

# THERMODYNAMICS

## INTRODUCTION

The study of energy transformations is the subject matter of thermodynamics. Various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. In a chemical reactions, energy stored by molecules can be released as heat. The chemical energy may also be used to do mechanical work when a fuel burns in an engine.

The laws of thermodynamics can be applied with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. More ever thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change.

### **Objectives and limitations of thermodynamics :**

#### **Objectives :**

- (1) Interrelate various energy changes during physical or chemical transformation.
- (2) Predict the feasibility of given change.
- (3) Deduce various laws, e.g. phase rule, distribution law, law of mass action etc. thermodynamically.
- (4) Derive at what conditions, the equilibrium is attained by a change.

#### **Limitations :**

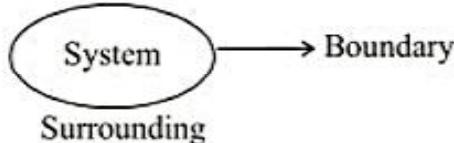
- (1) It's laws are valid for bulk of matter and does not provide information about individual atom.
- (2) It predicts feasibility of reaction but fails to suggest rate of reaction.
- (3) It fails to explain the systems which are not in equilibrium.

## SOME BASIC TERMS

### 1. System

A specified part of the universe with real or imaginary boundaries, on which studies of P, T etc are to be made.

A room, an engine human body etc. are examples of system.



### 2 . Surrounding

The rest part of the universe, adjacent to real or imaginary boundaries of the system .

Universe = System + Surrounding

**Note :** For practical purpose, surrounding means immediate surrounding rather than universe. For example in Lab experiment the room is considered as surrounding.

### 3. Types of system

#### (A) Based on exchange of mass and energy

- (i) **Isolated system :** A system is said to be isolated if it cannot exchange matter and energy with the surroundings. Example : coffee in a thermos flask.
- (ii) **Closed system :** A system is said to be closed if it can exchange energy but not matter. Example: Coffee in a closed stainless steel flask.
- (iii) **Open system :** A system is said to be open if it can exchange matter. Example : A thermos flask or a steel flask if not closed.

#### (B) Based on system composition

- (i) **Homogeneous systems :** A system having uniform nature throughout, made up of one phase only
- (ii) **Heterogeneous system :** A system not uniform throughout, consists of more than one phase.

## PROPERTIES OF A SYSTEM

The state of a system is defined by a particular set of its measurable quantities called properties, by which a system can be described for example, Temperature (T), Pressure (P) and volume (V) defines the thermodynamics state of the system in the same way, as particle co-ordinate is defined by (x, y, z) co-ordinate in physics. Properties can be categorised into extensive and intensive properties , on the basis of dependance of system size or mass.

**Intensive property** is one whose value is independent of the size (or mass) of the system.

**Extensive property** is one whose value depends on the size (or mass) of the system.

### Intensive & Extensive properties

1. Extensive properties are additive but intensive properties are non additive.
2. Ratio of two extensive property gives an intensive property.
3. An extensive property can be converted into intensive property by defining it per mole/ per gram/ per litre.

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

**Exercise**

1. Select the intensive and extensive properties from the following :

Entropy, specific entropy, triple point of water , volume of gas, pressure

**Ans.** Intensive property : Specific entropy, triple point of water, pressure,

Extensive property : Entropy,

A function may be state or path function depending on the dependence on path of the process or the end state.

- (A) **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.

**Mathematical Condition for a function to be a state function :**

There are three conditions that must be satisfied simultaneously for a function to be state function.

- (i) If  $\phi$  is a state function

$$\int_A^B d\phi = \phi_B - \phi_A$$

It means change in  $\phi$  depends only on end states and not on the path which it followed during the process.

- (ii) If  $\phi$  is a state function

$$\oint d\phi = 0$$

It implies, in cyclic integral as the end states are same, so  $\Delta\phi$  value will be zero.

- (iii) If  $\phi = f(x, y)$  is a state function, Euler's reciprocity theorem must be satisfied.

$$\frac{\partial}{\partial y} \left[ \left( \frac{\partial \phi}{\partial x} \right)_y \right]_x = \frac{\partial}{\partial x} \left[ \left( \frac{\partial \phi}{\partial y} \right)_x \right]_y$$

- (B) **Path function**

Functions which depend on the path means how the process is carried out to reach a state from another state depends on path e.g. work & heat.

**State function :** Pressure, volume, temperature, Gibb's free energy, internal energy, entropy

**Path function :** Work, Heat, Loss of energy due to friction

**Note :** S, U, H, V, T etc are state function but  $\Delta S$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta V$ ,  $\Delta T$ , etc. are not state function. In fact  $\Delta$  terms are not function itself and it is very misleading and frequently asked in the exams.

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**Illustration**

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1. Show that pressure of a fixed amount of an ideal gas is a state function  $V = \frac{nRT}{P}$

Sol.  $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$

$$\frac{\partial}{\partial P} \left[ \left( \frac{\partial V}{\partial T} \right)_P \right]_T = \frac{-nR}{P^2} \Rightarrow \left( \frac{\partial V}{\partial P} \right)_T = -\frac{nRT}{P^2}$$

$$\Rightarrow \frac{\partial}{\partial T} \left[ \left( \frac{\partial V}{\partial P} \right)_T \right]_P = \frac{-nR}{P^2}$$


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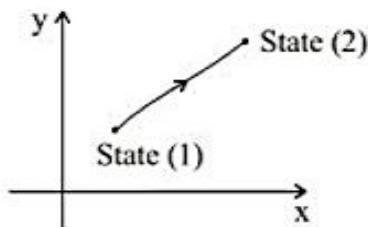
**Exercise**

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1. Show that Volume of a fixed amount of an ideal gas is a state function.
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**THERMODYNAMIC PROCESS**

The change of thermodynamic state from one condition to another condition is called thermodynamic process.



x and y are thermodynamic co-ordinate  
eg. P, T, V, S, U etc.

**(1) Reversible and Irreversible process**

A process which is carried out so slowly that the system and the surroundings are always in equilibrium during the process is known as a **Reversible Process (quasi-static)**. If this condition does not hold good, the process is said to be, **Irreversible**.

In a reversible process the driving force is infinitesimally larger than the opposing force.

A reversible process is very slow and takes infinite time. Whereas an irreversible process completes in finite time.

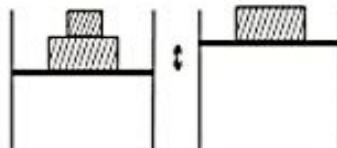
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**Note :**

- This thermodynamic reversible process is different from the “reversible reactions”. The term “Reversible reaction” only indicates that the reaction proceeds in both the directions.
- A process which proceeds without any external help is called a spontaneous process.
- All the real process are irreversible process



Reversible process



irreversible process

S.No.	Reversible process	Irreversible process
1.	Driving force is infinitesimally small.	Driving force is large and finite. PV work is done across pressure difference $\Delta P$
2.	PV work is done across pressure difference $dP$	Irreversible heat transfer take place across difference $\Delta T$
3.	A reversible heat transfer take place across temperature difference $dT$	It is a real process
4.	It is an ideal process.	It takes finite time for completion of process.
5.	It takes infinite time for completion of process.	It is a natural process and occurs in particular direction under given set of conditions.
6.	It is an imaginary process and can not be realised in actual practice.	The system is far away from state of equilibrium and exact path of process can not be defined as different part of the system are under different conditions
7.	Throughout the process, the system remain infinitesimally closer to state of equilibrium and exact path of process can be drawn	

**(2) Isothermal Process**

- i) A process in which temperature of the system does not change throughout the studies.
- ii)  $dT = 0$
- iii) It can be achieved by using thermostatic process.

**(3) Adiabatic Process**

- i) A process in which exchange of heat between system and surrounding does not take place.
- ii)  $q = 0$
- iii) It can be achieved by insulating the system boundaries for heat transfer.

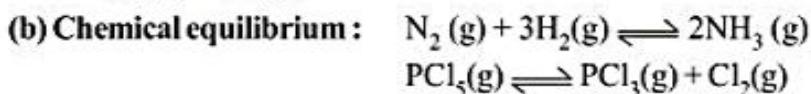
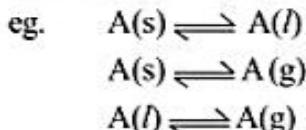
- (4) **Cyclic Process**
- (i) A process in which initial state of system is same after a series of operation
  - (ii) For a cyclic process  $\Delta E = 0$  and  $\Delta H = 0$
- (5) **Isochoric Process**
- (i) A process in which volume of the system remains constant throughout, the process.
  - (ii) For an Isochoric process  $\Delta V = 0$
- (6) **Isobaric process**
- (i) A process in which pressure of the system remains constant throughout the process.
  - (ii) Means  $\Delta P = 0$
- (7) **Equilibrium :** It is defined as when there is no change in thermodynamic property (P, V, T etc) of system with time.

## TYPES OF EQUILIBRIUM

System and surrounding equilibrium condition is considered in three broader terms :

1. **Thermal equilibrium :** Equality of temperature between system and surrounding
2. **Mechanical equilibrium :** Equality of pressure between system and surrounding
3. **Material equilibrium :** No. of moles of every substance in a definite phase remains constant with respect to time. Attained in closed vessel.

(a) **Physical or phase equilibrium :** Only physical changes are involved.



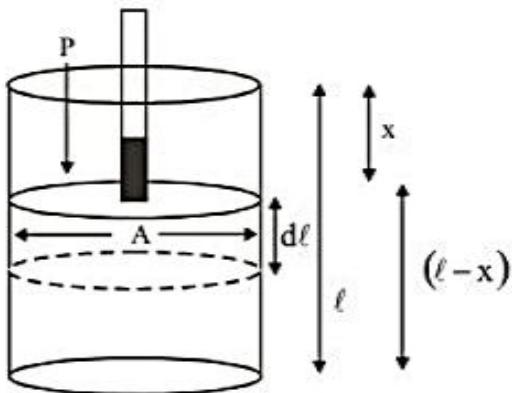
**In thermodynamics to deal with energy change during interaction of system and surrounding understanding of work (W) heat (Q, q) and internal energy (U,E) is very important.**

## WORK

Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved. This definition is consistent with our understanding of work as  $dw = Fdx$ . The force F can arise from electrical, magnetic, gravitational & other sources. It is a path function.

**Note :** Litre atmosphere term is unit of energy. It is useful to remember the conversion : 1 litre atm = 101.3 Joules = 24.206 Cal.

**PV- Work analysis :** Consider a cylinder fitted with a frictionless piston, which enclosed no more of an ideal gas. Let an external force F pushes the piston inside producing displacement in piston. Let distance of piston from a fixed point is x and distance of bottom of piston st the same fixed point is  $\ell$ . This means the volume of cylinder =  $(\ell - x)A$  where A is area of cross section of piston.



For a small displacement  $dx$  due to force  $F$ , work done on the system.

$$dw = F \cdot dx$$

$$\text{Also } F = PA$$

$$dW = PA \cdot dx$$

$$V = (\ell - x)A$$

$$\Rightarrow dV = -A \cdot dx \quad \Rightarrow \quad dW = -P_{\text{ext}} \cdot dV$$

$$\Rightarrow W_{PV} = - \int_{V_i}^{V_f} P_{\text{ext}} dV$$

**Note :** During expansion  $dV$  is positive and hence sign of  $w$  is negative since work is done by the system and negative sign representing decrease in energy content of system. During compression, the sign of  $dV$  is negative which gives positive value of  $w$  representing the increase in energy content of system during compression.

### Illustration

- Find the work done when 18 ml of water is getting vapourised at 373 K in open vessel (Assume the ideal behaviour of water vapour.)

**Sol.**  $PV = nRT$  [V in litre and T in Kelvin]

$$PV = 1 \times 0.0821 \times 373$$

$$PV = 30 \text{ litre}$$

$$V = 30 \text{ litre}$$

$$W = -P\Delta V$$

$$= -1 (30 - V_{\text{gas}}) \quad [18 \text{ ml is negligible as compared to 30 litre}]$$

$$= -1 \times 30 = -30 \text{ litre atm.}$$

- Calculate work done for the expansion of a substance from  $3m^3$  to  $5m^3$  against.

$$\text{Constant pressure} = 10^5 \text{ Pa}$$

**Sol.**  $W = -10^5 \times 2 = -2 \times 10^5 \text{ J}$

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**Exercise**

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1. Find the work done in each case :

(a) When one mole of ideal gas in 10 litre container at 1 atm, is allowed to enter a vacuated bulb of capacity 100 litre.

(b) When 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

Ans. (a)  $W = -P\Delta V$

But since gas enters the vacuum bulb and pressure in vacuums zero. This type of expansion is called free expansion and work done is zero.

Note :- Work done in free expansion is always zero.

(b)  $W = -P\Delta V = -1 (5 - 1) = -4 \text{ litre-atm.}$

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**HEAT**

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

According to IUPAC convention heat given by system is expressed with –ve sign heat given to system is expressed with +ve sign.

(i)  $q_V = nC_V dT$  (for constant volume process)

(ii)  $q_p = nC_p dT$  (for constant pressure process)

(iii)  $C_{p,m} - C_{v,m} = R$

(iv)  $C_v$  &  $C_p$  depends on temperature even for an ideal gas. ( $C = a + bT + cT^2 \dots$ )

(v) It is a path function

$C_v$ ,  $C_p$  are heat capacity of system and  $C_{v,m}$ ,  $C_{p,m}$  are heat capacity of one mole system at constant volume and pressure respectively.

**INTERNAL ENERGY (E & U)**

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy. Internal energy is stored in different forms inside the molecule.

$$U = U_{\text{Kinetic}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

**Note :**

1.  $U$  is a state function & is an extensive property.

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

2. It does not include kinetic energy of motion of system as a whole or its potential energy due to its position.

3.  $\Delta E = q_V$ , heat supplied to a gas at constant volume, since all the heat supplied goes to increase the internal energy of the gas.

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4. For a given system, if U is a function of T and Volume :

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

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

5. For isochoric process :  $dV = 0$

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

$$dU = C_V \cdot dT$$

$$\Delta U = \int C_V \cdot dT$$

6. For an ideal gas, change in internal energy with change in volume at constant temperature is zero.  
i.e.

$$\left( \frac{\partial U}{\partial V} \right)_T = 0$$

$$dU = C_V \cdot dT$$

$$\Delta U = \int C_V \cdot dT$$

**Internal energy is stored in the molecular motion and capacity to store energy depends upon degree of freedom of molecules**

## DEGREE OF FREEDOM AND EQUIPARTITION PRINCIPLE

According to Law of equipartition of energy

- (i) each translation and rotational degree of freedom in a molecule contributes  $1/2 RT$  to the thermal energy of one mole of a gas, and
- (ii) each vibrational degree of freedom in a molecule contributes  $RT$  to the thermal energy of one mole of a gas.

The **degree of freedom** in a molecule are given by the **number of coordinates** required to locate all the mass points (atoms) in a molecule. If a molecule contains only one atom (as in a monatomic gas), it has three degree of freedom corresponding to translational motion in the three independent spatial directions X, Y and Z. If a molecule contain N atoms, each atom contributes these three degree of freedom, so the molecule has a total of  $3N$  degree of freedom. Since three coordinates (degree of freedom) are required to represent the translational motion of the molecule, the remaining  $(3N - 3)$  coordinates represent what are called the **internal degree of freedom**. If the molecules is linear, it has two rotational degrees of freedom ; for a non-linear molecule, there are three rotational degree of freedom. The remaining degrees of freedom, that is  $3N - 5$  for linear and  $3N - 6$  for non-linear molecules are the vibrational degree of freedom. Table list the degrees of freedom for several molecular system.

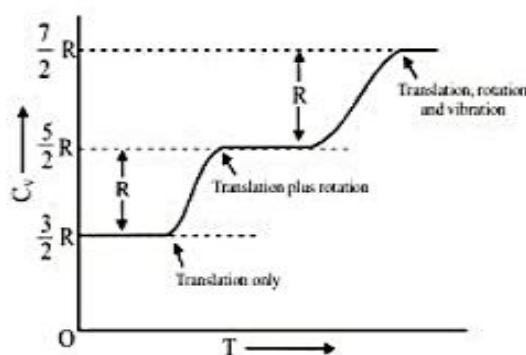
Atomicity	$n_{tr}$	$n_{R_0}$	$n_{vib}$	$C_V$		$C_p$		$\gamma$		
				Excl.Vib	Incl.Vib	Excl.Vib	Incl.Vib	Excl.Vib	Incl.Vib	
Mono	3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$	
Di	3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$	
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	$3R$	$6R$	$4R$	$7R$	$\frac{4}{3}$	$\frac{7}{6}$

In a monatomic molecule  $E = 3RT/2$  is in agreement with the simple model. For a diatomic molecule, there are three translational, two rotational (because the molecule is linear) and One vibrational degree of freedom making a total of six. The thermal energy per mole.

$$\bar{E} = \left(\frac{1}{2}RT\right)_{trans} + \left(\frac{1}{2}RT\right)_{rot} + (1RT)_{vib}$$

and  $\bar{C}_V = 3R/2 + R + R = 7R/2 = 7 \text{ cal deg}^{-1} \text{ mol}^{-1}$

Table shows that the observed of  $\bar{C}_V$  for diatomic deviate greatly from the predicted values. The fact that the observed values of  $5 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (which is close to  $5R/2$ ) is most common for simple diatomic molecules shows that vibration degree of freedom are active only at very high temperature. The following graph shows.



Variation of heat capacity at constant volume of a di atomic gas due to excitation of rotational and vibrational levels.

**Note :** Variation of  $C_V$  with temperature highlights the fact that with increase in the temperature the vibration modes of motion also contribute to the heat capacity

\* **Adiabatic exponent :** Adiabatic exponent ( $\gamma$ ) for a mixture of gas with different heat capacity is defined as :

$$\gamma_{mix} = \frac{n_1 C_{p_1} + n_2 C_{p_2} \dots}{n_1 C_{V_1} + n_2 C_{V_2} \dots}$$

where  $n_1, n_2 \dots$  are moles of different gases.

**Illustration**

1. Calculate change in internal energy of 10 gm of  $H_2$ , when its state is changed from (300K, 1 Atm) to (500 K, 2 Atm)

**Sol.** For ideal gas

$$\Delta U = nC_V(T_2 - T_1) = \left(\frac{10}{2}\right)\left(\frac{5}{2}R\right)(500 - 300) = 2500 R = 5 \text{ Kcal}$$

$C_V$  for  $H_2$  (diatomic) in low temperature range will be  $5R$  as vibrational part is not included.

2. Calculate change in internal energy for a gas under going from state-I (300 K,  $2 \times 10^{-2} \text{ m}^3$ ) to state-II (400 K,  $4 \times 10^{-2} \text{ m}^3$ ) for one mol. of vanderwaal gas.  
[ $C_V = 12 \text{ J/K/mol}$ ]

$$\left\{ \text{Given: } \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \right.$$

$$C_V = 12 \text{ J/k/mol}$$

$$a = 2 \text{ J.m./mol}^2 \quad \left. \right\}$$

**Sol.**  $\Delta U = C_V(T_2 - T_1) + a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) = C_V(100) + a \left( \frac{1}{4} \right) \times 10^2 = 12 \times 100 + 2 \left( \frac{1}{4} \right) \times 100 = 1250$

**Exercise**

1. Calculate change in internal energy of  $CO_2$  for two mole, if temperature change is 100 K in very high temperature range.

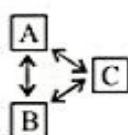
**Ans.**  $2 \times 100 \times \frac{13R}{2} = 1300 \text{ R}$

( $CO_2$  is triatomic linear molecule)

**FIRST LAWS OF THERMODYNAMICS**

Laws of thermodynamic are deduced from experimental observation with logical reasons. There are four laws :

1. **Zeroth law of thermodynamics :** It is bases on thermal equation two system in thermal equation with a 3rd system are also in thermal equation with each other.



## 2. First law of Thermodynamics

"Total energy of universe remain 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 now done on the system, the internal energy in the final state of the system,  $U_2$  is given by

$$U_2 = U_1 + q + w$$

$$\text{or } U_2 - U_1 = q + w$$

$$\Delta U = q + w,$$

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

1. The pressure of a fluid is a linear function of volume ( $P = a + bV$ ) and the internal energy of the fluid is  $U = 34 + 3PV$  (S.I. units). Find  $a$ ,  $b$ ,  $w$ ,  $\Delta E$  and  $q$  for change in state from (100 Pa, 3m<sup>3</sup>) to (400 Pa, 6m<sup>3</sup>)

**Sol.**  $w = - \int_{v_1}^{v_2} P dV$   $(100 = a + 3b ; 400 = a + 6b ; a = -200 \text{ & } b = 100)$

$$w = - \int_{v_1}^{v_2} (a + bV) dV = - \left\{ [aV] + \left[ \frac{bV^2}{2} \right] \right\}_{v_1}^{v_2}$$

$$= - [-600 + 13.5 \times 100] = -750$$

$$\Delta U = 6300$$

### Exercise

1. One mole of an ideal gas expands from state-I (1 Atm, 20 litre) to (2 Atm, 10 litre) isothermally. Calculate,  $w$  &  $\Delta U$ .

**Ans.**  $\Delta U = 0$ ,  $w = -nRT \ln \left( \frac{V_2}{V_1} \right) = P_1 V_1 \ln \left( \frac{V_2}{V_1} \right) = -20 \ln 2 = -14 \text{ lit-atm}$

### ENTHALPY

Enthalpy is a measure of the total energy of a thermodynamic system. It includes the internal energy, which is the energy required to create a system, and the amount of energy required to make space for it by displacing its environment and establishing its volume and pressure.

The enthalpy of a system is defined as:

$$H = U + PV$$

so

$$dH = dU + d(PV)$$

where

$H$  is the enthalpy of the system

$U$  is the internal energy of the system

$P$  is the pressure at the boundary of the system and its environment

$V$  is the volume of the system.

Note that the  $U$  term is equivalent to the energy required to create the system, and that the  $PV$  term is equivalent to the energy that would be required to "make space" for the system if the pressure of the environment remained constant.

#### Property of Enthalpy parameter

1. Enthalpy is a thermodynamic potential. It is a state function and an extensive quantity.
2. The total enthalpy, (absolute value)  $H$ , of a system cannot be measured directly. Thus, change in enthalpy,  $\Delta H$ , is a more useful quantity than its absolute value.
3. The unit of measurement for enthalpy (SI) is joule.
4. The enthalpy is the preferred expression of system energy changes in many chemical and physical measurements, because it simplifies certain descriptions of energy transfer. This is because a change in enthalpy takes account of energy transferred to the environment through the expansion of the system under study.
5. The change  $\Delta H$  is positive in endothermic reactions, and negative in exothermic processes.  $\Delta H$  of a system is equal to the sum of non-mechanical work done on it and the heat supplied to it.
6. For quasistatic processes under constant pressure,  $\Delta H$  is equal to the change in the internal energy of the system, plus the work that the system has done on its surroundings. This means that the change in enthalpy under such conditions is the heat absorbed (or released) by a chemical reaction.

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.

$$\Delta H = q_p - \text{Heat added at constant pressure}$$

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**Note :**

- 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.
- For a given system

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

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

- For isobaric process :  $dP = 0$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$dH = C_P \cdot dT$$

$$\Delta H = \int C_P dT$$

- For an ideal gas, change in enthalpy at constant temperature with change in pressure is zero.  
i.e.

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \Rightarrow dH = C_P \cdot dT \Rightarrow \Delta H = \int C_P dT$$

- (A) Relationship between  $\Delta H$  &  $\Delta U$  :** The difference between  $\Delta H$  &  $\Delta U$  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

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

- (B) Difference between enthalpy and internal energy :** Chemists routinely use  $H$  as the energy of the system, but the  $pV$  term is not stored in the system, but rather in the surroundings, such as the atmosphere. When a system, for example,  $n$  mole of a gas of volume  $V$  at pressure  $P$  and temperature  $T$ , is created or brought to its present state from absolute zero, energy must be supplied equal to its internal energy  $U$  plus  $pV$ , where  $pV$  is the work done in pushing against the ambient (atmospheric) pressure. This additional energy is, therefore, stored in the surroundings and can be recovered when the system collapses back to its initial state. In basic chemistry scientists are typically interested in experiments conducted at atmospheric pressure, and for reaction energy calculations they care about the total energy in such conditions, and therefore typically need to use  $H$ . In basic physics and thermodynamics. It may be more interesting to study the internal properties of the system and therefore the internal energy is used.

**Illustration**

1. 1 mole of a real gas is subjected to a process from (2 bar, 40 lit., 300K) to (4 bar, 30 lit., 400 K). If change in internal energy is 20 kJ then calculate enthalpy change for the process.

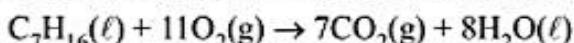
**Sol.**  $\Delta H = \Delta U + \Delta(PV)$

$$\Delta(PV) = P_2 V_2 - P_1 V_1 = 4 \times 30 - 2 \times 40 = 40 \text{ l-bar} = 4 \text{ kJ}$$

$$\Delta H = 20 + 4 = 24$$

**Exercise**

1. 1150 kcal heat is released when following reaction is carried out at constant volume 27°C



Find the heat change at const. pressure.

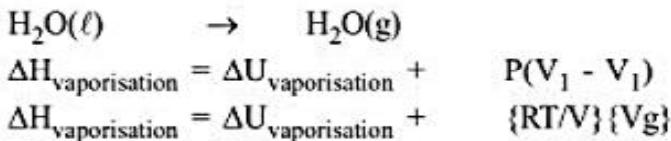
**Ans.** -1152.4 KCal

- (C) **Change in internal energy and enthalpy in phase transition :-** At certain temperature under one atmospheric pressure, one phase change into other phase by taking certain amount of Heat. The temperature at which this happens is called transition temperature and heat absorbed during the process is called Enthalpy of phase transition. Heat absorbed during transition is exchanged at constant pressure and temperature and it is significant to know that the process is reversible.

**Fusion :-** Solid ice at 273 K and 1 atm pressure reversibly changes into liquid water. Reversibly, isothermally and isobarically, absorbed heat is known as latent heat of fusion or enthalpy of fusion.

**Vaporisation :-** Water at 373K and 1 atm pressure changes into vapors absorbed heat is known as latent heat of vaporisation. The latent heat of vaporisation is heat exchanged isothermally, isobarically and reversibly to convert water into its vapour at boiling point.

Internal energy change of phase transitions involving gas phase has no practical significance because it is not possible to carry out  $\Delta U$  of phase transition directly through an experiment. However  $\Delta U$  of phase transition can be determined theoretically from experimentally obtained value of  $\Delta H$  of phase transition.



Ignore volume of liquid as it is very less compared to gas under normal pressure.

$$\Rightarrow \Delta H_{\text{vap.}} = \Delta U_{\text{vap.}} + RT$$

where R is gas constant and T absolute temperature for condensed phase transitions for solid liquid transitions

$$\Delta H_{\text{vap.}} \approx \Delta U_{\text{vap.}}$$

## CALCULATION OF WORK DONE IN VARIOUS PROCESS

- 1. Isothermal process :** In isothermal process, work done can be calculated as

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

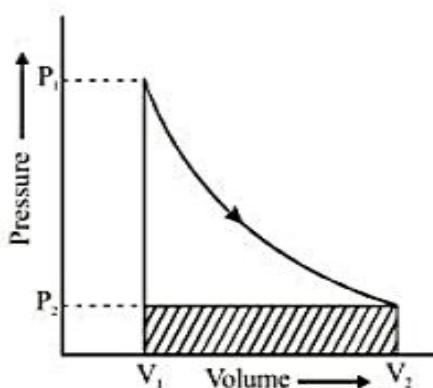
Since  $dT = 0 \Rightarrow dU = 0$  for an ideal gas

from 1<sup>st</sup> law  $q = -w$

- (A) If process is reversible

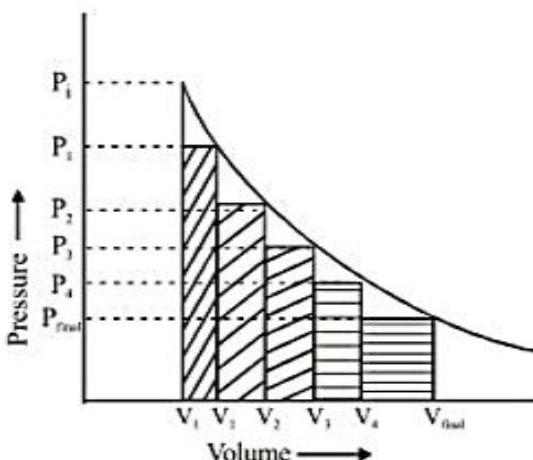
$$W = -nRT \ln \frac{V_2}{V_1}$$

- (B) **Irreversible isothermal expansion :** If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium of system is disturbed and piston rushes out : This type of P.V work is irreversible P.V work. To calculate irreversible P.V work. Law of conservation of energy is used. Suppose as a result of difference in pressure a piston moves out and acquire kinetic energy  $\Delta KE$  and in the process volume increase by  $\Delta V$  then  $w_{irr} = -P_{ext} \Delta V - \Delta KE$ . If after sufficient times piston come back to equilibrium state (off course in the process it moves up and down from equilibrium position many times),  $\Delta KE = 0$  : All the acquired kinetic energy is transferred back to ideal gas.



- (C) **Irreversible isothermal expansion and compression (Many steps)**

Consider an irreversible expansion of an ideal gas from initial pressure  $P_1$  to final pressure  $P_1$  in four steps. The gas is allowed to expand against constant external pressure of  $P_1, P_2, P_3$  and  $P_4$  and finally  $P_1$ . Hence the system passes on to final state through four equilibrium states. The work done in the process is shown graphically. The area under the isotherm is the magnitude of reversible work. Clearly the magnitude of reversible work of expansion is greater than irreversible work. As the number of intermediate steps in irreversible expansion is increased, the magnitude of work increases, and as number of steps tend to infinity  $w_{irr}$  tends to  $w_{rev}$ . The graphical comparison of irreversible and reversible work is shown in fig.



- (D) **Free expansion of ideal gas :** When ideal gas is allowed to expand against zero external pressure, the process is called free expansion.  $W=0$  for free expansion. During the free expansion, the ideal gas do not lose any energy, and hence temperature of ideal gas remains constant. Hence, free expansion of ideal gas is an example of isothermal, adiabatic irreversible process.

However if a real gas is allowed to expand in vacuum, the gas may be cooled or heated up depending upon temperature of the real gas. The temperature above which a gas gets heated up upon expansion is called **inversion temperature**.

#### Important points :

- If the reversible isothermal expansion is reversed by gradually increasing the pressure the system will return to initial state retracing it's path. This means path of reversible process can be exactly reversed if conditions are reversed.
- Work done by the system during reversible isothermal expansion is maximum possible work obtainable from system under similar condition.

#### Illustration

- One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Calculate  $q$ ,  $w$ ,  $\Delta U$  &  $\Delta H$  under the following conditions.
  - Expansion is carried out reversibly.
  - Expansion is carried out irreversibly

**Sol.** Isothermal process

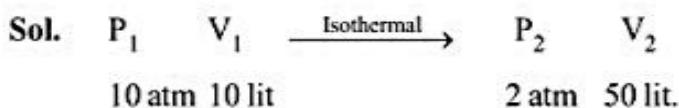
$$(i) \text{ For ideal gas } \Delta U = 0 \quad \Delta H = 0$$

$$q = -w$$

$$w_{rev} = -nRT \ln \frac{P_f}{P_i} = -1 \times R \times 300 \ln \frac{10}{1} = -690.9R$$

$$(ii) W_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right) = -1 \times 1 \times R \times 300 \left[ \frac{1}{1} - \frac{1}{10} \right] = -270R$$

2. One mol an ideal gas is expanded from (10 atm, 10 lit). (2 atm, 50 lit) isothermally. First against 5 atm then against 2 atm. Calculate work done in each step and compare it with single step work done.

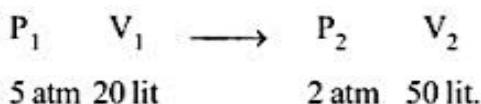


(i) Work done against 5 atm pressure  $\left( \begin{matrix} P_1 & V_1 \\ 10 \text{ atm} & 10 \text{ lit} \end{matrix} \longrightarrow \begin{matrix} P_2 & V_2 \\ 5 \text{ atm} & 20 \text{ lit} \end{matrix} \right)$

$$\text{Vol. of system at 5 atm} = \frac{10 \times 10}{5} = 20 \text{ lit.}$$

$$W_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -5(20 - 10) = -50 \text{ atm lit.}$$

(ii) Work done against 2 atm



$$W_{\text{irr.}} = -P_{\text{ext}}(V_2 - V_1) = -2 \times (50 - 20) = -60 \text{ atm lit.}$$

$$W_{\text{total}} = -50 - 60 = -110 \text{ atm lit.}$$

Total work done in single step.

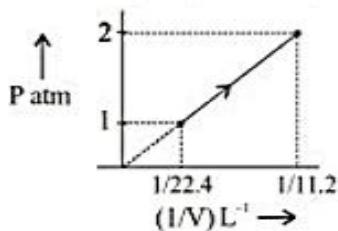


$$W = -2(50 - 10) = -80 \text{ atm lit.}$$

Magnitude of work done in more than one step is more than single step work done.

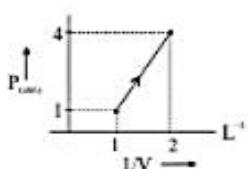
### Exercise

1. Calculate work done for an ideal gas ( $\ln 2 = 0.7$ )



**Ans.**  $W_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -P_1 V_1 \ln \frac{V_2}{V_1} = -22.4 \ln \frac{1}{2} = 22.4 \times 0.7 = 15.68 \text{ L atm.}$

2. Calculate  $w = ?$  ( $\ln 2 = 0.7$ )



**Ans.** P – V Relation from plot

$$P = \frac{3}{V} - 2 \quad \Rightarrow \quad w_{rev} = - \int P \, dv = - \int_1^2 \left( \frac{3}{V} - 2 \right) dv = 1.1 \text{ L atm.}$$


---

2. **Isobaric process :** In isobaric process, pressure remains constant during the process.

$$w = - \int_{V_1}^{V_2} P dV = - P_{ext} (V_2 - V_1) = - nR\Delta T \quad \& \quad \Delta H = q_p$$

3. **Isochoric process :** In isochoric process, volume remains constant during the process.

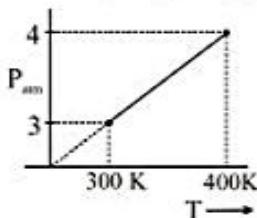
$$\text{Since } dV = 0 \quad \Rightarrow \quad W = 0$$

$$\text{from 1st law} \quad \Delta U = q$$

### Illustration

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1. For 1 mole of monoatomic gas. Calculate  $w, \Delta U, \Delta H, q$



**Sol.** Isochoric process

$$w = 0$$

$$q = dU = C_V (T_2 - T_1) = 3/2 \times (400 - 300) = 150 \text{ R}$$

$$\Delta H = C_P \Delta T = \frac{5}{2} R (400 - 300) = 250 \text{ R}$$


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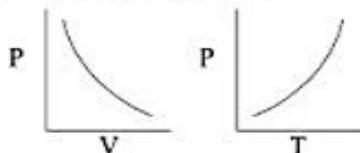
4. **Adiabatic process :** In adiabatic process, heat interaction between system and surrounding is zero

$$q = 0, \quad W = nC_v (T_2 - T_1) = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$


---

Note :

- For irreversible adiabatic process  $nC_V(T_2 - T_1) = -P_{ext} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$
  - Graphical representation of adiabatic process.



### *Illustration*

1. One mole of an non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm. Calculate Work done under the following conditions.

**Sol.**  $g = 0$

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

C<sub>v</sub> for triatomic non linear gas = 3R

(i) For rev. process.

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma \quad \gamma = \frac{4}{3}$$

$$T_2 = T_1 \left( \frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} = 300 \left( 2^4 \right)^{\frac{1}{4}} = 150 \text{ K}$$

$$\Delta U = w = 3R(150 - 300) = -450 \text{ J}$$

(i)  $n = 1$

$$-P_{ext}(V_2 - V_1) = C_V(T_2 - T_1)$$

$$-P_{ext} \left( \frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right) = 3R(T_2 - T_1)$$

$$-\frac{1}{16} \left( \frac{RT_2}{1} - \frac{RT_1}{16} \right) = 3R(T_2 - T_1), \quad -\frac{R}{16} (16T_2 - T_1) = 3R(T_2 - T_1)$$

$$-16T_2 + T_1 = 48T_2 - 48T_1$$

$$49T_1 = 64T_2$$

$$T_2 = \frac{49}{64} \times 300 \Rightarrow T_2 = 229.69$$

$$w_{irr} = C_v (T_2 - T_1) + 3R (229.69 - 300) = -210.93 \text{ R}$$

**Exercise**

1. One mole of a non linear triatomic ideal gas is compressed adiabatically at 300 K from 1 atm to 16 atm. Calculate Work done under the following conditions.

- (i) Expansion is carried out reversibly
- (ii) Expansion is carried out irreversibly

**Ans.** (i) 900 R      (ii) 3375 R

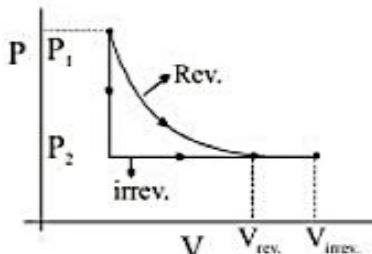
**COMPARISON OF VARIOUS PROCESSES UNDER DEFINED CONDITIONS**

- (A) Graphical comparison between adiabatic reversible and irreversible process:

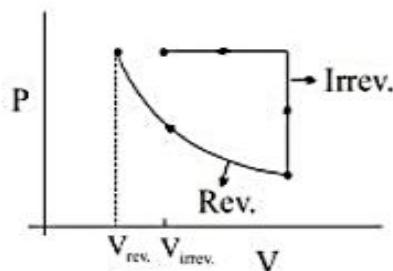
**Case-I :** For same final pressure

(a) Expansion:

$$PV^{\gamma} = \text{const.}$$

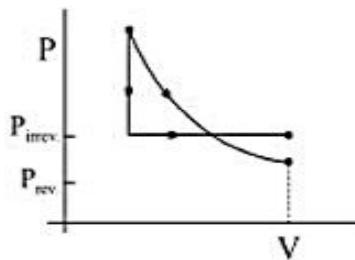


(b) Compression:

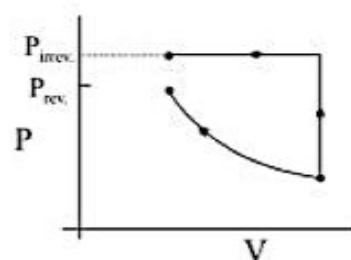


**Case-II :** For same final volume

(a) Expansion



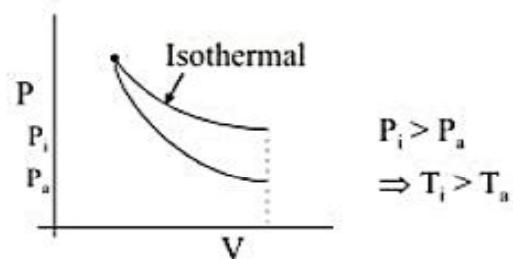
## (b) Compression



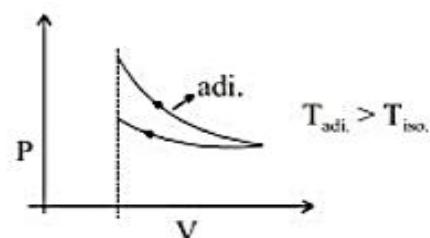
## (B) Comparison between isothermal &amp; adiabatic process:

Case-I : For same final volume

(a) Expansion :

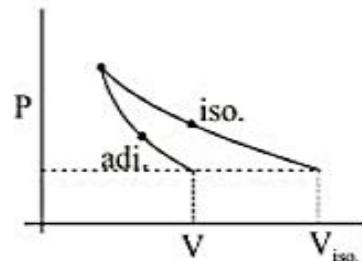


(b) Compression :

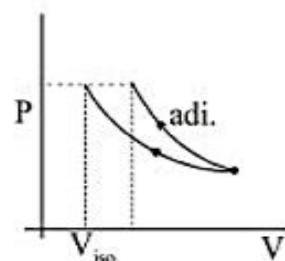


Case-II : For same final pressure

(a) Expansion

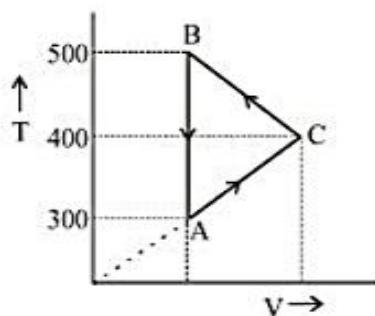


(b) Compression



**Illustration**

1. Calculate work done in process BC for 1 mol of an ideal gas if total 600 cal heat is released by the gas in whole process



**Sol.** For cyclic process

$$dU = 0$$

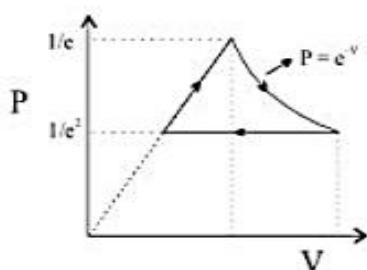
$$q = -w$$

$$q = -(w_{BA} + w_{AC} + w_{CB})$$

$$-600 = -(0 + (-) 2 \times (400 - 300) + w_{CB})$$

$$w_{CB} = 800 \text{ cal}$$

2.



**Sol.**  $w = ?$

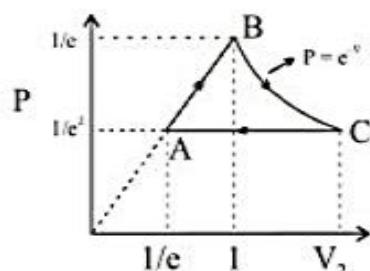
$$e^{-v}$$

$$P = KV$$

$$P = \frac{1}{e} V$$

$$\frac{1}{e^2} = KV_1$$

$$\frac{1}{e} = KV_2$$



$$\text{For AB } P = KV \Rightarrow P = \frac{1}{e} V \quad \frac{V_1}{V_2} = \frac{1}{e}$$

$$w_{AB} = - \int_{\frac{1}{e}}^1 \frac{1}{e} V dV = \frac{-1}{2e} \left[ 1 - \frac{1}{e^2} \right]$$

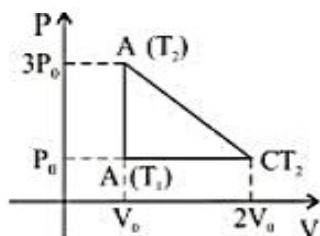
$$w_{BC} = - \int_1^2 e^{-V} dV = + [e^{-V}]_1^2 = + [e^{-2} - e^{-1}] = \frac{-1}{e} + \frac{1}{e^2}$$

$$w_{CA} = - \frac{1}{e^2} \left( \frac{1}{e} - 2 \right) = \frac{-1}{e^3} + \frac{2}{e^2}$$

$$w_{\text{Total}} = w_{AB} + w_{BC} + w_{CA} = \frac{-1}{2e} + \frac{1}{2e^3} + \frac{1}{e^2} - \frac{1}{e} - \frac{1}{e^3} + \frac{2}{e^2} = \frac{-1}{2e^3} + \frac{3}{e^2} - \frac{3}{2e}$$

**Exercise**

1. One mole of an ideal monoatomic gas is taken in cyclic process ABCA as shown in the figure



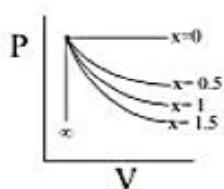
Calculate :

- (a) The work done by the gas
- (b) The heat rejected by the gas in the path CA
- (c) The net heat absorbed by the gas in the path BC
- (d) Maximum temperature obtained by the gas during the cycle.

**Ans.** (a)  $+ 3 P_0 V_0$       (b)  $- 5/2 P_0 V_0$       (c)  $+ P_0 V_0 / 2$       (d)  $+ 3 P_0 V_0 / R$

**Polytropic process :** For polytropic process, value of exponential constant are different for various process.

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



$x = 0$ , Isobaric process

$x = 1$ , Isothermal process

$x = \gamma$ , Adiabatic process

$x = \infty$ , Isochoric process

## SECOND LAW OF THERMODYNAMICS

The essence of first law is that all physical and chemical processes take place in such a manner that the total energy of the universe remain constant.

However, it is observed that all processes have a natural direction ,i.e. a direction in which they take place spontaneously. First law fails to answer this. Another feature of the spontaneous processes is that they proceed only until an equilibrium is achieved. The direction of a spontaneous process and that it eventually reaches equilibrium, can be understood on the basis of entropy concept introduced through the second law of thermodynamics.

**The second law can be expressed in alternative forms as below :**

**(A) Clausius statement**

Clausius is credited with the first formulation of the second law, now known as the Clausius statement  
*"No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature."*

Spontaneously, heat cannot flow from cold regions to hot regions without external work being performed on the system, which is evident from ordinary experience of refrigeration, for example. In a refrigerator, heat flows from cold to hot, but only when forced by an external agent, a compressor.

**(B) Kelvin statement**

The Kelvin statement expressed the second law in another form :

*"No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work."*

This means it is impossible to extract energy by heat from a high-temperature energy source and then convert all of the energy into work. At least some of the energy must be passed on to heat a low-temperature energy sink. Thus, a heat engine with 100% efficiency is thermodynamically impossible.

This also means that it is impossible to build solar panels that generate electricity solely from the infrared band of the electromagnetic spectrum without consideration of the temperature on the other side of the panel (as is the case with conventional solar panels that operate in the visible spectrum).

Note that it is possible to convert heat completely into work, such as the isothermal expansion of ideal gas However, such a process has an additional result. In the case of the isothermal expansion, the volume of the gas increases and never goes back without outside interference.

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**Corollaries:****(A) Perpetual motion of the second kind**

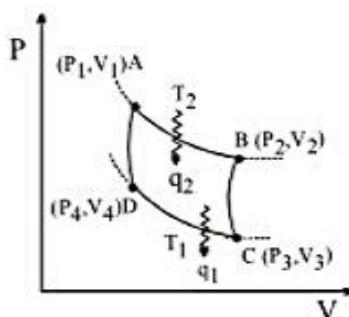
Prior to the establishment of the Second Law, many people who were interested in inventing a perpetual motion machine had tried to circumvent the restrictions of First Law of Thermodynamics by extracting the massive internal energy of the environment as the power of the machine. Such a machine is called a "perpetual motion machine of the second kind". The second law declared the impossibility of such machines.

**(B) Carnot theorem**

Carnot's theorem is a principle that limits the maximum efficiency for any possible engine. The efficiency solely depends on the temperature difference between the hot and cold thermal reservoirs. Carnot's theorem states:

- \* All irreversible heat engines between two heat reservoirs are less efficient than a Carnot engine operating between the same reservoirs.
- \* All reversible heat engines between two heat reservoirs are equally efficient with a Carnot engine operating between the same reservoirs.

**The thermodynamic cycle for carnot engine is given below :**

**Carnot cycle**

AB – Isothermal reversible expansion

$$q_2 = -w_{AB} = nRT_2 \ln \frac{V_2}{V_1}$$

BC – adiabatic reversible expansion

$$w_{BC} = C_V (T_1 - T_2)$$

CD – Isothermal reversible compression

$$q_1 = -w_{CD} = nRT_1 \ln \left( \frac{V_4}{V_3} \right)$$

DA – adiabatic reversible compression

$$w_{DA} = C_V (T_2 - T_1)$$

$$\text{Carnot efficiency } \eta = \frac{-w_{\text{Total}}}{q_2} = \frac{q_1 + q_2}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \text{ for rev. cycle}$$

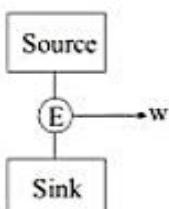
$$\oint \frac{dq_{\text{rev}}}{T} = \oint dS = 0$$

Entropy (denoted by S) is a state function.

$$\Delta S = \int \frac{dq_{rev}}{T}$$

### Statements of second law of thermodynamics

- (i) No cyclic engine is possible which take heat from one single source and in a cycle completely convert it into work without producing any change in surrounding.



### Illustration

1. Calculate maximum ' $\eta$ ' for an heat engine operating between  $27^\circ\text{C}$  to  $127^\circ\text{C}$ .

Sol.  $\eta = \frac{T_2 - T_1}{T_2} = \frac{400 - 300}{400} = 25\%$

## ENTROPY

Entropy is a thermodynamic property that can be used to determine the energy available for useful work in a thermodynamic process, such as in energy conversion devices. In thermodynamics, entropy is commonly associated with the amount of order, disorder, of a thermodynamic system.

$$dS = \frac{dq_{rev}}{T}$$

Thermodynamic entropy has the dimension of energy divided by temperature, and a unit of joules per Kelvin (J/K) in the International System of Units

To highlight the importance and developing below are various definitions of entropy:

- Entropy - a measure of the unavailability of a system's energy to do work; also a measure of disorder; the higher the entropy the greater the disorder.
- Entropy - a measure of disorder; the higher the entropy the greater the disorder.
- Entropy - in thermodynamics, a parameter representing the state of disorder of a system at the atomic, ionic, or molecular level; the greater the disorder the higher the entropy.

### Properties of entropy change ( $\Delta S$ ):

1. The value of the entropy of a system of atoms and molecules in a thermodynamic system is a measure of the disorder in the arrangements of its particles.
2. In solids, which are typically ordered on the molecular scale, usually have smaller entropy than liquids, and liquids have smaller entropy than gases and colder gases have smaller entropy than hotter gases.

3. Moreover, according to the third law of thermodynamics, at absolute zero temperature, crystalline structures are approximated to have perfect "order" and zero entropy.
4. Entropy and disorder also have associations with equilibrium. Entropy, from this perspective, is defined as a thermodynamic property which serves as a measure of how close a system is to equilibrium
5. In a stretched out piece of rubber, the arrangement of the molecules of its structure has an "ordered" distribution and has zero entropy, while the "disordered" kinky distribution of the atoms and molecules in the rubber in the non-stretched state has positive entropy
6. In a gas, the order is perfect and the measure of entropy of the system has its lowest value when all the molecules are in one place, whereas when more points are occupied the gas is all the more disorderly and the measure of the entropy of the system has higher value
7. The mathematical basis with respect to the association entropy has with order and disorder is given by famous Boltzmann formula:

$$S = k \ln W$$

Which relates entropy S to the number of possible states W in which a system can be found

8. It is obvious that entropy is a measure of order or, most likely, disorder in the system. Second law of thermodynamics, as famously enunciated by Clausius in 1865, states that: "The entropy of the universe tends to a maximum"
9. Entropy is also a measure of the tendency of a process, such as a chemical reaction, to be entropically favored, or to proceed in a particular direction

### **Physical significance of entropy**

One can think entropy as a measure of the degree of randomness or disorder in a system. The greater the disorder, in a system, the higher is the entropy.

#### ***Prediction of sign of $\Delta S$ using the concept of Randomness.***

- (i) With change in temperature at constant 'V'

$$\text{As } T \uparrow \text{es } S \uparrow \text{es} \Rightarrow \Delta S_{\text{sys}} > 0$$

- (ii) Change in volume at constant T

$$\text{As } V \uparrow \text{es } S \uparrow \text{es} \Rightarrow \Delta S_{\text{sys}} > 0$$

- (iii) For phase change

$$S_{\text{solid}} < S_{\text{liquid}} << S_{\text{gas}}$$

- (iv) In chemical reaction, entropy change ( $\Delta S$ )

- (a) Involving only solids and liquids entropy change will be small

eg. entropy of graphite > diamond (only when we know the structure or any other property).

- (b) Involving gases

$$\text{If } (\Delta n)_g > 0 \Rightarrow (\Delta S) > 0$$

$$\text{If } (\Delta n)_g < 0 \Rightarrow (\Delta S) < 0$$

$$\text{If } (\Delta n)_g = 0 \Rightarrow (\Delta S) \neq 0$$

(v) As atomicity  $\uparrow$  es disorder  $\uparrow$  es

$$1 \text{ mol.} \quad 1 \text{ mol}$$

$$S_{\text{NO(g)}} < S_{\text{NO}_2\text{(g)}}$$

$$S_{\text{CH}_4} < S_{\text{C}_2\text{H}_6}$$

(vi) For the molecules having same atomicity, entropy will be more for the substance having more molecular mass.

(vii) In an irreversible process entropy of universe increases but it remains constant in a reversible process.

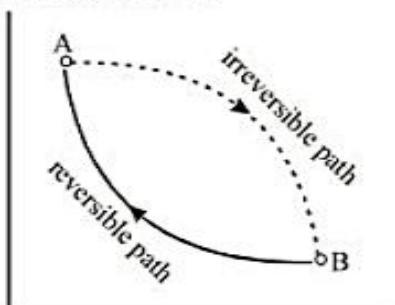
$$\Delta S_{\text{syst}} + \Delta S_{\text{surr}} = 0 \quad \text{for rev. process}$$

$$\Delta S_{\text{syst}} + \Delta S_{\text{surr}} > 0 \quad \text{for irrev. process}$$

$$\Delta S_{\text{syst}} + \Delta S_{\text{surr}} \geq 0 \quad (\text{In general})$$

### Entropy change in isolated system (isolated system = sys + surr)

Consider a system taken state A to state B by an irreversible path and returned to state A by a reversible path. Since one of the step is irreversible, according to classius inequality, sum of  $q/T$  over the cycle must be less than zero. Hence



$$\sum_{A \rightarrow B} \frac{q_{\text{irr}}}{T} + \sum_{B \rightarrow A} \frac{q_{\text{rev}}}{T} \leq 0 \Rightarrow \sum_{A \rightarrow B} \frac{q_{\text{irr}}}{T} \leq - \sum_{B \rightarrow A} \frac{q_{\text{rev}}}{T}$$

$$\text{But } - \sum_{B \rightarrow A} \frac{q_{\text{rev}}}{T} = \sum_{A \rightarrow B} \frac{q_{\text{rev}}}{T} \text{ since the process is reversible}$$

for infinitesimally small change

$$\left( \frac{dq_{\text{rev}}}{T} \right)_{A \rightarrow B} = dS_{\text{system} A \rightarrow B}$$

$$dS_{\text{system}} - \left( \frac{dq}{T} \right)_{A \rightarrow B} > 0$$

$$dS_{\text{system} A \rightarrow B} + dS_{\text{surr} A \rightarrow B} > 0$$

$$\Delta S_{\text{Total isolated sys}} > 0$$

Entropy calculation in process involving ideal gases.

From First law

$$dq = dU + PdV$$

$$\Rightarrow \frac{dq_{\text{rev}}}{T} = \frac{dU}{T} + \frac{PdV}{T}$$

But for ideal gas

$$\frac{dU}{T} = \frac{nC_V dT}{T} \quad \{\because dU = nC_V dT\}$$

$$\Rightarrow dS_{sys} = \frac{nC_V dT}{T} + \frac{nR}{V} dV$$

Integration gives

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \left( \frac{V_2}{V_1} \right)$$

General Expression, for any process

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

**Entropy calculation for various process is given below.**

**(A) Isothermal process**

Reversible & irreversible isothermal expansion and contraction of an ideal gas

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

For surroundings

$$\Delta S_{surr} = -\Delta S_{sys} \text{ (for reversible)}$$

$$\Delta S_{surr} = \frac{q_{surr}}{T} \text{ (for irreversible)}$$

**(B) Isobaric process**

$$\Delta U = C_V \Delta T$$

$$\Delta H = C_p \Delta T = q_p$$

$$\Delta S_{sys} = nC_p \ln \left( \frac{T_2}{T_1} \right)$$

For surroundings

$$\Delta S_{surr} = -\Delta S_{sys} \text{ (for reversible)}$$

$$\Delta S_{surr} = \frac{q_{surr}}{T} \text{ (for irreversible)}$$

**(C) Isochoric process**

$$\Delta U = C_V \Delta T = q_v$$

$$\Delta H = C_p \Delta T$$

$$\Delta S_{\text{sys}} = nC_V \ln \left( \frac{T_2}{T_1} \right)$$

For surroundings

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} \text{ (for reversible)}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ (for irreversible)}$$

#### (D) Adiabatic process

$$\Delta U = C_V \Delta T$$

$$\Delta H = C_P \Delta T$$

$$\Delta S_{\text{sys}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \text{ for irreversible process}$$

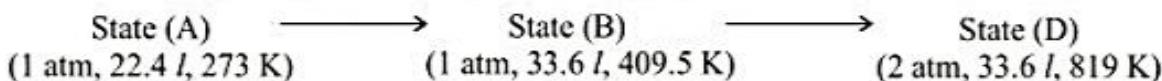
$\Delta S_{\text{sys}} = 0$  for reversible adiabatic compression and expansion.

For surroundings

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} \text{ (for irreversible)}$$

#### Illustration

1. Calculate entropy change in each step for an ideal gas (monoatomic)



Sol.  $\Delta S_{A-B} = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = nC_P \ln \frac{409.5}{273} = C_P \ln \frac{3}{2}$

$$\Delta S_{AC} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_V \ln \frac{546}{273} = C_V \ln 2$$

2. One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Find the values of  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  &  $\Delta S_{\text{total}}$  under the following conditions.

- (i) Expansion is carried out reversibly
- (ii) Expansion is carried out irreversibly
- (iii) Expansion is free.

Sol.(i)  $\Delta S_{\text{sys}} = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0 + R \ln 10 = R \ln 10$

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys}} = -R \ln 10$$

$$\Delta S_{\text{total}} = 0$$

(ii)  $\Delta S_{sys} = R \ln 10$

$$\Delta S_{surr} = \frac{-q_{irr}}{T}$$

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

$$q_{irr} = p_{ext} (v_2 - v_1)$$

$$q_{irr} = p_{ext} \left[ \frac{RT}{P_2} - \frac{RT}{P_1} \right] = RT \left[ \frac{1}{1} - \frac{1}{10} \right] = RT \times \frac{9}{10} = \frac{9}{10} \times R \times 300 = 270R$$

$$\Delta S_{surr} = \frac{-q_{irr}}{T} = \frac{-9R}{10} \Rightarrow \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = R \ln 10 - \frac{9R}{10}$$

(iii) Free expansion  $\Delta T = 0$

$$w = 0$$

$$q = 0$$

$$\Delta S_{sys} = R \ln 10$$

$$\Delta S_{surr} = \frac{-q_{irr}}{T} = 0$$

$$\Delta S_{total} = R \ln 10$$

### Exercise

1. One mole of a non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm. Find the values of  $\Delta S_{sys}$ ,  $\Delta S_{surr}$  &  $\Delta S_{total}$  under the following conditions.
- (i) Expansion is carried out reversibly
  - (ii) Expansion is carried out irreversibly
  - (iii) Expansion is free.

Ans. (i)  $\Delta S_{sys} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0, q = 0, \Delta S_{surr} = -\Delta S_{sys} = \Delta S_{total} = 0$

(ii)  $\Delta S_{sys} = 1.702 \text{ R}, \Delta S_{surr} = 0, \Delta S_{total} = \Delta S_{sys} = 1.702 \text{ R}$

(iii)  $\Delta S_{sys} = nR \ln \frac{P_1}{P_2} = 2.77 \text{ R}, \Delta S_{surr} = \frac{-q_{irr}}{T} = 0, \Delta S_{total} = \Delta S_{sys} = 2.77 \text{ R}$

### (E) Entropy changes for the reactions

$$\Delta S_r = \sum v_p S_{(products)} - \sum v_R S_{(reactants)}$$

Variation of  $\Delta S_r$  with temperature & pressure :

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_p)_r \ln \frac{T_2}{T_1}, \quad (\Delta S_r)_{P_2} - (\Delta S_r)_{P_1} = \Delta n_g R \ln \frac{P_1}{P_2}$$

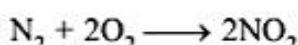
Similarly

$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1) \quad \text{[Krichoff's equation]}$$

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1)$$

### Illustration

1. For the reaction



Given: at 1 atm, 300 K

$$S_{N_2} = 180 \text{ J/mol/K}$$

$$C_p(N_2) = 30 \text{ J/mol/K}$$

$$S_{O_2} = 220 \text{ J/mol/K}$$

$$C_p(O_2) = 30 \text{ J/mol/K}$$

$$S_{NO_2} = 240 \text{ J/mol/K}$$

$$C_p(NO_2) = 40 \text{ J/mol/K}$$

- Calculate (i)  $\Delta S_{300 \text{ K}, 1 \text{ atm}}$   
(ii)  $\Delta S_{400 \text{ K}, 1 \text{ atm}}$

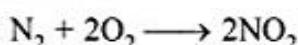
Sol.(i)  $(\Delta S_r)_{300} = 2S_{NO_2} - 2S_{O_2} - S_{N_2} = 2 \times 240 - 2 \times 220 - 180 = -140 \text{ J mol}^{-1}\text{k}^{-1}$

$$(\Delta C_p)_r = 2C_p(NO_2) - 2C_p(O_2) - C_p(N_2) = 2 \times 40 - 2 \times 30 - 30 = -10 \text{ J mol}^{-1} \text{ k}^{-1}$$

(ii)  $(\Delta S_r)_{400} = (\Delta S_r)_{300} + (\Delta C_p)_r \ln \frac{T_2}{T_1} = -140 - 10 \ln \frac{4}{3} = -142.88 \text{ J mol}^{-1} \text{ k}^{-1}$

### Exercise

1. For the reaction



Given: at 1 atm, 300 K

$$S_{N_2} = 180 \text{ J/mol/K}$$

$$C_p(N_2) = 30 \text{ J/mol/K}$$

$$S_{O_2} = 220 \text{ J/mol/K}$$

$$C_p(O_2) = 30 \text{ J/mol/K}$$

$$S_{NO_2} = 240 \text{ J/mol/K}$$

$$C_p(NO_2) = 40 \text{ J/mol/K}$$

- Calculate (i)  $\Delta S_{300 \text{ K}, 5 \text{ atm}}$   
(ii)  $\Delta S_{400 \text{ K}, 5 \text{ atm}}$

Ans. (i)  $(\Delta S_r)_{300, 5 \text{ atm}} = -126.62 \text{ J mol}^{-1} \text{ k}^{-1}$ .

$$(ii) (\Delta S_r)_{400, 5 \text{ atm}} = -129.5 \text{ J k}^{-1} \text{ mol}^{-1}.$$

- (F) **Entropy change during phase change :** During phase change entropy change is measured as

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

### **Illustration**

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1. Calculate entropy change



$$\Delta H_{\text{vap}} = 40 \text{ kJ/mol} \quad C_p(l) = 75 \text{ J/mol/K} \quad C_p(g) = 35 \text{ J/mol/K}$$

- Sol.  $\text{H}_2\text{O} (l, 2 \text{ atm}, 100^\circ\text{C}) \longrightarrow \text{H}_2\text{O} (g, 1 \text{ atm}, 100^\circ\text{C}) \longrightarrow \text{H}_2\text{O} (g, 2 \text{ atm}, 100^\circ\text{C})$
- (A) (B) (C)

$$\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40.000}{373}$$

$$\Delta S_{B \rightarrow C} = n R \ln \frac{P_2}{P_1} = 1 \times R \ln \frac{1}{2}$$


---

### **Exercise**

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1. Calculate entropy change



$$\Delta H_{\text{vap}} = 40 \text{ kJ/mol} \quad C_p(l) = 75 \text{ J/mol/K} \quad C_p(g) = 35 \text{ J/mol/K}$$

$$\text{Ans. } \Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40 \times 1000}{373}, \quad \Delta S_{B \rightarrow C} = n C_p(g) \ln \frac{T_2}{T_1} = 1 \times 35 \ln \frac{383}{373}$$


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## **THIRD LAW OF THERMODYNAMICS**

"At absolute zero, the entropy of a perfectly crystalline substance is taken as zero", which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{\text{rev}}}{T}$$

since  $S_{0K} = 0$

$$S_T = \int_0^T \frac{q_{rev}}{T}$$

Absolute entropies of various substances have been tabulated and these values are used to calculate entropy changes for the reactions.

## GIBBS FREE ENERGY (G) AND SPONTANEITY

Gibbs free energy is a thermodynamics potential that measures the "useful" work obtainable from a thermodynamic system at a constant temperature and pressure. Alternatively, Gibbs energy is the capacity of a system to do non-mechanical work and  $\Delta G$  measures the non-mechanical work done on it.

The term "free" was attached to Gibbs free energy for systems at constant pressure and temperature to mean "available in the form of useful work". However, an increasing number of books do not include the attachment "free", referring to G as simply "Gibbs energy". In 1988 IUPAC meeting the term 'free' was dropped.

IUPAC recommended name: Gibbs energy or Gibbs function

The Gibbs free energy is mathematically defined as:

$$G(p,T) = U + pV - TS$$

which is the same as:

$$G(p,T) = H - TS$$

where:

U is the internal energy (SI unit: joule)

p is pressure (SI unit: pascal)

V is volume (SI unit: m<sup>3</sup>)

T is the temperature (SI unit: kelvin)

S is the entropy (SI unit: joule per kelvin)

H is the enthalpy (SI unit: joule)

### Properties of Gibbs free energy

1. The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a closed system; this maximum can be attained only in a completely reversible process.
2. When a system changes from a well-defined initial state to a well-defined final state, the Gibbs free energy  $\Delta G$  equals the work exchanged by the system with its surroundings, minus the work of the pressure forces, during a reversible transformation of the system from the same initial state to the same final state.
3. Gibbs energy ( $\Delta G$ ) is also the chemical potential that is minimized when a system reaches equilibrium at constant pressure and temperature. Its derivative with respect to the reaction coordinate of the system becomes zero at the equilibrium point.

4. As such, it is a convenient criterion of spontaneity for processes with constant pressure and temperature.
5. The Gibbs free energy the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition.
6. Every system seeks to achieve a minimum of free energy.
7. The energy released equals the maximum amount of work that can be performed as a result of the chemical reaction. In contrast, if conditions indicated a positive  $\Delta G$ , then energy in the form of work would have to be added to the reacting system to make the reaction proceed.
8. Thus the direction of reaction will only be allowed if the total entropy change of the universe is equal to zero (an equilibrium process) or positive and correspondingly gibbs free energy criteria is:
  - A.  $\Delta G > 0$  the process is non-spontaneous
  - B.  $\Delta G = 0$  system is at equilibrium
  - C.  $\Delta G < 0$  the process is spontaneous

A new thermodynamic state function  $G$ , the Gibbs free energy is defined as :

$$G = H - TS$$

at constant temperature and pressure

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

If  $(\Delta G)_{T,P} < 0$  process is irreversible (spontaneous)

$(\Delta G)_{T,P} = 0$  process is reversible

$(\Delta G)_{T,P} > 0$  process is impossible (non spontaneous)

The use of Gibbs free energy has the advantage that it refers to the system only (and not surroundings).

To summaries, the spontaneity of a chemical reaction is decided by two factors taken together:

(i) the enthalpy factor and (ii) the entropy factor.

The equation  $\Delta G = \Delta H - T \Delta S$  takes both the factors into consideration.

$(\Delta H_r)_{T,P}$	$(\Delta S_r)_{T,P}$	$(\Delta G_r)_{T,P}$	Remarks
- ve	+ ve	Always - ve	Reaction is spontaneous
+ ve	- ve	Always + ve	Reaction non spontaneous
+ ve	+ ve	At low temperature, $\Delta G = +$ ve	Non spontaneous
		At high temperature, $\Delta G = -$ ve	Spontaneous
- ve	- ve	At low temperature, - ve	Spontaneous
		At high temperature, +ve	Non spontaneous

### Variation of Gibb's function (G) with temperature and pressure :

$$\begin{aligned} G &= H - TS \\ &= U + PV - TS \\ dG &= dU + PdV - TdS + VdP - SdT \\ dG &= VdP - SdT \end{aligned}$$

- (A) At constant temperature,  $dT = 0$   
for every substance

$$dG = VdP \text{ or } \left( \frac{\partial G}{\partial P} \right)_T = V$$

- (i) For an ideal gas, at constant temperature

$$dT = 0 \text{ and } V = \frac{nRT}{P}$$

So

$$dG = \frac{nRT}{P} dp = nRT/n \frac{p_2}{p_1}$$

- (ii) For solids / liquids, at constant temperature  
 $dT = 0$  and  $V$  is almost constant change in pressure  
So  
 $dG = vdp$  [v = constant]  
 $\Delta G = v(p_2 - p_1)$

- (B) At constant pressure,  $dP = 0$

For any substance

$$dG = -SdT$$

$$\left( \frac{\partial G}{\partial T} \right)_P = -S$$

If in a question, given that  $S = f(T)$ , by integrating  $\Delta G$  can be calculate.

### Relationship between $\Delta G$ & $W_{\text{non-PV}}$

Decrease in Gibb's function at constant temperature and pressure in a process given an estimate or measure of maximum non-PV work which can be obtained from system in reversible, manner.

The example of non-PV work is electric work done by chemical battery.

Expansion of soap bubble at for a closed system capable of doing non-PV work apart from PV work first law can b written as

$$dU = q + W_{\text{PV}} + W_{\text{non-PV}}$$

for reversible process at constant T & P

$$dU + pdV - TdS = W_{\text{non-PV}}$$

$$dH - TdS = W_{\text{non-PV}}$$

$$(dG_{\text{system}})_{T,P} = W_{\text{non-PV}}$$

$$-(dG_{\text{system}})_{T,P} = (W_{\text{non-PV}})_{\text{system}}$$

Non-PV work done by the system = decrease in gibbs free energy

Non-pV work done due to chemical energy transformation of due to composition change and decrease in Gibb's function in a isothermal and isobaric process provide a measure of chemical energy stored in bonds and intermolecular interaction energy of molecules.

### Some facts to be remembered :

(a) Standard condition

(i) For gases / solid / liquid : P = 1 bar

(ii) For ion / substance in solution : concentration = 1 M

$$(b) \Delta G_r = (\Delta G_f)_{\text{product}} - (\Delta G_f)_{\text{reactant}}$$

$$\Delta H_r = (\Delta H_f)_{\text{product}} - (\Delta H_f)_{\text{reactant}}$$

$$\Delta S_r = (\Delta S_f)_{\text{product}} - (\Delta S_f)_{\text{reactant}}$$

### THERMODYNAMIC RELATIONSHIP BETWEEN $\Delta G$ AND EQUILIBRIUM CONSTANT

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

$$G_2 = G_1 + RT \ln \frac{P_2}{P_1}$$

$$G_2 = G^\circ + RT \ln \frac{P_2}{1\text{bar}}$$

Consider a reaction A + B  $\longrightarrow$  C

$$G_A = G_A^\circ + RT \ln \frac{P_A}{1\text{bar}}$$

$$G_B = G_B^\circ + RT \ln \frac{P_B}{1\text{bar}}$$

$$G_C = G_C^\circ + RT \ln \frac{P_C}{1\text{bar}}$$

$$\Delta G_r = G_r^\circ + RT \ln \left( \frac{P_C}{\left( \frac{P_A}{1\text{bar}} \right) \left( \frac{P_B}{1\text{bar}} \right)} \right)$$

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q \quad [Q = \text{Reaction quotient}]$$

$$\Delta G_r^\circ = -RT \ln K_{eq} \quad (\text{At eqm. } (\Delta G_r)_{T,P} = 0)$$

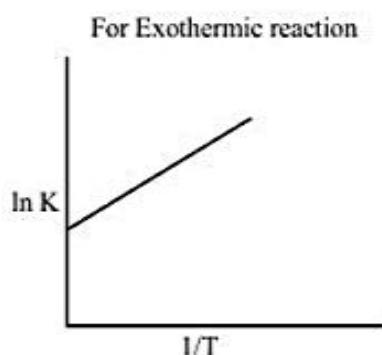
$$\Delta G_r^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K_{eq} = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

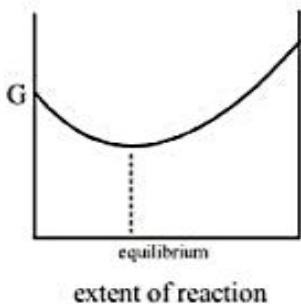
$$\ln K_1 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{KT_2}$$

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$



- \* **For a chemical reaction :** During a chemical reaction, reaction proceeds in that direction in which  $\Delta G < 0$  or value of  $G$  decreases and attains lowest value at equilibrium condition as shown in the figure. Moreover as equilibrium condition is changed in either direction, reaction always proceeds towards equilibrium condition



**Clausius Inequality :** Clausius inequality is another way for measuring the irreversibility and spontaneity of a process.

In mathematical term, it can be expressed as-

$$TdS \geq q$$

$$TdS \geq dU - w$$

at constant temperature & pressure

$$d(U - TS + PV) \leq 0$$

$$(H - TS) \leq 0$$

$$dG \leq 0$$

---

*Illustration*

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1. Calculate  $\Delta G$  for

- (i)  $H_2O(l, 1 \text{ atm}, 300 \text{ K}) \longrightarrow H_2O(g, 1 \text{ atm}, 300 \text{ K})$
- (ii)  $H_2O(l, 2 \text{ atm}, 373 \text{ K}) \longrightarrow H_2O(g, 2 \text{ atm}, 373 \text{ K})$

Given :  $\Delta H_{373} = 40 \text{ kJ}$

$$C_p(H_2O,l) = 75 \text{ J/mol/K}$$

$$C_p(H_2O,g) = 35 \text{ J/mol/K}$$

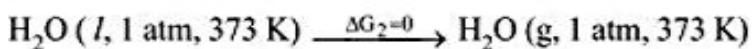
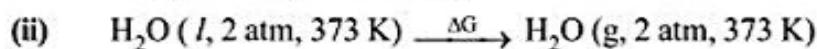
Sol.(i)  $\Delta H_{300} - \Delta H_{373} = (-40)(-73)$

$$\Delta H_{300} = 42920$$

$$\Delta S_{373} = \frac{40 \times 10^3}{373}$$

$$\Delta S_{300} = \Delta S_{373} + 40 \ln \frac{373}{300}$$

$$\Delta G_{300} = \Delta H_{300} - 300 \Delta S_{300}$$



$$\Delta G = V(1-2) + \Delta G_2 + nRT \ln \frac{2}{1}$$

---

*Exercise*

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1. Calculate  $\Delta G$  for

- (i)  $H_2O(l, 2 \text{ atm}, 300 \text{ K}) \longrightarrow H_2O(g, 2 \text{ atm}, 300 \text{ K})$
- (ii)  $H_2O(l, p \text{ atm}, 300 \text{ K}) \longrightarrow H_2O(g, p \text{ atm}, 300 \text{ K})$  Calculate  $p$  for which  $\Delta G = 0$

Given :  $\Delta H_{373} = 40 \text{ kJ}$

$$C_p(H_2O,l) = 75 \text{ J/mol/K}$$

$$C_p(H_2O,g) = 35 \text{ J/mol/K}$$

Ans. (i)  $\Delta G = V(P_2 - P_1) + [\Delta H_{300} - 300 \Delta S_{300}] + nRT \ln \frac{P_2}{P_1}$

(ii)  $P = 26.28 \text{ atm}$

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## SOLVED EXAMPLE

**Q.1** Value of ' $\gamma$ ' for  $\text{CH}_4$  molecule is (Consider vibrational degree of freedom to be active)

- (A)  $\frac{4}{3}$       (B)  $\frac{13}{12}$       (C)  $\frac{15}{14}$       (D)  $\frac{17}{15}$

**Ans.** (B)

**Sol.**  $C_V = 3R + 9R \Rightarrow 12R$

$$C_P = 13R$$

$$\gamma = \frac{C_P}{C_V} = \frac{13}{12}$$

**Q.2** ' $\gamma$ ' for  $\text{NH}_3$  including contribution from vibrational degree's of freedom is

- (A)  $\frac{4}{3}$       (B)  $\frac{10}{9}$       (C)  $\frac{7}{6}$       (D)  $\frac{13}{12}$

**Ans.** (B)

**Sol.**  $C_V = \frac{n_{\text{lf}}}{2}R + \frac{n_{\text{rot}}}{2}R + n_{\text{vib}}R = \frac{3}{2}R + \frac{3}{2}R + 6R = 9R$

$$C_P = 9R + R = 10R$$

$$\gamma = \frac{C_P}{C_V} = \frac{10}{9}$$

**Q.3** 1 mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 100 litre. Which of the following is false for the process?

- (A)  $\Delta T = 0$       (B)  $\Delta E = 0$       (C)  $\Delta H = 0$       (D) heat supplied ( $q$ ) = 0

**Ans.** (D)

**Hint:** For isothermal process involving ideal gas       $\Delta T = \Delta E = \Delta H = 0$

**Q.4** Pressure over 1 litre of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic condition. If the final volume of the liquid is 990 ml, calculate  $\Delta E$  and  $\Delta H$  of the process assuming linear variation of volume with pressure.

**Sol.** Assuming linear variation of volume with pressure

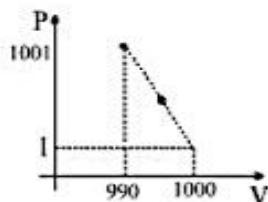
$$W = \text{area under the show line} = (10 \times 10^{-6}\text{m}^3) \times (10^5\text{N/m}^2) + \frac{1}{2}(1000 \times 10^5\text{N/m}^2) \times (10 \times 10^{-6}\text{m}^3)$$

$$= 1 \text{ J} + 500 \text{ J} = 501 \text{ Joule}$$

$$\Delta E = 501 \text{ Joule}$$

$$\begin{aligned} \Delta H &= \Delta E + P_2V_2 - P_1V_1 \\ &= 501 \text{ J} + (1001 \times 10^5 \text{ N/m}^2) \times (990 \times 10^{-6} \text{ m}^3) - (1 \times 10^5 \text{ N/m}^2) \\ &\quad \times (1000 \times 10^{-6} \text{ m}^3) \\ &= 501 \text{ J} + (99 \times 1001 \text{ J}) - (100 \text{ J}) \\ &= 99.5 \text{ kJ} \end{aligned}$$

**Ans.**



**Q.5** One mole of a real gas is subjected to a process from (2 bar, 30 lit., 300 K) to (2 bar, 40 lit., 500 K)

Given :  $C_v = 25 \text{ J/mol/K}$

$C_p = 40 \text{ J/mol/K}$

Calculate  $\Delta U$ ,

(A) 5000 J

(B) 6000 J

(C) 8000 J

(D) 10000 J

**Ans.** (B)

**Sol.**  $\Delta U = q + w$

$$= (40 \times 200) + (-2 \times 10 \times 100)$$

$$= 6000 \text{ J}$$

Ans.

**Q.6** One mole of ideal gas undergoes following cyclic process:

(I) Isochoric heating from  $(P_1, V_1, T_1)$  to double temperature.

(II) Isobaric expansion from to double volume.

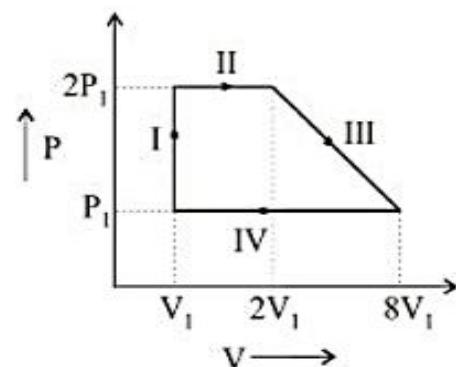
(III) Linear expansion (on PV curve) to  $(P_1, 8V_1)$ .

(IV) Isobaric compression to initial state.

Calculate the magnitude of work done in calories if initial temperature of the gas is 300 K?

Given :  $R = 2 \frac{\text{Cal}}{\text{mol} \cdot \text{K}}$

**Sol.** Magnitude of work  $= A = P_1 V_1 + \frac{1}{2} \times P_1 \times 6 V_1$   
 $= 4 P_1 V_1 = 4 nRT_1$   
 $= 4 \times 1 \times 2 \times 300$   
 $= 2400 \text{ cal}$



**Q.7** Determine the total work done by a gas (in Joule) if system follows an expansion process as shown in figure.

[Given : 1 Bar liter = 100 J]

**Sol.**  $P_B V_B^2 = P_C V_C^2$

or  $50 \times (0.4)^2 = P_C \times (0.8)^2$

or  $P_C = \frac{50 \times 0.4 \times 0.4}{0.8 \times 0.8} = 12.5$

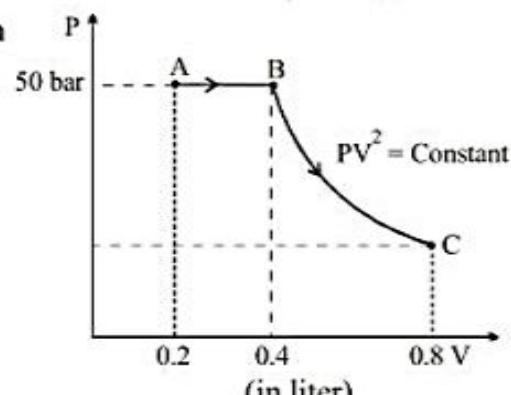
$w = w_{AB} + w_{BC}$

$$= -50(0.4 - 0.2) + \frac{P_C V_C - P_B V_B}{2-1}$$

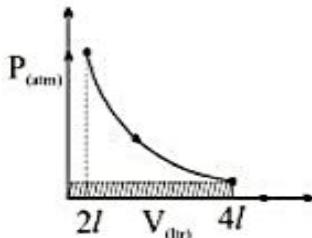
$$= -50 \times 0.2 + \frac{12.5 \times 0.8 - 50 \times 0.4}{1}$$

$$= -10 + (-10) = -20 \text{ bar liter} = -2000 \text{ J}$$

$w_{by} = 2000 \text{ J}$



- Q.9** A student is calculating the work during a reversible isothermal process, shown by 2 moles of an ideal gas. He by mistake calculated the area as shown in the PV graph (Shaded area) equal to 49.26 litre atm. Calculate the correct value of work (in litre atm) during the process.  
(Given :  $R = 0.0821 \text{ litre atm/mol/K}$ )

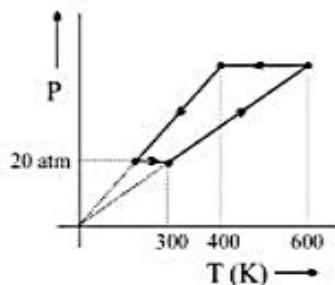


- (A) 49.26      (B) -34.14      (C) -78.63      (D) -98.52

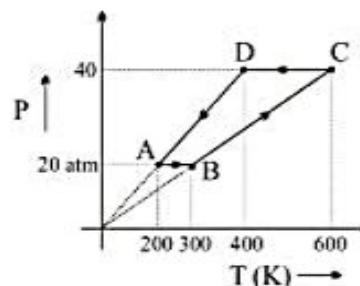
**Sol.** For isothermal process

$$\begin{aligned} W &= -nRT \ln \frac{V_2}{V_1} \\ &= -49.26 \times \ln 2 \quad [\text{Shaded area} = PV = nRT] \\ &= -34.14 \end{aligned}$$

- Q.10** Calculate the magnitude of work done (in atm lit.) for the given cyclic process involving 1 mol of an ideal gas. [Given :  $R = 0.08 \text{ atm lit./mol/K}$ ]



$$\begin{aligned} W_{AB} &= W_{CD} = 0 \\ W_{BC} &= -nR\Delta T = -1 \times R \times 300 = 300 R \\ W_{DA} &= -nR\Delta T = -1 \times R \times -200 = 200 R \\ W_{\text{total}} &= -100 R \\ \Rightarrow |W| &= 8 \text{ lit atm} \end{aligned}$$



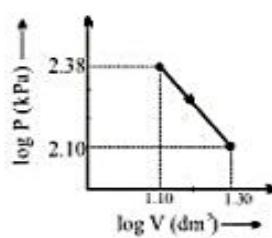
- Q.11**  $\log P$  vs  $\log V$  curve is plotted for an ideal gas, which is true for the gas?

- (A) Monoatomic & undergoing adiabatic change  
(B) Monoatomic & undergoing an isothermal change  
(C) Diatomic & undergoing an adiabatic change  
(D) Triatomic & undergoing an isothermal change

**Ans.** (C)

**Sol.** Equation of process

$$\frac{\log P - 2.38}{\log V - 1.10} = \frac{2.10 - 2.38}{1.30 - 1.10} = \frac{-0.28}{0.20} = \frac{-7}{5}$$



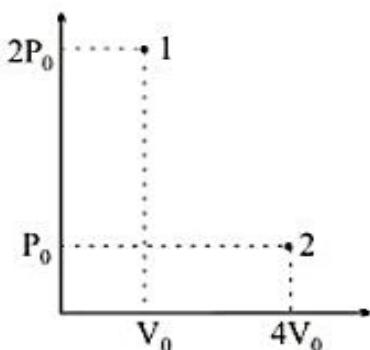
$$\begin{aligned}\Rightarrow (\log P - 2.38) \times 5 &= -7 (\log V - 1.1) \\ \Rightarrow 5 \log P + 7 \log V &= 19.60 \\ \Rightarrow \log P^5 + \log V^7 &= 19.60 \\ P^5 V^7 &= \text{antilog}(19.60) = \text{constant} \\ \text{or } PV^{1.4} &= \text{constant} \\ \therefore \gamma &= 1.4 - \text{diatomic \& adiabatic}\end{aligned}$$

- Q.12** A certain mass of a gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is 50 J/ $^{\circ}\text{C}$ . Calculate  $\Delta H$  (in kJ) of the process. (Given 1L atm = 100 J).  
(Fill your answer by multiplying it with 100)

**Sol.**  $\Delta U = Q + W$        $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\begin{aligned}&= 50 \times (600 - 300) - 1(4 - 1) \times 100 \quad \text{or} \quad \frac{10 \times 1}{300} = \frac{5 \times 4}{T_2} \\ &= 15000 - 300 \text{ J} \quad \text{or} \quad T_2 = 5 \times 4 \times 30 = 600 \text{ K} \\ &= 14700 \text{ J} \\ &= 14.7 \text{ J} \\ \Delta H &= \Delta U + (P_2 V_2 - P_1 V_1) \\ &= 14.7 + \frac{(20-10) \times 100}{1000} \\ &= 14.7 + 1 = 15.7 \text{ kJ} = 1570\end{aligned}$$

- Q.13** A liquid confined inside an adiabatic container is suddenly taken from state 1 to state 2 by a single stage process as shown, then  $\Delta H$  is



(A)  $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$       (B)  $\Delta H = -P_0 V_0$       (C)  $\Delta H = -3P_0 V_0$       (D)  $\Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$

**Ans.** (B)

**Sol.**  $Q = 0$

$$\begin{aligned}\Delta U &= Q + w = w \\ w &= -P_0(4V_0 - V_0) = -3P_0 V_0 \\ \Delta H &= \Delta U + (P_2 V_2 - P_1 V_1) \\ &= -3P_0 V_0 + (4P_0 V_0 - 2P_0 V_0) \\ &= -3P_0 V_0 + 2P_0 V_0 \\ &= -P_0 V_0\end{aligned}$$

- Q.14** One mole of Argon is heated using  $PV^{5/2} = \text{constant}$ . By what amount heat is absorbed during the process, when temperature changes by  $\Delta T = 26 \text{ K}$ .

(A) 100 J      (B) 200 J      (C) 180 J      (D) 208 J

**Ans.** (C)

**Sol.**  $n = 1$   $C_v = \frac{3}{2} R$ .  $PV^{5/2} = \text{constant}$ ,  $n' = 5/2$

$$q = n C \Delta T$$

$$= n \left[ C_v + \frac{R}{1-n'} \right] \Delta T = 1 \left[ \frac{3}{2} R + \frac{R}{1 - \frac{5}{2}} \right] 26 = \left[ \frac{3}{2} R - \frac{2}{3} R \right] 26 = \frac{5}{6} R \times 26 = \frac{5 \times 8.314 \times 26}{6} = 180 \text{ J}$$

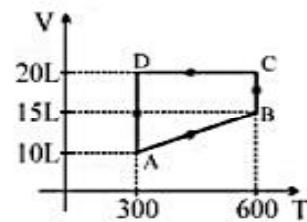
- Q.15** One mole monoatomic ideal gas was taken through process ABCD as shown in figure. Calculate

- $$(i) \quad w_{AB}, w_{BC}, w_{CD}, w_{DA}$$

- (ii)  $\mathbf{q}_{AB}, \mathbf{q}_{BC}, \mathbf{q}_{CD}, \mathbf{q}_{DA}$

- $$(iii) \quad \Delta H_{AB}, \Delta H_{BC}, \Delta H_{CD}, \Delta H_{DA}$$

[Use :  $\ln(3/2) = 0.40$ ;  $\ln(4/3) = 0.29$ ]



- Sol.(i)**  $w_{AB}$ : Along 'AB' pressure is variable

$$\text{from graph: } \frac{V-10}{T-300} = \frac{15-10}{600-300} \Rightarrow 60V - 600 = T - 300 \Rightarrow 60V - 300 = T$$

sub value of T in ideal gas equation

$$PV = R(60V - 300) \Rightarrow P = 60R - \frac{300R}{V}$$

$$w_{AB} = - \int_{10}^{15} P dV = - \int_{10}^{15} \left[ 60R - \frac{300R}{V} \right] dV = - 60R(V_2 - V_1) + 300R \ln\left(\frac{V_2}{V_1}\right)$$

$$= - 300R + 300 R(0.4) \quad \text{(take } \ln(3/2) = 0.40 \text{ data)}$$

$$W_{AB} = -180R = -1496.52 \text{ J Ans.}$$

$$w_{BC} = -RT \ln \frac{V_3}{V_2} = -RT \ln (4/3) \quad (\text{take } \ln (4/3) = 0.29 \text{ data})$$

$$= -8.314 \times 600 \times 0.29 = -1446.63 \text{ Joule Ans.}$$

$$w_{CD} = 0 \text{ Ans.}$$

$$w_{DA} = -nRT \ln \frac{V_f}{V_i} = -1 \times 8.314 \times 300 \ln \left( \frac{10}{20} \right) = +1728.84 \text{ Joule} \quad \text{Ans.}$$

$$(ii) \quad q_{AB} = \Delta E_{AB} - w = \frac{3}{2} R \times 300 + 1496.52 = 450 R + 180 R = 630 R = 5237.82 \text{ Joule Ans.}$$

$$q_{BC} = -w_{BC} = +1446.63 \text{ Joule Ans.}$$

$$q_{CD} = \Delta U = n C_V \Delta T = 1 \times \frac{3}{2} R \times (300 - 600) = - 3741.3 \text{ Joule} \quad \text{Ans.}$$

$$q_{DA} = -w_{DA} = 1728.84 \text{ Joule Ans.}$$

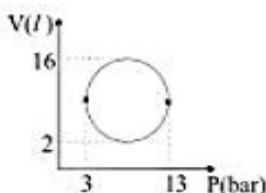
(iii)  $\Delta H_{AB} = C_p (T_2 - T_1) = \frac{5}{2} R \times 300 = 750 R = 6235.5 \text{ Joule Ans.}$

$\Delta H_{BC} = 0 \text{ Ans.}$

$\Delta H_{CD} = \Delta U_{CD} + nR \Delta T = n C_p \Delta T = 1 \times \frac{5}{2} R \times (-300) = -6235.5 \text{ Joule Ans.}$

$\Delta H_{DA} = \Delta U_{DA} + nR \Delta T = 0 \text{ Joule Ans.}$

**Q.16** Work done (in kJ) by the gas in the following cyclic process is



(A) -11

(B) -11000

(C) 11

(D) 11000

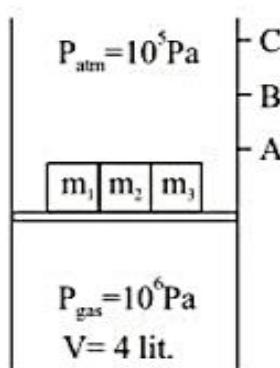
**Ans.** (A)

**Sol.**  $|w| = \pi ab = \frac{22}{7} \times 7 \times 5 = 110 \text{ bar lit.} = 11000 \text{ J} = 11 \text{ kJ}$

Final Answer = -11

**Q.17** Consider an isothermal cylinder and massless piston assembly in which ideal gas is filled. Cross sectional area of the cylinder =  $1\text{m}^2$ . Three masses  $m_1$ ,  $m_2$  and  $m_3$  are kept on the piston. When  $m_1$  is removed, piston moves upto point A. When  $m_1$  &  $m_2$  both are removed piston moves upto point B & when  $m_1$ ,  $m_2$  &  $m_3$  all the three are removed, piston moves upto point C. Calculate work done by the gas (in joule) when piston moves from point B to point C.

[Given :  $m_1 = 2 \times 10^4 \text{ kg}$ ,  $m_2 = 3 \times 10^4 \text{ kg}$ ,  $g = 10 \text{ m/s}^2$  ]



**Sol.** Initially piston is at eq,

$$10^6 = \frac{(2 \times 10^4 + 3 \times 10^4 + m_3) \times 10}{1} + 10^5$$

$$m_3 = \left( \frac{10^6 - 10^5}{10} \right) - 5 \times 10^4 = 10^4 (10 - 1) - 5 \times 10^4 = 10^4 (9 - 5) = 4 \times 10^4 \text{ kg}$$

since T = constant

$$P_i V_i = P_B V_B$$

$$10^6 \times 4 = (10^5 + 4 \times 10^5) \times V_B$$

$$V_B = \frac{4 \times 10^6}{10^5 \times 5} = \frac{40}{5} = 8 \text{ lit.}$$

Also,

$$P_B V_B = P_C V_C$$

$$10^5 \times 5 \times 8 = 10^5 \times V_C$$

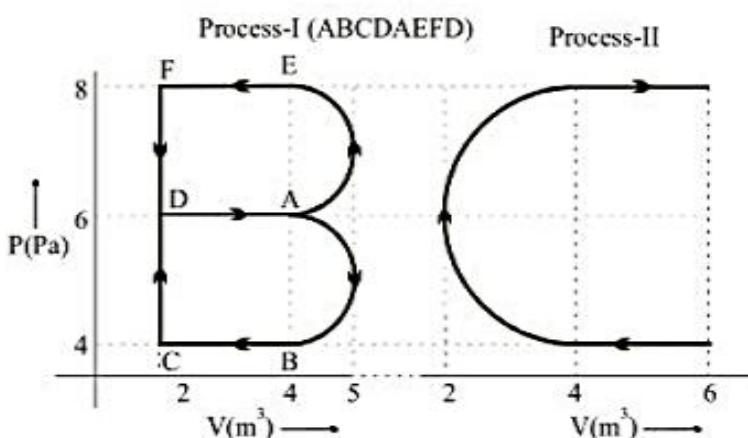
$$V_C = 40 \text{ L}$$

$$W_{BC} = -P_{\text{ext}}(V_C - V_B) = -10^5 (40 - 8) \times 10^{-3} = -3200 \text{ J}$$

$$W_{\text{by}} = 3200 \text{ J} \quad \text{Ans.}$$

- Q.18** Calculate difference in work done in process-I to process-II.

(Given :  $\pi = 3$ )



$$\text{Sol. Process-I : } W_{ABCDAEFD} = W_{ABCDA} + W_{AE} + W_{EF} + W_{FD}$$

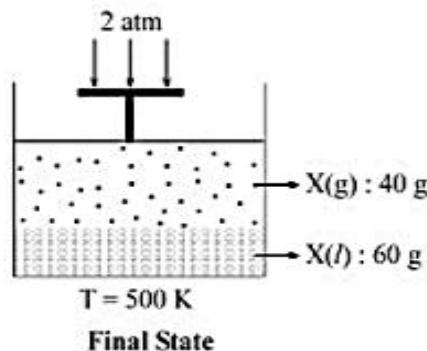
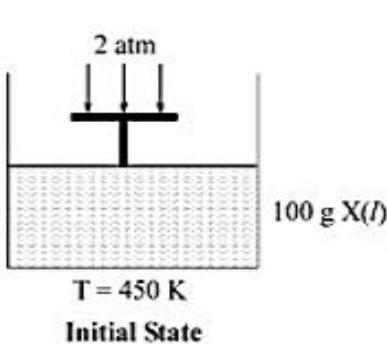
$$= - \left( 2 \times 2 + \frac{3 \times 1 \times 1}{2} \right) + \frac{3 \times 1 \times 1}{2} + 8 \times 2 + 0 = -5.5 + \frac{3}{2} + 16 = 12$$

$$\text{Process-II : } w = \left( \frac{3 \times 2 \times 2}{2} + 4 \times 2 \right) = -(6 + 8) = -14$$

$$\text{Difference in work done} = 12 - (-14) = 26 \quad \text{Ans.}$$

- Q.19** The external pressure 2 atm is applied on frictionless movable piston, fitted in a vessel containing 100 g of X(l) at 450 K. Now heat is supplied keeping pressure constant till 40 g of X is evaporated to form X(g) at 500 K (boiling point). Calculate change in internal ( $\Delta U$ ) energy in kJ for overall process.

Assume vapour of X(l) behaves like an ideal gas.



**Given:** Molar heat capacity of X ( $C_p$ ) = 60 J/mol.K;  $\Delta H_{\text{vaporisation}} = 30 \text{ kJ/mol}$ ;  $R = 8.3 \text{ J/mol-K}$   
At. weight of X = 20 g/mol.

[Fill your answer by multiplying it with 100.]

**Sol.**  $\Delta U = Q + w$

$$= n C_{p,m} \Delta T + n \Delta H_{\text{vap}} + w = \frac{100}{20} \times \frac{60}{1000} \times 50 + \frac{40}{20} \times 30 - \Delta n_g RT = 15 + 60 - \frac{2 \times 8.3 \times 500}{1000}$$

$$= 66.7 \text{ kJ} \Rightarrow 6670 \text{ Ans.}$$

**Q.20** An ideal gas with adiabatic exponent  $\gamma$  undergoes a process in which internal energy depends on volume as  $U = aV^\alpha$  then select the correct statement.

(A) Change in internal energy is  $\frac{(\gamma-1)}{\alpha} \Delta T$

(B) Molar heat capacity of process is  $\frac{R}{(1-\gamma)} + \frac{R}{\alpha}$

(C) Heat exchange in the process is given by  $\Delta U \left[ 1 + \frac{(1-\gamma)}{\alpha} \right]$

(D) Equation of process is  $PV^\alpha = \text{constant}$ , where  $\alpha > 0$  if  $\gamma < 1$ .

**Ans.** (D)

**Sol.**  $U = aV^\alpha \Rightarrow nC_v T = aV^\alpha$

$TV^{-\alpha} = a$

On comparing with,  $TV^{n-1} = \text{constant}$

Polytropic index,  $n = 1 - \alpha$

Molar heat capacity,  $= \frac{R}{\gamma-1} - \frac{R}{n-1} = -\frac{R}{1-\gamma} + \frac{R}{1-(1-\alpha)} = -\frac{R}{1-\gamma} + \frac{R}{\alpha}$

$q = C \Delta T$

$$= \left[ -C_V + \frac{R}{\alpha} \right] \Delta T = -C_V \Delta T + \frac{R}{\alpha} \Delta T = -\Delta U + \frac{R}{\alpha} \Delta T; \quad = -\Delta U + \frac{\gamma-1}{\gamma-1} \times \frac{R \Delta T}{\alpha}$$

$$= -\Delta U + \frac{R}{\gamma-1} \Delta T \times \frac{\gamma-1}{\alpha}; \quad = -\Delta U + \Delta U \cdot \frac{\gamma-1}{\alpha} = \Delta U \left[ \frac{\gamma-1}{\alpha} - 1 \right]$$

**Q.21** An adiabatic cylinder fitted with an adiabatic piston at the right end of cylinder, is divided into two equal halves with a monoatomic gas on left side and diatomic gas on right side, using an impermeable movable

adiabatic wall. If the piston is pushed slowly to compress the diatomic gas to  $\frac{3}{4}$  th of its original volume.

The new volume of monoatomic gas would be

(A)  $V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{4}{3} \right]^{\frac{25}{21}}$

(B)  $V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{7}{5} \right]^{\frac{3}{4}}$

(C)  $V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{3}{4} \right]^{\frac{21}{25}}$

(D)  $V_{\text{new}} = V_{\text{initial}} \times \frac{3}{4}$

**Ans. (C)**

**Sol.**  $Pv^\gamma = K$   
for diatomic gas

$$\frac{P_1}{P_2} = \left( \frac{V_2}{V_1} \right)^\gamma = \left( \frac{3}{4} \right)^{7/5}$$

for monoatomic gas

$$\frac{P_1}{P_2} = \left( \frac{V_{\text{new}}}{V_{\text{initial}}} \right)^{5/3} = \left( \frac{3}{4} \right)^{7/5} \Rightarrow V_{\text{new}} = V_{\text{initial}} \times \left[ \frac{3}{4} \right]^{21/5}$$

**Q.22** Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas from 300K and pressure 10 atm to 1 atm. ( $\gamma = 1.33$ ).

$$\text{Sol. } C_v(T_2 - 300) = -1 \left( \frac{RT_2}{1} - \frac{RT_1}{10} \right)$$

$$\gamma = 1.33 = \frac{4}{3} = \frac{C_p}{C_v} = \left( \frac{4}{3} \right) \quad C_p = C_v + R$$

$$3R(T_2 - 300) = -RT_2 + \frac{RT_1}{10}$$

$$4RT_2 = 30R + 900R$$

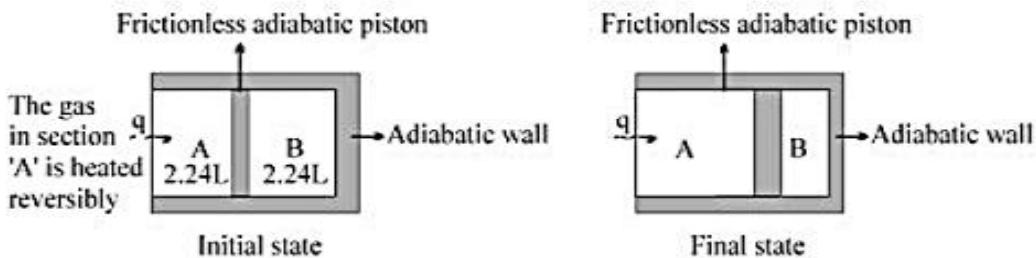
$$T_2 = \frac{930}{4} = 232.5 \text{ K}$$

$$W = 3R(232.5 - 300)$$

$$W = -202.5 \text{ R} = -1.683 \text{ kJ}$$

**Q.23** A cylindrical container of volume 4.48 litres is containing equal no. of moles of a monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gases was 273 K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes  $1/2\sqrt{2}$  of initial volume. Find total change in  $\Delta H$  for section A and B. (in cal/mole)

[ $C_v$  of monoatomic gas =  $3/2 R$ ,  $\gamma = 5/3$  ]



[Use  $R = 2 \text{ cal/mol}$  &  $\sqrt{2} = 1.4$ ]

**Sol.** Initial volume of sec. A = sec. B = 2.24 litres

$$\text{Final volume of sec. B} = \left[ \frac{2.24}{2\sqrt{2}} \right] \text{ litres}$$

The gas in sec. 'B' compressed reversibly and adiabatically

$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Rightarrow T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow T_2 = T_1 (2\sqrt{2})^{2/3} = 2T_1$$

$$\{\text{For monoatom gas } \gamma = \frac{5}{3}\}$$

The final pressure in sec. 'B'

$$P_f = \frac{P_1 V_1}{T_1}, \frac{T_2}{V_2} = P_1 \times \left( \frac{T_2}{T_1} \right) \cdot \left( \frac{V_1}{V_2} \right) P_1 \times 2 \times 2\sqrt{2} = 4\sqrt{2} \text{ atm}$$

$$\Rightarrow \text{Pressure in sec. 'A'} = 4\sqrt{2} \text{ atm} \quad \Rightarrow \text{Final temperature in sec. A } T_2 = \left( \frac{P_2}{P_1} \right) \left( \frac{V_2}{V_1} \right) T_1$$

$$T_2 = \left( \frac{P_2}{P_1} \right) \left\{ \frac{V_1 + V_1 - \frac{V_1}{2\sqrt{2}}}{V_1} \right\} T_1$$

$$4\sqrt{2} \left( 2 - \frac{1}{2\sqrt{2}} \right) T_1 = \left[ \frac{(4\sqrt{2}-1)(4\sqrt{2})}{2\sqrt{2}} \right] T_1$$

$$(4\sqrt{2}-1) 2T_1$$

$$[8\sqrt{2} T_1 - 2T_1 - T_1] = \{4\sqrt{2} T_1 - 3T_1\}$$

$$\Delta H_A = (0.1) \frac{5}{2} R \{8\sqrt{2} - 3\} \Rightarrow \Delta H_B = (0.1) \frac{5}{2} R \{273\} \\ 2(4\sqrt{2}-1)$$

$$\Delta H_T = (0.1) \frac{5}{2} R (273) \{2\} (4\sqrt{2}-1) = 1255.8 \text{ or } 5 \times 1255.8 = 6279 \text{ Ans.}$$

- Q.24** A gas ( $C_{v,m} = \frac{5}{2} R$ ) behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. Its initial temperature was 327°C. The molar enthalpy change (in J/mole) for the process is  
 (A) -1125 R                (B) -575 R                (C) -1575 R                (D) None of these

**Ans.** (C)

$$\text{Sol. } \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow T_2 = T_1 \left( \frac{1}{32} \right)^{\frac{7}{5}-1} = 600 \cdot \left( \frac{1}{2^5} \right)^{\frac{2}{5}} = 600(0.5)^2 = 150 \text{ K}$$

$$\Delta H_m = \frac{7}{2} R \times (150 - 600) = -1575 \text{ R} \quad \text{Ans.}$$

**Q.25** 1000 gm water is heated from 27°C to 47°C at a constant pressure of 1 bar. The coefficient of volume expansion of water is 0.002/°C and the molar volume of water at 0°C is 18.00 cm<sup>3</sup>/mol. The magnitude of work done (in J) by water is

**Sol.**  $V_{t^{\circ}\text{C}} = V_{0^{\circ}\text{C}} (1 + \gamma t)$        $\gamma = \text{coefficient of volume expansion}$   
 $V_{27^{\circ}\text{C}} = 1000 (1 + 0.002 \times 27)$        $t = \text{temperature in } ^{\circ}\text{C}$   
 $= 1054 \text{ ml}$

$$V_{47^{\circ}\text{C}} = 1000 (1 + 0.002 \times 47)$$

$$= 1094 \text{ ml}$$

$$W = -P\Delta V = \frac{-1 \times (1094 - 1054)}{1000} \text{ bar litre} = \frac{-4}{100} \text{ bar litre} = \frac{-4}{100} \times 100 \text{ J} = -4 \text{ J}$$

**Q.26** The temperature of a definite amount of an ideal monoatomic gas becomes four times in a reversible process for which heat exchange is zero. Which of the following is correct relation between the final and initial parameters of gas?

(A)  $V_f = 8V_i$       (B)  $P_f = 32 P_i$       (C)  $V_f = 16 V_i$       (D)  $P_f = \frac{1}{16} P_i$

**Ans.** (B)

**Sol.**  $\left(\frac{V_1}{V_2}\right) = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} = (3)^{3/2} = 8$

$$\frac{P_1}{P_2} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{1-\gamma}} = (3)^{\frac{5/3}{-2/3}} = (3)^{-5/2} = \frac{1}{32}$$

**Q.27** Inversion temperature  $\left(T_i = \frac{2a}{Rb}\right)$  is defined as the temperature above which if gas is expanded adiabatically it gets warm up but if temperature of gas is lower than  $T_i$  then it will cool down. What will happen to a gas if it is adiabatically expanded at 50°C if its Boyle's temperature is 20°C

- (A) heating      (B) cooling      (C) constant      (D) None of these

**Ans.** (B)

**Sol.** Boyle temperature,  $T_b = \frac{a}{Rb} = 20^{\circ}\text{C} = 293 \text{ K}$

inversion temperature,  $T_i = \frac{2a}{Rb} = 586 \text{ K} = 313^{\circ}\text{C}$

∴ at  $50^{\circ}\text{C} < T_i$ , on expansion cooling occurs

**Q.28** Which of the following statement(s) is/are correct :

Statement (a) : The entropy of isolated system with P–V work only is always maximized at equilibrium

Statement (b) : It is possible for the entropy of close system to decrease substantially in an irreversible process.

Statement (c) : Entropy can be created but not destroyed.

Statement (d) :  $\Delta S_{\text{system}}$  is always zero for reversible process in an isolated system

- (A) Statement a, b, c      (B) Statement b, d      (C) Statement a, b, d      (D) All

**Ans.** (D)

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- Q.29** 1 Kg stone at 27 °C falls 100 m into a lake whose temperature is 27 °C. Find the entropy change of  
 (a) the stone (b) the lake (c) the universe when  
 (i) stone is lowered reversibly  
 (ii) stone is dropped freely  
 Compare the loss of available energy in two cases

**Sol.(i)** If the stone is lowered reversibly no amount of heat will be produced. Also since term of stone remains the same

$$\Delta S_{\text{stone}} = 0 \quad \text{Ans.}; \\ q_{\text{rev}} = 0 \Rightarrow \Delta S_{\text{lake}} = 0 \quad \text{Ans.} \\ \text{and } \Delta S_{\text{total}} = \Delta S_{\text{universe}} = \Delta S_{\text{lake}} + \Delta S_{\text{stone}} = 0 \quad \text{Ans.}$$

**(ii)** If the stone is lowered irreversibly, the potential energy will be entirely lost in form of heat energy

$$q_{\text{actual}} = q_{\text{irr}} = mgh \\ \Delta S_{\text{stone}} = 0 \quad \text{Ans.}$$

$$\Delta S_{\text{lake}} = -\frac{q_{\text{irr}}}{T} = -\left(\frac{-1 \times 9.8 \times 1000}{300}\right) = \frac{980}{300} \text{ J/K} \\ = 3.26 \text{ J/K} \quad \text{Ans.} \\ \Delta S_{\text{total}} = 3.26 \text{ J/K} \quad \text{Ans.}$$

loss of available energy in first process = 0

loss of available energy in second process = 980 Joules

- Q.30** A mole of steam is condensed at 100°C, the water is cooled to 0°C and frozen to ice. What is the difference in entropies of the steam and ice? The heats of vaporization and fusion are 540 cal gm<sup>-1</sup> and 80 cal gm<sup>-1</sup> respectively. Use the average heat capacity of liquid water as 1 cal gm<sup>-1</sup> degree<sup>-1</sup>.

$$(A) 18\left(\frac{80}{373} + \frac{540}{273} + \ln\frac{373}{273}\right) \quad (B) 18\left(\frac{80}{273} + \frac{540}{373} + \ln\frac{373}{273}\right)$$

$$(C) 18\left(\frac{80}{273} + \frac{540}{373} + \ln\frac{273}{373}\right) \quad (D) 18\left(\frac{80}{273} + \frac{540}{373} + 100\right)$$

**Ans.** (B)

$$\text{Sol. } \Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vap}}}{T} = \frac{-540 \times 18}{373}$$

$$\Delta S_{\text{cooling}} = +nC_p \ln\left(\frac{T_2}{T_1}\right) = 18 \ln\left(\frac{273}{373}\right)$$

$$\Delta S_{\text{fusion}} = \frac{-80 \times 18}{273} \\ = -\left[18\left(\frac{80}{273} + \frac{540}{373}\right) + \left(18 \ln\frac{273}{373}\right)\right] \\ = -18\left(\frac{80}{273} + \frac{540}{373} + \ln\frac{373}{273}\right) \Rightarrow 36.95 \text{ cal /}^\circ \text{ Ans.}$$

- Q.31** Heat capacity of a solid A(s), is given by  $aT^3$  in vicinity at absolute zero. Taking heat capacity to be  $aT^3$  from 0 K to 10 K, b from 10 K to normal M.P. at 150 K and c from 150 K to 200 K, find the absolute entropy of A(l) at 200 K.

Given  $a = 0.5 \times 10^{-3} \text{ J/(K mole)}$

$b = 15 \text{ J/(K mole)}$

$c = 20 \text{ J/(K mole)}$

$\Delta H_{\text{fusion}} = +30 \text{ kJ/mole}$

$$\text{Sol. } S_T - S_{0 \text{ K}} = \int_{0 \text{ K}}^{10 \text{ K}} \frac{C(s).dT}{T} + \int_{10}^{150 \text{ K}} \frac{C(s).dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_M} + \int_{150}^{200 \text{ K}} \frac{C(l).dT}{T}$$

$$S_T = \int_{0 \text{ K}}^{10 \text{ K}} \frac{aT^3.dT}{T} + \int_{10}^{150} \frac{b.dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_M} + \int_{150}^{200} \frac{c.dT}{T}$$

$$S_T = a \left[ \frac{10^3}{3} - 0 \right] + b \ln \left( \frac{150}{10} \right) + \frac{30000}{150} + c \ln \left( \frac{200}{150} \right)$$

$$S_T = \frac{0.5}{3} + 15 \times \ln(15) + 200 + 20 \ln \frac{4}{3}$$

$$S_T = 0.166 + 40.62 + 200 + 5.8$$

$$S_T = 246.586 \text{ J / (mole. K)} \text{ Ans.}$$

- Q.32** For a perfectly crystalline solid  $C_{p,m} = aT^3 + bT$ , where a & b are constant. If  $C_{p,m}$  is 0.40 J/K-mol at 10 K and 0.92 J/K-mol at 20 K, then molar entropy at 20 K is

(A) 0.92 J/K-mol      (B) 8.66 J/K-mol      (C) 0.813 J/K-mol      (D) None

**Ans. (C)**

$$\text{Sol. } 0.40 = aT_1^3 + bT_1 \Rightarrow 0.40 = a \times (1000) + b \times 10 \quad \dots(1)$$

$$0.92 = aT_2^3 + bT_2 \Rightarrow 0.92 = a \times 8000 + 20b \quad \dots(2)$$

On solving

$$0.12 = 6000 a ; a = 2 \times 10^{-5}$$

$$0.40 = 2 \times 10^{-5} \times 1000 + b \times 10$$

$$\therefore b = 0.038$$

$$\begin{aligned} S_m &= \int \frac{aT^3 + bT}{T} dT \Rightarrow \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1] \\ &\Rightarrow \frac{2 \times 10^{-5} \times (8000 - 0)}{3} + b(20) \Rightarrow \frac{2 \times 10^{-5} \times 8000}{3} + 0.038 \times (20) \\ &\Rightarrow 0.053 + 0.76 \Rightarrow 0.813 \text{ J/K-mol} \end{aligned}$$

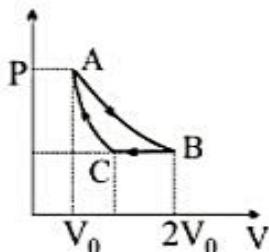
- Q.33** Two mole of an ideal gas is expanded irreversibly & isothermally at 27°C until its volume is doubled and 3.3 kJ heat is absorbed from surrounding. Determine  $\Delta S_{\text{system}}$  &  $\Delta S_{\text{surrounding}}$ .

$$\text{Sol. } \Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1} \Rightarrow 2 \times R \times \ln 2 \Rightarrow 11.52 \text{ J/K}$$

$$\Delta S_{\text{surrounding}} = -\frac{3.3 \times 1000}{300} \Rightarrow -11 \text{ J/K}$$

- Q.34** An ideal gas undergoing cyclic process ABCA consisting of isothermal expansion AB, isobaric compression BC & adiabatic compression CA. Find the % (approximate) efficiency of cycle.

[Given :  $T_A = T_B = 400 \text{ K}$ ;  $\gamma = 1.5$ ,  $\ln 2 = 0.7$ ,  $2^{-1/3} = 0.8$  ]



$$\text{Sol. } T_C = T_A \left[ \frac{P_A}{P_C} \right]^{\frac{1-\gamma}{\gamma}} = 400 \left[ \frac{2}{1} \right]^{\frac{1-1.5}{1.5}} = \frac{400}{2^{1/3}} = 400 \times 0.8 = 320$$

$$\eta = - \frac{W_{\text{Total}}}{q_{\text{absorbed}}}$$

$$w_{AB} = -nR \ln 2 = -280 \text{ nR}$$

$$w_{BC} = -nR(T_C - T_B) = -nR(320 - 400) = 80 \text{ nR}$$

$$w_{CA} = \frac{nR}{\gamma-1} (T_A - T_C)$$

$$= 2 \text{ nR} (400 - 320)$$

$$= 160 \text{ nR}$$

$$w_{\text{total}} = -280 \text{ nR} + 80 \text{ nR} + 160 \text{ nR}$$

$$q_{\text{absorbed}} = -w_{AB}$$

$$\% \eta = \frac{40 \text{ nR}}{280 \text{ nR}} \times 100 = \frac{100}{7} = 14.285 \approx 14 \text{ Ans.}$$

- Q.35** 0.5 mole of an ideal monoatomic gas at STP conditions undergoes a process, if the final volume of gas is  $(22.7 \times e)$  lit., then the entropy change in this process in J / K / mol is  
[Given : Process isobaric]

(Fill your answer by multiplying it with  $\frac{100}{R}$ )

$$\text{Sol. } \frac{V_1}{V_2} = \frac{T_1}{T_2} \Rightarrow \frac{22.7/2}{22.7 \cdot e} = \frac{273}{T_2} \Rightarrow T_2 = 273 \cdot (2e)$$

$$\Delta S = nC_p \ln \frac{T_2}{T_1} = 0.5 \times \frac{5}{2} R \times \ln \frac{(273)(2e)}{273}$$

$$= \frac{5}{4} R (\ln 2e) = \frac{5}{4} R (\ln 2 + \ln e) \quad \therefore \text{if } \ln 2 = 0.7$$

$$= \frac{5}{4} R \times (1.7) \times \frac{100}{R} = 212.5 \text{ Ans.}$$

- Q.36** When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into contact into thermal contact and isolated from its surrounding. The total change in entropy of system is given by

$$(A) C_v \ln \frac{T_c + T_h}{2T_c} \quad (B) C_v \ln \frac{T_2}{T_1} \quad (C) C_v \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c} \quad (D) C_v \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$$

Ans. (D)

Sol.  $C_v(T_h - T) = C_v(T - T_c) \Rightarrow T = \frac{T_c + T_h}{2}; \therefore \Delta S = \int_{T_1}^{T_2} \frac{C_v}{T} dT$

$$\Delta S_c = C_v \ln \frac{T}{T_c} \text{ & } \Delta S_h = C_v \ln \frac{T}{T_h}$$

$$\text{Total } \Delta S = C_v \ln \frac{(T_c + T_h)}{2T_c} + C_v \ln \frac{(T_c + T_h)}{2T_h} = C_v \ln \frac{(T_c + T_h)^2}{4T_c \cdot T_h}$$

- Q.37** A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000K and rejects heat to a reservoir at  $T_2$ . A second reversible engine B absorbs, the same amount of heat as rejected by the engine A, from the reservoir at  $T_2$  and rejects energy to a reservoir at 360K.

If the efficiencies of engines A and B are the same then the temperature  $T_2$  is

- (A) 680 K      (B) 640 K      (C) 600 K      (D) none

Ans. (C)

Sol. For heat engine A:  $\eta_A = \frac{1000 - T_2}{1000} \Rightarrow \eta_B = \frac{T_2 - 360}{T_2}$

$$\eta_A = \eta_B \\ \text{so } \frac{1000 - T_2}{1000} = \frac{T_2 - 360}{T_2} = T_2 = \sqrt{360 \times 1000} = 600 \text{ K Ans.}$$

- Q.38** Which of the following statement(s) is/are correct:

Statement (a) : In any closed system with P, V work only, G is always minimized at equilibrium.

Statement (b) :  $\Delta G$  is always zero for a reversible process in a closed system.

Statement (c) :  $\Delta G^\circ$  for an ideal gas reaction is a function of pressure.

Statement (d) : For an irreversible, isothermal, isobaric process in a closed system with P, V work only.  $\Delta G$  must be negative.

- (A) Statement a, b, d    (B) Statement b, c, d    (C) Statement c, d    (D) Only statement d

Ans. (D)

- Q.39** Select the correct statement(s).

(A)  $dG = Vdp - SdT$  is applicable for all process involving both 'PV' and 'non-PV' work in a closed system.

(B)  $\Delta S_{sys}$  can not be negative in any adiabatic process in a closed system.

(C)  $\Delta U = 0$  for the combustion of  $C_6H_6(g)$  in a sealed rigid diathermic container.

(D) In the presence of 'non-PV' work if  $(\Delta G_{sys})_{T,P} < 0$ , process must be spontaneous in a closed system.

Ans. (B)

- Sol.** (A)  $G = H - TS = U + PV - TS$   
 $dG = dU + PdV + VdP - TdS - SdT$   
 $= q + w + PdV + VdP - TdS - SdT$   
 For a reversible path  $q = TdS$   
 If there is no non-PV work  $w = -PdV$   
 $dG = VdP - SdT$
- (D)  $G = H - TS = U + PV - TS$   
 at constant 'T' & 'P'  
 $dG_{sys} = dU + PdV - TdS_{sys} = q + w_{PV} + w_{non-PV} + PdV - TdS_{sys}$   
 since  $w_{PV} = -PdV$   
 and in the absence of  $w_{non-PV}$   
 $dG_{sys} = q - TdS_{sys}$   
 $dG_{sys} = -T(dS_{sys} + dS_{sur})$

**Q.40** From the given T-S diagram of a reversible carnot engine, find

- (i) work delivered by engine in one cycle
- (ii) heat taken from the source in each cycle.
- (iii)  $\Delta S_{sink}$  in each cycle.

**Sol.(i)**  $W_{AB} = -nRT \ln \frac{V_2}{V_1}$

$$\begin{aligned}\Delta S &= \frac{q_{rev}}{T} = -\frac{W_{AB}}{T} \\ \Rightarrow -W_{AB} &= T\Delta S = 600 \times 100 \\ -W_{BC} &= -nC_V(T_1 - T_2) \\ -W_{CD} &= T\Delta S = 300 \times (-100) \\ -W_{DA} &= -nC_V(T_2 - T_1)\end{aligned}$$

net work delivered during one cycle  $= -W_{AB} - W_{BC} - W_{CD} - W_{DA} = 300 \times 100 = 30 \text{ kJ}$

**Note :** Net work done = area of the rectangle

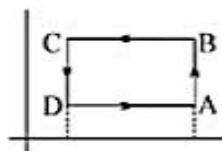
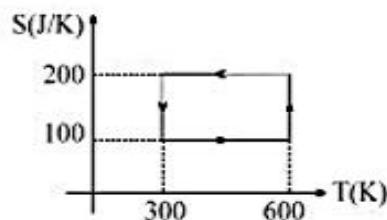
(ii)  $\frac{W_{net}}{q} = \eta \quad \text{and} \quad \eta = \frac{600 - 300}{600} = \frac{1}{2}$

$$\Rightarrow q = \text{heat taken from the source} = \frac{-W_{net}}{1/2} = \frac{30 \text{ kJ}}{1/2} = +60 \text{ kJ}$$

(iii)  $\Delta S_{sink} = -\frac{q_{sink}}{T} \quad \text{also} \quad (q_{source} + q_{sink}) = 30$

$$q_{source} = 60 \Rightarrow q_{sink} = -30 \text{ kJ}$$

$$\Rightarrow \Delta S_{sink} = \frac{-q_{sink}}{T} = \frac{-(-30000 \text{ J})}{100} = 100 \text{ J/K} \quad \text{Ans.}$$



- Q.41** Fixed amount of an ideal gas contained in a sealed rigid vessel ( $V = 24.6$  litre) at 1.0 bar is heated reversibly from  $27^\circ\text{C}$  to  $127^\circ\text{C}$ . Determine change in Gibb's energy ( $|\Delta G|$  in Joule) if entropy of gas  $S = 10 + 10^{-2} T$  (J/K)

**Sol.**  $dG = V.dP - S.dT$  ; at const. volume

$$\Delta G = V.\Delta P - \int (10 + 10^{-2}T).dT \quad \frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_2 = 1 \times 400/300$$

$$\Delta G = 24.6 \times \left( \frac{4}{3} - 1 \right) \times 100 - \left[ 10 \times 100 + 10^{-2} \times \left( \frac{T_2^2}{2} - \frac{T_1^2}{2} \right) \right]$$

$$\Delta G = 24.6 \times \frac{1}{3} \times 100 - [1000 + 10^{-2} \times \left( \frac{160000}{2} - \frac{90000}{2} \right)]$$

$$= 24.6 \times \frac{1}{3} \times 100 - 1000 - 350 = -530 \text{ J}$$

- Q.42** A reaction at 300 K with  $\Delta G^\circ = -1743 \text{ J/mol}$  consists of 3 mole of A(g), 6 mole of B(g) and 3 mole of C(g). If A, B and C are in equilibrium in 1 litre container then the reaction may be

[Given :  $2 = e^{0.7}$ ,  $R = 8.3 \text{ J/K - mol}$ ]

- (A)  $A + B \rightleftharpoons C$       (B)  $A \rightleftharpoons B + 2C$       (C)  $2A \rightleftharpoons B + C$       (D)  $A + B \rightleftharpoons 2C$

**Ans.** (C)

**Sol.**  $\Delta G^\circ = -RT \ln K_{eq}$

or,  $-1743 = -8.3 \times 300 \times \ln k_{eq}$

$k_{eq} = 2 = k_{eq}$  for reaction  $2A \rightleftharpoons B + C$  from given data.

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