frac{\partial^2 Q}{\partial T \cdot \partial V}$

So,  $Q$  is not a state function.

Q. When  $Q$  will be a state function?

A.  $H = U + P \cdot V$

$dH = du + PdV + VdP = dQ + VdP$

At const.  $P$ ,  $dH = dQ$

$\therefore Q = \int^2 dH = H_2 - H_1$ , so  $Q$  depends on final & initial enthalpies of system.

Q. Show that  $w$  is ~~not~~ a path function.

A. Now,  $dw = PdV$  and  $V = f(P, T)$

$dV = \left(\frac{\partial V}{\partial P}\right)_T \cdot dP + \left(\frac{\partial V}{\partial T}\right)_P \cdot dT$

$\therefore dw = P \cdot \left(\frac{\partial V}{\partial P}\right)_T \cdot dP + P \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot dT$

$\therefore \left(\frac{\partial w}{\partial T}\right)_P = P \cdot \left(\frac{\partial V}{\partial T}\right)_P$

$\therefore \frac{\partial^2 w}{\partial P \cdot \partial T} = P \cdot \left(\frac{\partial^2 V}{\partial P \cdot \partial T}\right) + \left(\frac{\partial V}{\partial T}\right)_P$  ——— ④

Again,  $\left(\frac{\partial w}{\partial P}\right)_T = P \cdot \left(\frac{\partial V}{\partial P}\right)_T \quad \therefore \frac{\partial^2 w}{\partial T \cdot \partial P} = P \cdot \frac{\partial^2 V}{\partial T \cdot \partial P}$  ——— ⑤

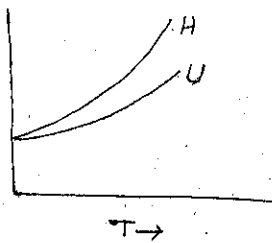
As,  $\frac{\partial^2 w}{\partial P \cdot \partial T} \neq \frac{\partial^2 w}{\partial T \cdot \partial P}$ , so,  $w$  is not path independent.

Q. When  $w$  will be a path independent?

In adiabatic process  $w$  is path independent.

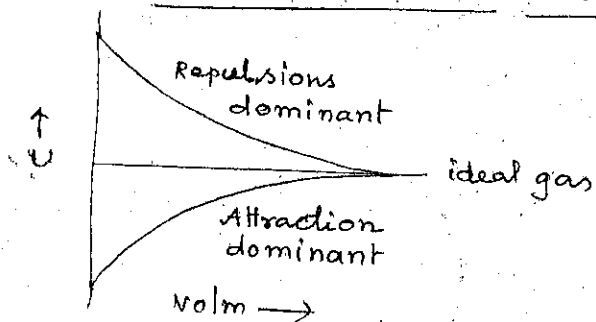
$W_{ad} = C_v (T_2 - T_1)$ ; it depends on final & initial state of a system.

Q. Why  $H$  increases more rapidly than  $U$  with  $T$ .



slope of  $H$  vs.  $T$  curve  $= \frac{dH}{dT} = C_p$   
 slope of  $U$  vs.  $T$  "  $= \frac{dU}{dT} = C_v$   $C_p > C_v$

Q. Draw  $U$  vs.  $V$  for ideal and real gases.



For an ideal gas  $U$  is independent with volume.

For a real gas, if attractions are dominant, the  $U$  increases with volume because the molecules become farther apart on average.

If repulsions are dominant, the internal energy decreases as gas expands.

Q. one mole of an ideal gas is expanded isothermally from  $T, P_1, V_1$  to  $T, P_2, V_2$  in two stages. First stage uses constant opposing pressure  $P'$  and second stage uses constant opposing pressure  $P_2$ . Show that the max<sup>n</sup> work,

$$W = 2RT \left\{ 1 - \left( \frac{P_2}{P_1} \right)^{1/2} \right\} \text{ and } P' = \sqrt{P_1 P_2}$$

Ans:

Step 1:  $(T, P_1, V_1) \longrightarrow (T, P', V')$

Step 2:  $(T, P', V') \longrightarrow (T, P_2, V_2)$

$$\therefore -W_1 = P' (V' - V_1) = P' \left( \frac{RT}{P'} - \frac{RT}{P_1} \right) = RT \left( 1 - \frac{P'}{P_1} \right)$$

$$-W_2 = P_2 (V_2 - V') = P_2 \left( \frac{RT}{P_2} - \frac{RT}{P'} \right) = RT \left( 1 - \frac{P_2}{P'} \right)$$

$$\therefore -W_{\max} = -W_1 + (-W_2)$$

$$= RT \left( 1 - \frac{P'}{P_1} \right) + RT \left( 1 - \frac{P_2}{P'} \right) = 2RT - \frac{RT \cdot P'}{P_1} - \frac{RT \cdot P_2}{P'}$$

At max<sup>n</sup> work,

$$-\frac{\partial W_{\max}}{\partial P'} = 0 - \frac{RT}{P_1} + \frac{RT P_2}{P'^2} = 0$$

$$\therefore \frac{RT}{P_1} = \frac{RT P_2}{P'^2} \quad \therefore P'^2 = P_1 P_2$$

$$P' = \sqrt{P_1 P_2}$$

(1)

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From ①,  $-W_{\max} = 2RT - \frac{RT}{P_1} (P_1 P_2)^{1/2} - \frac{RT \cdot P_2}{(P_1 P_2)^{1/2}}$

$$= 2RT - RT \left( \frac{P_2}{P_1} \right)^{1/2} - RT \left( \frac{P_2}{P_1} \right)^{1/2}$$

$$= 2RT \left\{ 1 - \left( \frac{P_2}{P_1} \right)^{1/2} \right\}$$

Q. For an ideal gas,  $\left( \frac{\partial H}{\partial P} \right)_T = 0$  and  $\left( \frac{\partial U}{\partial V} \right)_T = 0$ , which one is more important and why?

Ans:  $\left( \frac{\partial H}{\partial P} \right)_T = 0$  is the most important criteria for a gas to be ideal.

$\left( \frac{\partial U}{\partial V} \right)_T = 0$  and  $\left( \frac{\partial H}{\partial P} \right)_T = b$  for a gas obeying  $P(V-b) = RT$  eq<sup>n</sup>. but this is not ideal gas.

Q. Explain,  $PV^\gamma = \text{constant}$  is not an equation of state.

Ans: For  $PV = RT$ , the eq<sup>n</sup> of state of gas, as it correlates the intensive and extensive variables just required for defining the eq<sup>n</sup> of state.  $PV^\gamma = \text{const}$ , is not considered as eq<sup>n</sup> of state as it does not correlate extensive & intensive properties of system. and it is valid only for reversible adiabatic.

Q. Work in adiabatic process is path independent but it can not be defined as a state function.

Ans: Here i) work is not present in a system before and after transformation.

ii) work is not system's property

iii) work appears only during change of state

iv) and  $W_{ad} \neq W_2 - W_1$

Q. Show that  $C_p$  is independent with  $P$  and  $C_v$  is independent with volume. and also show that both  $C_p$  and  $C_v$  are independent with  $P$  &  $V$  for an ideal gas.

Ans:,  $C_p = \left(\frac{dH}{dT}\right)_P$

$$\left(\frac{dC_p}{dP}\right)_T = \frac{d}{dP} \left(\frac{dH}{dT}\right)_P = \frac{d}{dT} \left(\frac{dH}{dP}\right)_T$$

$$= \frac{d}{dT} \times 0 = 0$$

So,  $C_p$  is independent with  $P$

$C_v = \left(\frac{dU}{dT}\right)_V$

$$\left(\frac{dC_v}{dV}\right)_T = \frac{d}{dV} \left(\frac{dU}{dT}\right)_V = \frac{d}{dT} \left(\frac{dU}{dV}\right)_T$$

$$= 0$$

For ideal gas,

$$\left(\frac{dU}{dV}\right)_T = 0, \left(\frac{dU}{dP}\right)_T = 0$$

$$\left(\frac{dH}{dP}\right)_T = 0, \left(\frac{dH}{dV}\right)_T = 0$$

$C_p = \left(\frac{dH}{dT}\right)_P$

$$\left(\frac{dC_p}{dP}\right)_T = 0$$

Now we can write

$$\left(\frac{dC_p}{dP}\right)_T = \left(\frac{dC_p}{dV}\right)_T \cdot \left(\frac{dV}{dP}\right)_T = 0$$

As  $\left(\frac{dV}{dP}\right)_T \neq 0$ , so,  $\left(\frac{dC_p}{dV}\right)_T = 0$

$C_v = \left(\frac{dU}{dT}\right)_V$

$$\left(\frac{dC_v}{dV}\right)_T = 0 \text{ i.e., } \left(\frac{dC_v}{dP}\right)_T = \left(\frac{dC_v}{dV}\right)_T \cdot \left(\frac{dV}{dP}\right)_T = 0$$

As  $\left(\frac{dV}{dP}\right)_T \neq 0$ , so,  $\left(\frac{dC_v}{dP}\right)_T = 0$

Q. Is electronic rotation as an example of perpetual motion of 1st kind?

Ans: No, electronic rotation is due to coulombic force of attraction beth  $e^-$  & nucleus. So, it is not the example of said problem.

[\*] For reversible expansion,  $P_{\text{ext}} = P_{\text{system}} = P$   
 $= \frac{nRT}{V}$

$$dw = -P_{\text{ext}} \cdot dv$$

$$W = \int_{V_1}^{V_2} -P_{\text{ext}} \cdot dv = - \int_{V_1}^{V_2} P \cdot dv = - \int_{V_1}^{V_2} nRT \cdot \frac{dv}{V}$$

For irreversible expansion,  $P_{\text{ext}} = P_2$

$$dw = -P_{\text{ext}} (V_2 - V_1) = -P_2 (V_2 - V_1)$$

[\*] Explain — In rev. expansion, work is maximum &  
 In rev. compression, work is minimum.

Ans: In a rev. expansion, the system works against the maximum possible forces needed for expansion  
 p-dp : The work is maximum.

In a rev. compression, the system works against minimum possible external force needed. The work done is minimum.

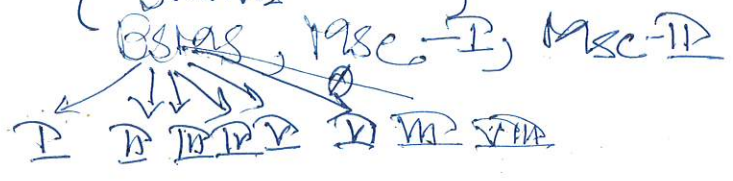


18th Jan 2017

Syllabus modification Analytical and instrumentation →

9:30 am, No project → Assignment do it timely.  
GUAN

FIST → O level, Attendance (is important specially



leaf late → instrument  
lab. Jam date: CCMN  
JAM.

Picnic MSc-IP, BSMS-VR

- 1. Presentation
- 2. Project

40

60

In dependent (1. Advanced) (2. Project).  
ment instruments you should learn. Choose a topic → this work has been done → we can do this the chemical has been assigned against MC & MR.  
BSMS-IP → Organic }  
                                } Inorganic

website → pr park.  
25 → PhD student  
Presentations & MR  
Team  
Instrumentation  
Publication  
Faculties  
4. PhD prog  
HOD  
Daphnion  
what is the  
research

18th Jan

18th Jan → Feb 2nd → give one presentation on rearranged syllabus. Submit syllabus. (Feb - 3rd Feb 2017)

NET-GATE

Class → Computer  
SG - co-ordinator for NET-GATE Class

Computing → chembiotech  
Chem Gen  
Lab  
Chungu  
Summer vac

- 1. MSc-IP
- 2. BSc-IP
- 3. BSMS-VR

A. Who ever does the class take the

- list.

Question bank from NET-GATE.

Good Feb Friday → presentation

SG will make syllabus → 4 teachers in one in inorganic + org + phy  
one coordinator  
4 teacher 4 teacher 4 teacher

Picnic → 28th Jan - Sat

venue → 21st Jan 2  
picnic  
MC + MR + MR + CS → Picnic.  
coordinator  
18th Jan  
SG + BS