4.

THERMODYNAMICS AND THERMOCHEMISTRY

1. INTRODUCTION

Thermodynamics, as the word suggests, is the heat in motion. The systems related to usage of heat for doing work. Every system was observed and accordingly laws were framed for categorising many such processes. In this Chapter, we would be learning about these laws and the systems governed by them.

1.1 Definition of Thermodynamics

Thermodynamics is a Greek word which means flow of heat in physical and chemical reactions.Thermodynamics is a branch of science dealing with study of different forms of energy and their inter conversions.

1.2 Importance of Thermodynamics

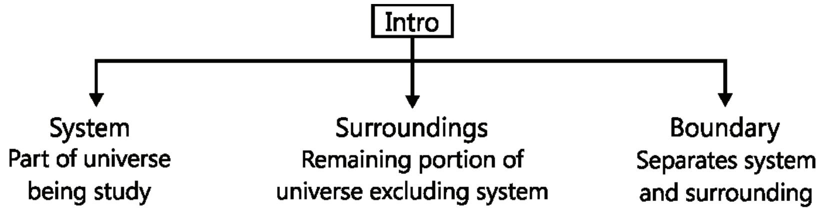
(a) Useful to predict whether any chemical reaction can occur under specified conditions.

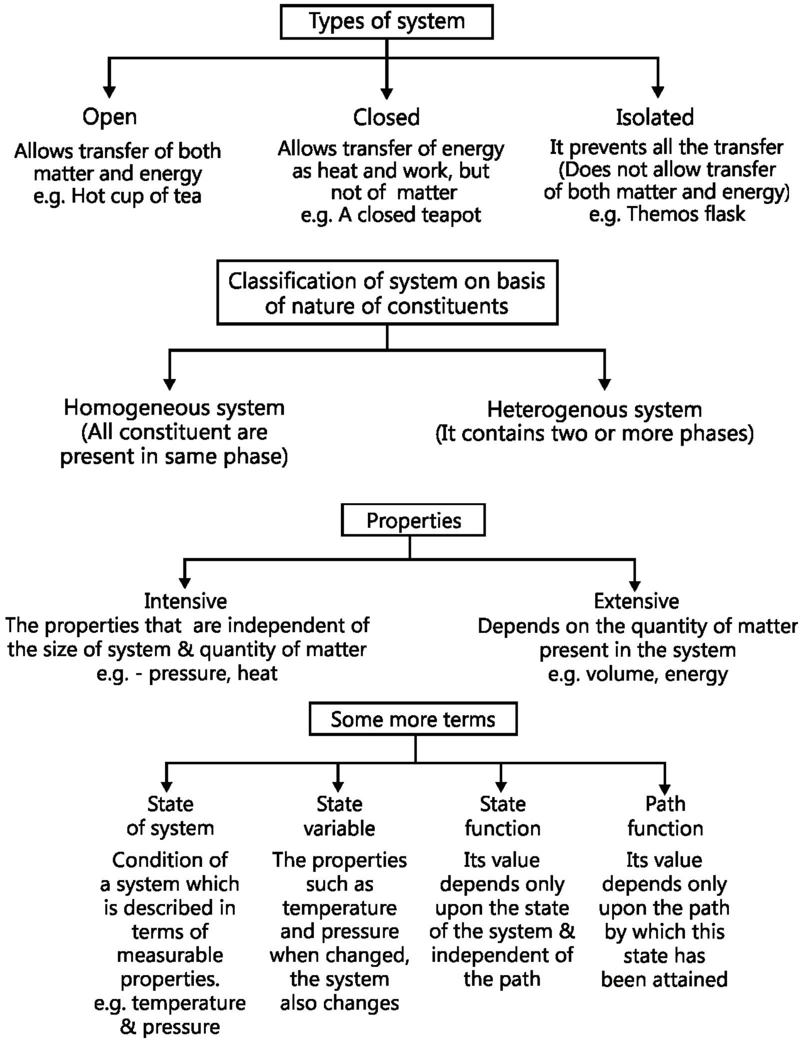
(b) Used to predict the extent of chemical reaction before equilibrium is reached.

(c) Used to derive important laws like law of equilibrium.

2. TERMS USED IN THERMODYNAMICS

Example: The fixed potential energy of a person standing on the top of a lighthouse stands as a state function, since it is not dependent on the path taken by the person. Whereas the work done by the legs of the person stands as a path function.





Flowchart 4.1: Terminology used Thermodynamics

2.1 Mathematics of State Function

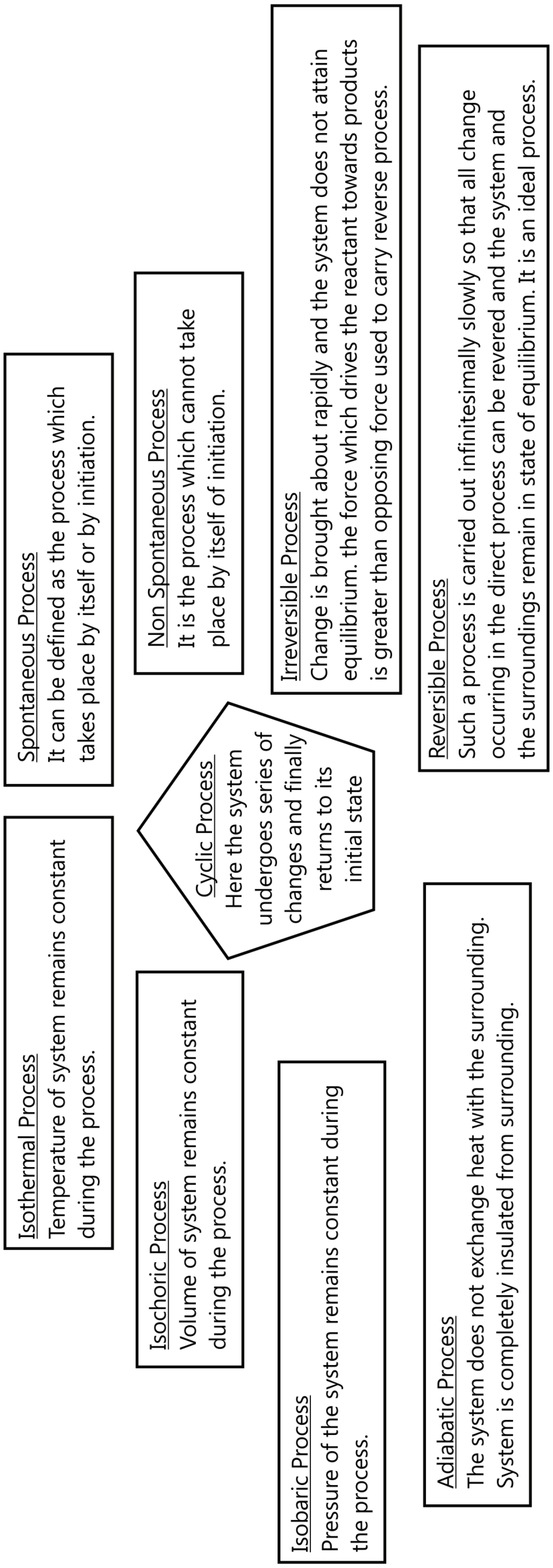
State functions can be thought of as integrals depending on three things: the function, the lower limit and the upper limit. Similarly, they depend on three more things: the property, the initial value, and the final value.

For example. $\int_{t_0}^{t_1} H(t)dt = H(t_1) - H(t_0)$; t_o gives the initial case and t_1 gives the final case. Thus, $\Delta H = H_{\text{final}} - H_{\text{initial}}$

Table 4.1: Difference between state and path functions

State Function	Path Function
Independent of path taken to establish property or value	Dependent on path taken to establish property or value
Can integrate using final and initial values.	Need multiple integrals and limits of integration in order to integrate.
Multiple steps result in same value.	Multiple steps result in different value.
Based on established state of systems (temperature, pressure, amount and identity of systems)	Based on how state of system was established.
Normally represented by an uppercase letter.	Normally represented by lowercase letter.

3. INTRODUCTION TO VARIOUS PROCESSES



Isothermal Process
Temperature of system remains constant during the process.

Spontaneous Process
It can be defined as the process which takes place by itself or by initiation.

Isochoric Process
Volume of system remains constant during the process.

Non Spontaneous Process
It is the process which cannot take place by itself of initiation.

Cyclic Process
Here the system undergoes series of changes and finally returns to its initial state

Isobaric Process
Pressure of the system remains constant during the process.

Irreversible Process
Change is brought about rapidly and the system does not attain equilibrium. the force which drives the reactant towards products is greater than opposing force used to carry reverse process.

Adiabatic Process
The system does not exchange heat with the surrounding. System is completely insulated from surrounding.

Reversible Process
Such a process is carried out infinitesimally slowly so that all change occurring in the direct process can be revered and the system and the surroundings remain in state of equilibrium. It is an ideal process.

Figure 4.1: (a) Various processes

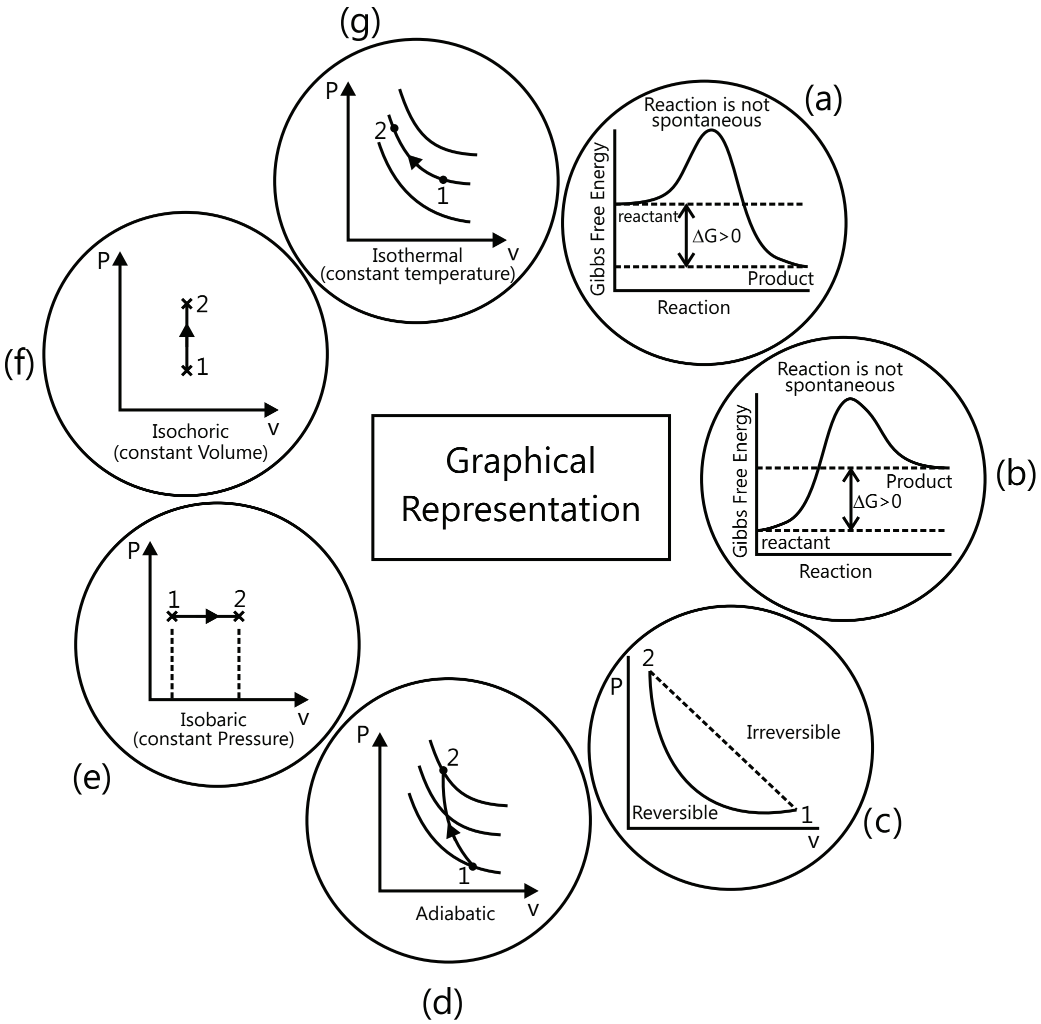


Figure 4.2 a to g: (b) Representation for the above processes

Illustration 1: Can you tell whether density is an intensive or extensive quantity? **(JEE MAIN)**

Sol: Intensive properties are those which does not depend on the amount of matter that is present whereas extensive properties vary with amount of matter present. Density is an intensive property. This is due to the fact that it does not depend on the amount of matter that is present. Different weights of the same matter will have the same density.

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How to check whether a quantity is intensive or extensive?

Suppose to measure a quantity q(S) relative to a system S. Now reproduce a copy of S and measure the same quantity for the system S+S composed of the two identical systems considered as a single system. If q(S+S) =q(S), then q is an intensive quantity.

If, for two different systems S and T, q(S+T) =q(S) +q (T), then q is an extensive quantity.

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4. MAJOR THERMODYNAMIC PARAMETERS: WORK, HEAT AND INTERNAL ENERGY

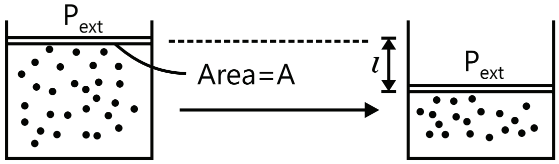
4.1 Work

Work is defined as a movement against force. It is a mode of energy transfer to or from a system with reference to surroundings.

Work: $W = \underset{\text{Applied Force}}{F}.\underset{\text{Distance}}{l}$

Mathematical Expression: If an object is displaced through a distance *l* against a force F, then the amount of work done is defined as **expansion work**.

Work associated with change in volume of a system against external pressure is called **mechanical work**.



Mechanical Work (=W) = $P_{ext}(V_2 - V_1) = P_{ext}\,\Delta$

Where P_{ext} =External pressure, ΔV =increase or decrease in volume.

4.1.1 Convention

'-' Sign	W>0 Positive work	ΔV<0	Work is done ON the system BY the surroundings
'+' Sign	W<0 Negative work	ΔV>0	Work is done BY the system ON the surroundings

If P_{ext} is not constant, then we have to look at infinitesimal changes.

$dw = - P_{ext}dV$ (d means this is not an exact differential)

Integral $w = -\int_1^2 P_{ext}dV$ (depends on the path)

Path dependence of W:

Example: Type of Process: Reversible process

Condition: = $P_{ext} = P$

Type of Work Done: Compression (by 2 paths)

$V_1 > V_2$ and $P_1 < P_2$

Table 4.2: To show path dependence of work

First Path	Second Path
$V_1 \rightarrow V_2$ at $P = P_1$ Then $P_1 \rightarrow P_2$ at $V = V_2$	$P_1 \rightarrow P_2$ at $V = V_1$ Then $V_1 \rightarrow V_2$ at $P = P_2$
$W_{(1)} = -\int_{V_1}^{V_2} P_{ext}dV - \int_{V_1}^{V_2} \cancel{P}_{ext}\cancel{dV}$ $= -\int_{V_1}^{V_2} P_1 dV$ $= -P_1(V_2 - V_1)$ $\boxed{W_{(1)} = P_1(V_1 - V_2)}$	$W_{(2)} = -\int_{V_1}^{V_2} \cancel{P}_{ext}\cancel{dV} - \int_{V_1}^{V_2} P_{ext}dV$ $= -\int_{V_1}^{V_2} P_2 dV$ $= -P_2(V_2 - V_1)$ $\boxed{W_{(2)} = P_2(V_1 - V_2)}$

W>0 ⟹ Work is done ON the system. It is compressed.

$\boxed{W_{(1)} \neq W_{(2)}}$

Illustration 2: Calculate the work done by 1 mole of an ideal gas in a piston fitted cylinder at the initial pressure of 24.83 atm pressure and 300 K to expand its volume to 10 litre if

(a) External pressure is reduced to 1 atm in single step.

(b) External pressure is reduced to 5 atm in 1st operation and then 1 atm in next step.

(c) Gas is allowed to expand into an evacuated space of 10 litre. **(JEE MAIN)**

Sol: By using ideal gas equation calculate the volume term and then calculate work done by the system by using pressure volume relationship.

$$P \times V_1 = nRT$$

$$V_1 = \frac{1 \times 0.0821 \times 300}{24.63} = 1\,\text{liter}$$

(a) $W = P\Delta V = -1 \times (10-1) = -9\ \text{L}-\text{atm}$

or $W_{\text{system}} = -9\ \text{L}-\text{atm}$ and $W_{\text{surr}} = +9\ \text{L}-\text{atm}$

(b) $[\because P_1V_1 = P_2V_2\ ; 24.63 \times 1 = 5 \times V_2;\ \therefore\ V_2 = 4.926]$

$$W = W_1 + W_2 = -5 \times (V_2 - V_1) + [-1 \times (10 - V_2)]$$

$$= -5 \times (4.926 - 1) + [-1 \times (10 - 4.926)]$$

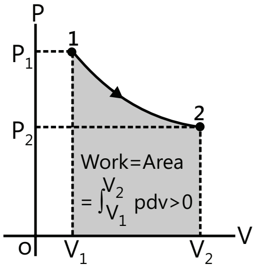
$$= -19.630 - 5.074$$

$$= -24.704\ \text{L}-\text{atm}$$

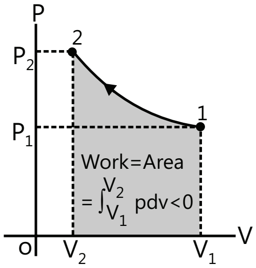
$\because W_{\text{sys}} = -24.704\ \text{L}-\text{atm};\ W_{\text{surr}} = +24.704\ \text{L}-\text{atm}$

(c) $W = -P \times \Delta V = -0 \times (10-1) = 0\,\text{L}-\text{atm}$

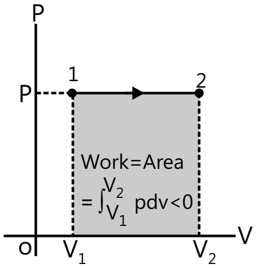
Work plots: In the following figures, observe how the sign of work changes on changing the volume.



Gas expands
dv > 0, W > 0



Gas compresses
dv < 0, W < 0



Constant P
$W = p\,(V_2 - V_1)$

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Work done is equal to the area under the P-V graph. But be careful about the sign. In case of expansion, the sign is negative while in compression, it is positive.

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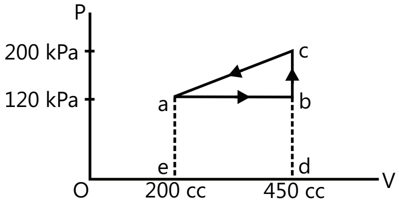
Illustration 3: Calculate the work done by a gas as it is taken from the state a to b, b to c and c to a as shown in figure. **(JEE MAIN)**



Sol: By using ideal gas equation calculate the volume term and then calculate work done by the system by using pressure volume relationship.

The work done by the gas in the process a to b is the area of abde

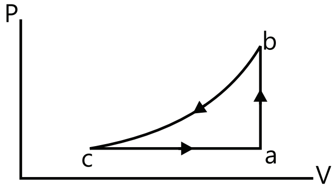
$$W_{ab} = (120\text{ kPa})\left(250\text{ cc}\right)$$
$$= 120 \text{ x } 10^3 \text{ x } 250 \text{ x } 10^{-6}\text{ J} = 30\text{ J.}$$

In the process b to c the volume remains constant and the work done is zero.

In the process c to a, the gas is Compressed. The volume is decreased and the work done by the gas is negative. The magnitude is equal to the area of caed. This area is cab + baed $= \frac{1}{2}\left(80\text{kPa}\right)\left(250\text{cc}\right)+30\text{J}$ = 10 J + 30 J= 40 J.

Thus, the work done in the process c to a is -40 J.

Illustration 4: A sample of an ideal gas is taken through the cyclic process abca. It absorbs 50 J of heat during the part ab, no heat during bc and rejects 70 J of heat during ca. 40 J of work is done on the gas during the part bc. (a) Find the internal energy of the gas at b and c if it is 1500 J at a (b) Calculate the work done by the gas during the part ca. **(JEE ADVANCED)**



Sol: By using the following equation find out the missing terms

$\Delta Q = \Delta U + \Delta W$.

(a) In the part ab, the volume remains constant. Thus, the work done by the gas is zero. The heat absorbed by the gas is 50 J. The increase in internal energy from a to b is $\Delta U = \Delta Q = 50$ J

As the internal energy is 1500 J at a, it will be 1550 J at b, in the part bc, the work done by the gas is

$\Delta W = -40$ J and no heat is given to the system. The increase in internal energy from b to c is

$\Delta U = -\Delta W = 40$ J

As the internal energy is 1550 J at b, it will be 1590 J at c.

(b) The change in internal energy from c to a is $\Delta U = 1500\text{J} - 1590\text{J} = -90\text{J}$

The heat given to the system is $\Delta Q = \Delta U + \Delta W$.

$\Delta W = \Delta Q - \Delta U = -70\text{ J} + 90\text{ J} = 20\text{ J}$

4.2 Heat and Internal Energy

The flow or exchange of energy between the system and the surroundings which can induce a change in the temperature of the system and/or the surroundings. Heat always flows from high temperature to low temperature.

It is expressed as q. Heat absorbed or evolved, $q = ms\Delta t$

m=Mass of substance, s=Specific heat and Δt =Tempearture difference.

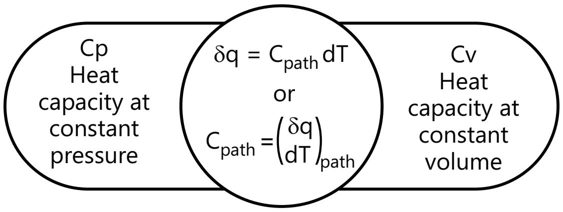
Heat is absorbed by the system	q= +ve
Heat is released by the system	q= -ve

Type of function: Path Function

Unit: Calories (1 cal = heat needed to raise the temperature of 1 g H_2O by 1^oC).

Also expressed as Joule (1 cal = 4.184J)

4.2.1 Heat Capacity



It is the amount of heat required to raise the temperature by one degree (usually expressed in Celsius or Kelvin). It is expressed in units of thermal energy per degree temperature.

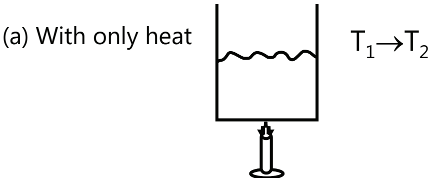
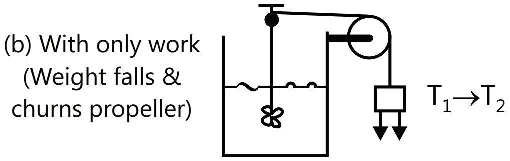
It is expressed as C.

Let dq be the amount of heat given to a system and the temperature of the system rises by dT.

Heat capacity= $\frac{dq}{dT}$

4.2.2 Relation of Work and Heat with Internal Energy

Temperature of water can be raised by-

Heating	**Doing work**
 **Figure 4.2:** (a) Heating to raise temperature	 **Figure 4.2:** (b) Doing work to raise temperature

But, $\oint(dw + dq) = 0$

⇒ (w + q) is independent of path

⇒ This implies that there exist a state function whose differential is dw + dq, known as **internal energy** or just energy. It is expressed as 'U'.

∴ dU = dw + dq

Internal energy can be given as:

$$U = U_{Kinetics} + U_{Potential} + U_{Electronic} + U_{nuclear} + \ldots\ldots$$

Illustration 5: A steam boiler made up of steel weighs 900kg. The boiler contains 400kg of water. Assuming 70% of the heat is delivered to boiler and water, how much heat is required to raise the temperature of the whole from 10°C to 100°C? Heat capacity of steel is 0.11 kcal/kg-K and heat capacity of water is 1 kcal/kg.K **(JEE MAIN)**

Sol: $\Delta q = (mS\Delta T)_{Boiler} + (mS\Delta T)_{Water}$

By using the above equation, first find out the ΔH required for complete heating and then by using the value of ΔH calculate the actual heat required when 70% is transferred to the system.

$\Delta q = (mS\Delta T)_{Boiler} + (mS\Delta T)_{Water}$

= 900 x 0.11 x 90 + 400 x 1 x 90 = 44910 kcal

Since, only 70% of heat given is used upto do so.

Thus, actual heat required = $\frac{44910 \times 100}{70}$ = 64157 Kcal.

Illustration 6: Assume an ideal gas obeys $\frac{P}{V}$ = constant. This gas confined in piston fitted cylinder having initial volume and pressure 2 litre and 1 atm is allowed to expand to occupy finally 6 litres. Calculate the work done by the system. **(JEE ADVANCED)**

Sol: From the given data calculate work done in terms of volume pressure relationship. i.e $W = -\int_{V_1}^{V_2} P\Delta V$

Given, $\frac{P}{V} = K \therefore K = \frac{1}{2} \text{atm } L^{-1}$ (initial condition)

$$W = -\int_{V_1}^{V_2} P\Delta V = -\int_{V_1}^{V_2} KV\Delta V = -K\int_{V_1}^{V_2} \frac{V^2}{2} = -K\left[\frac{V_2^2}{2} - \frac{V_1^2}{2}\right] = -\frac{1}{2}\left[\frac{36}{2} - \frac{4}{2}\right] = -8L - \text{atm}$$

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Always remember that the sign convention for work in physics and chemistry are both opposite. In physics the work done by the system is considered to be positive while in chemistry the work done on the system is considered to be positive. Hence in physics work = $\int PdV$ while in chemistry work = $-\int PdV$

Heat given to the system is considered to be positive while the heat extracted from the system is considered to be negative. This is same for both physics and chemistry.

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5. ZEROTH LAW OF THERMODYNAMICS

It was introduced after the 1st and 2nd law and thus got its name.

The law states: If two systems are in equilibrium with a third system, they are also in thermal equilibrium with each other. If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

Thermometers: Thermometers are common temperature measuring devices that are based on the zeroth law of thermodynamics.

Thermopile:

(a) Conversion of thermal energy into electrical energy can be done with the help of a thermopile, which is a device made up of multiple thermocouples connected in series.

(b) In accordance to the temperature increase in the thermocouples, proportional electrical output is received.

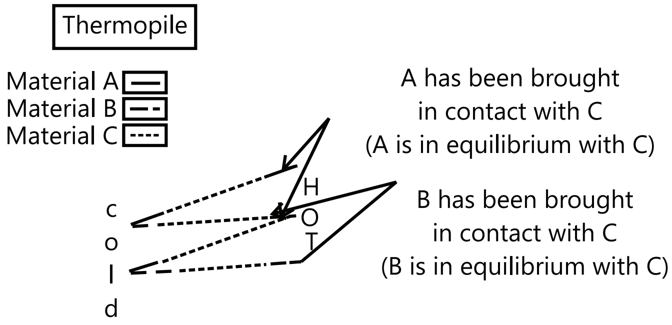


Figure 4.3: Thermopile

6. FIRST LAW OF THERMODYNAMICS

The increase in the internal energy of a thermodynamic system is equal to the amount of heat energy added to the system minus the work done by the system on the surroundings. When a system is changed from initial state to the final state it undergoes a change in the internal energy from E_i to E_f. Thus, ΔE can be written as: $\Delta E = E_f - E_i$

The change in internal energy can be brought about in two ways.

(a) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).

(b) By doing work on the system or the work done by the system.

Therefore, $E_f - E_i = q + w$ or $\Delta E = q + w$

Therefore, we can state that the change in internal energy of the system is equal to heat absorbed plus work done on the system

OR

The change in internal energy of the system is equal to heat absorbed minus work done by the system

OR

Energy is conserved; it can be neither created nor destroyed.

Therefore, it can be summarized as: $dU = dq + dw$

Or Mathematical statement: $\Delta U = q + w$ or $-\oint dq = \oint dw$

$$\Delta U_{system} = q + w;$$
$$\Delta U_{surroundings} = -q - w$$
$$\Rightarrow \Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0$$

Clausius statement of 1st law: The energy of the universe is conserved.

6.1 Enthalpy

Considering a system at constant pressure, the amount of heat which is released or absorbed is termed as **Enthalpy**. The change in enthalpy for a specific process is actually the change in internal energy associated with the changing volume.

$H = U + PV$

Enthalpy is a state function and an extensive property

Let a system at state-I be transformed to state – II at constant pressure condition $H = U + PV$

Table 4.2: Parameters for the given system

Parameters	State – I	State -II
Enthalpy	H_1	H_2
Internal energy	E_1	E_2
Pressure	P	P
Volume	V_1	V_2
	$H_1 = E_1 + PV_1$	$H_2 = E_2 + PV_2$
$H_2 - H_1 = \Delta H = (E_2 + PV_2) - (E_1 + PV_1)$ $= (E_2 - E_1) + P(V_2 - V_1)$ $\Delta H = \Delta E + P\Delta V$		

Also for an ideal gas $PV = nRT \Rightarrow$ $PV_1 = n_1RT$ and $PV_2 = n_2RT \Rightarrow P\left(V_2 - V_1\right) = \Delta n_gRT$

When $\Delta n_g = 0 \Rightarrow \Delta H = \Delta E$

When $\Delta n_g > 0 \Rightarrow \Delta H > \Delta E$

When $\Delta n_g < 0 \Rightarrow \Delta H < \Delta E$

Also $\Delta E = q_p - P\Delta V$ $q_p = \Delta E + P\Delta V$

And $\Delta H = q_p$ (i.e. Enthalpy change = heat exchange at constant pressure condition)

Also $\Delta E = q_v$, $\Delta H = \Delta E + P\Delta V$, $q_p = q_v + P\Delta V$

For a given system, H = f (T, P);

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial T}\right)_T dp$$

6.2 Degree of Freedom

Degree of freedom of gas molecules

A gas molecule can have following types of energies:

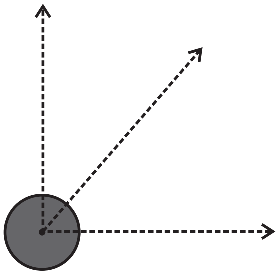
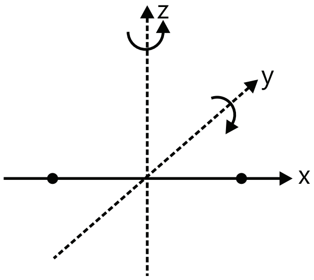
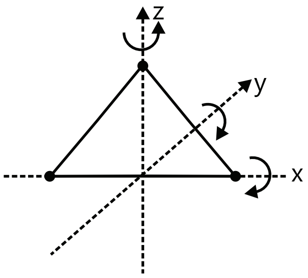
(a) Translational kinetic energy

(b) Rotational kinetic energy

(c) Vibrational energy (potential + kinetic)

Vibrational energy: The forces between different atoms of a gas molecule may be visualized by imagining every atom as being connected to its neighbours by springs. Each atom can vibrate along the line joining the atoms. Energy associated with this is called vibrational energy.

Table 4.4: Degree of Freedom

Degree of freedom	Explanation	Value of f	Diagram
Degree of freedom of monoatomic gas	1. A monoatomic gas molecule (like He) consists of a single atom. 2. Translational motion seen in any direction	3-all translational; due to its small moment of inertia, rotational kinetic energy is neglected	
Degree of freedom of a diatomic and linear polyatomic gas	Can not only move bodily but also rotate about any one of the three co-ordinate axes	f = 5 (3 translational + 2 rotational) at room temperatures and f = 7 (3 translational + 2 rotational + 2 vibrational) at high temperatures.	
Degree of freedom of nonlinear polyatomic gas	Can rotate about any of three co-ordinate axes	f = 6 (3 translational + 3 rotational) at room temperatures. and f = 8 (3 translational + 3 rotational + 2 vibrational) at high temperatures .	

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Degree of freedom of a diatomic and polyatomic gas depends on temperature since there is no clear cut demarcation line above which vibrational energy becomes significant. Moreover, this temperature varies from gas to gas. On the other hand for a monoatomic gas there is no such confusion. Degree of freedom here is 3 at all temperatures. Unless and until stated in the question ,you can take f = 3 for monoatomic gas, f = 5 for a diatomic gas and f = 6 for a non – linear polyatomic gas.

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6.3 Law of Equipartition of Energy

An ideal gas is the one which distributes internal energy equally in all degrees of freedom.

In each degree of freedom, energy of one mole of an ideal gas is $\frac{1}{2}$RT, where T is the absolute temperature of the gas. Thus, if f be the number of degrees of freedom, the internal energy of 1 mole of the gas will be $\frac{f}{2}$RT or internal energy of n moles of the gas will be $\frac{n}{2}$fRT.

Thus, $U = \frac{n}{2}fRT$.

For a monoatomic gas, f = 3

Therefore, $U = \frac{3}{2}RT$. (For 1 mole of a monoatomic gas.)

For a di and linear polyatomic gas at low temperatures, f = 5, so, $U = \frac{5}{2}RT$ (For 1 mole)

and for non-linear polyatomic gas at low temperatures, f = 6, so, $U = \frac{6}{2}RT$ (For 1 mole)

6.4 Specific Heats of Gases

The specific heats of gases are generally expressed as molar specific heats.

The expression for the internal energy is

$$U = nN_A\ KE_{avg} = nN_A\frac{3}{2}kT = \frac{3}{2}nRT$$

Two specific heats are defined for gases, one for constant volum (C_V) and one for constant pressure (C_P).

For a constant volume process with a monoatomic ideal gas, the first law of thermodynamics gives:

$$Q = C_v n\Delta T \qquad Q = \Delta U + P\Delta V = \Delta U$$

$$C_v = \frac{1\Delta U}{n\Delta T} = \frac{3}{2}R$$

Further application of the ideal gas law and first law gives the relationship $C_p = C_v + R$

Using first law of thermodynamics for a constant pressure process, $\Delta U + P\Delta V = nc_p\Delta T$

From the ideal gas law $(PV = nRT)$ under constant pressure condition it can be seen that,

$$P\Delta V = nR\Delta T \text{ so that } \frac{\Delta U}{\Delta T} + nR = nC_p$$

Since the constant volume specific heat is $c_v = \frac{1}{n}\frac{\Delta U}{\Delta T}$;

Thus, $C_p = C_v + R$

Ratio of heat capacity $\gamma = \frac{C_p}{C_v}$ depends on atomicity of gas.

6.5 Expansion of Ideal Gases

6.5.1 Isothermal Expansion

Isothermal Gas Expansion: In an isothermal gas expansion the temperature of the system remains constant throughout the process. Since, Internal energy depends on temperature, it follows that at constant temperature the total internal energy of the system remains constant. i.e $\Delta E = 0$

According to first law thermodynamics,

$\Delta U_{system} = q + w$; Since for isothermal expansion $\Delta U = 0\,; q = -w$

Also $\Delta H = \Delta U + \Delta(nRT)$ since ΔU and ΔT are zero, Hence $\Delta H = 0$

Gas (p_1, v_1, T) => gas (p_2, v_2, T) $(\Delta T = 0)$

Work done in reversible isothermal expansion:

The work done by the gas in each step of expansion can be given as

$$dw = -(P_{ext} - dp)\,dV = -P_{ext}.dV = -PdV$$

Total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is,

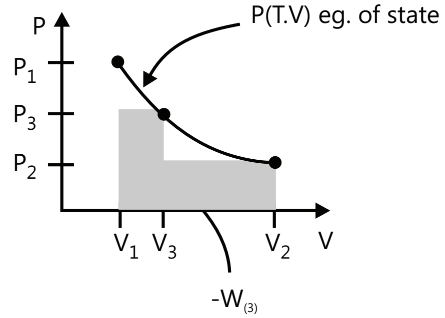

Figure 4.4: More work done to the surroundings

$$W_{rev} = \int_{V_1}^{V_2} PdV$$

For an ideal gas, $P = \frac{nRT}{V}$

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

Integrating, $w = -nRT\log_e\frac{V_2}{V_1} = -2.303nRT\log\frac{V_2}{V_1}$

At constant temperature, according to Boyle's Law, $w = -2.303nRT\log\frac{P_1}{P_2}$

Work done for Isothermal Compression: It has exactly same value as that of isothermal expansion but with opposite sign.

$$w = 2.303nRT\log\frac{V_1}{V_2} = 2.303nRT\log\frac{P_2}{P_1}$$

Work done for Irreversible Isothermal Expansion:

(a) Free expansion: In free expansion external work is zero thus work done is zero.

(b) Intermediate expansion:

$$w = \int_{V_1}^{V_2} P_{ext} \times dV = -P_{ext}(V_2 - V_1)$$

Maximum Work: Maximum work delivered to surroundings for isothermal gas expansion is obtained using a reversible path

For ideal gas: $W_{rev} = -\int_{V_1}^{V_2}\frac{nRT}{V}dV = nRT\ln\frac{P_2}{P_1}$

6.5.2 Adiabatic Expansion

Reversible adiabatic Expansion (or compression) of an Ideal Gas

1 mole gas (V_1. T_1) = 1 mole gas (V_2. T_2)

Adiabatic $\Rightarrow dq = 0$

Reversible $\Rightarrow dw = -PdV \Rightarrow$ Ideal gas

$$\text{From } 1^{st}\text{law } dU = -PdV \qquad \Rightarrow C_v dT = -PdV \text{ (along path)}$$

$$C_V\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V} \qquad \Rightarrow C_v\frac{dT}{T} = -R\frac{dV}{V} \quad (\text{using } P = \frac{RT}{V})$$

Integrating on both the sides

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

$$C_P - C_V = R\,;\ \frac{C_P}{C_V} - 1 = \frac{R}{C_V}\,;\ (\gamma - 1) = \frac{R}{C_V}$$

Putting the value in above equation we get, ; $\log\frac{T_2}{T_1} = \frac{R}{C_V}\log_e\frac{V_1}{V_2}$; $\log\frac{T_2}{T_1} = \log\left(\frac{V_1}{V_2}\right)^{\gamma-1}$; $\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

$$\text{For monoatamic ideal gas : } \gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} \qquad (> 1 \text{ generally})$$

In an adiabatic expansion ($V_2 > V_1$), the gas cools ($T_2 > T_1$) and in an adiabatic compression ($V_2 < V_1$), the gas heats up.

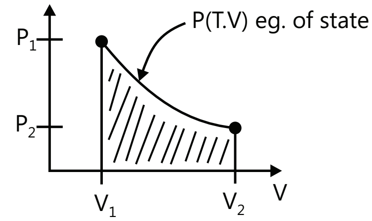

Figure 4.5: Comparison plots for different gases

For an ideal gas (one mole), $T = \frac{PV}{R}$

$$\Rightarrow \left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma} \Rightarrow P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$\Rightarrow PV^{\gamma}$ is constant in an adiabatic process

For an isothermal process (T = constant)

$\Rightarrow$ PV = constant.

Note that $V_2^{\ adiabatic} < V_2^{\ isothermal}$ because the gas cools during reversible adiabatic expansion

$$\text{Work done} = C_v.\Delta T = C_v(T_2 - T_1) = -\frac{R}{\gamma - 1}(T_2 - T_1)$$

$$\text{For n moles, } W = \frac{nR}{(\gamma - 1)}(T_1 - T_2)$$

Irreversible Adiabatic Expansion of an ideal gas against a constant external pressure

In free expansion, the external pressure is zero i.e. work done is zero. Accordingly ΔE which is equal to w is also zero. If $\Delta E = 0$, ΔT should be zero. Thus in free expansion $\Delta T = 0, \Delta E = 0, w = 0$ and $\Delta H = 0$

In intermediate expansion, the volume changes from V_1 to V_2 against external pressure $P_{ext.}$

$$w = -P_{ext}(V_2 - V_1) = -P_{ext}\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right) \qquad = -P_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right)\times R$$

or $$w = C_V(T_2 - T_1) = -RP_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right)$$

6.5.3 Isobaric Process

In an Isobaric process, $P = \text{constant}$

$$\Delta U = Q - W, W = \int PdV = \int_1^2 dV = P(V_2 - V_1)$$
$$Q = \Delta U + P(V_2 - V_1) = (U_2 - U_1) + P(V_2 - V_1) = (U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1 = \Delta H$$

6.5.4 Isochoric Process

Isochoric process is a Constant volume process, This implies, $V = \text{constant}$

$Q - W = \Delta U,\ W = \int PdV = 0$,no work done

$$Q = \Delta U = m\Delta u = m\int C_V dT$$

6.5.5 Polytropic Process

Polytropic Process: Its P-V relation can be expressed as PV^n = Constant, where n is a constant for a specific process

(a) Isothermal, T = Constant, if the gas is an ideal gas then PV = RT = constant, n = 1

(b) Constant-volume, V=constant, $V = \text{constant}(P)^{(1/n)}$, $n = \infty$ (For all substances)

(c) Adiabatic process, n=k for an ideal gas

$$P_1V_1^n = P_2V_2^n = PV^n$$
$$W = \int_1^2 PdV = \int_1^2 (P_1V_1^n)V^{-n}\,dV$$
$$= (P_1V_1^n)\int_1^2 V^{-n}dV = \frac{(P_1V_1^n)}{1-n}(V_2^{1-n} - V_1^{1-n}) = \frac{P_2V_2 - P_1V_1}{1-n}$$

6.6 Joule-Thomson Effect

A **Joule-Thomson effect** or a **process** is the change in temperature which was observed when a liquid or a gas was forced (or expands) through a small opening i.e. valve or a porous plug. This whole process being carried out in an isolated chamber prevented any heat exchange. Founded by Sir James Prescott Joule and Sir William Thomson, this was seen for almost a decent number of gases. But hydrogen, helium and neon seemed to behave differently. They heated up instead of cooling down. This instance was explained by the Inversion temperature i.e. a unique temperature possessed by every gas, below which it cools down on expansion.

Example - Diesel engines are used to power large trucks and other heavy equipment. In the cylinders of a diesel engine, air is compressed to very small volumes, raising the temperature to the point where fuel ignites spontaneously when injected into it.

6.7 Free Expansion

Adiabatic free expansion

(a) Expansion of gas in vacuum i.e. at zero external pressure, the system will give zero work.

(b) Thus, $W_{irr} = 0$

$$W_{irr} = 0$$
$$Q = 0$$
$$\Delta E = -W_{irr} = nC_v (T_2 - T_1)$$
$$\Delta H = nC_p (T_2 - T_1) = 0$$
$$T_1 = T_2$$

Considering an ideal gas, the above case is true. But, the final states of reversible and irreversible adiabatic transformations will be different. Thus, ΔE and ΔH will be different.

6.8 Limitations of First Law of Thermodynamics

Though the first law of thermodynamics gives us the exact equivalence of heat and work, whenever there is a change of heat into work or vice versa, it suffers from the following two limitations:

(a) No indication is available about the direction in which the change will proceed.

(b) This law can easily explain the heating of bullet when it strikes a block due to the conversion of kinetic energy into heat, but it fails to explain as to why heat in the block cannot be changed into kinetic energy of bullet and make it fly back from inside of the block.

(c) Practically it is not possible to convert the heat energy into an equivalent amount of work.

Illustration 7: One mole of a monatomic ideal gas is confined in to piston fitted cylinder occupying 10 litre at 300K. On heating the gas up to 400 K the gas also shows expansion and finally occupies 20 litres. Calculate **(JEE ADVANCED)**

(a) Change in internal energy in L-atm

(b) Change in heat enthalpy in L-atm

Sol: Using ideal gas equation to solve this problem to find out the pressure. Internal energy can be found out using heat content. Now we have calculated pressure and internal energy from these two terms , calculate the heat Enthalpy by the following equation.

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

$$P_1 = P_{initial} = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{10} = 2.463\,atm$$

$$P_1 - P_{final} = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 400}{20} = 1.642\,atm \quad ; \quad \Delta U = nC_v . \Delta T$$

$$\Delta U = 1 \times \frac{3R}{2} \times 100 = 300\,cal$$

$$\begin{aligned} \therefore \ \Delta H &= \Delta U + \Delta(PV) \\ &= 12.39 + P_1(V_2 - V_1) + V_2(P_2 - P_1) \\ &= 12.39 + 2.463x\ (20 - 10) + 20(1.642 - 2.463) \\ &= 12.39 + 24.63 - 16.42 = 20.6\ L - atm \end{aligned}$$

Illustration 8: A mole of a monoatmomic ideal gas at 1 atm and 273 K is allowed to expand adiabatically against a constant pressure of 0.395 bar until equilibrium is reached.

(a) What is the final temperature?

(b) What is the final volume?

(c) How much work is done by the gas?

(d) What is the change in internal energy? **(JEE MAIN)**

Sol: Let the initial and final volumes of the gas be V_1 and V_2 m^3 respectively. Given that the initial pressure (p_1) is 1×10^5 Pa, final pressure (p_2) is 0.395×10^5 Pa and the initial temperature is 273 K. Let the final Temperature be $T_{2.}$

We have,

$$P_1V_1 = n_1RT_1$$

$$V_1 = \frac{1 \text{ X}8.314 \text{ X}273}{1 \text{ X}10^5} = 0.022697 m^3$$

For an adiabatic expansion of 1 mole of monoatomic ideal gas against a constant external pressure (p_2), work done is given as

$$W = -p_2\left(V_2 - V_1\right) = C_v\left(T_2 - T_1\right) = \frac{3R}{2}\left(T_2 - T_1\right)$$

$$\text{Or} \quad -0.395 \times 10^5\left(V_2 - 0.022697\right) = (3 \times 8.314) / 2(T_2 - 273) \qquad \text{.... (i)}$$

$$\text{Again,} \quad p_2V_2 = nRT_2$$

$$0.395 \times 10^5 \times V_2 = 1 \times 8.314 \times T_2 \qquad \text{.... (ii)}$$

Solving eqns. (i) and (ii) we get,

(a) The final temperature, T_2 = 207 K

(b) The final volume, V_2 = 0.043578 m

Illustration 9: A quantity of air is kept in a container having walls which are slightly conducting. The initial temperature and volume are 27° C (equal to the temperature of the surrounding) and 800 cm^3 respectively. Find the rise in the temperature if the gas is compressed to 200 cm^3 (a) in short time (b) in a long time. Take $\gamma = 1.4$ **(JEE MAIN)**

Sol: By using the following equation calculate the missing terms

$$T_2V_2^{(\gamma-1)} = T_1V_1^{\gamma-1} \quad \text{or} \quad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

(a) Since compression of the gas takes place in a short time, the process is adiabatic.

$$\text{Thus,} \quad T_2V_2^{(\gamma-1)} = T_1V_1^{\gamma-1} \quad \text{or} \quad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(300 \text{ K}\right) \times \left[\frac{800}{200}\right]^{0.4} = 522k$$

Rise in temperature = T_2-T_1 = 222 K.

(b) Since compression of the gas takes place for a long time, the process is isothermal.

Thus, the temperature remains equal to the temperature of the surrounding that is 27° C.

The rise in temperature = 0.

Illustration 10: A gas undergoes a process such that $P \propto \frac{1}{T}$. If the molar heat capacity for this process is C = 33.25/ mol-K, find the degree of freedom of the molecules of the gas. **(JEE ADVANCED)**

Sol: As $P \propto \frac{1}{T}$ or PT = constant ... (i)

We have for one mole of an ideal gas PV = RT ...(ii) From Eq. (i) and (ii)

P^2V = constant or $PV^{1/2} = K$ (say) ... (iii)

From first law of thermodynamics,

$$\Delta Q = \Delta U + \Delta W \quad \text{Or} \quad C\Delta T = C_v\Delta T + \Delta W \quad \text{Or} \quad C = Cv + \frac{\Delta W}{\Delta T} \qquad \text{... (iv)}$$

Here, $\Delta W = \int PdV = K\int_{V_i}^{V_f} V^{-1/2}dV = \frac{P_fV_f - P_iv_i}{1-1/2} = \frac{R\left(T_f - T_i\right)}{1/2} = \frac{R\Delta T}{1/2}$

$\therefore \quad \frac{\Delta W}{\Delta T} = 2R$

Substituting in Eq. (iv), we have $C = C_V + 2R = \frac{R}{\gamma - 1} + 2R$

Substituting the values, $33.25 = R\left(\frac{1}{\gamma-1} + 2\right) = 8.31\left(\frac{1}{\gamma-1} + 2\right)$

Solving this we get $\gamma = 1.5$

Now, $\gamma = 1 + \frac{2}{F}$

Or degree of freedom $F = F + \frac{2}{\gamma - 1} = \frac{2}{1.5-1} = 4$

Illustration 11: 0.40 mole of a monoatomic gas fills a 1dm^3 container to a pressure 1.013×10^6 Pa. It is expanded reversibly and adiabatically until a pressure of 1.013×10^5 Pa is reached. Calculate:

(a) What is final volume of gas?

(b) Initial and final temperature of gas.

(c) Work done by gas during expansion. **(JEE ADVANCED)**

Sol: Volume of a gas can be calculated by using simple formula

PV^{γ} = constant of $P_1V_1^{\gamma}$

After calculating volume term, initial and final temperature can be calculated using following equation

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

As volume term and temperature term is known work done can be calculated either by using volume term or by using temperature term as follows:

Using temperature term, $w = \frac{nR}{\gamma-1}\left[T_2 - T_1\right]$

Using Volume term, $w = \frac{\left[P_2V_2 - P_1V_1\right]}{\gamma - 1}$

(a) We have PV^{γ} = Constant of $P_1V_1^{\gamma}$

$\therefore \quad 1.013 \times 10^6 \times 1^{\gamma} = 1.013 \times 10^5 \times V_2^{\gamma} \qquad (\therefore \gamma = \frac{5}{3})$

$\therefore \quad V_2 = 10^{\frac{3}{5}} = 3.98\text{dm}^3$

Also, we have $PV = nRT$

$P = 1.013 \times 10^6$, $V = 1\text{dm}^3 = 1 \times 10^3\text{m}^3$, $n = 0.40$, $R = 8.314$

For initial condition

$P = 1.013 \times 10^6 \times 10^{-3} = 0.40 \times 8.314 \text{ X } T_1$

$T_1 = 304.6$ K

also $TV^{\gamma-1}$ = constant or $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$\therefore\ 304.6 \times (1)^{\gamma-1} = T_2 \times (3.98)^{\gamma-1} \text{ or } T_2 = \frac{304.6}{(3.98)^{2/3}} \qquad \left(\therefore\ \gamma = \frac{5}{3}\right)$$

(c) Work done during expansion

(i) Either by : W

$$= \frac{nR}{\gamma-1}\left[T_2 - T_1\right] \left(\text{Since } T_2 \text{ and } T_1 \text{ are already evaluated}\right)$$

$$= \frac{0.4 \times 8.314}{\left(\frac{5}{3}-1\right)} \times \left[121.28 - 304.6\right] = -923.7\ \text{J}$$

$$\text{(ii) } W = \frac{\left[P_2V_2 - P_1V_1\right]}{\gamma-1} = \frac{1.013 \times 10^6 \times 1 \times 10^{-3} - 1.013 \times 10^5 \times 3.98 \times 10^{-3}}{\left(\frac{5}{3}-1\right)} = -923.7$$

7. SECOND LAW OF THERMODYNAMICS

First law showed the equivalence of work and heat.

$\Delta U = q + W$, $\oint dU = 0$ for cyclic process

$\Rightarrow q = -W$

(Suggests engine can run in a cycle and convert heat into useful work)

But second law puts restriction on useful conversion of q to w. It follows from observation of directionality to natural or spontaneous process. It provides a set of principles for determining the direction of spontaneous change and also for determining equilibrium state of a system.

Definition of Heat Reservoir: A very large system of uniform T, which doesn't change regardless of the amount of heat added or withdrawn. It is also called 'heat bath'. Real System can come close to this idealization.

Different statements of the Second Law

Kelvin: It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work at the same in the surroundings without transferring same heat to a colder reservoir.

Clausius: It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir at the same without converting some work into heat.

Alternative Clausius statement: All spontaneous processes are irreversible. (e.g. heat flows from hot to cold spontaneously and irreversibly)

Mathematical statement:

$$\oint \frac{dq_{rev}}{T} = 0 \ \textit{and}\ \oint \frac{dq_{irrev}}{T} < 0$$

$$\int \frac{dq_{rev}}{T} \text{ is a state function } - \int dS \ \rightarrow \ dS = \oint \frac{dq_{rev}}{T}$$

S = Entropy

$$\oint ds = 0 \rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T} > \int_1^2 \frac{dq_{irrev}}{T}$$

$$\text{for cycle } [1] \xrightarrow{\text{irrev}} [2] \xrightarrow{\text{rev}} [1]$$

$$\int_1^2 \frac{dq_{irrev}}{T} + \int_2^1 \frac{dq_{rev}}{T} = \oint \frac{dq_{irrev}}{T} < 0$$

$$\int_1^2 \frac{dq_{irrev}}{T} - \Delta S < 0 \Rightarrow \ \Delta S > \int_1^2 \frac{dq_{irrev}}{T}$$

7.1 The Carnot Cycle – A Typical Heat Engine

All paths are reversible

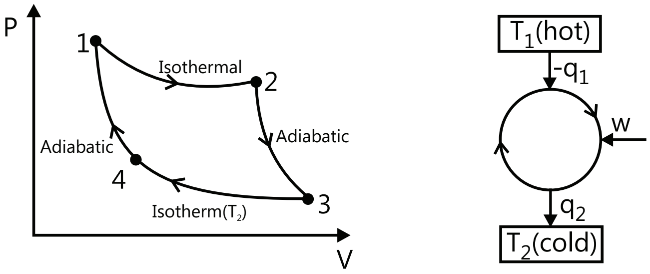

Figure 4.6: Carnot cycle

$1 \rightarrow 2$ isothermal expansion at T_1 (hot)	$U = q_1 - W_1$
$2 \rightarrow 3$ adiabatic expansion $(q = 0)$	$U = W_1'$
$3 \rightarrow 4$ isothermal compression at T_2 (cold)	$U = q_2 + W_2$
$4 \rightarrow 1$ adiabatic compression $(q = 0)$	$U = W_2'$

$$\text{Efficiency} \ = \frac{\text{Work output to surroundings}}{\text{Heat in at } T_1 \text{ (hot)}} - \frac{-\left(W_1 + W_1' + W_2 + W_2'\right)}{q_1}$$

$$1^{st}\text{Law} \quad \Rightarrow \oint dU = 0 \Rightarrow \ q_1 + q_2 = -\left(W_1 + W_1' + W_2 + W_2'\right)$$

$$\text{Efficiency} \equiv \varepsilon = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}$$

$$\text{Kelvin} \ : \ q_2 < 0 \ \rightarrow \ \text{Efficiency} \ \equiv \varepsilon < 1 \ \left(< \ 100\%\right) -W = \ q_1\varepsilon = \ \text{Work output}$$

Carnot cycle for an ideal gas

If cycle were run in reverse, then $q_1 < 0$, $q_2 < 0$, $w > 0$. It's a refrigerator.

$$1 \rightarrow 2 \qquad \Delta U = 0: \quad q_1 = -W_1 = \int_1^2 pdV = RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$2 \rightarrow 3 \qquad q = 0: \quad W_2' = C_v(T_2 - T_1)$$

$$\text{Rev adiabatic} \qquad \Rightarrow \ \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

$$3 \rightarrow 4 \qquad \Delta U = 0: \quad q_2 = -w_2 \int_3^4 pdV = RT_2 \ \ln\left(\frac{V_4}{V_3}\right)$$

$$4 \rightarrow 1 \qquad q = 0: \quad W_2' = C_v(T_1 - T_2)$$

Rev adiabatic $\Rightarrow \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$

$$\frac{q_2}{q_1} = \frac{T_2 \ln(V_4 / V_3)}{T_1 \ln(V_2 / V_1)} = \left(\frac{-T_2}{T_1}\right)$$

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \Rightarrow \left(\frac{V_4}{V_3}\right) = \left(\frac{V_1}{V_2}\right) \Rightarrow \frac{-q_2}{q_1} = \frac{T_2}{T_1}$$

Or $\left(\frac{q_1}{T_1}\right) + \left(\frac{q_2}{T_2}\right) = 0 \Rightarrow \oint \frac{dq_{rev}}{T} = 0$

Links heat engines to mathematical statement

Efficiency $\varepsilon = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$ → 100% as $T_2 \rightarrow 0$ K

7.2 Entropy

Carnot cycle for a reversible ideal gas:

$$\text{Efficiency}, \varepsilon = \frac{-W}{q_{rev}} = 1 + \frac{q_2^{rev}}{q_1^{rev}} = 1 - \frac{T_2}{T_1} \Rightarrow \frac{q_2}{T_1} + \frac{q_2}{T_2} - 0 \Rightarrow \oint \frac{dq_{rev}}{T} = 0$$

The efficiency of any reversible engine has to be the same as the Carnot cycle:

$\varepsilon = \frac{(-W)}{q_1}$ $\varepsilon' = \frac{(-W')}{q'_1}$ Assume $\in > \in'$

(Left engine is less efficient than Carnot cycle)

Since the engine is reversible. We can run it backwards. Use the work (-W') out of the Carnot engine as work input (W) to run the left engine backwards.

Total work out = 0 (-W' = W > 0)

But $\varepsilon' > \varepsilon \Rightarrow \frac{-W'}{q'_1} > \frac{-W}{q_1} \Rightarrow \frac{-W}{q'_1} > \frac{-W}{q_1} - \frac{W}{-q_1}$

This contradicts the 2nd law (Clausius). This says that we have a net flow of heat into the hot reservoir. But no work is being done!

∴ The efficiency of any reversible engine is ε = 1 – T_1/T_2

We can approach arbitrarily closely to any cyclic process using a series of only adiabats and isotherms.

∴ For any reversible cycle, $\oint \frac{dq_{rev}}{T} = 0$

This defines Entropy a function of state

$$dS = \frac{\hat{d}q_{rev}}{T} \Rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{\hat{d}q_{rev}}{T}$$

MASTERJEE CONCEPTS

Entropy is a state function, but to calculate ΔS requires a reversible path.

An irreversible Carnot (or any other) cycle is less efficient than a reversible one

$1 \rightarrow 2$

$$(-W)_{irrev} < (-W)_{rev} \quad \Rightarrow \quad W_{irrev} > W_{rev}$$

$$\Delta U = q_{irrev} + W_{irrev} = q_{rev} + W_{rev}$$

$$\therefore \quad q_{irrev} < q_{rev}$$

An irreversible isothermal expansion requires less heat than a reversible one.

$$S_{irrev} = 1 + \frac{q_2^{rev}}{q_1^{irrev}} \quad < \quad 1 + \frac{q_2^{rev}}{q_1^{rev}} = S_{rev} \qquad (q_2 < 0)$$

$$\text{also} \quad \frac{dq_{irrev}}{T} \quad < \quad \frac{dq_{rev}}{T} \quad \Rightarrow \quad \oint \frac{dq_{irrev}}{T} < 0$$

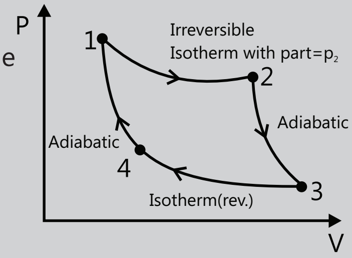

Figure 4. 7: (a) Process Plot

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The above equation (Note of MASTERJEE Concept) leads to Clausius inequality

$$\oint \frac{dq}{T} \le 0 \qquad \text{contains} \quad \left\{ \begin{array}{l} \dfrac{\hat{d}\, q_{rev}}{T} = 0 \\ \dfrac{\hat{d}\, q_{irrev}}{T} < 0 \end{array} \right.$$

Note that the entropy of an isolated system never decreases

Consider the system taken from 1 to 2, irreversibly as well as reversibly:

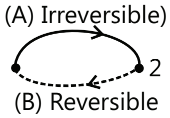


Figure 4.2: Cyclic process

(i) The system is isolated and irreversibly (spontaneously) changes from 1 to 2.

(ii) The system is brought into contact with a heat reservoir and reversibly brought back from 2 to 1.

Path (A) $q_{rev} = 0$ (isolated)

$$\text{Clausius} \quad \oint \frac{dq}{T} \le 0 \quad \Rightarrow \quad \int_1^1 \frac{dq_{rev}}{T} + \int_2^1 \frac{dq_{rev}}{T} \le 0\,; \qquad \int_2^1 \frac{dq_{rev}}{T} = S_1 - S_2 = \Delta S \le 0$$

$$\Delta S = S_2 - S_1 >= 0$$

This gives the direction of spontaneous change!

Irreversible Consider the universe as an isolated system containing our initial system and its surroundings.

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surr} > 0 \text{ therefore}$$

$$\Delta S_{surr} > -\Delta S_{system}$$

Reversible $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surr} = 0$ therefore,

$$\Delta S_{surr} = -\Delta S_{system}$$

Examples of a spontaneous process:

(a) Connect two metal blocks thermally in an isolated system (ΔU = 0)

Initially $T_1 \neq T_2$

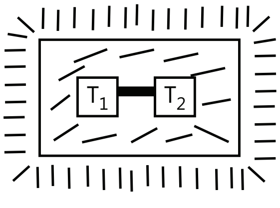


Figure 4.7: Spontaneity

$$dS = dS_1 - dS_2 - \frac{dq_2}{T_1} - \frac{dq_2}{T_1} - ds\frac{\left(T_2 - T_1\right)}{T_1 T_2}(dq_1 - dq_2)$$

dS > 0 for spontaneous process

$$\Rightarrow \quad \text{if} \quad \left.\begin{array}{l} T_2 > T_1 \Rightarrow dq_1 > 0 \\ T_2 < T_1 \Rightarrow dq < 0 \end{array}\right\} \begin{array}{c} \text{in both cases heat flows} \\ \text{from hot to cold as expected} \end{array}$$

(b) Joule expansion with on ideal gas

$$1 \text{ mol gas } \left(2V, T\right) = 1 \text{ mol gas } \left(V, T\right)$$

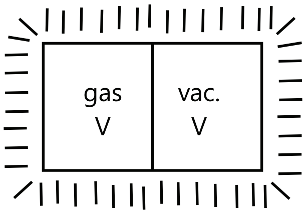


Figure 4.7: Joule expansion

$$\Delta S_{backwards} = \int \frac{\hat{d}q_{rev}}{T} = -\int \frac{dW}{T} = \int_{2v}^{v} \frac{Rdv}{V} = R\ln\frac{1}{2}$$

Therefore, Δ S-Rln2 > 0 (Spontaneous)

MASTERJEE CONCEPTS

- Entropy of a system increases when the temperature of system increases.
- Entropy of a system also increases during isothermal expansion
- Standard molar entropy is the molar entropy of pure substances at 25^{o}C and 1 bar pressure.
- Standard molar entropies increase as the complexity of a substance increases.
- The standard molar entropies of gases are higher than those of comparable solids and liquids at the same temperature.
- $\Delta S \geq 0$ for any process in an isolated system.
- At thermodynamic equilibrium $\Delta S_{total} = 0$.

Vaibhav Krishan (JEE 2009 AIR 22)

Entropy change for an ideal gas:

In going from initial to final state the entropy changes , ΔS for an ideal gas is given by the following relations,

(a) When T and V are two variables

$$\Delta S = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} \quad \text{Assuming } C_v \text{ is constant}$$

(b) When T and P are two variables,

$$\Delta S = nC_p \ln\frac{T_2}{T_1} - nR\ln\frac{p_2}{p_1} \quad \text{Assuming } C_p \text{ is constant}$$

(i) Thus for an Isothermal process (T constant)

$$\Delta S = nC_p \ln\frac{V_2}{V_1} \text{ or } = -nR\ln\frac{p_2}{p_1}$$

(ii) For isobaric process (p constant)

$$\Delta S = nC_p \ln\frac{T_2}{T_1} \text{ or } = nC_p \ln\frac{V_2}{V_1}$$

(iii) For isochoric process (V constant)

$$\Delta S = nC_v \ln\frac{T_2}{T_1} \text{ or } = nC_v \ln\frac{p_2}{p_1}$$

(iv) Entropy change during adiabatic expansion: In such process q=0 at all stages. Hence $\Delta S = 0$. Thus, reversible adiabatic processes are called isoentropic process.

7.2.2 Some Salient Features about Entropy Change

(a) For a reaction, entropy change ΔS is given by
$\Delta S = \sum S_{product} - \sum S_{reactants}$

(b) The units of entropy change are cal deg $^{-1}$ mol $^{-1}$and in S.I. units J K $^{-1}$ mol^{-1}

(c) At absolute zero temperature, i.e., zero Kelvin, the entropy of a pure crystal is zero. This is also referred as third law of thermodynamics.

Note: The entropies of CO, NO, NO_2, glassy solids, solid chlorine, etc., are not zero at absolute zero. These are exceptions to third law of thermodynamics.

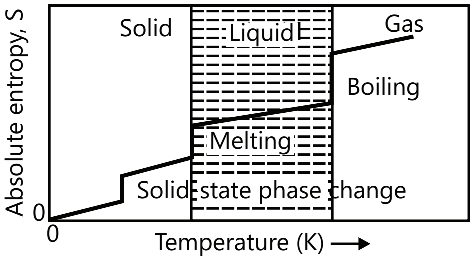


Figure 4.7: Plot of S vs T

MASTERJEE CONCEPTS

Misconception: Efficiency is not equal to 1- T_1/T_2 for all heat engines. It is only applicable to Carnot cycle. Maximum efficiency occurs only in Carnot's heat engine. But it is only a theoretical heat engine and practically such an engine is not possible because it involves reversible processes which take infinite time for completion of one cycle.

Vaibhav Krishan (JEE 2009 AIR 22)

Illustration 12: The enthalpy change, for the transition of liquid water to steam. ΔH_{vapour} is 40.8kJ mol^{-1}at 373 K. Calculation entropy change for the process. **(JEE MAIN)**

Sol: Here enthalpy and temperature is given, so entropy term can be calculated as follows:

$$\Delta S_{vapour} = \frac{\Delta H_{vapour}}{T}$$

The transition under consideration is :

$H_2O(l) \rightarrow H_2O(g)$

We know that, $\Delta S_{vapour} = \frac{\Delta H_{vapour}}{T}$

Given, $H_{vapour} = 40.8k.J\,mol^{-1} = 40.8 \times 1000\,Jmol^{-1}$; $T = 373K$

Thus, $\Delta S_{vapour} = \frac{40.8 \times 1000}{373} = 109.38\,JK^{-1}mol^{-1}$

Illustration 13: Heat supplied to a Carnot engine is 2x 10^3 J. How much useful work can be made by the engine working between 290 and 373 K? **(JEE MAIN)**

Sol: Using the following equation calculate the work done

$$\eta = \frac{W_{total}}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{W_{total}}{q_2} = \frac{T_2 - T_1}{T_2} \quad \text{or} \quad W = q_2\,\frac{T_2 - T_1}{T_2} = 2\ \text{x}10^3\,\text{x}\ \frac{373 - 290}{373} = 445\ \text{J}$$

Illustration 14: Calculation entropy change when 10 moles of an idea gas expands reversibly and isothermally from an initial volume of 10 litre to 100 litre at 300K. **(JEE MAIN)**

Sol: Here we are provided with initial volume and final volume so we have to use the following equation in order to calculate entropy term.

$$\Delta\ S\ =\ 2.303n\ R\ \log\left(\frac{V_2}{V_1}\right)$$

$$\Delta\ S\ =\ 2.303n\ R\ \log\left(\frac{V_2}{V_1}\right)\ =\ 2.303\ \text{x}\ 10\ \text{x}\ 8.314\ \log\left(\frac{100}{10}\right)\ =\ 191.24\ \text{J K}^{-1}$$

Illustration 15: Why would you expect a decrease in entropy as a gas condenses into liquid? Compare it with entropy decrease when a liquid sample is converted into solid? Or why is increase in entropy of the system greater for vaporization of a substance than for its melting? **(JEE MAIN)**

Sol: Gaseous molecules have free motion whereas liquid molecules have restricted motion or the entropy of gaseous molecules (more disorder) is higher than liquid molecules (relatively more ordered). Similarly, solid state has highly ordered arrangement thus possesses lowest entropy.

$$\Delta S_{condensation}\ =\ S_{(l)} - S_{(g)}\left(\Delta S = -ve;\ \text{a decrease}\right);\ \Delta S_{freezing}\ =\ S_{(s)} - S_{(l)}\left(\Delta S = -ve;\ \text{a decrease}\right)$$

$\Delta S_{condensation}$ Is much higher than $\Delta S_{freezing}$ for a substance as well as $\Delta S_{condensation}$ is almost constant for different liquids because $S_{(g)} >>> S$.

Illustration 16: Determine the standard entropy change for the reaction given below.$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ at 300K. If standard entropies of $H_2(g)$. $O_2(g)$ and $H_2O(l)$ are 126.6. 201.20 and 68.0 JK^{-1} mol^{-1} respectively. **(JEE ADVANCED)**

Sol: Here we are provided with standard entropies of reactant and products so entropy of reaction can be calculated using following equation

$$\Delta S_{Reaction} = \sum S^{o}{}_{product} - \sum S^{o}{}_{Reaction}$$

$$\Delta S_{Reaction} = \sum S^{o}{}_{product} - \sum S^{o}{}_{Reaction}$$

$$= 2 \times S^{2}{}_{H_2O} - \left[2 \times S^{o}{}_{H_2} + S^{o}{}_{O_2}\right] = 2\text{x}\ 68 - \left[2 \times 126.6 + 201.20\right]$$

$$\Delta S\ = -318.4\ \text{J K}^{-1}\text{mol}^{-1}$$

8. FUNDAMENTAL EQUATIONS, ABSOLUTE ENTROPY AND THE THIRD LAW

8.1 Fundamental Equations

From $dU\ =\ Tds\ -\ Pdv$

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T; \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

We can write similar equations for enthaipy

$$H = U + PV \Rightarrow dH = dU + d(PV) = dU + PdV + VdP$$

↖inserting dU =

$$\Rightarrow dH = TdS + VdP$$

The natural variables for H are then S and p.

From dH = TdS − VdP

$$\Rightarrow \left\{\frac{\partial H}{\partial S}\right\}_p = T\,;\left\{\frac{\partial H}{\partial P}\right\}_S = V$$

We can use these equations to find how S depends on T.

From dU= TdS+PdV

$$\Rightarrow \left\{\frac{\partial S}{\partial U}\right\}_V = \frac{1}{T}\,;\left\{\frac{\partial U}{\partial T}\right\}_V = \frac{C_V}{T}$$

From dH = TdS + VdP

$$\Rightarrow \left\{\frac{\partial S}{\partial H}\right\}_p = \frac{1}{T};\left\{\frac{\partial H}{\partial T}\right\}_p = \frac{C_p}{T}$$

8.2 Absolute Entropy

Absolute entropy of an ideal gas

$$\overline{S}(P.T) = \overline{S}^0(T) - R\ln P \;(\text{P in bar})$$

Then using $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$ we should be able to get $\overline{S}^0$ (T)

Consider the following sequence of processes for the substance A

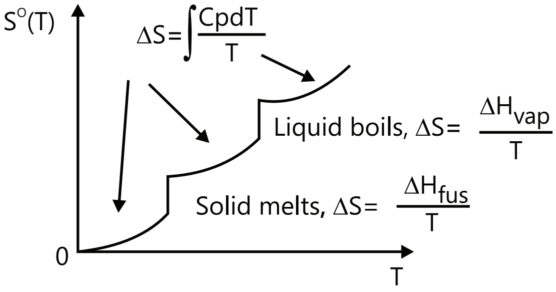


Figure 4. 8: Entropy plots for various processes

$$A(S,0K.1bar) \rightarrow A(S,T_m,1bar) \rightarrow A(l,T_m,1bar) \rightarrow (l,T_b,1bar) \rightarrow (g,T_b,1bar) \rightarrow (g,T,1bar)$$

$$\overline{S}(T,1bar) = \overline{S^\circ}(0K) + \int_0^{T_m}\frac{\overline{C}_p(s)dT}{T} + \frac{\Delta\overline{H}_{fus}}{T_m} + \int_{T_m}^{T_p}\frac{\overline{C}_p(\ell)dT}{T} + \frac{\Delta\overline{H}_{vapo}}{T} + \int_{T_m}^{T}\frac{\overline{C}_p(g)dT}{T}$$

Since ΔS° is positive for each of these processes. The entropy must have its smallest possible value at 0 K. If we take $\overline{S}^\circ(0K) = \text{zero}$ for every pure substance in its crystalline solid state, then we could calculate the entropy at any other temperature. This leads us to the Third law!

8.3 Third Law of Thermodynamics

Statement: The entropy of all perfectly crystalline solids is zero at the absolute zero temperature. Since entropy is a measure of disorder, it can be interpreted that at absolute zero, a perfectly crystalline solid has a perfect order of its constituent particles.

Application of the third law of thermodynamics is that it helps in the calculation of absolute entropies of the substance at any temperature T.

$$S_T = 2.303C_p\int_0^T \log T$$

Limitations of the Law:

(a) Glassy solids even at 0K has entropy greater than zero.

(b) Solids having mixtures of isotopes do not have zero entropy at 0 K.

9. CRITERIA FOR SPONTANEITY AND GIBBS FREE ENERGY

Gibbs free energy is defined as the energy available in the system for conversion into useful work.

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 irreversible

$(\Delta G)_{T,P} < 0$ Process is impossible (non-spontaneous)

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

To summarize the spontaneity of 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.

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

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

$$G = H - TS = U + PV - TS;\ dG = dU + PdV - TdS + VdP - SdT;\ dG = VdP - SdT$$

At constant temperature, $dG = VdP$ or $\left(\frac{\partial G}{\partial P}\right)_T = V$

At constant pressure, $dG = SdT \Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S$

Illustration 17: Calculate the boiling point of bromine from the following data:

ΔH° and S° value of Br_2 (l) $\rightarrow Br_2$ (g) are 30.91 KJ/ mole and 93.2 J/mol. K respectively. Assume that ΔH and ΔS do not vary with temperature. **(JEE ADVANCED)**

Sol: We are provided with standard enthalpy and standard entropy so temperature can be calculated by following equation

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

As entropy and enthalpy do not vary with temperature, ΔG becomes zero**.** Consider the process: Br_2 (l) $\rightarrow Br_2$ (g). The b. p. of a liquid is the temperature which the liquid and the pure gas coexist in equilibrium at 1 atm.

$\therefore \quad \Delta G = 0$

As it is given that ΔH and ΔS do not change with temperature

$$\Delta H = \Delta H^0 = 30.91 \text{ KJ}; \Delta S = \Delta S^0 = 93.2 \text{ J/K} = 0.0932 \text{KJ/K}$$

We have, $\Delta G = \Delta H - T\Delta S = 0$

$$\therefore \quad T = \frac{\Delta H}{\Delta S} = \frac{30.91}{0.0932} = 331.6 \text{ K}$$

This is the temperature at which the system is in equilibrium, that is, the b. p. of bromine.

Illustration 18: Estimate the temperature range for which the following standard reaction is product favoured

$$SiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow SiCl_4(g) + 2CO(g)$$

(JEE ADVANCED)

$$\Delta H^\circ = +32.9 \text{KJ/mole and } \Delta S^0 = 226.5 \text{J/mole.K}$$

Sol: In this problem, the factor ΔS° being positive, if favourable to spontaneity, whereas the factor ΔH° being positive is unfavourable. Thus the reaction becomes product-favoured above some temperature. We can set ΔG° equal to zero in the equation: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and solve for the temperature at which the reaction is at equilibrium and above which the reaction become product-favoured as then ΔG° becomes negative.

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{+32.9}{+0.2265} = 145.25 \text{ K}$$

Illustration 19: For the water gas reaction. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$. The standard Gibbs free energy of reaction (at 1000K) is -8.1 KJ/mol. Calculate its equilibrium constant. **(JEE ADVANCED)**

Sol: As standard free energy is given equilibrium constant can be calculated using the equation

$$K = \text{antilog}\left(\frac{-\Delta G^\circ}{2.303RT}\right) \quad \text{... (i)}$$

We know that, $K = \text{antilog}\left(\frac{-\Delta G^\circ}{2.303RT}\right)$ ... (ii)

Given that, $\Delta G^\circ = -8.1 \text{kJ/mol}$; $R = 8.314 \times 10^{-3} \text{KJK}^{-1} \text{ mol}^{-1}$; $T = 1000\text{K}$

Substituting these value in eq. (i), we get $K = \text{antilog}\left[\frac{-(-8.1)}{2.030 \times 8.314 \times 10^{-3} \times 1000}\right] = 2.65$

Illustration 20: The standard Gibbs free energies for the reactions at 1773 K are given below:

$$C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta G^0 = -380 \text{KJ mol}^{-1}$$

$$2C(s) + O_2(g) \rightleftharpoons 2CO_2(g); \quad \Delta G^0 = -500 \text{KJ mol}^{-1}$$

Discuss the possibility of reducing Al_2O_3 and PdO with carbon at this temperature.

$$4Al + 3O_2(g) \rightarrow 2Al_2O_2(s); \quad \Delta G^0 = -22500 \text{KJ mol}^{-1}$$

$$2Pd + O_2(g) \rightarrow 2PdO(s); \quad \Delta G^0 = -120 \text{KJ mol}^{-1}$$

(JEE ADVANCED)

Sol: Let us consider the reduction of Al_2O_3 by carbon

$$2Al_2O_3 + 3C(s) \rightarrow 4Al(s) + 3CO_2(g); \quad \Delta G^0 = -380 \times 3 + (22500) = +21360 \text{KJ}$$

$$2Al_2O_3 + 6C(s) \rightarrow 4Al(s) + 6CO_2(g); \quad \Delta G^0 = -500 \times 3 + 22500 = +21000 \text{KJ}$$

Positive value of ΔG° show that the reduction of Al_2O_3 is not possible by any of the above methods.

Now, let us consider the reduction of PdO.

$$2PbO_{(s)} + C \rightarrow 2Pb + CO_2; \qquad \Delta G^0 = +120 + \left(-380\right) = -260 KJ$$

$$2PbO_{(s)} + C \rightarrow 2Pb + CO_2; \qquad \Delta G^0 = +120 + \left(-500\right) = -380 \ KJ$$

Illustration 21: Calculate ΔG° for the following reaction

$$CO(g) + \left(\frac{1}{2}\right)O_2(g) \rightarrow CO_2(g); \ \ \Delta H^\circ = -282.84 KJ$$

Given, $S^\circ_{CO_2} = 213.8 JK^{-1}mol^{-1}$, $S^\circ_{CO_{(g)}} = 197.9 JK^{-1}mol^{-1}$, $S^\circ_{O_2} = 205.0 JK^{(-1)}mol^{(-1)}$. **(JEE ADVANCED)**

Sol: Here we are provided with standard entropies of reactant and products so entropy of reaction can be calculated using following equation

$$\Delta S_{Reaction} = \sum S^\circ_{product} - \sum S^\circ_{Reaction}$$

$$\Delta S^\circ = \sum S^\circ_{(products)} - \sum S^\circ_{(reactants)}$$

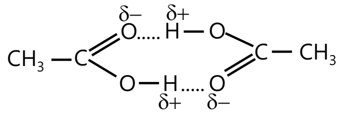
$$= \left[S^\circ_{CO_2}\right] - \left[S^\circ_{CO} + \frac{1}{2}S^\circ_{O_2}\right] = 213.8 - \left[197.9 + \frac{1}{2}205\right] = -86.6 kJ$$

According to Gibbs-Helmholtz equation,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = = -282.84 - 298 \times \left(-86.6 \times 10^{-3}\right) = -282.84 + 25.807 = -257.033 kJ$$

Illustration 22: Acetic acid CH_3COOH can form a dimer $(CH_3COOH)_2$ in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5kJ per mole of dimer. If at 25°C, the equilibrium constant for the dimerization is 1.3×10^3. Calculate ΔS° for the reaction. $2CH_3COOH(g) \rightarrow \left(CH_3COOH\right)_2 (g)$ **(JEE MAIN)**

Sol: We are provided with equilibrium constant and we have to calculate entropy term. Entropy term cannot be calculated directly, first we have to find out free energy change using equilibrium constant and then from free energy calculate the entropy term.



$$\Delta G^\circ = -2.303 RT \log K$$

$$= -2.303 \times 8.314 \times 298 \log\left(1.3 \times 10^3\right) = -17767.688 J = -17.767 kJ$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0; \ -17.767 = -66.5 - 298 \times \Delta S^0; \qquad \Delta S^\circ = \frac{-66.5 + 17.767}{298} = -0.163 kJ$$

THERMOCHEMISTRY

Thermochemistry is the branch of chemistry which deals with the heat changes in a chemical reaction.

10. THERMOCHEMICAL EQUATIONS

A Thermochemical equation presents a chemical reaction stating the amount of heat released or absorbed during the process. A thermochemical equation gives:-

(a) The physical state or the phase of the reactants and the products using the symbols s, l, g or aq(aqueous)).

(b) The allotropic form (if any) of the reactant.

(c) It tells whether a reaction proceeds with the evolution of heat or with the absorption of heat, i.e. heat change involved in the system. Heat changes of the system, heat of reactant and product are represented by ΔH, H_R and H_p respectively. $\Delta H = H_p - H_R$

Mathematically,

For Exothermic reactions, $H_R > H_P$ or ΔH is negative.

For endothermic reactions, $H_P > H_R$ or ΔH is positive.

11. HEAT OF REACTION AND KIRCHOFF'S EQUATION

Relation Between ΔH and ΔE

$\Delta H = \Delta E + P\Delta V$ $\Delta H = \Delta E + \Delta n_{(g)}RT$

Where $\Delta n_{(g)}$ = Number of moles of gaseous products-number of moles of gaseous reactants

Thus, is $\Delta n_{(g)} = 0$, ΔH = ΔE; $\Delta n_{(g)} > 1$, ΔH < ΔE; $\Delta n_{(g)} < 1$, ΔH < ΔE

For reactions involving only solids and liquids ΔH=ΔE; ΔH=22.0 kcal

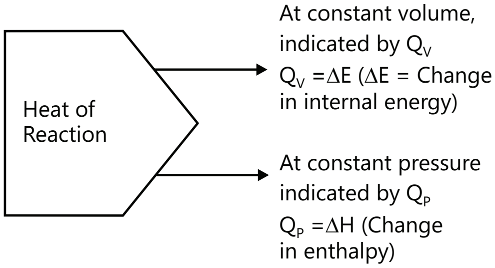


Figure 4.8: Heat of reaction

Factors Affecting Heat of Reaction

Among the various factors affecting heat of reaction, viz amount of reactants, physical state of reactants and products, pressure and temperature, temperature is the most important. The variation of heat of reaction with temperature is given by.

Kirchoff's Equations

(a) For heat of reactions at constant pressure, $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

(b) For heat of reactions at constant volume, $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$

Where ΔH_2=Heat of reaction at temperature T_2 at constant pressure

ΔH_1=Heat of reaction at temperature T_1 at constant pressure

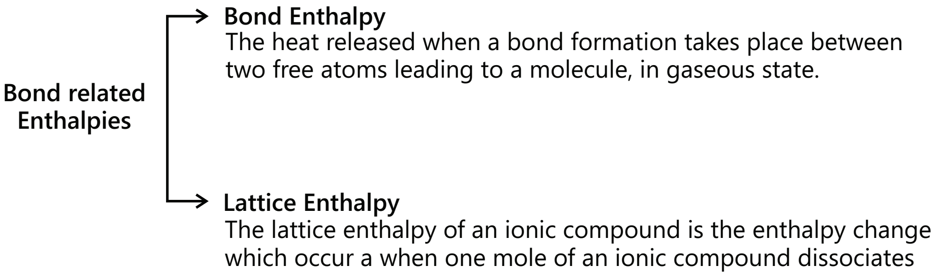
ΔE_2=Heat of reaction at temperature T_2 at constant pressure

ΔE_1=Heat of reaction at temperature T_1 at constant pressure

ΔC_p=Difference of heat capacities of products and reactants at constant pressure

ΔC_V=Difference of heat capacities of products and reactants at constant volume.

12. ENTHALPIES FOR VARIOUS PROCESSES



$$\Delta H_{reaction} = \left[\begin{array}{c}\text{Bond energy used for formation}\\ \text{of bond (to be taken as -ve)}\end{array}\right] + \left[\begin{array}{c}\text{Bond energy used for dissociation}\\ \text{of bond (to be taken as + ve)}\end{array}\right]$$

Figure 4.9: Enthalpies for various processes

$\Delta H_{reaction} = BE_{(R)} - BE_{(p)}$, taking Bond Energies as +ve values.

$Na^{+}Cl^{-}(s) \rightarrow Na^{+}(g) + Cl^{-}(g); \Delta_{lattice}H = +788 kJmol^{-1}$

Points to be noted:

(a) The bond enthalpy of diatomic molecules like H_2, Cl_2, O_2 etc. may be defined as the enthalpy change (always positive) when one mole of covalent bonds of a gaseous covalent substance is broken to form products in the gas phase, under conditions of constant pressure and temperature.

For example. Cl_2 (g) →2Cl (g); $\Delta H_{Cl\text{-}Cl} = +242 kJmol^{-1}$, O_2 (g) →2O (g); $\Delta H_{O\text{-}O} = +428 kJmol^{-1}$

(b) In case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. In such case, mean bond enthalpy is used. Mean bond enthalpy may be defined as the average enthalpy change to dissociate a particular type of bond in the compounds.

(c) In gas phase reaction, the standard enthalpy of reaction $\Delta_f H^\circ$ is related with the bond enthalpies of reactants and products as $\Delta_f H^\circ = \sum$ bond enthalpies (reactants) -$\sum$ bond enthalpies (products)

Electron Enthalpies

- **Ionization Enthalpy**
  It is the positive enthalpy change when an electron is removed form as isolated gaseous atom in its ground state under condition of constant temperature and pressure.
- **Electron Gain Enthalpy**
  It is the enthalpy change when an electron is added to a natural gaseous atom to convert it into a negative ion under condition of constant temperature and pressure.
  $X(g) + e^{-} \rightarrow X(g)$

Figure 4.9: Types of Electron Enthalpy

12.1 Enthalpy of atomization ($\Delta_a H$)

It is the enthalpy change (always positive) when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition

For example, $H_2(g) \rightarrow 2H(g)$; $\Delta_f H = 435.0 kJ\ mol^{-1}$ CH_4,(g)→C(g)+4H(g) ; $\Delta_f H = 1665 kJ\ mol^{-1}$

12.2 Heat/Enthalpy of Vaporization

In a system, a liquid is boiled and some of the molecules are converted to gas. The Heat of Vaporization corresponds to the heat that the liquid lost when the molecules phase changed. The Enthalpy of Vaporization, conversely, is the amount of heat applied to the system to boil the liquid. As a result, the temperature of the liquid remained constant, while the given heat was absorbed to convert the molecules. ΔH_{vap} = Heat of Vaporization

12.3 Standard Enthalpy of Formation

The definition of the standard enthalpy of formation is the change in enthalpy when one mole of a substance, in the standard state of 1 atm of pressure and temperature of 298.15 K, is formed from its pure elements under the same conditions.

For most chemistry problems involving standard enthalpies of formation, you will need the equation for the standard enthalpy change of formation:

$$\Delta H_f \text{reaction} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{Reactants})$$

Although this equation looks complicated, it essentially states that the standard enthalpy change of formation is equal to the **sum of the standard enthalpies of formation of the products** subtracted by the **sum of the standard enthalpies of formation of the reactants**.

There is an exception to ΔH_f^o values. In general practice, reference state, i.e., ΔH_f^o of P is taken to be white P despite that this allotropic form not being the most stable form but simply the most reproducible form.

MASTERJEE CONCEPTS

If we have a simple chemical equation with the variables A, B and C representing different compounds:
$A+B \leftrightharpoons C$

and we have the standard enthalpy of formation values as such:

$$\Delta H_f^o\left[A\right] = 433\ KJ/mol$$
$$\Delta H_f^o\left[B\right] = -256\ KJ/mol$$
$$\Delta H_f^o\left[C\right] = 523\ KJ/mol$$

The equation for the standard enthalpy change of formation is as follows:

$$\Delta H^o_{reaction} = \Delta H_f^o\left[C\right] - \left(\Delta H_f^o\left[A\right] + \Delta H_f^o\left[B\right]\right)$$
$$\Delta H^o_{reaction} = (1\cancel{mol})(523\ kJ/\cancel{mol}) - ((1\cancel{mol})(433\ kJ/\cancel{mol}) + (1\cancel{mol})(-256\ kJ/\cancel{mol}))$$

Since we have one mole of A, B and C, we multiply the standard enthalpy of formation of each reactant and product by 1 mole, which eliminates the mol denominator

$$\Delta H^o_{reaction} = \mathbf{346\ kJ}$$

We get the answer of 346 kJ, which is the standard enthalpy change of formation for the creation of variable "C".

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Illustration 23: What is the basic difference between enthalpy of formation and enthalpy of reaction? Illustrate with suitable example. **(JEE ADVANCED)**

Sol: Enthalpy of formation is the heat change during the formation of a compound from its components, e.g., enthalpy of formation of CO_2 is -94.3 =Kcal.

$$C + O_2 \rightarrow CO_2; \quad \Delta H = -94.3\ Kcal \qquad \text{... (i)}$$

Enthalpy of reaction is the heat change during the completion of any reaction, e.g.,

$$CO + \frac{1}{2}O_2 \rightarrow CO_2; \quad \Delta H = -68.0\ Kcal \qquad \text{... (ii)}$$

In some cases enthalpy of reaction and enthalpy of formation may be same as eq. (i) also enthalpy of reaction.

Illustration 24: Calculate $\Delta_f H^\circ$ for chloride ion from the following data: **(JEE ADVANCED)**

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g);\ \Delta_f H^\circ = -92.4KJ; \qquad HCl(g) + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq);$$

$$\Delta_f H^0 \text{of } H_3O^+(aq) = 0.0\ KJ$$

Sol: Given,

$$\frac{1}{2}H_2(g)+(aq)\rightarrow H^+(aq); \qquad \Delta H^0=0 \qquad \ldots \text{(i)}$$

$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\rightarrow HCl(g); \qquad \Delta H^0=-92.4\text{ kJ} \qquad \ldots \text{(ii)}$$

$$HCl(g)+H_2O(l)\rightarrow H_3O^+(aq)+Cl^-(aq); \quad \Delta H=-74.8\text{kJ} \qquad \ldots \text{(iii)}$$

By inspection method: eqs. (ii) + (iii) − (i) reveals that

$$\frac{1}{2}Cl_2(g)+(aq)\rightarrow Cl^-(aq); \qquad \Delta H=-167.2\text{ KJ}$$

i.e. Heat of Formation of $Cl^-(aq)=-167.2\text{KJ}$

12.4 Enthalpy of Combustion

The standard enthalpy of combustion is the enthalpy change when one mole of a reactant completely burns in excess oxygen under standard thermodynamic conditions (although experimental values are usually obtained under different conditions and subsequently adjusted).

Expressed as H_{comb} or H_c when the enthalpy required is not combustion, it can be denoted as H_{total}. Enthalpies of combustion are typically measured using bomb calorimetry, and have units of energy (typically kJ); strictly speaking, the enthalpy change per mole of substance combusted is the standard molar enthalpy of combustion (which typically would have units of kJ mol^{-1}).

12.4.1 Bomb Calorimetry

(a) Purpose of Bomb Calorimetry Experiments

Bomb calorimetry is used to determine the enthalpy of combustion, $\Delta_{comb}H$, for hydrocarbons:

$$C_xH_YO_z(s) + (2X+Y/2-Z)\ O_2(g) \longrightarrow X\ CO_2 + YH_2O$$

Since combustion reactions are usually exothermic (give off heat), $\Delta_{comb}H$ is typically negative. (However, be aware that older literature defines the "heat of combustion" as $\Delta_{comb}H$, so as to avoid compiling tables of negative numbers!

(b) Construction of a Bomb Calorimeter

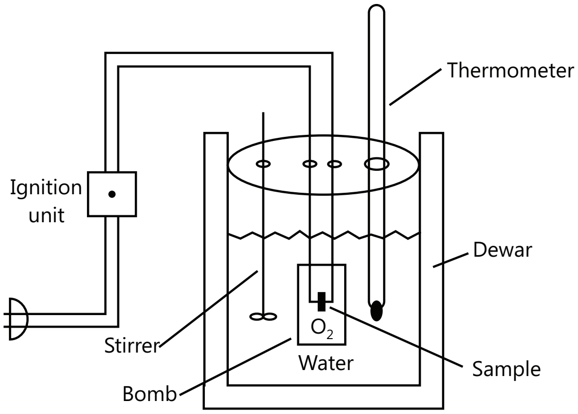


Figure. 4.9 Bomb calorimeter

Apparatus: Sample, oxygen, the stainless steel bomb, and water.

Role of Dewar: The dewar prevents heat flow from the calorimeter to the rest of the universe, i.e.,

$$q_{calorimeter} = 0$$

Since the bomb is made from stainless steel, The combustion reaction will occur at constant volume with no work, since the Bomb is of Stainless steel i.e.,

$$W_{calorimeter} = PdV = 0$$

Hence, ΔU, change in internal energy, is zero, for the calorimeter

$$\Delta U_{calorimeter} = q_{calorimeter} + W_{calorimeter} = 0$$

The calorimeter is isolated from the rest of the universe. This is the thermodynamic interpretation of the above equation.

Illustrations 25: Diborane is a potential rocket fuel, which undergoes combustion according to the reaction,

$B_2H_6(g)+3O_2(g)\rightarrow B_2O_3(s)+3H_2O(g)$

From the following data calculate the enthalpy change for the combustion of Diborane

$2B(s)+\frac{3}{2}O_2(g)\rightarrow B_2O_3(s);$ $\Delta H=-1273\text{kJ mol}^{-1}$ ... (i)

$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l);$ $\Delta H=-286\text{kJ mol}^{-1}$ ... (ii)

$H_2O(l)\rightarrow H_2O(g);$ $\Delta H=44\text{ kJmol}^{-1}$ ... (iii)

$2B(s)+3H_2(g)\rightarrow B_2H_6(g);$ $\Delta H=36\text{ kJ mol}^{-1}$ ... (iv) **(JEE ADVANCED)**

Sol: To get,

$B_2H_6(g)+3O_2(g)\rightarrow B_2O_3(s)+3H_2O(g)$

By inspection method $(i)+3\times(ii)+3\times(iii)-(iv)$

$2B(s)+(3/2)O_2(g)\rightarrow B_2O_3(s);$ $\Delta H=-1273\text{ kJ mol}^{-1}$ ... (i)

$3H_2(g)+(3/2)O_2(g)\rightarrow 3H_2O(l);$ $\Delta H=-286\text{ x}3$ ... (ii)

$3H_2O(l)\rightarrow 3H_2O(g);$ $\Delta H=44\text{ x}3$ ... (iii)

$2B(s)+3H_2(g)+3O_2\rightarrow B_2O_3(s)+3H_2O(g);$ $\Delta H=-1999\text{ kJ}$

$2B(s)+3H_2(g)\rightarrow B_2H_6(g);$ $\Delta H=36\text{ kJ}$

$B_2H_6(g)+3O_2(g)\rightarrow B_2O_3(s)+3H_2O(g)$ $\Delta H=-2035\text{ kJ mol}^{-1}$

12.5 Enthalpy of Solution

The enthalpy change of solution is the enthalpy change when 1 mole of an ionic substance dissolves in water to give a solution of infinite dilution. The other terms used for enthalpy of solution are;

(a) Integral enthalpy of dilution: It is the change in enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to other, e.g.,

$HCl(g)+40H_2O\rightarrow HCl(40H_2O);$ $\Delta H=-73.0\text{kJmol}^{-1}$ ...(i)

$HCl(g)+10H_2O\rightarrow HCl(10H_2O);$ $\Delta H=-69.5\text{kJmol}^{-1}$ ...(ii)

Also by eqs. (i) and (ii)

$HCl(10H_2O)+30H_2O(l)\rightarrow HCl(40H_2O);$ $\Delta H=-3.50\text{kJmol}^{-1}$

i.e. integral enthalpy of dilution of $HCl(10H_2O)$ to $HCl(40H_2O)$ is -3.50 kJ mol^{-1}

(b) Differential enthalpy of solution: It is the change in enthalpy when 1 mole of a solute is dissolved in excess of a solution of known concentration so that there occurs no appreciable change in the concentration of solution.

(c) Differential enthalpy of dilution: It is the change in enthalpy when 1 mole of a solvent is added to a large volume of the solution of known concentration so that there occurs no change in the concentration of solution.

Illustration 26: Calculate the enthalpy change when infinitely dilute solutions of $CaCl_2$ and Na_2CO_3 are mixed for respectively. **(JEE MAIN)**

Sol: The given reaction on mixing two solutions is $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

At infinite dilution, each species is 100% dissociated and thus,

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)\downarrow + 2Na^+(aq) + 2Cl^-(aq)$$

Or $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

The given reaction on mixing two solutions is $CaCl_2 \quad Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

At infinite dilution, each species is 100% dissociated and thus,

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)\downarrow + 2Na^+(aq) + 2Cl^-(aq)$$

Or $Ca^{2}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

$$\therefore \Delta H = \sum_{\text{Product}}^{0} - \sum_{\text{Reactant}}^{0} = \Delta_f H \sum{}^{o} CaCO_3 - \left[\Delta_f H^o Ca^{2+} + \Delta_f \sum{}^{o} CO_3^{2-}\right] \qquad \because (H^o = \Delta H^0_{\text{formation}})$$

$$= -288.5 - (-129.80 - 161.65)\ ;\ = 2.95 \text{ kcal}$$

12.6 Enthalpy of Hydration, $\Delta_{Hyd}H$

The negative enthalpy change observed when one mole of an anhydrous (or partly hydrated) combines with the required number of moles of water to form a specific hydrate at the specified temperature and pressure.

For example: $MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4(s).7H_2O(s)\ ;\quad \Delta_{hyd}H = -106.6 \text{ kJmol}^{-1}$

12.7 Enthalpy of Transition

It is the enthalpy change when one mole of one allotropic form changes to another under constant temperature and pressure.

For example: $C\ (\text{graphite}) \rightarrow C\ (\text{diamond})\ ;\ \Delta_{tra}H = 1.90 \text{ kJ mol}^{-1}$

12.8 Enthalpy of Neutralization $\Delta_{neut}H$

It is the enthalpy change (always negative) when one g-equivalent of an acid and one g-equivalent of a base undergo complete neutralization in aqueous solution and all the reactants & products are at the same specified temperature and pressure.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l);\ \Delta_{neut}H = -57.7 \text{ kJeq}^{-1}$$

The enthalpy of neutralization of strong acid and strong base is always constant (-57.7 kJ) independent from the acid and base taken. However the magnitude of enthalpy change of neutralization decreases when any one of the acid or base taken is weak.

Illustration 27: Whenever an acid is neutralized by a base, the net reaction is

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l); \Delta H = -57.1 \text{ kJ}$$

Calculate the heat evolved for the following experiments:

(i) 0.50 mole of HCl solution is neutralized by 0.50 mole of NaOH solution.

(ii) 0.50 mole of HNO_3 solution is mixed with 0.30 mole of KOH solution.

(iii) 100 mL of 0.2 M HCl is mixed with 100 mL of 0.3 M

(iv) 400 mL of 0.2 M H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution. **(JEE ADVANCED)**

Sol: According to the reaction, $H^+(aq) + OH^-(aq) \rightarrow H_2O(l);\ \Delta H = -57.1\,kJ$

When 1 mole of ions and 1 mole of ions are neutralized,1 mole of water is formed and 57.1 kJ of energy is released.

(i) 0.50 mole HCl $\equiv$ 0.50 mole H^+ ions

0.50 mole NaOH $\equiv$ 0.50 mole OH^- ions

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water = 57.1 x 0.5 = 28.55 kJ

(ii) 0.50 mole $HNO_3 \equiv$ 0.50 mole H^+ ions

0.30 mole KOH 0.30 mole OH^- ions

i.e., 0.30 mole of ions react with 0.30 mole of OH^- ions to form 0.30 mole of water molecules.

Heat evolved in the formation of 0.3 mole of water = 57.1 x 0.3 = 17.13 kJ

(iii) 100 mL of 0.2 M HCl will give $\left(\frac{0.2}{1000}\ x100\right) = 0.02$ mole of H^+ ions and 100 mL of 0.3 M NaOH will give $\left(\frac{0.3}{1000}\ x100\right) = 0.03$ mole of H^- ions i.e., 0.02 mole of ions react with 0.02 mole of ions to form 0.02 mole of water molecules. Heat evolved in the formation of 0.02 mole of water = 0.02 x 57.1 = 1.142 kJ

(iv) 400 mL of 0.2 M H_2SO_4 will give $\left(\frac{2x0.2}{1000}\ x400\right) = 0.16$ mole of H^- ions and 600 mL of 0.1 M KOH will give $\left(\frac{0.1}{1000}\ x600\right) = 0.06$ mole of OH^- ions i.e., 0.06 mole of ions react with 0.06 mole of ions to form 0.06 mole of water molecules.

Heat evolved in the formation of 0.06 mole of water = 0.06 x 57.1 = 3.426 kJ

12.9 Enthalpy of Sublimation $\Delta_{Sub}H$

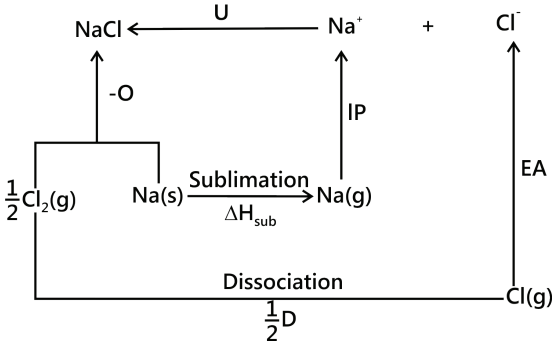
It is the enthalpy change when one mole of solid substance changes from solid state to gases state under conditions of constant temperature and pressure.

For example $Na_{(s)} \xrightarrow[\Delta_a]{\text{Substance}} Na_{(g)}\ \Delta_a\ H = x\ kJ\ mol^{-1}$

12.10 Born Haber Cycle

It is a series of steps (chemical processes) used to calculate the lattice energy of ionic solids, which is difficult to determine experimentally. You can think of BH cycle as a special case of Hess's law, which states that the overall energy change in a chemical process can be calculated by breaking down the process into several steps and adding the energy change from each step.

Example: Sodium chloride



Steps Involved :

(a) Sublimation (ΔH_{sub}) : Solid sodium changes into gaseous sodium.

(b) Ionization (IP) : gaseous sodium changes into sodium ion.

(c) Dissociation (D) : Dissociation of chlorine molecule.

(d) Electron affinity (EA) : Gaseous chlorine atom changes into chloride ions.

(e) Combination of ions to form neutral molecule.

Total energies evolved in the above reaction = $= \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$

Thus according to Hess's law, $-Q = \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$

Illustration 28: Which ions are present in MgO(s)?

Calculate the enthalpy change for the reaction $Mg(s) + ½O_2(g) \rightarrow MgO(s)$

What kind of enthalpy change is this? Standard enthalpy of formation of MgO is **(JEE MAIN)**

$\Delta H_{atm(O)} = +249 \text{ kJ mol}^{-1}$

$\Delta H_{atm(Mg)} = +148 \text{ kJ mol}^{-1}$

$\Delta H_{1st\ Ionisation\ energy(Mg)} = +738 \text{ kJ mol}^{-1}$

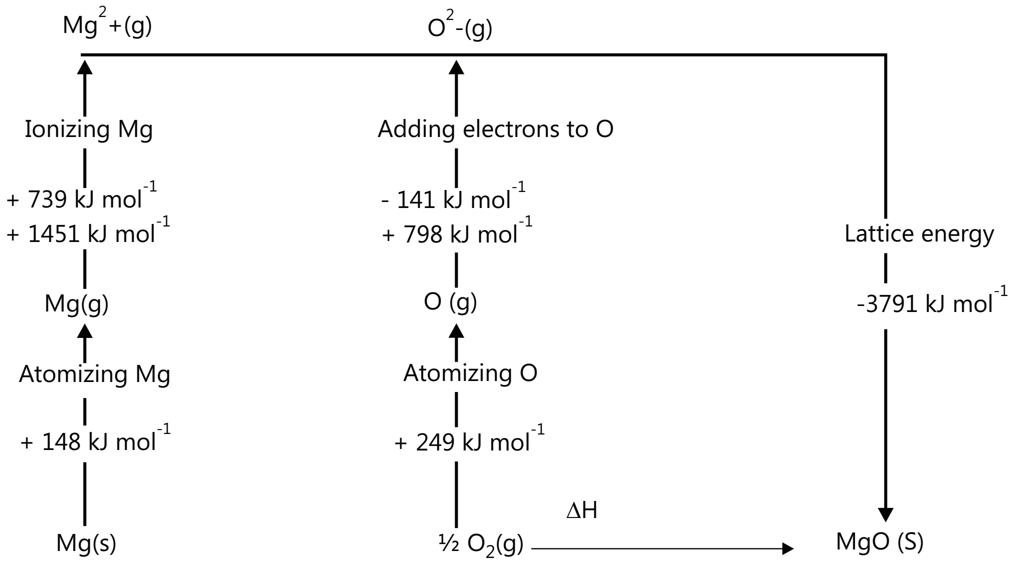
$\Delta H_{2st\ Ionisation\ energy(Mg)} = +1451 \text{ kJ mol}^{-1}$

$\Delta H_{1st\ electron\ affinity(O)} = +141 \text{ kJ mol}^{-1}$

$\Delta H_{2st\ electron\ affinity(O)} = +798 \text{ kJ mol}^{-1}$

$\Delta H_{lattice\ energy(MgO)} = +3791 \text{ kJ mol}^{-1}$

Sol:



$\Delta H \quad = \quad (148 + 1451 + 738) + (249 + 798 - 141) - 3791$

$\quad\quad = \quad 2337 + 906 - 3791 - 548 \text{ kJ mol}^{-1}$

The actual value for this reaction is -602 kJ mol^{-1} This is because there is a degree of covalent bonding in MgO. Therefore the bonds formed are slightly stronger than those predicted by a purely ionic model.

Illustration 29: Calculate the standard heat of formation of Carbon disulphide (l). Given that the standard heats of Combustion of Carbon (s), Sulphur (s) and Carbon disulphide (are – 393.3, 293.7 and 1108.76 kJ respectively.

Sol: Required equation is $C(s) + 2S(s) \rightarrow CS_2(l);\ \Delta H_f = ?$

Given, $C(s) + O_2(g) \rightarrow CO_2(g) \quad (\Delta H = -393.3 \text{ kJ})$ .... (i)

$S(s) + O_2(g) \rightarrow SO_2(g) \quad (\Delta H = -293.3 \text{ kJ})$ .... (ii)

$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) \quad (\Delta H = -1108.76 \text{ kJ})$ .... (iii)

First method: Multiply the eq. (ii) by 2.

$2S(s) + 2O_2(g) \rightarrow 2SO_2(g) \quad (\Delta H = -587.44 \text{ kJ})$ .... (iv)

Adding eqs. (i) and (iv) and subtracting eq. (iii),

$\left[C(s) + 2S(s) + 3O_2(g) - CS_2(l) - 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) - CO_2 - 2SO_2\right]$

$C(s) + 2S(s) \rightarrow CS_2(l)$

This is the required equation.

Thus, = -393.3 – 587.44 + 1108.76 = 128.02.kJ

Standard heat of formation of $CS_2(\ell)$ = 128.02 kJ

Second Method:

$C(s) + O_2(g) \rightarrow CO_2(g); \quad (\Delta H = -393.3 \text{ kJ})$ .... (i)

$S(s) + O_2(g) \rightarrow SO_2(g); \quad (\Delta H = -293.72\text{kJ})$ .... (ii)

$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g); \quad (\Delta H = -1108.76 \text{ kJ})$ .... (iii)

From eqs. (i) and (ii),

Enthalpy of CO_2 = -393.3 kJ; Enthalpy of SO_2= -293.72 kJ;

Enthalpy of O_2 = 0 (By convention)

ΔH of eq. (iii) Enthalpies of products Enthalpies of reactants

$-1108.76 = -393.3+2\,(-293.72) - \Delta HCS_2\,(l)$

$\Delta HCS_2\,(l) = (1108.76-980.74) = 128.02$ kJ

Enthalpy of CS_2 (l) = 128.02 kJ

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Enthalpy of reaction refers to entire chemical equation and not to any particular reactant or products. Alternatively, enthalpy of a reaction is the rate of change of Enthalpy of the system with the extent of reaction at constant P and T. If all the chemical species in a chemical equation are present in the respective standard state, i.e., at P=1 atm (better to say 1 Bar) and T = 298 K, the enthalpy of reaction is referred as standard enthalpy of reaction.

For reaction involving only solid or liquid state. (and if $\Delta V = 0$ of reactants and products, $\Delta H = \Delta U$, If temperature range is not small or C_P varies appreciably with temperature, Then, $C_P = \alpha + \beta T + \gamma T^2$ Where α, β and γ are constant for given species $\therefore \Delta C_P = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2$

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13. TROUTON’S RULE

Trouton’s rule: According to this rule, the ratio of heat of vaporization and the normal boiling point of a liquid is approximately equal to 88 J/mol, i.e., $\dfrac{\Delta_{vap}\ H}{T_b\left(\text{in K}\right)} = 88\ \text{J / mol}$