L-1/21

Thermodynamics

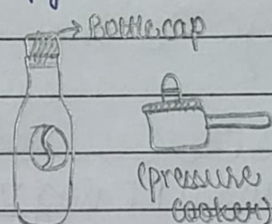
System: A specified portion of a universe under observation is called SYSTEM.

Surroundings: Except system, rest Part of the universe is called Surroundings.

Types of system →

OPEN	CLOSED	ISOLATED
can Exchange both Energy & Matter	can Exchange Energy not Matter	cannot Exchange both Energy & Matter

eg.



eg.
✓ Thermous flask
✓ vacuum flask

* NOTE: A system is seperated from surroundings by a Boundary & This Boundary can be real or Imaginary.

EXTENSIVE & INTENSIVE PROPERTY

EXTENSIVE → Amount Dependent

INTENSIVE → Amount Independent

*NOTE: Ratio of 2 Extensive properties is an INTENSIVE property.

STATE-FUNCTIONS

Property of a system depending on the Initial & Final States of the system not on the Path is called STATE-FUNCTIONS.

eg. Temp., Pressure, Internal Energy, Enthalpy, Entropy, Free Energy etc.

DATE : ___/___/____
PAGE : _____

NOTE: Heat & work done are Path Functions.

HEAT (Q) :-

It is a form of energy that flows from an object @ Higher Temp. to the object at lower Temp.

- ✓ Heat given to system → ⊕ ve
- ✓ Heat given by system → ⊖ ve

PRESSURE-VOLUME WORK DONE :

$W_{irr} = -P_{ext} \cdot \Delta V$ ⇒ Practically possible

- completes in "finite" Time
- flow in one dir^n (only compressible) or only Expansion

$W_{rev} = -2.303\, nRT \log \frac{V_2}{V_1}$ — completes in ∞ Time

$P_1 V_1 = P_2 V_2$ (Boyle's law)

$\Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$

$W_{rev} = -2.303\, nRT \log \frac{P_1}{P_2}$

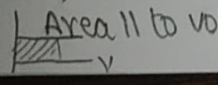
IN EXPANSION →

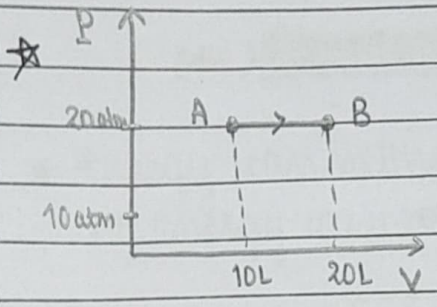
NOTE: $|W_{rev}| > |W_{irr}|$ ⇒ @ const. 'T'

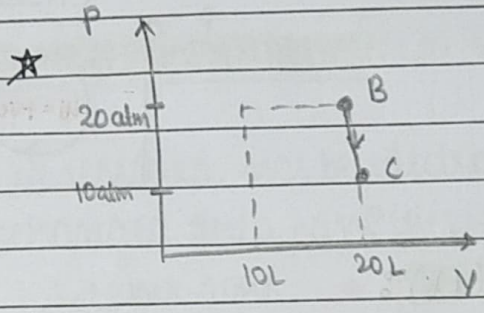
★ EXPANSION ⇒ work done by the ~~ster~~ system = −ve

★ COMPRESSION ⇒ work done on the system = +ve

★ In P-V graph, area under the vol. axis is work done.







$W_{A \to B} = -P_{ext} \cdot \Delta V$

$= -20 \text{ atm} (10\ L)$

$= -200 \text{ atm-L}$

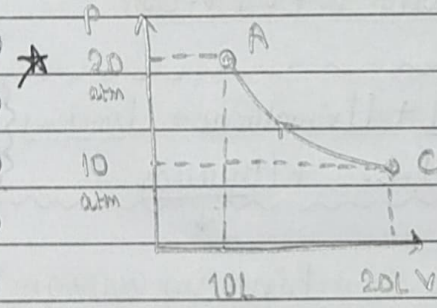
$1\ L\text{-atm} = 101.3\ J$

$\therefore (-200 \times 101.3)\ J$

$\Rightarrow -20260\ J$

$W_{B \to C}$

$W_{B-C} =$ ZERO.



When $PV = \text{constt}$

↳ Wrev is used

$W_{rev} = -2.303 \frac{nRT}{PV} \log \frac{V_2}{V_1}$

$= -2.303 \times 20 \times 10 \log \frac{10}{20}$

$\propto 10 \times 20$

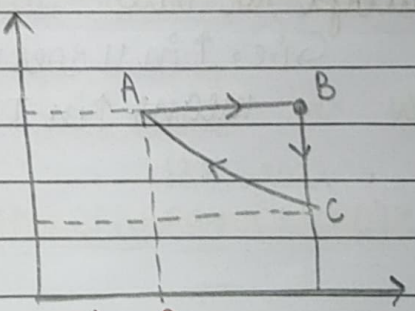
(Isothermal, $PV = \text{constt}$)

$= -2.303 \times 200 (\log 1 - \log 2)$

$= -2.303 \times 200 (0 - 0.3)$

$= 6909$ ~~L-atm~~

$= +13818$ L-atm

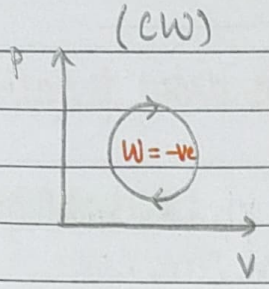
Ques^n :- 

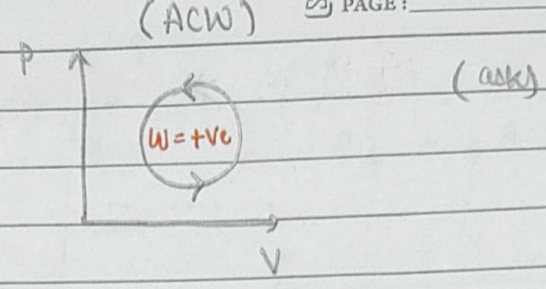
Sol^n :

$(-200 + 0 + 13818)$ L-atm

NOTE: In a cyclic Process, Work Done is the Area enclosed by the graph in the p-V graph

DATE: __/__/____
PAGE: _____



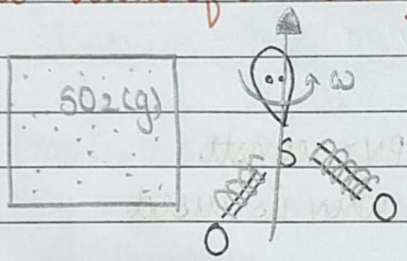


Internal energy (U):

Sum of all types of energies ⊕ in system is called:
INTERNAL ENERGY OF THE SYSTEM.

★ Internal energy (U) is a state function and we can only find the change in a state function.

★ Absolute value of a state function can't be Determined.



~~U = Utranslational = K.E. + P.E.~~

U = Utranslational + Uvibrational + Usotational
↳ K.E. + P.E. + Unuclear

Binding energy in Nucleons.

NOTE: Internal energy is the function of Temp.

i.e. $U = f(T)$

Increase in Temp. will increase the Internal energy of the system, but reverse is always not True
(i.e. ↑ in U does not Necessarily means ↑ in T

Ice ⇝ water
0°C 0°C

★ $U_{ice} < U_{water}$

"For ideal gas, change in Internal energy will always change its Temp & Vice versa."

DATE : ___/___/_____
PAGE : _____

FIRST LAW OF THERMODYNAMICS

★ Energy can neither be created nor be destroyed but one form of energy can be changed into another form.

$$\Delta U = q + W \quad \text{——} (1)$$

(W: work-done; q: Heat)

★ q & W are Path function but their sum i.e. $(q+W)$ is a state function

eqⁿ (1) is the mathematical form of 1st law of Thermodynamics

↦ Various form of $[\Delta U = q + W]$:
(for system of Ideal Gas)

① ISOTHERMAL - PROCESS (const^{tt} T) :

i.e. $\Delta U = 0$, $q = -W$ (for Ideal gas @ const^{tt} T)
Or $-q = W$

★ Heat given to the system is equal to work-done by the system at const^{tt} Temp.

or

Heat given by the system is equal to the work done on the system at const^{tt} T.

② ADIABATIC - PROCESS ($q = 0$) :-

$\Delta U = W$ i.e. work done is a state function in Adiabatic Process.

L-2/22 13 Dec 2022

③ ISOCHORIC - PROCESS ($\Delta V = 0$) :-

$\Delta U = q + W$

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

$\Delta U = q_v$ i.e. Heat is state function in Isochoric Process

Good Write

DATE: ___/___/____
PAGE: _____

Heat @ const. volume is change in internal energy.

④ ISOBARIC-PROCESS

$\Delta P = 0$

$\Delta U = q + W$ $\quad\quad$ $\Delta U = q - P\Delta V$

⑤ CYCLIC-PROCESS

NOTE: change in state function is zero in a cyclic process.

$\Delta U = q + W$

Zero $= q + W$

$q = -W$ $\quad$ like Isothermal

↓ ∴

Temp. is state function

ENTHALPY (H)

↳ state function

$H = U + PV$ $\quad$ Pressure Vol. work done $\quad$ —①

Enthalpy of the system is the sum of its INTERNAL ENERGY & PRESSURE-VOLUME work Done.

NOTE:

'H' is a state function and its absolute value cannot be determined, we can only find change in enthalpy (ΔH).

Differentiating eqⁿ ① :-

$dH = dU + PdV + dP.V$ —②

at const. P $(dp = 0)$ $\quad\quad$ at const. V $(dV = 0)$

$dH = dU + PdV$ $\quad\quad$ $dH = dU + VdP$

DATE: ___/___/____
PAGE: _____

$$\int_I^{II} dH = \int_I^{II} dU + \int_I^{II} P \cdot dV$$

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

↳ at const. P

$$\int_I^{II} dH = \int_I^{II} dU + \int_I^{II} V \cdot dP$$

$$\Delta H = \Delta U + V \cdot \Delta P$$

↳ at const. V

At constant constt P

$$\Delta H = \Delta U + P\Delta V$$
$$\Delta H = W + q + P\Delta V$$
$$\Delta H = -P\Delta V + q + P\Delta V \quad \text{(for rev. work)}$$

$$\Delta H = q_p$$

★ Heat @ constt 'P' is enthalpy-change (ΔH)

Ques" → calculate diff. b/w Heat at constt volume and Heat @ constt 'P' for the complete combustion of 1 mole solid Benzoic-Acid (C_6H_5COOH) @ 298 K. —

$$\Delta U - \Delta H = -nRT$$
$$= -RT$$

$$C_6H_5COOH + \frac{15}{2}O_2 \longrightarrow 7CO_2 + 3H_2O$$

12 + 3

const. n_r @ $\frac{15}{2}$

$PV = nRT$

$P\Delta V = \Delta n_g RT$

or

$P\Delta V = n R \Delta T$

↳ change in gaseous mole

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

$\Delta H = \Delta U + \Delta n_g RT$

↳ const. 'T'

$\Delta H = \Delta U + nR\Delta T$ (0.5)

$$C_6H_5COOH_{(s)} + \frac{15}{2}O_{2(g)} \longrightarrow 7CO_{2(g)} + 3H_2O$$

$n_p - n_r$

★ $n_p - n_r = \Delta n_g = 7 - \frac{15}{2} = -0.5$

Good Write Now, $\Delta U - \Delta H = -\Delta n_g RT = -(-0.5)RT = \frac{RT}{2}$ Ans

DATE : ___/___/____
PAGE : _____

Heat capacity

Amount of Heat required to raise the temp. of given Amount of substance by "1°C" is called: HEAT CAPACITY OF A SUBSTANCE.

NOTE: Heat capacity is extensive property.

Heat capacity

- specific Heat capacity
- Molar Heat capacity

= Intensive Properties

$q = m \times S \times \Delta T$

★ units of S → $J K^{-1} g^{-1}$

q → heat
m → mass in gram
S → specific Heat capacity
ΔT → change in temp.

• $m = 1g$, $\Delta T = 1°C$ or $1K$ (→ diff. in °C & K same)

⇒ $q = S$

↓

Amount of Heat required to raise temp. of 1g substance by 1°C is called: SPECIFIC HEAT CAPACITY OF SUBSTANCE

$q = n \times C \times \Delta T$

q → heat
n → no. of moles
C → molar Heat capacity

• $n = 1$; $\Delta T = 1°C$ or $1K$

⇒ $q = C$

↓

Amount of Heat req^{d} to raise temp. of 1 mole substance by 1°C is Called: MOLAR HEAT CAPACITY OF SUBSTANCE.

DATE: __/__/____
PAGE: _____

Molar Heat capacity at const. P (C_p)

$q_p = nC_p\Delta T$

$\Rightarrow \Delta H = nC_p\Delta T$ $\quad \star n = 1\,mole \longrightarrow$ $C_p = \left(\frac{\Delta H}{\Delta T}\right)_p$ → @ const P

Molar Heat capacity at const. V (C_v)

$q_v = nC_v\Delta T$

$\Rightarrow \Delta U = nC_v\Delta T$ $\quad \star n = 1\,mole \longrightarrow$ $C_v = \left(\frac{\Delta U}{\Delta T}\right)_v$ → at const V

$\because \Delta H = \Delta U + nR\Delta T$ (at const P) (at const V)

$\rightarrow n = 1$

$\Delta H = \Delta U + R\Delta T$

$\Rightarrow \left(\frac{\Delta H}{\Delta T}\right)_p = \left(\frac{\Delta U}{\Delta T}\right)_v + R$

$\Rightarrow C_p = C_v + R$

$\Rightarrow C_p - C_v = R$ for 1 mole

~~Monoatomic Gas~~

$C_p - C_v = R$

$\gamma = \frac{C_p}{C_v}$

Monoatomic Gas	$5/2R - \frac{3}{2}R = R$	$\star \frac{5}{3} = 1.67$
Diatomic Gas	$7/2R - 5/2R = R$	$\star \frac{7}{5} = 1.40$
Triatomic Gas	$4R - 3R = R$	$\star \frac{4}{3} = 1.33$

Good Write

DATE: __/__/____
PAGE: ____

HEAT OF REACTION / ENTHALPY OF Rx^n :- ($\Delta_r H$)

Amount of Heat Energy released or Absorbed in a given chemical rx^n is called: Heat of Rx^n

eg. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H_r = -92$ KJ/mole

$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$; $\Delta H_r = -46$ KJ/mole

@ standard cond^n : 25°C ; 1 bar

$$\Delta_r H^\circ = \sum \Delta_f H^\circ_{products} - \sum \Delta_f H^\circ_{reactants}$$

↳ enthalpy of formation

NOTE: standard enthalpy of formation for most stable thermodynamic form of an element is ZERO.

$$\Delta_r H^\circ = \sum \text{B.E. reactant} - \sum \text{B.E. Products}$$

↳ Bond energy

$$\Delta_r H^\circ = \sum \Delta_c H^\circ_{reactants} - \sum \Delta_c H^\circ_{products}$$

↳ enthalpy of combustion

* amount of Heat released in the complete combustion of 1 mole of a substance is its ENTHALPY OF COMBUSTION.

33, 40, 42, 49, 50, 57, 67 (PYQ)

Q. 33 pg 167

$\Delta_r H = \sum$ BE reactant $- \sum$ BE product

$4 \times C\text{-}H + 1 \times C{=}C + 1 \times H\text{-}H = 1 \times C\text{-}C + 6 \times CH$

$4 \times 410 + 1 \times 606.10 + 1 \times 431.37 - 1 \times 336.49 + 6 \times 410.5$

1642
606.10
431.37
2679.47

336.49
2463
2799.49

$1642 + 606.10 + 431.37$

$2679.47 - 2799.49$

$= -120.0$ KJ mol^{-1}

opt (2) Ans.

2799.49
2679.47
120.02

DATE: ___/___/____
PAGE: _____

Q.40 $\Delta H = \Delta U + \Delta n_g RT$ ($\Delta E \rightarrow \Delta U$)

Q.42 $C_6H_{10} + H_2 \longrightarrow C_6H_{12}$

$\Delta_c H = -3800$ $\quad \Delta_c H = -241$ $\quad \Delta_c H = -3920\ KJ$

$\Delta_r H = \sum \Delta_c H_{reactants} - \sum \Delta_c H_{product}$

$-4041 + 3920$

$-121\ KJ\ mol^{-1}$

Q.49: $x L : 2x L$ at 0°C, 1 Atm

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

$(5-x)L : 5(5-x)L$

$2x + 25 - 5x = 16L$

$3x = 9$

$x = 3L$

$\therefore CH_4 \longrightarrow x = 3L$.

$C_3H_8 \longrightarrow x = 2L$

Given: $\Delta H_{comb.}(CH_4) = 890\ KJ\ mol^{-1}$

for CH_4.

↓ i.e.

$1 mole = \Delta_c H = 890\ KJ$

$22.4L = 890\ KJ$

$3L = \left(\frac{890 \times 3}{22.4}\right) KJ = \Delta_c H_{CH_4}$

$\Delta_{comb.}(C_3H_8) = 2220\ KJ\ mol^{-1}$

↓ i.e.

$2L = \frac{2220}{22.4} \times 2 = \Delta_c H_{C_3H_8}$

$\frac{\Delta H}{R} = \Delta_c H_{reactants} = \frac{2670 + 4440}{22.4}$

$= \frac{71100}{224} \approx 317$ Ans.

Good Write

*Graphite → most stable 'C' thermodynamically

DATE: 17/12/22
PAGE:

L-3/23

Heat of formation

Enthalpy change when one mole of a substance is formed from its ~~consequent~~ constituent elements in most stable thermodynamic form is called:
Heat / enthalpy of formation of the substance.

(graphite)

* $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow 1C_2H_5OH$; $\Delta_r H = \Delta_f H_{Ethanol}$

* $Xe(g) + 3F_2(g) \longrightarrow XeF_6$; $\Delta_r H = \Delta_f H_{XeF_6}$

NOTE: "standard" enthalpy of formation for the most stable thermodynamic form of an element is taken as ZERO.

* $\Delta_f H^\circ_{graphite} = Zero$; $\Delta_f H^\circ_{diamond} = +ve$
  $\Delta_f H^\circ_{fullerene}$
* $\Delta_f H^\circ S_8$ (rhombic) = Zero
* $\Delta_f H^\circ Br$ (liquid) = Zero $\Delta_f H^\circ_{Br_2(gas)} = +ve$
* $\Delta_f H^\circ P_4$ (white) = Zero * EXCEPTION: $\Delta_f H$ P (Red, Black) = -ve

Enthalpy of Neutralization

1 g.eq. of an acid is Neutralised by 1 g eq. of a Base, is called: enthalpy of Neutralization.

$H^+ + OH^- \longrightarrow H_2O(l)$ * $\Delta_{neut.}H = -57.1$ KJ/g eq

when strong acid is neutralised by strong base
$\Delta_{neut.}H = -57.1$ KJ/g.eq

Ques^n: $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

$\Delta_r H^\circ = 2 \times (-57.1)$ KJ/mol

$\Delta_{neut} H^\circ = -57.1$ KJ/g eq

↳ fixed yes

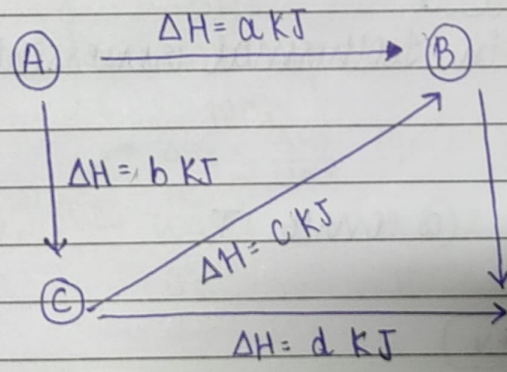
DATE : ___/___/_____
PAGE : _____

* If one of the Acid or Base is weak, energy released is less than -57.1 KJ/geq.

* When H-F (weak acid) is Neutralized by a strong base, energy released is more than 57.1 KJ/g.eq, Because High hydration energy of F^- due to its High charge Density.

HESS's LAW OF CONSTANT HEAT SUMMATION :-

enthalpy change for a chemical change remains constant whether it takes place in single-step or Multi-steps.



★ $a = b + c$

(Arrowdir^n Rev.)

★ $a = b + d - x$

ENTROPY :

↳ It is the Extent of randomness or disorderness of a system

Eg. $H_2O(s) \longrightarrow H_2O(l) \longrightarrow H_2O(g)$ (state)

entropy ↑ses

★ 1mole $H_2O(s)$ $-20°C$ $\longrightarrow$ 1mole $H_2O(s)$ $-10°C$ } $\Delta S = +ve$. (Temp.)

★ $H_2(g) \xrightarrow{2000K} 2H$ $\rightsquigarrow \Delta S = +ve$ (Amount ↑)

★ $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(l/s)$ $\rightsquigarrow \Delta S = -ve$. (state change)

Good Write

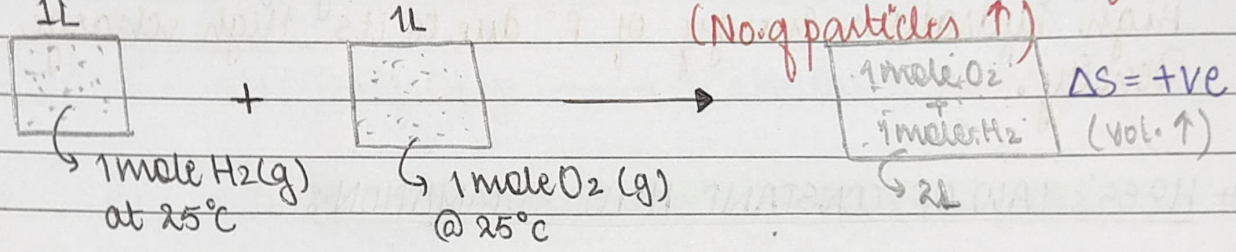
* $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ — No. of particles are equal on both sides → ΔS = zero

* Normal egg at 25°C ⟶ Boiled egg at 25°C. ΔS = +ve

↓

Due to denaturation of Proteins

(No. of particles ↑)

* 

NOTE: Entropy of mixing is always +ve

* $\Delta S = \frac{q_{rev}}{T}$ *

Unit: JK^{-1}

• q_{rev} ⟶ Heat involved in isothermal reversible process.

For An Ideal Gas,

$\Delta U = 0$ (@ const^{tt} T)

↓

$q_{rev} = -W_{rev}$

$$\Delta S = \frac{q_{rev}}{T} = -\frac{W_{rev}}{T} = \frac{-(-2.303\, nRT \log \frac{V_2}{V_1})}{T}$$

Use when there is change in 'P' (or V)

* $\Delta S = 2.303\, nR \log \frac{V_2}{V_1} = 2.303\, nR \log \frac{P_1}{P_2}$ for Ideal gas in Isothermal Process

L-4/24

$\because q = nC_p\Delta T$

For very small change in T,

$dq = nC_p dT$

Dividing by T

DATE: ___/___/____
PAGE: _____

$$\frac{dq}{T} = nC_p \frac{\Delta T}{T}$$

$$\Rightarrow dS = nC_p \frac{dT}{T}$$

Integrating b/w T_1 & T_2:

$$\int_1^2 dS = \int_1^2 nC_p \frac{dT}{T}$$

final ← 2, initial ← 1

$$\Rightarrow \Delta S = nC_p \ln \frac{T_2}{T_1}$$

$$\Rightarrow \Delta S = 2.303\, nC_p \log \frac{T_2}{T_1}$$

Ques^n: 18g Ice, $-20^\circ C$ → 18g water vapour, $120^\circ C$ — const^t 'p' — ★ Find ΔS.

Sol^n:

$$\underset{-20^\circ C}{\underset{H_2O(s)}{Ice}} \xrightarrow{\Delta S_I} \underset{0^\circ C}{Ice} \xrightarrow{\Delta S_{II}} \underset{0^\circ C}{water} \longrightarrow \underset{100^\circ C}{H_2O(l)} \longrightarrow \underset{100^\circ C}{H_2O(g)} \longrightarrow \underset{120^\circ C}{H_2O(g)}$$

$\Delta S_{II} = \frac{\Delta H_f}{273}$ ($q_p = \Delta H$) here f ⇒ fusion

$\Delta S = nC_p \ln \frac{T_2}{T_1}$ (when there is 'T' change) ; $\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$ (const^t 'p' const^T)

(when there is Phase change)

$$\Delta S_1 = 2.303\, nC_{p_{ice}} \log \frac{273}{253}$$

$$\Delta S_3 = 2.303\, nC_{p_{water}} \log \frac{373}{273}$$

$$\Delta S_4 = \frac{\Delta H_v}{373} \quad (v \rightarrow \text{vapourisation})$$

$$\Delta S_5 = 2.303\, nC_{p_{H_2O(g)}} \log \frac{393}{373}$$

★ $\Delta S_{tot^n} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$

Good Write

NOTE: entropy is a state function but its Absolute value can be determined.

DATE: ___/___/____
PAGE: _____

Q.44
pg 178

$$\Delta S_{vap} = \frac{\Delta H_v}{T}$$

$$150.6 = \frac{60.240 \times 10^3}{T}$$

$$T = \frac{60.24 \times 10^3}{150.6}$$

$$= \frac{6024 \times 10^3}{15060}$$

$$= \frac{6024 \times 10^2}{1506}$$

$$= 400\ K$$

Q.63
pg 169

$$\Delta S = \frac{q_{rev}}{T} = 2.303\, nR \log \frac{V_2}{V_1}$$

$$= 2.303 \times 2 \times 2 \log 10$$

$$= 9.212\ Cal\ K^{-1}$$

(G)

GIBBS FREE ENERGY →

H ⇝ ENGINE → TxS = lost energy

$$G = H - TS$$

↓

Max^m Amount of useful work-Done

@ const^t T

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

efficiency = $\eta = \frac{\Delta G}{\Delta H}$

Good Write

DATE : ___/___/_____
PAGE : _____

- ΔG = −ve ⇝ Process is said to be SPONTANEOUS
  i.e. $\Delta H < T\Delta S$ consider sign also

★ If ΔH = −ve & ΔS = +ve, then process must be SPONTANEOUS (T) ✓

- ΔG = +ve ⇝ Process is said to be Non-spontaneous,
  i.e. $\Delta H > T.\Delta S$

- $\Delta G = 0$ ⇝ Process is in eq^m
  i.e. $\Delta H = T\Delta S$ ⇒ $\boxed{\Delta S = \frac{\Delta H}{T}}$ Phase transition

$\Delta G = \Delta G^\circ + 2.303\,RT \log Q_c$

↓

At eq^m, $\Delta G = 0$; $Q_c = K_c$

$\Delta G^\circ = -2.303\,RT \log K_c$ also $\Delta G^\circ = -nF E^\circ_{cell}$

⇓

if $K_c = 1$; ΔG° = zero

SECOND LAW OF THERMODYNAMICS →

★ Entropy of universe is increasing.

$$\star\ \Delta S_{system} + \Delta S_{surrounding} = \Delta S_{universe} > 0$$

★ It is impossible to construct the engine with 100% efficiency. ($\Delta H \neq \Delta Q$)

★ Heat cannot flow from an object at lower Temp. to the object at Higher Temp. spontaneously.

DATE : ___/___/_____
PAGE : _____

THIRD LAW OF THERMODYNAMICS –

★ Absolute entropy of a perfectly crystalline substance @ Absolute zero temp is zero.

$S \neq 0$; @ $T = 0K$

CO	CO	CO	CO
OC	OC	CO	CO
OC	CO	OC	CO
CO	CO	CO	CO

$S = 0$; @ $T = 0K$

NO	NO	NO	NO
NO	NO	NO	NO
NO	NO	NO	NO
NO	NO	NO	NO

⇓

Perfectly crystalline

∴ @ 0K

$S = 0$