

UNIT : 6

CHEMICAL THERMODYNAMICS

Fundamentals:

a) Chemical Thermodynamics:

The study of the flow of heat or any other energy form into or out of system as it undergoes physical or chemical transformation is chemical thermodynamics.

b) System:

A system is the quantity of matter or a region selected for study.

c) Surroundings

Everything outside the system is called surrounding.

d) Boundary

Closed surface separating the system from its surroundings is called boundary.

e) Universe:

The combination of system, surrounding and boundary is called universe.

f) Thermodynamic system:

Based upon the nature of boundary, they are of three types:

- i) Open system ii) Closed system iii) Isolated system.

→ Movement of both mass and energy
→ Movement of energy but not mass
→ No movement of energy or mass

(g): Property:

Any characteristic of a system that can be measured or calculated is called property.

i) Extensiveii) Intensive

→ dependent upon the quantity of matter
→ independent upon the quantity of matter
→ They can be added up
→ They can't be added up.

Eg. Volume (V), No. of moles (n), → Eg. pressure, density, total energy (E), enthalpy, temperature, viscosity, entropy, Gibbs free energy. $R \cdot T$, concentration.

(h): State / State Variables

The condition at which a system exists is called state of the system.

State variables are the variables that define state of the system.

They are P (pressure), V (volume), T (temperature).

Any change in magnitude of P, V, T alters the system state.

A change in state function describes the difference between two states. It is independent of the pathway of said change.

$$\text{Let } PV = RT$$

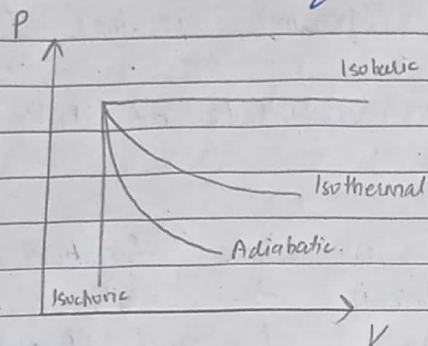
Here, if P and T are specified, value of V can be calculated.

Independent state variables are the variables that must be specified to define state. Here, P and T .

Dependent variables are the variables whose value depends upon the independent state variable. Here, V .

(i): Thermodynamic ^{process} systems:

- a) Isochoric: constant ~~pressure~~ ^{volume}, $dv = 0$
- b) Isobaric: constant pressure, $dp = 0$
- c) Isothermal: constant temperature, $dT = 0$
- d) Adiabatic: constant heat, $dq = 0$.



Work

The transfer of energy from one mechanical system to another is called work.

Mathematically,

$$\text{Mechanical work (W)} = F \times d.$$

$$\text{Workdone against gravity} = mgh$$

$$\text{Workdone due to change in velocity} = \frac{1}{2} (mv_2^2 - mv_1^2)$$

Thus, the workdone on simple mechanical system is numerically equal to change in its energy.

Pressure - Volume work:

The workdone in expansion or compression of a gas is called pressure-volume work.

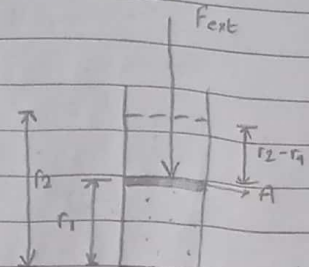
Let A = cross-sectional area of piston

F_{ext} = external force on piston

r_1 = initial point

r_2 = final point.

W = workdone during expansion



Now, we know,

$$W = -F_{\text{ext}} (r_2 - r_1) \quad \text{--- (i)}$$

[∵ '-' sign means system does work on surrounding]

In terms of pressure-volume,

$$W = -F_{\text{ext}} \times (r_2 - r_1) \times A \quad \text{--- (ii)}$$

Here, $\frac{F_{\text{ext}}}{A} = P_{\text{ext}}$ (external pressure), $A \times (r_2 - r_1) = \Delta V$ (change in volume).

So, eqⁿ (ii) becomes,

$$W = -P_{\text{ext}} \times \Delta V \quad \text{--- (iii)}$$

For infinitesimal volume change (dv), workdone is (dw) and external pressure is constant.

So, eqⁿ (iii) becomes,

$$dw = -P_{\text{ext}} \times dv \quad \text{--- (iv)}$$

Integrating (iv),

$$\int_0^w dw = \int_{V_1}^{V_2} -P_{ext} \times dV$$

$$W = -P_{ext} (V_2 - V_1)$$

$$\therefore W = -P_{ext} \Delta V.$$

At constant volume, $\Delta V = 0$ so, $W = 0$.

If compression, $W = \text{positive} = P_{ext} \Delta V.$

Workdone on the system

→ compression

→ positive work.

→ Workdone by the system

→ expansion

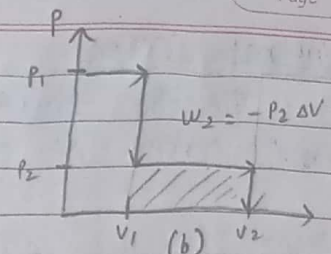
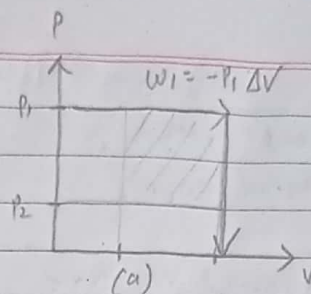
→ negative work.

Q: Prove that workdone is not state function:

Let us consider a gaseous system at P_1 and V_1 undergoes expansion and goes to P_2 and V_2 .

This can be done in two

ways:



In (a),

P_1 is constant and volume changes from V_1 to V_2

V_2 is constant and pressure changes from P_1 to P_2 .

path: $P_1 V_1 \xrightarrow{\text{work}} P_1 V_2 \xrightarrow{\text{work}} P_2 V_2$

$$\text{Work } (W_1) = -P_1 \Delta V$$

In (b),

V_1 is kept constant, pressure changes from P_1 to P_2 .

P_2 is kept constant, volume changes from V_1 to V_2 .

path: $P_1 V_1 \xrightarrow{\text{work}} P_2 V_1 \xrightarrow{\text{work}} P_2 V_2$

$$\text{Work } (W_2) = -P_2 \Delta V$$

From graph, $P_2 < P_1$ so, $W_1 < W_2$.

Thus, we can conclude the workdone depends upon path followed even though initial and final states are same.

So, work is not a state function.

Internal Energy

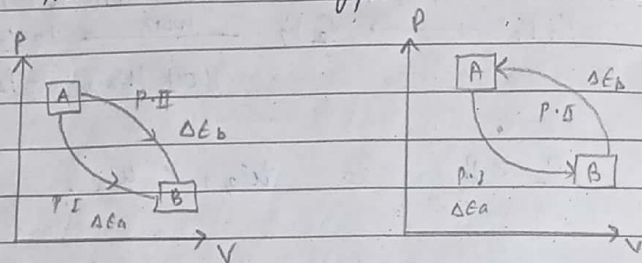
All the energy contained within a chemical system is called internal energy.

Internal Energy can be increased in three ways:

- Increase in temperature
- phase change
- initiation of chemical reaction.

Change in internal energy (ΔE) = $E_{\text{final}} - E_{\text{initial}}$.

<Q>: Prove internal energy is State Function.



Let us consider a system changes from state A to B from two paths E_a and E_b respectively.

Let $\Delta E_a > \Delta E_b$.

If this is the case, the system is continuous with cycle from A to B.

So, in doing so, extra energy is continuously generated i.e., $\Delta E_a > \Delta E_b$ i.e., $\Delta E = \Delta E_a - \Delta E_b$.

The creation of energy is not possible and violates 1st Law of thermodynamics.

So, internal energy is a state function.

First Law of thermodynamics

It is commonly known as 'Law of Conservation of Energy.'

Statement: Energy can neither be created nor be destroyed but can be converted into other forms of energy.

Let us consider the effect of adding energy to a system.

If 'q' heat is added to system doing no work then, change in internal energy is,

$$\Delta E = q \quad \text{--- (i)}$$

If no heat is supplied but work is done on the system then, change in internal energy

$$\Delta E = w \quad \text{--- (ii)}$$

If both processes are carried out together,

$$\Delta E = q + w \quad \text{--- (iii)}$$

$E_q^{(iii)}$ is mathematical expression for first law.

It states that internal energy of system can be increased by doing work or supplying heat.

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(*) Measurement of ΔE :

We know,

$$\Delta E = q + w \quad \text{--- (i)}$$

Now, pressure-volume work (w) = $-\int_{v_1}^{v_2} P \cdot dv$

Thus,

$$\Delta E = q - \int_{v_1}^{v_2} P \cdot dv \quad \text{--- (ii)}$$

If the chemical reaction occurs in a fixed volume, $dv=0$.

So, eqⁿ (ii) becomes,

$$\Delta E = q_v \quad (\text{heat change at constant volume}).$$

For exothermic, q_v is negative, so, $\Delta E = -ve$
For endothermic, q_v is positive, so, $\Delta E = +ve$.

(*) Calculation of Enthalpy:

We know,

$$H = E + PV \quad \text{--- (i)}$$

The change of enthalpy is given by -

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

$$\text{or, } \Delta H = q + w + \Delta(PV)$$

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$$\text{or, } \Delta H = q - P\Delta V + P\Delta V + V\Delta P$$

$$\therefore \Delta H = q + V\Delta P \quad \text{--- (ii)}$$

At constant pressure, $\Delta P = 0$.

So,

$$\Delta H = q_p \quad \text{--- (iii)}$$

For exothermic, $q_p = -ve$, so, $\Delta H = -ve \Rightarrow$ heat evolved.
For endothermic, $q_p = +ve$, so, $\Delta H = +ve \Rightarrow$ heat absorbed.

For solid or liquid, as $\Delta V \approx 0$.

$$\Delta H = \Delta E \quad \text{--- (iv)}$$

For gas,

$$\Delta H = \Delta E + \Delta nRT \quad \text{--- (v)}$$

$$\text{or } \Delta H = \Delta E + RT \Delta n \quad \text{--- (v) [at constant T]}$$

Terms for Enthalpy Changes

(a): Standard Enthalpy change for Reaction (ΔH°_{rxn})

The amount of heat change when chemical reaction occurs at standard condition (25°C , 1 atm pressure) is called standard enthalpy change of reaction.

b) Standard Enthalpy Change of Formation (ΔH_f°):

The amount of heat released for absorbed when one mole of a compound in its standard state is formed by from the elements at standard state.

Standard heat of formation for pure element = 0.

c) Standard Enthalpy Change of Combustion (ΔH_{com}°):

The amount of heat evolved when one mole of substance is completely combusted in standard form in the presence of excess oxygen.

x) Standard Enthalpy of reaction:

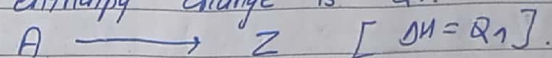
For reaction, Reactants \rightarrow products.

$$\Delta H_{rxn}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

Hess law of Constant Summation:

Statement: The total heat change for a direct reaction is equal to the sum of heat change in different steps of reaction.

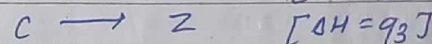
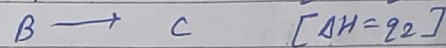
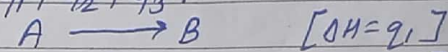
Let us consider A is directly converted to Z and enthalpy change is Q_1 .



Now, the same process is carried out in three steps.

$A \rightarrow B$, $B \rightarrow C$ and $C \rightarrow Z$ with enthalpy

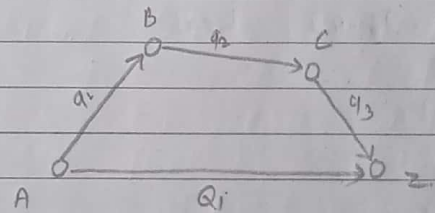
change q_1, q_2, q_3 .

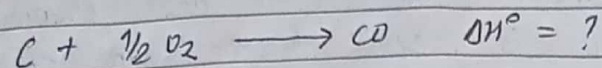
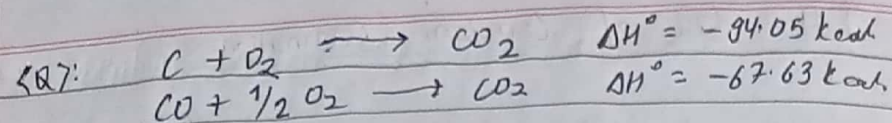


$$\text{So, } Q_2 = q_1 + q_2 + q_3.$$

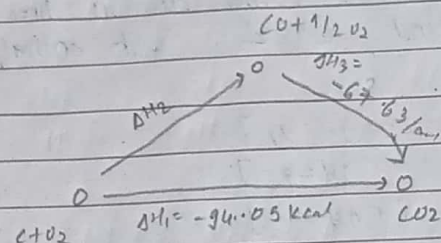
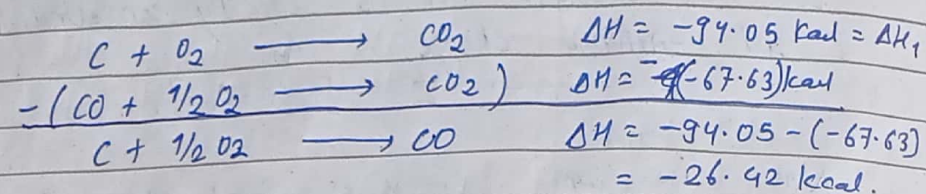
According to Hess law,

$$Q_1 = Q_2 \quad \text{So, } Q_1 = q_1 + q_2 + q_3.$$





Solⁿ:



From Hess law,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$\therefore \Delta H_2 = \Delta H_1 - \Delta H_3$$

$$= (-94.05) - (-67.63)$$

$$\therefore \Delta H_2 = -26.42 \text{ kcal.}$$

Molar Heat Capacity:

The amount of heat required to raise the temperature of one mole of substance through 1°C or 1K .

* Molar heat capacity at constant volume:

The amount of heat required to raise the temperature of one mole of gas through 1K at constant volume.

Mathematically,

$$C_v = \frac{dq_v}{dT} = \frac{dE}{dT} \quad \text{--- (i)}$$

* Molar heat capacity at constant pressure

The amount of heat required to raise the temperature of one mole of gas through 1K at constant pressure.

Mathematically,

$$C_p = \frac{dq_p}{dT} = \frac{dH}{dT} \quad \text{--- (ii)}$$

At constant pressure, amount of heat required to change from T_1 to T_2 , $dq_p = n C_p \Delta T$ --- (iii)

At constant volume, amount of heat required to change from T_1 to T_2 ,

$$dq_v = n C_v \Delta T \quad \text{--- (iv)}$$

(*) Relation between C_p and C_v :

We know,

$$H = E + PV \quad \text{--- (i)}$$

Diff. (i) w.r.t T on both sides,

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(PV)}{dT} \quad \text{--- (ii)}$$

For one mole of gas, $PV = RT$. So,

$$\frac{dH}{dT} = \frac{dE}{dT} + R \frac{d(RT)}{dT}$$

$$\text{or } \frac{dH}{dT} = \frac{dE}{dT} + R \quad \text{--- (iii)}$$

$$\text{We know } C_p = \frac{dH}{dT} \text{ and } C_v = \frac{dE}{dT}$$

So eqⁿ (iii) becomes.

$$C_p = C_v + R$$

So, $C_p > C_v$.

* ~~with~~

(*) Why $C_p > C_v$?

At constant volume, heat q_v is only used to increase the internal energy.

$$q_v = \Delta E \quad \text{--- (i)}$$

~~At~~ At constant pressure, the heat q_p is not only used to increase volume i.e. internal energy but also to overcome the pressure.

$$q_p = \Delta E + W \quad \text{--- (ii)}$$

Here, extra heat is required to overcome the constant pressure.

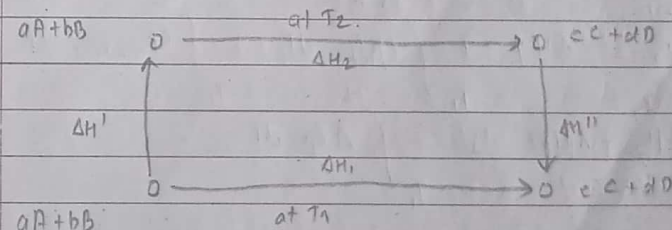
So, $C_p > C_v$.

Temperature Dependence of Enthalpy

The enthalpy change of a reaction is different at different temperatures.

Consider reaction,

$aA + bB \longrightarrow cC + dD$ be carried out at two different temperatures T_1 and T_2 . ($T_2 > T_1$)



Let us calculate enthalpy change using two paths.

First path:

Reactants at T_1 are heated to T_2 , reacted to give product at T_2 and cooled to T_1 .

$$\text{Total } \Delta H = \Delta H' + \Delta H_2 + \Delta H'' \quad \text{--- (i)}$$

Second path:

Reactant at T_1 are converted to product at T_1 .

$$\text{total } \Delta H = \Delta H_1 \quad \text{--- (ii)}$$

Equating (i) and (ii),

$$\Delta H_1 = \Delta H' + \Delta H_2 + \Delta H''$$

$$\begin{aligned} \Delta H_2 &= \Delta H_1 - \Delta H' - \Delta H'' \\ &= \Delta H_1 - \int_{T_1}^{T_2} C_{p, \text{reactant}} dT - \int_{T_2}^{T_1} C_{p, \text{product}} dT \end{aligned}$$

$$[\therefore \Delta H = \int_{T_1}^{T_2} n C_p dT]$$

$$\text{or } \Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} C_{p, \text{product}} dT - \int_{T_1}^{T_2} C_{p, \text{reactant}} dT$$

$$\text{or } \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT$$

$$\text{or } \Delta H = \int_{T_1}^{T_2} \Delta C_p dT \quad \text{--- (iii)}$$

$$\begin{aligned} \therefore \Delta C_p &= C_p(\text{product}) - C_p(\text{reactant}) \\ &= c C_p(C) + d C_p(D) - a C_p(A) - b C_p(B). \end{aligned}$$

Spontaneous and Non-spontaneous Change!

Non-spontaneous (Reversible)

- Process where state variables are changed by infinitesimal amount.
- It occurs in infinite numbers of infinitesimally small steps.
- It is very slow process.
- Imaginary process.

→ System is at equilibrium and can be reversed.

Spontaneous (Irreversible)

- Process where state variables are change by definite amount.
- It occurs in a single step.
- It is fast process.
- Real process.

→ System cannot be reversed.

→ Workdone in reversible process is always less than in irreversible process but heat change will be greater.

→ Workdone in irreversible process is always greater than in reversible process but heat change will be smaller.

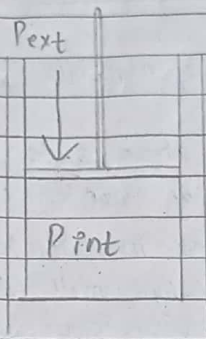
$$P_{\text{int}} = P_{\text{ext}} \pm dP_{\text{(very small)}} \rightarrow P_{\text{int}} = P_{\text{ext}} \pm dP_{\text{(large)}}$$

$$T_{\text{int}} = T_{\text{ext}} \pm dT_{\text{(very small)}} \rightarrow T_{\text{int}} = T_{\text{ext}} \pm dT_{\text{(large)}}$$

Q7: Workdone in Reversible Process is Always less than that in Irreversible Process.

So/D:

A cylinder is fitted with a movable piston.



We know,

$$\text{Workdone (W)} = -P \int_{V_1}^{V_2} dV$$

For compression, workdone is positive.

So,

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

In isothermal reversible compression, $P_{ext} \approx P_{int}$.

So,

$$W_{rev} = \int_{V_1}^{V_2} P_{ext} dV = \int_{V_1}^{V_2} P_{int} dV$$

We know,

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

So,

$$W_{rev} = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

or,

$$W_{rev} = nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{or } W_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right) \quad \text{--- (a)}$$

For irreversible compression, $P_{ext} = P_{int} + P$.

$$W_{irr} = \int_{V_1}^{V_2} P_{ext} dV$$

$$= \int_{V_1}^{V_2} (P_{int} + P) dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV + \int_{V_1}^{V_2} P \cdot dV$$

$$= nRT \int_{V_1}^{V_2} \frac{dV}{V} + P \cdot (V_2 - V_1)$$

$$\therefore W_{irr} = nRT \ln \left(\frac{V_2}{V_1} \right) + P(V_2 - V_1) \quad \text{--- (b)}$$

Subtracting (a) from (b),

$$W_{irr} - W_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right) + P(V_2 - V_1) - nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$\text{or } W_{irr} - W_{rev} = P(V_2 - V_1) \quad \text{--- (i)}$$

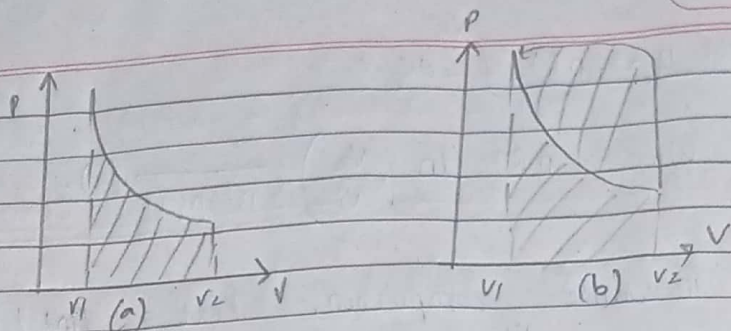
For compression, workdone is positive.

So,

$$W_{irr} - W_{rev} > 0 \quad \text{--- (ii)}$$

Hence,

$$W_{rev} < W_{irr} \quad \text{Hence, proved}$$



The shaded area shows work done.
 a) Reversible path b) Irreversible path.

<Q>: Prove that $q_{\text{irr}} < q_{\text{rev}}$.

Soln.

We know,
 From 1st law of thermodynamics,
 $\Delta E = q + w$

$$\text{or, } q = \Delta E - w.$$

For reversible process,

$$q_{\text{rev}} = \Delta E - w_{\text{rev}} \quad \text{--- (a)}$$

and for irreversible process,

$$q_{\text{irr}} = \Delta E - w_{\text{irr}} \quad \text{--- (b)}$$

Subtracting (b) from (a), we get.

$$q_{\text{rev}} - q_{\text{irr}} = \Delta E - w_{\text{rev}} - \Delta E + w_{\text{irr}}$$

$$\text{or, } q_{\text{rev}} - q_{\text{irr}} = w_{\text{irr}} - w_{\text{rev}}$$

We know, $w_{\text{irr}} - w_{\text{rev}} > 0$.

or,

$$q_{\text{rev}} - q_{\text{irr}} > 0$$

$$\therefore q_{\text{rev}} > q_{\text{irr}}$$

Hence, proved.

This also shows that heat is not a state function.