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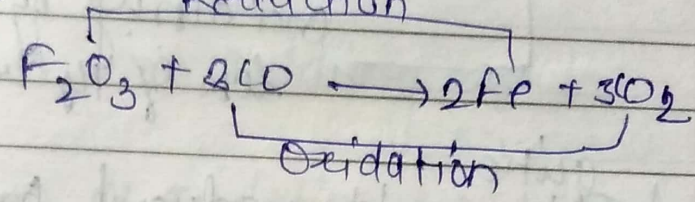
* Oxidation and Reduction :

1. In terms of oxygen transfer :
Oxidation is gain of oxygen
Reduction is loss of oxygen.

for Ex :



Here, Fe is oxidising agent and CO is reducing agent

- Oxidising agent give oxygen to another substance.
Reducing agent remove oxygen from another substance

2. In terms of hydrogen transfer :
Oxidation : Loss of Hydrogen
Reduction : Addition of Hydrogen

Oxidising agent : Remove Hydrogen
Reducing " : give Hydrogen.

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for ex: ethanol is oxidising to acid aldehyde using oxidising agent to remove Hydrogen

$CH_3CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3CHO$

Acidified with dil. H_2SO_4

oxidising by loss of Hydrogen

Acetic / citric acid reduced back to ethanol (by adding Hydrogen).

$CH_3CHO \xrightarrow{NaBH_4} CH_3CH_2OH$

Reducing a Reduction by gain of H

3. In terms of $e^\ominus$ transfer

oxidation : Loss of $e^\ominus$s

Reduction : gain of $e^\ominus$s

$Cu^{2+} + Mg \longrightarrow Cu + Mg^{2+}$

Reduction

Oxidation

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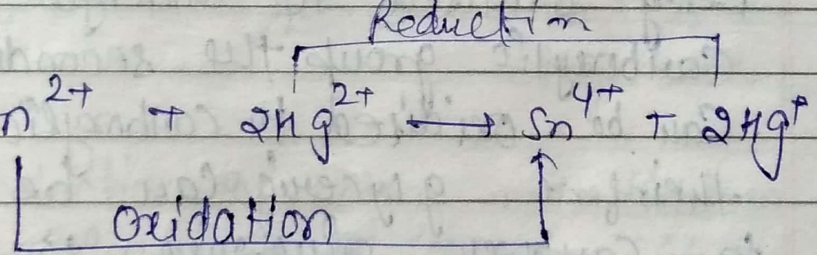
Here mg is Reducing Cu^{2+} ions by giving them e^- to to neutralised the charge. mg is Reducing agent

Cu^{2+} ion on the other hand Removing electron from mg to create the mg^{2+} ion

Cu^{2+} ion are oxiding agent

4. In term of oxidation No. :

- Increase in oxidation no. Oxidation
- Decrease " " " Reduction



* Oxidation :

different type of alcohol give diff. Product. In Presence of oxidising agent like ($KMnO_4 + H_2SO_4$) and ($Na_2Cr_2O_7 + H_2SO_4$)

1. Primary alcohol oxidised aldehyde and then into Carboxylic acid

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$CH_3CH_2OH \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[Na_2Cr_2O_7/H^+]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-OH$

2. Secondary alcohol are oxidised to ketone

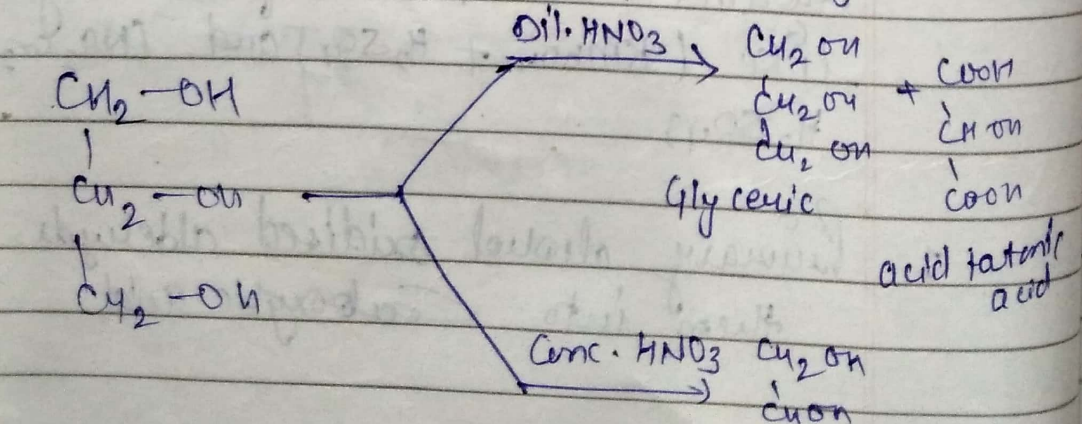
$CH_3-\overset{OH}{\overset{|}{C}}-CH_3 \xrightarrow[Na_2Cr_2O_7]{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$ (acetone)

3. tertiary alcohol do not go oxidation under Normal condition.

* Oxidation Reduction of Glyceric :

the two hydroxy groups in glyceric of being oxidised to aldehyde and then carboxylic group the secondary hydroxide can be oxidised to carboxylic group therefore glyceric can be oxidised to carboxy give rise to verity of oxidation product

depending on Nature of oxidising agent



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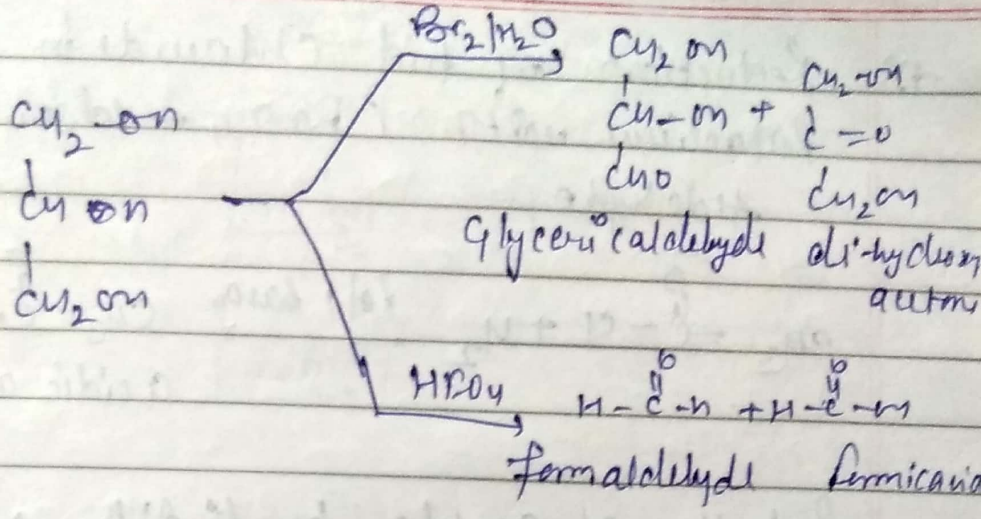

Glyceraldehyde dihydroxy acetone

Formaldehyde formic acid

* Reduction of aldehyde :

(1) Reduction of aldehyde with H_2/Ni give primary alcohol.

$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Ni} CH_3-CH_2-OH$$

ethyl alcohol

2. Reduction of ketone with Lithium Aluminium Hydride ($LiAlH_4$) give secondary alcohol.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2 \xrightarrow{LiAlH_4} CH_3-\overset{OH}{\overset{|}{C}}-CH_3$$

iso Propyl alcohol

3. Reduction of acid with $LiAlH_4$ give primary alcohol

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + H_2 \xrightarrow{LiAlH_4} CH_3-CH_2-OH$$

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4. Reduction of acid chloride in presence of Palladium on ($BaSO_4$ + $PdSO_4$) gives Aldehyde

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H + HCl$$

acidic acid

5. Reduction of amide by $LiAlH_4$ forms Primary secondry and tesery amine

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2$$

(1° amine)

$$R-\overset{O}{\overset{\|}{C}}-NHR' \xrightarrow{LiAlH_4} R-CH_2-NHR'$$

secondry amine

$$R-\overset{O}{\overset{\|}{C}}-NR_2' \xrightarrow{LiAlH_4} R-CH_2-NR_2'$$

(3° amine)

5) Reduction of Nitro compound (Nitro alkane) by Sn/HCl, Zn/HCl, H_2/Ni / $LiAlH_4$ formed Primary amine

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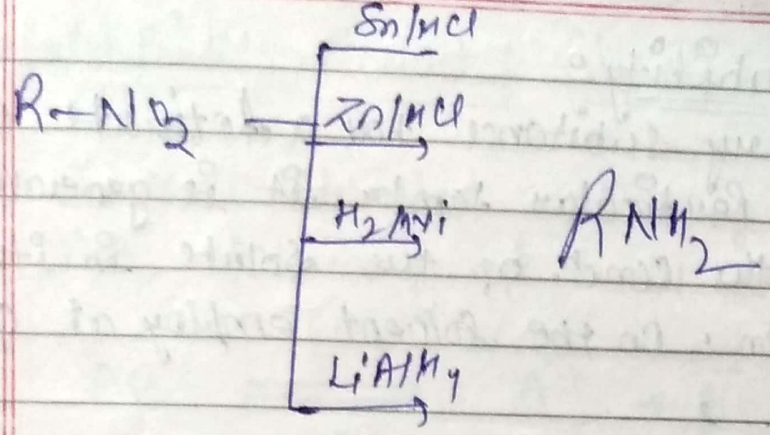

* Solubility equilibrium:

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* **Solubility :**

every substance has a definite solubility at a particular temp. It is generally defined as the conc^n. of the solute in its saturated solution. In the solvent employ at given temp.

It may also be defined as the amount of solute dissolved in 1000 gm of a solvent to form a saturated solution at a given temp. is termed as the solubility of the solute in the solvent at that temp.

Solubility is also express in terms of molarity i.e no. of moles of solute dissolved per litre of the solution at a given temp.

* **Solubility equilibria :**

Consider a the solubility of NaCl in water. the ions Na^+ and $Cl^\ominus$ are equilibrium with the solid NaCl.

$$NaCl(s) \rightleftharpoons Na^+ + Cl^\ominus$$

at eq^b. $$K = \frac{[Na^+] \times [Cl^\ominus]}{[NaCl]}$$

↑ Law of mass

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in saturated sol^n.

* Solubility Product : (K_{sp}) :

⇒ In the saturated solution of an electrolyte AB, following eq^b will exist.

$$AB \rightleftharpoons A^+ + B^- \quad \text{(Saturated solution)}$$

$$K = \frac{[A^+] * [B^-]}{[AB]}$$

$$K[AB] = [A^+] \cdot [B^-]$$

$$K_{sp} = [A^+][B^-]$$

Since solubility of substance remain const. therefore AB conc^n will also be constant.

therefore $K_{sp} = [A^+][B^-]$ ——(1)

Here K_{sp} is a new const. known as solubility product.

therefore, the product conc. of cations and anion present in a saturated solution of an electrolyte is known as solubility product.

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- The value of K_{sp} is constant at Given temp.

for ex: $NaCl \rightleftharpoons Na^{+} + Cl^{\ominus}$ (Sat)

$$K_{sp} = [Na^{+}] \cdot [Cl^{\ominus}]$$

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^{\ominus}$$

$$K_{sp} = [Ba^{2+}] \cdot [Cl^{\ominus}]^2$$

* Condition of ppt of electrolyte:
when ionic product is greater then solubility product, electrolyte is ppt

for ex: in case of NaCl

$$NaCl \rightleftharpoons Na^{+} + Cl^{\ominus}$$

when Na^{+} Conc^{n} $[Na^{+}] : [Cl^{\ominus}] > K_{sp}$
then ppt of NaCl will occur

* Relation b/w solubility product (K_{sp}) and solubility(s):

1. AB type electrolyte:

ex: NaCl, AgCl, $ZnSO_4$, etc.

$AB = K_{sp} = S^2$

AB_2 $K_{sp} = 4S^3$

$AB_3 = K_{sp} = 27S^4$

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electrolytes may be shown as

$$AB \rightleftharpoons A^+ + B^\ominus \quad \text{[saturated soln]}$$

S	0	0 (initially)
0	S	S

$K_{sp} = [A^+] \cdot [B^-]$

$= [S][S] = S^2$

$\boxed{K_{sp} = S^2}$

Here S is solubility in mole/litre

2. AB_2 type electrolyte :

Donisation of AB_2 type electrolyte may be as

$$AB_2 \rightleftharpoons A^{++} + 2B^\ominus$$

S	0	0
0	S	2S

$K_{sp} = [A^+] \cdot [B^-]^2$

$= [S](2S)^2$

$\boxed{K_{sp} = 4S^3}$

Such as: $BaCl_2$, PbF_2, etc.

$S^2, 4S^3, 27S^4$,

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3. For AB_3 type electrolyte :

Such as $AlCl_3$, $Fe(OH)_3$, etc.

Ionisation of AB_3 may be shown as

AB_3	$\rightleftharpoons$	A^{+++}	+	$3B^-$	Sat
S		0		0	Initiation
0		S		3S	After comp. ionisation

$$K_{SP} = [A^{+++}] \cdot [B^-]^3$$
$$= [S][3S]^3$$
$$\boxed{K_{SP} = 27S^4}$$

Qu: The solubility of NaCl is 2.5 mol/L. Calculate the solubility product of NaCl

$$K_{SP} = x\,(S)^2$$
$$= (2.5)^2 = 6.25$$

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* EMF or Cell Potential of a cell :

Electrochemical cell consist of two half cells. The electrode in these half cells have different Reduction Potential. Therefore they have different tendency to loss or gain of electrons.

The electrode having higher reduction potential will have higher tendency to gain electrons, rather it loses electrons. as a result of this, potential difference is developed.
there is a flow of e⁻s from the electrode with lower reduction pot. to the electrode with higher reduction potential.

" The difference b/w the electrode potential of the two electrodes constituting an electrochemical cell is known as EMF or a cell Potential "

Emf = Reduction Pot. of cathode − Reduction Pot. of anode.

$$E_{cell} = E_{cathode} - E_{anode}$$

Red. Oxid.

In Galvanic cell ... is ...

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Therefore Emf of the cell may be defined as the Pot. difference b/w two electrodes of the cell when either no or negligible current is allowed to flow in the circuit.

Book * **Nearst eq^n for Electrode :**

It tells us the effect of electrolyte conc^n on electrode potential.

Consider a general electrode equation

$$M^{n+}_{(aq)} + ne^{\ominus} \longrightarrow M_{(s)} \quad \text{---- i)}$$

for this electrode Rx^n the energy (ΔG) can be calculated provided standard free energy (ΔG°), gas constant (R), temperature (T), activity product ($a_{product}$) and activity Reactant ($a_{reactant}$) are known, using the following equation

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{a_{product}}{a_{reactant}}\right] \quad \text{---(2)}$$

Since $\Delta G = -nFE$ and

$\Delta G^\circ = -nFE^\circ$

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Hence $E = E^\circ - \frac{2.303RT}{nf} \log \left(\frac{a_{Product}}{a_{Reactant}} \right)$ — (3)

this is nernst equation where E is the Electrode Potential, E° is the Standard electrode potential f is faraday , T is temp., R is gas const. and a is activity

at $T = 298\,K$, Putting the value of $R = 8.314$ Joule/K/mol and $f = 96500\,C$ then we, get,

$$E = E^\circ - \frac{0.0591}{n} \log \left[\frac{a_{Product}}{a_{Reactant}} \right]$$

In dil. solution, activity may be replaced by molar concentration terms

$$E = E^\circ - \frac{0.0591}{n} \log \left(\frac{M_s}{M^{n+}_{(aq)}} \right)$$

for Pure solid $M_s = 1$

$$E = E^\circ - \frac{0.0591}{n} \log \left[\frac{1}{M^{n+}_{(aq)}} \right]$$

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The above eq^{n} is nernst eq^{n} for the electrode at 298 K.

and at any other temp. (T)

$$E = E^{0} - \frac{2.303RT}{nF} \log\left[\frac{1}{M^{n+}_{(aq)}}\right]$$

From the above eq^{n} it can be Concluded that

a) E increases as $\log[M^{n+}]$ is increased

b) The electrode Potential [E] decreases as temp is increase.

c) Nernst eq^{n} for a Cell :

* Nernst eq^{n} Can also be applied to any cell Rx^{n} such as

$$aA + bB \rightleftharpoons cC + dD$$

$$E_{cell} = E^{0}_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

Similarly for the cell Rx^{n}

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$$2M_{1(s)} + M_2^{2+}{}_{(aq)} \rightleftharpoons 2M_1^{+}{}_{(aq)} + M_{2(s)}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{2F} \log \frac{[M_1^{+}]^2}{[M_2^{2+}]}$$

Hence $M_{1(s)} = M_{2(s)} = 1$

* Application of Nernst eqⁿ:

(i) Nernst eqⁿ can be used to study the effect of electrolyte concⁿ on electrode potential.

Qᵉ A Zn rod is placed in a 0.1M solution of $ZnSO_4$ at 25°C. Calculate the potential of the electrode at this temp., assuming 96% dissociation of $ZnSO_4$ and $E^{\circ}(Zn^{2+}/Zn) = 0.76$ volt

$$E = 0.76 - \frac{0.0591 \times 8.314}{2 \times 96500} \log$$

Concⁿ of (Zn^{2+}) (96%) $= 0.1 \times \frac{96}{100}$

$= 96 \times 10^{-3}$ M

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Electrode Rx^{n}

$$Zn^{2+}_{(aq)} + 2e^{\ominus} \longrightarrow Zn_{(s)}$$

according to the Nernst eq^{n} the Potential of electrode is

$$E = E^{0} - \frac{RT}{nF} \ln\left[\frac{1}{(Zn^{2+}_{aq})}\right]$$

$$E = -0.76 - \frac{0.0591}{2} \ln\left[\frac{1}{96 \times 10^{-3}}\right]$$

$$E = -0.76 - \frac{0.0591}{2} \ln\left[\frac{1000}{96}\right]$$

$$E = -0.794 \text{ Volt}.$$

Q) Nernst eq^{n} can also be used for the Calculation of the Potential of a Cell under non standard Conditions.

Q. Calculate the Potential of the following electrochemical cell at 25°C.

$$Cu_{(s)} / Cu^{2+}_{(aq)} = (0.05\,M)$$

$$\parallel$$

$$H^{+}(0.01) / H_2(0.95 \text{ atm}), Pt$$

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Given $E^\circ_{cathode} = 0.000$

$E^\circ_{anode} = 0.34\ V$

Sol

$Cu^{2+} + 2e^{\ominus}$

$Cu_s + 2H^+ \rightleftharpoons Cu^{2+}(aq) + H_2$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \left(\frac{Cu^{2+}}{[H^+]^2} \right) P_{H_2}$$

$E^\circ_{cell} = -0.34$

$$= -0.34 - \frac{0.0591}{2} \log \left[\frac{0.05}{(0.01)^2} \right] \times 0.95$$

$$= -0.34 - \frac{0.0591}{2} \log \left(\frac{0.05}{(0.01)^2} \right) \times 0.95$$

$= -0.449$

3) determination of unknown conc^n of one of the ionic species in a cell is possible with the help of Nernst eq^n Predicted E°_{cell} and conc^n of other ionic species is known

4) the PH of the sol^n can be calculated from the measurement of Emf and nernst eq^n

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5] Nernst eq^{n} can also be used for finding the valency of an ion or the no. of $e^{\ominus}$s involved in the electrode Rx^{n}

In general oxidised state + $ne^{\ominus}$ $\rightleftharpoons$ reduced state

the Pott. of the electrode is given by

$$E = E^{\circ} - \frac{RT}{nF} \ln \left[\frac{\text{reduced state}}{\text{oxidised state}} \right]$$

Q Determine the Conc^{n} of Cd^{2+} ion in the following electrochemical cell

Fe, Fe^{2+} (0.1 M) / Cd^{2+} (x M), Cd,
assuming that activities equal Conc^{n}.
Given the Emf of the Cell E = −0.02V
and E° = 0.04 volt at 25°C

Sol^{n}

$$Fe_{(s)} + Cd^{2+} \rightleftharpoons Fe^{2+} + Cd_{(s)}$$

$$-0.02V = 0.04 - \frac{0.0591}{2} \log\left(\frac{(0.1)}{x}\right)$$

$$-0.02V - 0.04 = -\frac{0.0591}{2} \log \frac{(0.1)}{x}$$

$$0.06 = \frac{0.0591}{2} \log \frac{(0.1)}{x}$$

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$$\frac{0.06}{0.0591} \times 2 = \log \frac{(0.1)}{x}$$

$$\frac{0.12}{0.0591} = \log \frac{(0.1)}{x}$$

$$2.0304 = \log \frac{(0.1)}{x}$$

$$\frac{0.1}{x} = 4.614$$

$$x = \frac{0.1}{7.614}$$

$$x = 0.01313$$

Ans

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Thermodynamics

* **Internal Energy:**
The total of all the possible kind of energy of a system is called its internal Energy

It includes translational, rotational, Vibrational Energies of the molecules and also the kinetic and potential energy of nuclei and electron with in individual molecule.

It is state function because its value depends upon the state of a system and not on the Path followed to obtained it

It is an extensive property because its value depends of mass of the matter contain in a system.

It is a function of temp. of the system, pressure and volume, The thermodynamic Parameters also depends upon chemical nature of the substance

Internal Energy can not be determine by any means directly. It is the changely internal Energy accomp a chemical or Physical process which is measurable quantity

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Change in internal Energy

$$\Delta E = E_B - E_A$$

Where E_A and E_B are the internal energy of in initial and final state

SI unit is joule. and heat.

The Energy transfered due to the difference in the temperature b/w two systems is called heat. It flows from system at higher temp. to that at Lower temperature.

The amount of heat transfered (q) is Proportional to the difference in temp.

i.e $q \propto \Delta T$

$q = CT$

Here C is heat capicity of the system i.e quantity of heat required of raised the substance by 1°C.

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Note:
When heat is absorbed by the system
$$q = +w$$

When heat is given out by the system
$$q = -w$$

Work:
The energy of a system is its capacity to do work. a system may transfer the energy to another system or surrounding to work
It may also be in the form of expension or compression of the system
i.e Pressure, volume work
$$w = P\Delta V$$

Note: work is done by the system its energy decreases and work is done on the system. its energy increases

* first Law of Thermodynamics:
~~Energy~~ The total energy of an isolated system remains constant, though it may change from one form to another form.

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"Energy can neither be created nor destroyed" i.e total energy of the system is const.; it may change one form to another form.

$$\Delta E = q - w$$

q is amount of heat
w is work done by the system

$$\Delta E_r = E_A - E_B$$

E_A and E_B are the energy of initial and final state

Case:1 For a cyclic process involving isothermal expansion of an ideal gas

$$\Delta E = 0 \qquad E_A = E_B$$

Hence

$$q = w$$

Case-2 For an isocoric Process, (V=const.) System is under const. volume, no work of expansion

adiabatic = $q=0$ Isothermal = $\Delta E=0$

$w=0$ = isochoric = V

cyclic = $E=0$

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As $w = P\Delta V$

$\Delta V = 0$

$w = 0$

Hence

$\Delta E = q_v$ (at const vol.)

thus for system at const volume, heat involved clearly changes to internal energy

Case: for an adiabatic process no heat change is involved.

i.e $q = 0$

Hence $\Delta E = -w$

the decrease in internal energy is exactly equal to the work done on the system on the surr.

Case 4

for an isobaric process no change in pressure

$w = P\Delta V$

$\Delta E = q - P\Delta V$

$\Delta H =$

entropy, enthalpy

total disorder

total heat content present in system

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$\Delta V = V_B - V_A$

final initial volume.

Enthalpy or heat content of a system:

Total heat content of a system at constant pressure is equivalent to the internal energy

$$H = E + PV \quad \text{---} \quad (1)$$

If ΔH be the change in the enthalpy of a system in final state H_2 and initial state H_1

$H = E + P\Delta V$

$$\Delta H = H_2 - H_1$$

$$H_2 = E_2 + P_2V_2 - (E_1 + P_1V_1)$$

$$(E_2 - E_1) + (P_2V_2 - P_1V_1) =$$

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

If P is constant while the gas is expanding

$$\Delta H = \Delta E + P\Delta V$$

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$$\Delta H = \Delta E + W \quad \text{---(iii)}$$

According to first law

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

(q = Heat transferred)

from eq^{n} (iii) & (iv)

$$\boxed{\Delta H = q} \quad \text{or} \quad \Delta H = q_p$$

* For solid and liquid ΔP is very small

$$\Delta H = \Delta E$$

* for gases $P\Delta V$ is significant ($\Delta H > \Delta E$)

* for ideal gas $PV = nRT$

Therefore $\Delta H = \Delta E + \Delta nRT$

$\Delta n \Rightarrow$ difference b/w stiochiometric coefficient of gasious product and all gasious Reactant.

Note: ΔH is Positive ($H_2 > H_1$)

Rx^{n} 1

molar heat C = amount of heat Req. to raise temp

Stereochem
optical.

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Rx^n with Endothermic
ΔH is negative ($H_1 > H_2$)

Req^n Unit Kilocalories or kilo joules

* Molar Heat Capacity:
It is the amount of heat Req. to raise the temp. of 1 mole of the substance (system) by one calorie.
i.e molar heat capacity is the ratio of amount of heat absorbed to the rise in temp.

$$C = \frac{dq}{dt}$$

Unit - Calorie
SF. ~~J/kmole~~ J/kmole

molar heat capacity at Const. volume (Cv)
The Cv is the rate of change of internal energy with temp. at const. volume

$$dq = dE + pdv$$

divided by dt

$$\frac{dq}{dt} = \frac{dE}{dt} + \frac{Pdv}{dt}$$

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$dV = 0$

$$\frac{dq}{dt} = \frac{dE}{dt}$$

$$C_V = \left(\frac{dE}{dt}\right)_V$$

* molar heat capacity at Const. Pressure (C_V) is defined as the rate of change of Enthalpy with temp. at Const. Pressure

$$C_P = \left(\frac{dH}{dt}\right)_P$$

* Relation in C_P and C_V:

$$C_P = \left(\frac{dH}{dt}\right)_P \quad \& \quad C_V = \left(\frac{dE}{dt}\right)_V$$

I^st ~~E~~

∴ ~~H = PΔ~~ &

$H = E + PV$ and

for 1 mole of gas

$$H = E + RT \qquad (\because PV = RT)$$

diff. w.r.t T

$$\frac{dH}{dT} = \frac{dE}{dt} + R$$

and $C_P = C_V + R$

$$\boxed{C_P - C_V = R}$$

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Numerics

* Enthalpy of Rxn :
It is the amount of heat absorbed or evolved in a particular Rxn.
It is difference b/w the Heat Content or Enthalpy of product and Reactant

ΔH = Enthalpy of Product - Enthalpy of Reactant

It varies with temp.

Note ; $\Delta H \Rightarrow +ve \Rightarrow$ endothermic
$\Delta H \Rightarrow -ve \Rightarrow$ exothermic.

The heat change for a Rxn at 298 K and 1 atm is called Standard heat of Rxn or Standard enthalpy change (ΔH°).

Important

V. Imp

* Entropy :
Entropy is a thermodynamic state quantity i.e the measure of the randomness or disorder of the molecules of the system.

PYQ

Question

Entropy is a state fn and depends only on the initial and final states of the system.

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Entropy predicts whether a chemical Rxn or a physical change can occur spontaneously in an isolated system or not.

any process accompanied by an increase in entropy tend to be spontaneous

i.e $\Delta S = +ve$

$\Delta S = S_{final} - S_{initial}$

If any process is carried out reversibly so that dq is the amount of heat absorbed by the system by the surrounding at temp T. then the entropy change is given by

$$\boxed{ds = \frac{dq}{T}}$$

Thus increase in entropy (ds) in a reversible change is equal to the quantity of heat absorbed divided by the temp. on Kelvin Scale.

therefore change in entropy of a system (ΔS) from A to B is given by

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T}$$

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For adiabatic Reversible Process

$dq = 0$

$dS = \frac{dq}{T} \Rightarrow dS = 0$

$\boxed{S = Const}$

Entropy is thermal Property of the Substance which remains Const during an adiabatic cyclic change

$\Delta S_{system} + \Delta S_{surr.} = 0 \rightarrow$ Reversible Process.

$\Delta S_{sys.} + \Delta S_{surr.} > 0 \rightarrow$ Irreversible Process

Total Entropy change

$\Delta S_T = (\Delta S_{sys.} + \Delta S_{surr.})$

Note: Total Entropy change $\Rightarrow +ve \Rightarrow$ Spontaneous
Total " " $\Rightarrow -ve \Rightarrow$ non-Spontaneous
Total " " $\Rightarrow 0 \Rightarrow$ Process in eqb.

* Entropy of phase transition :

Case: 1 Transition from Solid phase to Liquid phase

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

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2 Transition from liquid phase to vapour phase

$$\Delta S_v = \frac{\Delta H_v}{T_v}$$

ΔH_f and ΔH_v heat of fusion and heat of vapourisation

T_f and T_v fusion and boiling point

Note:- fusion and vapourisation both accompanied with increase of entropy. Since ΔH_f and ΔH_v are both positive

Note-2 Transition from vapour to liquid and from liquid to solid (freezing of solid) are accompanied by decrease of entropy since ΔH_f and ΔH_v are both negative.

* Free Energy:
(1) Helmholtz free energy or work fn (A)
(2) Gibbs free energy (G).

$$A = E - TS$$

$$G = H - TS$$

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Helmholtz free Energy:

Consider an isothermal change at temp. T from the initial state indicated that 1 and final state as 2 then

$A_1 = E_1 - TS_1$ initial

$A_2 = E_2 - TS_2$ final

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

$$\boxed{\Delta A = \Delta E - T\Delta S}$$

ΔA is change in work function
ΔE is corresponding change in Energy
ΔS is change in Entropy in system

$$\Delta A = \Delta E - T\Delta S$$

$$\therefore \quad \Delta S = \frac{Q}{T}$$

$$\therefore \quad \boxed{Q = T\Delta S}$$

$$\therefore \quad \Delta A = \Delta E - Q$$

Acc. to first law of thermodynamics

$$Q = \Delta E + W$$

Hence $\boxed{\Delta A = -W}$

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for $-\Delta A = W$

decrease in the work fn A in any process at const. temp gives the max work that can be obtained from the system during and change.

In order to know quantitative the max. work obtained from the system during the given change, ~~Helmholtz~~ Helmholtz give fn of state A called work fn or Helmholtz fn

* Gibbs free Energy:

Consider a system which undergoes a change of state from one to two at const. temp. then

$$G_1 = H_1 - TS_1$$

$$G_2 = H_2 - TS_2$$

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

we know that at const. pressure

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

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$\Delta A = \Delta E - T\Delta S$

$\Delta G = \Delta E - T\Delta S + P\Delta V$

Hence $\Delta G = \Delta A + P\Delta V$ at const. pressure

and

$\Delta A = \Delta E - T\Delta S$

$\Delta G = \Delta A + P\Delta V$ at const pressure and T.

$P\Delta V$ represent work done against pressure

hence, $\Delta A = -w$

hence $\Delta G = -w + P\Delta V$

$-G = w - P\Delta V$

i-e decrease in free energy equal to max. work obtained in on the system - work done by system

Decrease in free energy $(-G)$ accompany a process taking place at const. temp. and pressure is equal to the max work obtainable from the system. other then the work of expansion

It is significant quantity in thermodynamic because the change in free energy is the measure of main work which may be electrical, mechanical or

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Decrease in free energy during a process is equal to the useful work obtainable from the process

$$G = H - TS$$

$$H = E + PV$$

$$G = E + PV - TS$$

$$dG = dE + (PdV + VdP) - (TdS + SdT)$$

$$dq = dE + dw \qquad \text{(first Law)}$$

$$-dw = PdV \qquad (dq = dE + Pv)$$

for reversible process

$$dS = \frac{dq}{T}$$

$$TdS = dq$$

therefore $TdS = dE + PdV$

$$dG = VdP - SdT$$

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Gibbs HelmHolz :

In terms of free energy and Enthalpy

$dG = VdP - SdT$ at const. Pressure

$dP = 0$

$dG = -SdT$

Let G_1 and G_2 be the free Energy in initial and final state of the system at temp. T. S_1 and S_2 are entropy in initial and final state.

$dG_1 = -S_1 dT$

$dG_2 = -S_2 dT$

$dG_2 - dG_1 = -(S_2 - S_1) dT$

$\Delta G = -\Delta S \, dT$

at const Pressure

$$\left(\frac{d\Delta G}{dT}\right)_P = -\Delta S \quad \text{— (1)}$$

$\Delta G = \Delta H - T\Delta S$ — (2)

Hence from eqⁿ (1) and (2)

$$\left(\frac{d\Delta G}{dT}\right)_P = \frac{\Delta G - \Delta H}{T}$$

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$$\Delta G = \Delta H + T\left(\frac{\partial G}{\partial T}\right)_P$$

It is Gibbs Helmholtz Eq^{n} in terms of free energy and enthalpy change at Constant Pressure.

Gibbs Helmholtz Eq^{n} also be written as

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

Q^{n} Calculate the standard entropy of formation (ΔS_f°) of $CO_2(g)$. Given the standard Entropies of $CO_2(g)$, Carbon(S), $O_2(g)$ which are 213.6, 5.740 and 205.0 J/K respectively

ΔS_f° =

$$\underset{(s)}{C} + \underset{(g)}{O_2} \longrightarrow \underset{(g)}{CO_2}$$

5.740 205.0 213.6

$$\Delta S_f^\circ = \sum \text{Product} - \sum \text{Reactant}$$

$\frac{5.740}{2}$

$$= 213.6 - (5.740 + 205.0)$$

$$= 2.86 \text{ J/K}$$

Heat of fusion

$\frac{\Delta H_F}{T_F}$

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Q Calculate of fusion of ice if its heat of fussion is 8.01 KJ/mole at 273 K

$$\frac{\Delta H_F}{T_F} = \frac{8.01}{273}$$

* Ellingem diagram.