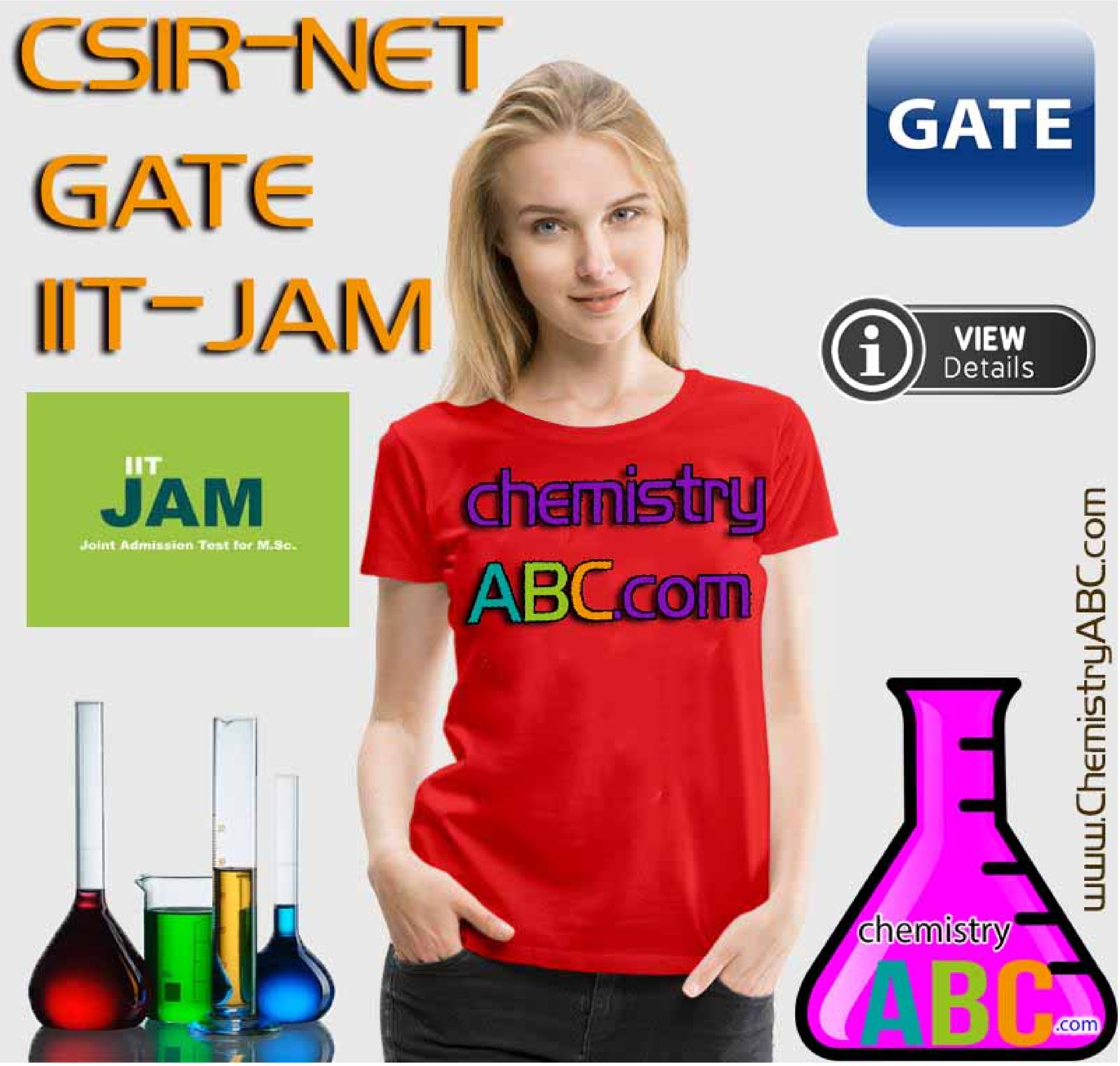
thermochemistry

Handwritten Notes with Assignment

Classnotes of Sahender Sir

Useful For CSIR NET & GATE



Thermodynamics

Quantum + Spectra = 5 units.
Thermodynamics = 2 units.
Kinetic & Surface Chemistry = 2 units
} most imp 85 marks

Remaining Chapters- Electrochemistry
Data Analysis
Group theory
Polymer
Surface Chemistry
Solid State.

Syllabus of thermodynamics:

(i) Unit conversion ~~of~~ In thermodynamics.

(ii) Maxwell thermodynamic Square.

(iii) Thermodynamic Coefficient & Elementary idea of Cyclic rule.

(iv) State function & path functions

↓

Euler's theorem and its Application.

(v) Sign convention in 1st law.

(vi) Heat capacity, Rel^n bet^n heat capacity (9 rel^n)

(vii) Rev. and Irreversible process for ideal and non-ideal gases.

(a) Isothermal (b) Adiabatic

Determination of w, z, ΔU, ΔH for above.

(viii) Thermodynamic eq^n of State (concept of internal pressure)

(ix) Joule thomson Coefficient.

X) Equipartion law of Entropy, Degree of freedom.

IInd Chapter:

XI) Carnot engine, Carnot refrigrator.

XII) Concept of Entropy.

Determination of entropy for rev & irrev. process.

- → Entropy of mixing
  - solid
  - liquid
  - gas
  - of ideal gas.
- → Third law of Entropy.

  Residual Entropy.

(Xiii) Maxwell thermodynamics potential

(xiv) Gibbs free Energy & Helmholtz eqn.

↓

Dependence of G on T & P.

(xv) Cleausius claperon eqn.

(xvi) Criteria of spontanity.

IIIrd chapter:

(xvii) Thermodynamics of Open System
- → partial molar Quantities
- → Chemical potential
- → Dep of chemical potential on T & P.
- → Gibbs Duhem eqn.
- → Concept of fugacity & Activity.

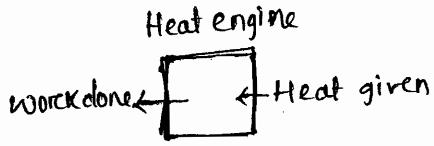
(xviii) Thermochemistry → Adiabatic flame temp

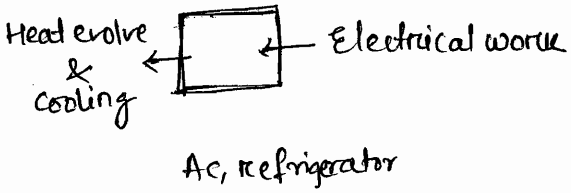
Kirchoff's eqn.

Unit Conversion:

→ Amount of material

→ Heat & work





Heat = ~~pdv~~ $dq = Tds$

work = ~~dr~~ $W = -pdv$.

Thermodynamic variables/parameters,

$\boxed{T, S, P, V}$, n (amount)

↓

Corresponding thermodynamics potentials/Energy.

$\boxed{\begin{matrix} U \\ H \\ A \\ G \end{matrix}}$

μ.

System → Under Observation

Surrounding → remaining part of Universe.

Closed System – Trasfer of heat & work

$P, V, S, T \longrightarrow G, H, A, U$ (correct potential)

Open System - Transfer of Amount Heat, work

↓

$n, P, V, S, T \longrightarrow \mu, G, H, A, U$ (correct potential)

↓

Chemical potential

we have to study with convenstion,

P = pressure

V = volume

S = Entropy $ds = \frac{dq}{T} = \frac{\text{Energy}}{T}$

T = Temp

{ G = Gibbs free energy

Energy form {

H = Enthalpy

A = Helmholtz func^n

U = Internal energy

W = work

q = Energy in form of heat / vice-versa.

∴, P, V, Energy] unit conversion Overall.

Volume Conversion :

$*\ 1m \times 1m \times 1m = 1000\,L$

$1m = 10\,dm$

$*\ 10dm \times 10dm \times 10dm = 1000\,L$

$$\therefore \boxed{1\,dm^3 = 1L} \text{ ——— } (1)$$

i.e., $10^3 dm^3 = 10^3 L$

$*\ 100\,cm \times 100\,cm \times 100\,cm = 1000\,L$

$$\boxed{10^3 cm^3 = 1\,L} \text{ ——— } (2)$$

$1L = 1000\,ml$

$= 10^3\,ml.$

$10^3 cm^3 = 10^3\,ml$

$$\boxed{1\,cm^3 = 1\,ml} \text{ ——— } (3)$$

Pressure Conversion :

$P = F/A = \frac{Newton}{m^2} = N/m^2$

$1\,atm = 101325\,N/m^2$

$= 101325\,Pa$

$= 101.325 \times 10^3\,Pa = 101.325\,KPa.$

$= 1.01325 \times 10^5\,Pa = 1.01325\,Bar$

$\therefore 10^5\,Pa = 1\,Bar = 10^5\,N/m^2$

So, $\boxed{1\,atm = 1.01325\,bar}$

$\therefore p = hdg$

$1\,atm = 76\,cm \times 13.6\,g \times cm^3 \times 980\,cm/s^2$

By converting it into mks unit,

$1\,atm = 760\,Cm\,Hg$

$= 760\,mmHg.$

$= 760\,Torr.$

1L bar $= 10^2$ Joule.

we know,

$1 m^3 = 1000 L$

$1 L = 10^{-3} m^3$

$1 \text{ Bar} = 10^5 \text{ Pa} = 10^5 N/m^2$.

∴, $10^{-3} m^3 \times 10^5 \text{ Pa}$.

$= 10^{-3} m^3 \times 10^5 N/m^2$

$= 10^2 Nm = 10^2$ Joule.

So, $\boxed{1 L \text{ bar} = 10^2 \text{ Joule.}}$

1 KPa L ⟶ Joule.

$1 KPa - 10^3 Pa$ $\quad 1L = 10^{-3} m^3$.

$10^3 N/m^2 \times 10^{-3} m^3$

$= 1 Nm = 1$ Joule.

$\boxed{1 KPa L = 1 J}$

$\boxed{1 MPa L = 1 kJ}$

Energy conversion :

Ex: 200 L-atm = ___ Joule.

Depends upon R.

$R = 8.314 J/K \text{ mole} = 2 \text{ cal}/K \text{ mole} = 0.821 L \text{ atm}/K \text{ mole}$.

$= 0.08314 L \text{ bar}/K \text{ mole}$.

$= 8.314 KPa \cdot L/K \text{ mole}$.

$\boxed{8.314\ J = 2\ cal = 0.0821\ L\,atm = 0.08314\ L\,bar = 8.314\ kPa\text{-}L}$

$0.0821\ L\text{-}atm = 8.314\ J.$

$\therefore, Q = 200\ L\,atm \Rightarrow$ ____ Joule.

$$200\ L\,atm = \frac{8.314 \times 200}{0.0821}\ J$$

$$= 200\ L\,atm \times \frac{R\ (Joule)}{R\ (L\ atm)}$$ → To unit change multiply.

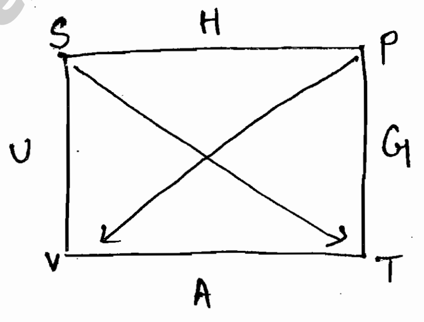
$$200\ \cancel{L}\,atm \times \frac{8.314\ J}{0.0821\ \cancel{L}\,atm}$$

$$= 20253.3\ Joule.$$

Maxwell – Thermodynamics Squares:

Given by Max. Born,

Study Close System
↓
Transfer
W　　　q
↓　　　↓
−pdv　　Tds



Or, some Hard Problem Go Throw A

$\therefore$, P, V, S, T (for variables. Very Easy Solution.

G H A U → for potential.

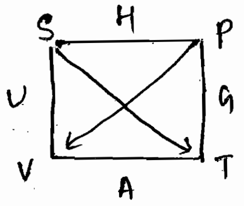
Maxwell Relation –

Relate the change in thermodynamic potential with variable.

Variables
Free Variables　　Bounded variables.

Free Variable	Bounded variable	
$S \longrightarrow$	dH	Change in variable.
$T \longrightarrow$	dG	
$P \longrightarrow$	dA	
$V \longrightarrow$	dU	

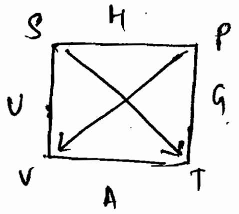
① $dH = Tds + Vdp$



→ Since H in betn S and P so, change in ds and dp.

→ Arrow away from S and P. so both +ve.

② $dG = Vdp - SdT$



→ In T the arrow is in near and in P the arrow is far away (+ve)

③ $dA = -Pdv - SdT$

④ $dU = Tds - Pdv$

$\therefore$,

$$\boxed{\begin{array}{l} dp \text{ के साथ } +V \\ ds = +T \\ dT = -S \\ dv = -P \end{array}}$$

Maxwell thermodynamic Relations:

The Relationship b/w Partial derivative of thermodynamic variables

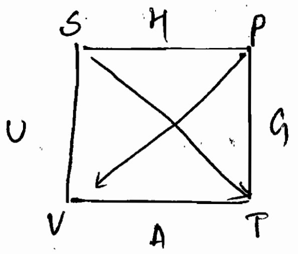
$\downarrow$ δ = ~~cons~~ it is attached with a const.

$\downarrow$ P, V, S, T.

d = complete

δ = Partial.

(i) Rel^n between S and p



$$\boxed{+\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial p}{\partial T}\right)_V}$$

or,

$$\left(\frac{\delta V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial p}\right)_V$$ (reverse is also same)

(ii) $$\boxed{\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p}$$

or, $$\left(\frac{\partial p}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_p$$

(iii) $$\frac{V}{S} = \frac{T}{p}$$

$$\boxed{-\left(\frac{\partial V}{\partial S}\right)_p = -\left(\frac{\partial T}{\partial p}\right)_S}$$

or $$\left(\frac{\partial S}{\partial V}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_S.$$

$$\boxed{PV = ST}$$
↓
In every rel^n.

(iv) $$\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$$

or, $$\boxed{\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_S}$$

∴, 4 eq^n and 4 thermodynamic rel^n.

Criteria of Spontanity Chem:

Spontanity increases → Stability increases → Energy decreases.

So, $\Delta E = -ve$

$$\boxed{\Delta E < 0}$$

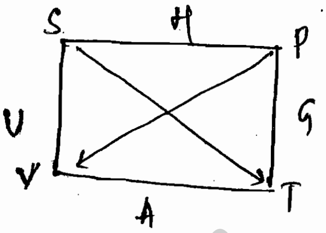
we have Energy term,

i.e., $\Delta G < 0$

$\Delta H < 0$

$\Delta A < 0$

$\Delta U < 0$



Imp

* G is in b/w P & T, so, put their constants,

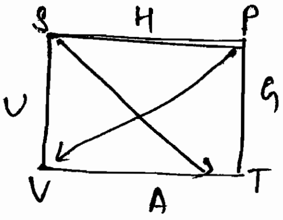
$$\therefore,\ \left.\begin{aligned}(\Delta G)_{P,T} &\leq 0\\ (\Delta H)_{S,P} &\leq 0\\ (\Delta A)_{V,T} &\leq 0\\ (\Delta U)_{S,V} &\leq 0\end{aligned}\right\}$$

'=' sign for reversible

'<' sign for Irreversible.

These are the spontanities in terms of potentials and energies.

Spontanity in terms of Variables: (S, P, V, T)



$$(dT) \begin{cases} (dT)_{P,G} < 0 \\ (dT)_{V,A} < 0 \end{cases}$$

$$dS \begin{cases} (dS)_{H,P} > 0 \\ (dS)_{U,V} > 0 \end{cases}$$

$$(dV) \begin{cases} (dV)_{S,U} < 0 \\ (dV)_{T,A} < 0. \end{cases}$$

$$dp \begin{cases} (dp)_{H,S} > 0 \\ (dp)_{G,T} > 0 \end{cases}$$

Dpp-1

① 20 L-bar — KJoule

1 L bar = 100 Joule

∴, 20 Lbar = 20×100

= 2 KJ

② 100 J — 1 L-atm

8.314 J = 0.0821 L-atm

$$1\,J = \frac{0.0821}{8.314}\ L\text{-atm}.$$

$$100\,J = \frac{0.0821}{8.314} \times 100\ L\text{-atm}.$$

$$= < 1$$

⑥ $(\Delta G)_{T,P} < 0$ ✓ (const right symbol wrong)

$(\Delta U)_{S,V} > 0$

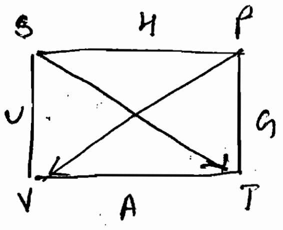
$(\Delta S)_{U,V} > 0$

⑩ a) wrong

b) correct

c) correct

d) wrong

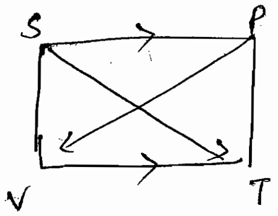


⑳ $(\ )_{V,S} \longrightarrow \therefore (U)_{V,S}.$ ✓ $(dS)_{S,U} \geq 0$

(29) $(dU)_{S,V} \geq 0$ check const and symbol $(dG)_{T,V} \leq 0.$

$(dA)_{T,V} \geq 0$

④



$$\left[-\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V\right]$$

$$\therefore \left(-\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$$

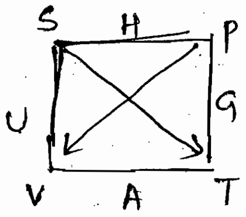
Its reverse will be,

$$-\left(\frac{\partial T}{\partial V}\right)_P = \left(\frac{\partial P}{\partial S}\right)_T$$

⑤ $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$.

⑨ After Cyclic rule,

i) $\left(\frac{\partial U}{\partial S}\right)_V = ?$ ii) $\left(\frac{\partial U}{\partial V}\right)_S = ?$



$dU = TdS - PdV$

$\left(\frac{\partial U}{\partial S}\right) = T$

(iv) $\left(\frac{\partial G}{\partial T}\right)_P = ?$

2) $\left(\frac{\partial U}{\partial V}\right)_S = -P$

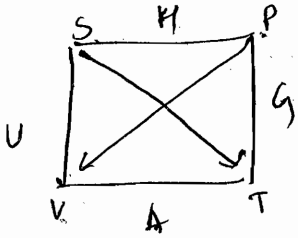
$\left(\frac{\partial G}{\partial T}\right) = -S$.

3) $\left(\frac{\partial G}{\partial P}\right)_T =$

$dG = -SdT + VdP$

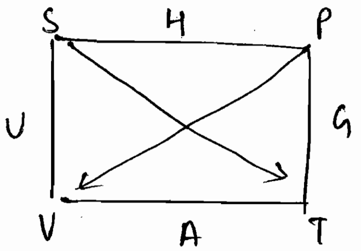
$\left(\frac{\partial G}{\partial P}\right) = V$

⑫



$T = \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial U}{\partial S}\right)_V$.

⑬



$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

⑭ P is expressed in terms of A & U.

⑮ $\left(\frac{\partial G}{\partial T}\right)_p$ $dG = Vdp - SdT$

$$\left(\frac{\partial G}{\partial T}\right) = -S$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -\left(\frac{\partial A}{\partial T}\right)_V$$

⑯ $\left(\frac{dH}{dP}\right)_S$ $dH = TdS + Vdp$

$$\left(\frac{dH}{dP}\right)_S = V$$

⑰ $$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

⑱ $$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

⑲ $\left(\frac{\partial U}{\partial S}\right)_V = T$ $dU = TdS - pdV.$

㉑ $$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left[\frac{\partial}{\partial p}\left(\frac{nRT}{P}\right)\right]_T$$

so not n/p

(22) $\left(\frac{\partial G}{\partial P}\right)_T = V$ Isothermal process graph b/w G & P at const T with

Slope $\left(\frac{\partial G}{\partial P}\right)_T$.

$dG = Vdp - SdT$.

Q. Show that

(1) $\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V$

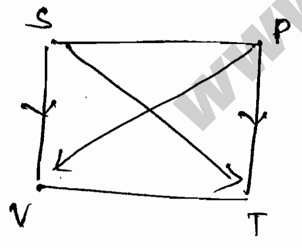
$$\alpha = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial V}\right)_T$$

Using Cyclic rule, $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$

$$\therefore, \alpha = -\left(-\frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}\right) = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\boxed{\alpha = \left(\frac{\partial P}{\partial T}\right)_V}$$

Now,



d → small change

∂ → " " at const

Δ → large change

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\therefore \alpha = \left(\frac{\partial S}{\partial V}\right)_T$$

(ii) $\alpha = \beta\gamma P$

T.P → $\frac{\alpha}{\beta} = \gamma P$

we know,

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$.

$\gamma = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$

$\left(\frac{\partial P}{\partial T}\right)_V = P\gamma$

$\therefore, \frac{\alpha}{\beta} = P\gamma$

$\alpha = \beta P\gamma$.

Mathematics involved in Thermodynamics

$z = z(x,y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

↓ complete differe^n of z.

complete diff. of x & dy.

↓ Partial diff. of z with respect to x at const. y.
or $\left(\frac{\text{change in } z}{\text{change in } x}\right)_y$.

Mathematics formulae used in thermodynamics:

① $\frac{d}{dx} x^n = n x^{n-1}$ ↳ new func^n

↳ func^n

$\frac{d}{dx}$ ↓ operator

② $\frac{d}{dx} c = 0$.

③ $\frac{d}{dx} c x^n = c \cdot n x^{n-1}$.

④ $\frac{d}{dx}(u_{(x)})V(x) = u\frac{dv}{dx} + v\frac{du}{dx}$.

⇒ $z = z(x,y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \xrightarrow[z = \text{const.}]{\text{If we introduce}} z \text{ constant } dz = 0.$$

$$\therefore, \; 0 = \left(\frac{\partial z}{\partial x}\right)_y (\partial x)_z + \left(\frac{\partial z}{\partial y}\right)_x (\partial y)_z$$

complete diff (d) change to partial diff (∂) & does not affect partial differe^n & independent identity.

$\therefore$, $\underbrace{dG = Vdp - SdT}_{P = \text{constant}}$

$\therefore dp = 0$.

$(\partial G)_p = V \times 0 - S(\partial T)_p$

$= -S(\partial T)_p$

$\therefore$, $S = -\left(\frac{\partial G}{\partial T}\right)_p$

dG (complete diff)

$\downarrow$

Changes to ∂G (partial diff.)

$\Rightarrow \Delta S = -\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$

$= -\left(\frac{\partial}{\partial T}(-nFE)\right)_P$

$$\boxed{\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P}$$

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

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

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

Gibbs Helmholtz eqⁿ.

$\Rightarrow$ 1 maxwell eqⁿ से 2 independent Variable nikalenge.

e.g., $dG = Vdp - SdT$.

① $\boxed{dG = Vdp - SdT}$

If we have to find S the $Vdp = 0$ $\swarrow$ $dp = 0$

If we have to find V $SdT = 0$. $\searrow$ $dT = 0$

$(\partial G)_P = -S(\partial T)_P$

$S = -\left(\frac{\partial G}{\partial T}\right)_P$

$(\partial G)_T = V(\partial P)_T - S \cdot 0$

$V = \left(\frac{\partial G}{\partial P}\right)_T$

∴, we can calculate 2 independent variable from energy eqⁿ

②
$$\begin{tikzcd}[column sep=small] & \underbrace{dU = TdS - PdV} \arrow[dl, "\substack{dS=0 \\ S\ \text{const}}"'] \arrow[dr, "\substack{dV=0 \\ V\ \text{const.}}"] & \\ \left(\frac{\partial U}{\partial V}\right)_S = -P & & \left(\frac{\partial U}{\partial S}\right)_V = T \end{tikzcd}$$

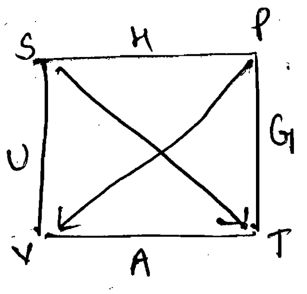
③
$$\begin{tikzcd}[column sep=small] & \underbrace{dA = -PdV - SdT} \arrow[dl, "\substack{dV=0 \\ V\ \text{const}}"'] \arrow[dr, "\substack{dT=0 \\ T=\text{const}}"] & \\ \left(\frac{\partial A}{\partial T}\right)_V = -S & & \left(\frac{\partial A}{\partial V}\right)_T = -P \end{tikzcd}$$

④
$$\begin{tikzcd}[column sep=small] & \underbrace{dH = TdS + VdP} \arrow[dl, "\substack{dS=0 \\ S\ \text{const}}"'] \arrow[dr, "\substack{dP=0 \\ P\ \text{const}}"] & \\ \left(\frac{\partial H}{\partial P}\right)_S = V & & \left(\frac{\partial H}{\partial S}\right)_P = T \end{tikzcd}$$

$$\left.\begin{aligned} \therefore,\ P &= -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial A}{\partial V}\right)_T \\ S &= -\left(\frac{\partial A}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P \\ V &= \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \\ T &= \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \end{aligned}\right]$$

So, Square diagram से variable Change की value भी calculate कर सकते हैं।

⇓



$$T = +\left(\frac{\partial H}{\partial S}\right)_P = +\left(\frac{\partial U}{\partial S}\right)_V$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

~~eq~~

$$V = +\left(\frac{\partial G}{\partial P}\right)_T = +\left(\frac{\partial H}{\partial P}\right)_S$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial A}{\partial T}\right)_V$$

Maxwell Squares gives →

1. Change in potential e.g. $ds = Vdp - SdT$.

2. Relation b/w partial derivatives of S, P, V, T $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

3. Criteria of Spontanity

4. To determine the value of variables in terms of Potential change of

$$S = \left(-\frac{\partial G}{\partial T}\right)_P$$

Q. for $z = x^2y^2$

Sol^n- Partial differ^n

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

① $\left(\frac{\partial z}{\partial x}\right)_y = \left[\frac{\partial}{\partial x} \cdot z\right]_y$

$$= \left[\frac{\partial}{\partial x} \cdot x^2y^2\right]_y = y^2\left[\frac{\partial}{\partial x^2}\, x^2\right] = y^2 \cdot 2x = y^2 2x,$$

Steps → ① Identity function & operator.

② put value of func^n in the form of operator.

③ Remove the Constants from operations.

④ Operate the operator.

② $\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}\cdot z\right)_x = \left[\frac{\partial}{\partial y}\left(x^2y^2\right)\right]_x = x^2\left[\frac{\partial}{\partial y}\left(y^2\right)\right]_x$

$= x^2\, 2y = 2x^2y$.

③ $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

$= 2xy^2dx + 2x^2y\, dy$.

④ $\frac{dz}{dx} = \frac{2xy^2dx}{dx} + \frac{2x^2y\, dy}{dx}$

$= 2xy^2 + 2x^2y\frac{dy}{dx}$

⑤ $\frac{dz}{dy} = \frac{2x^2y\, dx}{dy} + \frac{2x^2y\,\cancel{dy}}{\cancel{dy}}$

$= 2x^2y\frac{dx}{dy} + 2x^2y$.

Q. for $PV=RT$

Find $\left(\frac{\partial P}{\partial T}\right)_V, \left(\frac{\partial V}{\partial T}\right)_P, \left(\frac{\partial P}{\partial V}\right)_T, \left(\frac{\partial V}{\partial P}\right)_T$, dP, dV, $\frac{dP}{dT}$, $\frac{dV}{dT}$.

Q. for $PV = RT$

① $\left(\frac{\partial P}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right]_V = \frac{R}{V}\left[\frac{\partial}{\partial T}(T)\right]_V = \frac{R}{V}$

② $\left(\frac{\partial V}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{RT}{P}\right)\right]_P = R/P.$

③ $\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{RT}{V}\right)\right]_T = RT\left[\frac{\partial}{\partial V}\left(\frac{1}{V}\right)\right]_T = \frac{-RT}{V^2}$

④ $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$

⑤ $\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R}$ (opp of ①)

⑥ $\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R}$ (opp. of ②)

⑦ $dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right) dV$

$= \left[\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right]_V dT + \left[\frac{\partial}{\partial V}\left(\frac{RT}{V}\right)\right] dV = \frac{R}{V}.dT \quad \frac{RT}{V^2}.dV$

⑧ $dV = \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial P}\right) dP$ $\qquad V = \frac{RT}{P}.$

$= \frac{R}{P}\, dT. \frac{V^2}{RT}\, dP$

⑨

⑩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Thermodynamic coefficient & Cyclic Rule :

एक variable के change होने से दूसरे मे कितना Change hoga, at some const. variable

e.g., $\left(\frac{dv}{dT}\right)_P$

Now, Thermal expansivity

$\downarrow$ Temp

$\downarrow$ Relative vol. Change $\left(\frac{dv}{V}\right)$

$$\alpha = \left(\frac{\frac{dv}{V}}{dT}\right) \text{ at const } P.$$

Relative change in volume w.r.t change in ~~pressure~~ temp at const P.
If const is there then d changes to ∂.

$$\therefore \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Thermodynamic Coefficient :

Describes the effect of change in one variable on the change in other variable, keeping other variable const apart from those two variables.

(i) Thermal Expansivity : (Expansion)

Relative change in volume wrt to change in temp at const. p is known as thermal expansion or called Isobaric thermal exp. coefficient.

$$\alpha = \left(\frac{\frac{dV}{V}}{dT}\right)_P \quad \therefore \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$\alpha \rightarrow$ small in case of solid & liquid vol^m change less.

α is considerable in gases.

$$\boxed{dV = \alpha V dT}$$

α less but T change is less than v change so, dv increases.

② Compressibility factor:

Relative negative change in volume w.r.t change in pressure at const T is called thermal compressibility factor.

Isothermal compressibility factor

Pressure based

Negative Change in volume

$$\beta = \left(\frac{-\frac{dv}{V}}{dp} \right)_T$$

$$\boxed{\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

⇒ β is also small in case of solid & liquid.

At Critical pt. (above which no liquefication takes place) because,

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = 0 \qquad \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \infty.$$

③ Isochoric Temp based pressure change coefficient:

V = const.

$$\gamma = \left(\frac{\frac{dp}{P}}{dT} \right)_V = \frac{1}{P}\left(\frac{\partial p}{\partial T}\right)_V$$

Q. Find value of α and β for 1 mole of ideal gas.

we know, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$$\alpha_{ideal} = \frac{1}{V_{ideal}} \left(\frac{\partial V}{\partial T}\right)_{P_{ideal}} \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$= \frac{1}{V_{ideal}} \cdot \frac{R}{P_{ideal}}$$

$$= \frac{P}{PV} = \frac{R}{RT} = \frac{1}{T}$$

$$\boxed{\alpha_{ideal} = \frac{1}{T}}$$

Now, $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

For 1mole of ideal gas,

$\beta = -\frac{1}{V}\left(-\frac{RT}{P^2}\right)$ (as calculated earlier)

$$= \frac{\cancel{RT}}{P.\cancel{RT}} = \frac{1}{P}$$

$$\boxed{\beta_{ideal} = 1/P}$$

Similarly, $\gamma_{ideal} = 1/P$

So, In case of ideal gases

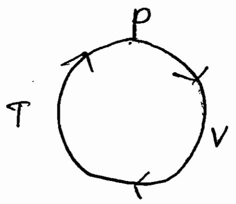
α = Temp based $= \frac{1}{T}$

β = pressure based $= 1/P$.

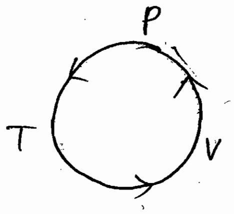
γ = Temp based $= \frac{1}{T}$

Cyclic Rule :

The solution between the partial derivative of these interdependent variables may be ~~separated~~ representation on a cycle as,



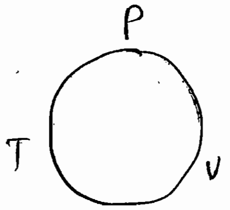
or



$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1.$$

Q. verify the Cyclic rule for 1mole of ideal gas $PV = RT$.

Soln.



$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \longrightarrow ①$$

L.H.S

$$\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{RT}{V}\right)\right]_T = RT\left[\frac{\partial}{\partial V}\left(\frac{1}{V}\right)\right]_T = \frac{-RT}{V^2}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\left(\frac{RT}{P}\right)\right)_P = \frac{R}{P}.$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \left[\frac{\partial}{\partial P}\left(\frac{PV}{R}\right)\right]_V = \frac{V}{R}$$

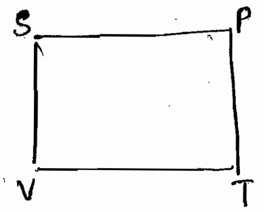
Put in ①,

$$-\frac{RT}{V^2} \times \frac{\cancel{R}}{P} \times \frac{V}{\cancel{R}} = \frac{-RT}{PV} = \frac{-RT}{RT} = -1.$$

$\underline{RHS}$

DPP-1

(Q23)



$$\frac{S}{P} = \frac{V}{T}$$

$$\frac{S}{V} = \frac{P}{T}$$

$$\Delta S = \Delta V \cdot \alpha/\beta \qquad \frac{\Delta S}{\Delta V} = \frac{\Delta P}{\Delta T}$$

$$\frac{\Delta S}{\Delta V} = \frac{\alpha}{\beta}.$$

(Q25) $\alpha = \beta\gamma P$

(24) $dG = Vdp - SdT$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

(21) $$\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\frac{nRT}{V-nb}\right] = \frac{nR}{V-nb}$$

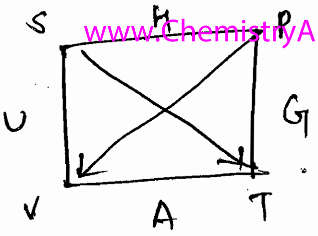
(27) $\beta = \infty$ at critical point.

$$\boxed{\alpha = \infty} \qquad \because \alpha = \beta P\gamma.$$

$$= \infty \times P \times \gamma$$

$$\therefore \alpha = \beta$$

(28)



$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

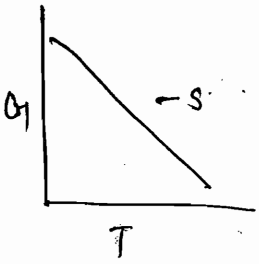
$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial A}{\partial T}\right)_V$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial U}{\partial S}\right)_V$$

DPP-2

①



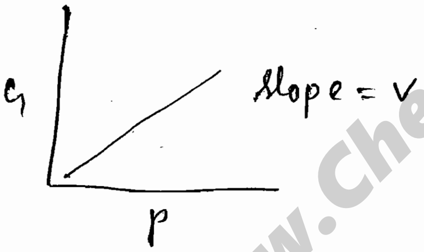
Slope = $\left(\frac{\partial G}{\partial T}\right)_P$

So, $dG = Vdp - SdT$

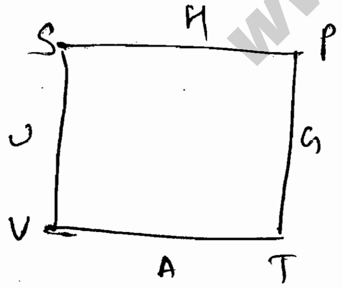
$\left(\frac{dG}{dT}\right)_P = -S$

∴ $-ve$ S (i.e., negative slope)

⑫ $\left(\frac{\partial G}{\partial p}\right)_T = V$ ($\because \Delta G = Vdp - SdT$)



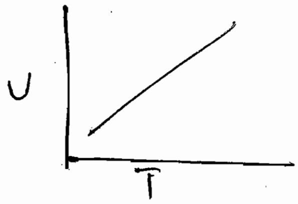
②



at const S, V

$dU < 0$ for spontaneous.

⑦ $\left(\frac{dU}{dT}\right)_V = C_V$



⑩ $\left(\frac{dH}{dT}\right)_P = C_p$

⑱ mass of water = 54 gms

$T_1 = 15°C$, $T_2 = 75°C$

$dT = 60°C$, $dH = ?$

$C_p = 75\ J/K\ mole.$

$C_p = \left(\frac{dH}{dT}\right)_P$

$dH = nC_p dT$

$60°C = 60\ K$

$= \left(\frac{54}{\cancel{18}_{3}}\right) \overset{15}{\cancel{75}} \times \overset{10}{\cancel{60}}$

$= 8100.$

= ___ kJ.

⑲ ΔH (energy supplied at const enthalpy) = 229 J

$dT = 2.55\ K$

$\Delta H = nC_p dT$

$229 = 3 \times C_p \times 2.55$

$C_p = \text{——}\ J/K\ mole$

$C_p - C_v = R$

$$\frac{229}{3 \times 2.55}\frac{J}{K\,mole} - C_v = 8.314\ J/K \cdot mole$$

↓

R value must taken in J/K mole.

$= C_v.$

<u>After ans Internal Pressure,</u>

⑤ $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$\left(\frac{\partial U}{\partial V}\right)_V = C_v,\ \left(\frac{\partial H}{\partial T}\right)_p = C_p\ \left(\frac{\partial G}{\partial T}\right)_p = -S.$$

⑥ $\left(\frac{\partial H}{\partial P}\right)_T =$

$$\frac{energy}{p} = \frac{work}{p} = \frac{PV}{P} = V$$

or $dH = Tds + vdp$

$$\frac{dH}{dp} = T\frac{ds}{dp} + V$$

⑪ Adiabatic free expansion

$dq = 0$ $\qquad$ $P_{ext} = 0.$

$w = -PdV$

$w = 0.$

$dq = dU - w$

$\therefore$, $\boxed{dU = 0}$

$\therefore$, U const.

(14) $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$ for V.well

$\therefore$, $\propto \frac{1}{V^2}$

(16) $\left(\frac{\partial U}{\partial V}\right)_T = 0$, $\left(\frac{\partial H}{\partial V}\right)_T = 0$

(24) $U = U(V,T)$

$\left(\frac{dU}{dT}\right)_p = ?$

$dU = \left(\frac{\partial U}{\partial T}\right)_V dp + \left(\frac{\partial U}{\partial V}\right)_T dV$

$dU = C_V\, dT + \pi_T\, dV$

Divide by dT,

$\left(\frac{\partial U}{\partial T}\right) = C_V + \pi_T \left(\frac{\partial V}{\partial T}\right)$

$$\left(\frac{\partial U}{\partial T}\right)_p = \overset{\text{const.}}{C_V} + \pi_T \left(\frac{\partial V}{\partial T}\right)_p$$

$\left(\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right)$

$\left(\frac{\partial U}{\partial T}\right)_V = C_V + \pi_T \cdot \alpha V$

Heat and Heat Capacity

Heat – It is not a energy but it is mode of transfer of energy. It is the entity which is transfere of energy by virtue of transfer.

Heat is a fluid or form of energy. It can't be decided yet. (Zemnansky Hitmann) so, it is considered mode of transfer of energy.

e.g., 25°c → 35°c pani करना तो Heat देना पडेगी।

from $T_1 \longrightarrow T_2$ is called heat Capacity.

$$C = \frac{dq}{T_2 - T_1} = \frac{dq}{dT}.$$

$$\boxed{dT = 1^\circ C = 1K}$$

$\because$, $T_1 = 100^\circ C$ $T_1 = 200 + 273K = 473K$

$T_2 = 300^\circ C$ $T_2 = 573K$

$dT = 100^\circ C$ $dT = 100K$

$C_p, C_v \rightarrow$ is the path func^n since heat Capacity is a path func^n.

It is defined as to raise the temp of substance from $T_1 — T_2$.

The ratio of heat required by system & temp is known as heat capacity.

or, $C = \frac{dq}{dT}$.

If $dT = 1^\circ C = 1K$

Then, $C = dq$

$\therefore$, Heat capacity may be defined as,

To raise the temp 1°c or 1K, heat required by the system is called Heat Capacity.

If The amount of substance is also taken into account then if amount = 1 mole then it is called molar heat capacity.

⇒ If amount = 1 gm then called Specific heat capacity.

Heat capacity may be defined as,

To raise the temp 1°C or 1K, heat required by the system is called heat capacity.

⇒ If Amount of substance is also taken into account then if amount = 1 mole then it is called molar heat capacity.

⇒ If amount = 1 gm then called Specific heat Capacity.

⇒ Heat Capacity is a path func^n so before study heat capacity we have to specify the path.

∴, Heat Capacity is studied via two paths —

1. Const. pressure path ⟶ at const P ⟶ C_p

2. const volume path ⟶ at const V ⟶ C_v

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

$$C_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{T\,ds}{dT}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p = \frac{\partial q_p}{\partial T}.$$

$$\therefore,\ C_v = \left(\frac{dq}{dT}\right)_v = \left(\frac{T\,ds}{dT}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial q_v}{\partial T}\right)$$

$\therefore$ If $dT = 1°C$ or $1K$

$$\boxed{C_p = dq_{V_p}}$$

To raise the temp 1°C of substance the heat required by the system at const P is called C_p.

Similary at const V.

$$\boxed{C_p = dq_{V_p}}$$

Sign Convention in first law of Thermodynamics & work done

IUPAC $w = -P_{ext}\, dV$

$= -P_{against}\, dV$

Expansion - volume increases.

$$V_2 > V_1$$

$$dv = V_2 - V_1 = +ve.$$

$$w = -P(+dV)$$

$$= -pdv$$

$$\therefore \boxed{W = -ve}$$

$\therefore$ work done by the system (expansion) $= -ve$.

Heat given by the system (expansion) $= -ve$

compression - Volume decrease

$$V_1 > V_2$$

$$dV = V_2 - V_1 = -ve$$

$$w = +ve$$

work done on the system = +ve.

Heat given on the system = +ve.

work done will never by +ve.

But $w = -ve$ (expansion) when work is done by the system.
$w = +ve$ (compression) when work is done on the system.

So, $dq = dU - w$

$dq = dU + w$

$q = 40J$, work done by the system $= 20J$.

$dU = q - w$

$dU = 40 - 20 = 20\ J$.

$\therefore$, $\boxed{dq = dU - w}$ is correct for 1st law of thermodynamics.

Prove,

$dq = dU - w$

$dq + U_1 = U_2 - w$

$dq = U_2 - U_1 - w$

$\boxed{dq = dU - w}$

Basic features of heat and heat Capacity:

① Heat is either internal energy or enthalpy in transit depending upon experimental condition.

At const V, $dq_v = dU$

At const P, $dq_p = dH$

To Prove, $dq_v = dU$

first Law, $dq = dU - w$

$= dU - (-pdV)$

$= dU + pdV$

at constant V

$\boxed{dq_v = dU}$ Heat taken by the System at const V is equal to Change in internal energy

$$C_v = \frac{dq_v}{dT}$$

$\therefore dq_v = C_v dT$

$dU = C_v dT$ for 1 mole

$\boxed{dU = nC_v dT}$

U is the function of T.

$\because$ V is const all the heat is converted to internal energy.

2. $dq_p = dH$

Heat taken by the System at const pressure is equal to Change In enthalpy.

Mathematic defination of enthalpy,

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

From 1st Law,

$dq = dU + PdV \quad (w = -PdV)$

$\therefore \boxed{dU = dq + VdP}$

at const P $= dH = dq_p$.

$$C_p = \frac{dq_p}{dT}$$

$dq_p = C_p dT$.

$\therefore dq_p = dH$

$\therefore C_p = \frac{dH}{dT}$.

$\boxed{dH = C_p dT}$ for 1 mole

$\boxed{dH = n C_p dT}$ for n mole

$\therefore$ H is function of T.

Problems:

$W = -PdV$ always in dU, dH [why].

* When heat is absorbed by the System the temp may or may not change depending upon

ex→ A material on melting ~~point~~ temp does not expense. Any change in temp.

Ice water

$$s \longrightarrow l$$

$$0^\circ c \longrightarrow 0^\circ c$$

→ Heat Capacity is extensive property

→ Specific heat Capacity is intensity property.

→ Heat Cap. may be +ve, 0, ∞ depending upon the process, system undergoes during the heat transfer.

→ Heat capacity has definite value at def. process

$$\underset{0^\circ c}{S} \xrightarrow{\downarrow dq \text{ (latent heat)}} \underset{0^\circ c}{l}$$

$$C = \frac{dq}{dT} = \frac{dq}{0} = \infty$$

∴ Heat capacity is infinite.

→ In rev. phase transfer process, Heat Capacity infinite.

$$C = \frac{dq}{dT} \quad \left(\text{with un heat temp increase}\right)$$

∴ c decreases.

* C_p is always greater than C_v because heat supplied at const p, the gas expands & work against the pressure. So heat is required to raise the temp as well as to do some work.

But if heat is supplied at const V, no work is done so heat is required only to raise the temp. means less heat is required to raise the temp means less heat is required at const volume then the heat required at const pressure to make the change of same amount of heat.

$$C_p = \frac{dq_p}{dT} = dU - w$$
$$= dU + pdV$$

C_p in Temp.

* In case of Ideal gas,

① C_v is function of T only.

C_p is function of T & $\boxed{C_p > C_v}$

② ∴, $C_p - C_v$ is not a func^n^ of T.

③ $\frac{C_p}{C_v} = \gamma$ is a func^n^ of T.

* Generally heat capacity of liquid is higher than heat Cap. of solid because liquid can absorb more heat (∵ translated + Vib motion) than solid (vib. motion) with in same temp range.

In solid the vib. motion is in the form of "phonons".

Relations between C_p & C_v :

1. $C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

2. $C_p - C_v = -T\left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial V}{\partial P}\right)_T$

3. $C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$

4. $C_p - C_v = \frac{\alpha^2 T V}{\beta}$

5. $C_p - C_v = T E \alpha^2 V$

6. $C_p - C_v = R$ (for ideal)

7. $C_p - C_v = R\left(1 + \frac{2a}{RTV}\right)$ for vanderwall.

8. $C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left[\left(\frac{\partial V}{\partial T}\right)_P\right]$

9. $C_p - C_v = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$.

E = Elasicity

Stress ∝ strain

Stress = E. Strain

$$E = \frac{\text{stress}}{\text{strain}} = \frac{dP}{\frac{dV}{V}}$$

Stress = F/A (change in pressure)

P = F/A

Strain = Relative change in volm

If, P increases, V decreases, T const.

$$\Rightarrow \left(\frac{dP}{-\frac{dV}{V}}\right)_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\beta}$$

$$\boxed{E = \frac{1}{\beta}}$$

$\therefore$, $C_p - C_v = \frac{\alpha^2 TV}{\beta}$ & $C_p - C_v = E\alpha^2 TV$.

Thermodynamic Equation of states:

① 1st thermodynamic eqⁿ of state – "Concept of internal pressure".

Change in internal energy w.r.t change in volume at const T is generally known as 1st thermodynamic eqⁿ of state.

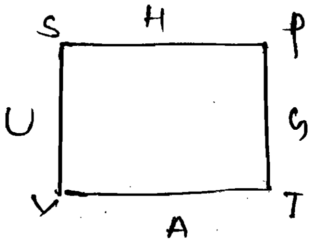
→ The study of variation of internal energy with volume, OR to check that internal energy is a function or not

$\left(\frac{dU}{dV}\right)_T = ?$ Have to calculate

If $\left(\frac{dU}{dV}\right)_T = 0$, then it is not a function of V.

To find, $\left(\frac{dU}{dV}\right)_T$

We take the value of dU from the eq.



$dU = TdS - PdV$

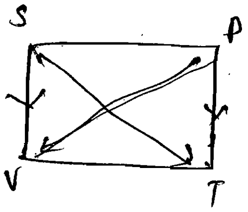
Divide by dV.

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{TdS}{dV} - \frac{PdV}{dV}$$

$$= T\frac{dS}{dV} - P$$

At const T, $\left(\frac{\partial U}{\partial V}\right)_T = T\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\text{eq}^n \text{ of state must be in } P, V, T.} - P$

so change it



$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

∴, $\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_T - P}$ so, unit of all are same. i.e of pressure

For ideal gas = $\left(\frac{\partial U}{\partial V}\right)_T = T\left[\frac{\partial}{\partial}\left(\frac{RT}{V}\right)\right] - P = T\cdot\frac{R}{V} - P$

$= P - P = 0$.

∴, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ Also, $\left(\frac{\partial U}{\partial P}\right) = 0$

∴, U is not a function of V in case of ideal gas.

$$\boxed{\left(\frac{\partial H}{\partial V}\right)_T = 0 \; , \left(\frac{\partial H}{\partial P}\right) = 0}$$

For vanderwaal eqn:

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$= T\left[\frac{\partial}{\partial T}\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)\right] - P$$

$$= T\left[\frac{R}{V-b} - 0\right] - P$$

$= \cancel{p} + \frac{a}{V^2} - \cancel{p}$

$= \frac{a}{V^2}$.

$\therefore \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}}$. U is function of V in case of vandewall also of T.

Conclusion-

For ideal gas → $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ $\left(\frac{\partial H}{\partial T}\right)_V = C_p$

$\left(\frac{\partial U}{\partial V}\right)_T = 0$ $\left(\frac{\partial H}{\partial V}\right)_T = 0$

$\left(\frac{\partial U}{\partial P}\right)_T = 0$ $\left(\frac{\partial H}{\partial P}\right)_T = 0$.

$\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gas

$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$ → for vanderwaal eqn

Gaseous state :

Ideal gas → $PV = RT$

Vander wall eqn;

$\left(P + \underbrace{\frac{a}{V^2}}_{\text{vanderwall}}\right)(V-b) = RT$

$(P+P_i)(V-V_i) = PT$

↓
ideal

$(P+0)(V-0) = RT$

Second thermodynamics equation of state :

variation of enthalpy with pressure at const temperature. Mathematically,

$$\left(\frac{dH}{dP}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T$$

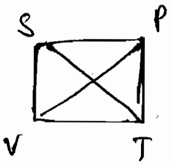
$dH = nC_p dT.$

From M.T.s,

$$dH = Tds + vdp$$

dividing by dp at const T,

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T + v \quad \text{at const } T.$$



$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

Q.12 (DPP-3)

for $P(v-b) = RT$

$$\left(\frac{\partial H}{\partial P}\right)_T = ?$$

soln: $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$

$P(v-b) = RT$ (for this we bring $\left(\frac{\partial V}{\partial T}\right)_P$

$$P(v-b) = RT$$

$$v-b = \frac{RT}{P}$$

$$V = \frac{RT}{P} + b.$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\cdot V\right]_P = \left[\frac{\partial}{\partial T}\left(\frac{RT}{P}+b\right)\right]_P$$

$$\underset{\substack{\downarrow \\ \frac{R}{P}\frac{\partial}{\partial T}T}}{\left[\frac{\partial}{\partial T}\cdot\frac{RT}{P}\right]} + \underset{\substack{\downarrow \\ 0}}{\left[\frac{\partial}{\partial T}b\right]_P} = \frac{R}{P}.$$

Ideal gas $= \left(\frac{\partial V}{\partial T}\right)_P = R/P.$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\cdot\frac{R}{P} + V = -\frac{RT}{P} + V = -V + V = 0.$$

Ideal $(PV = RT)$	vander wall $\left(P + \frac{a}{V^2}\right)(V - b) = RT$
(i) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ 0	a/V^2 for 1 mole
(ii) $-T\left(\frac{\partial V}{\partial T}\right)_P + V = \left(\frac{\partial H}{\partial P}\right)_T$ 0	$\frac{n^2 a}{V^2}$ for n mole $b - \frac{2a}{RT}$ $n\left(b - \frac{2a}{RT}\right)$

$\left(P + \frac{a}{V^2}\right)(v - b) = RT$ $\left(\frac{\partial H}{\partial P}\right)_T = b - \frac{2a}{RT}$ (vanderwall)

$P(v - b) = RT$ $\left(\frac{\partial H}{\partial P}\right)_T = b$ (Reduced vanderwall)

For $P(v-b) = RT$ (Reduced vanderwall)

$$\frac{\partial P}{\partial T} = \frac{R}{v-b}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = R/P$$

For PV=RT (Ideal)

a) $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$ $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$

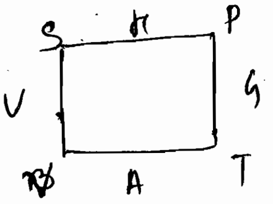
b) $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V}$ $\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{V^2}$

For $\left(P+\frac{a}{V^2}\right)(V-b) = RT$ (vanderwall Eq^n)

a) $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$

b) $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left(P+\frac{a}{V^2}\right) - \frac{2a(V-b)}{V^3}}$

Q.4. $Z = \frac{PV}{RT}$ $P = \frac{ZRT}{V}$



$\left(\frac{\partial U}{\partial V}\right)_T = ?$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\cdot P\right) = \left[\frac{\partial}{\partial T}\cdot\frac{ZRT}{V}\right]_V = \frac{R}{V}\left[\frac{\partial}{\partial T}\overset{1st}{Z}\overset{2nd}{T}\right]_V$$

$$= \frac{R}{V}\left[Z\cdot\frac{\partial}{\partial T}T + T\frac{\partial}{\partial T}Z\right]_V = \frac{R}{V}\left[Z + T\frac{\partial Z}{\partial T}\right]_V$$

$$= \frac{RZ}{V} + \frac{RT}{V}\left(\frac{\partial Z}{\partial T}\right)_V$$

$$= \frac{RT^2}{V}\left\{\frac{\delta Z}{\delta T}\right)_V .$$

Q.7. $\left(\frac{\delta p}{\delta T}\right)_v \quad \left(\frac{\delta v}{\delta T}\right)_p \quad \left(\frac{\delta v}{\delta p}\right)_T$

$\frac{R}{V} \quad \frac{R}{P} \quad \frac{-RT}{p^2}$

$= \frac{R^2}{pV} \times \frac{-RT}{p^2}$, $PV = RT$

$= \frac{R^2}{\cancel{RT}} \times \frac{-\cancel{RT}}{p^2}$

$= -\frac{R^2}{p^2}$

Q.11 $nC_p dT = \frac{200}{18} \times c \times (T_2 - T_1)$

$= \frac{200}{18} \times c \times (80 - 40)$

b) $\frac{200}{18} \times c \times (80 - 20)$

✓ c) $\frac{150}{18} \times c \times (80 - 50)$ least.

d) $\frac{300}{18} \times c \, (80 - 30)$ least.

State function & path function :

State function are those which values are depend on initial and final state not on the path that is taken to acheive the state.

Essential Criteria of being a state function.

(i) depends upon initial & final state.

(ii) Cyclic Integral of this function = 0.

If z is state function

$\oint dz = 0$.

dz is exact function.

(iii) These function follow Eular's theorem

(iv) Almost all thermodynamic entities are state function except w, q, heat capacity.

S G

P H Mi

V A

T . U state.

$\oint dw = 0$ ×

$\oint dq = 0$ ×

not a state funcⁿ.

Eular's theorem :

Let us consider a equation, $dz = M\,dx + N\,dy$.

$z = z(x,y)$ when $= \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

z is a state funcⁿ.

when the variable of z; (x & y)

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$

Q. Ideal gas eqⁿ P stable funcⁿ

$P = \frac{RT}{V}$ $P = P(T,V)$

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right]_V$$

$$\frac{\partial}{\partial V}\cdot\frac{R}{V} \qquad\qquad \frac{\partial}{\partial T}\cdot\frac{-RT}{V^2}$$

$$= -\frac{R}{V^2} \qquad\qquad = \frac{-R}{V^2}\cdot 1.$$

So, P is a state funcⁿ.

Q. Show that V is state funcⁿ for 1mole of Ideal gas.

$$PV = RT$$

$$V = \frac{RT}{P}.$$

$$V = V(T, P)$$

$$dV = \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{M} dT + \underbrace{\left(\frac{\partial V}{\partial P}\right)_T}_{N} dP$$

$$dV = M\,dT + N\,dP$$

$$M = \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\frac{RT}{P}\right)_P = \frac{R}{P}. = -RP^{-2}$$

$$N = \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\frac{RT}{P}\right)_T =$$

$$= RT\left(\frac{\partial}{\partial P}\frac{1}{P}\right)$$

$$= -\frac{RT}{P^2}$$

$$\left(\frac{\partial M}{\partial P}\right)_T$$

$$= \left(\frac{\partial}{\partial P}\cdot M\right)_T$$

$$\downarrow$$

$$= \left(\frac{\partial}{\partial P}\cdot\frac{R}{P}\right)_T$$

$$= R\left(\frac{\partial}{\partial P}\cdot\frac{1}{P}\right) = R\frac{\partial}{\partial P}P^{-1} = R(-1)P^{-1-1}$$

$$\left(\frac{\partial N}{\partial T}\right)_P$$

$$= \left(\frac{\partial}{\partial T}\cdot N\right)_P$$

$$= \frac{\partial}{\partial T}\left[\frac{-RT}{P^2}\right]_P$$

$$= \frac{-R}{P^2}\frac{\partial}{\partial T}T = -RP^{-2}.$$

Q. Show that w is a path Function..

$$dw = -pdv$$
$$dw = -RdT + vdp$$

$$PV = RT$$
$$d(PV) = d(RT)$$
$$= pdv + vdp = RTd + T\cancel{dR}^{0}.$$
$$= pdv = RTd - vdp.$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y.$$

$$= \left(\frac{\partial R}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P.$$

$$0 \neq R/P.$$

∴ w is a path func^n

As our func^n G, H, A, U are state func^n. So, they would follow eulan theorem.

When we apply eulan theorem on Maxwell rel^n as.

(i) $dG = vdp - sdT.$

As G is state func^n follows Euler's theorm.

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}$$

(ii) $dU = Tds - pdv$

Apply euler

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

(iii) $dA = -pdv - sdT$

$$\boxed{-\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T}$$

(iv) $dH = Tds + vdp$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$dz = M\,dx + N\,dy$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y .$$

Q. The rel^n $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

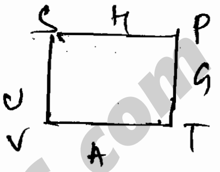
a) = $dG = Vdp - SdT$

b) $du = Tds - pdv.$

✓ c) $dA = -pdv - sdT.$

d) $dH = Tds + vdp.$

Q. $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$ comes from which rel^n.



$U = Tds - \cancel{vdp}\, pdv.$

⑤ $x\,dy$

b) $dx - (x/y)\,dy$

c) $ydx - xdy$

d) $(1/y)\,dx - (x/y^2)\,dy.$

(b) $\left[\frac{\partial}{\partial y}\frac{1}{y}\right]_x \neq -\left[\frac{\partial}{\partial x}(x/y)\right]_y$

$\downarrow$

$0 \neq -\frac{1}{y}\left[\frac{\partial}{\partial x}x\right]$

$0 \neq -1/y$

(c) $\left(\frac{\partial y}{\partial y}\right) \neq -\left(\frac{\partial x}{\partial x}\right)$

$1 \neq -1.$

(d) $\cancel{\left(\frac{\partial y}{\partial y}\right)}\left(\frac{\partial}{\partial y}\frac{1}{y}\right) = \left[\frac{\partial}{\partial x}\left(-\frac{x}{y^2}\right)\right]$

$= -\frac{1}{y^2} = -\frac{1}{y^2}\left(\frac{\partial x}{\partial x}\right).$

⑥ $C_p = 300\ JK^{-1}$

$C_p - C_v = nR$

$300\ J/K - C_v = 10\ mole \times 8.314\ J/K\ mole$

$= 300\ J/K - C_v = 83.14\ J/K$

$C_v = 300\ J/K - 8314.\ J/K$

$= 217\ J/K.$

Q.8 $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial v}{\partial T}\right)_p$

$P(V-nb) = nRT$

$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{V-b}$ (1 mole)

$\left(\frac{\partial v}{\partial T}\right)_p = R/P$ (1 mole)

[illegible] $P(V-nb) = nRT$ $\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$. (n-mole)

$\left(\frac{\partial v}{\partial T}\right)_p = \frac{nR}{p}$

$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial v}{\partial T}\right)_p$

$= T.\frac{R}{V-nb}.\frac{nR}{P}$

$= \frac{nRT \, . \, nR}{p(V-nb)}$

$= \frac{nRT \, . \, nR}{nRT}$

$= nR$.

⑮ $\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p + V$

$\alpha = \frac{1}{V}\left(\frac{\partial v}{\partial T}\right)_p$

$\left(\frac{\partial v}{\partial T}\right)_p = \alpha V$

⑲ $\Delta H - \Delta U$

$nC_p dT - nC_v dT$

$= n(C_p - C_v)dT$

$= nR\,dT$

$= 2\text{ mole} \times 8.314\ J/K\,mol \times (400-300)K$

㉑ $H = U + PV$

$\Delta H = \Delta U + P\Delta V + V\overset{0}{\Delta P}$.

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

$\Delta H = \Delta U + P(V_v - V_l)$ $(V_v > V_l)$

$\Delta H = \Delta U + PV_v$

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

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

$= 40.66 \times 10^3\ J/mol - 8.314\ J/K \times 373K$.

$\Delta H = 40.66\ kJ$

$\left(\frac{\partial H}{\partial p}\right)_T = -T\alpha V + V$

$= V(1 - \alpha T)$

㉓ $dH = nC_p dT$

$=$ T = const (Isothermal)

$dT = 0$

$dH = 0$.

(24) $\left(P+\frac{a}{V^2}\right)(V-b) = RT$ $\qquad \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

$= \quad a = 0 \qquad\qquad a = 0.$

$P(V-b) = RT \qquad\qquad \left(\frac{\partial U}{\partial V}\right)_T = 0.$

(25) $\frac{(C_p - C_v)_{Ideal}}{(C_p - C_v)_{vanderwall}} = \frac{R}{R\left(1+\frac{2a}{RTV}\right)} = \frac{1}{\left(1+\frac{2a}{RTV}\right)}$

$(1+x)^n = 1+nx$

If x value is small then power go inside

(26) $\left(\frac{\partial H}{\partial T}\right)_V \qquad = \left(1+\frac{2a}{RTV}\right)^{-1} = 1-\frac{2a}{RTV}.$

$\partial H = Tds + vdp.$

$\frac{\partial H}{\partial T} = \frac{T\,ds}{dT} + \frac{v\,dp}{dT}$

$C_v = \left(\frac{dq}{dT}\right)_V = \left(\frac{T\,ds}{dT}\right)_V = T\left(\frac{\partial s}{\partial T}\right)_V.$

at const V: $\left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V$

$\left(\frac{\partial P}{\partial T}\right)_V = \alpha/\beta.$

$= C_p + V\cdot\frac{\alpha}{\beta}.$

(27) $PV = RT \qquad dw = -pdv.$

$pdv + \underset{0}{vdp} = RdT$

$Pdv = R\,dT$

$dw = -RdT$

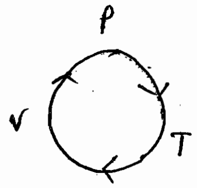
$= -R(2)$

$= -2R$

Relation betⁿ heat Capacity:

① $C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

If we put $\left(\frac{\partial P}{\partial T}\right)_V$ in Cyclic rule,



$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

$$C_p - C_v = -\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \; T$$

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T.$$

② $C_p - C_v = R$ (To Prove).

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

$$= -T\left(\frac{R}{P}\right)^2 \left(\frac{-RT}{V^2}\right)$$

$$= \frac{T^2 R^2 R}{P^2 V^2}$$

$$= \frac{(PV)^2 R}{P^2 V^2} = R.$$

$$C_p - C_v = \frac{\alpha^2 TV}{\beta}.$$

from fundamental $C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\beta V}$$

$$C_p - C_v = -T(\alpha V)^2 \left(-\frac{1}{\beta V}\right)$$

$$= \frac{\alpha^2 TV}{\beta};$$

③ $C_p - C_v = \frac{\alpha^2 TV}{\beta}$

$\alpha = \frac{1}{T}$

$\beta = \frac{1}{P}$

$$= \frac{\left(\frac{1}{T}\right)^2 TV}{\frac{1}{P}}$$

$$= \frac{PV}{T} = R$$

imp

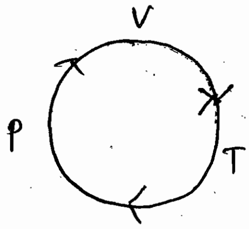
④ $C_p - C_v = \frac{\alpha^2 TV}{\beta}$

$$E = \frac{1}{\beta}$$

$$\boxed{C_p - C_v = TE\alpha^2 V.}$$

⑤ $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$

Put $\left(\frac{\partial V}{\partial T}\right)_p$ in Cyclic rule,



$$\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_T} = -\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T$$

Putting in fundamental eqⁿ

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left[\left(-\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T\right]$$

So,

$$\boxed{C_p - C_v = -T\left(\frac{\partial p}{\partial T}\right)_V^2 \left(\frac{\partial V}{\partial p}\right)_T}$$

⑥ $T\left(\frac{\partial p}{\partial T}\right)_V = \left[\pi_T + p\right]$

$$\pi_T = \left(\frac{\partial U}{\partial V}\right) = T\left(\frac{\partial p}{\partial T}\right)_V - P$$

$$C_p - C_v = \left[\pi_T + P\right]\left\{\left(\frac{\partial V}{\partial T}\right)_p\right\}$$

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p.$$

⑦ $\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$

$$T\left(\frac{\partial V}{\partial T}\right)_p = V - \left(\frac{\partial H}{\partial p}\right)_T$$

⑧ $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}\left(\frac{\partial V}{\partial T}\right)_p$$

$$= \frac{R}{\left(P + \frac{a}{V^2}\right) - \frac{2a(V-b)}{V^3}}$$

$$= \boxed{C_p - C_v = R\left(1 + \frac{2a}{RTV}\right)}$$

In case of solid and liquid, $\boxed{C_p \approx C_v}$

But in case of ideal gas $C_p > C_v$.

Fundamental eqⁿ $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$ may be obtained by Tds eqⁿ in thermodynamics

Let us consider S is a function of T & v.

$$S = S(T, v)$$

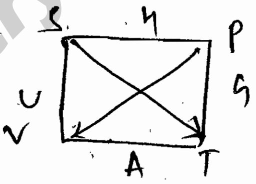
$$dS = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial v}\right)_T dv$$

multiply with T $= Tds = T\left(\frac{\partial S}{\partial T}\right)_v dT + T\left(\frac{\partial S}{\partial v}\right)_T dv$

$$= C_v\,dT + T\left(\frac{\partial S}{\partial v}\right)_T dv$$

$$\boxed{Tds = C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv}$$

$$\boxed{ds = C_v \frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)_v dv}$$



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

$C_v = \left(\frac{dq}{dT}\right)_v$

$= \left(\frac{Tds}{dT}\right)_v = T\left(\frac{\partial S}{\partial T}\right)_v$.

$C_p = \left(\frac{dq}{dT}\right)_p$

$= \left(\frac{Tds}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$

imp

we can find out Entropy change in term of T & V of any gaseous state from the above eqⁿ

Now,

$$Tds = C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv.$$

divide by dT.

$$= \frac{Tds}{dT} = \frac{C_v\,dt}{dT} + T\left(\frac{\partial p}{\partial T}\right)_v \frac{dv}{dT}$$

$$= C_p = C_v + T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$$

$$= \boxed{C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_v}$$

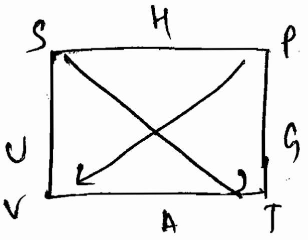
Let us consider $S = S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \cdot$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= C_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= C_P dT + T\left\{\left(-\frac{\partial V}{\partial T}\right)_P\right\} dP$$



$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

we can find out entropy in terms of P and T.

for making it ~~in de~~ C_V, divide dT.

$$\frac{TdS}{dT} = \frac{C_P dT}{dT} - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{dP}{\partial T}\right)_V$$

$$C_V = C_P - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{dP}{\partial T}\right)_V$$

$$= \boxed{C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

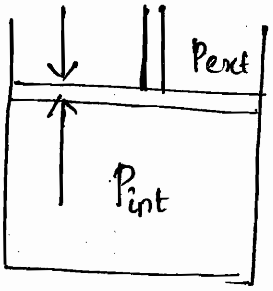
Concept of work and value of work, q, ΔV, ΔH for various Type of process:

P, V, W occurs when the volume V of the Sys. Charge. pdv work = area under the process curve plotted on the P V diagram (indicator diagram). work in thermodynamic is define as any quantity of energy that flows across the boundary b/w the System and surround that can used to change the height of mass in the surrounding.

In thermo, we generally consider mechanical work.

Features:

(1) work generally occour on the boundary work. But it is called Boundarywork



$P_{int} > P_{ext}$ (gas expands or expansion)

System work on the ~~System~~ surrounding.

$P_{ext} > P_{int}$ (gas compress or compression)

~~System~~ Surrounding work on the System.

② work is a path func^n so before study the work we have to specify the path (generally process).

③ P-V work is almost negligible in case of liquid & solid.

④ when pressure is applied on the System apart from mechanical work. There ~~are~~ exist several type of non-mechanical work.

Non-Mechanical work

i) Surface work = $\gamma\, dA$ γ = Surface Tension dA = Area.

ii) Electrical work = $V\, dq$ V = potential dq = Charge.

iii) Elongation work = $F\, dl$ F = force dl = length.

$$dq = dU - W_T$$
$$= dU - (W_{mech} + W_{non})$$

Later on we prove that at const T & p gibbs free energy is equal to non-mech. work. That is source of Introduction of 'G' in number of branch in physical chemistry.

⑤ work involved in a chemical rea^n generally depend on no. of mole of gas that is evolved in the rea^n.

Ex: work involved in the eletrolysis of water at a perticuler temp 27° at 1 atm may be obtain as,

$$H_2O_{(l)} \longrightarrow \underset{(g)}{H_2} + \underset{(g)}{\tfrac{1}{2}O_2}.$$

$$w = -pdv$$

$$= -dn_g RT \qquad n_g(\overset{(g)}{1}+\overset{(g)}{\tfrac{1}{2}}-\overset{(l)}{0})$$

$$= -\frac{3}{2}RT \qquad = \left(\frac{3}{2}-0\right) = \frac{3}{2}.$$

$$PV = nRT$$

$$Pdv + \underset{0}{Vdp} = Rn\underset{0}{dT} + TRdn.$$

$$PdV = TRdn.$$

DPP-4

④ $W = W_{A\to C} + W_{C\to B}$

$= 0 + 9 - pdV$

$= -1(5-1) = -4$ L atm.

⑧ vol^m of solid > liq in case of water. Density ice is > water.

$$\begin{array}{ccc} \text{Ice} & \longrightarrow & \text{water} \\ 0^\circ C & & 0^\circ C \\ 1\,atm & & 1\,atm. \end{array}$$

$$w = -pdv$$

$$= -p(V_{water} - V_{ice})$$

$$= -p\left(\frac{M}{d_{water}} - \frac{M}{d_{ice}}\right)$$

$$= -1\,atm\left(\frac{18\ gm/mole}{1\times10^{3}\ gm/L} - \frac{18\ gm/mole}{0.9\times10^{3}\ gm/L}\right)$$

$$= -1\left[18 - \frac{18}{0.9}\right]\times10^{-3} = -1\left[18-20\right]\times10^{-3}$$

$$= 2\times10^{-3}.$$

Reversible & Irreversible :

*(6) In case of free expⁿ $P_{ext} = 0$, $w = 0$. (In Vacuum)

Reversible	Irreversible
① The difference b/w driving force and opposing force is very small. $P_{int} \approx P_{ext}$.	① The difference between P_{int} & P_{ext} is considerable.
② The process may be reversed back at any stage of transfⁿ by making a minute change in the surrounding.	② The process can not be reversed easily.
③ process takes infinite step in complition.	③ process takes finite steps in complition
④ Ideal process. ↓	④ Natural process. ↓
⑤ Integration possible ↓ pressure does not play dominant role.	not possible intgrⁿ. ↓ Pressure play dominant role.

Ideal Isothermal reversible :

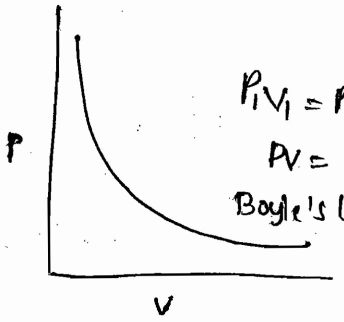
q, w, ΔV & ΔH for Rev isothermal Tranfⁿ of an ideal gas

Let us consider n mole of ideal gas is transformed

A to B

(P_1, V_1, T_1) (P_2, V_2, T_2)

$P_1V_1 = nRT$ $P_2V_2 = nRT$.



$P_1V_1 = P_2V_2$

$PV = $ Const.

Boyle's law.

$W = P_{ext}\, dv$

$= -P_{int}\, dv$

$= -P_{ideal} dV$

$w = \frac{-nRT}{V} dv.$

$w = -nRT \int_{V_1}^{V_2} \frac{dv}{V} = -nRT \ln \frac{V_2}{V_1}$

$\boxed{w = -2.303\, nRT \log ~~\log~~ \frac{V_2}{V_1}}$ work done in Isothermal process.

$\int_{x_1}^{x_2} \frac{dx}{x} = \ln \frac{x_2}{x_1}$

$\ln x = 2.303 \log x.$

* Change in Internal energy for Ideal gas

$dU = n\, C_v\, dT$

Since Isothermal $T = const$, $T = 0$.

Ideal Isothermal $\Delta U = 0$ $\because$ $\pi_T = 0$

But

vanderwall Isthermal $\Delta U \neq 0$ $\because$ $\pi_T = \frac{a}{V^2}$

$U = U(T,V)$

$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \partial V$

$dU = C_v dT + \pi_T dv.$

① Ideal $\pi_T = 0$

$dU = C_v dT$

② vandwall $\pi_T = \frac{a}{V^2}$

$dU = C_v dT + \frac{a}{V^2} dv$

* Change in Enthalpy for ideal gas.

$\because$ Isothermal $T = const$ $\Delta T = 0.$

$\Delta H = n\, C_p\, dT$

$\boxed{\Delta H = 0}$

work done

$W = -nRT \ln \frac{V_2}{V_1}$

$= -2.303\, nRT \log \frac{V_2}{V_1}$

$= -2.303\, nRT \log P_1/P_2$

$= -2.303\, P_1V_1 \log P_1/P_2$

$= -2.303\, P_2V_2 \log P_1/P_2$

$= -2.303\, P_1V_1 \log V_2/V_1$

$= -2.303\, P_2V_2 \log V_2/V_1$

$P_1V_1 = P_2V_2$

$P_1V_1 = nRT$

$P_2V_2 = nRT$

Irreversible Isothermal Ideal

Ⓐ ⟶ Ⓑ

$P_1 V_1 T$ $\qquad$ $P_2 V_2 T$

$w = -P_{ext}\,dV = -P_{ext}(V_2 - V_1)$

$= -P_2\,dV$ (If P_2 is written, then it is P_{ext}) (If 2 is given P_{final} is P_{ext})

$= -P_2(V_2 - V_1)$

$= -P_2\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$

$= -nRT\left(\frac{P_2}{P_2} - \frac{P_2}{P_1}\right)$

$= -nRT\left(1 - \frac{P_2}{P_1}\right)$

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

$= -nRT\left(\frac{P_{ext}}{P_2} - \frac{P_{ext}}{P_1}\right)$ If 3 pressure is given. (5 atm to 3 atm change against a const ext. pressure 1 atm).

Internal energy change for ~~[illegible]~~ Irreversible Ideal Isothermal:

$dU = nC_v\,dT$

Ideal

T = const $dT = 0$. $\boxed{dU = 0}$

Enthalpy Change for Irrever. Ideal Isothermal:

$\partial H = nC_p\,dT$.

Ideal

T = const $dT = 0$.

$\boxed{\boxed{dH = 0}\ \boxed{\partial H = 0}}$

work done

$$W = -P_{ext}\, dv$$

$$= -P_2 (V_2 - V_1)$$

$$= -P_2 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$= -nRT \left(1 - \frac{P_2}{P_1}\right)$$

$$= -nRT \left(1 - \frac{V_1}{V_2}\right)$$

$$= -P_1 V_1 \left(1 - \frac{V_1}{V_2}\right)$$

$$= -P_2 V_2 \left(1 - \frac{V_1}{V_2}\right)$$

$$\boxed{P_1 V_1 = P_2 V_2. \quad \frac{P_2}{P_1} = \frac{V_1}{V_2}}$$

Heat

$$\begin{tikzcd} dq = \Delta U - w \arrow[d, "\text{Ideal, Isothermal}"] \\ \boxed{dq = -w} \end{tikzcd}$$

Q. Show that work involved in Rev isothermal exp^n of an ideal gas is greater than work involved in Irr. Isothermal exp^n of an ideal gas.

Ans.

Adiabatic Transformation of Ideal gas :

$\Delta q = 0$. $\quad \underset{P_1 V_1 T_1}{\textcircled{A}} \longrightarrow \underset{P_2 V_2 T_2}{\textcircled{B}}$

wheather exp^n or Compr^n press charges and Temp change.

→ In adiabtic exp^n temp decreases.

→ In adiabatic Compr^n temp increases.

→ In Adiabatic Transform^n (exp^n or compresn^n) not only P & V but also temp changes as → $P_1 V_1 T_1 \longrightarrow P_2 V_2 T_2$.

→ In case of adiabatic exp^n of ideal gas

$$dq = 0.$$

$$dq = du - w$$

$$\downarrow$$

$$0 = du - w$$

$$\downarrow$$

$$du = w \quad (exp = -ve)$$

$$\boxed{du = -ve}$$

$$du = C_v dT = C_v (T_f - T_i) = -ve$$

$$T_f - T_i = -ve$$

$$T_f - T_i < 0$$

$$\boxed{T_f < T_i}$$

q, w, ΔU & ΔH in Rev. Adiabatic transf^n of an ideal gas:

Let us consider 1 mole of an Ideal gas is transformed from a state A to State B. Rel^n b/w Initial & final variable is generally governed by Poisson eq^n:

$$\text{(A)} \longrightarrow \text{(B)}$$
$$P_1 V_1 T_1 \qquad P_2 V_2 T_2$$

In isothermal (Ideal) in generally governed by Boyle's law, Rel^n b/w initial & final is governed by Boyle law.

$$P_1 V_1 T \longrightarrow P_2 V_2 T.$$

$$P_1 V_1 = RT \qquad P_2 V_2 = RT$$

$$P_1 V_1 = P_2 V_2 \qquad PV = \text{const}$$

(i) $\boxed{P_1 V_1^{\gamma} = P_2 V_2^{\gamma}}$ ✓

$$\Rightarrow PV^{\gamma} = \text{const}$$

$\gamma = C_p/C_v$ (atomicity of the gas).

$$\boxed{C_p > C_v}$$

Rev. Adi (Ideal) = $PV^{\gamma} = \text{Const} \Rightarrow P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

Imp

Poission eq^n in terms of T & V

$$PV^{\gamma} = \text{const}$$

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

$$\frac{RT}{V} \cdot V^{\gamma} = \text{const}$$

$$\Rightarrow T V^{\gamma-1} = \frac{\text{const}}{R} = \text{const}$$

$$TV^{\gamma-1} = \text{const}.$$

$\boxed{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}}$ ✓

Poission eqⁿ in terms as T & P :

$PV^{\gamma} = \text{const}$

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

$P\left(\frac{RT}{P}\right)^{\gamma} = \text{const}$

$\Rightarrow P \cdot \frac{R^{\gamma}T^{\gamma}}{P^{\gamma}} = \text{const}$

$= P^{1}P^{-\gamma}T^{\gamma} = \frac{\text{const}}{R} = \text{const}.$

$P^{1-\gamma}T^{\gamma} = \text{const}$

$$\boxed{P_1^{1-\gamma}T_1^{\gamma} = P_2^{1-\gamma}T_2^{\gamma}}$$

Rev. Iso Ideal

$Ⓐ \longrightarrow Ⓑ$

$P_1V_1T \longrightarrow P_2V_2T$

$PV = \text{const}$

$P = \frac{\text{const}}{V^{1}}$

Rev Adiabatic Ideal

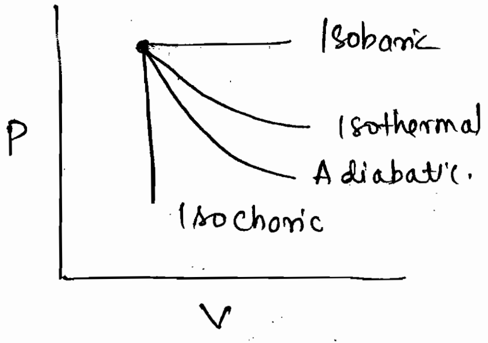
$Ⓐ \longrightarrow Ⓑ$

$P_1V_1T_1 \longrightarrow P_2V_2T_2$

$PV^{\gamma} = \text{const}$

$\gamma > 1.$

$P = \frac{\text{const}}{V^{\gamma}}$



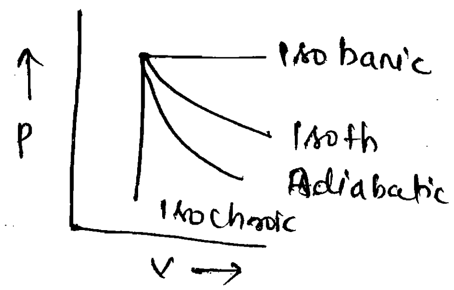
Ad ka PV ka slope Isothermal ke PV slope se stip hota hai.

- Slope of P-V diagram for Adiabatic process is higher then isothermal process.
- Adiabatic P-V Curve is steeper than Iso P-v curve.

Q.1 Show that $\left(\frac{\partial P}{\partial V}\right)_{adi} > \left(\frac{\partial P}{\partial V}\right)_{Iso}$.

slope of P-V curve in adiabatic process is greater than slope of p-V curve in Isothermal

Order of work done P-V curve:



(-w) Isobaric > (-w) Iso > (-w) Adia > (-w) Isochoric

ans-1

Isothermal Ideal

$PV = const$

$d(PV) = d(const)$

$pdv + vdp = 0$

$pdv = -vdp$

$\left(\frac{dP}{dV}\right)_{Iso} = -P/V$

Adiabatic Ideal

$PV^\gamma = const$

$d(PV)^\gamma = d(const)$

$pdv^\gamma + v^\gamma dp = 0$.

Dividing & multiplying dv.

$p\frac{dv^\gamma}{dv}dv + v^\gamma dp = 0$. (diff of v^γ)

$p\gamma v^{\gamma-1}dv + v^\gamma dp = 0$.

$-p\gamma v^{\gamma-1}dv = v^\gamma dp$

$\frac{-\gamma p v^{\gamma-1}}{v^\gamma} = \frac{dp}{dv}$

$= -\gamma\frac{P}{V} = \left(\frac{dp}{dv}\right)_{adiabatic}$

$$\left(\frac{dp}{dv}\right)_{adia} = -\gamma \frac{P}{V}$$

$$\left(\frac{dp}{dv}\right)_{iso} = -\frac{P}{V} .$$

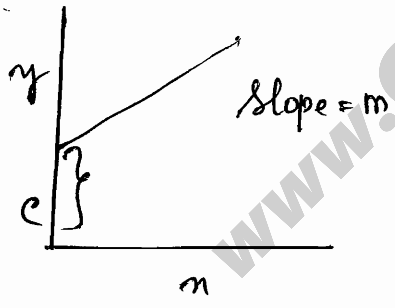
$$\boxed{\frac{\left(\frac{dp}{dv}\right)_{adia}}{\left(\frac{dp}{dv}\right)_{iso}} = \gamma}$$

so, $\boxed{\left(\frac{dp}{dv}\right)_{adia} = \gamma \left(\frac{dp}{dv}\right)_{iso}}$

Gate

Q If we plot of graph b/w ln P vs ln V for Rev. Adiabatic exp^n of an Ideal gas.

Sol^n: $PV^{\gamma} = K$



$m = \frac{dy}{dx}.$

$C_p - C_v = R$

$\frac{C_p}{C_v} - \frac{C_v}{C_v} = \frac{R}{C_v}$

$\gamma - 1 = R/C_v$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$\boxed{T_1V_1^{R/C_v} = T_2V_2^{R/C_v}}$

$\ln(PV^{\gamma}) = \ln K$

$\ln P + \ln V^{\gamma} = \ln K$

$\ln P + \gamma \ln V = \ln K.$

$\boxed{\underbrace{\ln P}_{y} = \underbrace{\ln K}_{c} - \underbrace{\gamma \ln V}_{mx}}$

$\boxed{\text{Slope} -\text{ve} = -\gamma}$

$$\boxed{\gamma_{mono} > \gamma_{dia}}$$

$\gamma_m = 1.66$

$\gamma_D = 1.40$

DPP-4

Q112

$$\begin{tikzcd}
& T_i \arrow[dl, "M"'] \arrow[dr, "D"] & \\
T_m & & T_D
\end{tikzcd}$$

In Adi expⁿ T decreases, So Ti is more.

γ of mono > γ of di

$T_1V_1^{\gamma-1} = \text{const}$

$T_D \propto \frac{1}{V_D^{\gamma-1}}$ $\quad T \propto \frac{1}{V^{1.4-1}}$

$$\boxed{T \propto \frac{1}{V^{.4}}}$$

$$\boxed{T_i > T_D > T_m}$$

$T_M \propto \frac{1}{V^{\gamma_m-1}}$

$\propto \frac{1}{V^{1.66-1}}$

$$\boxed{T_m \propto \frac{1}{V^{0.66}}}$$

Q.12 $\quad C_p = 29.234\ J/K.mole$

Rev Adiabatic

$A \rightarrow B$

$V_1 = 1\,dm^3 \quad V_2 = 10\,dm^3 \qquad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$T_1 = 750K \quad T_2 = ?$

$C_p = 29.234$ J/K mole.

Ideal, $C_p - C_v = R$

$C_v = C_p - R.$

$C_v = 29.234 - 8.314$ J/K mole.

$= 20.9.$

$$\gamma = \frac{C_p}{C_v} = \frac{29.234}{20.9} = 1.4$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$= 750 \times \left(\frac{1}{10}\right)^{1.4-1}$$

$$= 750 \times \left(\frac{1}{10}\right)^{1.4-1} = \underline{\underline{750 \times (0.1)^{0.4}}}$$

ⓐ 1000 ✗

ⓑ 750 ✗

ⓒ 300 ✓

ⓓ 100

<u>**Q.13**</u> $PV^a = \text{const}$ (expⁿ) (Ideal)

In Cooling Temp decrease

$\boxed{\gamma > 1}$

But in heating $\boxed{\gamma < 1}$ or $\boxed{a < 1}$.

<u>another method</u> $T_2 > T_1$

$V_2 > V_1$

$PV^a = \text{const}$

$\frac{RT}{V} V^a = \text{const}$

$T V^{a-1} = \text{const}$

$T_1 V_1^{a-1} = T_2 V_2^{a-1}$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{a-1}$$

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

$$= a-1 \ln\left(\frac{V_2}{V_1}\right).$$

$-ve = (a-1)(+ve)$

$a-1 = -ve \Rightarrow a-1 < 0,\ a < 1$

16

$U = 3.5\, PV + K$

$V_1 = 0.25\ dm^3 \quad V_2 = 0.86\ dm^3$

$1\ dm^3 = 10^{-3}\ m^3$

$P_1 = 5\ N/m^2$

$\Delta U = ?$

$PV^{1/3} = \text{const}$

$P_1 V_1^{1/3} = P_2 V_2^{1/3}$

$P_2 = \left(\frac{V_1}{V_2}\right)^{1/3} P_1$

$= 5 \times \left(\frac{0.25}{0.86}\right)^{0.33}.$

$U = 3.5\, PV + K.$

$U_1 = 3.5\, P_1 V_1 + K$

$U_2 = 3.5\, P_2 V_2 + K.$

$\Delta U = U_2 - U_1$

$= 3.5\, P_2 V_2 - 3.5\, P_1 V_2.$

(17) Poisson eqn

$P_1^{1-\gamma}\, T_1^{\gamma} = P_2^{1-\gamma}\, T_2^{\gamma}$

$\frac{P_1^{1-\gamma}}{P_2^{1-\gamma}} = \left(\frac{T_2}{T_1}\right)^{\gamma}$

$\left(\frac{P_1}{P_2}\right)^{1-\gamma} = \left(\frac{T_2}{T_1}\right)^{\gamma}$

$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$

$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$

$$\boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}}$$

⑮ $C_v = 1.5R$ $\quad C_p - C_v = R$ $\quad \gamma = \frac{C_p}{C_v} = \frac{2.5}{1.5} = 5/3 = 1.66.$

$T_1 = 500K$ $\quad C_p = R + C_v$

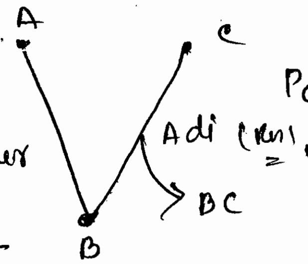
$P_1 = 1 atm$ $\quad C_p = 1 + 1.5 = 2.5R$

$P_2 = 2 atm.$

$P_A = 1 atm$

$T = 500K$

Rev. Isother



$P_c = 1.0 atm$

$V_c = ?$

$P_B V_B^{\gamma} = P_c V_c^{\gamma}$

$T_B = 500K$
(∵ Isothermal)

$P_B = 2 atm$

$V_B = \frac{RT_B}{P_B}$

$V_B = \frac{0.0821 L atm/K mol \times 500K}{2 atm}$

$= 20.5 L$

$P_B V_B^{\gamma} = P_c V_c^{\gamma}$

$2 (20.5)^{1.66} = 1 \times (V_c)^{1.66}.$

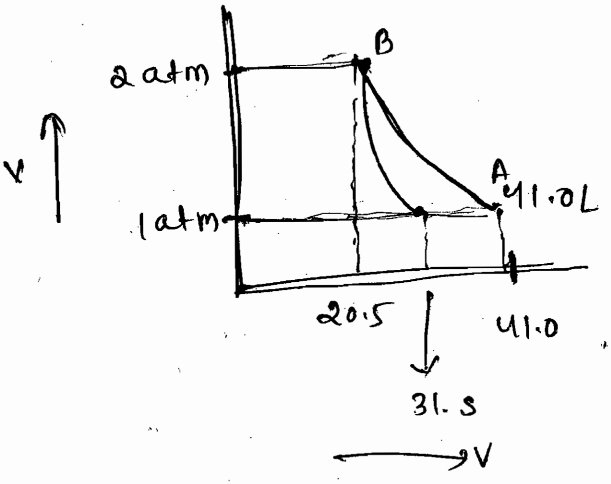
another

Ⓐ $P_a = 1 atm$

$T_A = 500K$

$V_A = \frac{RT_A}{P_A} = \frac{0.0821 \times 500}{1}$

$= 41.0L$



Ⓑ $P_B = 2 atm$

$T_B = 500K$

$V_B = \frac{RT_B}{V_B} = \frac{0.0821 \times 500}{2} = 20.5 L$

Proof of Poission Equation:

The rel^n b/w Initial & final variable for a Rev adiabatic exp^n of an ideal gas was proposed by poission.

Poission eq^n is the appl^n of 1st law of thermodynamic from 1st law of thermo.

From 1st law of thermodynamics:-

$$dq = du - w$$

Adiabatic

$$dq = 0.$$

$$0 = du - w$$

$$du = w$$

ideal ↓ ↘ Rev

$$w = -P_{ext}\, dv$$

$$= -P_{int}\, dv$$

$$= -P\, dv$$

$$C_v dT = -P dv$$

$$C_v dT = -\frac{RT}{V} dv$$

Eq^n $\int_{T_1}^{T_2} \frac{dT}{T} = -R/C_v \int_{V_1}^{V_2} \frac{dv}{V}$

$$\boxed{\ln \frac{T_2}{T_1} = -\frac{R}{C_v} \ln \frac{V_2}{V_1}}$$

we know = $\gamma - 1 = R/C_v$.

$$\boxed{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}}$$

$$\ln \frac{T_2}{T_1} = -(\gamma-1) \ln V_2/V_1$$

$$\ln \frac{T_2}{T_1} = (\gamma-1) \ln \frac{V_1}{V_2}$$

$$\ln T_2/T_1 = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Poission eq^n well not applicable in Irr. adiabic expa^n

w, q, ΔU & ΔH

From Ist law of thermo,

$$\Delta U = \Delta q - w$$

(adiabatic) $= dq = 0$

$$\Delta U = -w$$

$$dU = C_v dT = C_v(T_2 - T_1)$$

$$dU = \frac{R}{\gamma-1} d(T_2 - T_1)$$

$$= \frac{1}{\gamma-1}(RT_2 - RT_1)$$

$$\boxed{dU = \frac{1}{\gamma-1}(P_2V_2 - P_1V_1)}$$

we know, $C_p - C_v = R$

$$\frac{C_p}{C_v} - 1 = R/C_v$$

$$\gamma - 1 = R/C_v.$$

$$C_v = \frac{R}{\gamma-1}.$$

	Rev. Adiabatic	Irrev. Adiabatic
q	0	
w	$C_v(T_2 - T_1)$	$C_v(T_2 - T_1)$
	$\frac{R}{\gamma-1}(T_2 - T_1)$	$\frac{R}{\gamma-1}(T_2 - T_1)$
	$\frac{1}{\gamma-1}(P_2V_2 - P_1V_1)$	$\frac{1}{\gamma-1}(P_2V_2 - P_1V_1)$
ΔU	$C_v(T_2 - T_1)$	$C_v(T_2 - T_1)$
ΔH	$C_p(T_2 - T_1)$	$C_p(T_2 - T_1)$

cont ✓ In Adia Irreversible we find out from Ist law,

$$dq = dU - w$$

$$0 = dU - w$$

$$dU = w$$

$$\boxed{C_v(T_2 - T_1) = -P_2(V_2 - V_1)} = \boxed{C_v(T_2 - T_1) = -\frac{RT_2}{V_2}(V_2 - V_1)}$$

But in case of reversible Adiabatic, we apply poission eq^n

$$\rightarrow \boxed{P_1V_1^{\gamma} = P_2V_2^{\gamma}}$$

$$\boxed{T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}}$$

$$\boxed{P_1^{1-\gamma}T_1^{\gamma} = P_2^{1-\gamma}T_2^{\gamma}}$$

Q. Using transf^n Poission $PV^{\gamma} = \text{const}$. Show that work Involved in Rev. Adiabatic

$$w = \frac{1}{\gamma-1}\left[P_2V_2 - P_1V_1\right]$$

$$w = \frac{R}{\gamma-1}\left[T_2 - T_1\right]$$

$$= C_V\left(T_2 - T_1\right).$$

Mathematics

1) $\int x^n = \left[\frac{x^{n+1}}{n+1}\right]$

$\frac{d}{dx}x^n = nx^{n-1}.$

② $\frac{d}{dT}\cdot\frac{1}{T} = T^{-1}$

$= -1\,T^{-1-1}$

$= -1\,T^{\cancel{2}-2}$

$= \frac{-1\,T^{-2\cancel{+1}}}{-2\cancel{+1}} = \frac{-1\,T^{-1}}{\cancel{-1}}$

$= \left(-\frac{1}{T}\right)$

2) $\int \frac{1}{T}\,dT = \ln_e T = 2.303\log_{10}T$

$$\int_{T_1}^{T_2} T^2\,dT = \frac{T^3}{3}\,dT = \frac{1}{3}\,\cancel{d}\left[T^3\right]_{T_1}^{T_2}$$

$$= \frac{1}{3}\left[T_2^3 - T_1^3\right] =$$

③ $\int_{T_1}^{T_2}\frac{1}{T}\,dT = \int_{T_1}^{T_2}\ln_e T\,dT$

$= \ln T_2 - \ln T_1$

$= \ln\frac{T_2}{T_1}$

ln character

① $\ln_e x = 2.303\,\ln_{10}x$

② $\ln(mn) = \ln_e m + \ln_e n$

③ $\ln\frac{m}{n} = \ln_e m - \ln_e n$

④ $\ln m^n = n\ln m.$

⑤ $\ln\frac{m}{n} = -\ln\frac{n}{m}.$

Q. $PV^{\gamma} = K$ $\quad P = \frac{K}{V^{\gamma}} = KV^{-\gamma}$

So, $P_1V_1^{\gamma} = K$ $\quad P_1 = \frac{K}{V_1^{\gamma}} = KV_1^{-\gamma}$

$P_2V_2^{\gamma} = K$ $= P_2 = \frac{K}{V_2^{\gamma}} = KV_2^{-\gamma}$

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$W = -Pdv$

$= -Kv^{-\gamma}dv$

$= -K\int_{v_1}^{v_2} v^{-\gamma}$

$= -K\int_{v_1}^{v_2} \frac{v^{-\gamma+1}}{-\gamma+1}$

$= \frac{-K}{-\gamma+1}\left[v^{-\gamma+1}\right]_{v_1}^{v_2}$

$= \frac{K}{\gamma-1}\left[V_2^{-\gamma+1} - V_1^{-\gamma+1}\right]$

$= \frac{K}{\gamma-1}\left[V_2^{-\gamma}V_2 - V_1^{-\gamma}V_1\right]$

$= \frac{1}{\gamma-1}\left[KV_2^{-\gamma}V_2 - KV_1^{-\gamma}V_1\right]$

$= \frac{1}{\gamma-1}\left[P_2V_2 - P_1V_1\right]$ (prove)

Q. $U = aT^2 + bT^4$

$dU = Tds - Pdv$

$V = const$

$dU = T\,ds$

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

$dU = \cancel{aT^2dT + baT^4dT}$

$= daT^2 + dbT^4$

$= a\frac{d}{dT}T^2dT + b\frac{d}{dT}T^4dT$

$= \int \frac{2aTdT + 4bT^3dT}{T}$

$= \int \frac{2aTdT}{T} + \frac{4bT^3dT}{T}$

$= 2a\int dT + 4b\int T^2dT$

$= 2aT + 4b\frac{T^3}{3}$

Various types of process :

(Ideal)

	w	ΔU	ΔH	dq
Rev. Isothermal	$= -nRT \ln \frac{V_2}{V_1}$ $= -2.303\, nRT \log V_2/V_1$	0	0	$-w$
Irrev. Isothermal	$= -P_{ext}(V_2 - V_1)$ $= -nRT\left(1 - \frac{V_1}{V_2}\right)$	0	0	$-w$
Rev. Adiabatic	$= nC_v(T_2 - T_1)$ $w = \frac{1}{\gamma - 1}(P_2V_2 - P_1V_1)$	w	$nC_p(T_2 - T_1)$	0.
Irrev. Adiabatic	"	"	"	"

$dU = w$

$C_v(T_2 - T_1) = -P_{ext}\, dV.$

The expression for $w, q, \Delta U, \Delta H$ in Rev. Adiabatic & Irrev Adia.

The expression for $w, q, \Delta U, \Delta H$ in Rev Adiabatic & Irrev adiabatic transformation of an Ideal gas, are same but value differs. Because the rel^n b/w initial and final variable differ.

$dS_{reversible} = 0$

$dS_{irreversible} > 0.$

Rel^n between P & V	$P_1V_1^{\gamma} = P_2V_2^{\gamma}$	$C_V\left(\frac{P_2V_2}{R} - \frac{P_1V_1}{R}\right) = -P_2(V_2 - V_1)$
Rel^n between T & V	$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$	$C_V(T_2 - T_1) = -\frac{RT_2}{V_2}(V_2 - V_1)$
Rel^n between P & T	$P_1^{1-\gamma}T_1^{\gamma} = P_2^{1-\gamma}T_2^{\gamma}$	$C_V(T_2 - T_1) = -P_2\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$

$$\boxed{\begin{array}{l} dU = w \\ C_V(T_2 - T_1) = -P_2(V_2 - V_1) \\ P_1V_1 = RT_1 \qquad P_2V_2 = RT_2 \end{array}}$$

Q. $(-w)_{\underset{\text{iso}}{\text{rev}}} > (-w)_{\underset{\text{iso}}{\text{irrev}}}$

$$= (-w)_{\underset{\text{iso}}{\text{rev}}} - (-w)_{\underset{\text{iso}}{\text{irrev}}} > 0.$$

$$= RT\ln\frac{V_2}{V_1} - RT\left(1 - \frac{V_1}{V_2}\right)$$

$$= RT\ln\left[1 + \underbrace{\boxed{\frac{V_2}{V_1} - 1}}_{x}\right] - RT\left(1 - V_1/V_2\right)$$

$\ln(1+x) = x$ exp^n of Log till 1 term.

$$= ~~RT\ln[1+x~~ = RT\left[\frac{V_2}{V_1} - 1 - 1 + \frac{V_1}{V_2}\right]$$

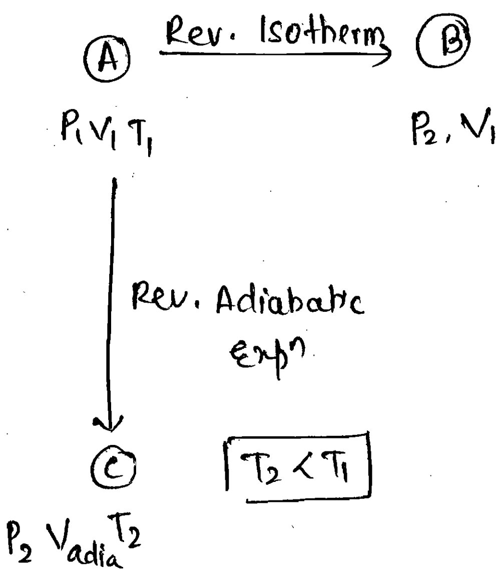
$$= RT\left[\frac{V_2}{V_1} - 2 + \frac{V_1}{V_2}\right]$$

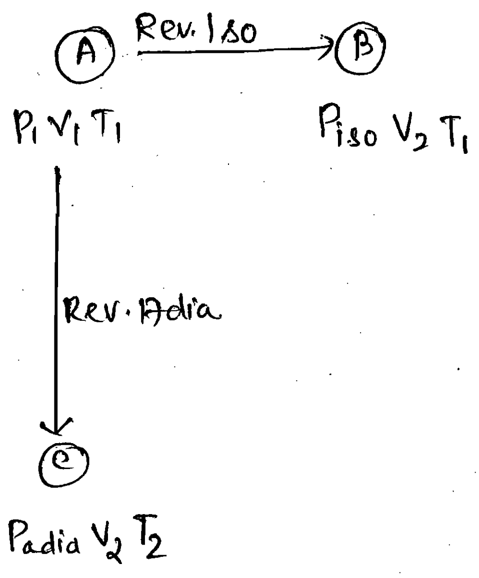
$$= RT\left[\frac{V_2^2 - 2V_1V_2 + V_1^2}{V_1V_2}\right]$$

$$= RT\left[\frac{(V_1 - V_2)^2}{V_1V_2}\right]$$

$= +$ve.

Comparison between Rev. Isothermal & Rev. Adiabatic expⁿ of Ideal gas :





we compare these two process Rev Iso, Rev adia expⁿ of an Ideal gas under 2 catagory.

(i) Comparing of final volᵐ in Initial State $(P_1 V_1 T_1)$ and final pressure are same.

In Process AB (Rev. Iso) ideal.

Boyle's law Apply, $P_A V_A = P_B V_B$.

$$P_1 V_1 = P_2 V_{iso}$$

$$\boxed{\frac{P_1}{P_2} = \frac{V_{iso}}{V_1}} \quad --- ①$$

In process AC (Rev Adia)

Poisson eqⁿ Apply, $P_A V_A^\gamma = P_C V_C^\gamma$

$$= P_1 V_1^\gamma = P_2 V_{adi}^\gamma$$

$$\boxed{\frac{P_1}{P_2} = \frac{V_{adi}^\gamma}{V_1^\gamma}} \quad -- ②$$

from ① & ②,

$$\frac{V_{iso}}{V_1} = \left(\frac{V_{adia}}{V_1}\right)^{\gamma}$$

$$\ln \frac{V_{iso}}{V_1} = \ln\left(\frac{V_{adia}}{V_1}\right)^{\gamma}$$

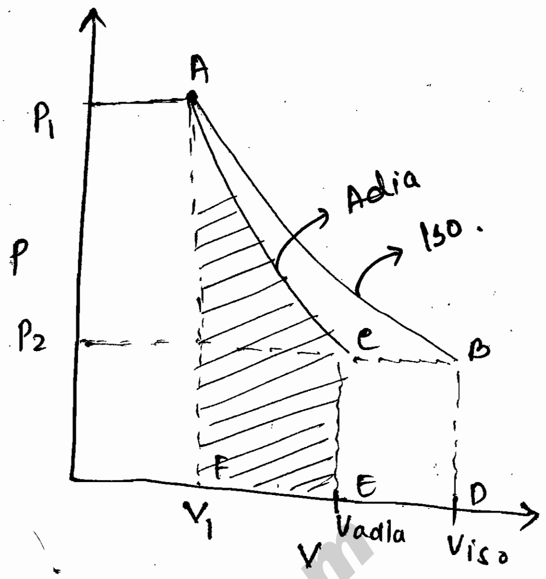
$$\Rightarrow \ln \frac{V_{iso}}{V_1} = \gamma \ln \frac{V_{adia}}{V_1}$$

$$\because \boxed{\gamma > 1}$$

$$\ln \frac{V_{iso}}{V_1} > \ln \frac{V_{adia}}{V_1}$$

$$\Rightarrow \frac{V_{iso}}{V_1} > \frac{V_{adi}}{V_1}$$

$$\Rightarrow \boxed{V_{iso} > V_{adia}}$$



i) Area under ACEFA = work involved in adiabatic process.

ii) Area under ABDFA = work involved in Isotherma process.

iii) Area under ABDECA = Enhanced work in Isothermal process.

② Comparision of Final pressure if initial state variable (P_1V_1) and final volume are same

$$\begin{tikzcd}
(P_1 V_1)\ A \arrow[r, "\text{Rev - Iso}"] \arrow[d, "\text{Rev, Adia}"] & B\ (P_{iso}, V_2) \\
C\ (P_{adia}, V_2) &
\end{tikzcd}$$

In process AB (Rev Iso)

Boyle's law

$$P_AV_A = P_BV_B$$

$$P_1V_1 = P_{iso}V_2$$

$$\boxed{\frac{P_1}{P_{iso}} = \frac{V_2}{V_1}} \longleftarrow ①$$

In process AC (Rev Adia)

$$P_A V_A^\gamma = P_C V_C^\gamma$$

$$P_1 V_1^\gamma = P_{adia} V_2^\gamma$$

$$\frac{P_1}{P_{adia}} = \left(\frac{V_2}{V_1}\right)^\gamma \quad \text{—②}$$

$$\frac{P_1}{P_{iso}} = \frac{V_2}{V_1} \quad \text{—①}$$

$$\frac{P_1}{P_{adia}} = \left(\frac{V_2}{V_1}\right)^\gamma \quad \text{—②}$$

$$\frac{P_1}{P_{adia}} = \left(\frac{P_1}{P_{iso}}\right)^\gamma$$

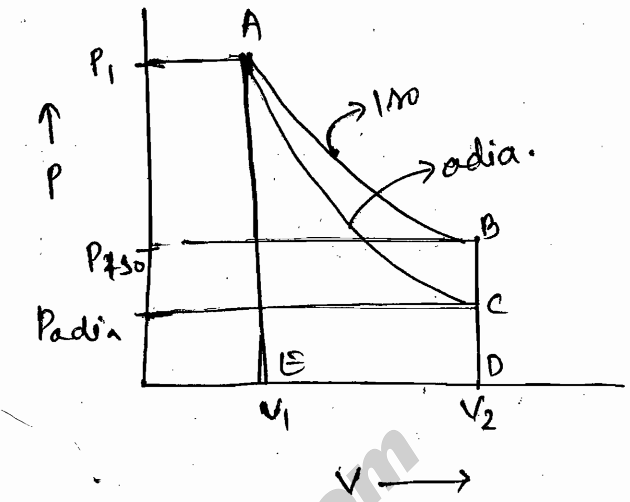
$$\ln \frac{P_1}{P_{adia}} = \ln \left(\frac{P_1}{P_{iso}}\right)^\gamma$$

$$\ln \frac{P_1}{P_{adia}} = \gamma \ln \frac{P_1}{P_{iso}}$$

$\because \gamma > 1.$

$$\frac{P_1}{P_{adia}} > \frac{P_1}{P_{iso}}$$

$$\boxed{P_{iso} > P_{adia}}$$



i) Area under ABDEA = ~~area~~ work involved in Isothermal.

ii) Area under A~~B~~CDEA = work involved in adia.

iii) Area under =

work involved in expansion –

Rev > Irre.

Iso > Adia

Expansion

So, $\boxed{W_{rev\,iso} > W_{irrev\,iso} > W_{irre\,adia}}$

compression – $\boxed{W_{rev\,iso} < W_{irr\,iso} < W_{irr.\,adia}}$

Degree of freedom & Law of Equipartition of energy

1. Translational $\Delta E <<< KT$.

2. Rotational $\Delta E < KT$.

3. Vibrational $\Delta E \approx KT$.

KT more (T more) $\Delta E < KT$.

KT less (T less) $\Delta E > KT$.

4. Electronic $\Delta E >> KT$.

we know,

$$\boxed{\Delta E_{elec} > \Delta E_{vib} > \Delta E_{rot} > \Delta E_{Tran}}$$

- The internal energy is summation of energy contributed by total degree of freedom.

- Degree of freedom of movement of atom in the molecule or molecules in the space.

- for molecule with atom N total D.O.F = 3N.

	Tr	Rot	vib
Linear	3	2	3N-5
Non-linear	3	3	3N-6

According to Equipartion law of energy.

Energy contributed by each degree of freedom, to the Internal energy is always same.

i.e., $-\frac{1}{2}KT$ | molecule, $\frac{1}{2}KT$ | mole.

Each Trans → Contribute $= \frac{1}{2}KT$

Each rot^n → contribute $= \frac{1}{2}KT$.

Each Vibr^n → contribute $= KT$ → high temp.

0 → low temp.

$$U = \left[\text{Total Transl}^{n}\ D.O.F \times \tfrac{1}{2}kT\right] + \left[\text{Total Rot. } D.O.F \times \tfrac{1}{2}kT\right] + \left[\text{Total Vib } D.O.F \times kT\right]$$

$$U_{linear} = \left[3\times\tfrac{1}{2}kT\right] + \left[2\times\tfrac{1}{2}kT\right] + (3N-5)\times kT$$

$$\boxed{= \underset{\overset{\uparrow}{Tr}}{\left[3\times\tfrac{1}{2}RT\right]} + \underset{\overset{\uparrow}{rot}}{\left[2\times\tfrac{1}{2}RT\right]} + \underset{\overset{\uparrow}{Vib}}{(3N-5)RT}.}$$

$$\boxed{U_{non\text{-}linear} = 3\times\tfrac{1}{2}RT + 3\times\tfrac{1}{2}RT + (3N-6)RT}$$

$$C_v = \frac{dU}{dT}$$

① $C_{v\,linear} = 3\times\frac{1}{2}R + 2\times\frac{1}{2}R + (3N-5)$

② $C_{v\,non\text{-}linear} = 3\times\frac{1}{2}R + 3\times\frac{1}{2}R + (3N-6)$

Monoatomic : N=1 (There is no vib^nal energy so there is no effect of temp in monoatomic)

D.O.F = Transl^n = 3.

$3\times\frac{1}{2}R = 3/2\,R.$

$$\boxed{C_v = 3/2\,R.}$$

$C_p - C_v = R$

$C_p = R + C_v$

$C_p = R + \frac{3}{2}R$

$$\boxed{C_p = 5/2\,R}$$

$$\gamma = \frac{C_p}{C_v} = \frac{5/\cancel{2}\cancel{R}}{3/\cancel{2}\cancel{R}} = 5/3\,R$$

$$\boxed{\gamma = 1.66.}$$

Diatomic

O_2

vib D.O.F Contri = 100% high Temp. ↙ ↘ Low Temp D.O.F = 0.

$C_v = 3\times\frac{1}{2}R + 2\times\frac{1}{2}R + 3N-5R.$

$= \frac{3}{2}R + R + (3\times2-5)R$

$= 1.5R + R + R = 3.5R$ (linear)

$C_v = 3.5R$

$C_p = 4.5R$

$\gamma = \frac{4.5}{3.5}$

$C_v = 3\times\frac{1}{2}R + R$

$= \frac{3}{2} + R = 2.5R$

$C_p = C_v + R = 3.5R$

$\gamma = \frac{3.5R}{2.5R} = 7/5 = 1.40.$

DPP-5

② $w = -nRT \ln\frac{V_2}{V_1}$

$= -2.303 nRT \ln V_2/V_1$ or P_1/P_2

③ $\Delta H = nC_p dt$

$= \frac{72\,gm}{18\,gm/mole} \times 75\,J/K\,mole \times 50\,K$

18 gm = 1 mole

72 gm = 4

$= 15000\,J = 15\,kJ$

4 mole ⟶ 15 kJ

1 mole $= \frac{15}{4} = 3.75$ kJ/mole.

④ $C_v = 1.5R$

$C_p = 2.5R \qquad T_1 = 750.$

$\gamma = \frac{C_p}{C_v} = 1.66 \qquad V_1 = 1\ dm$

$V_2 = 10$

Applying poimmon eq^n,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$= T_2 = \frac{T_1 V_1^{\gamma-1}}{V_2^{\gamma-1}}$$

$$= T_2 = 750\left[\frac{1}{10}\right]^{\gamma-1}$$

$$T_2 = 750\left(\frac{1}{10}\right)^{0.66}$$

Irr. Adia

$dq = dU - W$

$dq = 0.$

$dU = W.$

$C_v(T_2 - T_1) = -P(V_2 - V_1)$

$C_v(T_2 - T_1) = -\frac{RT_2}{V_2}(V_2 - V_1)$

$C_v(T_2 - T_1) = RT_2\left(1 - \frac{V_1}{V_2}\right)$

$1.5\cancel{R}(T_2 - 750) = -\cancel{R}\,T_2\left(1 - \frac{1}{10}\right)$

$1.5T_2 - 1125 = -0.9T_2$

$1.5T_2 + 0.9T_2 = 1125$

$2.4T_2 = 1125$

$T_2 = ?$

Temp is more decrease in reversible than that of Irreversible.

$\boxed{T_{irr} > T_{rev}}$

⑧ $C_V = 1.5R$

$C_P = 2.5R$

$\frac{C_P}{C_V} = 1.66.$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$T_1 = 300K$, $V_1 = 1L$, $V_2 = 10L$

$\Delta H = nC_P(T_2 - T_1)$

$T_2 = ?$

⑨ SO_2 (non-linear).

$3N-6 = 3\times3-6$

$= 9-6 = ③$

$C_V = 3\times\frac{1}{2}RT + 3\times\frac{1}{2}RT + 3RT$

$= \frac{3}{2}RT + \frac{3}{2}RT + 3RT$

$= 6RT + 3RT$

$= 6RT.$

$C_P = 7R.$

$\gamma = C_P/C_V = 7/6 = 1.16$

⑩ $U = 3PV$

$TV^{\gamma-1} = const$

$U = 3RT$

$C_V = \frac{\partial U}{\partial T} = 3R$

$C_P = 4R$

$\gamma = C_P/C_V = \frac{4}{3}$

$TV^{\frac{4}{3}-1} = const$

$TV^{1/3} = const.$

⑪ $O=C=O$ (Linear)

$U = 3\times\frac{1}{2}RT + 2\times\frac{1}{2}RT + (3N-5)RT$

$= \frac{3}{2}RT + RT + KT$

$= \frac{3}{2}KT + 4KT = 6.5KT.$

⑫ In room temp taken as low temp (neglect vib)

$O_2 = C_v = 3\times\frac{1}{2}R + 2\times\frac{1}{2}R +$

$N_2 = C_v = 3\times\frac{1}{2}R + 2\times\frac{1}{2}R$

$CO_2 = C_v = 3\times\frac{1}{2}R + 2\times\frac{1}{2}R$

} 2.5R (linear)

$SO_2 = C_v = 3\times\frac{1}{2}R + 3\times\frac{1}{2}R = \frac{3}{2}R + \frac{3}{2}R$

$= 3R$

$= 3\times 8.314$

$= 25$ J/kmol

⑬ Linear Translational

$\downarrow$

$3 \nearrow$

$U_m(T) = U_m(0) + \frac{3}{2}RT$

ⓑ Linear Tr & Rot

$U_m(T) = U_m(0) + 2.5RT$

$3\times\frac{1}{2}RT + 2\times\frac{1}{2}RT = \frac{3}{2}RT + RT = 2.5RT.$

ⓒ non-liner (Tr + Rot)

$3\times\frac{1}{2}RT + 3\times\frac{1}{2}RT$

$= 3KT$

ⓓ N-L (Trans)

$= 3\times\frac{1}{2}RT + U_m(0).$

$w, q, \Delta U, \Delta H$ for Rev. Isothermal Tranfn of Vanderwall:

Let us consider 1 mole of vanderwall gas is transfored Rev & Isothermally form.

State A ⟶ State B

$P_1 V_1 T$ $\quad$ $P_2 V_2 T$

$$w = -P_{ext}\, dv$$

$$= -P_{int}\, dv$$

$$= -P_{vanderwall}\, dv.$$

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

$$P + \frac{a}{V^2} = \frac{RT}{V-b}$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$w = -\int\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)dv$$

$$= -\int\frac{RT}{V-b}dv - \int\frac{a}{V^2}dv$$

$$w = -RT\int\frac{dv}{V-b} + a\int\frac{1}{V^2}dv$$

$$\int_{V_1}^{V_2}\frac{1}{V^2}dV$$

$$= \int_{V_1}^{V_2} V^{-2}\, dv$$

$$= \frac{V^{-2+1}}{-2+1}\, dv$$

$$= \frac{V^{-1}}{-1}\, dv$$

$$= -\left[\frac{1}{V}\right]_{V_1}^{V_2}$$

✓ $$\boxed{w = -RT \ln\frac{V_2-b}{V_1-b} - a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]}$$

for 1 mole

for n mole,

✓ $$\boxed{w = -nRT \ln\frac{V_2-nb}{V_1-nb} - an^2\left[\frac{1}{V_2} - \frac{1}{V_1}\right]}.$$

Internal Energy:

As we know U is the func^n of T, V in case of vanderwall

$$U = U(T,V)$$

In Isothermal T=0

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv$$

$$dT = 0.$$

$$dU = C_V dT + \pi_T\, dv$$

so, $\boxed{dU = \pi_T \, dv}$

$$dU = \frac{a}{V^2}\, dv$$

$$dU = a\int_{V_1}^{V_2} \frac{1}{V^2}\, dv$$

$$\Delta U = -a\left[\frac{1}{V_2} - \frac{1}{V_1}\right].$$

For Isothermal expan^n in vanderwaal, the internal energy increases.

$$\Delta U = a\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

$$\Delta U = a\left[\frac{V_2 - V_1}{V_1 V_2}\right]$$

$$= V_2 > V_1$$

$$\boxed{\Delta U = +ve}$$

If we will put $a=0$, $b=0$ in vanderwaal's eq^n we will get Ideal rev. Isother eq^n.

$$W = -RT \ln\frac{V_2 - b}{V_1 - b} - a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

$$\Big\downarrow \begin{array}{l} a=0 \\ b=0 \end{array}$$

$$\boxed{W_{\text{rev iso Ideal}} = -RT \ln\frac{V_2}{V_1}}$$

Rev. Iso vanderwaal: $\Delta U = -a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$

$$\Big\downarrow a=0$$

$$\boxed{\boxed{\Delta U = 0} \quad \text{Rev iso ideal.}}$$

Enthalpy Change:

$H = U + PV$ (From mathematical defination)

$H_2 = U_2 + P_2V_2$

$H_1 = U_1 + P_1V_1$

$\Delta H = H_2 - H_1$

$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$

$\Delta H = \Delta U + P_2V_2 - V_1V_1$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P + \frac{a}{V^2} = \frac{RT}{V-b}$$

$$\boxed{P = \frac{RT}{V-b} - \frac{a}{V^2}}$$

$$P_2 = \frac{RT}{V_2-b} - \frac{a}{V_2^2}$$

$$P_1 = \frac{RT}{V_1-b} - \frac{a}{V_1^2}$$

$$\Delta H = -a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \left(\frac{RT}{V_2-b} - \frac{a}{V_2^2}\right)\cdot V_2 - \left(\frac{RT}{V_1-b} - \frac{a}{V_1^2}\right)\cdot V_1$$

$$= -a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \frac{RTV_2}{V_2-b} - \frac{a}{V_2} - \frac{RTV_1}{V_1-b} + \frac{a}{V_1}$$

$$= -a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + RT\left(\frac{V_2}{V_2-b} - \frac{V_1}{V_1-b}\right) - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= -2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + RT\left(\frac{V_2}{V_2-b} - \frac{V_1}{V_1-b}\right)$$

$$\boxed{\Delta H = -2U + RT\left(\frac{V_2}{V_2-b} - \frac{V_1}{V_1-b}\right)}$$

$$U = -a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\Delta H = -2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + RT\left[\frac{V_2 - b + b}{V_2 - b} - \frac{V_1 - b + b}{V_1 - b}\right]$$

$$= -2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + RT\left[1 + \frac{b}{V_2-b} - 1 - \frac{b}{V_1-b}\right]$$

$$= -2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + RT\left[\frac{b}{V_2-b} - \frac{b}{V_1-b}\right]$$

$$\Delta H = -2a\left[\frac{1}{V_2} - \frac{1}{V_1}\right] + bRT\left[\frac{1}{V_2-b} - \frac{1}{V_1-b}\right]$$ for 1mole

$$\Delta H = -2n^2a\left[\frac{1}{V_2} - \frac{1}{V_1}\right] + n^2bRT\left[\frac{1}{V_2-b} - \frac{1}{V_1-b}\right]$$ for n-mole.

Rev- Adiabatic Vandenwall :

Let us consider 1 mole of vandenwall gas is expanded Rev & adiabatically from state A to state B.

$$\begin{array}{cc} \downarrow & \downarrow \\ P_1V_1T_1 & P_2V_2T_2 \end{array}$$

Poission eqⁿ: $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ Ideal

$$T_1(V_1-b)^{R/C_v} = T_2(V_2-b)^{R/C_v} \longrightarrow \text{vanderwall}$$

We know, In adiabatic $dq = 0$

$$\boxed{dw = \Delta U}$$

$$U = U(T,V)$$

$$\boxed{\Delta U = C_v(T_2 - T_1) - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \parallel w.}$$

$$dU = \left(\frac{\partial V}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv$$

$$dU = C_v dT + \pi_T dv$$

$$\int dU = \int C_v dT + \int \frac{a}{v^2} dv$$

$$\Delta U = C_v \int_{T_1}^{T_2} dT - a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

$$\Delta U = C_v (T)_{T_1}^{T_2} - a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

Enthalpy change in case of Reversible adiabatic vanderwall

$$H = U + PV$$

$$H_2 = U_2 + P_2V_2$$

$$H_1 = U_1 + P_1V_1$$

$$\Delta H = H_2 - H_1 = (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$= \Delta U + P_2V_2 - P_1V_1$$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$P_2 = \frac{RT_2}{V_2 - b} - \frac{a}{V_2^2}$$

$$P_1 = \frac{RT_1}{V_1 - b} - \frac{a}{V_1^2}$$

$$\Delta H = \Delta U + P_2V_2 - P_1V_1$$

$$C_v(T_2 - T_1) - a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \left(\frac{RT_2}{V_2 - b} - \frac{a}{V_2^2}\right)V_2 - \left(\frac{RT_1}{V_1 - b} - \frac{a}{V_1^2}\right)V_1$$

$$=$$

The expression for w, q, ΔU & ΔH, in rev. Adia & Irrev. Adia transf^n of vanderwall gas are same value is diff.

Irreversible Isothermal vanderwall :

$$\boxed{A} \longrightarrow \boxed{B}$$

$$P_1V_1T \qquad P_2V_2T$$

Rev iso } Poision
Rev Adia } imp.

1st part * *
imp
Carnot
open syst
entropy

$$w = -P_{ext}\, dV$$

$$= -P_2\, dV$$

$$= -P_2 (V_2 - V_1)$$

$$\boxed{w = -\left(\frac{RT}{V_2 - b} - \frac{a}{V_2^2}\right)(V_2 - V_1)}$$

$$\boxed{\Delta U = -a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

$$\boxed{dq = \Delta U - w}$$

$$\boxed{\Delta H_{irr\ iso} = \Delta H_{rev\ iso}}$$

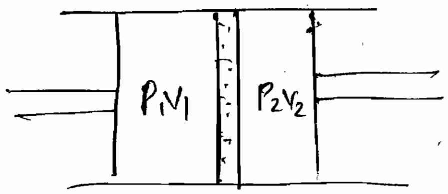
Joule-Thomson Experiment :

when a gas in expanded adiabatically from high pressure region to low pressure region the change in temp with respect to change in pressure at const enthalpy is known as J.T. coefficient & the experiment conducted to study it is known as J.T experiment.

$$\boxed{\mu_{J\cdot T} = \left(\frac{dT}{dP}\right)_H = \left(\frac{\partial T}{\partial P}\right)_H}$$

$\Delta p = -ve$
$\because$ High pressure to low pressure.

Process in Adiabatic as well as Isoenthalpic.



Work involved in left chamber

$V_1 = V_1$
$V_2 = 0$
p

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

$$= -P_1(0 - V_1) = P_1V_1$$

work involved in right Chamber

$V_1 = 0$

$V_2 = V_2$

$P_{ext} = P_2$

$w = -P_2(V_2 - V_1)$

$= -P_2(V_2 - 0)$

$\boxed{w = -P_2 V_2}$

Total work = $P_1V_1 - P_2V_2$

from 1st law,

$dq = dU - w$

∵ it is a adiabatic process.

$0 = dU - w$

$dU = w$

$U_2 - U_1 = P_1V_1 - P_2V_2$

$U_2 + P_2V_2 = P_1V_1 + U_1$

$\boxed{H_2 = H_1}$

$\left(\frac{\partial H}{\partial T}\right)_p = C_p$

$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p +$

$\left(\frac{\partial H}{\partial p}\right)_T$ ideal $= 0$

$\left(\frac{\partial H}{\partial p}\right)_T$ vander $= \frac{b - 2a}{T}$

Determination of Joule-Thomson coefficient :

$H = H(P, T)$

$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$

$= \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT.$

$\boxed{dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp}$

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

Enthalpy = const.

$dH = 0$.

~~$0 = C_p dT$~~

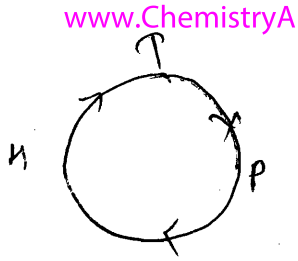
$$0 = C_p(\partial T)_H + \left(\frac{\partial H}{\partial p}\right)_T (\partial p)_H$$

$$C_p(\partial T)_H = -\left(\frac{\partial H}{\partial p}\right)_T (\partial p)_H$$

✓ $$\boxed{\left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T}$$

↓ Isoenthalpic Joule Thomson Coefficient

↓ Isothermal J.T coefficient



$$\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p = -1$$

$$\mu_{J.T} \left(\frac{\partial p}{\partial H}\right)_T C_p = -1$$

$$\mu_{J.T} = -\frac{1}{C_p} \frac{1}{\left(\frac{\partial p}{\partial H}\right)_T} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T.$$

$$\boxed{\mu_{J.T} = -\frac{1}{C_p}\phi_{J.T}}$$

$$\boxed{\mu_{J.T} = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{C_p}\phi_{J.T}}$$

① For ideal gas,

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

$$\mu_{J.T} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{C_p}\cdot 0 = 0$$

$$\mu_{J.T} = \left(\frac{\partial T}{\partial p}\right)_H = 0$$

↓ -ve

$dT = 0$ neither heating nor cooling.

$\boxed{T_1 = T_2}$

for vandenwall gas,

$$\left(\frac{\partial H}{\partial P}\right)_T = b - \frac{2a}{RT}$$

$$\mu_{J.T} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_p}\left[b - \frac{2a}{RT}\right]$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]}$$

Hence coolig taus place

$\Delta T = -ve.$

$\Delta P = -ve$

so, +ve $= \frac{1}{C_p}\left[\frac{2a}{T} - b\right]$

a = attractive $\quad \frac{2a}{T} > b$ (+ve)

b = repul^n

Inversion Temp:

↓

Inverse.

The temp at which real gas behave ideally is known as inversion temp.

or

The temp at which $\mu_{J.T} = 0$. in $\mu_{J.T}$ eq^n of real gas.

$$\mu_{J.T} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

$$\Big\downarrow \begin{array}{l} T = T_i \\ \mu_{J.T} = 0. \end{array}$$

$$0 = \frac{1}{C_p}\left[\frac{2a}{RT_i} - b\right]$$

$$\frac{2a}{RT_i} = b$$

$$\boxed{T_i = \frac{2a}{Rb}}$$

imp

✓ $T_{critical} = \frac{8a}{27Rb}$

✓ $T_{boyel} = \frac{a}{Rb}$

✓ $T_{inversion} = \frac{2a}{Rb}$

$T_i > T_b > T_c$

$P_c = \frac{a}{27b^2}$ = critical pressure

$V_c = 3b$

① case of cooling:

$T_f < T_i$

$dT = T_f - T_i = -ve$

$q_p = -ve$ through Out

$$\mu_{J.T} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

$$\left(\frac{-ve}{-ve}\right) = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

$$\frac{1}{C_p}\left[\frac{2a}{RT} - b\right] = +ve$$

$$\frac{1}{C_p}\left[\frac{2a}{RT} - b\right] > 0.$$

$$\frac{2a}{RT} - b > 0$$

$$\boxed{\frac{2a}{RT} > b}$$

$$\frac{2a}{Rb} > T$$

$\boxed{T_i > T}$ most of the gas.

② Case of Heating:

$T_f > T_i$

$dT = T_f - T_i = +ve$

$$\mu_{J.T} = \left(\frac{\partial T}{\partial P}\right)_H$$

$$\mu_{J.T} = \frac{+ve}{-ve} = -ve$$

$\mu_{J.T} < 0$

$$\frac{1}{C_p}\left(\frac{2a}{RT} - b\right) < 0$$

$$\frac{2a}{RT} < b$$

$$\frac{2a}{Rb} < T$$

$\boxed{T_i < T}$ Gases like H_2, He

③ Neither cooling nor heating :

$T_i = T_f$

$dT = 0$

$\mu_{J\cdot T} = \left(\frac{\partial T}{\partial P}\right)_H = 0.$

$\downarrow$

$\frac{1}{C_p}\left[\frac{2a}{RT} - b\right] = 0$

$\frac{2a}{RT} - b = 0$

$\boxed{\frac{2a}{RT} \geq b} = \frac{2a}{Rb} = T = \boxed{T_i = T}$

Conclusion

i) when $T_i > T$ → cooling takes place.

ii) when $T_i < T$ → heating takes place.

iii) when $T_i = T$ → neither cooling nor heating.

Chart

Case	$\mu_{J\cdot T}$	$\phi_{J\cdot T}$	Comments
1. Heating $T_2 > T_1$ $dT = +ve$	$\mu_{J\cdot T} = \left(\frac{\partial T}{\partial P}\right)_H$ $= +ve/-ve$ $\boxed{= -ve}$ $\mu_{J\cdot T} < 0$ $\frac{2a}{RT} < b$ $T_i < T$	$\mu_J = -\frac{1}{C_p}\phi_{J\cdot T}$ → $\boxed{+ve}$	H and He at ordinary temp. most gases at very high temp.
2. cooling $T_2 < T_i$ $dT = -ve$	$\mu_{J\cdot T} = \frac{-ve}{-ve} = \left(\frac{\partial T}{\partial P}\right)_H$ $\mu_{J\cdot T} = +ve$ $\frac{2a}{RT} > b$ $T_i > T$		→ most gases shows cooling at ordinary temp. H_2 He at very low Temp.

	$\mu_{J.T}$	$\psi_{J.T}$	commens
③ Neither heating non cooling.	$\mu_{J.T} = 0$ $\frac{2a}{RT} = b$ $T_i = T$	0	→ Ideal gas at ordinary temp. → Vanderwall gas at Inversⁿ temp.

Relⁿ b/w T_i and α.

$\boxed{\alpha = \text{expansion}}$

$$\mu_{J.T} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T \qquad \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V.$$

$$\mu_{J.T} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

$$\mu_{J.T} = \frac{1}{C_p}\left[T\alpha V - V\right]$$

$$= \frac{V}{C_p}\left[\alpha T - 1\right]$$

$$\boxed{\mu_{J.T} = \frac{V}{C_p}\left[\alpha T - 1\right]}$$

$T = T_i \qquad \mu_{J.T} = 0.$

$$0 = \frac{V}{C_p}\left[\alpha T_i - 1\right]$$

$$\alpha T_i - 1 = 0$$

$$\boxed{T_i = \frac{1}{\alpha}}$$

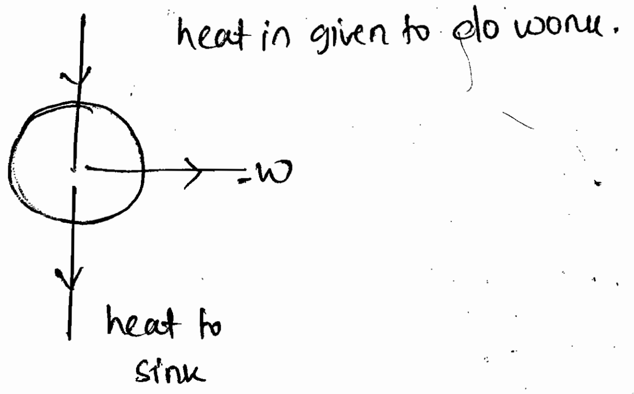
DPP-6

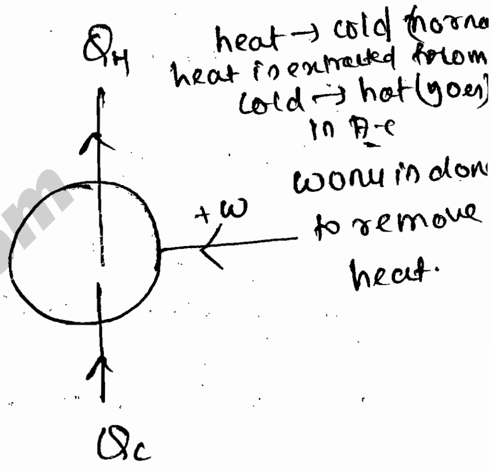
1. $T = 300K$
   $p = 25$

$P_1 = 50$ atm
$P_2 = 1$ atm.
$T_1 = 300$ K
$T_2 = ?$

$$\mu_{J \cdot T} = 0.173 \ K/atm = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T_2 - T_1}{P_2 - P_1}$$

Carnot Engine and Refrigerator:





efficiency = Output/Input

$$= \frac{-w}{+Q_H}$$

Heat is taken from hot source to do mechanical work.

Electrical work done on the system to extract heat from cold body

$$\eta = -\frac{Q_c}{w}$$

Basic features of Carnot Engine :

① Most efficient engine (but not 100 % efficient)

② Rev
  ^ Ideal in Nature.

③ Efficiency of Carnot engine does not depend upon Nature of work up substance but engine is Ideal.

④ Temp diff. is responsible for the value of efficiency.

⑤ Carnot engine efficiency is amount Independent

$$\eta = 1 - \frac{T_c}{T_w} = \frac{T_H - T_c}{T_H}$$

T_H = Temp of Source

T_c = Temp of sink.

⑥ Engine Involved four steps orderly as,

$$\boxed{\eta = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}}$$

a) Isothermal exp^n → heat has taken

b) Adiabatic exp^n → neither take

c) Isothermal comp^n → heat will be given

d) Adiabatic compr^n. – none give heat

T_2 = Source

T_1 = Sink.

$$\boxed{w = q_2 - q_1}$$

For Isothermal exp^n → it is keep in source

For Isothermal compr^n → " " " " sink

Adiabatic → kept in insulating

a) <u>Iso-thermal Expansion</u> :

To obtain this process put the working Substance Cylinder on the hot source, remove the weight by using piston. Gas expands isothermally

Let us consider from

$$\text{Ⓐ} \longrightarrow \text{Ⓑ}$$

$$P_1 V_1 T \longrightarrow P_2 V_2 T$$

System takes heat let us consider Q_R

From 1st law,

$dq = du - w$

Isothermal ideal $du = nC_v dT$
$= 0 \; (dT = 0)$

$dq = -w$

$q_H = -w$

$$\boxed{w_1 = -RT_h \ln \frac{V_2}{V_1}}$$

b) Adiabatic exp^n

Shift the working Substance Cylinder from the source to the Insulated stand. Remove the weight, gas expand adiabatically temp fall down.

Let us consider from
B to C

$$P_2V_2T_H \longrightarrow P_3V_3T_C.$$

$dq = U - \omega$

$dq = 0$

$dU = \omega$

$C_V(T_C - T_H) = W_2$

③ Isothermal compression:

Shift the working substance Cylinder from the insulated stand to the sink. Raise the weight by using piston. Gas compressed isothermally heat reject.

$$\underset{P_3, V_3, T_C}{\overset{C}{\downarrow}} \quad \text{to} \quad \underset{P_4, V_4, T_C}{\overset{D}{\downarrow}}$$

$P_3 < P_4$

$V_3 > V_4$

Let us consider Q_C.

$dq = U - \omega$

Isothermal $\Delta U = C_V dT$

$\Delta U = 0$ $\quad dT = 0.$

$$\boxed{dq = -\omega}$$

~~te~~ $\omega = -RT_C \ln \frac{V_4}{V_3}$

$dq = -\omega$

$Q_C = -\omega_3 = RT \ln \frac{V_4}{V_3}$

ⓓ Adiabatic Compression:

Shift the Cylinder on the Stand, raise the weight, gas compressed adiabatically. Cycle complete from D to A.

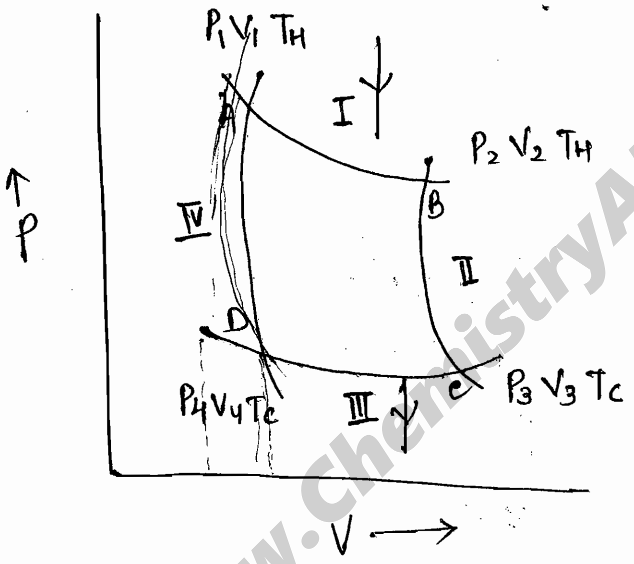
$$\begin{array}{cc} D & A \\ \downarrow & \downarrow \\ P_4V_4T_c & P_1V_1T_H \end{array}$$

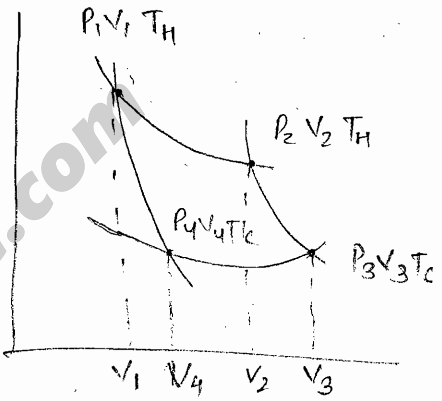
Adiabatic $dq = 0$.

$dq = du - w$

$0 = du - w$

$du = w_4 = C_v(T_H - T_c)$





Net work $W_{net} = w_1 + w_2 + w_3 + w_4$

$$= -RT_H \ln\frac{V_2}{V_1} + C_v(T_c - T_H) - RT_c \ln\frac{V_4}{V_3} + C_v(T_H - T_c)$$

$$\boxed{W_T = -RT_H \ln\frac{V_2}{V_1} - RT_c \ln\frac{V_4}{V_3}}$$

Relation between V_1 V_2 V_3 V_4:

To reduce the parameter,

(From In process BC rev. adiabatic Ideal = $T_B V_B^{\gamma-1} = T_c V_c^{\gamma-1}$
Poission eqn)

$$T_H V_2^{\gamma-1} = T_c V_3^{\gamma-1}$$

$$\left(\frac{T_H}{T_c}\right) = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad \text{-----} ①$$

In process D to A Rev, Adiabatic [illegible] $T_D V_D = T_A V_A$

$$T_c V_4^{\gamma-1} = T_H V_1^{\gamma-1}$$

$$\frac{T_H}{T_c} = \frac{V_4^{\gamma-1}}{V_1^{\gamma-1}} \quad \text{---} ②$$

from eqn ① & ②,

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

$$= \boxed{\frac{V_4}{V_1} = \frac{V_3}{V_2}}$$

$$= \boxed{V_1 V_3 = V_4 V_2}$$

$$= \boxed{\frac{V_4}{V_3} = \frac{V_1}{V_2}}$$

$$W_T = -RT_H \ln\frac{V_2}{V_1} - RT_c \ln\frac{V_4}{V_3}$$

$$= -RT_H \ln\frac{V_2}{V_1} - RT_c \ln V_1/V_2$$

$$= -RT_H \ln\frac{V_2}{V_1} + RT_c \ln V_2/V_1$$

$$W_T = -R \ln\frac{V_2}{V_1}(T_H - T_c)$$

$$\boxed{Q_H = RT_H \ln V_2/V_1}$$

Efficiency

$$\eta = \frac{-W_T}{-Q_H} = \frac{R \ln V_2/V_1 \, (T_H - T_c)}{R\, T_H \ln V_2/V_1}$$

$$\eta = \frac{T_H - T_c}{T_H}$$

$$\eta = \frac{T_H}{T_H} - \frac{T_c}{T_H}$$

$$\boxed{\eta = 1 - T_c/T_H}$$

Since, it is a cyclic process,

$\Delta U = 0$ (path func^n)

imp The internal energy $= 0$ for the whole process.

$$W = Q_H - Q_c$$

$$\boxed{\eta = \frac{-W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{Q_c}{Q_H}}$$

$$= \cancel{\frac{T_H - T_c}{T_H}} = 1 - \frac{T_c}{T_H}$$

$$= \cancel{T}$$

$$\boxed{\eta = -\frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = \frac{T_H - T_c}{T_H} = 1 - \frac{T_c}{T_H} = 1 - \frac{Q_c}{Q_H}}$$

Efficiency only depends upon the difference of temp.

$$\frac{T_H - T_c}{T_H} = \frac{Q_H - Q_c}{Q_H}$$

$$= 1 - \frac{T_c}{T_H} = 1 - \frac{Q_c}{Q_H}.$$

$$= \frac{T_c}{T_H} = \frac{Q_c}{Q_H}$$

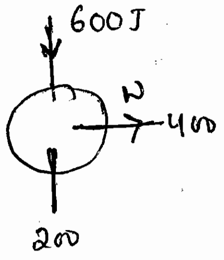
$$= \boxed{\frac{Q_H}{T_H} = \frac{Q_c}{T_c}}$$

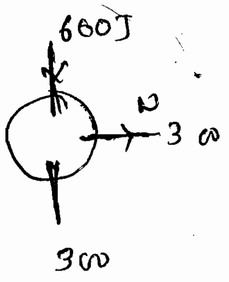
17th July

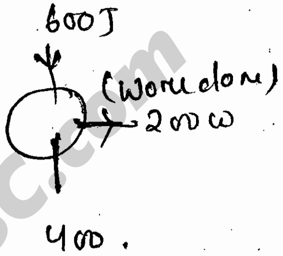
If any engine show more efficiency than the carnot engine it is Impossible engine.

If any engine shows less efficiency than the carnot engine — Irreversible engine.

If ~~so~~ taking same heat amount and gives less energy than ~~it is~~ a Carnot engine then it is a impossible engine. If given more energy then it is the Irreversible engine.







$\eta = 0.66$ (impossible engine)

$\eta = \frac{1}{2}$ (carnot engine)

$\eta = 0.33$. (Irreversible engine)

DPP-6

Q

$T_H = T_2$

$T_c = T_1$

$Q_H = Q_2$

$Q_c = Q_1$

$w = -400\ J$

$-w = 400\ J$

$$\eta = \frac{-w}{Q_H} = \frac{T_H - T_c}{T_H} = \frac{Q_H - Q_c}{Q_H} = \frac{1 - Q/3}{3} = 1 - \frac{1}{3} = 2/3.$$

$$\eta = \frac{-w}{Q_h}$$

$$\frac{2}{3} = \frac{400}{Q_h} = 1200 = 2Q_h$$

$$\boxed{Q_h = 600}$$

$$Q_c = \frac{Q_H}{3} = \frac{600}{3} = 200\ J.$$

$$\boxed{Q_c = 200\ J}$$

$$\eta = \frac{T_H - T_C}{T_H}$$

$$\frac{2}{3} = \frac{200}{T_H}$$

$$T_H = \frac{3 \times 200}{2} = \frac{600}{2} = 300.$$

$$T_H - T_C = 200$$

$$300 - T_C = 200$$

$$T_C = 100.$$

DPP.

(c) $\left(\frac{\partial C_v}{\partial V}\right)_T = 0$ for Ideal & van (CT)

(ii) $\left(\frac{\partial C_p}{\partial P}\right)_T = 0$ for ideal & van (F).

(i) $\left(\frac{\partial C_v}{\partial V}\right)_T = \left[\frac{\partial}{\partial V} \cdot \left(\frac{\partial U}{\partial T}\right)_V\right]_T$

↓ U is state funcⁿ.

$\left[\left(\frac{\partial}{\partial T}\right)\left(\frac{\partial U}{\partial V}\right)_T\right]_V.$

↓

$\left(\frac{\partial}{\partial T}\pi_T\right)_V$

ideal: $\pi_T = 0$

$\frac{\partial}{\partial T} \cdot 0$

↓

0

vand: $\pi_T = \frac{a}{V_m^2}$ $\left(\frac{\partial}{\partial T} \cdot \frac{a}{V^2}\right) = 0.$

(ii) $\left(\frac{\partial C_p}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right]_T$

↓ E.T

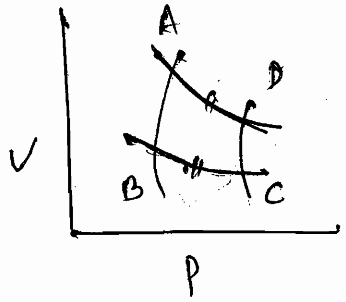
$\left[\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right]_P$

find these

$\left(\frac{\partial H}{\partial P}\right)_T = 0$ (Idle

$\left(\frac{\partial H}{\partial P}\right)_T = b - \frac{2a}{RT}$

11.



$$\left(\frac{\partial P}{\partial V}\right)_{Adia} > \left(\frac{\partial P}{\partial V}\right)_{Iso}$$

But Here, $\left(\frac{\partial V}{\partial P}\right)_{Iso} > \left(\frac{\partial V}{\partial P}\right)_{Adia}$.

Adiabtic compression,

① BC or AD → Adiabatic. (Slope from V-P diagram)

② Adiabtic compression

DC → exp^n or compr

CD → exp^n.

So, BC Adi Compression.

15. 90J $Q_H = 90J$

$T_H = 300 J$.

$$\frac{Q_C}{T_C} = \frac{Q_H}{T_H} = \frac{90}{300} = ? \frac{3}{10}.$$ $\frac{6}{2}$

(i) $Q_C = 60$, $T_C = 200 = \frac{60}{200} = 3/10$. $\left(\because \frac{Q_C}{T_C} = \frac{Q_H}{T_C}\right)$

(ii) $Q_C = 50$, $T_C = 200$, $\frac{50}{200} = 1/4$.

(14) Heat $\xrightarrow{\text{can't convert 100\%}}$ work

work → Heat
↓
Can convert 100%.

$$\eta = \frac{-w}{Q_H} = \frac{T_H - T_C}{T_H}$$

$$= \frac{-w}{1000J} = \frac{500-200}{500}$$

$-w = 600J$.

T-S diagram from Carnot engine:

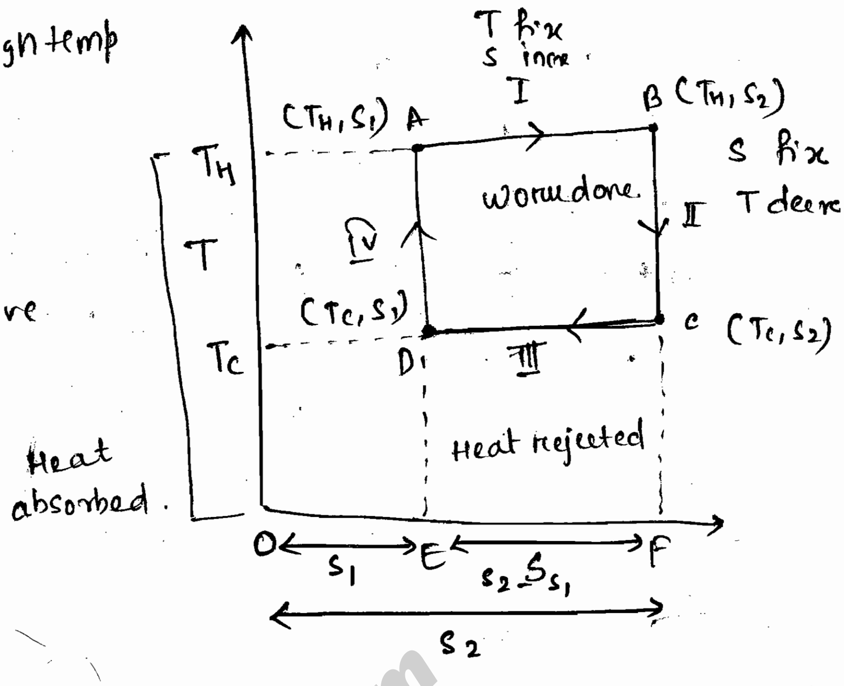
(i) Isothermal Expansion - High temp

→ take heat by the system.

→ Temp const

$ds = \frac{dq}{T} = \frac{Q_h}{T_h} = \frac{+ve}{const} = +ve$

∴, Entropy increase



ii). Adiabatic expⁿ:

→ Temp fall

→ $dq = 0$

$ds = \frac{dq}{T} = 0$ (S const).

(iii) Isothermal compression

T = fix (const

T = low

(heat reject)

$ds = \frac{dq}{T} = \frac{-ve}{const} = -ve.$

S decrease.

(iv) Adiabatic compression:

$ds = 0$

S = Const

T = increase

Area under ABFE = Total heat taken = Q_h

$= AB \times AE$

$= EF \times AE$

$Q_H = (S_2 - S_1) \times T_H.$

Area under ABCD = Total work done = $-\omega$

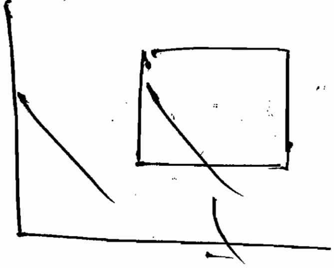
$AB \times AD$

$= EF \times (AE - ED)$

$\eta = \frac{-\omega}{Q_h} = \frac{T_h - T_c (S_2 - S_1)}{T_H (S_2 - S_1)}$ $\quad -\omega = (S_2 - S_1) \times (T_H - T_c)$

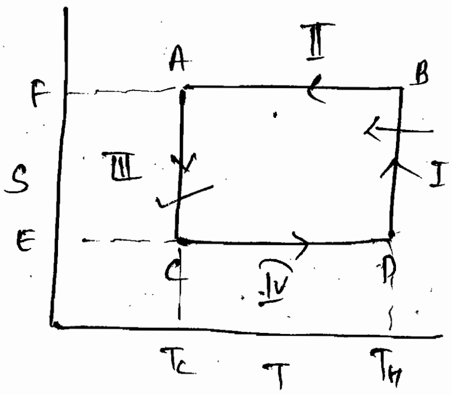
Qe.

$= \frac{T_h - T_c}{T_h}$



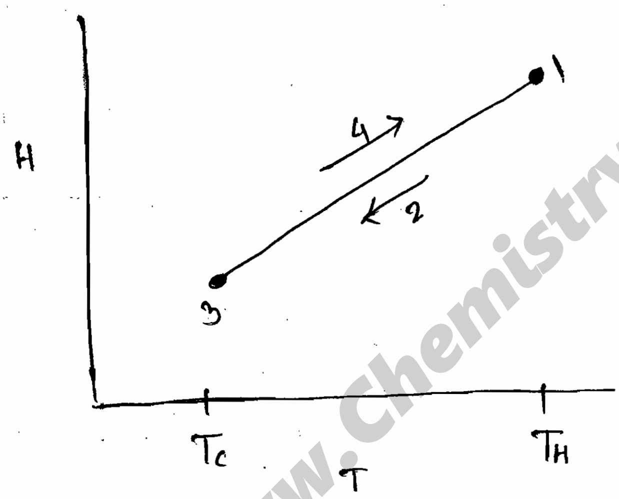
Area under CDEF = Heat rejected.

S T curve



In which case process heat rejected
soln = AC. (Isothermal compression)

H-vs T curve



① Isothermal expn:

$T = \text{const}, \; dT = 0$

$dH = nC_p dT$

$dH = 0$

$H = \text{const}$

② Adiabatic expn:

Temp fall down.

$dT = -ve$

$dH = nC_p \underset{-ve}{\underset{\downarrow}{dT}}$

$dH = -ve$

$H \downarrow$.

③ Isothermal comprsn

$T = \text{Const} \; dT = 0$.

$dH = nC_p dT = 0$

$H = \text{const}$

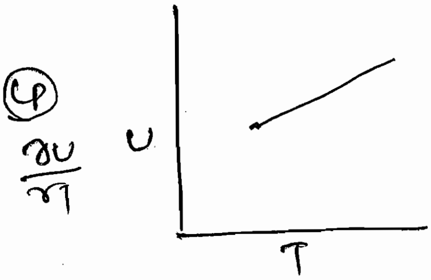
④ Adiabatic compression

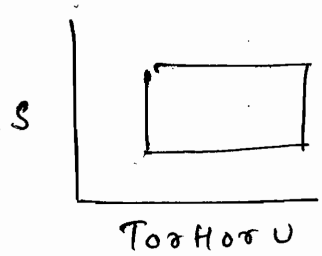
$T = +ve$

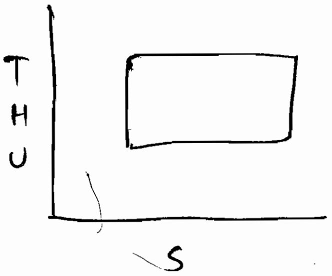
$\Delta H = +ve$

U Vs T

$$\boxed{C_p > C_v}$$



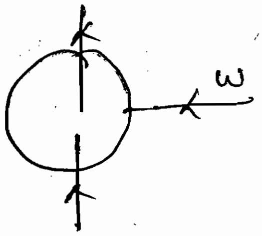




Elementary Idea of Refrigirator:

$$\eta = \frac{-w}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_H}.$$

Thermodynamically, the functioning of Carnot refrigirator is reverse of functioning of Carnot heat engine. The expression for determing efficiency of refrigirator is generally known as COP (coefficient of performance). COP is the ratio of heat rejected from cold body and work done on the system to reject that heat generally represented by β.



$$\beta = COP = \frac{\text{Output}}{\text{Input}} = \frac{-Q_c}{w} = \frac{Q_c}{Q_h - Q_c} = \frac{T_c}{T_H - T_c}$$

Relation b/w η & β

$$\eta = \frac{T_H - T_c}{T_H} \qquad \beta + 1 = \frac{T_c}{T_H - T_c} + 1 = \frac{T_c + T_H - T_c}{T_H - T_c} = \frac{T_H}{T_H - T_c}$$

$$\beta = \frac{T_c}{T_H - T_c} \qquad \boxed{\beta + 1 = \frac{1}{\eta}} \rightarrow \beta = \frac{1}{\eta} - 1 = \frac{1-\eta}{\eta}$$

$$\boxed{\eta_{\text{Carnot Engine}} = \frac{1}{\eta_{\text{Carnot heat pump}}} = \frac{1}{1+\beta_{\text{refrigerator}}}}$$

$$\eta_{\text{Heat pump}} = \frac{T_h}{T_h - T_c}$$

(18.) Latent heat

$\Delta H_{melt} = 6.01\ KJ$ mole.

$$s \xrightarrow{\downarrow 6.01\,KJ} l$$

or

$$\underset{1\text{ mole}}{l} \xrightarrow{\uparrow 6.01\,KJ.} \underset{1\text{ mo}}{s}$$

1 mole = 18 gm water in convert to Ice, heat removed = 6.01 KJ

$$100\ gm = \frac{6.01 \times 100}{18}$$

$$Q_c = -\frac{6.01 \times 100 \times 10^3}{18}$$

$$\beta = \frac{-Q_c}{+W} = \frac{T_c}{T_h - T_c} = \frac{-\frac{(-6.01 \times 10^3 \times 100)}{18}}{W} = \frac{273\,K}{298 - 273.}$$

Entropy: Entropy is a measurement of degree of randomness or degree of disorderness that is definations that is attributed to statistical thermodynamics. From the Boltzmann rel^n,

$$S = K \ln W.$$

1) perfectly ordered systems

$W = 1 \qquad S = 0$

2) If disorderd

$W \neq 1 \qquad S \neq 0.$

Thermodynamics does not define ~~change~~ in entropy but define change in entropy. If the heat taken by system Δq_{rev} at temp T than change in entropy is the ratio of heat taken and the temp at which heat is taken.

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

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

$$ds > \frac{dq_{irr}}{T}$$ (Clausius Inequalities)

Entropy change in a Reversible Transformation of an Ideal gas:

- → phase same
- → state diff (variable diff)
- → Reversible process.
- → Ideal system.

Let us consider 1 mole of an Ideal gas is transformed reversible from State A to State B.

$$\begin{array}{cc} A & B \\ \downarrow & \downarrow \\ P_1 V_1 T_1 & P_2 V_2 T_2 \end{array}$$

$dq = du - w$ (1st law)

$w = -pdv$

$dq = du + pdv$

$\downarrow du = nC_v dT$

$$\boxed{dq = C_v dT + pdv}$$

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

$$\boxed{ds = \frac{C_v dT + pdv}{T}}$$

$$ds = C_v \frac{dT}{T} + p\frac{dv}{T}$$

In terms of p & v,

Replace p by $PV = RT$

$$P = \frac{RT}{V}.$$

$$ds = C_v \cdot \frac{dT}{T} + R\frac{dv}{V}$$

$\downarrow$ C_v is Temp Indep.

$$\int ds = C_v \int \frac{dT}{T} + R\int \frac{dv}{V}$$

without limit,

$$\boxed{S = C_v \ln T + R \ln V}$$

with limit

$$\int_{S_1}^{S_1} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R\int_{V_1}^{V_2} \frac{dv}{V}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln V_2/V_1$$

$$\boxed{\Delta S = 2.303\, C_v \log \frac{T_2}{T_1} + 2.303\, R \log V_2/V_1}$$ for 1mole

$$\boxed{\Delta S = 2.303 n C_v \log \frac{T_2}{T_1} + 2.303\, nR \log V_2/V_1}$$ for n mole,

(ii) <u>In terms of T & P</u>

$$ds = C_v dT + Pdv$$

$$ds = \frac{C_v dT + RdT - vdp}{T}$$

$$ds = \frac{(C_v + R)dT - vdp}{T}$$

$$\int ds = \frac{C_p dT - vdp}{T}$$

$PV = RT$

$dPV = dRT$

$Pdv + vdp = RdT$

$Pdv = RdT - vdp$

$$\boxed{\begin{aligned} ds &= C_v \frac{dT}{T} + R\frac{dv}{V} \\ ds &= C_p \frac{dT}{T} - R\frac{dp}{P} \end{aligned}}$$

without limit,

$$\int ds = C_p \int \frac{dT}{T} - R\int \frac{dp}{P}$$

$$= C_p \ln T - R \ln p + S_0$$

with limit,

$$\int_{S_1}^{S_2} ds = C_p \int_{T_1}^{T_2} \frac{dT}{T} - R \int_{P_1}^{P_2} \frac{dp}{P}$$

$$\boxed{\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln {P_2}/{P_1}}$$

In terms of P & T

$$\Delta S = C_p \frac{dT}{T} \mp R \frac{dp}{P}$$

$$S = C_v \ln T - R \ln P + S_0$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln {P_2}/{P_1}$$

$$\Delta S = 2.303\, n C_p \log \frac{T_2}{T_1} - 2.303\, n R \log {P_2}/{P_1}$$

Term of P,V

$$ds = C_v \frac{dp}{P} + C_p \frac{dv}{V}$$

$$S = C_v \ln p + C_p \ln v + S_0$$

$$\Delta S = C_v \ln {P_2}/{P_1} + C_p \ln {V_2}/{V_1}$$

$$\Delta S = 2.303\, n C_v \log {P_2}/{P_1} + 2.303\, n C_p \log {V_2}/{V_1}.$$

DPP-7

⑫ 1 Ar (300 K, 1 bar) ⟶ 1 Ar (200 K, 10 bar)

$T_1 = 300K$ Ar → mono atomic

$P_1 = 1$ bar $U = 3/2\ RT$

$T_2 = 200K$ $C_v = 3/2\ R.$

$P_2 = 10$ bar $C_p = C_v + R = \frac{3}{2}R + R = 5/2\ R.$

$\Delta S = 2.303\ C_p \log \frac{T_2}{T_1} - 2.303\ R \log P_2/P_1$ [For = 1 mole]

⑮ Const = volm

$V_2 = V_1$ $T_1 = 300$, $T_2 = 500K$ $n = 2$ mole.

$\Delta S = 2.303\ nC_v \log \frac{T_2}{T_1} + 2.303\ nR \log V_2/V_1$

$= 2.303 \times 2\text{mole} \times 3/2 \cdot R \log \frac{500}{300}$

$= 2.303 \times 2\text{ mole} \times 1.5 \times 8.314 / \text{K.mole} \times \log \frac{500}{300}$

$= 12.74\ J/K.$

2 mole →

1 mole $= \frac{12.74}{2}\ J/K\ \text{mole}^{-1}.$

⑬ $C_p = 6.955$ cal deg^{-1} mol⁻¹

n = 10 mole.

Ⓐ 10 atm Ⓑ 100 at 600 K

$C_p = 6.955$ cal/degree-mole

$\Delta S = 2.303\, nC_p \log T_2/T_1 - 2.303\, nR \log P_2/P_1$

$= 2.303 \times 10\,\text{mole} \times 6.955\ \text{cal/k mole} \times \log \frac{800}{300} - 2.303 \times 10\,\text{mole} \times$

$2\ \text{cal/k mole}$

⑯ $V_1 = V \qquad T_1 = T$

$V_2 = V/4 \qquad T_2 = 2T.$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln V_2/V_1$$

$$= C_v \ln \frac{2T}{T} + R \ln \frac{V}{4.V}$$

$$= C_v \ln 2 + R \ln \frac{1}{4}$$

$$= C_v \ln 2 - R \ln 4.$$

$$= C_v \ln 2 - R \ln 2^2$$

$$= C_v \ln 2 - 2R \ln 2$$

$$= (C_v - 2R) \ln 2 .$$

⑲ $T_1 = 300\,K$

$T_2 = 400\,K$

$C_p = 5 + 0.1\,T \qquad P = \text{const} \quad dp = 0.$

$$dS = C_p \frac{dT}{T} - \boxed{R \frac{dp}{P}} = 0.$$

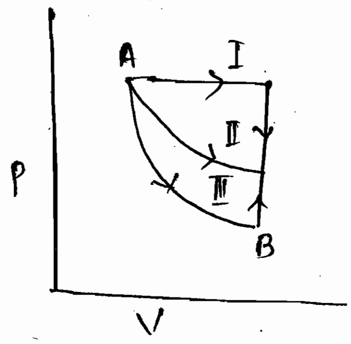
$$dS = (5 + 0.1\,T) \frac{dT}{T}. \quad = \int_{T_1}^{T_2} 5 \frac{dT}{T} + \int_{T_1}^{T_2} 0.1 \frac{dT}{T}.$$

$$= 5 \ln \frac{T_2}{T_1} + 0.1\,[T]_{T_1}^{T_2}$$

$$= 5 \ln \frac{T_2}{T_1} + 0.1(T_2 - T_1)$$

$$5 \times 2.303 \log \frac{T_2}{T_1} + 0.1 \ (T_2 - T_1$$

⑳



$\Delta S_1 = \Delta S_2 = \Delta S_3$ ($\because$ S is a state funⁿ)

only depends on AB.

~~Energy chan~~ Entropy Change in Reversible phase Transformation:

Reversible phase transformation are those transformation in which phase differ but variable (especially T & P) remains same, and T and P are corresponds to each other.

Ex: $H_2O(l) \longrightarrow H_2O(s)$

0°c 0°c

1 atm 1atm (Reversible phase transfⁿ)

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

-10°c -10°c

1 atm 1atm (Not reversible)

do not freeze in -10°c.

(iii) $H_2O(l) \longrightarrow H_2O(v)$ (Reversible)

100°c 100°c

1atm 1atm

(iv) $H_2O(l) \longrightarrow H_2O(v)$ (Irreversible)

100c 100c

2 atm 2 atm

(v) $A(l) \longrightarrow A(v)$

$T_b \quad\quad T_b$ (Revrible)

1atm $\quad$ 1atm

(vi) $A(s) \longrightarrow A(l)$

$T_m \quad\quad T_m$ (Reversible)

1atm $\quad$ 1atm.

* M.P, boiling point & Sublimation are Reversible phase transformation.

In case of rev phase transfn,

$$\Delta S = \frac{\text{Heat transfer during the phase tranfn}}{\text{Temp at which Tran sfn takes place}}$$

$$\begin{array}{cc} l & \longrightarrow & V \\ T_b & & T_b \\ 1\text{atm} & & 1\text{atm} \end{array}$$

$$\boxed{\Delta S_v = \frac{\Delta H_v}{T_b}}$$

i) Vapourisation:

$\Delta G = 0$, ($\because dp = 0, dT = 0$).

$$\begin{array}{ccc} A(l) & \longrightarrow & A(v) \\ H_2O(l) & \longrightarrow & H_2O(v) \\ T_b & & T_b \\ 1\text{atm} & & 1\text{atm} \end{array}$$

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

$$S_v - S_l = \frac{\Delta H_v}{T_b}$$

$$S_v = S_l + \frac{\Delta H_v}{T_b}$$

$$\boxed{\therefore S_v > S_l}$$

(ii) Melting:

$$\begin{array}{ccc} A(s) & \xrightarrow{+} & A(l) \\ H_2O(s) & \longrightarrow & H_2O(l) \\ 0^\circ C & & 0^\circ C \\ T_m & & T_m \end{array}$$

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

$$S_l - S_s = \frac{\Delta H_m}{T_m}$$

$$S_l = S_s + \frac{\Delta H_m}{T_m}$$

$$\boxed{S_l > S_s}$$

Condensed, } same
freezing } magnitude
← -ve sign.

Sublimation :-

$S \longrightarrow V$

$A(s) \longrightarrow A(g)$

T_{sub} T_{sub}

$$\Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}}$$

$$S_v - S_s = \frac{\Delta H_{sub}}{T_{sub}}$$

$$\boxed{S_v = S_s + \frac{\Delta H_{sub}}{T_{sub}}}$$

Crystalliz^n

$\alpha(\text{sulphur}) \longrightarrow \beta(\text{sulphur})$

$$\boxed{\Delta S = \frac{\Delta H_{Transf}}{T_{Transf}}}$$

DPP-7

Q ⑦ $H_2O(v) \xrightarrow{\text{cond}^{n}ed} H_2O(l)$

$\Delta H_{vap} = 40.66$ kJ/mole.

$$\Delta S = \frac{\Delta H}{T} = \frac{-40.66 \times 10^3 \text{ J/mole}}{373} = 5/18 \text{ mole}.$$

⑧

If $n \rightarrow$ mole, $C_p \rightarrow$ per mole } no ~~con~~ unit conv^n

$n \rightarrow$ gm, $C_p \rightarrow$ gm } no conv^n.

$dS = \frac{dq}{T} = J/K$

$C_p = 4.184$ J/K. gm

$$\Delta S = 2.303\, n C_p \log\frac{T_2}{T_1} - 2.303 \int nR \log P_2/P_1$$

$$= 2.303 \times 100\text{ gm} \times 4.184 \text{ J/K gm} \times \log\frac{273+75}{273+50}.$$

⑨ ethene $\longrightarrow$ polyethene

$(g) \longrightarrow (s)$ decreases so $\Delta S = -ve$.

⑩ (i) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$\Delta S = -ve$.

(ii) $s \longrightarrow L$ $\Delta S = +ve$.

(iii) $s \longrightarrow v$ $\Delta S = +ve$

(iv) $l \longrightarrow g$ $\Delta S = +ve$.

⑭ water $\longrightarrow$ Ice

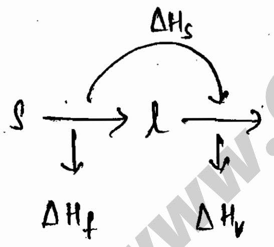
$(l) \longrightarrow (s)$

freezing (heat evolved) $\Delta S = -ve$.

$$\Delta S = \frac{\Delta H}{T} = \frac{-6000\ J/mole}{273\ K}.$$

$$\Delta S = -22\ J/K\ mole^{-1}$$

(18)



$$\Delta H_{sub} = \Delta H_f + \Delta H_v$$

Trouton's Rule :

Troutnon has observed that most of the liquid do not form H-bond and have the b.p higher than 150 K, fore those liquid,

$$\boxed{\Delta S_{vap} \approx 10.5 R}$$

Best Example that follow this rule, Benzene, Toulene etc.

water (a liquid) does not follow trouton rule. bcoz it form H-bond.

No Such Rules are exist in fusion & sublimation process.

$$\Delta S_{vap} = 10.5R$$

$$\downarrow$$

$$\boxed{\frac{\Delta H_{vap}}{T_b} = 10.5R}$$

Q.17 $n = 3$ mole

$$T_b = 80^\circ C = 273 + 80$$
$$= 353K$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

$$88.3\ J\,K^{-1} mol^{-1} = \frac{\Delta H_{vap}}{353K.}$$

$$\Delta H_{vap} = 88.3\ \frac{J}{K.mole} \times 353K$$

$$\Delta H = 88.3 \times 353\ J/mole.$$

$$= 88.3 \times 353 \times 3\cancel{mole} \times J/\cancel{mole}$$

(22) $S_{Tr} = R\ln \underset{\uparrow}{q_{Tr}} + \frac{U}{T}$

$S_{Rot} = R\ln q_{rot} + \frac{U}{T}$

m↑, q↑, S↑.

(23) (d)

(21) with increase in mass → q increase → with q increase → S increase

$$S = R\ln q + \frac{U}{T} \quad m\uparrow\ q\uparrow$$

↳ Partⁿ.

$$q_{Tr} = \frac{(2\pi mkT)^{3/2}}{h^3}.V$$

DPP-8

① $\eta = 1/6$

$$\frac{1}{6} = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H}$$

$$1/6 = 1 - \frac{T_C}{T_H} \quad \text{——} ①$$

$$\frac{1}{3} = 1 - \frac{T_C - 65}{T_H} \quad \text{---} ②$$

$$\frac{1}{3} = 1 - \frac{T_C}{T_H} + \frac{65}{T_H}$$

$$\frac{1}{3} = 1/6 + \frac{65}{T_H}$$

$$\frac{1}{3} - \frac{1}{6} = \frac{65}{T_H}$$

$$\frac{1}{6} = \frac{65}{T_H}$$

$$T_H = 6 \times 65 = 390.$$

② $\frac{q_H}{T_H} = \frac{q_C}{T_C}$

③ d) $= 0$: closed vessel.

④ $\alpha = \frac{1}{T}$ (Ideal gas)

⑤ $\Delta H_{vap} = 0$ at Critical point.

At critical pt. we are not able to distinguish b/w liq & vap phase.

$\boxed{\Delta H_{vap} = 0}$ ⟶ Mathematically derived from clausius clapeyron.

⑥ $C_p = 30 - 4T$

$$dH = nC_p\,dT$$

$$\int dH = \int n(30 - 4T)\,dT$$

~~for~~ $\Delta H = \int 30\,dT - \int 4T\,dT.$

$$\Delta H = n\,30[T] - 4\frac{T^2}{2}$$

$$= n\,30[T_2 - T_1] - 2[T^2]_{T_1}^{T_2}$$

$$= n\,30[T_2 - T_1] - 2[T_2^2 - T_1^2]$$

$$= n\,30[T_2 - T_1] - 2[T_2 + T_1](T_2 - T_1)$$

(ii) $\Delta S = nC_p\frac{dT}{T} - \cancel{nR\frac{dp}{p}}^{0}$

$$= n\int(30 - 4T)\frac{dT}{T}$$

$$= n\int 30\frac{dT}{T} - \int 4\cancel{T}\frac{dT}{\cancel{T}}$$

$$= \int_{T_1}^{T_2} 30\ln T - 4[T]_{T_1}^{T_2}$$

$$= 1.75\;30\ln\frac{T_2}{T_1} - 4[T_2 - T_1]$$

$$= 1.75\;30 \times 2.303\,\frac{273 + 75}{273} - 4(75$$

⑦ $w = 1.50 \times 10^3$ W

$= 1.50 \times 10^3$ J/s

$= 1.50 \times 10^3$ J/sec $\times 24 \times 60 \times 60$

$$\beta = \frac{-Q_c}{+w}.$$

⑪ $n = 2$ mole

$P_1 = 5 \quad T_1 = 298$

$P_2 = 1 \quad T_2 = 298$ } Iso.

$$\Delta S = 2.303\, n C_p \log \frac{T_2}{T_1} - 2.303\, nR \log P_2/P_1$$

$T_0 = 0$.

Entropy Change in Irreversible phase Transformation:

① Not only phase but also variable (T & P) Changes.

$H_2O(l) \longrightarrow H_2O(l)$ same phase.

25°C — 125°C

1 atm — 1 atm → variable Change.

② The phase tranf^n that ~~the~~ are not reversible in Nature.

Ex: $H_2O(l) \longrightarrow H_2O(s)$

0°C — 0°C

2 atm — 2 atm.

$A(s) \longrightarrow A(l)$

Tm — Tm

1 atm — 1 atm.

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

−10°C — −10°C

2 atm — 2 atm.

To calculate $\Delta H, \Delta U, \Delta S$ × ΔG for irrev phase transf.. we have to convert them in reversible phase transf.

* Phase same, varible diff –

$$\Delta S = nC_p \ln \frac{T_2}{T_1} - R \ln P_2/P_1$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + R \ln V_2/V_1$$

$$\Delta S = nC_p \ln \frac{V_2}{V_1} + nC_v \ln P_2/P_1$$

* phase diff, variable (T, P) same -

$$\Delta S = \frac{\Delta H}{T}$$

⑬ $H_2O\ (l, 300K, 1atm) \longrightarrow H_2O\ (v, 600K, 1atm)$

Irreversible → convert to Reversible.

$H_2O(l) \longrightarrow H_2O(v)$

100°C + 273 = 373°C

100°C + 273°C = 373 °C.

① $H_2O\ (l) \longrightarrow H_2O(l)$

300°C → 373°C

1 atm → 1 atm.

$\Delta S = 2.303 \times C_{p_l} \log \frac{T_2}{T_1}$

P const = 0.
(same phase)

$= 2.303 \times 36 \times \log \frac{373}{300}.$

② $H_2O\ (l) \longrightarrow H_2O\ (v)$

373°C → 373°C

1 atm → 1 atm

$\Delta S_2 = \frac{\Delta H_v}{T} = \frac{40.6 \times 10^3}{373}$

③ $H_2O(v) \longrightarrow (H_2O)(v)$

373°C → 600

1 atm → 1 atm,

$\Delta S_3 = 2.303\ C_{p_v} \log \frac{T_2}{T_1} = 2.303 \times 35 \times \log \frac{600}{373}.$

$\Delta H_1 = C_p dT = C_{p,l}(T_2 - T_1)$

$= 36(373 - 300)$

$\Delta H_2 = 40.6 \times 10^3$

$\Delta H_3 = C_p dT$

$= 35(600 - 373)$

$=$

⑩ $H_2O\,(l, T = 263$
$= -10^\circ C \longrightarrow H_2O(s)$ $[T = -10^\circ C$
$= 263K$

$P = 0.1 MPa$

$= 1\ atm$

$P = 0.1 MPa.$

$= 1\ atm.$

① $H_2O(l) \longrightarrow H_2O(l)$

$-10^\circ C$ | $0^\circ C$

$(263K)$ | $(273K)$

$1\ atm$ | $1\ atm.$

② $H_2O(l) \longrightarrow H_2O(s)$

$0^\circ C\ (273K)$ | $0^\circ C\ (273K)$

③ $H_2O(l) \longrightarrow H_2O(s)$

$0^\circ C$ | $-10^\circ C$

273 | 263

$1\ atm$ | $1\ atm.$

$\Delta S_1 = C_{p,l} \ln \frac{T_2}{T_1}$

$= 76 \ln \frac{273}{263}$

$= 76 \times [\ln 273 - \ln 263]$

$= 76 \times [5.61 - 5.57]$

$\Delta S_2 = \frac{\Delta H}{T} = -\frac{6006}{273}.$

$\Delta S_3 = C_{p,s} \ln \frac{T_2}{T_1} = 38 \times \ln 263 - \ln 273)$

$\Delta H_1 = C_{p,l}(T_2 - T_1)$

$= 76($

$\Delta H_2 = -6006$

$\Delta H_3 = C_{p,s}(T_2 - T_1) = 36(263 - 273)$

Irreversible → $\underset{\substack{(s)\\ T\\ P=1atm}}{A} \longrightarrow \underset{\substack{(v)\\ T'\\ P=1atm.}}{A}$

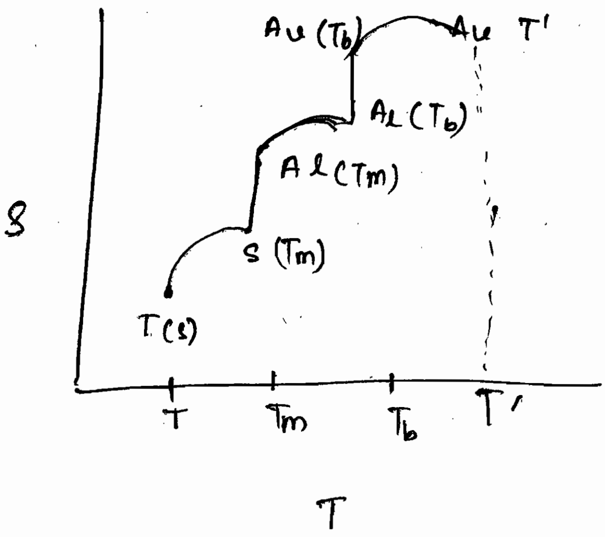
Rev, ① $\underset{\substack{(s)\\ T\\ 1\,atm}}{A} \longrightarrow \underset{\substack{(s)\\ T_m\\ 1\,atm}}{A}$ $\Delta S_1 = C_{p,s} \ln \frac{T_m}{T}$

② $\underset{\substack{(s)\\ T_m\\ 1\,atm}}{A} \longrightarrow \underset{\substack{(l)\\ T_m\\ 1\,atm}}{A}$ $\Delta S_2 = \frac{\Delta H_m}{T_m}$

③ $\underset{\substack{(l)\\ T_m\\ 1\,atm}}{A} \longrightarrow \underset{\substack{(l).\\ T_b\\ 1\,atm}}{A}$ $\Delta S_3 = C_{p,l} \ln \frac{T_b}{T_M}$

④ $\underset{\substack{(l)\\ T_b\,(1atm)}}{A} \longrightarrow \underset{\substack{(v)\\ T_b\,(1atm)}}{A}$ $\Delta S_4 = \frac{\Delta H_v}{T_b}$

⑤ $\underset{T_b}{A(v)} \longrightarrow \underset{T'}{A(v)}$ $\Delta S_5 = C_{p,v} \ln \frac{T'}{T_b}.$



$\Delta H_{vap} > \Delta H_{fus^n}.$

A/C to Debye,

If T = 0 Kelvin

we can't take $\Delta S = C_p \int \frac{dT}{T}$

exp.

If Initial state A, (0 K, 1 atm)

Then in the rel^n $dS = C_p \frac{dT}{T}$

$\therefore$ C_p is not Independent at temp. but the value is generally determined by T^3 law (Debye)

$$\boxed{C \propto T^3}$$

⑮ $\underset{(360K)}{\underset{(s)}{I_2}} \longrightarrow \underset{(410K)}{\underset{(l)}{I_2}}$

Sol^n $\underset{360}{\underset{(s)}{I_2}} \longrightarrow \underset{387}{\underset{(s)}{I_2}}$ $\quad \Delta S_1 = 2.303\, \overset{54.44}{C_{p,s}} \log \frac{T_2}{T_1}$

$\underset{387}{\underset{(s)}{I_2}} \longrightarrow \underset{387}{\underset{(l)}{I_2}}$ $\quad \Delta S_2 = \frac{\Delta H_{vap}}{T} = \frac{7.87 \times 10^3 \text{ J mole}}{387}$

$\underset{387}{\underset{(l)}{I_2}} \longrightarrow \underset{410.}{I_2(l)}$ $\quad \Delta S_3 = 2.303 = \underset{80.67}{C_{p,l}} \times 2.303 \log \frac{T_2}{T_1}$

21 July

DPP-8

16. H_2O (l, 1 atm) $\longrightarrow$ H_2O (g, 0.1 atm) at 100°c
100°c 100°c

H_2O (l, 1 atm) $\longrightarrow$ H_2O (v, atm) $\Rightarrow S = \frac{\Delta H_v}{b} = \frac{40670 \text{ J/mole}}{373 \text{ K}}$.
100°c 100°c

H_2O (v, 1 atm) $\longrightarrow$ H_2O (v, 0.1 atm)
100°c 100°c

$S = -2.303 \times R \times \log P_2/P_1$
$= -2.303 \times 8.314 \log \frac{0.1}{1}$
$= -2.303 \times 8.314 \times (-1)$.

DPP-9

18. H_2O (s, 0°c) $\longrightarrow$ H_2O (v, 100°c).
1 atm 1 atm.

Soln: H_2O (s, 0°c) $\longrightarrow$ H_2O (l, 0°c) $\frac{\Delta H}{T} = \Delta S$

$\frac{\Delta H}{T} = \Delta S$.

H_2O (l, 0°c) $\longrightarrow$ H_2O (l, 100°c) $\Delta S = 2.303 \times C_{p_l} \ln \frac{T_2}{T_1}$

H_2O (l, 100°c) $\longrightarrow$ H_2O (v, 100°c) $\Delta S \; \frac{\Delta H_v}{T_b} = \frac{40650}{373}$

DPP-8

⑬ Total heat content $= \Delta H$.
vapour $\rightarrow$ liquid which can liquify $C_p \approx C_v$ (in case of liq)

(i) $\Delta H = \Delta U + P\cancelto{0}{\Delta V}$

$\Delta H = \Delta U$

$\Delta U = C_v \, dT$ $C_p \approx C_v$

$\Delta U = \Delta H$

(ii) $\Delta H_2 = \Delta U_2 + P\Delta V$ (Phase do not charge.

(same phase)
In liq with charge
in temp volm do
not charge.

$\Delta H_2 = \Delta U_2 + P\Delta V$

$= \Delta U_2 + P(V_v - V_l)$

$\Delta H_2 = \Delta U_2 + PV_v$ (Idealgas)

$\Delta H_2 = \Delta U_2 + RT$

$\Delta U_2 = \Delta H_2 - RT.$

$= 40600 - 8.314 \times 373$

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

$= \Delta U + 1RT$

$\Delta U_2 = \Delta H - RT.$

(iii) $\Delta U_3 = C_v dT$

$= (C_p - R)(T_2 - T_1)$

$= (35 - 8.3)(600 - 373)$

Entropy of Mixing: (Temp must be diff)

(i) solid-solid mixing → $\overset{\text{cold}}{\text{Cu}}$ in $\overset{\text{hot}}{\text{Fe}}$

(ii) liquid-liquid mixing. → $\underset{T_h}{\text{milk}}$ in $\underset{T_c}{\text{water}}$, $\underset{T_h}{\text{water}}$ in $\underset{T_c}{\text{milk}}$.

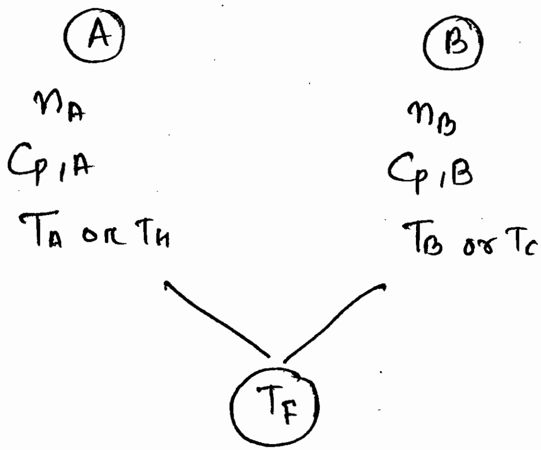
(iii) solid-liquid mixing. $\underset{T_h}{\text{Fe}}$ in $\underset{T_c}{\text{water}}$

solid-liquid mixing (If solid melt in liquid)

$\underset{0^\circ c}{\text{Ice}} - \underset{T_H.}{\text{water}}$

Let us consider substance A with Temp T_H, T_A amount n_A and heat capacity $C_{p,A}$ is mixed with substance B with Temp T_C or T_B. amount n_B and heat capacity $C_{p,B}$ at cost.p.

The Entropy change in this case is surely depend upon the final temp on equilibrium attained by the system.



$$\Delta S = nC_p \ln\frac{T_2}{T_1} - n\cancel{R\ln}^{0}\frac{P_2}{P_1} \quad (\because \text{~~atms~~ presn} = 1\,\text{atm})$$

$$\Delta S = nC_p \ln T_2/T_1$$

$$\boxed{\begin{aligned} \Delta S_A &= n_A C_{p,A} \ln\frac{T_2}{T_1} \\ \Delta S_B &= n_B C_{p,B} \ln\frac{T_2}{T_1} \end{aligned}}$$

To get final temp (T_f) we apply the Conservation of heat law.

Heat given by hot body = heat taken by cold body.

$$-n_A C_{p,A}(T_f - T_A) = n_B C_{p,B}(T_f - T_B)$$

$$= -n_A C_{p,A} T_f + n_A C_{p,A} T_A = n_B C_{p,B} T_f - n_B C_{p,B} T_B.$$

$$= n_A C_{p,A} T_A + n_B C_{p,B} T_B = n_B C_{p,B} T_f + n_A C_{p,A} T_f.$$

$$= n_A C_{p,A} T_A + n_B C_{p,B} T_B = [n_B C_{p,B} + n_A C_{p,A}] T_f.$$

$$\boxed{T_f = \frac{n_A C_{p,A} T_A + n_B C_{p_B} T_B}{n_A C_{p,A} + n_B C_{p,B}}}$$

$$\boxed{T_f = \frac{n_H C_{p,H} T_H + n_C C_{p,C} T_C}{n_H C_{p,H} + n_C C_{p,C}}}$$

Case-I

Substance same, amount diff, Temp diff

$C_{p,A} = C_{p,B}$

$C_{p_c} = C_{p_H}$

$$\boxed{T_f = \frac{n_A T_A + n_B T_B}{n_A + n_B}}$$

Case-II

same substance, amount same, Temp diff

$n_h = n_c = n$

$$\boxed{T_f = \frac{T_h + T_c}{2}}$$

DPP-9

⑥ ① 393 K 50 g ⓒ 323 K 100 gm (Sub same amount diff)

$T_h = 393K$ $T_c = 323K$

$m_h = 50gm$ $m_c = 100gm$

$C_{p,h} = 0.4184\ J/K\,gm.$ $C_{p,c} = 0.4184\ J/Km$

$$T_f = \frac{m_H T_h + m_c T_c}{m_H + m_c} = \frac{50 \times 393 + 100 \times 323}{150}$$

$$\Delta S_H = m_h C_{p,h} \times 2.303 \times \log \frac{T_f}{T}$$

$$= 50 \times 0.4184 \times \frac{J}{K\,gm} \times 2.303 \log \frac{T_f}{393}.$$

$$\Delta S_c = m_c C_{p,c} \times 2.303 \log \frac{T_f}{T}.$$

$100\ gm \times 0.4184\ J/K\,gm \times 2.303 \times \log T_f/323.$

Case-IV → solid → liquid (solid melts in liquid)
(specific case)

when solid is dropped in liquid and solid starts melts in liquid.

Let us consider, m_c gram of, ice of $0°c$ is dropped in m_H gm of water at T_H.

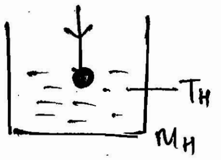
① Final Temp

② ΔS_c / ΔS_H.

Heat given by hot body = Heat taken by cold body.

$$\underset{0°c}{\text{Ice}} \longrightarrow \underset{0°c}{\text{liquid}} \quad (\text{Ice is conved to water}) \quad \Delta H_f \quad \Delta S = \frac{\Delta H_f}{273}$$

$$\underset{0°c}{\text{liquid}} \longrightarrow \underset{T_H}{\text{liquid}} \qquad \Delta S = m_c C_{p,wat} \ln\frac{T_H}{273}$$



$$\underset{T_H}{\text{liquid}} \longrightarrow \underset{T_f}{\text{liquid}}$$

$$\Delta S_h = m_h C_{p,water} \ln\frac{T_f}{T_h}.$$

$$\boxed{-m_h C_{p,water}(T_f - T_h) = m_c \Delta H_f + m_c C_{p,w}(T_f - 273)}$$

गरम पानी का T_f पर पहुँचना

ice convert $0°c$

water का $0°c$ से T_f का reach करना.

① $$\Delta S_c = \frac{m_c \Delta H_f}{273} + m_c C_{p,water} \ln\left(\frac{T_f}{273}\right)$$

② $$\Delta S_h = m_h C_{p,wat} \times \ln\frac{T_f}{T_h}$$

⑦ $m_c = 5 gm$

$T_c = 273 K = 0^\circ C$

$m_H = 30 gm$

$T_H = 323 K$.

$C_{P,\,water} = 4.184 \ J/K gm$ $\quad \Delta H_f = 334.72 \ J/K.gm$

Heat given by hot wat to reach at T_f = heat taken by ice to convert into cold water + heat taken by cold water to reach at T_f.

$$= -m_h C_{P\,wat} [T_f - T_h] = m_c \Delta H_f + m_c C_{P,\,wat} (T_f - T_c)$$

$$-30 \ gm \times 4.184 \frac{J}{K gm} (T_f - 323) = 5 \times 334.72 \frac{J}{K gm} + 5 gm \times 4.184 \ J/K gm \ (T_f - 273)$$

$$\Delta S_c = \frac{m_c \Delta H_f}{273} + m_c C_{P,\,water} \times 2.303 \times \log \frac{T_f}{273}$$

$$= \frac{5 gm \times 334.72}{273} + 5 gm \times 4.184 \ J/K gm \times 2.303 \times \log \frac{T_f}{273}.$$

Entropy of mixing of gas:

(i) Ideal mixing of ideal gas –

Conditions: (E.P.V) *

(i) $\Delta V_{mix} = 0$.

(ii) $\Delta H_{mix} \neq 0$

(iii) Isothermal & Isobaric

(iv) No chemical rea^n should be there

(v) gas behave ideally.

(vi) $\Delta U_{mix} = 0$

✓ (vii) $\Delta S_{mix} = +ve$

✓ (viii) $\Delta G_{mix} = -ve$.

$$\boxed{\Delta S_{mix} = -2.303\, R \sum n_i \log x_i}$$ $$\boxed{\Delta S_{mix} = -R \sum n_i \ln x_i}$$

n_i = mole of ith gm.

$x_i = \frac{n_i}{\sum n_i} = \frac{n_i}{N}$ x_i = mole frac^n

* If two gas with amount n_1 & n_2 are mixed ideally,

$$\Delta S_{mix} = -2.303R\left[n_1 \log x_1 + n_2 \log x_2\right] \quad x_1 = \frac{n_1}{n_1+n_2},\ x_2 = \frac{n_2}{n_1+n_2}$$

* If 3 gases with amount n_1, n_2 & n_3 are mixed ideally,

$$\Delta S_{mix} = -2.303R\left[n_1 \log x_1 + n_2 \log x_2 + n_3 \log x_3\right]$$

8)

$\Delta S_{mix} = -2.303\ R\ J\ K^{-1} mol^{-1} \sum n\ mol\ \log x_i$

unit = J/K. ΔS_{mix} = +ve.

$\log(x_i) = \log(\text{frac}) = -ve.$

① $\Delta S = \frac{\Delta H}{T}$ ΔH_{vap} : water vapourising at 100°C.

$= \frac{44\ kJ/mole}{1\ atm.}$

$= 44 \times 10^{3}$ [illegible]

373 [illegible]

$= 110\ J/K$

$$\Delta G_{mixing} = \Delta H_{mix} - T\Delta S_{mix}$$

$\downarrow$ Ideal

0

$$\Delta G_{mix} = -T\Delta S_{mix}$$

$$\boxed{\Delta G_{mix} = +2.303\, RT \sum n_i \log x_i}$$ $\log x_i = -ve.$

$\Delta G_{mix} = -ve.$

Total entropy of mixing $\Delta S_{mix} = -R \sum n_i \ln x_i$. (for n mole)

molar entropy of mixing (for 1 mole)

$$\underset{(molar)}{\Delta S_{mix}} = -R \sum \frac{n_i}{n} \ln x_i$$

$$\boxed{\underset{total}{\Delta S_{mix}} = -nR \sum x_i \ln x_i}$$

$$\boxed{\Delta S_{mix} = -R \sum x_i \ln x_i}$$

(14) $n_1 = 10$ mole

$n_2 = 10$ mole

$$x_1 = \frac{n_1}{n_1+n_2} = \frac{10}{10+10} = \frac{1}{2}$$

$$x_2 = \frac{n_2}{n_1+n_2} = \frac{10}{10+10} = \frac{1}{2}.$$

$$\Delta S = -2.303R\left[n_1 \log x_1 + n_2 \log x_2\right]$$

$$= -2.303\ 8.314\left[10\log\frac{1}{2} + 10\log\frac{1}{2}\right]$$

$$= -2.303 \cdot 8.314\left[-10\log 2 - 10\log 2\right]$$

(15) $$\Delta S = -2.303\left[n_1\log x_1 + n_2\log x_2 + n_3\log x_3\right]$$

$$x_1 = \frac{n_1}{n_1+n_2+n_3} = \frac{2}{2+3+2}$$

$$x_2 = \frac{3}{2+3+2}$$

$$x_3 = \frac{2}{2+3+2}.$$

(12) $n_1 = 1$ $\quad x_1 = \frac{1}{1+1+2} = \frac{1}{4}$

$n_2 = 1$ $\quad x_2 = 1/4,\ x_3 = 2/4 = 1/2.$

$n_3 = 2$

$$\ln\frac{m}{n} = -\ln\frac{n}{m}$$

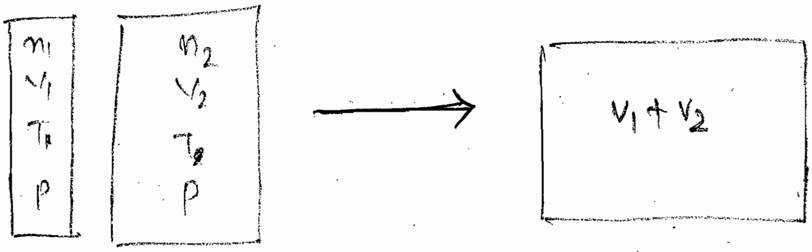
$$\Delta S_{mix} = -R\left[n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3\right]$$

$$= -R\left[1\ln 1/4 + 1\ln 1/4 + 2\ln 1/2\right]$$

The expression ΔS_{mix} may be justified by the, Entropy depends depen mole.

$$\Delta S_{Isothermal} = nR \ln V_2/V_1$$

Let us consider,



$$\Delta S_1 = n_1 R \ln \frac{V_f}{V_1} = n_1 R \ln \frac{V_1+V_2}{V_1}$$

$$\Delta S_2 = n_2 R \ln \frac{V_f}{V_2} = n_2 R \ln \frac{V_1+V_2}{V_2}$$

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= n_1 R \ln \frac{V_1+V_2}{V_1} + n_2 R \ln \frac{V_1+V_2}{V_2}$$

$$= n_1 R \ln \frac{V_1}{V_1+V_2} - n_2 R \ln \frac{V_2}{V_1+V_2}$$

$$V_1 = \frac{n_1 RT}{P}$$

$$V_2 = \frac{n_2 RT}{P}$$

$$\frac{V_1}{V_1+V_2} = \frac{n_1}{n_1+n_2} = x_1$$

$$\frac{V_2}{V_1+V_2} = \frac{n_2}{n_1+n_2} = x_2.$$

$$\Delta S = -R \sum n_i \ln x_i$$

$$\Delta S = -R [n_1 \ln x_1 + n_2 \ln x_2]$$

$$\boxed{\Delta S = -n_1 R \ln x_1 - n_2 R \ln x_2.}$$

Gibb's Paradox:

For entropy of mixing to exist mixed molecular species must be chemically or physically distinct if molecular species are identical there is no entropy change on mixing them. Hence, Gibbs free entropy of is also zero. It is considered that there is no mass transfer no thermodynamically recognised process of mixing is generally known as "Gibb's paradox".

Ex: 1 mole N_2
2 mole N_2
1 mole N_2
} same gas.
$\Delta S_{mix} = 0$
$\Delta G_{mix} = 0$.

1 mole N_2
2 mole N_2 = 3 mole N_2
2 mole O_2 — 2 mole O_2
$\Delta S \neq 0$.

Q. Show that for binary mixture of ideal gas the entropy of mixing is maxᵐ when mole fracⁿ of both gases are equal.
[It is considered that gas is mixed ideally]

* <u>Binary gas mixture</u> (when two gas are given we have to see their moles)
$\Delta S_{mix} = max$
$x_1 = x_2 = 1/2$
$\Delta G_{mix} = min$

* <u>Ternary gas mix</u>
$\Delta S_{mix} = max$ $x_1 = x_2 = x_3 = 1/3$.
$\Delta G_{mix} = min$

<u>imp</u> For 3 type of gas ΔS_{mix} = max when all the 3 gas have same fracⁿ of magnitude

* If n gas are mixed ideally,
$\Delta S_{mix} = max$ $x_1 = x_2 = \cdots\cdots \frac{1}{n}$
$\Delta G_{mix} = min$ $x_1 = x_2 = \cdots\cdots 1/n$.

<u>To Proof:</u>

ⓐ $\Delta S_{mix} = -nR \sum x_i \ln x_i$

$$= -nR\left[x_1 \ln x_1 + x_2 \ln x_2\right]$$

For binary mix = $x_1 + x_2 = 1$

$$\boxed{x_2 = 1 - x_1}$$

$$\Delta S_{mix} = -nR\left[x_1 \ln x_1 + (1-x_1)\ln(1-x_1)\right]$$

ΔS_{mix} is max in terms of mole frac^n only when $\frac{\partial \Delta S_{mix}}{\partial x_1} = 0$

$$\frac{\partial \Delta S_{mix}}{\partial x_1} = 0 = -nR\left[\frac{\partial}{\partial x_1} x_1 \ln x_1 + \frac{\partial}{\partial x_1}(1-x_1)\ln(1-x_1)\right] = 0$$

$$\frac{\partial}{\partial x_1} x_1 \ln x_1 = \overset{I}{x_1}\frac{\partial}{\partial x_1}\ln \overset{II}{x_1} + \ln \overset{II}{x_1}\frac{\partial}{\partial x_1}\overset{I}{x_1}$$

$$= x_1 \cdot \frac{1}{x_1} + \ln x_1 \cdot 1$$

$$= 1 + \ln x_1.$$

$$\frac{\partial}{\partial x_1}\overset{I}{(1-x_1)}\ln\overset{II}{(1-x_1)}$$

$$= \overset{I}{(1-x_1)}\frac{\partial}{\partial x_1}\ln\overset{II}{(1-x_1)} + \ln\overset{II}{(1-x_1)}\frac{\partial}{\partial x_1}\overset{I}{(1-x_1)}$$

$$= (1-x_1)\frac{-1}{1-x_1} + \ln(1-x_1)[-1]$$

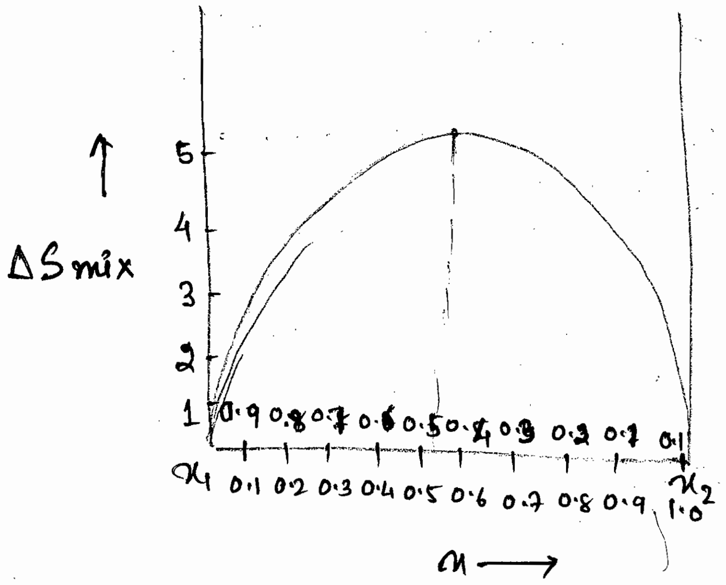
$$= -1 - \ln(1-x_1)$$

$$\frac{\partial}{\partial x}(1-x_1)$$

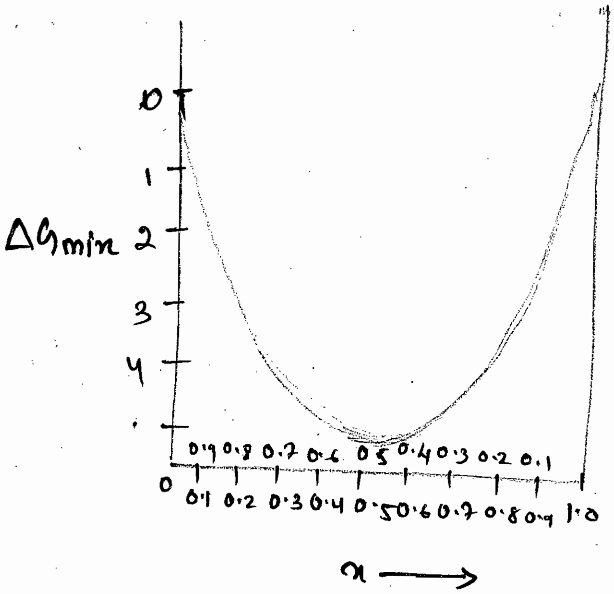
$$= \frac{\partial}{\partial x_1}1 - \frac{\partial}{\partial x_1}x_1$$

$$= 0 - 1 = -1.$$

("Reverse Bowl Shape")



("Bowl Shape")



Non-Ideal mixing of ideal gas :

If only one or more Condition corresponding to Ideal mixing of ideal gas is violated then it becomes under the category of non-ideal mixing of ideal gas. And conventional formula for entropy change in terms of P,V,T apply.

$$\Delta S = 2.303\, n C_v \log \frac{T_2}{T_1} + 2.303\, nR \log V_2/V_1.$$

$$\Delta S = 2.303\, n C_p \log \frac{T_2}{T_1} - 2.303\, nR \log P_2/P_1.$$

Q. 1 dm^3 of methane at 298K and 1atm with 3 dm^3 of N_2 at 298K and 1 atm is forcefully poured into a 2 dm^3 evacuated container. Find the entropy change.

soln $$\Delta S_{methane} = \cancel{2.303\, n C_v \log \frac{T_2}{T_1}} + 2.303\, nR \log \frac{V_2}{V_1}$$

T fix.

$$\Delta S_{methane} = n_{methane} \times 2.303 \times R \times \log \frac{V_f}{V_i}$$

V_i methane = 1 dm^3

$V_f = 2 dm^3$

$$n_{methane} = \frac{PV}{RT} = \frac{1\,atm \times 1\,dm^3}{0.0821\, \frac{L\,atm}{K\,mole} \times 298K}.$$

$$n_{N_2} = \frac{PV}{RT} = \frac{1\,atm \times 3\,dm^3}{0.0821\,\frac{dm^3.atm}{K\,mole} \times 298\,K}$$

$$\Delta N_2 = 2.303\, n_{N_2} R \log \frac{V_f}{V_{i,N_2}} \qquad V_i = 3dm^3 \quad V_f = 2dm^3.$$

② 2 mole of He.
1 mole of N_2 in mixed ideally ΔS_{He}, ΔS_{N_2}

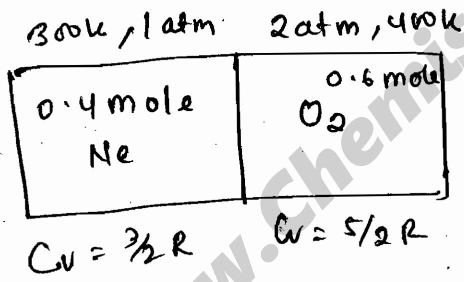
Sol^n $\Delta S = -2.303\, R\left[n_{He} \log x_{He} + n_{N_2} \log x_{N_2}\right]$

$= -2.303\, R\, n_{He} \log x_{He} - 2.303\, R\, n_{N_2} \log x_{N_2}.$

$\Delta S_{He} = -2.303 R\, n_{He} \log x_{He}$

$= -2.303 \times 8.314 \times 2 \times \log 2/3.$

Q.



A container is partitioned into 2 part as given in the fig. the gases filled at diff variable in the container is shown. If the partition is removed than what is value of ΔS_{mix}.

sol^n: $\Delta S_{Ne} = 2.303\, n\, C_v \log \frac{T_2}{T_{1\,Ne}} + 2.303\, n\, R \log \frac{V_f}{V_{i\,Ne}}$

$$V_{i,Ne} = \frac{n_{Ne} R T_{Ne}}{P_{Ne}} = \frac{0.4\,mole \times 0.0821\,\frac{L.atm}{K.mole} \times 300\,K}{1\,atm.}$$

$$V_{i,O_2} = \frac{n_{O_2} R T_{O_2}}{P_{O_2}} = \frac{0.6\,mole \times 8.314\,J/K.mole \times 400\,K}{2\,atm.}$$

To get T_f apply conserⁿ of heat law,

$$T_f = \frac{n_{Ne} C_{v,Ne} T_{Ne} + n_{O_2} C_{v,O_2} T_{O_2}}{n_{Ne} C_{v,Ne} + n_{O_2}, C_{v,O_2}}.$$

$T_{i,Ne} = 300\,K.$

$$\Delta S_{N_2} = 2.303\, n_{Ne} C_{v,Ne} \log \frac{T_f}{N_{i\,Ne}}$$

DPP-10

③ . $n_1 = 2\text{mole}$

$n_2 = 3\,\text{mole}$

$$x_1 = \frac{2}{2+3} = 2/5$$

$$x_2 = \frac{3}{5}.$$

$$\Delta G = 2.303\,RT\,[n_1 \log x_1 + n_2 \log x_2]$$

DPP-9

(12) N_2 O_2 =

$V_f = 44.8$ $V_f = 44.8$

$V_i = 33.6\,L$ $V_i = 22.4$

$T = 300\,K$, 1atm $T = 300\,k$

$$n_{N_2} = \frac{PV}{RT}.$$

$$n_{O_2} = \frac{PV}{RT}$$

$22.4 + 33.6 = 56\,L$ (Non-ideal)

$$\Delta S_{N_2} = 2.303\, \cancel{n C_v}\, \log \frac{T_2}{T_1} + 2.303\, nR\, \ln \frac{V_f}{V_{i\,N_2}},$$

Clayperon - Clasius eq^n:

Change in Temp w.r.t change in pressure. ($\frac{dT}{dp}$)
(Transition point)
or
Change in pressure w.r.t Change in temp ($\frac{dP}{dT}$) in a case of a Reversible phase Tran^n was studied by "Clayperon."

It is generally differential form. Further it was Integrated by "Clasius."

Clayperon eq^n is applicable to "First Order phase trans^n".

- → 1st derivate of G changes (i.e S and V)
- → But G_P = do not change, it is contineous.
- → S changes, V changes.
- → The 1st derivative of gibbs free energy(s) (i.e S,V) Changes during the phase trans^n.
- → Derivative of G are discontineous.

Clayperon - Equation:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

$$\begin{array}{ccc} S & \longrightarrow & L \\ T_m & & T_m \\ 1\,atm & \longrightarrow & 1\,atm \end{array}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H_m}{T\Delta V}}$$

The change in p w.r.t T depends on entropy change, Vol^m & enthalpy change

$$S \xrightarrow{\Delta H = +ve} L \qquad \boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}, \quad \frac{dT}{dP} = \frac{T\Delta V}{\Delta H}}$$

$$\Delta V = V_l - V_s.$$

$l \longrightarrow s$

$$\boxed{\frac{dp}{dT} = \frac{\Delta H}{T\underset{V_s - V_l}{\underset{\downarrow}{\Delta V}}}, \quad \frac{dT}{dp} = \frac{T\Delta V}{\Delta H}}$$

$l \rightarrow v$

$$\boxed{\frac{dp}{dT} = \frac{\Delta H_v}{T\Delta V} = \frac{\Delta H_v}{T(V_v - V_l)}}$$

$V \rightarrow l$

$$\boxed{\frac{dp}{dT} = \frac{\Delta H_{vap}}{T(V_l - V_v)}}$$

$s \rightarrow v$

$$\boxed{\frac{dp}{dT} = \frac{\Delta H_{sub}}{T(V_v - V_s)}}$$

Let us consider a rev phase transfⁿ from A to B occur at temp T, Press P.

$A \longrightarrow$	B
T	T
P	P
V_A	V_B
S_A	S_B
G_A	G_B
$\Delta G = 0$	~~Δ~~ $G_A = G_B$

Now pressure p is changed by dp if corresponding change in temp is dT press G_A becomes $G_A + dG_A$

G_B becomes $G_B + dG_B$.

$A \longrightarrow$	B
$T + dT$	$T + dT$
$P + dp$	$p + dp$.
V_A	V_B
S_A	S_B
$G_A + dG_A$	$G_B + dG_B$.

$$\Delta G = 0$$

$$G_B + dG_B - G_A - dG_A = 0.$$

$$dG_B = dG_A$$

$$V_B dp - S_B dT = V_A dp - S_A dT.$$

$$(V_B - V_A) dp = (S_B - S_A) dT$$

$$\frac{dp}{dT} = \frac{(S_B - S_A)}{(V_B - V_A)} = \frac{\Delta S}{\Delta V}$$

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

$$\frac{dp}{dT} = \frac{T\Delta S}{T\Delta V}.$$

$$\boxed{\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}}$$

Application of Clayperon eqⁿ :

1. Effect of pressure on B.P :

$$\begin{array}{ccc} L & \longrightarrow & V \\ T_b & & T_b \\ 1\,atm & & 1\,atm \end{array}$$

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{T(V_v - V_L)} = \frac{+ve}{+ve} = +ve.$$

$$\boxed{\frac{dp}{dT} = +ve.}$$

If P increases	$dp = +ve.$	$dp = -ve$
If T increase	$dT = +ve.$	$dT = -ve$

So, with increase in pressure Boiling point increases and vice-versa.

(ii) Effect of pressure on M.P:

$$S \longrightarrow L$$

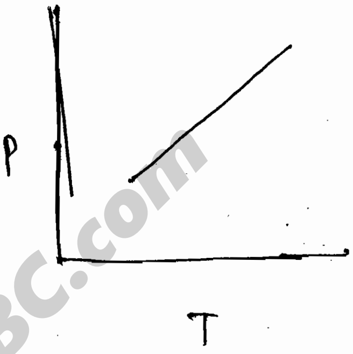
$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = +ve.$$

$$\Delta V \begin{cases} +ve \\ -ve. \end{cases}$$

(i) If ΔV is positive $V_l > V_s$ (sulphur, wax)

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{T(V_l - V_s)} = \frac{+ve}{+ve} = +ve.$$

with increase in pressure, m.p increases.

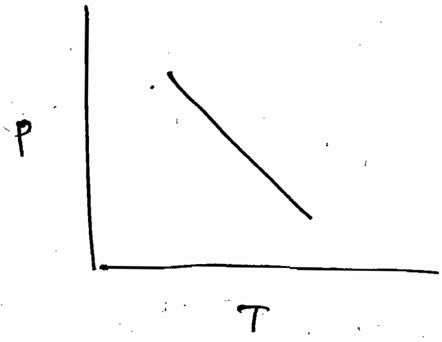


(ii) If ΔV is $-ve$ $V_s > V_l$ (water)

$$\Delta V = V_l - V_s = -ve.$$

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{+ve}{-ve} = -ve.$$

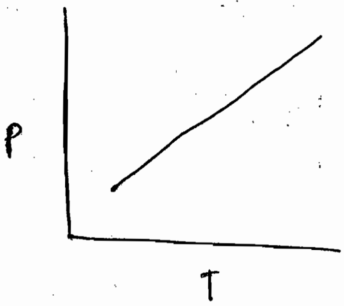
with increase in pressure, m.p decreases.



(iii) $S \longrightarrow V$

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{T(V_v - V_s)} = +ve$$

$$\frac{dP}{dT} = +ve \qquad V_v > V_s.$$

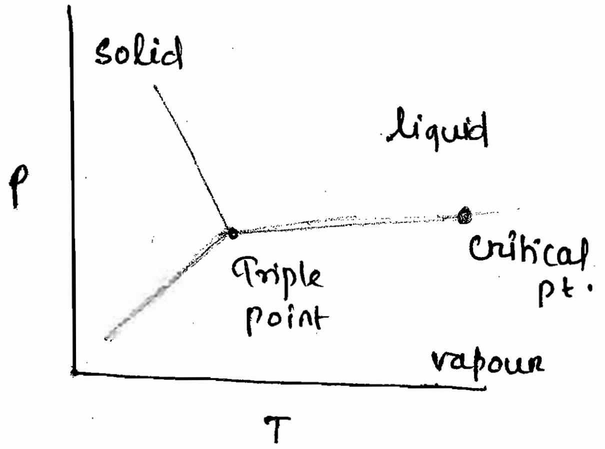


(water) (Note)

$l \rightarrow V$ $dP/dT = +ve.$

$S \rightarrow V$ $dP/dT = +ve$

$S \rightarrow L$ $dP/dT = -ve.$



8) $\frac{dP}{dT} = 400K.\ 8\times10^{-3}$ bar/K.

$T = 400K.$

$V_v = 200$ L/mole.

$V_l = 0$

$\Delta H = ?$

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_v - V_l)}$$

$$\frac{dP}{dT} = \frac{\Delta H}{400K(200)\,L/mole.}$$

$\Delta H = 8\times10^{-3}\ \frac{bar}{\cancel{K}} \times 400\cancel{K} \times 200$ L/mole

$= 8\times10^{-3} \times 80000$ L.bar/mole

L.bar = 100 J.

$= 64\times10^{-3}\times10^{6}$

$= 64\times10^{3}$ J/mole.

$= 64$ kJ/mole.

㉔ $l \longrightarrow s \qquad s \longrightarrow l$

$V_l = 1.001\ \frac{mL}{gm} \qquad T = 0^{\circ}C = 273K.$

$V_s = 1.0907\ \frac{mL}{gm}$

$\downarrow$
ice

$\Delta H_f = 333.88$ J/gm $\qquad \frac{dT}{dP} = ?$ K/atm

$l \longrightarrow s \qquad \Delta H = -ve.$

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_s - V_l)}$$

$$\frac{dT}{dP} = \frac{T(V_s - V_l)}{\Delta H}$$

$$= \frac{273K(1.0907 - 1.001)\times10^{-3}\ L/gm}{-333.88\ J/gm.}$$

$$= -\frac{273\cancel{K}\ 0.089\times10^{-3}\ \cancel{L}.K}{333.8\cancel{J}\times\frac{0.0821\cancel{L}atm}{8.314\cancel{J}}}$$

$= -0.0075$ K/atm.

14

$l \longrightarrow v$

contineous

$\Delta G =$ contineou.

Integreated form of Clayperon equation

[Clanius - clayperon Equation]

(i) In case of melting:

$$s \longrightarrow l$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad \frac{dP}{dT} = \frac{\Delta H}{T\Delta V}.$$

$\downarrow$

$$dP = \frac{\Delta S}{\Delta V}\, dT$$

It is considered that ΔS & ΔV is Independent of Temp.

$$\int_{P_1}^{P_2} dP = \frac{\Delta S}{\Delta V}\int_{T_1}^{T_2} dT$$

$$P_2 - P_1 = \frac{\Delta S}{V_l - V_s}(T_2 - T_1)$$

$$\boxed{P_2 = P_1 + \frac{\Delta S}{V_l - V_s}(T_2 - T_1)}$$

$\downarrow$

$$\int_{P_1}^{P_2} dP = \frac{\Delta H}{\Delta V}\int_{T_1}^{T_2} \frac{dT}{T}.$$

$$P_2 - P_1 = \frac{\Delta H}{\Delta V}\ln\frac{T_2}{T_1}$$

$$P_2 = P_1 + \frac{\Delta H}{V_l - V_s}\ln\frac{T_2}{T_1}$$

$$\boxed{P_2 = P_1 + \frac{\Delta H}{V_l - V_s} \times 2.303 \log\frac{T_2}{T_1}}$$

ml → L → J → bar

(18) Ice → water

$T_1 = 0°C \qquad P_1 = 1$ bar

$T_2 = -10°C \qquad P_2 = ?$

$\Delta S = 22.04$ J/K mole

$V_l = 18.01$ ml/mole

$V_s = 19.64$ ml/mole

Integrated from of clayperon eqn in the form of vapourisation :

(ii) In case of vapourisation,

$l \rightarrow v.$

$$\frac{dp}{dT} = \frac{\Delta H_v}{T(V_v - V_l)}$$

$V_v >> V_l$

$$\frac{dp}{dT} = \frac{\Delta H_v}{T V_v}$$

If vapour behave ideally,

$$V_v = \frac{RT}{P}.$$

So, $\frac{dp}{dT} = \frac{\Delta H_v}{T \frac{RT}{P}}$

$$\boxed{\left(\frac{dp}{dT}\right)_{l \rightarrow v} = \frac{\Delta H_v}{RT^2} \cdot P}$$

slope of diagram of P vs T in the vapour. $(l \rightarrow v)$

$$\frac{dp}{p} = \frac{\Delta H_v}{R} \cdot \frac{dT}{T^2}$$

If is considered that ΔH_v is Independent of temp,

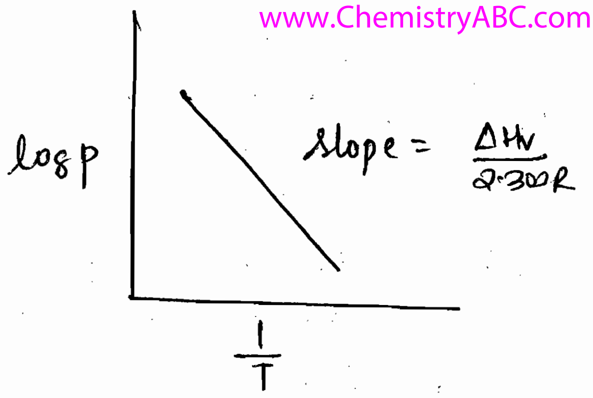
$$\int \frac{dp}{p} = \frac{\Delta H_v}{R} \int \frac{1}{T^2} dT \quad \text{(with out limit)}$$

$$\ln p = \frac{\Delta H_v}{R} \left[-\frac{1}{T}\right] + \text{const.}$$

$$\boxed{\ln p = -\frac{\Delta H_v}{R} \frac{1}{T} + \text{const}}$$

$$2.303 \log P = -\frac{\Delta H_v}{R} \cdot \frac{1}{T} + \text{const}$$

$$\boxed{\log P = -\frac{\Delta H_v}{2.303 R} \cdot \frac{1}{T} + \text{const}}$$



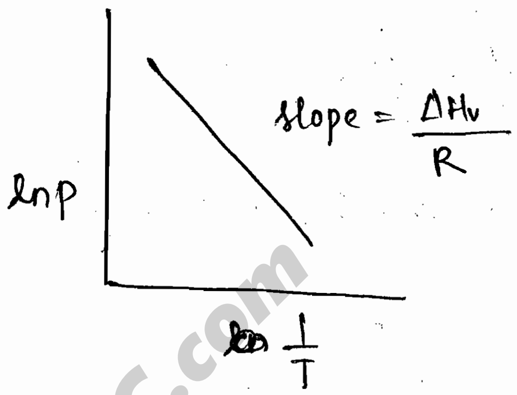
Integrⁿ with limit

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{1}{T^2}\, dT$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2}$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_v}{R} \left[\frac{1}{T} \right]_{T_1}^{T_2}$$

$$= -\frac{\Delta H_v}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$



$$\int \frac{1}{T^2} dT = \int T^{-2} dT$$

$$= \frac{T^{-2+1}}{-2+1}$$

$$= \frac{T^{-1}}{-1}$$

$$= -\frac{1}{T}$$

$$\boxed{\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\boxed{\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]}$$

(21) $P_1 = 2.02 \times 10^3$ N/m² $T_1 = 293$ K.

$\Delta H_{vap} = 41$ kJ/mole.

$T_b = T_2 = ?$ $P_2 = 1$ atm $= 101325$ N/m² $= 1.01325 \times 10^5$ N/m²

$$\log P_2/P_1 = \frac{\Delta H_v}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right].$$

⑨ $C_6H_6(l) \longrightarrow C_6H_6(v)$

$\Delta H = 33.90 \frac{kJ}{mole}$.

$\Delta S = 96.4\ J/K\ mole$.

$$\Delta S = \frac{\Delta H}{T_b}$$

$$T_b = \frac{\Delta H}{\Delta S} = \frac{33.90\times10^3}{96.4} = 352$$

$T_1 = T_b = 352$, $P_1 = 1\ atm = 760\ Torr$.

T_2 ?? $P_2 = 35\ torr$.

$$\log\frac{P_2}{P_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Integration form of clayperon eq^n for $subli^m$ +ve process:

$$S \longrightarrow V$$

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_v - V_s)}$$

$$V_v > V_s.$$

$$\frac{dp}{dT} = \frac{\Delta H_{sub}}{T V_v}$$

$$V_v = \frac{RT}{P}$$

$$\frac{dp}{dT} = \frac{\Delta H_{sub}}{T\cdot\frac{RT}{P}} = \boxed{\left(\frac{dp}{dT}\right)_{s\to v} = \frac{\Delta H_{sub}}{RT^2}\cdot p}$$

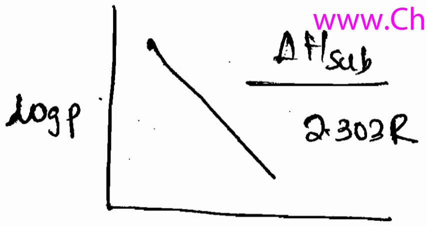
$$\frac{dp}{P} = \frac{\Delta H_{sub}}{R}\frac{dT}{T^2}$$

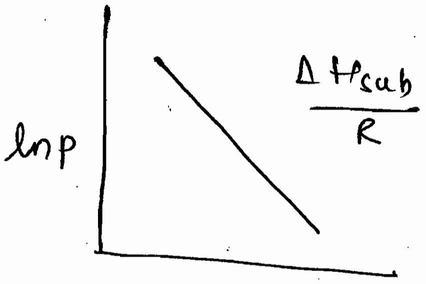
$$\int\frac{dp}{P} = \frac{\Delta H_{sub}}{R}\int\frac{dT}{T^2}$$

without limit

$$\boxed{\ln p = -\frac{\Delta H_{sub}}{R}\cdot\frac{1}{T} + \text{const}}$$

$$\boxed{\log p = -\frac{\Delta H_{sub}}{2.303R}\cdot\frac{1}{T} + \text{const}.}$$





with limit Integr^n

$$\int_{P_1}^{P_2}\frac{dp}{p} = \frac{\Delta H_{sub}}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{sub}}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2}$$

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H_{sub}}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

$$\boxed{\ln\frac{P_2}{P_1} = \frac{\Delta H_{sub}}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]}$$

$$\boxed{\log\frac{P_2}{P_1} = \frac{\Delta H_{sub}}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]}$$

⑦ $\log_e p^{solid} = 24 - \frac{3900}{T}$

$\log_e p^{liquid} = 18 - \frac{2600}{T}$

$\log_e p^{solid} = -\frac{\Delta H_{sub}}{R}\cdot\frac{1}{T} + \text{const}$

$= \text{const} - \frac{\Delta H_{sub}}{R}\cdot\frac{1}{T}$

$\frac{\Delta H_{sub}}{R}\cdot\frac{1}{T} = \frac{3900}{T}$

$\Delta H_{sub} = 3900R$

$\log_e \text{liquid} = 18 - \frac{2600}{T}$

$= \text{const} - \frac{\Delta H_{vap}}{RT}$

$\frac{\Delta H_{vap}}{RT} = \frac{2600}{T}$

$\Delta H_{vap} = 2600R$

$$\frac{\left(\frac{dp}{dT}\right)_{s\to v}}{\left(\frac{dp}{dT}\right)_{l\to v}} = \frac{3900R}{2600R} = 1.5$$

(b) $P_1 = 5333$ Pa

$T_1 = 7.6°C = 273 + 7.6 = 280.6$ K.

$P_2 = 53330$ Pa

$T_2 = 60.6 = 273 + 60.6 = 333.6$ K.

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$T_b = T_3 = ?$ $\quad T_3 = 1\,atm = 101325$ Pa.

$$\log \frac{P_3}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_3 - T_1}{T_1 T_3}\right]$$

Q.17 At triple $S \rightarrow L$, $L \rightarrow V$ trans^n met with each other.

$\ln p^{solid} = -8750\frac{K}{T} + 34.143$ ①

$\ln p^{liq} = -4053\frac{K}{T} + 21.10$ — ②

$$-8750\frac{K}{T} + 34.143 = -4053\frac{K}{T} + 21.10$$

$T_{Tr} = ?$

To get P_{Tr} put T_{Tr} in any eq^n given above.

⑲ $\log p = 10 - \frac{1800}{T}$ (solid)

$\log p = 8 - \left(\frac{1400}{T}\right)$ (liquid)

At triple point,

$$10 - \frac{1800}{T} = 8 - \frac{1400}{T}$$

$$(10 - 8) = \frac{1800 - 1400}{T}$$

$$2 = \frac{400}{T}$$

$$\boxed{T_{Tr} = 200}$$

⑳ $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = 10.5R$

$$\frac{\Delta H_{vap}}{273 + 110} = 10.5 \times 8.314$$

$$\boxed{\Delta H_{vap} = 10.5 \times 8.314 \times 383}$$

$T_1 = 100°C = 373$ K

$P_1 = ?$

$T_b = T_2 = 273 + 110 = 383$

$P_2 = 1$ atm.

(13) $X_2O_4(l) \longrightarrow 2XO_2(g)$

$\Delta U = 9000\,J$ $T = 298\,K$

$\Delta S = 84\,J/K$ $\Delta n_g = 2$

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

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

(40) ② $V \xrightarrow{cond} l$ $\Delta H = -ve$

exo.

$\Delta S = \frac{\Delta H}{T} = -ve$

$S_l - S_v = -ve$

$S_v > S_l$ (True)

b $\overset{L}{w} \longrightarrow V$

$\Delta S = +ve.$

$S_v - S_l = +ve.$

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

$= \Delta U + P(V_v - V_l)$

$\Delta U - \Delta H = -P(+ve)$

$\Delta U - \Delta H < 0.$

$$\boxed{\left(\frac{dp}{dT}\right)_{s\to l} > \left(\frac{dp}{dT}\right)_{s\to v} > \left(\frac{dp}{dT}\right)_{l\to v}}$$

Note

At 100°c $l \longrightarrow V$

$\Delta G = 0$ $\Delta G = 0.$

(non-spont)

when temp goes on

i.e 105°c . . .

$\Delta G = -ve.$

(spontaneous)

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

$0 = -$

$\boxed{\Delta G = -ve}$

DPP-11

1. $P_2 = P_1 + \frac{\Delta S}{V_l - V_s}(T_2 - T_1)$

$T_1 = 0^\circ c$, $P_1 = 1 ban$
$= 273 K.$

$T_2 = -10^\circ c = 263 K$ $P_2 = ?$

$P_2 = 1 ban + \frac{16.3 J/K}{18.01 mL - 19.64 mL}(263 - 273) K.$

$= 1 ban + \frac{16.3}{-1.63 mL}(-10)$

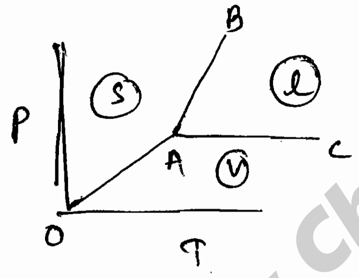
$= 1 ban + \frac{163}{1.63 \times 10^{-3} L} = 1 ban + \frac{163 \times 10^{-2} L bar}{1.63 \times 10^{-3} L}$

$1 L bar = 10^2 J.$

$1 J = 10^{-2} L b$

$= 1 ban + \frac{1}{10^{-3}} ban = 1 + 1000 = 1001 ban.$

2.



$\tan\theta = \frac{\sin\theta}{\cos\theta}$

$\tan\theta = \frac{1}{\cot\theta}.$

$\left(\frac{dp}{dT}\right)_{s \to l} = \tan \pi/3$ ~~tan~~ $\left(\frac{dp}{dT}\right)_{l-v} = \tan \pi/6.$

$\left(\frac{dp}{dT}\right)_{s \to v} = \tan \pi/4$

$s \to l$; $T = 300 K$, $\Delta H = 3 kJ = 3000 J.$

$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}.$ $\Delta V = \frac{10}{\tan \pi/3}$

$\tan \pi/3 = \frac{3000 J}{300 K \Delta V} =$ $= 10 \cot \pi/3.$

At equlm
$\Delta G = 0$
So, p const
T = const

④ $\Delta S = -2.303\, R\, n_{Ne} \log x_{Ne}$.

$= -2.303\, R \times 3 \log 3/5$

⑤ $\ln p = 23 - (3863/T) = \cancel{s}$

$\ln p = 19 - (3063/T)$

At triple point,

$$23 - \left(\frac{3863}{T}\right) = 19 - \left(\frac{3063}{T}\right).$$

⑯ $\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{0} = \infty$.

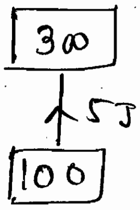
$\frac{dp}{dT} = \infty,\ \frac{dT}{dp} = 0$.

$dT = 0$

T = const. (1).

⑰ At triple point only 3 phases meet.

⑳ $\beta = -\frac{Q_c}{w} = \frac{T_c}{T_H - T_c}$



Criteria of Spontanity:

$dS_{system} + dS_{surrounding} = 0$ (for reversible).

$dS_{sys} + dS_{surr} > 0$ (for Irreversible)

$dS_{sys} + dS_{surr} = dS_{universe}$.

In case of reversible process, (Ideal)

Surrounding gives heat dq at T.

$$dS_{surr} = -\frac{dq}{T}$$

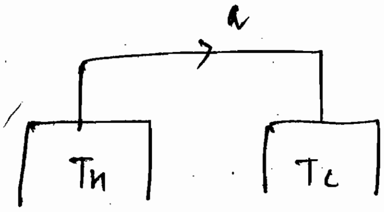
Sys takes heat rev dq at T

$$dS_{sys} = +\frac{dq}{T}.$$

$$\boxed{dS_T = 0}$$

Irreversible process (Natural)

So, we can take an ex from nature.



heat flow from hot body to cold body

$$\Delta S_H = -\frac{q}{T_h}$$

$$\Delta S_c = +\frac{q}{T_c}$$

$\Delta S_h + \Delta S_c$

$$= \frac{q}{T_c} - \frac{q}{T_h} = q\left[\frac{T_h - T_c}{T_h T_c}\right] = +ve \quad T_h = +ve.$$

(11) $n = 1$ mole

Isothermally $T_1 = T_2$

$V_1 = 1.0\ dm^3$

$V_2 = 10.0\ dm^3.$

$$\Delta S_{sys} = 2.303\ \cancel{nC_v \log \frac{T_2}{T_1}}^{\,0} + n\,2.303\ R \log V_2/V_1$$

(Isothermal)

$$= 2.303 \times 2\ \frac{cal}{K} \log 10.$$

$$= 4.606\ cal/K.$$

$$dS_{sys} + \Delta S_{surr} = 0.$$

$$dS_{surr} = -\Delta S_{sys}.$$

$$= -4.6.$$

Let us consider Surrounding gives heat dq at temp T.

$$dS_{surr} = -dq/T.$$

$$dS_{sys} - \frac{dq}{T} = 0.$$

$$\boxed{ds \geq \frac{dq}{T}}$$ Clausius Inequality. $\oint ds \geq \oint \frac{dq}{T}$

$$\boxed{ds > \frac{dq}{T} \text{ for Irrev}}$$

$$\boxed{ds = \frac{dq}{T} \text{ for Reversible}}$$

$$0 \geq \oint \frac{dq}{T}$$

$$\oint \frac{dq}{T} \leq 0.$$

In Adiabatic condition,

(Rev- Adiabatic)

$$dS_{sys} = \frac{dq}{T} = 0$$

$$dS_{sys} = 0$$

$$dS_{surr} = 0$$

$$dS_{universe} = 0.$$

(Irreversible- Adiabatic)

$$dS_{sys} > \frac{dq}{T}$$

$$dS_{sys} > 0$$

$$dS_{surr} = 0.$$

$$dS_{universe} = dS_{sys} + dS_{surr}$$

$$dS_{universe} > 0$$

$$ds = C_v \ln \frac{T_2}{T_1} + nR \ln V_2/V_1$$

Rev Adiabatic proof $dS = 0$.

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

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

$$\ln T_1/T_2 = \gamma-1 \ln (V_2/V_1)$$

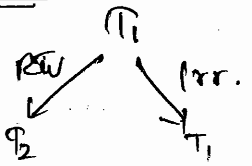
$$-\ln \frac{T_2}{T_1} = \frac{R}{C_v} \ln (V_2/V_1)$$

$$C_v \ln T_2/T_1 = R \ln (V_2/V_1)$$

$$\left(C_v \ln T_2/T_1\right)_{Rev, Adia} = -R \ln V_2/V_1$$

$$= 0.$$

Irrev



$$(T_2')_{Ir} > (T_1)_{Rev}$$

$$\left(C_v \ln \frac{T_2}{T_1}\right)_{Irr} > \left(C_v \ln \frac{T_2}{T_1}\right)_{Rev\ Adia.}$$

$$\left(C_v \ln \frac{T_2}{T_1}\right)_{Irrev} > -R \ln V_2/V_1$$

$$= \left(C_v \ln \frac{T_2}{T_1}\right)_{Irr} + n \ln \frac{V_2}{V_1} = 0 .$$

$dS_{Irr\ Adi} > 0$. (proof)

$$\boxed{\begin{array}{ll} \text{Rev. Adia} & \Delta S_{sys} = 0 \\ & \Delta S_{surr} = 0 \\ & \Delta S_{uni} = 0 \\ \text{IrRev. Adia} & \Delta S_{sys} = \Delta S_{univ} > 0 . \\ & \Delta S_{surr} = 0 . \end{array}}$$

⑫ $T_1 = 300K$

$P_1 = 10$

$P_2 = 2$ $\quad C_v = 1.5R$

$T_2 = ?$ $\quad C_p = 2.5R.$

(i) Rev. Adi $dS_{surr} = 0$.

(ii) Irr. Adia = $dS = C_p \ln \frac{T_2}{T_1} - R \ln P_2/P_1$

$$= 2.303\, C_p \log \frac{T_2}{T_1} - 2.303\, R \log P_2/P_1$$

Irreversible Adia की Initial and final

$dq = dU - w$

$0 = dU - w$

$dU = -w$

$C_v (T_2 - T_1) = -P_2 (V_2 - V_1)$

$C_v (T_2 - T_1) = -P_2 \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$

$1.5R\,(T_2 - 300) = -R\left(\frac{T_2 \cancel{P_2}}{\cancel{P_2}} - \frac{P_2 T_1}{P_1}\right]$

$= 1.5\,(T_2 - 300) = -T_2 - \frac{P_2 T_1}{P_1}$

$= 1.5\,(T_2 - 300) = -\left[T_2 - \frac{2 \times 300}{10}\right]$

$= 1.5T_2 - 450 = -T_2 \times 60$

$1.5T_2 + T_2 = 450 + 60$

$2.5T_2 = 510$

$\boxed{T_2 = 204}$

$= \frac{510}{2.5}$

$= \frac{510}{5} \times 2$

$= 102 \times 2$

$= 204$

In rev. [illegible]

[illegible]

∴ P-term place

But in Irreversible

[illegible]

[illegible]

[illegible] applied.

Rev. Adia T_f

[illegible]

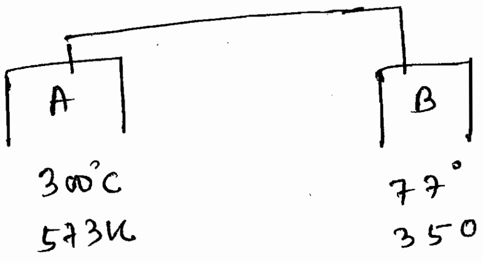
IrR Adia T_f (more

more

$\Delta S =$

⑬ 1- True 2- True 3- False.

⑭



$\Delta S_A = \frac{-10460}{573}$ $\Delta S_B = \frac{10460}{350}$

$\Delta S_T = \Delta S_A + \Delta S_B$

~~Gate~~

Gate - 2006

㉙ ΔS°_{uni} for the following reacⁿ at 298K in,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$\Delta S^\circ_{sys} = -197\ J/K.$

$\Delta H^\circ_{sys} = -91.8\ kJ$

$\Delta S_{surr} = 91.8\ kJ.$

(Syst gives heat → Surr. [illegible] (entropy)).

Solⁿ: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr.}$

$= 197\ J/K = \frac{91.8 \times 10^3 J}{298\ K}.$

Criterian of spontanity in terms of, G, H, A, U, S.

$dS_{syst} - \frac{dq}{T} \geq 0.$

$Tds - dq \geq 0$

from 1st law $dq = du - w$ $w = -pdv$

$dq = du + pdv.$

$Tds - (du + pdv) \geq 0.$

$$\boxed{Tds - du - pdv \geq 0}$$

1. $Tds - du - pdv \geq 0$

$s = \text{const}$, $v = \text{const}$; $ds = 0$, $dv = 0$

$-dU_{s,v} \geq 0$

$$\boxed{dU_{s,v} \leq 0}$$

$v = \text{const}$ $dv = 0$
$U = \text{const}$ $du = 0$.

$Tds_{U,v} \geq 0$.

$$\boxed{dS_{U,v} \geq 0}$$

$\rightarrow$ U & s const

$du = 0, ds = 0$.

$(-pdv)_{U,s} \geq 0$.

$$\boxed{\therefore (pdv)_{U,s} \leq 0}$$

Mathematical defn of enthalpy,

$H = U + PV$

$dH = du + pdv + vdp$.

$$\boxed{-du - pdv = -dH + vdp}$$

2. $Tds - dH + vdp \geq 0$

$S \& P = \text{const}$; $ds = 0$, $dp = 0$

$-dH_{s,p} \geq 0$

$$\boxed{dH_{s,p} \leq 0}$$

$H = \text{const}$ $dH = 0$
$P = \text{const}$ $dp = 0$.

$TdS_{H,p} \geq 0$

$$\boxed{dS_{H,p} \geq 0}$$

As, $G = H - Ts$

$dG = dH - Tds - sdT$

$Tds - dH = -dG - sdT$

Putting this eq 2.

③ $-dG - sdT + vdp \geqslant 0$

$\swarrow$ T = const, P = const

$-dG_{T,P} \geqslant 0$

$$\boxed{dG_{T,P} \leqslant 0}$$

④ $-dA - SdT - Pdv \geqslant 0$

T = const, V = const

$-dA_{T,V} \geqslant 0$.

$$\boxed{dA_{T,V} \leqslant 0}$$

As, $A = U - TS$.

$dA = dU - TdS - SdT$

Putting this in eqn ①.

Maxwell - Thermodynamic potential :

From the combination of mathematical reepresentation of First law and second law. First thermodynamic potential (Internal energy) was Introduced as,

From 1st law,

$dq = dU - w \qquad w = -pdv$

$dq = dU + pdv$ ——(i)

From 2nd law,

$dq = Tds$ ——(ii)

from eq(i) and eq(ii),

$Tds = dU + pdv$

$$\boxed{dU = Tds - pdv}$$

The natural variable of U are S & V.

Out of U variable only T & P can controlled in lab. not S & V.

So, [illegible]

S & V

(i) Extremic in nature

(ii) Not easily controlable in lab.

(iii) Intrinsic prop.

So, we have to Introduce those potential which are easily controllable.

So, to introduce new thermodynamic func^n we use [Legandre Transf^m]

↓

The new func^n may be obtained by adding/substracting the multiplication of two conjugate variable to the old func^n

One Interensic

Other extremic.

from 1st law,

$$dq = du - w \qquad w = -pdv.$$

$$dq = du + pdv$$

at const p

$$pdv = d(pv)$$

$$dq = du + d(pv)$$

$$= d\,[U + PV]$$

→ Intensive.

↳ extensive

↓

follow Legendre func^n.

$$\boxed{H = U + PV}$$

$$H = U + PV$$

$$dH = du + pdv + vdp$$

↓

$$dH = Tds - pdv + pdv + vdp$$

$$\boxed{dH = Tds + vdp}$$

Uncontrol   Control

Now, to get other potential take the eq^n corresponds to,

$$du = Tds - pdv$$

$$du - Tds = -pdv$$

at const Temp, $d(Ts) = Tds$.

$$du - d(Ts) = -pdv$$

$$d\,[U - Ts] = -pdv$$

↳ Legendre cond^n.

$A = U - TS$

$dA = dU - TdS - SdT$

$\downarrow$

$= TdS - pdV - TdS - SdT$

$$\boxed{dA = -pdV - SdT}$$

Intrinsic Extrinsic

Extensive Intensive.

To get other potential we take the rel^n,

$dH = TdS + VdP$

$dH - TdS = VdP$ at const T.

$TdS = d(TS)$

$d(H - TS) = VdP$

Legendre cond^s.

$G = H - TS$

$dG = dH - TdS - SdT$

$\downarrow$

$= TdS + VdP - TdS - SdT$

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

Extrinsic controllable.

Kirchoff's Equation:

To control the heat content by of a chemical rea^n (occur at const p) by controlling the temp, the eq^n was proposed by Kirchoff known as a Kirchoff's eq^n.

Let us consider a reac^n,

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

If at T_1 heat Transfer is ΔH_{T_1} at T_2 heat transfer ΔH_{T_2} may be obtained as,

from the rea^n

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p.$$

for a chemical rea^n,

$$\left[\frac{\partial \Delta H}{\partial T}\right]_p = \Delta C_p$$

$$\Delta C_p = C_{p,P} - C_{p,R}$$

$$\int_{T_1}^{T_2} [\partial \Delta H] = \Delta C_p \int_{T_1}^{T_2} \partial T$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_p (T_2 - T_1)$$

$$\boxed{\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p (T_2 - T_1)}$$

Q. 45 Gate (2003)

ΔH°_{298} for the rea^n.

$C_2H_4O_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$ is −16.0 kJ. From the given data evaluate the temp at which ΔH will be 0.

Substance	C_2H_4O	CH_4	CO
	50	36	30

Sol^n $T_1 = 298$ $\Delta H_{T_1} = -16.0$ kJ

$= -16000$ J

$T_2 = ?$ $\Delta H_{T_2} = 0$.

$\Delta C_p = C_{p,P} - C_{p,R}$

$= [C_{p,CH_4} + C_{p,CO}] - [C_{p,C_2H_4O}]$

$= 36 + 30 - 50 \quad \Delta C_p = 16\,J/K.$

$\Delta C_p = 16\,J/K.$

$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p (T_2 - T_1)$

$0 = -16000\,J + 16\,J/K\,(T_2 - 293)$

Q. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$P = 8.76$

$\Delta S^\circ_{298} = 16.kJ$

$\Delta S^\circ_{308} = ?$

$\Delta S = C_p \ln T_2/T_1 - \cancel{R \ln P_2^\circ/P_1}$

$\Delta\; S_{T_2} - S_{T_1} = C_p \ln T_2/T_1$

$\Delta S_{T_2} - \Delta S_{T_1} = \Delta C_p \ln T_2/T_1$

$$\boxed{\Delta S_{T_2} = \Delta S_{T_1} + \Delta C_p \ln T_2/T_1}$$

[illegible] transf^n take place then

$\Delta S = nC_p \ln \frac{T_2}{T_1} - nR \ln P_2/P_1$

But when there is a chemical reac^n,

$\Delta S_{T_2} - \Delta S_{T_1} = \Delta C_p \ln T_2/T_1$

Gibb's free Energy:

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

① Exothermic $\Delta H = -ve$ $\Delta S = +ve$ $\Delta G = -ve$ (spontaneous)

② Endothermic $\Delta H = +ve$ $\Delta S = -ve$ $\Delta G = +ve$ (non-Spontaneous)

③ Exothermic $\Delta H = -ve$ $\Delta S = -ve$ [low Temp] $\Delta G = -ve$ (spontaneous)
[high Temp] $\Delta G = +ve$ (non-spontaneous).

④ Endothermic $\Delta H = +ve$ $\Delta S = +ve$ [high Temp] $\Delta G = -ve$ (Spontaneous)
[low Temp] $\Delta G = +ve$ (non-spontanu

Dependence on G on P and T:

(i) Dependence of G on P at const T: (Isothermal)

$$\left(\frac{\partial G}{\partial P}\right)_T$$

(a) In case of Solid and liquid

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

at const $dG = Vdp$

$dG = Vdp \cdot SdT$
const T ∴ $dT = 0$.
$(\partial G)_T = V(\partial P)_T - S \cdot 0$

In case of liq. & solid on change the pressure, volume almost remains const.

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \int \partial G = V \int \partial P$$

$$G_2 - G_1 = V(P_2 - P_1)$$

If, we apply above concept for a chemical reac^n (that involve only liq & solid)

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$$

$$\Delta G_2 - \Delta G_1 = \Delta V (P_2 - P_1)$$

$$\boxed{\Delta G_2 = \Delta G_1 + \Delta V (P_2 - P_1)}$$

At minm pressure $\Delta G = 0$,
At eqm.

Qn: At 1 Bar at 298 K for the process, $A(s) \longrightarrow A(l)$ the ΔG is 200 J/mole and $\Delta V_m = -2\times10^{-6}$ m³/mole. The minn pressure at which at becomes Spontaneous at 298 K (1bar = 10^5 pa)

Soln: $P_1 = 1$ bar $\Delta G_{P_1} = 200$ J/mole

$P_2 = ?$ $\Delta V = -2\times10^{-6}$ m³/mole $\Delta G_{P_2} = 0$.

$$\Delta G_{P_2} = \Delta G_{P_1} + \Delta V (P_2 - P_1)$$

$$0 = 200\text{ J/mole} + \left(-2\times10^{-6}\frac{m^3}{mole}\right)(P_2 - 1\text{ bar})$$

$$-200\text{ J/mole} = \left(2\times10^{-6}\frac{m^3}{mole}\right)(P_2 - 1\text{bar})$$

$$\frac{200\text{ J/mole}}{2\times10^{-6}\text{ m}^3\text{/mole}} = (P_2 - 1\text{bar})$$

$$= \frac{200\ N-\cancel{m}}{2\times10^{-6}\ m^{\cancel{3}2}} = P_2 - 1\text{bar}.$$

$$= 100\times10^{6}\text{ Pa} = P_2 - 1\text{bar}$$

$$1000\times10^{5}\text{ Pa} = P_2 - 1\text{bar}.$$

$$P_2 = 1001\text{ bar}.$$

DPP-12

⑥ Graphite → Diamond.

$\Delta G^\circ = 2900$ J/mole

$P_1 = 1$ bar $\quad \Delta G_{P_1} = 2900$ J/mole.

$P_2 = ? \quad \Delta G_{P_2} = 0$.

$$\Delta G_{P_2} = \Delta G_{P_1} + \Delta V (P_2 - P_1)$$

$$0 = 2900 \frac{J}{mole} + (V_d - V_g)(P_2 - 1)$$

$$0 = 2900 \; J/mole + \left(\frac{12 \; gm/mole}{3.51 \; gm/cm^3} - \frac{12 \; gm/mole}{2.25 \; \frac{gm}{cm^3}}\right)(P_2 - 1)$$

$cm^3 - L$

$J = L\,bar$

In Case of Ideal Gas :

As $\left(\frac{\partial G}{\partial P}\right)_T = V \qquad (\partial G) = V(\partial P)$

In case of ideal gas $PV = nRT$

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

$$\int_{G_1}^{G_2} \partial G = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\int_{G_1}^{G_2} \partial G = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\boxed{\Delta G = G_2 - G_1 = nRT \ln P_2/P_1}$$

Gas is ideal process is Isothermal,

$P_1V_1 = nRT \qquad P_2V_2 = nRT$

$P_1V_1 = P_2V_2 \qquad PV = const$

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

$$\boxed{\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}}$$

$$\Delta G_{P_2} - \Delta G_{P_1} = nRT \ln \frac{P_2}{P_1}$$

If the above concept is applied for a chemical reacⁿ involving gaseous species

$$\Delta G_2 - \Delta G_{P_1} = \Delta n_g RT \ln P_2/P_1$$

④ $n = 1$ mole , $P_1 = 1$, $P_2 = 2$, Process = Iso Gas = Ideal.

$$\Delta G = nRT \ln P_2/P_1 = RT \ln 2.$$

③ $n = 1$ mole

$V_1 = 1.0\,L$

$V_2 = 4.0\,L$

Isothermal

$T = 300\,K$

$$\Delta G = nRT \ln \frac{V_1}{V_2}$$

$$= 1 \cdot R \times 300K \ln \frac{1}{4}$$

$$= -300 R \ln (2)^2$$

$$= -600 R \ln 2.$$

(1) - $\frac{1}{2}$ -(1

1 -

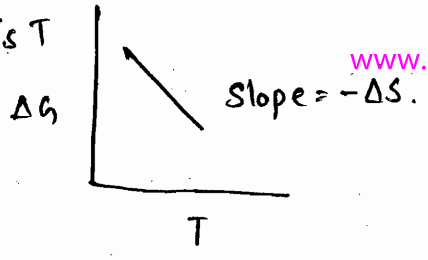
① $CO_{(g)} + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\Delta C_p = \Delta C_{p,CO_2} - [C_{p\,O_2} + \frac{1}{2} C_{p,O_2}]$

$T = 298$ $\Delta H_{298} = -394 - [-110 + 0]$

$T = 400$ $\Delta H = ?$

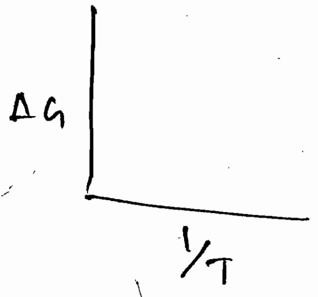
② $\underset{\downarrow y}{\Delta G} = \Delta H - \underset{\downarrow x}{T\Delta S}$.

ΔG Vs T



$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \frac{T\Delta S}{T}.$$

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



Dependence of G on T at const. P:

$$\left(\frac{\partial G}{\partial T}\right)_p$$

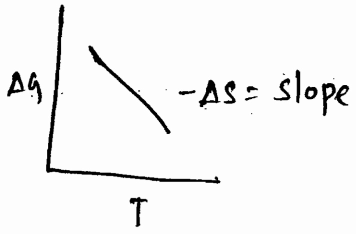
from the maxwell eqⁿ $dG = vdp - sdT$.

if $p = const$

$dp = 0$

$$(\partial G)_p = v\cdot 0 - s(\partial T)_p$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$



In chemical reaⁿ, $\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$.

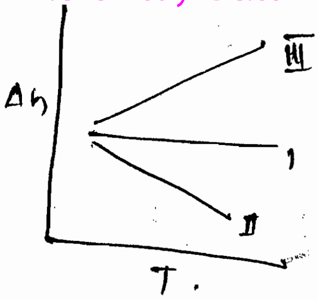
$$\left[\frac{\Delta G_2 - \Delta G_1}{\Delta T_2 - T_1}\right]_p = -\Delta S.$$

⑱ $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\frac{\partial \Delta G}{\partial T} = 0$, $\Delta G = const$

$\Delta S \approx 0$.

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta S = +ve$, Slope = −ve

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta S = -ve$ slope = +ve.



⑰ $\Delta G = \Delta H - T\Delta S \rightarrow$ len the 25°C
$\downarrow$
with decrease in Temp

$\Delta H = -ve$
$\Delta G = +ve$.

⑬ $X_2O_4(l) \longrightarrow 2XO_2(g)$

$\Delta U = 9\,kJ$
$\Delta S = 84\,J/K$.

$\Delta n_g = 2$.

$\Delta G = \Delta H - T\Delta S$
$= \Delta U + \Delta n_g RT - T\Delta S$.

From the mathematical repn of Gibbs funcn,

Application of above Reln:

I> Introductn of function ΔG in Electro:

$$\left[\frac{\partial \Delta G}{\partial T}\right]_P = -\Delta S$$

$\Delta G = -nFE$ (At const T & P
ΔG = non-mechanical)

$$\left[\frac{\partial(-nFE)}{\partial T}\right]_P = -\Delta S$$

$$-nF\left[\frac{\partial E}{\partial T}\right]_P = \Delta S$$

$$\boxed{\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF}}$$

Remember
Gibb's Helmoltz eqn

① $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

② $\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$

③ $\left[\frac{\partial(\Delta G/T)}{\partial(1/T)}\right]_P = \Delta H$.

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

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

$$-nFE = \Delta H + T\left[\frac{\partial}{\partial T}(-nFE)\right]_P.$$

$$\boxed{\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P}$$

② In kinetics and Equilibria.

$$\boxed{\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}}$$

$$\downarrow \; \Delta G = -RT \ln K_{eq} \text{ (from equ}^n\text{)}$$

$$\left[\frac{\partial(-RT\ln K_a)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$$

$$\boxed{\left[\frac{\partial \ln K_{eq}}{\partial T}\right]_P = \frac{\Delta H}{RT^2}}$$ Van't hoff eq^n,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$\cancel{\left[\frac{\partial \ln K_{eq}}{\partial T}\right]}.\left(\frac{\partial \ln k_1/k_{-1}}{\partial T}\right)_P = \frac{\Delta E}{RT^2} = \frac{E_1 - E_{-1}}{RT^2}$$

$$\frac{\partial \ln k_1}{\partial T} - \frac{\partial \ln k_{-1}}{\partial T} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2}$$

$$\frac{\partial \ln k}{\partial T} = \frac{E_1}{RT^2}$$

$$\boxed{\frac{\partial \ln k}{\partial T} = \frac{E_a}{RT^2}} \rightarrow k = Ae^{-E_a/RT}$$

$$\searrow \ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Remember:

1. $\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p$.
2. $\Delta G = -nFE$
3. $\Delta H = \Delta G + T\Delta S$
4. $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_p = -\frac{\Delta H}{T^2}$
5. $\left[\frac{\partial \ln K_{eq}}{\partial T}\right]_p = \frac{\Delta H}{RT^2}$

⑧ $\left(\frac{\partial G}{\partial T}\right)_p = -S$

$\frac{\Delta S}{nF}$.

⑦ $\Delta G = -nFE$

$\left(\frac{\partial E}{\partial T}\right)_p$

$S = -\left(\frac{\partial G}{\partial T}\right)_p$

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\left[\frac{\partial}{\partial T}(-nFE)\right] = nF\left(\frac{\partial E}{\partial T}\right)_p$$

$$\boxed{\left(\frac{\partial E}{\partial T}\right)_p = \Delta S/nF}$$

⑥ $\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S}{nF}$

$\partial E = \frac{\Delta S}{nF}\partial T$

$\int \partial E = \frac{\Delta S}{nF}\int dT$

$E_2 - E_1 = \frac{\Delta S}{nF}(T_2 - T_1)$

$$\boxed{E_2 = E_1 + \frac{\Delta S}{nF}(T_2 - T_1)}$$

$T_1 = 250$

$T_2 = 850$

$E_1 = 1.26\,V$

$E_2 = ?$

$n = 2$, $\Delta S = -96.5\,J$

$nF = 965$

① $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

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

$$\boxed{\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P}$$

② $\Delta G = \Delta H - T\Delta S$

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S.$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = \left[\frac{\partial}{\partial T}\left(\frac{\partial H}{T}\right)\right]_P - \left[\frac{\partial}{\partial T}\Delta S\right]_P$$

$$\boxed{\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}}$$

③ $\left[\frac{\partial\left(\frac{\Delta h}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$

$$-T^2\left[\frac{\partial \Delta G/T}{\partial T}\right]_P = \Delta H$$

$$\left[\frac{\partial\left(\frac{\partial G}{T}\right)}{\left(-\frac{1}{T^2}\right)\partial T}\right]_P = \Delta H.$$

$$\left[\frac{\partial \Delta G/T}{\partial(1/T)}\right] = \Delta H.$$

Gibb's Helmoltz eqⁿ:

Gibb's

$G = H - TS$

$\downarrow$

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

$dG = VdP - SdT$

$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$

Helmoltz

$A = U - TS$

$\downarrow$

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

$dA = -PdV - SdT$

$\left(\frac{\partial A}{\partial T}\right)_V = -S$

$\left[\frac{\partial \Delta A}{\partial T}\right]_V = -\Delta S$

① $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$

② $\left[\frac{\partial (G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$

③ $\left[\frac{\partial(\Delta G/T)}{T}\right] = \Delta H$

① $\Delta A = \Delta U + T\left(\frac{\partial \Delta A}{\partial T}\right)_V$

② $\left[\frac{\partial(\Delta A/T)}{\partial T}\right]_V = -\frac{\Delta U}{T^2}$

③ $\left[\frac{\partial(\Delta A/T)}{(\partial 1/T)}\right] = \Delta U$

Q. Show that at const T & P Gibb's free energy change is equal to non-mech work

Solⁿ: If we introduce all form of work in 1st law,

$$\boxed{dq = dU - w_T}$$

$w_T = w_{mech} + w_{non\text{-}mech}$

$-PdV + w_{el} + w_{sur} + w_{ele} +$

From Gibbs funcⁿ

$G = H - TS$

$G = U + PV - TS$

$dG = dU + PdV + VdP - TdS - SdT$

$dG = T\cancel{dS} + w_T + PdV + VdP - T\cancel{dS} - SdT$

$= w_T + PdV + VdP - SdT$

at const T & const P

$$dT = 0,\ dP = 0.$$

$$dG = w_T + pdv$$

$$dG = w_T - (-pdv)$$

$$dG = w_T - W_{mech}$$

$$\boxed{dG = W_{non\text{-}mech}}$$ (proved)

Third Law of Thermodynamics : [concept of Residual entropy]

$$\underset{(s)}{\underset{0^\circ K}{A}} \longrightarrow \underset{(s)}{\underset{T\,K}{A}}$$

$$\Delta S = C_p \ln T_2/T_1$$

$$dS = C_p \frac{dT}{T}$$

$$dS = C_p \frac{dT}{T} = C_p \int \frac{dT}{T}$$

$$dS = \int_0^T C_p \frac{dT}{T}.$$

$$S_T - S_0 = \int_0^T C_p \frac{dT}{T}$$

$$S_T = S_0 + \int_0^T C_p \frac{dT}{T}.$$

S_T = Entropy at Temp T.

S_0 = Entropy at temp 0°K.

Debye law, $0 < T < 10\,K$.

Let 1 mole of solid at const press. is heat from 0°K to some Temp 'T', below its m.p. According to entropy equ^n.

Since, the entropy fun^c increases with increase in Temp it may be expected that it has a min^m value at zero K. Max planck suggested that min^m entropy may be assigned zero value for a pure perfectly crystalline substance. This sugge^n is known as 3rd law of thermodynamics.

Perfect Crystalline,

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

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

Ordinarily measurement of solid have in determine to a lower temp that lie in the range of 10 to 15. Below that temp Heat Capacity of solid is determined for "Debye T^3 law",

$$C \propto T^3$$

$$\boxed{C = aT^3}$$

$$S_T = \int_0^{T_{min}} aT^3 \frac{dT}{T} + C_p \int_{T_{min}}^{T} \frac{dT}{T}.$$

$$S_T = a \int_0^{T_{min}} T^2 \, dT + C_p \ln \frac{T}{T_{min}}$$

$$S_T = a \left[\frac{T^3}{3}\right]_0^{T_{min}} + C_p \ln T/T_{min}$$

a = Debye const.

Residual Entropy:

There are many Crystals that do not fulfill the requirement of perfectly ordered arrangement even at the absolute zero of temp.

For, this Crystals entropy at 0°K is not zero. Entropy stores in the form of residual entropy and may be obtained by a rel^n.

$$\boxed{S = k \ln w}$$

k = Boltzmann const

w = arrangement

$T = 0$ perfectly order crystal $w = 1$ $S = 0$.

$T = 0$ Imperfectly " " $w \neq 1$, $S \neq 0$.

1 molecule (CO) have 2 orie^n w.

2 molecule have 2^2 orie^n.

N_A molecules have 2^{N_A} orie^n.

$$w = 2^{N_A}$$

$$S = k \ln w$$

$$= k \ln 2^{N_A}$$

$$= N_A k \ln 2$$

$$\boxed{w = R \ln 2}$$

Thermodynamics of Open System :

Thermodynamic relationship that are derived earlier are applicable to closed System. Because only heat and work transfer. Now, we will consider those system in which not only work and heat but also transfer of metal takes place. Here, the amount of various substance are treated as variables like any other thermodynamic variable.

Ex: G is not a func^n of (T,P) but also a

For simplicity let us consider a two component System,

$$G = G(T, P, n_1, n_2)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{n_1,n_2,T} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} dn_2$$

~~$= -SdT + V$~~

In this equation,

entity $\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}$ and $\left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1}$ are partial molar free energy of component 1 & 2.

So,

$$dG = -SdT + VdP + \bar{G}_1 dn_1 + \bar{G}_2 dn_2 .$$

Partial molar quantity :

Partial molar value of Y is the change in Y when 1 mole of component Y is transfered keeping other variables constant.

(add^n or subs^n)

$$\boxed{Y_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n_i}}$$

Chemical potential :

It is the partial molar thermodynamic potential. It may be represented in the form of every Thermodynamic potential.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \quad i \neq j$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} \quad i \neq j$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} \quad i \neq j$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} \quad i \neq j$$

Now,

$$\boxed{dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2}$$

For multi component System,

$$U = U(S, V, n_1, n_2)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_1,n_2} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_1,n_2} dV + \left(\frac{\partial U}{\partial n_1}\right)_{V,S,n_2} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{V,S,n_1} dn_2$$

$$\boxed{dU = TdS - pdV + \mu_1 dn_1 + \mu_2 dn_2}$$

$\downarrow$ For multicomponent System

$$\boxed{dU = TdS - pdV + \sum \mu_i dn_i}$$

Maxwell eq^n in open System

$$dG = -SdT + Vdp + \sum \mu_i dn_i$$

$$dH = TdS + Vdp + \sum \mu_i dn_i$$

$$dU = TdS - PdV + \sum \mu_i dn_i$$

$$dA = -SdT - pdV + \sum \mu_i dn_i$$

Dependance of Chemical potential on Temp and pressure :

(i) Change in chemical potential w.r.t change in T at const P :

$$\left(\frac{\partial \mu_i}{\partial T}\right)_P = \left[\frac{\partial}{\partial T}\cdot \mu_i\right]_P = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right]$$

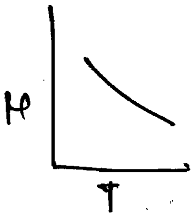
(As G (state func^n) follow

$$= \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right)_P\right]_{T,P,n_j}$$

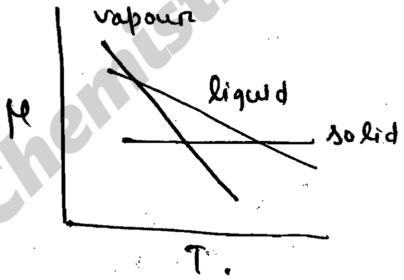
$$= \left[\frac{\partial}{\partial n_i}(-S)\right]_{T,P,n_j}$$

$$= \cancel{\frac{\partial}{\partial n_i}\{\partial G} \quad = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}.$$

$$\bar{S}_i = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}.$$



μ = -ve.



$S_v > S_l > S_s$.

Slope = -ve.

⑫ $\alpha \underset{T}{\rightleftharpoons} \beta$

$T_P \qquad T_P$

$T_\alpha = T_\beta$

$P_\alpha = P_\beta$

$\mu_\alpha = \mu_\beta$

$G_\alpha = G_\beta$

(ii) Change in chemical potential w.r.t Change in P at const T.:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right] = \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_T\right]_{T,P,n_j}$$

(∵ G is a stat func^n]

$$= \left[\frac{\partial}{\partial n_i}(V)\right]_{T,P,n_j} = \bar{V}_i$$

So, $\boxed{\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i}$

For ideal gas,

$$\bar{V}_i = \frac{RT}{P}$$

$$\frac{\partial \mu_i}{\partial P} = \frac{RT}{P}$$

$$\int_{\mu_i^\circ}^{\mu_i} \partial \mu = \int_{P^\circ}^{P} \frac{RT}{P}\,\partial P$$

$$\mu_i - \mu_i^\circ = RT\int_{P^\circ}^{P}\frac{dP}{P}$$

$$\mu_i = \mu_i^\circ + RT\ln\frac{P}{P^\circ}$$

Note (imp)

μ_i° [illegible]

$\mu_i^\circ = \mu_i^\circ(T)$ [illegible] on T not on P.

∵ $P^\circ = 1$ bar. (Const)

μ_i: vary with P & T

$\mu_i = \mu_i(P, T)$

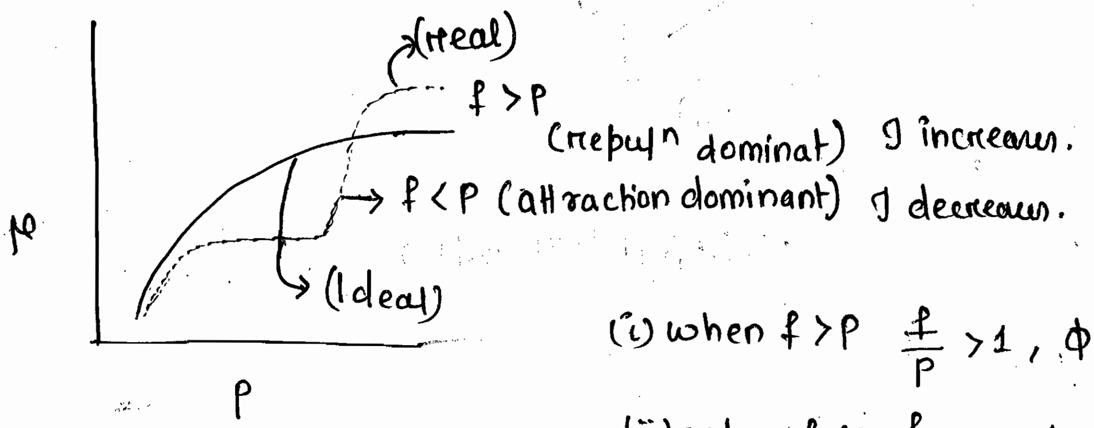
$P^\circ = 1$ bar

$$\boxed{\mu_i = \mu_i^\circ + RT\ln P}$$

$$\mu_i = \mu^\circ + RT\ln\frac{P}{P_0 = 1}$$

$$\boxed{d\mu = \mu_i - \mu_i^\circ = RT\ln P}$$

Imp For ideal gas graph



(i) when f > P $\frac{f}{P} > 1$, $\phi > 1$.

(ii) when f < P $\frac{f}{P} < 1$, $\phi < 1$.

Equation $\mu = \mu^\circ + RT \ln P$ so that chemical potential varies with the natural logarithm of P. A plot of μ Vs P is general,

However measurement on real gas so that rel^nship b/w μ and p are not so exact. At very low gas pressure all gas approach ideal behaviour at moderate pressure for a given potential, the pressure is very lower than expected. This is because real gas molecule attract each other slightly and the measured pressure is lower than Ideal. At very high pressure, the pres. for real gas is higher than expected becoz gaseous molecule so densly packed so they repel each other. The actual behaviour of the chemical potential Vs real pressure of a gas is show above.

For real gas thermodynamics define a scaled pressure called "Fugacity".

$$\boxed{f = \phi P}$$

φ = fugacity coefficient

Representation of fugacity coefficient in terms of Z :

$$\boxed{Z = \frac{PV}{RT}}$$

Z = Compressibility factor

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V}$$

$$\boxed{\begin{aligned} d\mu_{real} &= \bar{V}_{real}\, dP \\ d\mu_{ideal} &= V_{ideal}\, dp. \end{aligned}}$$

$$d\mu_{real} - d\mu_{ideal} = (V_{real} - V_{ideal})\, dp$$

$$= \left(\frac{zRT}{P} - \frac{RT}{P}\right) dp$$

$$= \frac{(z-1)RT}{P}\, dp \quad \text{— ②}$$

$$\left.\begin{aligned} \mu_i &= \mu_i^\circ + RT \ln \frac{P}{P^\circ} \quad \text{(ideal)} \\ \mu_i &= \mu_i^\circ + RT \ln \frac{f}{f_0} \quad \text{(real)} \\ \mu_i &= (d\mu)_{ideal} = RT \ln \frac{P}{P_0} \quad \text{(Ideal)} \\ \mu_i &= (d\mu)_{real} = RT \ln \frac{f}{f_0} \quad \text{(real)} \end{aligned}\right\} \text{eq}^n\text{- A}$$

$$d\mu_{real} - d\mu_{ideal} = RT \ln \frac{f/f_0}{P/P_0} \quad \text{— ①}$$

$$= RT \ln \frac{f/f_0}{P/P_0} = \frac{(z-1)RT}{P}\, dp. \quad \text{(from (1) and (2))}$$

$$\ln \frac{(f/f_0)}{(P/P_0)} = \int_{P_i}^{P_f} \frac{z-1}{P}\, dp$$

$\ln P_i \Rightarrow 0$ $\boxed{P^\circ = f^\circ}$

So, $\boxed{\ln \frac{f}{P} = \int_0^P \frac{(z-1)}{P}\, dp}$

$$\boxed{\ln \phi = \int_0^P \frac{(z-1)}{P}\, dp}$$

1. $\ln\phi = \int_0^P \frac{z-1}{P}\,dp$.

$$\ln\phi = \int_0^P \frac{Pb}{RT}\cdot\frac{dp}{P}$$

$$\ln\phi = \frac{b}{RT}\int_0^P dp$$

$$= \frac{b}{RT}\cdot P$$

$$\ln\phi = \frac{bP}{RT}$$

$$\phi = e^{bP/RT}$$

$$\frac{f}{P} = e^{bP/RT}$$

$$f = Pe^{bP/RT}$$

$$P + \cancel{\left(\frac{a}{v^2}\right)}^{0}(v-b) = RT$$

$P(v-b) = RT$ (when attn is not dominated)

$$Pv - Pb = RT$$

$$\frac{Pv}{RT} - \frac{Pb}{RT} = 1$$

$$z - \frac{Pb}{RT} = 1$$

$$z = 1 + \frac{Pb}{RT}$$

$$z - 1 = Pb/RT.$$

⑥ $\phi = e^{bP/RT}$

⑨ $PV = RT + BP$

$$P(V-B) = RT$$

$$f = Pe^{BP/RT}$$

$$z = \frac{Pv}{RT}$$

$$z = 1 + BP/RT.$$

⑪

From eqn we can represent,

$$P + \frac{a}{V^2} (V-b) = RT$$

R-dominatn

$$P(V-b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb$$

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$Z = 1 + \frac{Pb}{RT}$$

$$\ln \frac{f}{P} = +ve$$

$$\boxed{f > P.}$$

A-dominant.

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = 1 - \frac{a}{RTV}$$

$$Z < 1$$

$$\ln f/P = -ve$$

$$\boxed{f < P}$$

Concept of Activity :

Introduction of term activity was proposed by lewis. "To determine the transfer tendency of material from one state to other state in a liquid and solid".

According to him chemical potential eqn in terms of activity may be represented as

$$\boxed{\mu = \mu^\circ + RT \ln a}$$

This eqn is applicable to gas, solid, liquid phase.

For vanderwaall $a = f/f_0$

For ideal $a = P/P^\circ$

In case of solid & liquid activity may be determined as,

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V}$$

$$d\mu = \bar{V}\, dP$$

$$\mu - \mu^\circ = \bar{V}(P - P^\circ)$$

$$\boxed{(d\mu)_{l \text{ or } s} = \bar{V}(P - P^\circ)} \quad \text{—(1)}$$

From the chemical potential eqⁿ,

$$\mu = \mu^\circ + RT \ln a$$

$$\mu - \mu^\circ = RT \ln a$$

$$\boxed{d\mu = RT \ln a} \quad \text{——(2)}$$

from eqⁿ ① & ②,

$$RT \ln a = \bar{v}(p - p^\circ)$$

$$\ln a = \frac{\bar{v}(p-p^\circ)}{RT}$$

$$\boxed{a = e^{\bar{v}(p-p^\circ)/RT}}$$

⑧ $P = 11$ bar $T = 298K$

$\bar{v}$ = molar vol^m

= 1 mole = 18gm = 18 ml

$P^\circ = 1$ bar

$$a = e^{\bar{v}(P-P^\circ)/RT}$$

$$a = e^{(18\times10^{-3}L)(11-1)\,\text{bar}/0.08314\,\frac{L\,\text{bar}}{K\,\text{mole}}\times 298K}$$

Gibb's Duhem's Equation:

This describes the relative tendency of one component w.r.t other component in a 2 component system. For a 2 component Syst. the chemical potⁿ of one species increases then c.p of other species decreases. This eqⁿ is also applicable for other thermodynamic entities.

for any of other partial quantities if P and T are kept const,

$$\sum n_i d\mu_i = 0.$$

For a 2 component system in form of chemical potential equⁿ,

$$\sum n_i d\mu_i = 0$$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0.$$

$$n_1 d\mu_1 = -n_2 d\mu_2 \quad \boxed{d\mu_1 = -n_2 d\mu_2}$$

The eqⁿ also represent change in c.p caused by variation in composition of solⁿ containing two constituent.

It is also applicable for volume:

$$x_1 dv_1 + x_2 dv_2 = 0.$$

$$\sum n_i d\mu_i = 0$$

$$\sum \frac{n_i}{n} d\mu_i = 0$$

$$\boxed{\sum x_i d\mu_i = 0.}$$

From, the maxwell eqⁿ for open system,

$$dG = vdp - sdT + \sum \mu_i dn_i \quad \text{—①}$$

$$dG = \left(\frac{\partial s}{\partial T}\right)_p$$

From the defⁿ of chemical potential,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

$$\partial G = \mu_i \partial n_i$$

$$\int \partial G = \int \mu_i \partial n_i$$

$$G = \sum \mu_i n_i$$

$$\boxed{dG = \sum \mu_i dn_i + \sum x_i d\mu_i} \text{ —②}$$

At const T & P, equating eqⁿ(1) & (2),

$$\sum \mu_i dn_i = \sum \mu_i dn_i + \sum n_i d\mu_i$$

$$\sum n_i d\mu_i = 0$$

$$\sum \frac{n_i}{n} d\mu_i = 0$$

$$\boxed{\sum x_i d\mu_i = 0}$$

(22) $T_1 = 20°C$

$E_1 = 0.2699V$

$T_2 = 30°$

$E_2 = 0.2669\ V.$

$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)$

$= nF\left(\frac{E_2 - E_1}{T_2 - T_1}\right) = -ve.$

(27) $2Cl \rightarrow Cl_2$

$Cl + Cl \rightarrow Cl_2$

$\Delta S = -ve$

$\Delta G = -ve$

$\Delta H = -ve.$

(23) $\Delta S_{ys} = -96\ J/K\ mole.$

$T = 27°C = 273 + 27 = 300K.$

$\Delta S_{surr} = \frac{45000J}{300\ K}$
$= 150$

$\Delta S_T = 150 - 96 = 54.$

(26) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$\Delta H°\ (25°C) = -92.2\ kJ.$

$T_1 = 25°C = 298K$

$\Delta H_1 = -92200\ J$

$T_2 = 100°C = 373K$

$\Delta H_2 = ?$

$\Delta C_p = (C_p)_P - (C_p)_R$

$= 2C_{p(NH_3)} - [3C_{p_{H_2}} - C_{p_{N_2}}]$

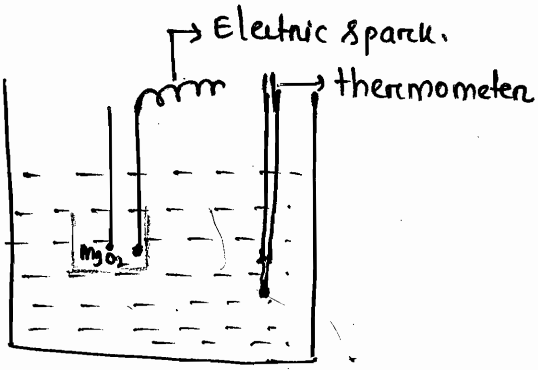
$= 2 \times 35.1 - [3 \times 28.8 + 29.1] = -ve$

$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$

$= -92200 + (-ve)$

Bomb Calorimetry :

Enthalpies of combust^n are usually measured by placing a known mass of a compound in a closed steel container known as Bomb Calorimeter. filled with O_2 at about 30 bar pressure Bomb Calorimeter is surrounded by known mass.



Entire apparatus is kept in an insulated jacket to prevent heat entering into or leaving from apparatus. Sample is ignited electrical to bring about the comb^n rea^n. Heat evolved is used in raising the temp of water and Calorimeter.

$$q_{Bomb} = -\left(q_{water} + E_{Calorimeter}\right)$$

$$= -\left(n_{water}\, C_{wat}\, dT + \underset{\underset{\text{mole}}{\downarrow}}{n_{Bomb}}\ \underset{\underset{\text{J/K mole.}}{\downarrow}}{C_{Bomb}}\ dT\right)$$

$$q_{Bomb} = -\left[n_{wat}\, C_{wat} + \underset{\underset{\text{J/K.}}{\downarrow}}{C_{bomb}}\right] dT$$

Since, the experiment is carried out at a const pressure. The heat released per unit amount of substance will be,

$$\Delta U = \frac{q_{Bomb}}{n_{mole}}$$

To get ΔH we use,

$$\boxed{\Delta H = \Delta U + \Delta n_g RT.}$$

⑬ $q_{comb} = -n_{wat} C_{wat} + C_{bomb}\, dT$

2.5 kJ/mole $\quad \downarrow$ J/K.

$E_{com} = -2.5 \dfrac{\text{kJ}}{\cancel{\text{K}}} \times 4\cancel{\text{K}}$

$= -10 \text{ kJ}$.

$A \rightarrow \dfrac{0.5 \text{ gm}}{500 \text{ gm/mole}} = \dfrac{1}{100} = 10^{-2} \text{ mole}$

$10^{-2} \text{ mole} \rightarrow -10 \text{ kJ}$

$1 \text{ mole} \rightarrow \dfrac{-10}{10^{-2}}$

$= -1000 \text{ kJ}$.

DPP 1 Thermodynamics Sahendra Kumar

1. The value of 20 L-bar is equal to
(a) =2 KJ (b) >2 KJ (c) < 2KJ (d) none of these

2 The value of 100Joule =xlitreatm than the value of x is
(a) >1 (b) <1 (c) =1 (d) none

3 The partial derivative $(\delta v/\delta T)_p$ is equal to **CSIR JRF II 2016**
a) $-(\delta P/\delta S)_T$ b) $-(\delta P/\delta S)_V$ c) $-(\delta P/\delta S)_n$ d) $-(\delta P/\delta S)_H$ (c) $-\left(\frac{\partial S}{\partial P}\right)_T$

4 The partial derivative $(\delta T/\delta V)_p$ is equal to **CSIR JRF II 2016**
a) $-(\delta P/\delta S)_T$ b) $-(\delta P/\delta S)_V$ c) $-(\delta P/\delta S)_n$ d) $-(\delta P/\delta S)_H$ →

5 Consider an ideal gas of volume V at temperature T and pressure P . If the entropy of the gas is S , the partial derivative $(\delta P/\delta S)_V$ is equal to **IIT GATE 2017**
a) $(\delta T/\delta P)_S$ b) $(\delta T/\delta V)_P$ c) $-(\delta T/\delta V)_S$ d) $(\delta T/\delta S)_P$

Q 6 Of the following inequalities, the criterion/criteria for spontaneity of a chemical reaction is/are **IIT GATE 2017**
(i) $(\Delta G_{T,P}) < 0$ (ii) $(\Delta U)_{S,V} > 0$ (iii) $(\Delta S)_{U,V} > 0$
(A) (i) only (B) (ii) only (C) (i) and (ii) (D) (i) and (iii)

Q 7 The internal energy E of a system is given by $E=\{bS^3/VN\}$, where b is a constant and other symbols have their usual meaning . The temperature of this system is equal to CSIR JRF P
(a) bS^2/VN (b) $3bS^2/VN$ (c) $3bS^3/VN$ (d) $\{S/N\}^2$

Q 8 The internal energy E (T) of a system at a fixed volume is found to depend on the temperature T as $E = aT^2 + bT^4$. Then the entropy S (T), as a function of temperature, is
(a) $\{aT^2/2\} + \{bT^4/4\}$ b) $\{2aT^2\} + \{4bT^4\}$ CSIR JRF P
(c) $\{2aT^2\} + \{4bT^4/3\}$ d) $\{2aT\} + \{\frac{4bT^3}{3}\}$

$2aT + \frac{4}{3}bT^3$

(only T difference

Q 9 Match the following **Gate 2004 Chemistry**

P. $(\delta U/\delta S)_V$ I A
Q. $(\delta U/\delta V)_S$ II –S
R $(\delta G/\delta P)_T$ III T
S $(\delta G/\delta T)_P$ IV -P
V H
VI V

P = III
Q = IV
R = VI
S = II

$dU = TdS - PdV$

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

$dU = 2aT\,dT + 4bT^3\,dT$

$dS = 2a\,dT + 4bT^2$

$= 2aT + \frac{4bT^3}{3}$

Q 10 Which of the following thermodynamic relation(s) is/are correct? **JAM 2015 Chemistry(MSQ)**
(A) $(\partial T/\partial V)_S=(\partial P/\partial S)_V$ (B) $(\partial T/\partial P)_S=(\partial V/\partial S)_P$
(C) $(\partial S/\partial V)_T=(\partial P/\partial T)_V$ (D) $(\partial S/\partial P)_T=(\partial V/\partial T)_P$

Q 11 In thermodynamics of open system thermodynamic parameter included are
(a) T,P,V,S (b) T,P,V,S,n (c) T,P,n (d) n only

Q 12 Which one of the following defines the absolute temperature of a system?
(a) $(\partial U/\partial S)_V$ (B) $(\partial A/\partial S)_V$ (c) $(\partial H/\partial S)_V$ (d) $(\partial G/\partial S)_V$ **Gate 2015 Chemistry**

Q 13 The correct thermodynamic relations among the following is **CSIR Dec 2013**

(a) $(\partial U/\partial V)_S = -P$ (b) $(\partial H/\partial V)_S = -P$ (c) $(\partial G/\partial V)_S = -P$ (d) $(\partial A/\partial V)_S = -S$

Q 14 From Maxewell thermodynamic relation,The value of P may be obtained in terms of first partial derivatives of thermodynamic potential (a)G,U (b) G,A (c) A,U (d) H,U

Q 15)The value of $(\delta G/\delta T)_P$ is equal to

a) $(\delta A/\delta T)_V$ (b) $(\delta A/\delta V)_T$ (c) $(\delta U/\delta T)_V$ (d) $(\delta A/\delta T)_P$

16) The change in Enthalpy with respect to change in pressure at constant entropy is equal to

(a) Temperature (b) Volume (c) Pressure (d) Entropy

Q 17 The value of $(\delta S/\delta P)_T$ is equal to

a) $(\delta V/\delta T)_P$ (b) $-(\delta V/\delta P)_T$ (c) $-(\delta V/\delta T)_P$ (d) $(\delta V/\delta P)_T$

Q 18 For a system of constant composition the pressure P is given by **CSIR Dec 2011**

a) $-(\partial U/\partial S)_V$ b) $(\partial U/\partial V)_S$ c) $(\partial V/\partial S)_T$ d) $(\partial U/\partial V)_T$ $dU = -PdV + TdS$

Q 19The change in internal energy with respect to change in entropy at constant volume is

a)Pressure (b) Volume (c) Temperature (d) Entropy

20) A process is carried out at constant volume and at constant entropy. It will be spontaneous if:

$\Delta G<0$ (b) $\Delta U<0$ (c) $\Delta A<0$ (d) $\Delta H<0$ **June 2011 CSIR-JRF**

Q 21The value of isothermal compressibility factor β for n mole of an ideal gas is Jam Physics

(a)$1/P$ (b)n/P (c) $1/P^2$ (d)$-1/P^2$

22).The change in value of thermodynamic potential G with respect to P at constant temperature is (a)V (b) –S (c)P (d) –V

Q 23 The entropy change in terms of α ,β and ΔV is

(a)$\Delta S = \alpha\Delta V/\beta$ (b)$\Delta S=\alpha\beta/\Delta V$ (c) $\Delta S=1/\alpha\beta\Delta V$ (d)can not determine

Q 24 TheMaxewell relation that may be obtained by $dG=VdP - SdT$ is **CSIR 2013 Dec**

(a)$(\delta V/\delta T)_P=(\delta S/\delta P)_T$ (b)$(\delta V/\delta T)_P=-(\delta S/\delta P)_T$ (c)$(\delta S/\delta V)_T=(\delta P/\delta T)_V$ (d)none

Q 25 .The relation between α ,β ,γ and P is use Euler Theorem

(a) $\alpha\beta=\gamma P$ (b)$\alpha\gamma=\beta P$ (c)$\alpha\beta\gamma =P$ (d) $\alpha=\beta\gamma P$

Q 26 The value of α/β for $P(V-nb)=nRT$ is

(a)$R/V\text{-}nb$ (b)$nR/V\text{-}b$ (c) $nR/V\text{-}nb$ (d) nR/V

Q 27 The value of Isothermal compressibility factor at critical point is $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

a) Zero (b) Infinite (c) 1 (d) any real number

Q 28 Which among the following sets of Maxewell relation is correct **Gate 2010 Phy**

a)$T=(\partial U/\partial V)_S$ and $P=(\partial U/\partial S)_V$ b) $V=(\partial H/\partial P)_S$ and $T= (\partial H/\partial S)_P$

c)$P=-(\partial G/\partial V)_T$ and $V=(\partial G/\partial P)_S$ d) $P==-(\partial A/\partial S)_T$ and $S=--(\partial A/\partial P)_V$

Q 29 The criteria of spontaneous change in terms of state function is **Gate Chemistry 2004**

a) $dU_{S,V}\geq 0$ b) $dA_{T,V}\geq 0$ c) $dS_{U,V}\geq 0$ d) $dG_{T,V}\leq 0$

30 Choose the correct criterion of spontaneity in terms of properties of system alone

a) $dS_{U,V}> 0$ b) $dS_{T,P}> 0$ c) $dS_{H,P}> 0$ d) $dG_{T,,V}> 0$ (Both) **Gate Chemistry 2001**

31 The thermodynamic potential which must be negative for spontaneous process at constant Temperature and at constant Pressure (a) G (b) H (c) A (d) U **CSIR JRF**

32Which of the following is path function a) G b) H c) μ d) w

DPP 2 Thermodynamics Science Zone Sahendra Kumar

Q 1 For a pure substance , the slope of the plot of Gibbs free energy (G) against T at constant pressure is a) S [✓ b) –S] c) –H d) $-C_P$ GATE EXAM 1995

Q 2 The parameter which always decreases during a spontaneous process at constant S and V, is
a) H [✓ b) U] c) C_P d) q CSIR JRF II 2016

Q 3 The value of $P/T)_V \cdot P/V)_T \cdot V/T)_P$ for 1 mole of an ideal gas is equal to
a) $-(R^2/P^2)$ b) $-(R^2/V^2)$ [✓ c) (R^2/V^2)] d) -1 Gate 2004

Q 4 When we plot a graph between U vs T at constant volume the slope in the plot is
a) C_P [✓ (b) C_V] (c) 1 (d) can not determine

Q 5 For an ideal gas at 300 K CSIR JRF 2016
[✓ a) $(\delta U/\delta V)_T = 0$] b) $(\delta U/\delta T)_V = 0$
c) $(\delta H/\delta T)_P = 0$ d) $(\delta G/\delta T)_P = 0$

6 $(\delta H/\delta P)_T$ has the dimension of CSIR JRF 2016
a) Pressure [✓ b) Volume] c) Temperature d) Heat Capacity

7. The value of $(\delta U/\delta T)_V$ is equal to
a) C_P [✓ b) C_V] c) 0 d) R

8 The criterian of spontaneity in terms of helmholtz function is
a) $dA_{T,V} > 0$ b) $dA_{T,P} > 0$ [✓ c) $dA_{T,V} < 0$] d) $dA_{T,P} < 0$

Ⓜ 9 For an ideal gas $(\delta U/\delta V)_T + (\delta H/\delta P)_T + (\delta U/\delta P)_T$ is equal to
a) P b) C_P c) R [✓ d) 0]

10.For an ideal gas $(\delta H/\delta T)_P$ is equal to
[✓ a) C_P] (b) C_V (c) 0 (d) 1

11 Incorrect statement from the given statement is
i) In adiabatic free expansion , internal energy remains constant True
ii) In a refrigerator, electrical energy is used to extract heat from the inside of the device and to release it in the surroundings True iii) The relationship between P and V for the process under consideration is represented graphically in what is called an indicator diagram.
the correct above are a) ii,iii (b) i,ii (c) i,iii [✓ (d) all are correct]

12 $(\delta G/\delta P)_T =$ GATE EXAM 2011
[✓ a) V] b) S c) –S d) –V

~~13 The internal pressure $_T$ of a real gas is related to compressibility factor /RT by –~~
~~$_T$ =RT($_T$ (b)( )$_T$ = CSIR JRF 12~~
~~$_T = _v$ (d) $_T = _v$~~

14The internal pressure of a vanderwaal gas is GATE
a)Independent of molar volume
b)Inversely proportional to molar volume
[✓ c) Inversely proportional to square of molar volume]
d)Directly proportional to the molar volume

$\Pi_T = \frac{a}{V^2}$

15 The internal pressure for one mole a vanderwaal gas is --- GATE

$\left(\frac{\partial U}{\partial T}\right)_V$ ✓ $\left(\frac{\partial U}{\partial V}\right)$

$\left(\frac{\partial U}{\partial T}\right)_V = C_V$; $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$\left(\frac{\partial U}{\partial P}\right)_T = 0$

a) (b) (c) zero (d) $\frac{3}{2}$ ✓

16 Consider the statement

self i) U remains constant in every isothermal process in closed system

ii) if q=0 then the process must be isothermal. iii) C_V is independent of volume in case of ideal gas. The true statements above are

(a) i,ii (b) i,ii,iii (c) I only (d) iii only (i, iii)

17.Consider the statements

i) q=0 for every cyclic process ii) P –V work is usually negligible in case of solid and liquid

iii) A thermodynamic process is specified by specifying the initial and final state of the system

iv) Change in temperature is equal to zero for every adiabatic process

the true statements above are (a) ii,iii (b) i,ii and iii (c) ii only (d) iii only

dq = -dw

du = Tds

18 The temperature of 54 gm of water is raised from 15°C to 75°C at constant pressure , the change in enthalpy ΔH is {C_P = 75 J/K-mole} Gate 2007

a) 6 KJ b) 9 KJ c) 12 KJ d) 13.5 KJ

19 229 J of energy is supplied to 3 mole of an ideal gas at constant pressure , the temperature of gas rises by 2.55 K . The value of C_P and C_v . Gate 1996

Q 20 128 For an ideal gas in closed system at constant temperature T , what are the value of {δU/δV} and {δH/δP} ? TIFR 2016

a) {δU/δV} =0 and {δH/δP} =0 b) {δU/δV} > 0 and {δH/δP} < 0

c) {δU/δV} < 0 and {δH/δP} > 0 d) {δU/δV}> 0 and {δH/δP} > 0

Q 21 If U, F, H, and G represent internal energy, Helmholtz free energy, enthalpy, and Gibbs free energy respectively, then which one of the following is a correct thermodynamic relation?

(A) dU =PdV- TdS (B) dH= VdP+ TdS (C) dF=- PdV+ SdT (D) dG =VdP+ SdT IIT J

False Q 22 Consider the statement

i) For liquid and solid the value of $(\delta U/\delta V)_T$ is zero.

ii) for P(v-b)=RT the value of internal pressure is zero.

iii) If dZ=xdy+ydx than z is a state function.

The true statements above are a)I,ii b)ii,iii c) I,iii d) all e) none

23 Consider the statements

i) The cyclic integral of an inexact differential is usually not zero.

ii) work appear on the boundary of the system

iii) heat capacity at constant volume is rate of increase of energy with temperature at constant volume.

The true statements above are a)I,ii b)ii,iii c) I,iii d) all e) none

24 If U is a function of V and T, $(\delta U/\delta T)_P$ is equal to (π and α are the internal pressure and the coefficient of thermal expansion, respectively.)

a) C_P b) C_V c) C_P- π V α d) π V α + C_V CSIR JRF 2016

25 An example of extensive property is GATE EXAM 1994

a) Temperature b) Internal energy

c) Viscocity d) Molar heat capacity

$$\boxed{dU = Tds - PdV}$$ $$\boxed{\frac{\partial U}{\partial V}}$$ $$\frac{dU}{dV}$$

ideal $\frac{\partial U}{\partial T}$ | ideal $\frac{\partial U}{\partial V}$ $\frac{\partial U}{\partial P}$

DPP 3 Thermodynamics SCIENCE ZONE

Q 1 Indicate which of the following relation is not correct CSIR JRF I 2012

a) $-\{\delta T/\delta V\}_S = \{\delta P/\delta S\}_V$ [✓ b)] $-\{\delta T/\delta P\}_S = \{\delta V/\delta S\}_P$ Wrong 2 Ans should

c) $-\{\delta S/\delta V\}_T = -\{\delta P/\delta T\}_V$ $\boxed{\text{d) } -\{\delta S/\delta P\}_S = -\{\delta V/\delta T\}_P}$

Q 2 For a system subjected to only P-V work , entropy is given by IIT GATE 2016 More than 1 Ans

[✓ i)] $-\{\delta G/\delta T\}_P$ ii) $\{\delta G/\delta P\}_T$ iii) $-\{\delta A/\delta V\}_T$ [✓ iv)] $-\{\delta A/\delta T\}_V$

Q 3 Which of the following statement is not true about cyclic process CSIR JRF I 2013

N.T [✓ i)] cyclic integral of heat is equal to zero ii) Cyclic integral of work is zero N.T

(Not true) → iii) Heat can be completely converted into work Explained by Carnot engine

iv) Work can be completely converted into ~~work~~ . Heat → True only

Q 4 The internal pressure $\{\delta U/\delta V\}_T$ of a real gas is related to compressibility factor $Z = \{PV/RT\}$ by CSIR JRF II 2013

i) $\{\delta U/\delta V\}_T = RT\,\{\delta Z/\delta V\}_T$ ii) $\{\delta U/\delta V\}_T = \{RT/VZ\}$

[✓ iii)] $\{\delta U/\delta V\}_T = \{RT^2/V\}\,\{\delta Z/\delta T\}_V$ iv) $\{\delta U/\delta V\}_T = \{V/RT^2\}\,\{\delta Z/\delta V\}_T$

Q 5 The exact differential df of a state function f(x,y) among the following is CSIR JRF II 2014

a) xdy b) dx – (x/y) dy c) ydx-xdy [✓ d)] $(1/y)\,dx - (x/y^2)\,dy$

Q 6 The heat capacity of 10 mole of an ideal gas at a certain temperature is 300 JK^{-1} at constant pressure .The heat capacity of the same gas at the same temperature and at constant volume is given by CSIR JRF II 2013

a) 383 $J\,K^{-1}$ [✓ b)] 217 $J\,K^{-1}$ c) 134 $J\,K^{-1}$ d) 466 $J\,K^{-1}$

Q 7 For one mole of an ideal gas $\{\delta P/\delta T\}_V \{\delta V/\delta T\}_P \{\delta V/\delta P\}_T =$ IIT GATE 2004

a) -1 [✓ b)] $-\{R^2/P^2\}$ c) +1 d) R^2/P^2

Q 8 If a Gas obeys the equation of state $P\{V-nb\} = nRT$, then the ratio $[\{C_P - C_V\}/\{C_P - C_V\}_{ideal}]$ is IIT GATE 2008

a) > 1 b) <1 [✓ c)] 1 d) (1-b)

Q 9 For an ideal gas IIT GATE 2010

a) $\{\delta P/\delta T\}_V \{\delta T/\delta V\}_P \{\delta V/\delta P\}_T = 0$ [✓ b)] $\{\delta P/\delta T\}_V \{\delta T/\delta V\}_P \{\delta V/\delta P\}_T = -1$

c) $\{\delta P/\delta T\}_V \{\delta T/\delta V\}_P \{\delta V/\delta P\}_T = +1$ d) $\{\delta P/\delta T\}_V \{\delta T/\delta V\}_P \{\delta V/\delta P\}_T = +2$

Q 10 Among W (Work) Q (heat) U (Internal energy) and S (Entropy)

a) W and U are path function but Q and S are state function IIT GATE 2010

b) W and S are Path function but Q and U are state function

c) S and U are path function but Q and W are state function

[✓ d)] W and Q are path function but U and S are state function

Q 11 Among the following the system that would require the least amount of thermal energy to bring its temperature to 80°C is IIT GATE 2009

a) 200 gm of water at 40°C b) 100 gm of water at 20°C

[✓ c)] 150 gm of water at 50°C d) 300 gm of water at 30°C

Q 12 The equation of state for one mole of a gas is given by P(V-b) =RT where b and R are constant the value of $\{\delta H/\delta P\}_T$ is CSIR JRF II 2016

a) V-b [✓ b)] b c) 0 d) $\{RT/P\} + b$

$\left(\frac{\partial U}{\partial V}\right)_T$ → for ideal & vanderwaal

$\left(\frac{\partial H}{\partial P}\right)_T$ → Also learn these value

Q 13 If the pressure P (system) is greater than P (surrounding) then CSIR II 2015

a) Work is done on the system by the surrounding

[✓ b) Work is done on the surrounding by the system]

c) Work is done on the system by the surrounding is equal to Work is done on the surrounding by the system

d) Internal energy of the system decreases

Q 14 The Maxwell relationship derived from the equation dG =VdP –S dT is

a) $\{\delta V/\delta T\}_P = \{\delta S/\delta P\}_T$ b) $\{\delta P/\delta V\}_T = \{\delta T/\delta S\}_P$ CSIR JRF 2013

[✓ c) $\{\delta V/\delta T\}_P = -\{\delta S/\delta P\}_T$] d) $\{\delta P/\delta V\}_T = -\{\delta T/\delta S\}_P$

Q 15 The value of $(\delta H/\delta P)_T$ in terms of thermal expansivity α is

[✓ a) V (1- αT)] b) V (1 + αT) c) V (1- α/T) d) (1- αT)

Q 16 The incorrect relation between heat capacity at constant pressure and constant volume are

(a) $C_P - C_V = T(\delta P/\delta T)_V (\delta V/\delta T)_P$ [✓ (b) $C_P - C_V = T(\delta P/\delta T)_V^2 (\delta V/\delta P)_T$]

(C) $C_P - C_V = R$ (for 1 mole of ideal gas) (d) $C_P - C_V = R(1+2a/RTV)$ (For real gas)

Self

Q 17 The temperature of 100 gm of water is raised from 50°C to 100°C at constant pressure the change in enthalpy approximately is (Cp for water is 4.184 J/k-gm)

[✓ (a) 20.91 KJ] (b) 3.76 KJ (C) 104.54 KJ (d) 0 e) None

Q 18 Among the quantities q_{rev}, w , q_{rev}/T and q_{rev} – w the state function are CSIR JRF M

[✓ (a) q_{rev}/T, $q_{rev} - w$] (b) q_{rev}, $q_{rev} - w$ (c) q_{rev}, q_{rev}/T (d) q_{rev}, T , W

19 The temperature of 2 moles of an ideal gas is raised from 300 K to 400 K .The value of ΔH-ΔE for this process is a)0 J (b) 83 J (c) 830 J [✓ (d) 1660 J] CSIR JRF 11

$dU = dq + ~~dw~~$

$= q - PdV$

when V const.

$\boxed{dq_V = C_V dT}$

Proof

20 Internal energy of an ideal gas depends on:

a) Presure (b) volume [✓ (c) temperature] (d) all

For ideal gas

$\left(\frac{\partial U}{\partial T}\right)_V = C_V$, $\boxed{\left(\frac{\partial U}{\partial P}\right)_T = 0}$ $\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$

∴ It gives value only with T so It is function of internal energy Tree

21 Standard enthalpy of vapourisation $\Delta_{vap}H$ for water at 100° C is 40.66 kJmol⁻¹. The internal energy of vapourisation of water at 100°C (in kJmol⁻¹) is

a) + 43.76 (b) 40.66 [✓ (c) 37.56] (d) -43.76

22 For an ideal gas (MSQ) TIFR

a)$(\delta U/\delta T)_P=0$ [✓ (b) $(\delta U/\delta P)_T=0$] (c) $(\delta U/\delta T)_V=0$ [✓ (d) $(\delta U/\delta V)_T=0$]

23 A sample of Argon Gas at 1 atm and 27 °C expands reversibly and isothermally from 1.25 litre to 2.50 litre The change in enthalpy approximately is

a)11.5 Joule (b) 272 Joule (c) 115 Joule [✓ (d) 0]

ΔH, ΔU = 0 for ideal (Rev. & isotherm)

= 0 // (irrev. & //)

24 The value of internal pressure for 1 mole of an real gas with equation P(V-b) = RT is equal to

[✓ a) 0] b) R c) >R d) <R

25 If a gas obey the vanderwall equation of state the ratio of $(C_P-C_V)_{Ideal}$ and $(C_P-C_V)_{Vanderwall}$ is [✓ (a) $\{1+(2a/RTV)\}$] [✓ (b) $\{1-(2a/RTV)\}$] (c) 0 (d) 1

26 The value of $(\delta H/\delta T)_V$ in terms of α and β is

[✓ a) $C_v + \alpha V/\beta$] b) $C_v - \alpha V/\beta$ c) $C_v + \alpha/\beta$ d) $C_v + \alpha V\beta$

27 Work done in increasing the temperature of 1 mole of gas by 2°C at constant pressure is

[✓ a) 2R] (b) R (c) 3R (d) R/2 IISC

→ Problem Solve

Why W = −PdV (mostly)

↓

Because in Thermo we consider only Mechanical work = −PdV

28 Which mechanism of heat transfer is involved in heating a pot within water on a stove

[✓ (a) convection] (b) conduction (c) radiation (d) induction

(a) ↓ Mol. move from 1 to another place

(b) Pass 1→2→3 – ↓ In solid

(c) ↓ Packet Brake fakde ↓ light

(d) ↓ To charge something.

DPP 4 Thermodynamics Science zone

Q 1 (a)Show that for n moles of vanderwall gas is $(\partial U/\partial V)_T=(n^2a/V^2)$. ✓ Subjective (done) $\boxed{\text{Do it}}$

(b)Can a gas that obeys the equation of state P(V-nb)=nRT be liquefied? Explain. IIT J 2012 C

Q 2 $\boxed{2}$ mole of zinc is dissolved in HCl at 25^{0}C The work done in open vessel is [Work done in open vessel considered but not in closed vessel ∵ dV = 0 in closed vessel. (Pressure cooker eg)

a) -2.47 KJ ✓b) -4.95KJ c) 0.0489 KJ d) None

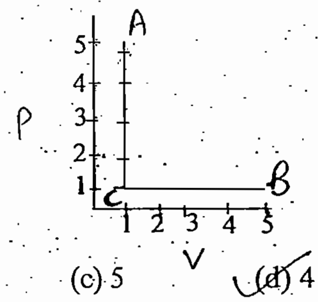
Ans Half value

$\boxed{\text{Q 3}}$ 2 mole of an ideal gas at 27^{0}C expands isothermally and reversibly from a volume of 4 litre to 400 litre then the work done by the gas is

a) -28.72 KJ b) -11.48 KJ c) -5.73 KJ d) -4.98 KJ e) none

−22.976KJ

Q 4 The figure below represents the path followed by gas during exp^n from A to B the work done in {L-atm} is CSIR NETI 2014



$$W = W_{A\to C} + W_{C\to B}$$
$$= (-PdV)_{A-C} - (PdV)_{C-B)}$$
$$= 0 - 1(5-1)$$
$$= 4$$

from A→C dV = 0

P = 1
dV = 5−1

(a) 0 (b) 9 (c) 5 ✓(d) 4

Q 5 When 18 gm of water is heated from 300 K to 600 K at constant volume then the change in internal energy is if (C_V=1.5 R) is

✓a) 450 J/K-mole R b) 45 J/K-mole c) 810 J/K-mole d) 81 J/K-mole

Q 6 The temperature of an ideal gas increase in an

✓a) adiabatic expansion ↓se b) isothermal expansion

✓c) adiabatic compression ↑se d) Isothermal compression

Q 7 One mole of ideal gas is expanded from 1 dm^3 to 10 dm^3 with various different type of processes the correct order of work

✓a) $-W_{isobaric} > -W_{isothermal} > -W_{adiabatic} > -W_{isochoric}$ b) $-W_{isobaric} > -W_{adiabatic} > -W_{isothermal} > -W_{isochoric}$

c) $-W_{isobaric} < -W_{isothermal} < -W_{adiabatic}$ d) $-W_{isothermal} > -W_{isobaric} > -W_{adiabatic} > -W_{isochoric}$

Q 8 When 1 mole of ice is converted to water at 0^{0}C and 1 atm , the work done in (L-atm) is (given density of ice = 0.9 ×10^{3}gm/L , given density of ~~ice~~ water = 1 ×10^{3}gm/L) IIT JAM

a) 1.1 × 10^{-4} ✓b) 2.0 × 10^{-3} c) 2.0 × 10^{-4} d) 1.1 × 10^{-5}

Q 9 Adiabatic reversible expansion of a monoatomic gas (M) and a diatomic gas (D) at an initial temperature Ti, has been carried out independently from initial volume V_1 to final volume V_2. The Final temperature (Tm for monoatomic and T_D for diatomic) attained will be:GATE 2003

(a) $T_M = T_D > T_i$ ✓(b) $T_M < T_D < T_i$ (c) $T_M > T_D > T_i$ (d) $T_M = T_D = T_i$

Q 10 For an ideal gas following adiabatic reversible expansion, plot of log P versus log V is linear with a slope equal to ($\gamma = C_P/C_v$) IIT GATE 2000

a) γ b) 1/γ ✓c) − γ d) − 1/γ

calculation Not solved

[Q 11 2 mole of an ideal diatomic gas (C_v =5/2 R) at 300 K and).507 MPa to be expanded adiabatically to a final pressure of 0.203 MPa against a constant pressure of 0.101 MPa ,the final temperature is

a) 236 K b) 270 K c) 300 K d) none

$$\frac{750}{10^{0.4}} = \left(\frac{750}{10^{0.5}}\right) 250$$

750
1000
100
300

∴ Poisson's eqn

Q 12 One mole of an ideal gas (C_P =29.234 J/K-mole) is expanded reverissibly and adiabatically from 1 dm^3 to 10 dm^3 .If the initial temperature is 750 K , the final temperature would be

a) 1000 K b) 750 K c) 300 K d) 100 K IIT Gate 1996

Q 13 An ideal gas expands by following an ideal gas equation PV^a = constant .In which case one does expect heating ? CSIR June 2011

a) 3>a>2 b) 2>a>1 [✓ c) 0<a< 1] d) -1 <a < 0 (Range of γ ⟶ γ>1)

Q 14 Show that $(\delta x/\delta y)_Z\ (\delta y/\delta z)_x\ (\delta z/\delta x)_y = -1$. IIT GATE 1991

Q 15 One mole of an ideal gas (C_V=1.5 R) at a temperature of 500 K is compressed from 1 atm to 2 atm by a reversible isothermal path .Subsequently , it is expanded back to 1.0 atm by a reverisible adiabatic path .The volume of final state in litre is ~~CSIR JRF~~ 2004 GATE

a) 15.6 b) 20.5 [✓ c) 31.1] d) 41.0

Q 16 The internal energy of an ideal gas follow the equation U=3.5 PV + k , where k is constant .The gas expands from an initial volume of 0.25 dm^3 to a final volume of 0.86 dm^3 .If the initial pressure is 5 Nm^{-2} the change in internal energy (in joule) is (given $PV^{1/3}$ = constant) .... IIT GATE 2015

Q 17 The ration of T_2/T_1 in terms of pressure from the Poission equation is

a) $\{P_1/P_2\}^{\gamma-1/\gamma}$ [✓ b) $\{P_2/P_1\}^{\gamma-1/\gamma}$] c) $\{P_1 P_2\}^{\gamma-1/\gamma}$ d) None

Q 18 The minimum work involved in compression of 1 mole of an ideal gas to double of its initial pressure at 300 K is

[✓ a) 300 R ln 2] b) 600 R ln 2 c) 300 ln 2 d) can not determine because process is not given

Q 19 Assume that the only change in volume is due to production of hydrogen , when 2.0 mole of Zn is dissolved in hydrochloric acid ,the work done at 35 ^{0}C and 1 atm is

a) -51 KJ b) -512 KJ [✓ c) -5 KJ] d) -5120 KJ

Q 20 The work involved in reversible adiabatic transformation when 1 mole of monoatomic ideal gas (C_V =1.5 R) when its temperature change from 200 K to 600 K is

a) 300 R b) 450 R [✓ c) 600 R] d) temperature does not change in adiabatic process

Q 21 Work (w) involved in reverissible isothermal expansion of an ideal gas from Vi to Vf of n mole of an ideal gas is CSIR JRF II 2013

[✓ a) $w= -nRTln\ (V_f/V_i)$] b) $w= nRTln\ (V_f/V_i)$

c) $w= -nRT\ (V_f/V_i)$ d) $w= -nRT\ log\ (V_f/V_i)$

Q 22 For isothermal free expansion of an ideal gas into vaccum , which one of the following set of values are correct ? IIT JAM 2015

dU=0 w=0 ∴ q=dU-w =0

a) ΔU =0 , q > 0 , w <0 b) ΔU > 0 , q > 0 , w =0

[✓ c) ΔU =0 , q = 0 , w =0] d) ΔU <0 , q = 0 , w <0

Q 23 Two mole of an ideal gas is expanded isothermally and reversibly from 5 to 1 bar at 27^{0}C , find the value of W ,Q ,ΔU and ΔH for this transformation.

Q 24 Intensive variable is/ are MSQ IIT JAM 17

[✓ a) Temperature] b) Volume [✓ c) Pressure] [✓ d) Density]

Q 25 In case of adiabatic expansion temperature always

[✓ i) Decreases] ii) Increases iii) remains same iv) 0

Z=?

19/2023

DPP 5 Thermodynamics SCIENCE ZONE

Q 1 The value of γ is independent of temperature in case of

[✓ a) Monoatomic] b) Diatomic c) Triatomic d) Always

Q 2 The 2 mole of an ideal gas is expanded reverisibly and isothermally from 1 atm to 1o atm the work involved in this process is

a) 2.303 RT [✓ b) 4.606 RT] c) 6.909 RT d) 2 RT

Q 3 The temperature of 72 gm of water is heated from 25^0 C to 75^0 C at constant pressure the change in enthalpy is $C_P = 75$ J/K-mole

a) 20 KJ/mole b) 15 KJ /mole [✓ c) 3.75 KJ/mole] d) 10 KJ/mole

Q 4 One mole of ideal gas is expanded i) reverrisibly and adiabatically ii) Ireverrisibly and adiabatically from1 dm^3 to 10 dm^3 if initial temperature is 750 K what is the final temperature in both cases given that $C_V = 1.5$ R.

Q 5 The value of C_V is independent of temperature in case of

[✓ i) Monoatomic] ii) Diatomic iii) Triatomic d) Never

$N = 1 \rightarrow \boxed{U = \frac{3}{2}KT} + 0 + (3N-5)$ ×

Total = ③ N=3

Q 6 One mole of monoatomic gas at temperature 300 K and volume 1 L is expanded reverrisbly and adiabatically till the volume becomes 10 L , what is the value of change in enthalpy for the Gas

Q 7 Consider the statement

i) In reversible adiabatic expansion of an ideal gas change in temperature is higher than ireversible adiabatic expansion of an ideal gas .

ii) Adiabatic Curve in a P-V diagram is steeper than isothermal curve in case of expansion of the ideal gas True

2and relate the ~~intil and final variable~~

The correct statement above are

[✓ a) I,ii] b) ii ,iii c) I,iii d) ALL

Q 8 The contribution made by degree of freedom to internal enrgy that is strongly dependent on temperature is

a) Traslational b) Rotaional [✓ c) Vibrational] d) Electronic

Q 9 The value of γ for SO_2 by Using Equipartition law of energy, if it is considered that all vibrational ode are active, is

a) 1.33 [✓ b) 1.16] c) 1.40 d) 1.66

Q 10 If internal energy for an ideal gas is related with the P and Volume by the relation U=3 PV than the Poission equation in terms of Temperature and volume is

a) TV^3 =Constant b) TV^2 =Constant [✓ c) $TV^{1/3}$ =Constant] d) $TV^{2/3}$ =Constant

Q 11 For CO_2 molecule the energy according to equipartition lw of energy is IIT JAM 2005

a) 3.5 kT b) 4.5 kT [✓ c) 6.5 kT] d) 5.5 kT

Q 12 The molar heat capacity at constant volume for a colourless gas is found to be 25 J/K-mole at room temperature the gas would be IIT JAM 2006

a) N_2 b) O_2 c) CO_2 [✓ d) SO_2]

Q 13 For a cyclic process performed by an ideal gas , changes in some thermodynamic function is zero ,Indicate the set in which ll function is zero

a) w , ΔE ,ΔH ,ΔG b) q , ΔS ,ΔH ,ΔA c)q ,ΔE ,ΔS,ΔG [✓ d) ΔE ,ΔS ,ΔH, ΔA]

$\oint dE = 0$

i.e all state functions zero

Q 14 The molar internal energy of a gas at temperature T is $U_m(T)$ .The molar internal energy at T=0 is $U_m(0)$ .The correct expression that relates these two appropriate contribution is

a) $U_m(T) = U_m(0) + 3\,RT$ { Linear molecule , translational only }
b) $U_m(T) = U_m(0) + 2.5\,RT$ { Linear molecule ,Translational and rotational only}
c) $U_m(T) = U_m(0) + 1.5\,RT$ { Non- Linear molecule , Translational and rotation only}
d) $U_m(T) = U_m(0) + RT$ {Non- Linear molecule Translation Only}

Q 15 Among CH_3Cl , CH_2Cl_2 , $CHCl_3$, CH_3Br and CH_3I in the gaseous state , the one having highest molar entropy value at room temperature is Gate2003chemistry
a) $CHCl_3$ (b) CH_3Cl (c) CH_3Br (d) CH_3I

Q 16 For air at 300K and 25 atm, μ_{JT} is 0.173K atm^{-1}. If a Joule–Thomson expansion is carried out from a pressure of 50.00 atm to a pressure of 1.00 atm, the final temperature is (if the initial temperature is 300 K)
a) 292 K (b) 308 K (c) 284 K (d) none

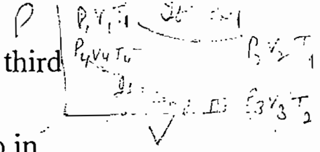
Q 17The relation between critical temp (Tc) inversion temp (Ti) and Boyle temp(T_B) is
a) $T_c > T_i > T_B$ (b) $T_i > T_B > T_c$ (c) $T_i > T_c > T_B$ (d) none of these

Q 18 The maximum work done when pressure on 10 gm of hydrogen is reduced from 20 atm to 1 atm at constant temperature of 273 K .The gas behave ideally . The value of internal energy change ΔU and q respectively are
a) 0, 8180 calorie b) -8180 calorie , 8180 calorie c) 8180 calorie, 0 d) 0,0

Q 19 Assume that the only change in volume is due to production of hydrogen , when 2.0 mole of Zn is dissolved in hydrochloric acid ,the work done at 35 ^0C and 1 atm is
a) -51 KJ b) -512 KJ c) -5 KJ d) -5120 KJ

Q 20 Define isothermal Joule Thomson coefficient and isoenthalpic Joule Thomson coefficient and find a relation between these two. IIT Gate 1995

Q 21 Consider the statements
1 At critical temperature heat of vaporization is zero because it is not possible to distinguish between liquid phase and vapor phase.
2 In Carnot engine in very fist process entropy increases and pressure decreases in third process entropy decrease and pressure increase



3 In carnot engine in isothermal process internal energy change is not equal to zero in individual step but overall internal energy change is zero. F

Entry ↑se ← $V_2 > V_1$, P_2 decrease
Entry ↓se $V_4 < V_3$, P_4 ↑se

The true statements above are a)1,2 (b)1,2,3 (c)2,3 (d)1,3

Q22 Consider the statement
1 There is a natural asymmetry in the efficiency of converting work to heat and converting heat to work.
2 The maximum work that can be done by reversible heat engine operating between 500 K and 200 K if 1000 J is absorbed at 500K is 600 J.
3 The efficiency of heat pump is inverse of efficiency of carnot engine because it works in reverse of refrigeratorThe true statement above are
a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3

Q 23 A carnot engine operating between 127^{0}C and 527^{0}C absorbs 500 J of heat from the high temperature source the maximum efficiency of the engine
a)0.53 (b) 0.75 (c) 0.87 (d) 0.50

Any Q 24 A carnot engine operates at 55 % efficiency . If the temperature of reject steam is 105^{0}C then the absolute temperature of input steam is ....IIT GATE 2014 $T_h = 840.0K$

Q 25 At critical point Heat of vapourisation is ...0...........

$\mu_{J,T} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T_2 - T_1}{P_2 - P_1}$ $T_2 = ✓$

DPP 6 Thermodynamics Science Zone

Q 1 For air at 300K and 25 atm, μ_{JT} is 0.173K atm^{-1}. If a Joule–Thomson expansion is carried out from a pressure of 50.00 atm to a pressure of 1.00 atm, the final temperature is (if the initial temperature is 300 K)

[✓ a) 292 K] (b) 308 K (c) 284 K (d) none

Q 2 The relation between critical temp (Tc) inversion temp (Ti) and Boyle temp(T_B) is

a) Tc>Ti>T_B [✓ (b) Ti>T_B>Tc] (c) Ti>Tc>T_B (d) none of these

Ask in DMS

Q 3 Consider the statements

1 At critical temperature heat of vaporization is zero because it is not possible to distinguish between liquid phase and vapor phase.

2 In Carnot engine in very fist process entropy increases and pressure decreases in third process entropy decrease and pressure increase

3 In carnot engine in isothermal process internal energy change is not equal to zero in individual step but overall internal energy change is zero.

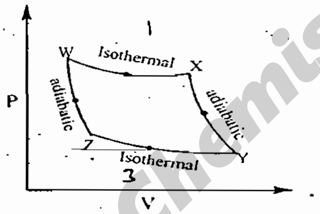
The true statements above are a)1,2 (b)1,2,3 (c)2,3 (d)1,3

Q 4 Assume that the only change in volume is due to production of hydrogen , when 2.0 mole of Zn is dissolved in hydrochloric acid ,the work done at 35 ^{0}C and 1 atm is

a) -51 KJ b) -512 KJ [✓ c) -5 KJ] d) -5120 KJ

Q 5 Write the expression for the vibrational contribution to the total energy of CH_4 (g) at 500 K All the vibrational mode are ative at this Temperature. Find U_m for CH_4 (g).IIT JAM 2009

Q 6 From the carnot cycle undergone by an ideal gas, identify the process in which the change in internal energy is NoN- zero GATE 2015



1,3 → isothermal
$dU = 0$

$dU = C_v dT$

a)I and II [✓ (b) II and IV] (c) II and III (d)I and IV

Q 7 Acarnot cycle operates on a temperature difference of 200K. one third of heat absorbed from the source at T_2 is discharged as waste heat to sink ot T_1. The cycle does 400 J of work. Calculate q_1, q_2 , T_1 and T_2 GATE 1996

T_c T_h q_h

8 A carnot engine operates between 600 and 800 K and absorbs 2,000 calories from the source per cycle. The work done (in cal) per cycle is - GATE

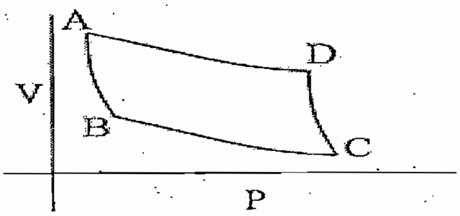
$\eta = \frac{-W_T}{q_h} = \frac{T_h - T_c}{T_h}$

9 A carnot engine operates at 55% efficiency. If the temperature of reject steam at 105^{0}C, then the absolute temperature of input steam is ……….. GATE 2014

$T_h = ✓$

10Define isothermal Joule – Thomson coefficient and isenthalpic Joule – Thomson coefficient and find a relation between the two. Gate 1995

11 The figure below describes how a Carnot engine works. It starts from the adiabatic compression step denoted by CSIR JRF 2016



Opp. figure given

Q9, $\eta = 55\% = \frac{55}{100} = 0.55$

$T_c = 105^0C = 378K$

$T_h = ✓$

$\eta = 1 - \frac{T_c}{T_h}$

a) AB ✓b) BC c) DC d) AD

12 The equation of state for one mole of a gas is given by P(V-b)= RT , where a and R are constants. The value of $(\delta H/\delta P)_T$ is CSIR JRF II 2016

a) v-b ✓b) b c) 0 d) (RT/P)+b`

13 For an ideal gas at 300 K is CSIR JRF 2016

✓a) $(\delta U/\delta V)_T = 0$ b) $(\delta U/\delta T)_V = 0$ c) $(\delta H/\delta T)_P = 0$ d) $(\delta G/\delta T)_P = 0$

14 Consider the statement

1 There is a natural asymmetry in the efficiency of converting work to heat and converting heat to work.

2 The maximum work that can be done by reversible heat engine operating between 500 K and 200 K if 1000 J is absorbed at 500K is 600 J.

3 The efficiency of heat pump is inverse of efficiency of carnot engine because it works in reverse of refrigerator The true statement above are

a) 1,2 ✓(b) 2,3 (c) 1,3 (d) 1,2,3

15 A carnot takes up 90 J of heat from the source kept at 300 K .The correct statement among the following is CSIR DEC C 2012

✓a) It transfer 60 J of heat to the sink at 200 K .

b) It transfer 50 J of heat to the sink at 200 K

c) It transfer 50 J of heat to the sink at 250 K

d) It transfer 60 J of heat to the sink at 250 K

$\frac{Q_c}{T_c} = \frac{Q_h}{T_h}$

$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

16 The coefficient of performance of perfect refrigerator working reversibly between the temperature T_h and T_c is given by IIT GATE C 2004

a) $(T_c - T_h) / T_c$ b) $(T_h - T_c) / T_c$ ✓c) $T_c/(T_h - T_c)$ d) $T_h/(T_h - T_c)$

$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$

17 A carnot cycle operates on a working substance between two reservoir at temperature T_1 and T_2 with $T_1 > T_2$. During each cycle , an amount of heat Q_1 is extracted from the reservoir at T_1 and amount Q_2 is delivered at temperature T_2 . Which of the following statement is incorrect

?

IIT GATE P 2011

Heat engine cyclic Process

entropy → state function zero

a) work done in one cycle is $Q_2 - Q_1$ b) $(Q_1/T_1) = (Q_2/T_2)$

c) Entropy of hotter reservoir decreases ✓d) Entropy of the universe increases ←

18 Assume that a Carnot Engine is working in reverse of refrigerator , with perfect thermodynamic efficiency . Calculate the amount of work needed i) to freeze 100 gm of water at 0^0C , the temperature of surrounding being 25^0 C ii) to withdraw same amount of heat from a body at 10^{-5} K, the surrounding being 1 K . (ΔH_{melt} = 6.01 KJ/mole) TIFR C 2010

$1 - \frac{T_c}{T_h}$

a) i) 601 KJ ii) 601 KJ b) i) 33.4 KJ ii) 33.4 KJ

✓c) i) 3.06 KJ ii) 33.4 KJ d) i) 33.4 KJ ii) 33.4×10^{-5}KJ

$Q_c = \frac{100 \times 6.01 \times 10^3}{18}$

19 Consider a Carnot engine operating between temperature of 600 K and 400 K . The engine performs 1000 J of work per cycle .The heat (in Joules) extracted per cycle from high temperature reservoir is

Ans ?

……2839.3……J IIT JAM 2017 P

$T_c = 10^{-5}$

$T_h = 1K$

20 Which of the following feature is not correct about Joule Thomson experiment

a)The change in pressure is negative throughout experiment

b)The inversion temperature of H_2 and He is very low so it shows heating at ordinary temperature

c)This process is adiabatic, isoenthalpic and also known as throttling process

d)If attractive part dominate over repulsive term than gas does not liquefy.

All correct

✓ Q19. $T_h = 600$

$T_c = 400$

$\therefore dU = -W = 1000 J$ (cyclic so $dU = 0$)

$Q_c = ?$

$Q_h - Q_c = -W$

$\eta = -\frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h}$

$= 1 - \frac{T_c}{}$

$dU_1 = 0$

$dU_2 = C_V (T_c - T_h)$

$dU_3 = 0$

$dU_4 = C_V (T_h - T_c)$

DPP -7 Thermodynamics Sahendra Kumar

Q 1 Acarnot engine operating between 227⁰C and 727⁰C absorbs 500 J of heat from the high temperature source the maximum efficiency of the engine

a)0.53 (b) 0.75 (c) 0.87 [✓ (d) 0.50]

Q 2 The area under temperature entropy curve (T-S) of any thermodynamic process represents

a)Heat absorbed (b) Heat rejected [✓ (c) ~~either~~ both heat rejected or heat absorbed] (d) none

Q3For an isothermal free expansion of an ideal gas into vaccum ,which one of the value is correct

a) $\Delta U=0$,$q>0$, $w<0$ b) $\Delta U>0$,$q>0$, $w=0$ IIT JAM C 2015

[✓ c) $\Delta U=0$,$q=0$, $w=0$] d) $\Delta U<0$,$q=0$, $w<0$

Q 4 For an ideal gas undergoing reversible Carnot Cycle,the plot of Enthalpy H versus Entropy S is IIT JAM C 2011.

Q 5 The number of normal modes of vibration in naphthalene is

a) 55 b) 54 [✓ c) 48] d) 49 IIT JAM 2017 C

Q 6 The work done during the free expansion of one mole of an ideal gas at 27⁰C to twice its original volume is given (given RT = 2494 Jmole⁻¹ ,ln 2=.7 ,log 2=.3) IIT JAM C 2010

a) 1746 J/mole b) -1746 J/mole [✓ c) zero] d) 748.2 J/mole

Q 7 The heat of vapourization of water at 100⁰C is 40.66 KJ / mole , the entropy change when 5 gm of vapor condense is ✓ $v \rightarrow l$

a) -3.02 J/K [✓ (b) -30.2 J/K] (c) -302 J/K (d) +302 J/K e) none

Q 8 The entropy change when 100 gm of water is heated from 50⁰C to 75⁰C at 1 atm pressure is
vapour no cp ✓ given $\rightarrow C_p = 4.184 \frac{J}{K}$-

a) 3.12 J/K [✓ (b) 31.2 J/K] (c) -3.12 J/K (d) – 31.2 J/K e) none

Q 9The conversion of ethylene in form of polyethelene accompanied by the change in

(a) Positive entropy [✓ (b) Negative entropy] (c) Entropy does not change (d) cant say

Q 10Among the following the relation that is accompanied by decrease in entropy IIT JAM

[✓ (a) N_2 (g) + $3H_2$ (g) → $2NH_3$ (g)] [✓ (b) $C_6H_{12}O_6$ (s) + $6O_2$ (g) →6 CO_2 (g) +$6H_2O$ (l)] b/z no of mole decrease. So entropy decrease

(c)PCl_5 (s)→PCl_3 (g) +Cl_2 (g) (d) $2H_2O$ (l) →$2H_2$ (g) +O_2 (g)

Q 11The maximum efficiency of an engine operating between 110⁰ C and 25⁰ C will be

(a) 30.5 % (b) 20.25 % [✓ (c) 22.20 %] (d) 33.3 %

Q 12 For the process 1 Ar (300 K, 1 bar) → 1 Ar (200 K ,10 bar) assuming ideal gas behavior the change in molar entropy is Gate 2011

[✓ a) -27.57 J/K-mole] b) 27.57 J/K-mole c) -24.20 J/K-mole d) 24.20 J/K-mole

Q 13 Ten mole of a gas is allowed to expand from a state A at 10 atm and 300 K to a state B at 100 atm and 600 K . If the value of C_P is 6.955 cal deg⁻¹ mol⁻¹ calculate the entropy change for the process Gate 1998

Q 14 The entropy change associated with freezing of 1 mole of water at 0⁰C and 1 atm is (Heat of fusion under these condition is 6 KJ/mole) Gate 1999

a) -6 J/K [✓ b) -22 J/K] c) 22 J/K d) 6 J/K

Q 15 Then change in entropy when 2 moles of argon gas are heated at constant volume from 300 K to 500 K is Gate 2010

a) -12.74 J/K-mole b) -6.37 J/K-mole [✓ c) 6.37 J/K-mole] d) 12.74 J/k-mole

Q 16 The change in entropy when 1 mole of an ideal gas is compressed to one fourth of its initial volume and simultaneously heated to twice its initial temperature is Gate 2004

a) $(C_V-R)\ln 4$ ✓ b) $(C_V-2R)\ln 2$ c) $(C_V-2R)\ln 4$ d) $(C_V+2R)\ln 2$

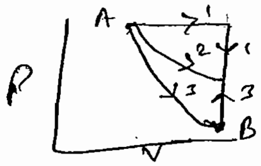
V.Imp Q 17The change in enthalpy when 3 mole of liquid benzene transform to the Vapor state at its boiling temperature (80^0C) and at 1 bar pressure is ....kJ. Gate 2013 chemistry → Useful information of $\Delta S_{Vap} = \frac{88.3 J}{\uparrow T}$

Q 18 The enthalpy of fusion of ice at 273 K is 6.01 KJ/mole and the enthalpy of vaporization of water at 273 K is 44.83 KJ/mole. The enthalpy of sublimation (in KJ/mole) is ...... Gate 2014C

Q 19 One mole of a substance is heated from 300 K to 400 K at constant pressure.. The C_p of the substance is C_p (J/k-mole)=5+0.1 T . The change in entropy in J/k-mole of the substance is .... Gate Chemistry 2015

Q 20 The state of 2 moles of an ideal gas is changed from the point A to the point B along three different paths, as shown in the following P-V diagram. If the change of entropy of the gas in changing its state from state A to B along the path i is denoted ΔSi, then which of the following statements is correct?

Given Graph



a) $\Delta S_1 > \Delta S_2 > \Delta S_3$ B) $\Delta S_1 < \Delta S_2 < \Delta S_3$ C) $\Delta S_1 \neq \Delta S_2 \neq \Delta S_3$ ✓ D) $\Delta S_1 = \Delta S_2 = \Delta S_3$ TIFR 2013C

? Q 21 Calculate the change in the molar entropy of a perfect gas when it is compressed isothermally from a pressure of 1 bar to 10 bar

a) 83.1 JK^{-1} $mole^{-1}$ b) 7.6 $JK^{-1}mole^{-1}$ ✓ c) 19.1 $JK^{-1}mole^{-1}$ d) 183 KJ K^{-1} $mole^{-1}$

Imp → Q 22 The boiling temperature of ethylbenzene is 136 °C. Use Trouton's rule to estimate the enthalpy of vaporization of ethylbenzene at this temperature. m = ?

✓ a) 35 KJ $mole^{-1}$ b) 12 KJ mol^{-1} c) 23 KJ $mole^{-1}$ d) 4.8 KJ $mole^{-1}$

Q 23 One mole of gaseous oxygen is expanded from 10 dm^3 and 298 K to 20 dm^3 and 400 K , If C_P=29.4 J/K-mole then change in entropy in this expansion would be

✓ a) 12.0 J/K-mole (b) 6 J/K-mole (c) 120 J/K-mole (d) 60 J/K-mole

Q 24 Consider the statement Given fig.

Check
1 When we increase the temperature of solid the amplitude of vibration increases so entropy increases
2. In reversible adiabatic expansion increased disorder may be balanced by cooling of the gas
3 For reversible phase transformation ΔS=(ΔH/T).The correct statement above are

a) 1,2 (b) 2,3 (c) 1,3 ✓ (d) 1,2,3

Q 25 Among CH_3Cl , CH_2Cl_2 , $CHCl_3$, CH_3Br and CH_3I in the gaseous state , the one having highest molar entropy value at room temperature is Gate 2003 chemistry

a) $CHCl_3$ (b) CH_3Cl (c) CH_3Br ✓ (d) CH_3I

Q 26 At room temperature which of the molecule show maximum rotational entropy

✓ a) O_2 b) H_2 c) D_2 d) N_2 CSIR JRF 2011

m relate to ↑ rotational partition funct ↑

$S = R\ln q + \frac{U}{T}$

Q 27 Large deviation from Trouton Rule is observed for system which are CSIR C Model

a) having more ordered structure b) having more disordered structure

c) having low melting point ✓ (d) having low boiling point

m↑, q↑, S↑

14 + Cl Br I CH3Cl

DPP 8 Thermodynamics

Sahendra Kumar

Q 1 The efficiency of Carnot engine is 1/6 .On decreasing the temperature of the sink by 65 K , the efficiency increases to 1/3 .The temperature of source is

i) 390 K ii) 325 K iii) 65 K iv) 165 K

Q 2 A carnot engine operate between temperature 600 K and 390 K .It absorb 120 Cal of heat from the source . The heat rejected to the sink

i) 90 Cal ii) 120 cal iii) 60 Cal iv) 140 Cal 78 Cal

Q 3 Whn Fe (s) is dissolved in a closed vessel , the work done is ....IIT GATE 1994

Q 4 The isobaric thermal expansion of an ideal gas is IIT GATE 1995

a) 1/T b) 1/P c) R d) 0

Imp Q 5 The enthalpy of vapourisation of water is zero at IIT GATE 1995

a) at 0^0C b) at the critical pressure

c) at the boiling point d) under no condition

Q 6 Calculate ΔH and ΔS if the temprature of 1.75 mole of Hg(l) is increased from 0^0C to 75^0C at 1 bar . Over this temperature range $C_P = 30 - 4T$

Q 7 An air conditioner consume 1.50×10^3 W of electric power and idealised as reversible carnot refrigerator .If COP of this device is 2.5 then How much heat is extracted from House in 24 Hours is

a) 3.24×10^8 J b) 3.24×10^5 J c) 3.24×10^3 J d) 1.67×10^8 J e) none

Q 8 For which of the following case ΔS = {ΔH}/T IIT GATE CHEMISTRY

a) A Process for which $\Delta C_P = 0$ b) An adiabatic process

c) A constant pressure process d) An isothermal reverisible phase transformation

Q 9 If $\Delta H_{vap} = 30$ KJ/mole and $\Delta S_{vap} = 75$ J/K-mole the value of boiling point is

a) 400 K b) 250 K c) 300 K d) Can not determine

Ans check Imp Q 10 Calculate ΔH_m and ΔS_m for the process

$$H_2O\ (l)\{T=263\ K, P=0.1\ MPa\} \rightarrow H_2O\ (s)\{T=263\ K, P=0.1\ MPa\}$$

Assume that at 273 K the molar enthalpy of fusion of ice is 6006 J /mole the heat capacity of ice is 38 J/K-mole and heat capacity of liquid water is 76 J/K-mole , Consider the heat capacity to be constant (given ln 263 = 5.57 , ln 273 = 5.61) IIT JAM 2010

Q 11 When 2 mol of an ideal gas is expanded isothermally and reverissibly from 5 bar to1 bar at 298 K .The change in entropy (in J K^{-1}) of the system is ....IIT JAM 2015

Q 12 The change in entropy for the following transformation is respectively (+ indicate increase , indicate decrease , 0 indicate no change) IIT JAM 2015

i) $SO_2Cl_2\ (g) \rightarrow SO_2\ (g) + Cl_2\ (g)$ ii) $n\ CH_2 = CH_2 \rightarrow$ polymer (s)

iii) $I_2\ (s) \rightarrow I_2\ (v)$ ↑ΔS iv) Adiabatic reversible transformation of ideal gas

a) + , -,0 ,+ b) + , - , 0,0 c) - ,+,0 ,0 d) +, -,+,0

Ans check Q 13 Find the value of ΔU , ΔH and ΔS for the transformation

$$H_2O(l, 300\ K, 1\ atm) \rightarrow H_2O\ (v, 600\ K, 1\ atm)$$

C_P (l) = 36 J/k-mole , C_P (v) = 35 J/k-mole , ΔH_{vap} =40.6 KJ/mole

Q 14 Determine the overall change in entropy for the following process using 1 mole of He

Ans = ?

$He\ (300\ K,\ 1.5\ atm) \rightarrow He\ (600\ K,\ 15\ atm)$

The Heat capacity of He is 20.8 J/K-mole.

Q 15 Calculate the change in the entropy when 1 mole o solid iodine , I_2 at a temperature of 360 K is heated at constant pressure to produce liquid iodine at a temperature of 410 K . The constant pressure molar heat capacity of solid iodine is 54.44 J/K-mole , and of liquid iodine is 80.67 J/K-mole . The melting temperature of iodine is 387 K , and molar enthalpy of fusion of iodine is 7.87 KJ/mole TIFR 2014 Chemistry

a) 8.6 J/K-mole [✓ b) 28.9 J/K-mole] c) 20.3 J/K-mole d) 11.7 J/K-mole

Q 16 Calculate the entropy change for the transformation IIT GATE 1996

Ans ?

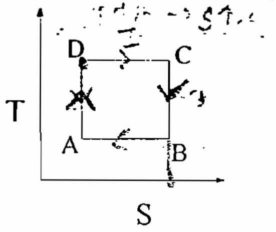
$H_2O\ (liq,\ 1atm) \rightarrow H_2O\ (g,\ 0.1atm)$ at 100^0 C

ΔH_{vap} for H_2O is 40670 J.

Q 17 The correct form Trouton rule is

[✓ (a) $\Delta S = (\Delta H_{vap}/T)$] (b) $\Delta H_{vap} = (\Delta S_{vap}/T)$ (c) $\Delta S_{vap}/\Delta H_{vap} = R$ (d) none

Q 18 If the Carnot cycle in entropy temp diagram look as below IISC



Then the system rejects heat to the surrounding is going from

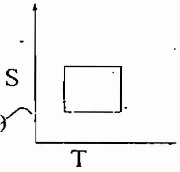
[✓ (a) B → A] (b) A → B (c) D → C (d) C → D

Q 19) A Carnot engine works between the temperature 300 K and 400 K and takes 6 KJ energy. Then what is work done GATE

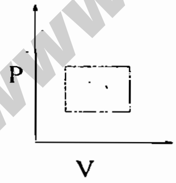
a) 1 KJ [✓ (b) 1.5 KJ] (c) 2.5 KJ (d) 2.0 KJ

20 The Plot that describe the Carnot cycle is GATE

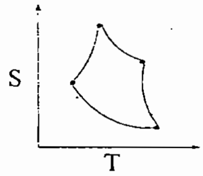
[✓ (a)]



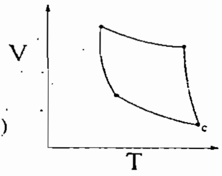
(b)



(c)



(d)



21 Liquid water is to be circulated to transfer from a source to sink at 1 atm . Considering the arrangement as Carnot engine , calculate the maximum theoretical efficiency that can be expected from the system . IIT JAM 2008

Ans check ?

Max. eff. depends upon Max temp diff & for water T_h, T_c $T_h = 100$ $T_c = 0°C$ η ✓

22 Assume that a Carnot engine is working in reveries in a refrigerator, with perfect thermodynamic efficiency. Calculate the amount of work needed (i) to freeze 100 g of water at 0^0C, the temperature of surrounding being 25^0C (ΔH_{melt} = 6.01 KJ/mol)

a) 601 KJ (b) 33.4 KJ (c) 3.06 KJ [✓ (d) 3.06 KJ]

23) A Carnot engine operates between 600 and 800 K and absorbs 2000 cal from the source per cycle. The work done (in cal) per cycle is GATE 1998

a) 1000 [✓ (b) 500] (c) 666 (d) 200

$ds = \frac{dq}{T}$ rev. $dS = 0$

$ds > \frac{dq}{T}$ $ds > 0$

DPP 9 Thermodynamics SCIENCE ZONE

1. According to equipartition law of energy , The molar heat capacity at constant volume for CO_2 (g) ,SO_2 (g) and H_2O (g) follows the trend is JAM Chemistry
(a) $CO_2 = SO_2 = H_2O$ (b) $CO_2 > SO_2 = H_2O$ (c) $CO_2 < SO_2 = H_2O$ (d) $CO_2 = H_2O > SO_2$

2. Calculate the change in entropy when 1 mol of solid iodine, I_2, at a temperature of 360 K is heated at constant pressure to produce liquid iodine at a temperature of 410 K. The constant pressure molar heat capacity of solid iodine is 54.44 J K^{-1} mol^{-1} and of liquid iodine is 80.67 J K^{-1} mol^{-1} . The melting temperature of iodine is 387 K, and the molar enthalpy of fusion of iodine is 7.87 kJ mol^{-1} . TIFR 2014
A) 8.6 J K^{-1} mol^{-1} B) 28.9 J K^{-1} mol^{-1} C) 20.3 J K^{-1} mol^{-1} D) 11.7 J K^{-1} mol^{-1}

3. Consider the statement
1. ΔS when 1 mol of N2(*g*) goes irreversibly from 25°C and 10 L to 25°C and 20 L must be the same as ΔS when 1 mol of N2(*g*) goes reversibly from 25°C and 10 L to 25°C and 20 L.
2. $\Delta S = 0$ for every adiabatic process in a closed system.
3. The entropy of 5 g of Fe at 20°C and 1 atm or 10 g of Fe at 20°C and 1 atm is same.
The correct statement above are
a) 1 (b) 1,2 (c) 1,3 (d) 1,2,3 (e) none of these

4 The entropy change accompanying the transfer of 10460 J of heat from a body A at 300 ^{0}C to a body B at 77^{0}C is 11.6 J/K
a) 11.6 J/k b) 1.2 J/K c) 12 J/K d) 1160 J/K

Ans 5 An ideal gas at 27^{0}C expands isothermally and reversibly from 10 to 1 bar against a pressure that is gradually reduced. Calculate q per mole and w per mole and each of the thermodynamic quantities ΔU ΔH ,ΔS . IIT JAM

Imp 6 A 50 g mass of Cu at a temperature 393 K is placed in contact with a 100 gm mass of copper at a temperature of 393 K in a thermally insulated container .The final temperature and total entropy change respectively are { given that specific heat capacity of water =0.4184 J/K-gm)

Ans
a) 333 K , 4.85 J/K-mole 346 b) 303 K , .485 J/K-mole
c) 303 K , 4.85 J/K-mole d) 333 K , .485 J/K-mole

Q 7 5 gm of ice at 273 K is added to 30 gm of water at 323 K in a thermally insulated container the final temperature and entropy change corresponding to ice is
{Given that C_p(w)=4.184 J/k-g , Heat of fusion of ice =334.72 J/g}
a) 304 K , 8.40 J/K b) 304 K , .840 J/K
c) 324 K ,8.40 J/K d) 324 K , .840 J/K

Q 8 10 gm of ice is heated to become vapor at 373 K and 101325 kPa .Calculate change in entropy for the system {given that Given that C_p(ice)=4.184 J/k-g , Heat of fusion of ice =334.72 J/g , Heat of vaporization 2259.36 J/g}
a) 8.58 J/k b) 85.8 J/k c) 858 J/k d) .858 J/k

Q 9 For water ΔH_{vap}= 41 KJ mole^{-1} .The molar entropy of vaporization at 1 atmospheric pressure is approximately CSIR JRF C 2012
a) 410 J/K-mole b) 110 J/K-mole c) 41 J/K-mole d) 11 J/K-mole

Ans - 2 Q 10 N atom of ideal gas are enclosed in a container of volume V .The volume of the container is changed to 4 V , while keeping total energy constant , the change in entropy of the gas in unit of $Nk_B \ln 2$ is .... Gate P 16

T=0

Q 11 During isothermal expansion of an ideal gas which of the following happen:
(i) Temperature does not change (ii) Process is spontaneous → $\Delta S = nR\ln\frac{V_2}{V_1}$ ∴ $V_2 > V$
(iii) The energy of the system does not change (iv) Entropy increases TIFR 17 ΔS +ve
A) i and iii only B) i, ii, and iv only C) i, iii, and iv only D) i, ii, iii and iv ∴ spontaneous

→ Q 12 Under what circumstances $\Delta S = -nR \in x_i \ln x_i$ valid . What is ΔS for isothermal mixing at 300 K of 33.6 litre of O_2 and 22.4 litre of N_2 at 1 atm pressure is mixed in such a way the final volume becomes 44.8 litre. Gate Chemistry

Q 12 1 mole CO_2 , 1 mole of N_2 and 2 mole of O_2 were mixed at 300 K . The entropy of mixing is ✓(a) 6 R ln 2 (b) 8R ln 2 (c) 8R ln 2/300 (d) 16 R ln 2 CSIR JRF NET

13 At 273 K temperature , 1 atm pressure 1 mole of N_2 and 4 mole N_2 are mixed together. What will be the entropy of mixing TIFR
a)0.69 J/K (b) 20.8 J/K (c) 0 (d) 4.16 J/K

14 The entropy of mixing of 10 moles of helium and 10 moles of oxygen at constant temperature and constant pressure , assuming both to be an ideal gas is Gate chemistry
check a)115.3 J/K (b) 5.8 J/K (c) 382.9 J/K (d) 230.6 J/K

15 Assuming that there is no chemical reaction , the change in entropy when 2 moles of N_2 , 3 moles of H_2 and 2 moles of NH_3 are mixed at constant temperature is Gate chem
a) -62.79 J/K ✓(b) 62.79 J/K (c) 125.58 J/K (d) -125.58 J/K

16 Consider the statement

MCQ → 1. The entropy change for reversible as well as irreversible adiabatic process is equal to 0.
$\frac{dq}{T} = 0$
? 2. When we plot a graph between G vs T at constant pressure then the slope is generally $-\boxed{T}$ and the value of slope is maximum in liquid phase than solid and vapour phase.
$ds > \frac{dq}{T}$
3. In irreversible phase transformation entropy change may be calculated by converting irreversible phase transformation to revrisible phase transformation.
70
The true statement above are
a)1.2 (b) 2,3 (c) 1,3 (d) 1,2,3

$\left(\frac{\partial G}{\partial T}\right)_P = -S$

17 One mole of a substance is heated from 300 K to 400 K at constant pressure . The C_p of the substance is C_p (J/k-mole) = 5+ 0.1 T . The change in entropy in J/k-mole of the substance is .... Gate Chemistry 2015

18 The melting point of water at the pressure of interest is 0.00^0C and the enthalpy of fusion is 6.010 KJ mol^{-1} the boiling point is 100^0C and the enthalpy of vaporization is 40.65 KJ mol^{-1} Calculate for transformation ......[heat capacity of liquid water at 1 atm is 75.3J/K-mole]
$H_2O(s, 0^0C \rightarrow H_2O(g, 100^0C)$

19 The Helmholtz free energy of a photon gas is given by $F = -\frac{a}{3}VT^4$ where a is constant the entropy S and pressure P of the photon gas are GATE-2007- PHY
✓(a) $S = \left(\frac{4}{3}\right) aVT^3, P = \left(\frac{a}{3}\right)T^4$ (b) $S = \left(\frac{1}{3}\right) aVT^4, P = \left(\frac{4}{3}\right) aT^3$
(c) $S = \left(\frac{4}{3}\right) aVT^4, P = \left(\frac{a}{3}\right)T^3$ (d) $S = \left(\frac{1}{3}\right) aVT^3, P = \left(\frac{4}{3}\right) aT^4$

20 Standard entropy of crystalline carbon monoxide (J/K-mole) at 0K is around
(a) 0.03 (b) 2.50 (c) 0 (d) 5.76

21 One mole of an ideal gas expands isothermally (at 300K) from 1.0dm^3 to 10dm^3 an finally attains a mechanical equilibrium. What are the entropy change of the system and tha of surrounding respectively (R = 2cal-K-mole)
(a) 4.6 Cal/K and – 4.6 Cal/K (b) 4.6 Cal/K and – 1.8 Cal/K
(c) 1.8 Cal/K and – 4.6Cal/K (d) 1.8 Cal/K and – 1.8 Cal/K

Q 22 At 20 °C, the standard EMF of a certain cell is +0.2699V, and at 30 °C it is +0.2669V. What can you say about the standard entropy of this reaction? Assume that the standard ΔH° and ΔS° are independent of temperature. TIFR EXAM 2012

$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)$

$= nF\left(\frac{E_2 - E_1}{T_2 - T_1}\right)$

A) ΔS° = 0 B) ΔS° = +ve C) ΔS° = −ve D) Not enough information is given

23 For the following reaction

$CO_2 + H_2O \rightarrow H_2CO_3$

The entropy change (ΔS_{system}) was calculated to be -96 J/K-mole. The enthalpy change (ΔH) was measured to be -45kJ/K-mole The reaction is considered to be spontaneous The total entropy change in entropy ($\Delta S_{system} + \Delta S_{surrounding}$) is TIFR EXAM 2014 Ans = +ve

a) + 54 J/K-mole b)-96 J/K-mole c)-45096 J/K-mole d)-44004 J/K-mole

Q 24 82 For a pure substance , the slope of the plot of Gibbs free energy (G) against T at constant pressure is a) S b) –S c) –H d) $-C_P$ GATE EXAM 1995

25 ΔH^0_{298} for the reaction $C_2H_4O\ (g) \rightarrow CH_4\ (g) + CO\ (g)$ is -16.0 kJ . From the given data ; evaluate the temperature Which ΔH will be zero ? GATE EXAM 2002

Substance	C_2H_4O (g)	CH_4 (g)	CO(g)
C_P (J/K-mole)	50	36	30

a)1298 K b) 1000 K c) 1298 ⁰C d) 1100 ⁰ C

26 Consider the following reaction use the data given below GATE EXAM 2001

$N_2\ (g) + 3H_2(g) \rightarrow 2\ NH_3\ (g)$ ΔH^0 (25⁰ C) =-92.2 kJ)

Substance	N_2 (g)	H_2 (g)	NH_3 (g)
C_P (J/K-mole)	29.1	28.8	35.1

→ n [illegible] Multiply or add ?

Assuming C_P to be independent of temperature , the reaction at 100⁰C compared to that at 25⁰C will be a) endothermic b) less exothermic c) more exothermic d) having ΔH^0 =0

27 For the reaction $2Cl(g) \rightarrow Cl_2\ (g)$ the thermodynamic properties GATE EXAM 2003

a) ΔG , ΔH and ΔS are positive b) ΔG , ΔH and ΔS are negative

c) ΔG , ΔH are negative and ΔS are positive d) ΔG is negative , ΔH and ΔS are positive

28 For an irreversible adiabatic expansion of a perfect gas from volume Vi to Vf, the change in entropy of the gas is – GATE

(a) nR ln (Vf/Vi) (b) zero (c) less than zero (d) greater than zer

29 Consider 2 mole of an ideal diatomic gas at 300 K and 5 atm to be expanded adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. The final temperature is (given C_V=2.5 R)

a) 220 K (b) 250 K (c) 150 K (d) 270 K

30 1 mole of an ideal gas undergoes reversible isothermal expansion from an initial volume of V to final volume 10 V and does 10 KJ of work .If the initial pressure was 10^7 Pa the value of V_1 is

a) $4.34 \times 10^{-3}\ m^3$ b) $4.34 \times 10^{-4}\ m^3$

c) $4.34 \times 10^{-2}\ m^3$ d) $4.34 \times 10^{-1}\ m^3$ e) none

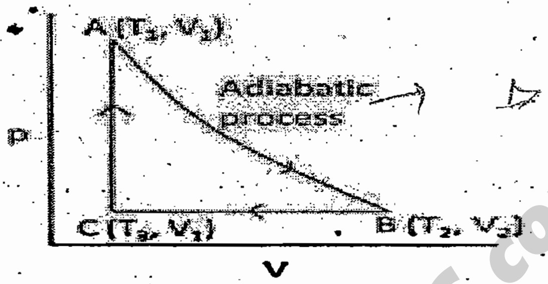
31 The graph corresponding to P vs V for the expansion of an ideal gas for isothermal expansion , adiabatic expansion ,isobaric and isochoric process are ………………

32 The free energy change accompanying the compression of 1 mole of gas at 57^0C from 25 atm to 200 atm is
a) 3.4 kJ b) 6.3 kJ c) 8.6 kJ d) 5.7 kJ

33 The value of $\Delta U - \Delta H$ for the reaction
$Fe_2O_3 + 3\,C(S) \rightarrow 2\,Fe(S) + 3CO(g)$ CSIR 2015
[✓ a) -3 RT] b) 3RT c) RT d) –R T

34 Consider the progress of a system along the path shown in the figure . ΔS (B→C) for one mole of an ideal gas is given by

check



$\Delta S = 0$

a) $C_V \ln (T_3/T_1)$ b) $C_V \ln (T_3/T_2)$ c) $R \ln (V_2/V_1)$ d) None

35 Adiabatic reversible expansion of a monoatomic gas (M) , a diatomic gas (D) and triatomic gas has been carried out independently from initial volume V_1 to final volume V_2. The Final temperature (Tm for monoatomic and TD for diatomic and T_T for triatomic) attained will be:
(a) $T_M = T_D > T_T$ (b) $T_M < T_D < T_T$ (c) $T_M > T_D > T_T$ (d) $T_M = T_D = T_T$

Q 36 Of the following inequalities the criteria for spontaneity of a chemical reaction is/are
i) $\Delta G_{T,P} < 0$ ii) $\Delta U_{S,V} > 0$ iii) $\Delta S_{U,V} > 0$ iii) $\Delta A_{T,V} < 0$
A) i only b) I,iii only [✓ c) i,iii,iv] d) all

Q 37 The internal pressure $\left(\frac{\partial U}{\partial V}\right)_T$ of a real gas is related to Second virial coefficient B is { if Z is related with B by equation Z= {1 +(B/V)}
a) $\left(\frac{\partial U}{\partial V}\right)_T = RT^2\left(\frac{\partial B}{\partial V}\right)_T$ (b) $\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{(\bar{V}B)}$
c) $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{RT^2}{\bar{V}2}\right)\left(\frac{\partial B}{\partial T}\right)_V$ (d) $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\bar{V}}{RT^2}\right)\left(\frac{\partial B}{\partial T}\right)_V$

Q 38 The entropy change for a chemical reaction $N_2\,(g) + 3\,H_2(g) \rightarrow 2NH_3\,(g)$at pressure 1 bar is 100 J/K than entropy change corresponding to 10 bar is
a) 100 + 2.303 R b) 100 – 2.303 R c) 100 + 4.606 R [✓ d) 100-4.606 R] e) none

Q 39 The value of $\{\delta C_v/\delta V\}_T$ for 1 mole of vanderwall gas is
a) >1 b) <1 c) 0 d) 1

$S = k \ln W$

Q 40 The number of configuration in the most probable state according to Boltzmann formulae is
[✓ a) $e^{s/kb}$] b) $e^{-s/kb}$ c)) $e^{E/kbT}$ d)) $e^{-G/kbT}$ CSIR JRF 14

$W = e^{S/k}$

Q 41 The molar entropy of crystalline CO is Gate
a) zero [✓ b) R ln 2] c) –R ln 2 d) 2 R ln 2

Q 42 For one mole of mono atomic ideal gas the relation ship between P , volume V and average kinetic energy ε is IIT GATE 2011
a) $P = (N_A\,\varepsilon) / V$ b) $P = (N_A\,\varepsilon) / 3V$ c) $P = (2N_A\,\varepsilon) / 3V$ $P = (2N_A) / V\varepsilon$

DPP 10 Thermodynamics

Q 1 Which of the following properties are characteristic of an ideal solution

[✓ i)] ΔG_{mix} is negative [✓ (ii)] ΔS_{mix} is positive (iii) ΔV_{mix} is positive (iv) ΔH_{mix} is negative

a) i and iv [✓ (b)] i and ii (c) i and iii (d) iii and iv Gate 2015 Chemistry

?

Q 2 Consider ideal mixing of 2 moles of toluene and 2 moles of benzene at 1 atm and 300 K. Calculate the value of ΔV_{mix}, ΔU_{mix} , ΔH_{mix} , ΔG_{mix}, ΔS_{mix}. JAM 2012 Chemistry

S_{mix} formula apply for gases so here ?

Q 3 A container is partitioned into two compartment one of which contains 2 mole of He while the other contains 3 mole of Ar. The gases are ideal .The temperature is 300 K and the pressure is 1 bar If the partition between two compartments is removed and the gas are allowed to mix, then what is Gibbs free energy of mixture. What is the change in entropy in this process.JAM2009C

Ans ?

Q 4 For mixing of two ideal gas at 25^{0}C and 1 atm which one is incorrect GATEChem

(a) $\Delta T_{mix}=0$ (b) $\Delta H_{mix}=0$ (c) $\Delta V_{mix}=0$ [✓ (d)] $\Delta S_{mix}=0$

Q 5 For a binary mixture of an ideal gas Gibbs free energy of mixing

ΔG_{mix} = nRT [xlnx + (1-x)ln(1-x)] where x is the mole fraction of one of the component what are the enthalpy change and entropy of mixing. CSIR JRF CHEMICAL SCIENCE

This is for ideal mixing

a) $\Delta H_{mix} > 0$, $\Delta S_{mix} > 0$ b) $\Delta H_{mix} < 0$, $\Delta S_{mix} < 0$

[✓ c)] $\Delta H_{mix} = 0$, $\Delta S_{mix} > 0$ d) $\Delta H_{mix} > 0$, $\Delta S_{mix} = 0$

Q 6 The vapour pressure of Benzene is 5333 Pa at 7.6^{0}C and 53330 Pa at 60.6^{0}C calculate the heat of vaporization of benzene and normal boiling point of benzene. JAM 2014 Chemistry

why T_1 or T_2 used

Q7 Thevapour pressure of solid and liquid is given as

$\log_e P^{solid} = 24 - (3900/T)$ and $\log_e P^{liquid} = 18 - (2600/T)$

whereP_{solid} and $P_{liquid}$are the vapour pressure (in torr) of solid and liquid chlorine near the triple point respectively and T is the absolute temperature. The ratio of slope of solid gas curve to the slope of liquid gas curve at the Triple point in P-T diagram is ....JAM 2013 Chemistry

Q 8 . For the liquid to vapourequillibirium of a substance dP/dT at 1 bar and 400 K is 8×10^{-3} bar K^{-1}.If the molar volume in the vapour form is 200 L mole^{-1} and molar volume in liquid form is negligible than molar enthalpy of vapourization is CSIR JRF

a) 640 KJ/mole (b) 100 KJ/mole (c) 80 KJ/mole [✓ (d)] 64 KJ/mole

Q 9 If the enthalpy change and entropy change for the process C_6H_6 (l)→C_6H_6 (v) are respectively 33.90 KJ/mole and 96.4 J/K-mole, the temperature at which the vapour pressure of C_6H_6(g) is 35 torr will be

(a) 352 K (b) 507 K [✓ (c)] 278 K (d) 273 K

Q 10 Consider the statement

(1) on increasing the pressure generally boiling point of water increases and melting point decreases

(2)The entropy of liquid phase is smaller than entropy of vapour phase because condensation is an exothermic process.

$(\therefore \Delta S = \frac{\Delta H}{T} = -ve)\ \Delta H = -ve$

(3)when water converted into vapour and behave ideally than difference in internal energy change and enthalpy change is greater than zero.

?

The correct statement above are (a) 1 [✓ (b)] 1,2 (c) 2,3 (d) 1,2,3

13 For the reaction X_2O_4 (l) → 2 XO_2(g) at 298 K, given the value ΔU = 9KJ and

$\Delta S = 84 JK^{-1}$ ΔG is GATE-2013

a) – 11.08KJ (b) 11.08KJ (c) – 13.55KJ (d) 13.55KJ

14 Consider the transition of liquid water to steam as water boils at a temperature of 100^{0}C and 1 atm .Which one of the following entity does not change discontinuously at the transition CSIR NET PHYSICS ? ?

a) The gibbs free energy (b) The internal energy (c) the entropy (d) the specific volume ✓

15 Consider the statement (i)On the mountain cooking is difficult because on mountain the pressure is low so boiling point increases. ?

ii)If any engine reject more heat as waste than carnot engine than impossible engine. irreversible shall be

True statement above are a) 1,2 (b)2 (c)1,3 (d) 1,2,4 (e) None ✓

16 The normal boiling temperature of benzene is 353.24 K, and the vapor pressure of liquid benzene is ,1.19×10^4 Pa at 20.0°C. The enthalpy of fusion is 9.95 KJ/mole and the vapor pressure of solid benzene is 137 Pa at -44.3^{0}C . The ΔS_{vap} and ΔH_{vap} respectively are ……. ………….

17 The variation of the vapor pressure of the liquid and solid forms of a pure substance near the triple point are given by $\ln(P_{solid}/Pa)$ = -8750(K/T) +34.143 and $\ln(P_{liquid}/Pa)$ = -4053(K/T) +21.10.The temperature and pressure at the triple point respectively are ………… …………

18 Estimate the pressure necessary to melt water at -10°C if the molar volume of liquid water is 18.01 mL and the molar volume of ice is 19.64 mL. ΔS for the process is +22.04 J/K and you can assume that these values remain relatively constant with temperature. You will need this conversion factor: 1 L bar = 100 J.

19 The Temperature dependence of vapour pressure of solid A can be represented by log P = 10-(1800/T) and that of liquid A is represented log P = 8-(1400/T) . The temperature of triple point of A is (a) 200 K (b) 300 K (c) 400 K (d) 500 K CSIR-JRF-CHEMICAL SCIENCE

20 Calculate the vapour pressure of toluene at 100^{0}C assuming that Trouton rule is obeyed .The boiling point of toluene is 110^{0}C. IIT GATE 2002

21 A liquid has a vapor pressure of 2.02×10^3 N m^{-2} at 293 K and heat of vaporization is 41 KJ mole^{-1}. The boiling point of liquid in Kelvin is ……….Gate 2015 Chemistry

22 The non spontaneous process among the following is CSIR JRF Chemical Science

a) Vapourization of superheated water at 105^{0}C and 1 atm pressure .
b) Expansion of gas in vaccum
c) Freezing of super cooled water at -10^{0}C and 1 atm pressure.
✓ d) Freezing of water at 0^{0}C and 1 atm

23 The temperature dependence of vapour pressure of solid A can be represented by $\log P = 10 - (\frac{1800}{T})$ and that of liquid A is represented $\log P = 8 - (\frac{1400}{T})$ the temperature of triple point of A is CSIR NET JRF 2015

a) 200K (b) 300K (c) 400K (d) 500K

Q 24 The specific volume of liquid water is 1.001 mL/g and that of ice is 1.0907 mL g^{-1} at 0^{0}C. If the heat of fusion of ice at this temperature 333.88 J/g , The rate of change of melting point of ice with pressure of deg atm^{-1} will be GATE 2007

-ve & +ve check

✓ a) -0.0075 b) 0.0075 c) 0.075 d) -0.075

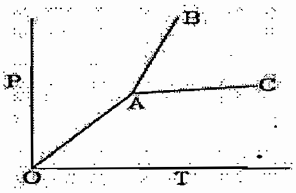
//

DPP Thermodynamics

Imp for NET

Q 1 Estimate the pressure necessary to melt ice at -10^0 C if molar volume of liquid water is 18.01 ml and molar volume of solid ice is 19.64 , The entropy change for melting process is 16.3 J/K (assume that entropy change and volume remains constant in this temperature range) (1L-bar=100J) IITJAM2012

Q 2 . Phase diagram of a compound is shown below: CSIR JRF 2016

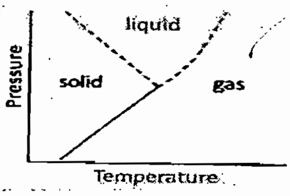


The slope of line OA, AC and AB are tan π/4 , tan π/6 and tan π/3 respectively , if melting point and Δ H of meltting respectively are 300 K and 3 KJ/mole respectively the change in volume of melting is

a) 10 tan π/3 b) 10 tan π/4 c) 10 cot π/3 d) 10 cot π/4

Q 3 Determine the incorrect statement regarding the given graph

NET (Section-A)



(For water)

a) M.P increase with pressure b) M.P decrease with pressure

c) B.P increase with pressure d) solid liquid gas can coexist at same pressure and temperature

Q 4 .2 mole of He is mixed with 3 mole of Ne ideally ΔS corresponding to Ne is............

Q 5 The vapour pressure P of a solid at temperature T is expressed by lnP=23 - (3863/T) and that of liquid phase is ln P = 19 – (3063/T) the triple point (in Kelvin) of the material is Gate 2007 P

a) 185 K b) 190 K c) 195 K d) 200 K

Q 6 Two gases separated by an impermeable but movable partition are allowed to freely exchange energy. At equilibrium, the two sides will have the same Gate physics 2013

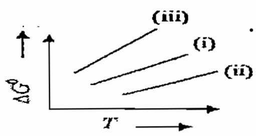
(A) pressure and temperature (B) volume and temperature ΔG = 0 , T, P same

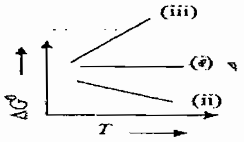
(C) pressure and volume (D) volume and energy

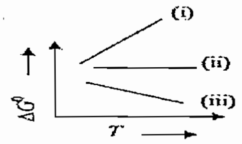
Q 7 The residual entropy of the asymmetric molecule N_2O in its crystalline state is 5.8 J/K –mole at absolute zero . The number of orientation that can be adopted by N_2O in its crystalline state is Gate 2008

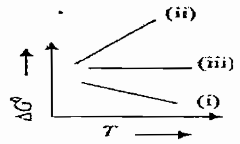
a) 4 b) 3 c) 2 d) 1

Q 8 The standard Gibbs free energies of the following reactions, ΔG^0 , have been determined at various temperatures. (i) $C(s) + O_2(g) \rightarrow CO_2(g)$ (ii) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ (iii) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ Which of the following plots would represent most likely the temperature dependence of ΔG^0 ?TIFR

(A)


(B)


(C)


(D)


Q 9 Hydrogen adsorption on platinum surface is IIT GATE
a) Endothermic with positive ΔS and positive ΔG b) Endothermic with positive ΔS and negative ΔG
c) Exothermic with negative ΔS and negative ΔG d) Endothermic with positive ΔS and negative ΔG

10 Standard entropy of crystalline carbon monoxide (in J/K-mole) at 0K is around
a) 0.03 b) 2.50 c) zero d) 5.76 IIT GATE

Check standard of [illegible]

11 One mole of an ideal gas expands isothermally (at 300 K) from 1.0 dm^3 to 10 dm^3 and finally attains a mechanical equillibrium .What are the entropy change of the system and that of surrounding respectively (R=2 Cal/K-mole) CSIR
a) 4.6 Cal /K and -4.6 Cal/K b) 4.6 Cal /K and -1.8 Cal/K
c) 1.8 Cal /K and -4.6 Cal/K d) 1.8 Cal /K and -1.8 Cal/K

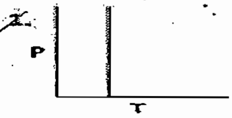
Q 12 One mole of an ideal gas initially at 300 K and a pressure of 10 atm undergoes adiabatic expansion . (i) reversibly (b) irreversibly against a constant external pressure of 2 atm until the final pressure becomes equal to the external pressure.Find the value of ΔS_{system} for (i) and (ii) in the terms of R (heat capacity at constant volume is Cv=1.5 R) IIT JAM 2011

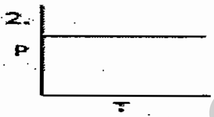
Q 13.Consider the statement
1.Classiusclayperon equation is applicable to first order phase transformation.
2.The slope of liquid gas coexistence curve is smaller than slope of solid liquid coexistence curve in P-T diagram $(l \to g) < (s \to l)$
3 solid gas coexistence curve ends at critical point , liquid gas coexistence curve ends at triple point
Which of the above statement is true (a) 1,2 (b) 1,2,3 (c) 1 only (d) 2 only

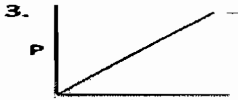
Q 14 The entropy change accompanying the transfer of 10460 J of heat from a body A at 300 ^{0}C to a body B at 77^{0}C is
a) 116 J/k b) 1.2 J/K c) 12 J/K d) 1160 J/K

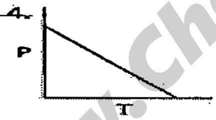
Q 15 Vapour pressure of water at 95^{0}C and 100^{0}C are 634 mm and 760 mm respectively the molar heat of vaporisation of water between 95^{0}C and 100^{0}C is
a)41363 J/mole b) 46562 J/mole c) 56234 J/mole d) 64532 J/moe

Q 16 The volume change in a phase transition is zero. From this, we may infer that the phase boundary is represented by

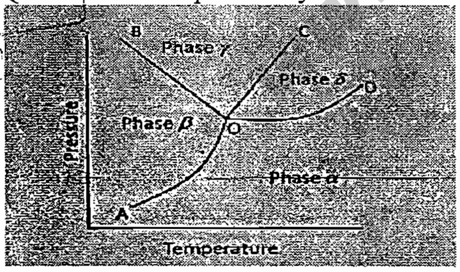
1.


2.


3.


4.


Q 17 A one component system with the associated phase diagram CSIR JRF



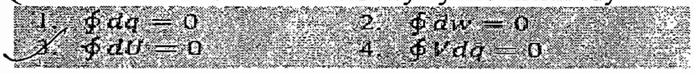
Choose incorrect.

4 phase. can't exist at triple point

a) OB has a negative value b) OC has a positive value
c) Both OB and OC are linear d) OB,OC and OD can not coexist , given OA

Q 18 A phase transition process is always CSIR JRF
a) Isothermal -isoentropic b) Isochoric –isothermal c) isobaric-isochoric d) isothermal –isobaric

Q 19 The correct statement for any cyclic thermodynamic process is CSIR JRF


1. $\oint dq = 0$ 2. $\oint dw = 0$
3. $\oint dU = 0$ 4. $\oint V dq = 0$

Why

Q 20 The minimum work required by an engine to transfer 5 J of heat from a reservoir at 100 K to a reservoir at 300 K is CSIR JRF
a) 5 J b) 10 J c) 15 J d) 20 J

DPP 12 Thermodynamics Sahendra Kumar

Q 1 The ΔH^0 for the reaction $CO(g) + ½\ O_2(g) \rightarrow CO_2(g)$ at 400K in KJ mol^{-1} is....given at 298 K JAM-2016-CHEMISTRY

	ΔH^0 KJ mol^{-1}	C_p^0 J mol^{-1} K^{-1}
O_2	0	29.4
CO	– 110	29.1
CO_2	– 394	37.1

Q 2 ΔH of a reaction is equal to slope of the plot of NET-2015

(a) ΔG versus $\frac{1}{T}$ (b) ΔG versus T (c) $\frac{\Delta G}{T}$ versus T [✓ (d) $\frac{\Delta G}{T}$ versus $\frac{1}{T}$]

Q 3 A reversible expansion of 1.0 mol of an ideal gas is carried out from 1.0 L to 4.0 L under isothermal condition at 300K. ΔG for this process NET-2015

(a) 300 R ln 2 (b) 600 R ln 2 [✓ (c) – 600 R ln 2] (d) – 300 R ln 2

Q 4 .The free energy change ΔG for 1 mole of an ideal gas that is compressed isothermally from 1 atm. to 2 atm. is GATE-2009

[✓ (a) RT ln 2] (b) – 2RT (c) – 2RT ln 2 (d) 2RT

Q 5.$\left(\frac{\partial G}{\partial P}\right)_T = ?$ GATE-2011

[✓ (a) V] (b) S (c) – S (d) – V

Q 6 .Calculate the equilibrium pressure for the conversion of graphite to diamond at 25^0C. The densities of graphite and diamond may be taken to be2.25 and 3.51 g cm^{-3}, respectively, independent of pressure, in calculating the change of ΔG with pressure. Means Dependence of G on P,T, Both Solids

$\Delta G^0 = 2900$ J/mole

Q 7 (a) Given that ΔG = – nFE, derive the expression for the temperature dependence of the cell potential in terms of change in entropy ΔS

(b) For a cell reaction E at (25^0C) = 1.26 volt, n = 2, ΔS = – 96.5J/K-mole, calculate ΔS at 85^0C by assuming ΔS to be independent of temperature IIT-JAM-2011

ΔE_2

Q 8 The temperature dependence of an electro chemical cell potential is NET-2015

(a) $\frac{\Delta G}{nFT}$ (b) $\frac{\Delta H}{nF}$ [✓ (c) $\frac{\Delta S}{nF}$] (d) $\frac{\Delta S}{nFT}$

Q 9 Hydrogen adsorption on platinum surface is GATE

(a) Endothermic with positive ΔS and positive ΔG

(b) Endothermic with positive ΔS and negative ΔG

[✓ (c) Exothermic with negative ΔS and negative ΔG]

(d) Endothermic with positive ΔS and negative ΔG

Q 10The activity of water at 11 bar and 298K is GATE-2011

a)1.101 [✓ (b) 1.007] (c) 0.998 (d) 0.898

Q 11 For the reaction $X_2O_4\ (l) \rightarrow 2\ XO_2(g)$ at 298 K, given the value ΔU = 9KJ and ΔS = 84JK^{-1} ΔG is GATE-2013

[✓ a)– 11.08KJ] (b) 11.08KJ (c) – 13.55KJ (d) 13.55KJ

Q 12 The activity of water at 11 bar and 298K is GATE-2011

(a) 1.101 [✓ (b) 1.007] (c) 0.998 (d) 0.898

Q 13 For the reaction X_2O_4 (*l*) → 2 XO_2(g) at 298 K, given the value ΔU = 9KJ and
ΔS = 84JK^{-1} ΔG is GATE-2013
(a) – 11.08KJ (b) 11.08KJ (c) – 13.55KJ (d) 13.55KJ

Q 14 The following reaction are carried out at 1 atm and 300 K
$2H_2 (g) + O_2(g) \rightarrow 2H_2O(l)$ JAMChemistry
ΔU for the above reaction is 550 kJ. Assuming ideal gas behavior for H2 and O2 calculate the value of ΔH.

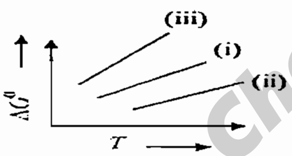
Q 15 (a)Given that ΔG =-nFE ,derive the expression for the temperature dependence of the cell potential in terms of change in entropy ΔS. (b)For a cell reaction E (at 250C) =1.26 volt , n=2,ΔS = -96.5 J/K-mole , calculate ΔS at 850C by assuming ΔS to be independent of temperature. JAMChemistry

16 The temperature dependence of Gibbs free energy G is given obtain the temperature dependence of equillibirium constant H=A+BT. JAMChemistry

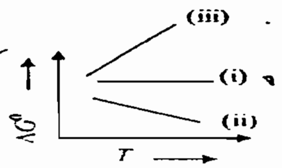
17 21 A reaction has a negative (and approximately temperature independent) enthalpy change. It does not proceed spontaneously at room temperature (25 ^{0} C). At which of the following temperatures is the reaction more likely to become spontaneous? TIFR 2013 chem
A) –50 ^{0} C B) 50 ^{0} C C) 100 ^{0} C D) 1000 ^{0} C

18 The standard Gibbs free energies of the following reactions, ΔG^0, have been determined at various temperatures. (i) $C(s) + O_2(g) \rightarrow CO_2(g)$ (ii) $C(s) + ½O_2(g) \rightarrow CO(g)$ (iii) $CO(g) + ½O_2(g) \rightarrow CO_2(g)$ Which of the following plots would represent most likely the temperature dependence of ΔG^0 ? TIFR

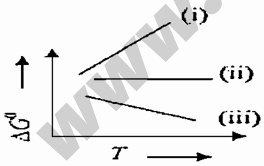
(A)



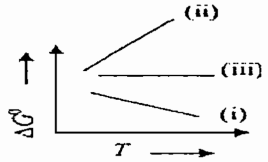
(B)



(C)



(D)



19 The residual entropy of the asymmetric molecule N_2O in its crystalline state is 5.8 J/K –mole at absolute zero . The number of orientation that can be adopted by N_2O in its crystalline state is Gate 2008
a) 4 b) 3 c) 2 d) 1

20 The chemical potential of ith species may be written as Gate
a) $\mu_i = (\delta G/\delta n_i)_{S,V,n_j}$ b) $\mu_i = (\delta H/\delta n_i)_{S,V,n_j}$
c) $\mu_i = (\delta A/\delta n_i)_{S,V,n_j}$ d) $\mu_i = (\delta U/\delta n_i)_{S,V,n_j}$

21 In the μ versus T diagram for the differnet phase of the same substance at one atmospheric pressure the line A,B and C compound to GATE 2010
I)What does A ,B and C represents in the abive diagram
II) What does D, E , and F represent

DPP 13 Thermodynamics Sahendra Kumar

Q 1 The fugacity coefficient Φ is given by $\ln \Phi=\int_0^P (z-1)dP/P$ where z is the compressibility factor and P is the pressure The fugaity of the gas governed by $P(V-b)=RT$ is GATE 2004

a) $P\ln(V/RT)$ b) $Pe^{bP/RT}$ c) $Pe^{-bP/RT}$ d) $e^{bP/RT}$

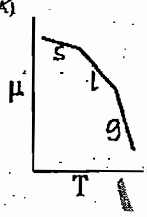
Q2 The fugacity of a gas depends on pressure and the compressibility factor $Z=PV/RT$ through the relation

For most gas at temperature T and up to moderate pressure the equation show that

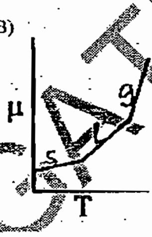
a) f<P if T→0 b) f<P if T→infinity c) f>P if T→0 d) f=P if T=0 CSIR 2012

Q 3 Of the following plot which represent the correct representation of chemical potential versus temperature for a pure substance is (S , l and g represent the solid liquid and gas phase respectively Gate 2014

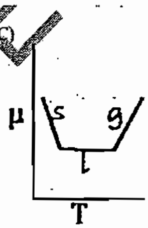
(A)



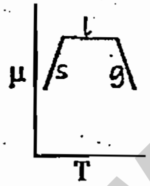
(B)



(C)



(D)



All negative

Q 4 At high pressure the fugacity coefficient of a real gas is greater then one because

i) Attractive term overweigh the repulsive term CSIR NET EXAM 2015

ii) Repulsive term overweigh the Attractive term

iii) Repulsive term is equal to attractive term

iv) The system is independent of both attractive term and repulsive term

Q 5 Given the following two relation CSIR NET EXAM 2014

$$X_1 d\mu_1 + X_2 d\mu_2 = 0$$
$$X_1 dV_1 + X_2 dV_2 = 0$$

For a binary liquid of mixture at constant temperature and pressure the true statement is that

a) both the relation are correct b) relation A is correct B is not

c) relation B is correct A s not d) both the relation are incorrect except for very dilute solution

Q 6 At any temperature T , the fugacity coefficient γ is given by GATE EXAM 2010

Where Z is compressibility factor . The fugacity coefficient of real gas governed by $P(V-b)=RT$ with b a constant is given by

a) RT/bP b) bP/RT c) $e^{-bP/RT}$ d) $e^{+bP/RT}$

Q 7 Across a first order phase transition, the free energy is

(A) proportional to the temperature (B) a discontinuous function of the temperature

(C) a continuous function of the temperature but its first derivative is discontinuous

(D) such that the first derivative with respect to temperature is continuous Gate P 2013

In earlier dpp

Q 8 1. The activity of water at 11 bar and 298 K is GATE EXAM 2011

a) 1.101 b) 1.007 c) 0.998 d) 0.898

Q 9 A gas is known to obey equation of state $PV=RT+BP$ with $B=8.026\times10^{-6}$ m^3/mole .What is the fugacity of the gas at 300 atm (and 300 K) ? Gate 1991

Q 10 The chemical potential of μ_i of ith component is defined as CSIR JRF 2013
a) $\mu_i = (\delta U/\delta n_i)_{T,P}$ b) $\mu_i = (\delta H/\delta n_i)_{T,P}$ c) $\mu_i = (\delta A/\delta n_i)_{T,P}$ d) $\mu_i = (\delta G/\delta n_i)_{T,P}$

Q 11 The chemical potential of component 1 in the solution of binary mixture $\mu_i = \mu_1^0 + RT \ln p_1$ when p1 is the partial pressure of component 1 vapor phase , the tansard state μ_1^0 is CSIR 2011
a) independent of temperature and pressure b) depends on temperature and pressure both
[✓ c)] Depends on temperature only d) Depends on pressure only

→ Q 12 Given two phase α and β of a species in equilibrium . The correct relation observed among the variable T,P and μ are CSIR JRF
a) $T_\alpha = T_\beta$, $P_\alpha \neq P_\beta$, $\mu_\alpha = \mu_\beta$ b) $T_\alpha \neq T_\beta$, $P_\alpha = P_\beta$, $\mu_\alpha = \mu_\beta$
[✓ c)] $T_\alpha = T_\beta$, $P_\alpha = P_\beta$, $\mu_\alpha = \mu_\beta$ d) $T_\alpha \neq T_\beta$, $P_\alpha = P_\beta$, $\mu_\alpha \neq \mu_\beta$

Q 13 In a bomb calorimeter , the combustion of 0.5 gm of compound A (molar mass 50 gm/mole) increases the temperature by 4 K , if heat capacity of calorimeter along with the material is 2.5 KJ /K the molar internal energy of combustion in KJ is CSIR JRF 14
a) 1000 [✓ b)] -1000 c) 20 d0 -20

Q 14 The fugacity of real gas is less than pressure of an ideal gas at the same temperature T only when (T_b is the Boyle temperature of real gas) CSIR JRF 2017 $f < P$ $T_b = \frac{a}{Rb}$
a) high P , $T < T_b$ [✓ b)] Low P , $T < T_b$
c) high P , $T > T_b$ d) Low P , $T > T_b$

attraction dominate
if Pressure mod. i.e. → low

If $T > T_b$
$RbT >$
Repulsion T
$\boxed{T < T_b}$
$RT b < a$
∴ Att. d

Q 15 The residual entropy of the asymmetric molecule N_2O in its crystalline state is 5.8 J/K – mole at absolute zero . The number of orientation that can be adopted by N_2O in its crystalline state is Gate 2008
$S = R \ln(\text{arrangement})$
$S = 2.303 R \ln(W)$
$W = $
a) 4 b) 3 [✓ c)] 2 d) 1

Q 16 A thermodynamic equation that relates chemical potential and chemical composition of mixture is CSIR——
a) Gibbs Helmholtz equation b) Kirhoff equation
[✓ c)] Gibbs Duhem equation d) Planck Equation

Q 17 When 100 gm of water is reversibly heated from 50°C to 75° C at 1 atm the change in entropy (J/K) of the universe is (a) -0.31 (b) 0.31 [✓ (c)] 0 (d) 3.1 IIT JAM

Q 18 An ideal gas is expanded irreversibly and adiabatically from state A (Vi,Pi) to a state B(Vf,Pf) then the value of ΔS_{system} would be IIT GATE
a) RT ln {Vf/Vi} b) R ln (Vf/Vi) c) -R ln (Vf/Vi) [✓ d)] Greater than zero

→ Q 19 The standard enthalpy of formation ($\Delta_f H^0$) at 1 bar and 300 K for the formation of CF_2ClCF_2Cl (g) from its constituent element is -900kJ/mole The standard molar internal energy of formation (($\Delta_f U^0$) is (a) -905 kJ/mole (b) -895 kJ/mole (c) 895 kJ/mole (d) 905 kJ/mole IIT JAM 2012

Q 20 The enthalpy of vaporization is zero at IIT JAM 2012 Chemistry
(a) Boyle temperature [✓ (b)] critical temperature (c) inversion temperature (d) Boiling emperature

Q 21 One mole of Vanderwall gas undergoes reversible isothermal transformation from an initial state V_1 to V_2 the expression for work done is ………… IIT JAM 2011 Chemistry

↓
formula

Surprise Test

DPP Thermodynamics Science zone

Q 1 If the pressure p (system) is greater than the p(Surrounding) then CSIR JRF 2015

[✓ a) Work is done on the system by surrounding]

b) Work is done on the surrounding by the system

c) Work is done on the system by surrounding is equal Work is done on the surrounding by the system

d) Internal energy of the system increases

Q 2 The relation between internal pressure (π_T) , thermal expansivity α and isothermal compressibility factor β is

a) $\{(\pi_T + P)T\} = (\alpha / \beta)$ b) $\{(\pi_T + P)/T\} = (\alpha\, \beta)$

[✓ c) $\{(\pi_T + P)/T\} = (\alpha / \beta)$] d) $\{(\pi_T - P)/T\} = (\alpha / \beta)$

Q 3 The temperature of 72 gm of substance A (molar mass 36 gm/mole) is raised from 300 K to 400 K at constant pressure when substance absorbs 72 KJ of heat the heat capacity at Constant pressure

a) 10 J/K-gm b) 10 J/K-mole c) 36 J/K-mole d) 36 J/K-gm

Q 4 The change in internal energy (In KJ) when the temperature of 1 mole of substance is raised from 100 K to 200 K , If $C_V = 5 + T$ is

[illegible] a) 10.5 b) 20 c) 2 d) 1.05 e) none

Q 5 Consider the following thermodynamics system

i) $TdS = C_V dT + (\delta V/\delta T)_P$ [✓ ii) $TdS = C_P dT - T(\delta V/\delta T)_P dP$]

[✓ iii) $TdS = C_V dT + T(\delta P/\delta T)_V dV$] iv) $TdS = C_V dT + T(\delta V/\delta T)_P dv$

The correct relations above are

a) I ,ii b) ii ,iii c) ii,iv d) ii only

Q 6 The temperature of one mole of ideal gas ($C_V = 1.5$ R) is doubled at constant pressure the change in entropy is

a) 4.5 R b) .45 R c) 7.5 R d) .75 R

Q 7 The enthalpy change when 36 gm of water is heated from 27^0 C to 37^0 C at 1 atm pressure . The molar heat capacity of water (18.1 Cal /k-mole) remains constant in this temperature range is

[✓ a) 362 Cal /mole] b) 36.2 Cal /K-mole c) 52.4 Cal / k-mole d) 524 Cal /K-mole

Q 8 Consider the statement

i) The cyclic integral of an inexact differential is usually not zero .

ii) Work appear on the boundary of the system

iii) Heat capacity at constant volume is rate of increase of energy with temperature at constant volume .

The true statement above are a) I,ii b) ii,iii c) I,iii [✓ d) all] e) none

→ Q 9 Correct statement regarding the heat capacity

i) Heat capacity are path function and inexact differential .

ii) Heat capacity of solid is higher than the liquid ✗ nearly equal

iii) The ratio of heat capacity is known as atomicity of the gas and depend on the number of atom

a) I ,ii b) ii,iii [✓ c) I,iii] d) all e) none

Q 10 Consider the statement

i) For liquid and solid the value of $(\delta U/\delta V)_T$ is zero. → $\pi_T \neq 0$ for liquid & gas

ii) For P(V-b) =RT the value of $(\delta U/\delta V)_T$ is zero.
iii) If dz= xdy + ydx than z is state function.
The true statement above are
a) I , ii [✓ b) ii , iii] c) I,iii d) all

Q 11 Consider the statement regarding the state function
i) These are exact differential ii) The cyclic integral of these function is zero
iii) The summation of two inexact differential never be equal to exact differential
[✓ a) I,ii] b) ii ,iii c) I,iii d) all e) none

$dq = dU - W$

$\boxed{dq + w = dU}$

Q 12 Consider the statement given below
i) $\{\delta C_V / \delta V\}_T = 0$ for ideal as well as for vanderwall gas
ii) $\{\delta C_P / \delta P\}_T = 0$ for ideal as well as for Vanderwall gas
iii) The dimension of $\{\delta U / \delta V\}_T$ is equal to Pressure ✓
The correct statements above are
a) a) I , ii b) ii , iii c) I,iii d) None

Q 13 In thermodynamic a process is said to be reversible is
a) Surrounding and system change into one another
b) There is no boundary between system and surrounding
c) The surrounding are always equilibrium with system
d) The system changes in surrounding spontaneously

Q 14 The value of ΔH for the transformation of one mole of an ideal gas from 27^0 C and 1 atm to 327^0C and 1 atm is {gven that C_P= 20 +0.04 T J/k-mole}
a) 9 KJ/mole b) 20 KJ/mole c) 24 KJ/mole d) None

Q 15 The expansion work done when 50 gm of water is electrolysed under costant pressure at 25^0 C is
a) -100 KJ b) -10 KJ c) – 1 KJ d) none

Q 16 The temperature of an ideal gas increase in an
a) Adiabatic Expansion b) Isothermal Expansion
[✓ c) Adiabatic Compression] d) IsothermalCompression

Q 17 The minimum work involved in compression of 1 mole of an deal gas to double of its initial pressure at 300 K is
a) 300 R ln 2 b) 600 R ln 2 c) 300 ln 2 d) can not determine because process is not given

Q 18 Two mole of a gas at 1 bar and 298 K are compressed at constant temperature by use of constant pressure of 5 bar ,
i) The work is done on the gas is
a) 198.2 KJ b) 1.982 KJ c) 1982 KJ d) 19.82 KJ
ii) If the compression is driven by 100 Kg Mass , how far will it fall in the earth gravitational field (g=9.8 m/s^2)
a) 20.22 m b) 202.2 m c) 2.022 m d) 2022 m

Q 19 Consider the statement
i) Internal pressure for 1 mole of Vanderwall Gas is inversely proportional to the volume of the gas.
ii) In adiabatic free expansion for an ideal gas from initial state A to B the internal energy decreases.
The correct statement above are a) I,ii b) ii c) ii,iii d) none

Q 20 Heat Capacity of species is independent of temperature if it is
a) Tetraatomic b) Triatomic c) Diatomic d) Monoatomic

SCIENCE ZONE

Batch – 1 Answer Key DPP - Thermo

DPP – 1

1.a 2.b 3.a 4.a 5.c 6.d 7.b 8.e 2aT + 4b
9. P-III,Q-IV,R-VI,S-II 10.b,c 11.b 12.a 13.a 14.c 15.a 16.b 17.c
18.b 19.c 20.b 21.a 22.a 23.a 24.b 25.d 26.c 27.b 28.b 29.c
30.a 31.a 32.d

DPP – 2

1.b 2.b 3.b 4.b 5.a 6.b 7.b 8.c 9.d 10.a 11.d 12.a
13.e ()v 14.c 15.() 16.d 17.c 18.d 19. Cp=29.93JK^{-1}mole^{-1}Cv=21.62Jk^{-1}mole^{-1}
20.a 21.b 22.b 23.d 24.d 25.b

DPP – 3

1.b,d 2.i,iv 3.d 4. ()v 5.d 6.b 7.b 8.c 9.b 10.d 11.c 12.b
13.b 14.c 15.a 16.b 17.a 18.a19.d 20.c 21.c 22.b,d 23.d 24.a 25.b
26.a27.a 28.a

DPP – 4

1. 2.b 3. 4.d 5.e 450R 6.c 7.a 8.b 9.b 10.c 11.b 12.c 13.c
15.c 16.-1.36joule 17.b 18.a 19.c 20.c 21.a 22.c
23.W =-8030J, Q=8030J,ΔH=ΔU=0 24.a,d 25.i

DPP – test

1.b 2.c 3.360J/Kmole 4.e 5.b 6.1.7R 7.a 8.d 9.c 10.b 11.a 12.c
13.c 14.d 15.b 16.c 17.a 18.d 18.a 19.b 20.d

DPP – 5

1.a 2.4.606RT 3.b 4.(i)T = 164K (ii)468K 5.i 6.ΔH=-4871.3J/mole 7.a 8.c
9.b 10.c 11.c 12.d 13.d 14.b 15.d 16.a 17.b 18.a 19.c
21.a 22.a 23.d 24.567°C 25.zero

DPP – 6

1.a 2.b 3.a 4.c 5.(3N-6)RT and 49.884KJ/mole 6.b
7.T_1=100k, T_2=300k, q_1=200J q_2=600J 8.500Cal 9.567°C 11.b 12.b 13.a
14.a 15.a 16.c 17.d 18.c 19.3000J 20.d

DPP – 7

1.d 2.d 3.c 5.c 6.c 7.b 8.b 9.b 10.a 11.c 12.a 13. 2.119Cal/kmole
14.b 15.c 16.b 17. 92.45kj 18. 50.8 19.11.43J/kmole 20.d 21.c 22.a
23.a 24.d 25.d 26.a 27.d

DPP – 8

1.i 2. 78 Cal 3.zero 4.a 5.d 6. ΔH= -15.9kJ, ΔS= -512.2J/k 7.a 8.d 9.a
10.ΔH= - 5626J/mole, ΔS =-20.48 J/Kmole 11. 26.7 12.d
13.ΔH=51.143KJ/mole, ΔS=133.31J/Kmole, ΔU=46.184KJ/mole
14.ΔS= -4.72J/k mole 15.b 16.128.17J/kmole
17.a 18.a 19.b 20.a 21. 0.26 22.c 23.b

DPP – 9

1.b 2.b 3.a 4.c 5. ΔU = ΔH = O, W = -5743 J, ΔS = 19.14J/K, Q = 5743J 6.d 7.a
8.b 9.b 10. 2 11.d 12.8.43J/K 12.a 13.c 14.a 15.b 16. 3only
17. 11.43J/k mole 18. ΔS= 154.5J/k mole 19.a 20.d 21.a

DPP – 10

1.b 2. ΔS = 23.05 J/K mole,ΔG= -6.9 KJ/mole, ΔV = ΔU=ΔH=0
3.ΔS=27.9J/k mole, ΔG= -8.39kJ/mole 4.d 5.c 6. ΔH_V = 33.81KJ/mole, T = 352K
7.1.5 8.d 9.a 10.b 13.a 14.a 15.none 16. ΔS=86.55 J/K ΔH=30.575 KJ
17.T=360K, P=18860Pa 18. 1353bar 19.a 20. 0.7546atm 21. 381K 22.d
23.a 24.a

DPP – 11

1.1001bar 2.c 3.a 4. 12.74J/k 5.d 6.a 7.c 8.b 9.c 10.d 11.a
12.(i)zero (ii) 0.6R 13.a 14.c 15.a 16.a 17.d 18.d 19.3 20.b

DPP – 12

1. -284.683 kJ/mol 2.d 3.c 4.a 5.a 6.-1.52×10^{4}bar 7. 1.23V 8.c 9.c 10.b
11.a 12.b 13.a 14.542.517KJ 15. 1.23V 17.a 18.b 19.c 20.d
16. Ln(=

DPP -- 13

1.b 2.a 3.a 4.ii 5.a 6.d 7.c 8.b 9.330atm 10.d 11.c 12.c 13.b 14.b
15.c 16.c 17.c 18.d 19.b 20.b 21. –RT ln()+ a() 22.c 23.a
24.b 25.a 26.c 27.b 28.d 29.d 30.b 32.d 33.a 34.d 35.b 36.c 37.c 38.c
39.c 40.a 41.b

If any doubt meet Yogesh Sir will be available 6:00pm to 7:30pm