

We know, $W_{irre} - W_{rev} > 0$.

or,

$$q_{rev} - q_{irre} > 0$$
$$\therefore q_{rev} > q_{irre}$$

Hence, proved.

This also shows that heat is not a state function.

Entropy:

The measure of degree of disorderness of the system is called entropy.

$$S_{solid} < S_{liquid} < S_{gas}.$$

Change in entropy: $\Delta S = \int_1^2 \frac{dq_{rev}}{T} = \frac{q_{rev}}{T}$

Second law of thermodynamics:

Statement: The entropy of the universe in reversible process remains the same but increases in irreversible process.

ie, the energy of the universe is constant but available energy is decreasing.

Mathematically,

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surrounding} = 0 \quad (\text{For reversible})$$
$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surrounding} > 0 \quad (\text{For irreversible})$$

Entropy Change in Terms of Volumes

Entropy change in terms of volume occurs at constant temperature.

From kinetic theory of gas, $E_{\text{trans}} = \frac{3}{2} RT$

At constant temperature, $E_{\text{trans}} = E$ (total internal energy)

and $\Delta E = 0$.

From first law of thermodynamics, we get.

$$\Delta E = q + w$$

$$\therefore q = -w$$

So,

$$q_{\text{rev}} = -w_{\text{rev}}$$

$$q_{\text{rev}} = - \left(- nRT \ln \left(\frac{V_2}{V_1} \right) \right)$$

$$\therefore q_{\text{rev}} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

So,

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{nRT \ln \left(\frac{V_2}{V_1} \right)}{T}$$

$$\therefore \Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

If $V_2 > V_1$, gas expands, entropy increased
If $V_2 < V_1$, gas compresses, entropy decreased.

* Isothermal reversible and irreversible expansion of gas

In reversible expansion,

$$\Delta S_{\text{gas}} = \frac{q_{\text{rev}}}{T}$$

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

So,

$$\Delta S_{\text{system uni}} = \Delta S_{\text{gas}} + \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{rev}}}{T} = 0$$

It is justified by 2nd law of thermodynamics.

In irreversible expansion,

$$\Delta S_{\text{gas}} = nR \ln \left(\frac{V_2}{V_1} \right)$$

From 1st law, $q = \Delta E - w = 0$

Since there is no heat gain/lost to surrounding,

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

$$\begin{aligned} \Delta S_{\text{system uni}} &= \Delta S_{\text{system}} + \Delta S_{\text{surr}} = nR \ln \left(\frac{V_2}{V_1} \right) - 0 \\ &= nR \ln \left(\frac{V_2}{V_1} \right) > 0 \end{aligned}$$

It justifies second law of thermodynamics.

Isothermal reversible and irreversible expansion of gas is feasible.

(*) Irreversible Isothermal Compression:

Gas is compressed from V_1 to V_2 .

So,

$$\Delta S_{\text{gas}} = nR \ln \left(\frac{V_2}{V_1} \right)$$

Since $V_2 < V_1$, no outside influence.

$$\Delta S_{\text{sur}} = 0.$$

$$\Delta S_{\text{uni}} = nR \ln \left(\frac{V_2}{V_1} \right) - 0 = nR \ln \left(\frac{V_2}{V_1} \right) < 0.$$

This violates second law of thermodynamics.
So, irreversible isothermal compression not feasible.

Criterion for Spontaneity:

When two blocks at different temperature (T_c & T_h) come together:

(i): If cold body absorbs heat from hot body,
 $ds > 0$

second law is obeyed.

(ii): If hot body absorbs heat from cold body,
 $ds < 0$,

second law is not obeyed.

The reaction not feasible.
process

Temperature Dependence of Entropy

We know,

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} \quad \text{--- (i)}$$

The process may occur at constant pressure or constant volume.

At constant pressure,

$$dq_{\text{rev}} = nC_p dT \quad \text{--- (ii)}$$

At constant volume,

$$dq_{\text{rev}} = nC_v dT \quad \text{--- (iii)}$$

So,

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_p dT}{T} \quad \text{--- (iv)}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_v dT}{T} \quad \text{--- (v)}$$

For small temperature change, $C_p \approx C_v = \text{constant}$.

So

$$\Delta S = nC_p \ln \left(\frac{T_2}{T_1} \right) \quad \text{--- (vi)}$$

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right) \quad \text{--- (vii)}$$

Molecular Interpretation of Entropy:

Macroscopic ^{properties} ~~provides~~ are the properties that describes the system as a whole/bulk.

Microscopic properties are the properties that of the system including properties of individual units.

Entropy is the measure of number of microstates associated with particular macro-state.

Entropy increases molecular chaos of the system.

* Disordered System:

The system with relatively small amount of information about its microscopic properties is called disordered system.

Entropy Change Associated with Phase change,

a) Entropy of Fusion:

The change in entropy when one mole of substance change from solid to liquid at its melting point.

Mathematically,

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}}$$

b) Entropy of Vapourization:

The change in entropy when one mole of substance changes from liquid to gas at boiling point. Mathematically,

$$\Delta S_{\text{vapourization}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b.p.}}}$$

Third law of thermodynamics:

Statement: The entropy of perfect crystal of all pure element / compound is zero at absolute temperature.

It is used to calculate absolute entropy of solid, liquid or gas at temperature T .

We know,

$$S_T^0 = S_T - S_0.$$

$$S_0 = 0$$

For solid,

$$S_T^0 = \int_0^T \frac{C_p dT}{T}$$

For liquid,

$$S_T^0 = \int_0^{T_f} \frac{C_p dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^T \frac{C_p' dT}{T}$$

For gas,

$$S_T^0 = \int_0^{T_f} \frac{C_p dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_{\text{mp}}} \frac{C_p' dT}{T} + \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} + \int_{T_{\text{vap}}}^T \frac{C_p'' dT}{T}$$

Here,

C_p = molar heat capacity of solid at c.p.

C_p' = molar heat capacity of liquid at c.p.

C_p'' = molar heat capacity of gas at c.p.

(x): Standard Entropy Change for Reaction

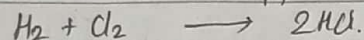
for reaction,
 $aA + bB \longrightarrow cC + dD$

$$\Delta S^\circ = \sum S^\circ_{\text{product}} - \sum S^\circ_{\text{reactant}}$$

$$\therefore \Delta S^\circ = cS^\circ(C) + dS^\circ(D) - aS^\circ(A) - bS^\circ(B)$$

$$\begin{aligned} \text{Unit} &= \text{J K}^{-1} \text{mol}^{-1} \text{ [EU]} \rightarrow \text{SI} \\ &= \text{cal K}^{-1} \text{mol}^{-1} \text{ [eU]} \rightarrow \text{CGS.} \\ 1 \text{ eU} &= 4.8 \text{ EU} \end{aligned}$$

(a): Calculate entropy change for reaction.



$$[S^\circ_{\text{H}_2} = 131.0, S^\circ_{\text{Cl}_2} = 223.0, S^\circ_{\text{HCl}} = 187.01 \text{ J/Kmol}]$$

For H_2 ,

$$S^\circ_{\text{H}_2} = 131.0$$

For HCl ,

$$S^\circ_{\text{HCl}} = 187.01$$

for 2HCl ,

$$\Delta S^\circ_{2\text{HCl}} = 374.02 = \sum S^\circ_{\text{product}}$$

For Cl_2 ,

$$S^\circ_{\text{Cl}_2} = 223.0$$

Now,

$$\begin{aligned} \sum S^\circ_{\text{product}} &= S^\circ_{\text{H}_2} + S^\circ_{\text{Cl}_2} \\ &= 131 + 223 \end{aligned}$$

$$\therefore \sum S^\circ_{\text{product}} = 354$$

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= \sum S^\circ_{\text{product}} - \sum S^\circ_{\text{reactant}} \\ &= 374.02 - 354 \end{aligned}$$

$$\therefore \Delta S^\circ_{\text{rxn}} = 20.02 \text{ J K}^{-1} \text{mol}^{-1}$$

Free Energy / Gibbs Free Energy

We know,

$$G = H - TS \quad \text{--- (i)}$$

Taking the differential of eqⁿ (i),

$$dG = dH - d(TS)$$

$$\text{or } dG = dH - S \cdot dT - T \cdot ds \quad \text{--- (ii)}$$

We know, $T \cdot ds = dq_{\text{rev}}$ and $dH = dq$.

So, eqⁿ and

At constant P and T, $dT = 0$ and $dH = dq$.

So,

$$dG = dq - dq_{\text{rev}} \quad \text{--- (iii)}$$

In reversible process, $dq = dq_{\text{rev}}$.

So,

$$dG = 0 \quad \text{--- (iv)}$$

In irreversible process, $q < q_{\text{rev}}$. So, $dq < dq_{\text{rev}}$.

Hence,

$$dG < 0 \quad \text{--- (v)}$$

For finite changes;

$$\Delta G = 0 \quad (\text{for reversible})$$

$$\Delta G < 0 \quad (\text{for irreversible})$$

Note: Evaporation of water is not spontaneous but condensation of supersaturated vapour is feasible.

Free Energy and Equilibrium Constant:

1) Standard Free Energy change:

The free energy change accompanying the conversion of reactants to products in standard state.

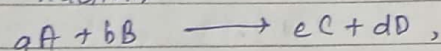
* Standard Free Energy change of Formation

The free energy change occurring when one mole of compound in standard state is formed from its elements in standard states.

For all pure elements, standard free energy change of formation is zero.

* Standard Free Energy Change for Reaction:

For reaction,



$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \sum \Delta G^\circ_f(\text{product}) - \sum \Delta G^\circ_f(\text{reactant}) \\ &= c\Delta G^\circ_f(C) + d\Delta G^\circ_f(D) - a\Delta G^\circ_f(A) - b\Delta G^\circ_f(B)\end{aligned}$$

At equilibrium, $\Delta G^\circ_{\text{rxn}} = 0$.

(*) Free Energy in terms of Pressure & Equilibrium Constant:

We know,

$$G = H - TS \quad \text{--- (i)}$$

$$\text{or } G = E + PV - TS \quad \text{--- (ii)}$$

Differentiating (ii), we get

$$dG = dE + PdV + VdP - Tds - SdT$$

Since, $W = -PdV$,

$$dG = dG - PdV + PdV + VdP - Tds - SdT$$

$dG = Tds$ and $dT = 0$ since, T is constant.

So, we get

$$dG = dG - VdP \quad \text{--- (iii)}$$

For one mole of gas, $dG = \frac{RT}{P} dP$ --- (iv)

on Integrating $G^\circ \rightarrow G$ and $P^\circ \rightarrow P$,

$$\int_{G^\circ}^G dG = \int_{P^\circ}^P \frac{RT}{P} dP$$

$$\text{or } G - G^\circ = RT \ln \left(\frac{P}{P^\circ} \right)$$

$$\text{or } G - G^\circ = RT \ln P \quad \text{--- (v)}$$

For n mole of gas,
 $nG = nG^\circ + nRT \ln P$

For reaction $aA + bB \rightarrow cC + dD$,

$$\Delta G^\circ = cG^\circ(c) + dG^\circ(d) + cRT \ln P_c + dRT \ln P_d - aG^\circ(a) - bG^\circ(b) - aRT \ln P_a - bRT \ln P_b$$

So, eqⁿ (x) becomes-

$$\Delta G = \Delta G^\circ + RT \ln \left| \frac{(P_c)^c \times (P_d)^d}{(P_a)^a \times (P_b)^b} \right| \quad \text{--- (vi)}$$

or, $\Delta G = \Delta G^\circ + RT \ln Q \quad \text{--- (vii)}$

Hence, $Q = \frac{(P_c)^c \times (P_d)^d}{(P_a)^a \times (P_b)^b}$

At equilibrium condition,
 $Q = K, \Delta G = 0$.

So, $\Delta G^\circ = -RT \ln K \quad \text{--- (viii)}$

Eqⁿ (viii) can be written as

$$K = e^{-\Delta G^\circ / RT} = 10^{\frac{-\Delta G^\circ}{2.303 RT}} \quad \text{--- (ix)}$$

If $\Delta G^\circ < 0$, $K > 1$. So forward reaction
 If $\Delta G^\circ > 0$, $K < 1$. So, backward reaction.

We know, $\Delta G = \Delta H - T\Delta S$.

So,

eqⁿ (ix) can be written as,

$$K = 10^{\frac{\Delta S^\circ}{2.3R}} \times 10^{\frac{-\Delta H^\circ}{2.3RT}} \quad \text{--- (x)}$$

Temperature Dependence of Equilibrium:

We know,

$$\Delta G^\circ = -RT \ln K \quad \text{--- (i)}$$

and

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{--- (ii)},$$

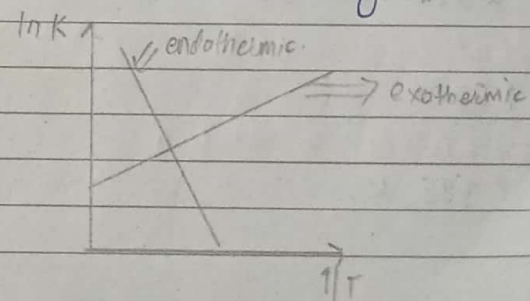
Equating (i) and (ii), we get.

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\text{or } \ln K = \left(\frac{-\Delta H^\circ}{R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad \text{--- (iii)}$$

which is in form of $y = mx + c$.

If ΔH° & ΔS° independent of temperature then,
 $\ln K$ is linear function of $1/T$.



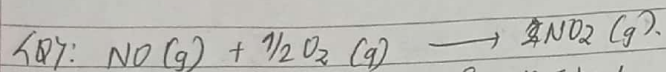
At different temperature T_1 and T_2 ,

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad \text{--- (i)}$$

$$\ln K_2 = \left(\frac{-\Delta H^\circ}{R} \right) \frac{1}{T_2} + \frac{\Delta S^\circ}{R} \quad \text{--- (ii)}$$

Combining (i) and (ii),

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



$$\Delta G^\circ = -8.33 \text{ kcal} \quad \Delta H^\circ = -13.5 \text{ kcal}$$

Calculate eqm constant at 298 K and 598 K.
Soln:

Given

$$\Delta G^\circ = -8.33 \text{ kcal}$$

$$\Delta H^\circ = -13.5 \text{ kcal}$$

We know, At 298 K.

$$K_1 = 10^{\frac{-\Delta G^\circ}{2.303 RT}}$$

$$= 10^{\frac{-(-8.33)}{2.303 \times 298 \times 8.31}}$$

$$\therefore K_1 = 1.0033$$

Now at 598 K,

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

$$\text{or } \ln \left(\frac{K_2}{1.0033} \right) = \frac{-(-13.5)}{8.31} \left(\frac{1}{598} - \frac{1}{298} \right)$$

$$\text{or } \ln \left(\frac{K_2}{1.0033} \right) = -2.73$$

$$\text{or } \frac{K_2}{1.0033} = e^{-2.73}$$

$$\text{or } K_2 = e^{-2.73 \times 1.0033}$$

$$\therefore K_2 = 0.06463$$

Nernst Equation:

We know,

$$G = H - TS \quad \text{--- (i)}$$

For small change in free energy,

$$dG = dH - d(TS)$$

$$\text{or } dG = dq + PdV + VdP - Tds - SdT$$

$$[\because H = E + PV]$$

$$\text{or } dG = dq + dw + PdV + VdP - Tds - SdT \quad \text{--- (ii)}$$

At constant temp and pressure, $dP=0, dT=0$
and $dq = Tds$.

So, we get / eqn (ii) becomes.

$$dG = dq + dw + PdV + 0 - dq - 0$$

$$\text{or } dG = dw + PdV \quad \text{--- (iii)}$$

Here, $dw =$ all work done.

So, $dw = dw_{elec} + dw_{pv}$.

Since PV work is negative,

(in eqⁿ(iii),

$$dG = dw_{elec} - PdV + PdV$$

$$\text{or, } dG = dw_{elec} \quad \text{--- (iv)}$$

for infinite change,

$$\Delta G = w_{elec} \quad \text{--- (v)}$$

We know, $w_{elec} = -nF\Delta E$ --- (vi).

Here, $\Delta E =$ potential change.

$F =$ Faraday constant = 96500 C.

Equating (v) and (vi), we get.

$$\Delta G = -n\Delta E F \quad \text{--- (vii)}$$

At standard condition,

$$\Delta G^\circ = -nF\Delta E^\circ \quad \text{--- (viii)}$$

and

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{--- (ix)}$$

From (vi), (vii), (viii) + (ix).

$$-n\Delta E F = -nF\Delta E^\circ + RT \ln Q$$

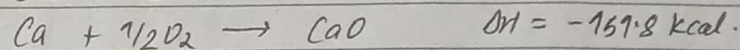
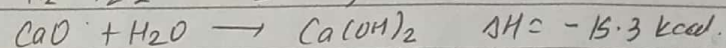
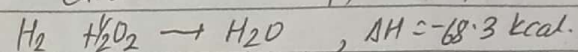
$$\text{or, } \Delta E = \Delta E^\circ - \frac{RT}{nF} \ln Q.$$

$$\text{or, } \Delta E = \Delta E^\circ - \frac{8.31 \times 298}{n \times 96500} \times 2.303 \log Q$$

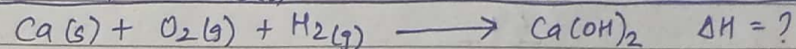
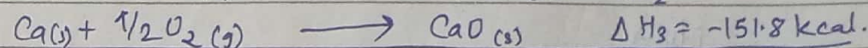
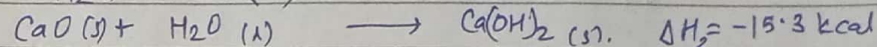
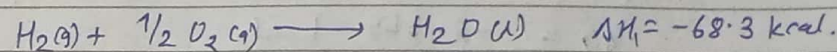
$$\therefore \Delta E = \Delta E^\circ - \frac{0.059}{n} \log Q. \quad \text{--- (x)}$$

Eqⁿ (x) is the Nernst equation.

Q7: Calculate enthalpy of formation of Ca(OH)_2 .



Solⁿ.



From Hess law of constant summation,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \\ = (-68.3 - 15.3 - 151.8) \text{ kcal.}$$

$$\therefore \Delta H = -235.4 \text{ kcal}$$

(Q7): Calculate ΔG° and K at 25°C for
reaction $\text{NO} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{NO}_2(\text{g})$.
Data given in chapter 8.
Solⁿ:

Here,

$$\Delta H^\circ = \sum H_f^\circ(\text{product}) - \sum H_f^\circ(\text{reactant})$$
$$= 8.09 - 21.6 = -13.51 \text{ Kcal.}$$

$$\Delta S^\circ = \sum S_{\text{product}} - \sum S_{\text{reactant}}$$
$$= 57.5 - (50.3 + 49/2)$$
$$\therefore \Delta S^\circ = -17.3 \text{ eu}$$

Now,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -13.51 \text{ Kcal} - 298 \times (-17.3)$$
$$\therefore \Delta G = -8.355 \text{ Kcal.}$$

Now

$$K = 10^{\frac{-\Delta G^\circ}{2.303RT}}$$
$$= 10^{\frac{-(-8.355)}{2.303 \times 8.31 \times 298}}$$

$$\therefore K = 1.0033$$