11/07/17

Thermodynamics Part : 2

* Heat cycle or Heat Engine :

for any heat engine if q_1 = Heat given to engine ((+)ve), q_2 = heat released by engine (Negative (−))

W = workdone by engine (−ve).

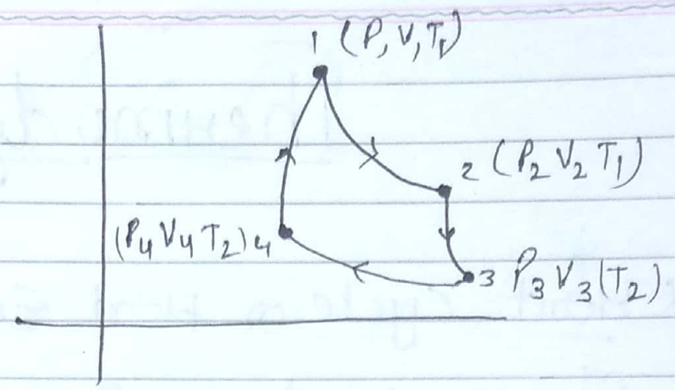
$$|W| = |q_1| - |q_2| = q_1 + q_2$$

Efficiency
$$\eta = \frac{|W|}{|q_1|} = \frac{-W}{q_1}$$
$$= \frac{|q_1| - |q_2|}{|q_1|} = \frac{q_1 + q_2}{q_1}$$
$$\eta = 1 - \frac{|q_2|}{q_1} = 1 + \frac{q_2}{q_1}$$

* Effeciency of a reversible engine will be greater than effeciency is irreversible engine.

$$W_{irr} > W_{rev.}$$
$$|W_{irr}| < |W_{rev}|$$
$$\frac{|W_{irr}|}{|q_1|} < \frac{|W_{rev.}|}{|q_1|}$$
$$\eta_{irr} < \eta_{rev}$$

* Carnot Cycle:



1-2 rev. Isothermal expansion.

$q_1 + w = 0$

$q_1 = -w$

$q_1 = +nRT_1 \ln\left(\frac{V_2}{V_1}\right)$ —— (i)

2-3 rev. adiabatic Expansion

$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$ —— (ii)

3-4 rev isothermal Compression

$q_2 + w = 0$

$q_2 = -w$

$q_2 = +nRT_2 \ln\left(\frac{V_4}{V_3}\right)$ —— (iii)

4-1 rev. adiabatic compression

$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$ —— (iv)

$\eta = \frac{|w|}{|q_1|} = |q_1|$

$\eta = 1 - \frac{\left|nRT_2 \ln\left(\frac{V_4}{V_3}\right)\right|}{\left|nRT_1 \ln\left(\frac{V_2}{V_1}\right)\right|}$

(ii) ÷ (iv)

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

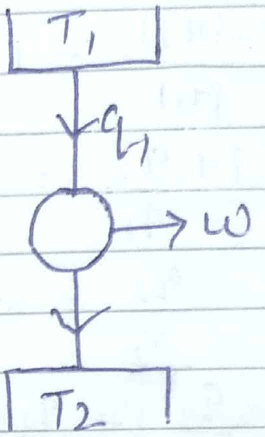
Adiabatic ball

$$\eta = 1 - \frac{\left|T_2 \ln\left(\frac{V_1}{V_2}\right)\right|}{\left|T_1 \ln\left(\frac{V_2}{V_1}\right)\right|}$$

$$\eta = 1 - \frac{\left|T_2 \ln \frac{V_2}{V_1}\right|}{\left|T_1 \ln\left(\frac{V_2}{V_1}\right)\right|}$$

$$\eta = 1 - \frac{|T_2|}{|T_1|}$$

$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$



$T_2 \Rightarrow$ Temp. of lower temp. sing
$T_1 \Rightarrow$ Temp. of higher temp. sing

$$\frac{|w|}{|q_1|} = \frac{|q_1| - |q_2|}{|q_1|} = 1 - \frac{|q_2|}{|q_1|}$$

$\Rightarrow \eta_{rev} > \eta_{irr}$

* $1 - \frac{|q_2|}{|q_1|} = 1 - \frac{T_2}{T_1}$ [for any reversible engine operating b/w T_1 & T_2 temp.

$1 - \frac{|q_2|}{|q_1|} < 1 - \frac{T_2}{T_1}$ [for any irreversible engine operating b/w T_1 & T_2)

$1 - \frac{|q_2|}{|q_1|} > 1 - \frac{T_2}{T_1}$ [Impossible]

* For any reversible cycle:

$$1-\frac{|q_2|}{|q_1|} = 1 - \frac{T_2}{T_1}$$

$$1+\frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

$$\oint \frac{dq_{rev.}}{T} = 0$$

$$\oint ds = 0 \qquad ds = \frac{dq_{rev.}}{T}$$

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

$$\oint \frac{dq}{T} = \frac{q_1}{T_1} + \frac{q_2}{T_2}$$

1−2

$$\Rightarrow \frac{dq_1}{T_1} + \frac{dq_2}{T_1} + \frac{q_{q_3}}{T_1} - - \frac{q_1}{T_1} = 0$$

* As the cyclic integration of $\frac{dq_{rev.}}{T}$ is zero it means it will definately denote a change in a state function this state fn is called antropy

* For any irreversible cycle:

$$1 - \frac{|q_2|}{|q_1|} < 1 - \frac{T_2}{T_1}$$

$$\cancel{1} + \frac{q_2}{q_1} < \cancel{1} - \frac{T_2}{T_1}$$

$q + w = \Delta U$

$$\frac{q_2}{T_2} < -\frac{q_1}{T_1}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} < 0$$

$$\oint \frac{dq_{irr}}{T} < 0$$

~~dq irr.~~ Cyclic integration of $\frac{dq_{irr.}}{T}$ is not equal to zero is means it will not denote change in any state.

* Clausius Inequality :-

$$\left\{ ds = \frac{dq_{rev}}{T} \right\}$$

$$dq_{irr} < dq_{rev.}$$

$$\frac{dq_{irr}}{T} < \frac{dq_{rev}}{T}$$

$$ds > \frac{dq_{irr}}{T}$$

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

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

$\hookrightarrow$ clausius inequality.

Start.

Imp. Topic's

* Clausius inequality for an Isolated System:-

($dq = 0$)

$ds \geq 0$
$ds > 0$ {Possible irreversible process or spontaneous process}

$ds = 0$ [reversible process)

$ds < 0$ [impossible process or non-spontaneous process}

Imp.

⇒ Entropy of an Isolated System can never decrease during a process in Isolated System

⇒ Entropy will be maximum at eq^{b}. in a Isolated System.

⇒ Universe is an Ideal example of Isolated System. So all the results of Isolated system can be applyed for universe.

* Second law of Thermodynamics:-

Statement given by Clausius:

Total Entropy of a universe during a process can never decrease either it will increase in a spontanious or remain constant in a reversible Process.

$dq = 0$

$\Delta S_{univ.} \geq 0$

$\Delta S_{system} + \Delta S_{surr} > 0$ [Process Irreversible Process or Spontaneous process]

$\Delta S_{system} + \Delta S_{surr} = 0$ [reversible process or at Equilibrium)

$\Delta S_{syst.} + \Delta S_{surr} < 0$ [Impossible process or non-Spontaneous Process]

Although individual value of Entropy of system or Entropy of Surrounding can decrease.

* Entropy: (S):- Entropy is a measurement of dispersion of Energy, Unuseful energy or Randomness of particles of the system

Important Point:- gasious molecules which have higher value of atomicity will have value of entropy as

$S_{NH_3} > S_{H_2}$

$S_{H_2} < S_{O_2}$

$\boxed{H < H_2 < \begin{matrix} NH_3 \\ O_2 \end{matrix}}$

$S_H < S_{H_2}$

2) If atomicity are equal we will compare by Size of molecules

Size ↑ S ↑

3] Entropy of gas >>> Entropy of liquid >>> Entropy of Solid

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

Ex:- i) $2NH_{3(g)} \longrightarrow N_{2(g)} + 3H_{2(g)}$ $\Delta n_g > 0$ $\Delta S > 0$

(ii) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta n_g < 0$ $\Delta S < 0$

(iii) $H_2O_{(s)} \longrightarrow H_2O_{(l)}$ $\Delta n_g = 0$ $\Delta S \neq 0$

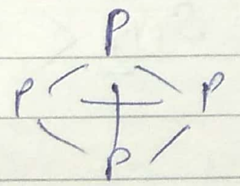
$\Delta S > 0$.

4] On mixing of two gases or two liquids or two solids Entropy will increase.

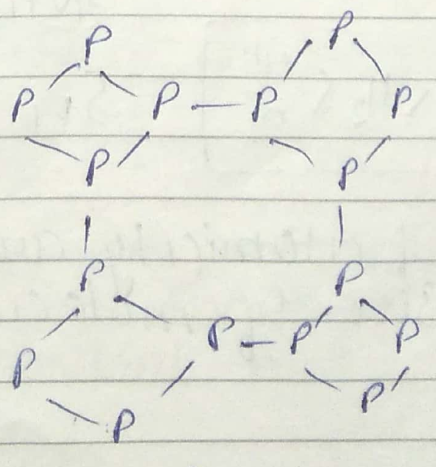
5) Alotrophic form of a substance which have batter arrangement of particle ~~which~~ will have lower value of Entropy.

$S_{C(diamond)} < S_{C(graphite)}$.

$S_{P(white)} > S_{P(red)}$



white



red

$C_m = \frac{c}{n}$ H-W: ⑥ J-A

Que: In which of the following options Entropy will decrease.

~~1)~~ during precipitation Process ↓
~~2)~~ During streching of Rubber. ↑↓
~~3)~~ Boiling of Egg. ↑ Due to Dinaturation of Protein.
~~4)~~ Absorption of a gas on a solid ↓
5) Dissolution of a solid in a liquid. ↑

* Calculation of entropy change:

* for non Reacting Substances:

(i) If molar heat capacity of process is provided:

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

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_m dT}{T}$$

(ii) If Cm is constant:

$$\Delta S = nC_m \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = C \ln(T_2/T_1)$$

* for non Reacting Ideal gas:

$$dq + w = du$$

$$dq - PdV = nC_m dT$$

$$\frac{dq}{T} - \frac{P\,dv}{T} = \frac{n C_{vm}\,dT}{T}$$

$$dS = \frac{P}{T}dv + \frac{n C_{vm}\,dT}{T}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{nR}{V}\,dv + \int_{T_1}^{T_2} \frac{n C_{vm}\,dT}{T}$$

Learn

$$\boxed{\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) + n C_{vm}\ln(T_2/T_1)}$$

If Cvm is const.

$$\Delta S = nR\ln\frac{\frac{nRT_2}{P_2}}{\frac{nRT_1}{P_1}} + n C_{vm}\ln(T_2/T_1)$$

$$\Delta S = nR\ln\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right) + n C_{vm}\ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = nR\ln\left(\frac{P_1}{P_2}\right) + nR\ln\left(\frac{T_2}{T_1}\right) + n C_{vm}\ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = nR\ln\left(\frac{P_1}{P_2}\right) + n(C_{vm} + R)\ln\left(\frac{T_2}{T_1}\right)$$

Learn

$$\boxed{\Delta S = nR\ln(P_1/P_2) + n C_{pm}\ln(T_2/T_1)}$$

Always [illegible]

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

Valid for non Reacting ideal gas in every process

$PV = \underline{\boxed{nR}}T$

$\downarrow$ $\boxed{0.0821}$

V ↑	S↑
P ↑	S↓
T ↑	S↑
m ↑	S↑

Que:- molar heat capacity for an ideal gas in a isochloric process is $C_{vm} = (1 + .01T)$ Joule/mol·K. If isocholicly this gas heated from 27°C to ~~100~~ 127°c then calculate change in molar Entropy for this ideal gas.

$$\Delta S = \int_{T_1}^{T_2} \frac{dq}{T} = \int_{300}^{400} \frac{n C_{vm}\, dT}{T} = \int_{300}^{400} \frac{(1)(1 + .01T)\, dT}{T}$$

Que:- A gas is taken from 2 atm to 30 litre to (4 atm, 90 litre) by a certain process then calculate chang in molar Entropy ΔS of gas. Suppose gas is a ~~di~~ ideal Diatonic gas.

$C_{vm} = \frac{5}{2}R.$

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

$$\Delta S = (1)R \ln\left(\frac{90}{30}\right) + (1)\left[\frac{5}{2}R\right] \ln\left(\frac{P_2 V_2}{P_1 V_1}\right) \qquad PV = RT$$

* Entropy Change for Surrounding:-

1. If process is a reversible process in the system

$$\Delta S_{system} + \Delta S_{surr} = 0$$

$$\boxed{\Delta S_{surr} = -\Delta S_{system}}$$ Learn.

2) If process is Irreversible process in the system.

$$\Delta S_{system} + \Delta S_{surr} > 0$$

$$\Delta S_{surr} = \int \frac{dq_{surr}}{T_{surr}} = \frac{\int dq_{surr}}{T_{surr}} = \frac{q_{surr}}{T_{surr}}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}}$$

Imp

$$\boxed{\Delta S_{surr} \begin{cases} \xrightarrow{rev} -\Delta S_{system} \\ \xrightarrow{irr} -\dfrac{q_{sys}}{T_{surr}} \end{cases}}$$ learn

learn

Imp

$$\Delta S_{sys} = nR\ln\left(\frac{V_2}{V_1}\right) + nC_{vm}\ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S_{sys} = nR\ln\left(\frac{P_1}{P_2}\right) + nC_{pm}\ln\left(\frac{T_2}{T_1}\right)$$

Isoth:- $\Delta U = 0$ Isobar $q = \Delta H \Rightarrow nC_{pm}\Delta T$ $q = \Delta U - w$

* Calculation of ΔS_{system}, $\Delta S_{surr.}$ and $\Delta S_{universe}$ for different process:-

(1) In Isochoric Process:-

(i) ΔS_{sys} for rev/irr Isochoric process:

$$\boxed{\Delta S_{sys.} = nC_{vm} \ln\left(\frac{T_2}{T_1}\right)}$$

ii) ΔS_{surr} if process is rev. process $= -\Delta S_{sys.}$

(iii) ΔS_{surr} if process is irr process =

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = -\frac{(\Delta U - \overset{0}{\cancel{w}})}{T_{surr}}$$

$$\Delta S_{surr.} = -\frac{nC_{vm}\cdot(T_2 - T_1)}{T_{surr.}}$$

* $T_{surr} = T_2$ if value of T_{surr} not given in question.

* In Isobaric process:

(i) ΔS_{sys} for rev/irr Isobaric process:

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

(ii) $\Delta S_{surr.}$ if process is rev process $= -\Delta S_{sys.}$

(iii) ΔS_{surr} if process is irr process =

$$\text{Isothel} = W = -P_{ext}(T_2 - T_1)$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = \frac{-(\Delta U - W)}{T_{surr}}$$

$$-\frac{(nC_{vm}\Delta T + nR\Delta T)}{T_{surr}}$$

$$-\frac{(n(C_{vm} + R)\Delta T)}{T_{surr}}$$

$$-\frac{nC_{pm}(T_2 - T_1)}{T_{surr}}$$

* In Isothermal process :-

(i) ΔS_{sys} for rev/irr process !

$$\Delta S_{sys} = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln(P_1/P_2)$$

(ii) ΔS_{surr} if process is reversible process $= -\Delta S_{sys}$

(iii) ΔS_{surr} if process is irreversible process =

$$\Delta S_{surr.} = \frac{-q_{sys}}{T_{surr}} = \frac{-(\Delta U - W_{irr})}{T_{surr}}$$

$$\Delta S_{surr} = \frac{W_{irr}}{T_{surr}}$$

$$\Delta S_{surr} = \frac{-P_{ext}(V_2 - V_1)}{T_{surr}}$$

$$S_{surr} = \frac{-P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)}{T_{surr}}$$

$$T_{surr} = T_2 = T$$

✗ ~~In isothermal process~~!

In Adiabatic Process

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

$$\Delta S = nC_{pm}\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)$$

These formulas are also ~~app~~ aplicable for adiabatic process if we solve for reversible adiabatic process then

$$\boxed{\Delta S_{sys} = 0.}$$

If we solve for irreversible adiabatic process then

$$\boxed{\Delta S_{sys} > 0}$$

Proof! $\Delta S = nC_{vm}\left[\ln\left(\frac{T_2}{T_1}\right) + \underset{\substack{\Downarrow \\ \gamma-1}}{\left(\frac{R}{C_{vm}}\right)}\ln\left(\frac{V_2}{V_1}\right)\right]$

$$\Delta S = nC_{vm}\left[\ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{V_2}{V_1}\right)^{\gamma-1}\right]$$

$$\Delta S = nC_{vm}\left[\ln\frac{T_2 V_2^{\gamma-1}}{T_1 V_1^{\gamma-1}}\right]$$

(ii) ΔS_{surr} if process is rev process $= -\Delta S_{sys} = 0$

(iii) ΔS_{surr} if process is irr process =

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = 0$$

*free Expansion of Ideal gas :

free Expansion of Ideal gas is a irr. adaiabatic and irr. Isothermal process simultaneously.

$$\Delta S_{sys} = nR\ln\left(\frac{V_2}{V_1}\right) + nC_{v,m}\ln\cancel{\left(\frac{T_2}{T_1}\right)}^{0}$$

In free Expansion

$$\boxed{\Delta S_{sys} > 0}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = 0$$

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

*for Cyclic Process in System :

(i) for rev/irr cyclic Process :

$$\Delta_{sys} = 0$$

611 Pascal

T.D-2 O-1 = 1 to 10

T.D-1 S-II => 1 to 5

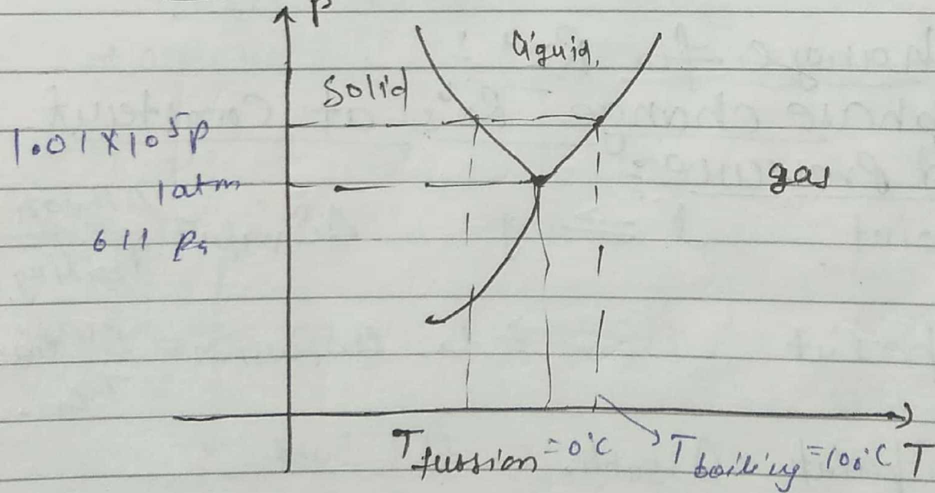
(ii) ΔS_{surr} if process is rev process $= -\Delta S_{sys} = 0$

(iii) ΔS_{surr} if process is irr. process:

$$\Delta S_{surr} = \frac{-q_{sys}}{T_{surr}} = \frac{-(\overset{0}{\cancel{\Delta U}} - w)}{T_{surr}} = \frac{w_{irr}}{T_{surr}}$$

* If System Restored to its initial position in a cyclic process then it is not compolsory that surrounding will also Restored to its initial position.

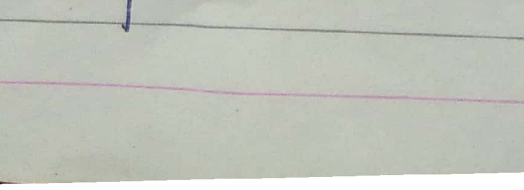
* ~~fo~~ phase diagram for water:



$V_{H_2O(s)} > V_{H_2O}$ liquid,

Phase diagram for H_2O

for a general substance:



V (Solid) < V (Liq)

* At Boiling point liquid will be in eq with gas/vapour.

* Boiling point at 1 atm pressure called normal boiling point

* Boiling point at 1 bar pressure called Standard boiling point.

* At fussion point solid will be in eq^b with liquid.

for general ~~solid point~~ substence T_{fusion} ↑ P ↑

for H_2O substance ~~for~~ T_{fusion} ↑ P ↑

* Entropy change for Rx^n :

(1) ΔS for phase change Rx^n's at Constant temp. and Pressure :

* At boiling point $l \rightleftharpoons g$. $\Delta S_{vap.} = \frac{\Delta H_{vap}}{T_{boiling\ point}}$

* At fussion point $s \rightleftharpoons l$ $\Delta S_{fussion} = \frac{\Delta H_{fus.}}{T_{fus.}}$

* At Sublimation point $\Delta S_{subli.} = \frac{\Delta H_{Subli.}}{T_{sub.}}$

$s \rightleftharpoons g$.

$$\Delta S = \int \frac{dq}{T}$$

* $\Delta S = \int \frac{dq}{dT} = \frac{\int dq}{T} = \frac{\Delta q}{T} = \frac{\Delta H}{T}$ [because Pressure is constant]

(526) Coun Counselling

1(53) 2'' (

Que! Enthalpy of Vaporisation for H_2O liquid is 40 kcal per gram. if Condensation of 1 mol. H_2O Vapour occurs at 100°C and 1 atm pressure then calculate value of ΔS condensation for 1 mol of H_2O.

Ans)

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{boiling\ point}}$$

$$\Delta S_{vap} = \frac{40 \times 18}{373}$$

$$\Delta S_{condensation} = -\frac{40 \times 18}{373}$$

* $$H_2O(l)\ (1.atm, 100°C) \rightleftharpoons H_2O(g)\ (atm, 100°C) \qquad \Delta S = \frac{\Delta H_{vap}}{T_b}$$

$$\begin{tikzcd}
H_2O(l)\ (1atm\ 150°C) \arrow[r] \arrow[d, "\Delta S_1 = \int \frac{dq}{T} \int_{423}^{373} \frac{nC_{pm}(l)\,dT}{T}"'] & H_2O(g)\ (1atm, 150°) \\
H_2O(l)\ (1atm, 100°C) \arrow[r, shift left, "\Delta S_2 = \frac{\Delta H_{vap}}{T_b}"] & H_2O(g)\ (1atm, 100°C) \arrow[l, shift left] \arrow[u, "\Delta S_3 = \int_{373}^{423} \frac{nC_{pm}(g)\,dT}{T}"']
\end{tikzcd}$$

$$\Delta S = \frac{\Delta H_{vap}}{T_b} \quad \text{X}$$

90-

Que: for a solid Cp.m 40 J/mol. ΔH fussion = 50 kJ/m, n = 1 mol, Normal fussion = 27°C then Calculate ΔS

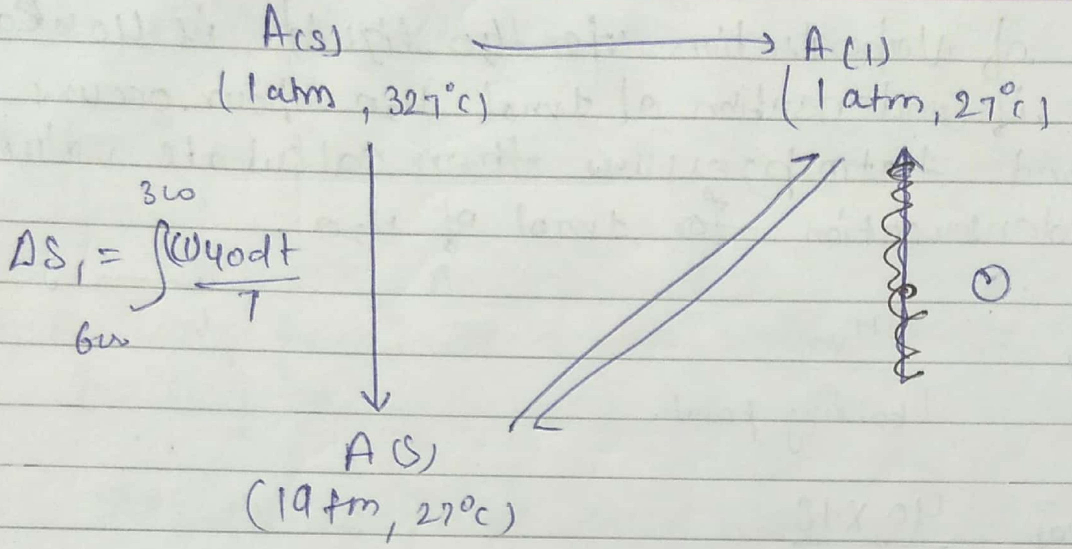
Qr. $$\overset{\rightharpoonup}{A}(s)\ (1 atm\ 327°C) \longrightarrow A(l)\ (1atm, 27°C)$$

[n = 1]

Δ n o

$\frac{50}{40}$ =

=



(2) If exect Value of Molar Entropy of different Reactant or product given in the question.

$$aA + bB \longrightarrow cC + dD \quad \Delta S_{Rxn} = ?$$

$$\Delta S_{Rxn} = (cS_C + dS_D) - (aS_A + bS_B)$$

Here S_a, S_b, S_c, and S_D are molar Entropy of A, B, C and D respectively.

$$\Delta H_{Rxn} = (cH_C + dH_D) - (aH_A + bH_B)$$

S.T.P	standard Condition
P = 1 bar	P = 1 bar
T = 273	T = any definate Temp.
	If a Quantity is given under standard Condition then this is measure under these given Condition. If any liquid species is present then Conc= 1 molar Ex: S°, H°, ΔS°, ΔG°.

$\boxed{dq = -ve}$

T.D : Part 1 full
0-2

↑ 80
10↑

* Third Law of Thermodynamics:

At 0K temp Entropy of a perfectly Crystallin Solid will be minimum and this minimum value Can be assume to equal to zero

$$\boxed{S_{0\,kelvin} = 0}$$

with the help of Third Law of Thermodynamics ~~exact~~ exact value of entropy of a substance Can be calculated

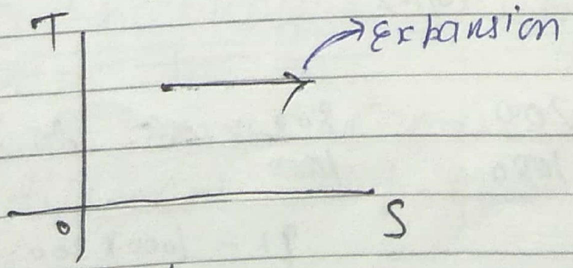
$$\underset{0\,K}{H_2O(s)} \xrightarrow{\Delta S_1 = \int_0^{273} \frac{nC_{pm(s)}\,dT}{T}} \underset{273\,K}{H_2O(s)} \xrightleftharpoons{\Delta S_2 = \frac{\Delta H_{fusion}}{T_{fusion}}} \underset{373}{H_2O(l)} \xrightleftharpoons{\Delta S = \frac{\Delta H_{vap}}{T_b}}$$

$$\underset{373}{H_2O(g)} \xrightarrow{\Delta S = \int_{373}^{600} \frac{nC_{pm(g)}\,dT}{T}} \underset{600\,K}{H_2O(g)}$$

$$\Delta S = S_{600K} - \cancel{S_{0K}}^{\,0} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

* T–S diagram for Carnot cycle!

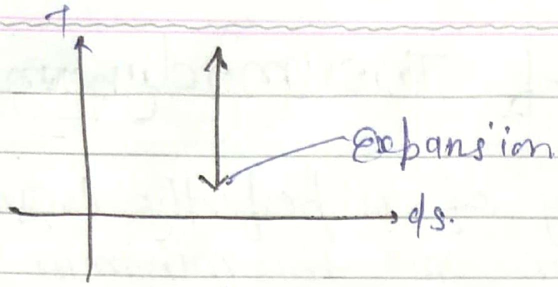
(i) T–S diagram for rev. isothermal process:



(ii) T–S diagram for rev. adiabatic Process:–

$\omega^{+} \ne C^{-}$ B↓ = ada.

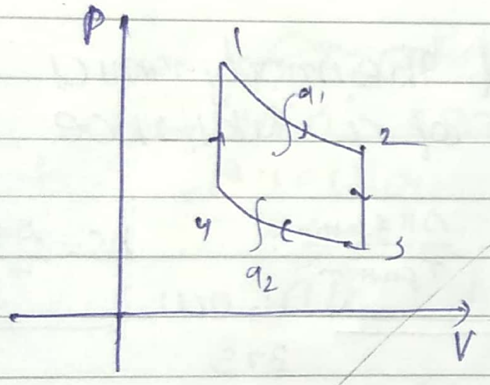
NVIM

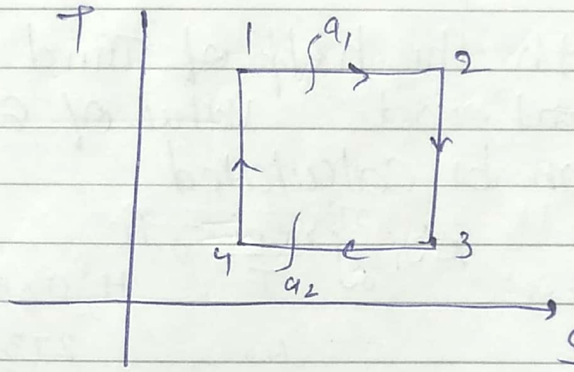


$= \int y\,dn$
$= \int T\,ds$
$= \int dq$

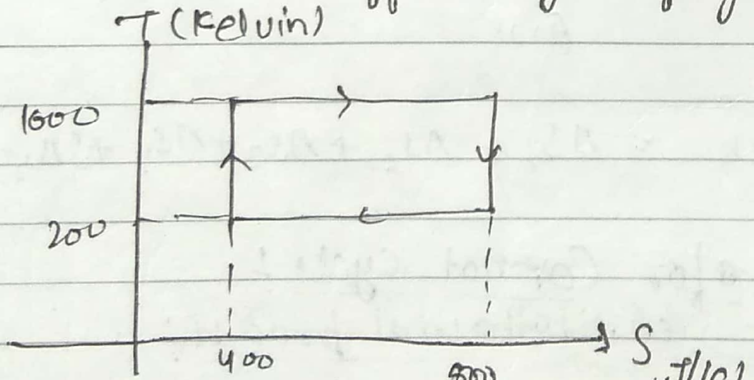
- * If rev. adeabatic process antropy of system remain constant so it is also called iso antropic process

- * Area Under T-S curve denote magnitude of Heat change in the process





Que: Calculate efficiency of given Carnot cycle:



C alo

M-1. $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{200}{1000} = \frac{800}{1000} \times 100 = 80\%$.

$q_1 = 1000 \times 200 =$

M.2 $\eta = \frac{|W|}{|q_1|} = \frac{|q_1| - |q_2|}{|q_1|}$

~~Topic~~
Not very Important

Habson - releam

Que: Calculate work done by engine per cycle

Ans

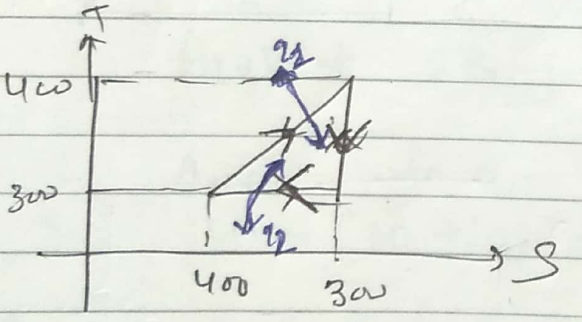
$$|q_1| = 100000 \text{ Joule.}$$
$$|q_2| = 20000 \text{ Joule}$$
$$|w| = |q_1| - |q_2| = 80000 \text{ J.}$$

(iii) If be eliminate 10000 bulb each of 40 watt ~~to~~ Capacity by given carnote engine then calculate no. of cycle that are required te Eliminate these bulb.

~~40000 / 80000~~ = m
.. 5 m

$$40 \times 10000 = \quad = 80000 \times n$$
$$m = 5 \text{ cycle}$$

Que: Calculate efficiency of given ~~carnot~~ cyle



$$|q_2| = 100 \times 300$$
$$|q_1| = \frac{1}{2}(700)(100)$$

* Krichhoff's equation:

Let a rx^n Occurs Const. Pressure and two different temp. t_1 and t_2

$$\begin{tikzcd}
n_1 R \arrow[r, "\Delta_r H_{T_1}"] \arrow[d, dash, "\Delta H = n_1 C_{pm(R)} \Delta T"'] & n_2 P \arrow[d, "\Delta H' = n_2 C_{pm(P)} \Delta T"] \\
n_1 R \arrow[r, "\Delta_r H_{T_2}", "T_2 K"'] & n_2 P
\end{tikzcd}$$

$$\Delta_r H_{T_2} + n_1 C_{pm(R)} \Delta T = \Delta_r H_{T_1} + n_2 C_{pm(P)} \Delta T$$

$$\Delta_r H_{T_2} - \Delta_r H_{T_1} = n_2 C_{pm(P)} \Delta T - n_1 C_{pm(R)} \Delta T$$

$$\Delta_r H_{T_2} - \Delta_r H_{T_1} = [n_2 C_{pm(P)} - n_1 C_{pm(R)}] \Delta T$$

$$\boxed{\Delta H_{T_2} - \Delta H_{T_1} = \Delta_r C_p \Delta T} \Rightarrow \Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta_r C_p \, dT$$

m

Ex: $aA + bB \longrightarrow cC + dD$

$$\Delta_r C_P = (c C_{pm(C)} + d C_{pm(D)}) - (a C_{pm(A)} + b C_{pm(B)})$$

* for internal energy change at different temp. T_1 and T_2

$$\boxed{\Delta_r U_{T_2} - \Delta_r U_{T_1} = \Delta_r C_v (\Delta T)}$$

Note: for a rxn if $\Delta_r C_p = 0$ then $\Delta_r H$ will be independent from temp

$\Delta_r C_P$

then $\Delta_r H$

$$\frac{d(\Delta_r H)}{dT} = 0$$

Ques) $A_{(g)} + 2B_{(g)} \longrightarrow C_{(g)}$

Enthalpy change for Rxn at ~~20~~ 27 °C is -10 kJ then calculate enthalpy change for Rxn at 127 °C. if molar heat capacity at constant pressure for a, b, and c are in ratio of 1 : 0.5 : 1 and Cpm for A gas is 10 J/mol.K.

Ans: $\overset{10}{A_{(g)}} + \overset{5}{2B_{(g)}} \longrightarrow \overset{10}{C_{(g)}}$

~~27°c — -10 kJ~~

$\Delta_r C_p$! $-$ ~~$\frac{10}{27} \times 127$~~

$\Delta_r C_P = -10$ J.

$10 - (10 + 10) = -10$ J/mol K

$$\Delta_r H_{400} - \Delta_r H_{300} = \Delta_r C_p (T_2 - T_1)$$

$$\Delta_r H_{400} - (-10000) = -10(400 - 300)$$

$$\Delta_r H_{400} = -11000 \text{ Joule}$$

Q:- Inorganic if Cpm for $A_{(g)}$ is $(1 + \cdot 02\,T)$ J/mol k.
then calculate $\Delta_r H$ at 127 °C

* Gibbs free Energy :

$$ds \geq \frac{dq}{T}$$

by Gibbs

$P = C$, $T = C$

$dq = dH$

$ds \geq \frac{dH}{T}$

$Tds \geq dH$

$dH - Tds \leq 0$

$dH - dTS \leq 0$

$d(H - TS) \leq 0$

$dG \leq 0$

by Helmholtz

$V = C$, $T = C$

$dq = dU$

$d(U - TS) \leq 0$

$dA \leq 0$

↳ Helmholtz energy

* Gibbs free energy : (G) :

$$G = H - TS$$

at constant temp. & Pressure

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

* Relation b/w ΔG and ΔS universe :

at $P = C$ & $T = C$

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$$

Thelu: Part-1: S-2: 6 to 11 + S-4: 23-24
Part 2. 1 to 6. S-1
9 to 11

$$\Delta S_{universe} = \Delta S_{sys.} - \frac{\Delta H}{T}$$

$$T\Delta S_{univ.} = T\Delta S_{sys.} - \Delta H.$$

$$-T\Delta S_{univ.} = \Delta H - T\Delta S_{sys.}$$

$$\boxed{-T\Delta S_{universe} = \Delta G}$$

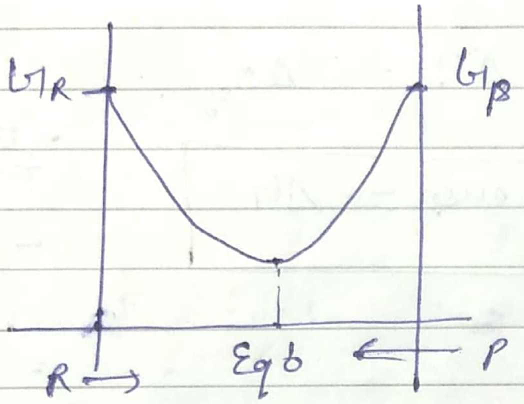
$$\begin{tikzcd}
 & \Delta S_{surr.} \arrow[dl, "rev."'] \arrow[dr, "irr"] & \\
-\Delta S_{sys.} & & \frac{-q_{sys}}{T} \\
-\int \frac{dq}{T}_{sys} & & \\
-\frac{1}{T}\int dq_{sys} = & & \frac{-\Delta h}{T} \\
-\frac{q_{sys}}{T} & & \\
= \frac{-\Delta h}{T} \arrow[uurr, leftrightarrow] & &
\end{tikzcd}$$

	$\Delta S_{univ.}$	$\Delta G.$
spontaneous process	>0	<0
rever. process or at Equilibrium	$=0$	$=0$
non-spontaneous process	<0	>0

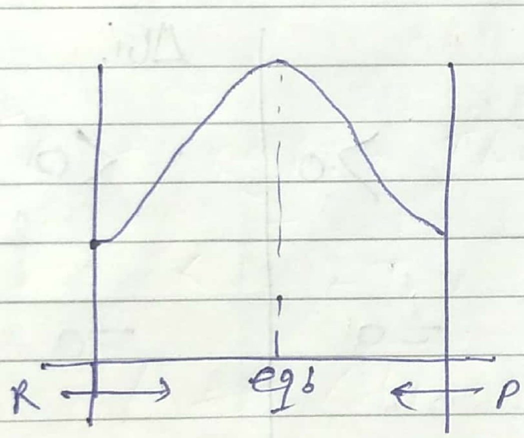
* Spontinuity criteria can be defined by ΔS universe in every condition But spontinuity criteria can be defined by ΔG only at const. P & const. Temp

① During a process gibbs free energy (G) will be minimum at eqb. and $S_{universe}$ will be maximum at eqb.

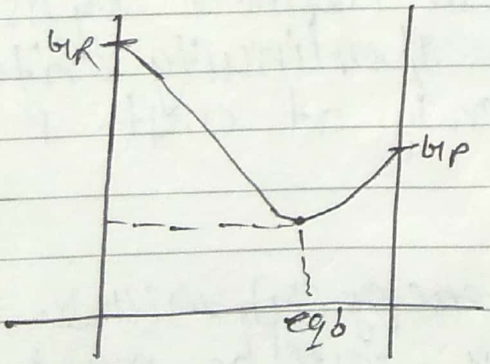
3)* for chemical eqb Rx^n graph of gibbs energy and entropy of univers can be plotted as

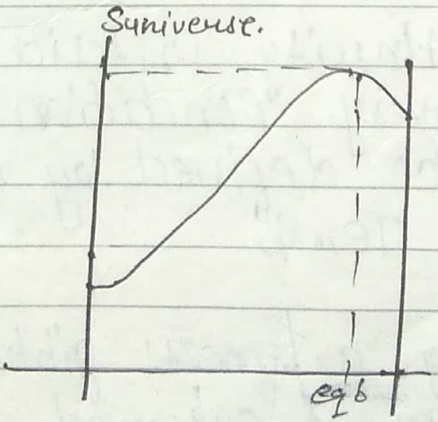


S universe:



for a chemical eqb Rx^n if value of eq^b const is quit high

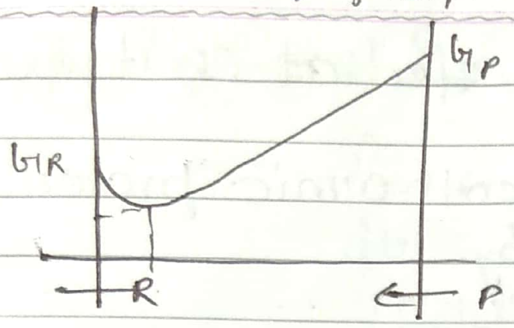


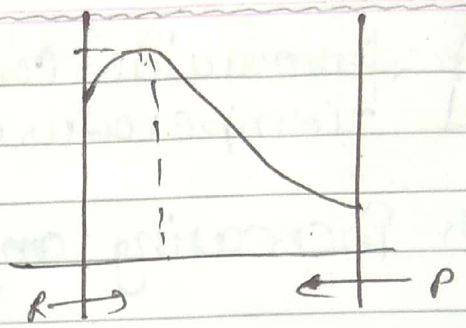


Sponanueous: Possible.

for eq const. eqⁿ ↑ high.

Juniuuse





$$K_{eq} = \frac{[P]\downarrow}{[R]\uparrow}$$

* Analysis of Spontinuity of Rxⁿs by ΔG. Occurs at Const. Pressure and Temp:-

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

ΔH	ΔS	ΔG	
−ve	+ve	−ve	always spontanuous.
+ve	−ve	+ve	always non-spontanuous.
+ve	+ve	T↑, −ve	Spontaneous at high temp
		T↓, +ve	nonspontaneous at low temp
−ve	−ve	T↑, +ve	
		T↓, −ve	Spontaneous at low temp.

* Most favourable condition for at const Pressure and Temperature

is exothermic process with increasing ~~on~~ entropy.

Que:- $2A_{(g)} \longrightarrow B_{(g)} + C_{(s)}$ $\Delta S = 1000$ cal/mol·K

$\Delta U = 99.8$ kcal/mol.

~~Ans~~ Calculate the temp above which reaction will be spontaneous

k−k

$\Delta G < 0$

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

$\Delta H = \Delta U + \Delta n_g \overset{2}{R}T$.

$\Delta h = 99.8$ kcal/mol.

$= \cancel{\Delta H} =$

$\Delta U + \Delta n_g RT - T\Delta S < 0$

$99.8 \times 1000 - (2)T - T(1000) < 0$

$99800 < 1002T$.

* Calculation of ~~ΔG~~ ΔG. if Temp. & Pressure is not Constant:

This calculation can be done only for a rev. process.

$G = H - TS$

$G = U + PV - TS$

$dG = du + Pdv + vdp - Tds - SdT$

$= dq + vdp - dq - SdT$

$$\boxed{dG = vdp - SdT}$$

$dq + w = du$

$dq - Pdv = du$

$dq = du + Pdv$

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

$Tds = dq$.

* Only if ~~temp~~ Pressure is constant: (In Isobaric Process).

$$P = \text{constant}$$
$$dG = -SdT$$
$$\left(\frac{dG}{dT}\right)_P = -S$$

*1) At constant Pressure slope of G v/s T Curve will ~~to~~ be equal to $-S$

$$S_{gas} >>> S_{liquid} > S_{solid}$$

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

2) Only if temperature is Constant:

(In Isothermal Process):

$$dG = VdP$$

$\left(\frac{dG}{dP}\right)_T = V$ slope of.

$$V_{gas} >> V_{liquid} > V_{solid}.$$

Case: (1) ΔG for solid & liquid in an Isothermal Process:

$$dG = VdP$$
$$\Delta G = \int_{P_1}^{P_2} VdP$$

$\Delta G = V(P_2 - P_1)$ $\boxed{\Delta G = V\Delta P}$

Case :- 2: ΔG for Ideal gas in an Isothermal Process:

$$\Delta G = \int_{P_1}^{P_2} V\,dP$$

$$\Delta G = \int_{P_1}^{P_2} \frac{nRT}{P}\,dP$$

$$\Delta G = nRT \ln(P_2/P_1)$$

$$\Delta G = -nRT \ln\left(\frac{P_1}{P_2}\right) = W_{isothermal}.$$

Qu: Calculate Sign of ΔH, ΔU, ΔS, ΔG, ΔS_{surr}, $\Delta S_{universe}$ for given process.

$H_2O_{(l)}$ (1atm, 150°C) $\longrightarrow$ $H_2O_{(g)}$(1atm, 150°C)

$\Delta H > 0$ Physical state
$\Delta U > 0$ $(g) > (l) > (s)$
$\Delta S > 0$

$\Delta S_{surr} = -\frac{q_{system}}{T}$ $q > 0$ $q > 0$

$\Delta S_{surr} < 0$

$\Rightarrow$ Process will be spontaneous
$\Delta G < 0$
$\Delta S_{universe} > 0$

(ii) $H_2O(l)$ $\longrightarrow$ $H_2O(s)$

(2 atm, 0°C) (2 atm, 0°C)

$\Delta H < 0$

$\Delta U < 0$

$\Delta S < 0$

$\Delta S_{surr} = \frac{-q_{sys}}{T}$ $q < 0$

$\Delta S_{surr} > 0$

Non-spontinuous

* Process will be non spontaneous

$\Delta G > 0$

$\Delta S_{universe} < 0$

Que) Boiling at freezing point

$\Delta H > 0$ $\Delta S_{surr} = \frac{-q_{system}}{T}$ $\because q > 0$

$\Delta U > 0$

$\Delta S > 0$ $\Delta S_{surr} < 0$

* process will be non-spontaneous.

$\Delta G > 0$

$\Delta S_{universe} < 0$

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

Solid & liquid $\Delta G = V\Delta P \Rightarrow T$ Constant.

gas $= -nRT\left(\frac{P_1}{P_2}\right) \Rightarrow T = $ Const

0-1 ⇒ Complete ≠ 22, 23, 30

* Calculate ΔG for ~~1 mol~~ conversion of 1 mol $H_2O\,(l)$

$$H_2O_{(l)} \longrightarrow H_2O_{(g)}$$

$$\begin{tikzcd}
\begin{matrix} H_2O(l) \\ (2\,atm, 100^\circ C) \end{matrix} \arrow[r] \arrow[d, "\Delta G_1 = V\Delta P"'] & \begin{matrix} H_2O\,(g) \\ (2\,atm, 100^\circ C) \end{matrix} \\
\begin{matrix} H_2O\,(l) \\ (1\,atm, 100\,C) \end{matrix} \arrow[r, shift left] & \begin{matrix} H_2O_{(g)} \\ (1\,atm, 100^\circ C) \end{matrix} \arrow[l, shift left] \arrow[u, "\Delta G_3 = -nRT\ln\left(\frac{P_1}{P_2}\right)"']
\end{tikzcd}$$

$$\Delta G_1 = V\Delta P = \frac{18}{1000}(1-2) \text{ atm.litre.}$$

$$\Delta G_3 = -1\,(R)\,(373)\ln(1/2)$$

$$\Delta G = -\frac{1.8}{1000}(101.3) - (8.3)(373)\ln(1/2)$$

* **Relation b/w ΔG, ΔG° and Q:**

V. Imp. $\boxed{\Delta G = \Delta G^\circ + RT\ln Q}$ $\boxed{Q = \frac{R}{P}}$

at eq^b

$\Delta G = 0$

$Q = K_{eq}$ → K_p = gaseous equilibrium
→ K_c ⇒ liquid eq^b.

$$0 = \Delta G^\circ + RT\ln K_{eq}$$

$$\boxed{\Delta G^\circ = -RT\ln K_{eq}}$$

$\Delta G = -RT \ln K_{eq} + RT \ln Q$

$\Delta G = RT \ln \left(\frac{Q}{K_{eq}}\right)$

$\Delta G < 0$ spontaneous Rxn in forward direction — $Q < K_{eq}$ [Forward]

$\Delta G = 0$ Equilibrium — $Q > K_{eq}$ (backward]

$\Delta G > 0$ Non-spontaneous in forward dirn. — $Q > K_{eq}$ [backward]

Que: $2A_{(g)} \rightleftharpoons 3B_{(g)}$ $K_P = 10$

In at any instant $P_A = .01$ KPA & $P_B = 1$ KPa then calculate value of ΔG at 27°C and what will with be direction of rxn to achieve Equilibrium?

$H_2O_{(g)}$

1 bar $= 10^5$ Pa

Ans:

~~$\frac{P_B^{3}}{P_A^{2}}$ = [illegible]~~

$$Q = \frac{P_B^3}{P_A^2} = \frac{(1000 \times 10^{-5})^3}{(.01 \times 1000 \times 10^{-5})^2}$$

$Q = 100$

$\Delta G = \Delta G^\circ + RT \ln Q$

$\Delta G = -RT\ln keq + RT\ln Q$

$\Delta G = RT\ln(Q/keq)$

~~ΔG~~ $\Delta G = -RT\ln 10 + RT\ln 100$

$\Delta G = RT\ln\frac{100}{10}$

$\Delta G = RT\ln 10$

backward direction

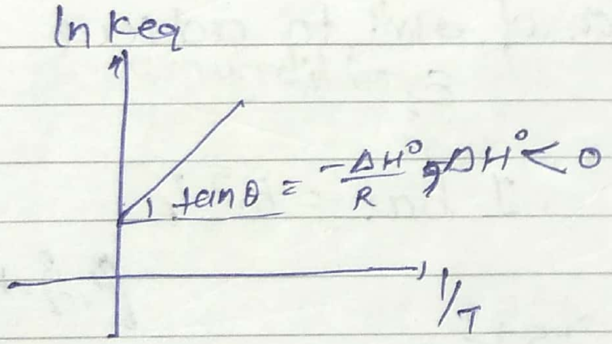
* Relation b/w ΔH°, ΔS° & $\ln keq$:

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

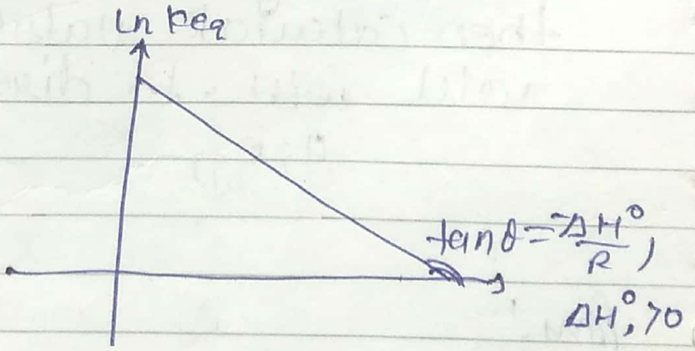
$-RT\ln keq = \Delta H^\circ - T\Delta S^\circ$

$\ln keq = \left(\frac{-\Delta H^\circ}{R}\right)\frac{1}{T} + \frac{\Delta S^\circ}{R}$

$y = m\ x + c$



Exothermic Rxn



Endothermic Rxn

* Physical Significance of ΔG:

At constant Pressure and Temp. in a Rev. Process ΔG will be equal to non-PV work.

$C'\Delta T$

Qn useful work in the ~~to~~ process
useful work is also called available energy of System :

$$dq + w = du$$
$$dq + w_{PV} + w_{non-PV} = du$$
$$dq - PdV + w_{non-PV} = du$$
$$w_{non-PV} = \underbrace{du + PdV} - dq$$
$$w_{non-PV} = dH - TdS$$

$$\boxed{w_{non-PV} = dG}$$

Q. 500 ml ~~R~~ 0.2 M HCl solution is mixed with 400ml 0.1 M Solution of NaOH in a calorie meter due to the reaction temp. of Solution increase by 0.6°C. then Calculate ΔH for Given Rxn.

$$HCl + NaOH \rightarrow NaCl + H_2O \quad \Delta H_{Rxn}$$

Suppose density of Resulting solⁿ is 1g/ml and specific heat capacity of solⁿ is 1 Cal/gramK and heat capacity of container is zero.

$$\overset{500ml}{HCl} + \overset{400ml}{NaOH} \rightarrow NaCl + H_2O \quad \Delta H_{Rxn}$$

100 mi = 0.1 mol

40 mill. = 0.04 mol

$$= \frac{\Delta H}{S.P} = \frac{\Delta H}{1} \times 0.04 = -mC_s\Delta T$$

$$\Delta H_{Rxn} \times 0.04 = -(900)(1)(0.6)$$

$$\Delta H_{Rxn} = -13500 \text{ cal.}$$

9:00 Am to 1:00 PM

* Defination of different types of Enthalpies

1. Enthalpy of formation (ΔH°_f) :-

Define for ~~&~~ formation of 1 mole Substance from its elements and elements must be present in their Standard state.

Most abundance of element in Nature considered its standard state

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^\circ_{Rxn} = \Delta H^\circ_f(H_2O(l))$$

$$H_2\underset{\uparrow}{(l)} + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ_{Rx^n} \neq \Delta H^\circ_f[H_2O(l)]$$

C → graphite ✓
C → diamond ×
C → fulrine ×

P → white ✓
P → red ×
P → black ×

S → Rhombic ✓
S → monoclinic ×