

$$S = k_B N \ln \left[\frac{V}{h^3} \left(\frac{mE}{N} \right)^{3/2} \left(\frac{1}{N!} \right) \right]$$

①
IN CLASS
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NOROS
2/6/23

1) $\frac{1}{T} = \frac{\partial S}{\partial E} \Big|_{N, V}$

a) $S = k_B N \left[\ln V - \ln h^3 + \frac{3}{2} \ln \left(\frac{mE}{N} \right) - \ln N! \right]$

b) $\frac{\partial S}{\partial E} \Big|_{N, V} = k_B N \left(\frac{3}{2} \frac{1}{E} \right)$

c) $\therefore E = \frac{3}{2} N k_B T$ (v.1) (1x)

⊕ $N = n \text{ (mols)} \cdot \frac{N_A \text{ particle}}{(1 \text{ mol})}$

$\therefore (1x) \Rightarrow E = \frac{3}{2} n K_B N_A T$ (**)

⊕ $K_B N_A = \bar{R}$

$(1.38)(10^{-23}) \left(\frac{J}{K} \right) \cdot \frac{6.023(10^{23})}{\text{mol}}$

$\bar{R} = 8.134 \frac{J}{\text{mol} \cdot K}$

⊕ $E = \frac{3}{2} n \bar{R} T = J$

III) Given $U = U(S, \tilde{V}, N)$
experimental

(6)

a) $T = \left. \frac{\partial U}{\partial S} \right|_{\tilde{V}, N}$

b) $P = \left. \frac{\partial U}{\partial \tilde{V}} \right|_{S, N}$

c) $\mu = \left. \frac{\partial U}{\partial N} \right|_{S, \tilde{V}}$

d) $dS = [S]$

i) \tilde{V}, N fixed

ii) $ds = \frac{du}{T}$

iii) $\int_{S_{ref}}^S ds = \int_{u_{ref}}^u \frac{du}{T}$

U is known
 then du
 $du = 0$ in
 u w/ \tilde{V}, N
 fixed

$[S] - [S]_{ref} =$

\Rightarrow exp. where \tilde{V}, N

Prep
Notes
2/6/23

$$1) S = k_B N \ln \left[\frac{h^3}{h^3} \left(\frac{m E}{N} \right)^{3/2} \left(\frac{1}{N!} \right) \right]$$

$$2) \frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{N, V} = k_B N \left(\frac{3}{2} \right) \frac{1}{E}$$

$$\rightarrow E = \frac{3}{2} N k_B T = \tilde{U}$$

$$3) N = n_{mol} \cdot \frac{N_A}{mol}$$

$$N_A \cdot k_B = \bar{R}$$

$$\therefore \tilde{U} = \frac{3}{2} n \bar{R} T$$

$$U = \frac{\tilde{U}}{mass} = \frac{\frac{3}{2} n \bar{R} T}{n M W}$$

$$U = \frac{3}{2} R_{gas} T$$

$$6) C_V = \left. \frac{\partial E}{\partial T} \right|_{V, T}$$

$$= \frac{3}{2} N k_B$$

$$= \frac{3}{2} n \bar{R}$$

$$6a) C_V = \frac{3}{2} n \bar{R}$$

$$C_V = \frac{3}{2} R_{gas}$$

$$C_V = \left. \frac{\partial U}{\partial T} \right|_{V, N} = \frac{3}{2} k_B N$$

$$7) C_P = \left. \frac{\partial (E + P V)}{\partial T} \right|_P$$

$$= \frac{\partial}{\partial T} \left[N \frac{3}{2} k_B T + k_B N T \right]$$

$$C_P = \left. \frac{\partial H}{\partial T} \right|_{P, N} = \frac{\partial}{\partial T} [U + P V]$$

$$4) \frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{N, E}$$

$$= \frac{\partial}{\partial V} \left[\frac{k_B N}{V} \right]$$

$$\frac{\partial S}{\partial V} \Big|_{N, E} = \frac{\partial H}{\partial E} \Big|_{N, S}$$

$$\frac{\partial E}{\partial S} \Big|_{N, V} = T$$

$$\Rightarrow \frac{\partial S}{\partial V} \Big|_{N, E} = \frac{\partial E}{\partial S} \Big|_{N, S}$$

$$5) \therefore (P V = k_B N T) = k_B N N_A T = n \bar{R} T$$

$$= \frac{\partial E}{\partial S} \Big|_{N, S}$$

$$1) S = k_B N \ln \left[\frac{V}{h^3} \left(\frac{mE}{N} \right)^{3/2} \right] \quad \text{erL} \quad \textcircled{1}$$

$$2) \frac{1}{T} = \frac{\partial S}{\partial E} \Big|_{N,V} = k_B \frac{3N}{2E}$$

$$\Rightarrow \left[E = \frac{3N}{2} k_B T \right] \quad \leftarrow \partial$$

$$3) \frac{P}{T} = \frac{\partial S}{\partial V} \Big|_{N,E} = \frac{k_B N}{V} = \frac{\partial S}{\partial V} \Big|_{N,E} \frac{\partial E}{\partial V} \Big|_{N,E}$$

$$\Rightarrow PV = k_B N T$$

$$\frac{\partial U}{\partial S} \Big|_{N,V} = T$$

$$N = n \text{ mol} \frac{N_A}{1 \text{ mol}}$$

$$\Rightarrow N = n N_A$$

$$\frac{\partial S}{\partial V} \Big|_{N,E}$$

$$\left[PV = \bar{P} n \bar{V} \right]$$

$$\Rightarrow \bar{P} = k_B N_A$$

$$\left[N k_B = n \bar{P} \right]$$

$$= \frac{1}{T} \frac{\partial U}{\partial V} \Big|_{N,E}$$

$$= - \left(\frac{\partial U}{\partial V} \right)_{N,E}$$

$$4) \bar{C}_V = \frac{\partial E}{\partial T} \Big|_{N,V} = \frac{\partial}{\partial T} \left(\frac{3}{2} N k_B T \right)$$

$$= \frac{3}{2} N \frac{\partial}{\partial T} \left(\frac{3}{2} n \bar{P} T \right) = R/T$$

$$= \frac{3}{2} n \bar{P}$$

$$C_V = \frac{\bar{C}_V}{\text{mass}} = \frac{3/2 n \bar{P}}{M} = \frac{3}{2} R_{\text{molar}}$$

$$\bar{C}_P = \frac{\partial}{\partial T} (U + PV) \Big|_{N,P} = \bar{C}_V + \frac{k_B N}{n \bar{P} k_B} = \bar{C}_V + \frac{3}{2} n \bar{P}$$

5000	C_V	$R_{\text{molar}} C_{V, \text{SEFF}} = \frac{3}{2}$
Air	$\sim 0.75 \text{ kJ/kg}\cdot\text{K}$	$8.314 \text{ kJ/mol}\cdot\text{K}$
N ₂	$\sim 0.77 \text{ ''}$	$0.445 = \frac{5}{2} n \bar{P}$
O ₂	$\sim 0.72 \text{ ''}$	
CO ₂	$\sim 0.825 \text{ ''}$	

Fund. reln

U) G1 \Leftrightarrow $\boxed{du = Tds - Pd\tilde{v} + u dN}$
 $\Leftrightarrow \boxed{u = u(s, \tilde{v}, N)}$

G2) a) $h \equiv u + Pv$

b) $dh \equiv du + Pd\tilde{v} + \tilde{v}dP$
 $= Tds - Pd\tilde{v} + u dN + Pd\tilde{v} + \tilde{v}dP$

$\boxed{dh = Tds + \tilde{v}dP + u dN}$

$\Rightarrow \boxed{h = h(s, P, N)}$

G3) a) $A \equiv u - Ts$

b) $dA = du - Tds - s dT$
 $= Tds - Pd\tilde{v} + u dN - Tds + s dT$

c) $\boxed{dA = -Pd\tilde{v} + u dN - s dT}$
 $\boxed{A = a(\tilde{v}, T, N)}$

G4) a) $G = H - Ts$

b) $dg = dh - Tds - s dT$

c) $\boxed{dg = \tilde{v}dP + u dN - s dT}$

$\boxed{g = g(P, T, N)}$

III) max from Therm eqs

(3)

A) $f = pt. P_n \Leftrightarrow$ calc. only depends on location of P_n & volume. any Ω study

B) ~~sol~~ $f = f(x, y, z)$ points put in index

C) $df = f_{,x} dx + f_{,y} dy + f_{,z} dz$ etc
 $f_{,x|y} = f_{,y|x}$ is an exact differential
 $df = f_{,x} dx + f_{,y} dy$

D) calc $\int_{exact} M(x,y) dx + N(x,y) dy$
 $dA = M(x,y) dx + N(x,y) dy$

E) \Rightarrow $M_{,y|x} = N_{,x|y}$ \Leftrightarrow $\frac{\partial}{\partial x} (f_{,y|x}) = \frac{\partial}{\partial y} (f_{,x|y})$
Maxwell rels

IV) Maxwell rels
 $\frac{\partial}{\partial S} \left(\frac{\partial A}{\partial N, V} \right) = T$

A) G1: $\frac{\partial}{\partial S} \left(\frac{\partial A}{\partial S, N} \right) = \frac{\partial}{\partial S} \left(\frac{\partial A}{\partial S, V} \right)$

(C1) $du = T ds - P d\tilde{V}$
 a) $= M dx + N dy$
 b) $= M dx + N dy$
 c) $\therefore M_{,y|x} = N_{,x|y}$
 or $T, \tilde{V}|_s = -P, s|\tilde{V}$

$$a) du = T ds - p d\tilde{v}$$

$$Q.S = S(\tilde{v}, T)$$

$$ds = S_{,v}|_T d\tilde{v} + S_{,T}|_{\tilde{v}} dT$$

$$b) \therefore du = T [S_{,v}|_T d\tilde{v} + S_{,T}|_{\tilde{v}} dT] - p d\tilde{v}$$

$$= T S_{,T}|_{\tilde{v}} dT + [T S_{,v}|_T - p] d\tilde{v}$$

$$c) \quad \frac{\partial u}{\partial T}|_{\tilde{v}} = T S_{,T}|_{\tilde{v}} = C_v$$

$$\Rightarrow \underline{S_{,T}|_{\tilde{v}} = C_v / T}$$

(4)

u
h
a
s

Therm ~~and~~ relationships can
be. \Rightarrow when ~~we~~ know
stated ~~of~~ in terms of
nat. vls each can
be used to get
all thermo props.

obj. 1 Gibbs and Maxwell
vls

obj. 2

derive ~~and~~ dH, dG, dA
for dU, dH, dS
in terms of directly
meas vls

max

max ~~and~~ meas props.

1) Let $f, x, y, z \Rightarrow$ any any 3
of h, u, etc

2) f, x, y are pk vars

\oplus path ind

\oplus have exact d.f

3)
3)

have ~~prop~~

$$df = M(x,y)dx + N(x,y)dy$$

N! corrections due to indistinguishability

(1)

3 - I am placing a box w/ simple ptcl

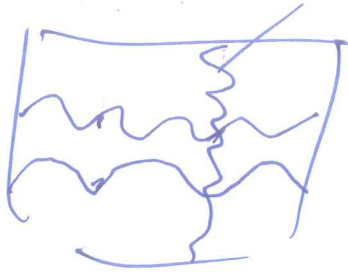
3 avail Q states $\epsilon_1, \epsilon_2, \epsilon_3$

where each ϵ_i corresponds to a sp.

n_x, n_y, n_z and as well as

a "spin state" as well as

vibration rotation



Ψ_{sys}

classical limit

$$\Psi_{sys}^{(1)} = \psi_1(a) \psi_2(b) \psi_3(c)$$

$$\Psi_{sys}^{(2)} = \psi_2(c) \psi_3(b)$$

$$\Psi_{sys}^{(3)} = \psi_3(a) \psi_2(b)$$

(b) (c)

since a, b, c indistinguishable

only one Ψ_{sys} for N or 5

when counting

②

$$G.11 \quad du = T ds - P d\tilde{V} + \sum_i \mu_i dn_i$$

b) $s = s(V, T, \mu)$

c) $ds = S_{,T} / T dT + S_{,V} / V dV$

d) $\therefore du = T [S_{,T} / T dT + S_{,V} / V dV] - P d\tilde{V}$
 $= [T S_{,T} / T - P] d\tilde{V} + T S_{,V} / V dT$

e) but $du = C_V dT$

for $u = u(T, V)$

$$du = C_V dT + u_{,V} / V dV$$

$$\therefore \boxed{T S_{,T} / T = C_V}$$