

Tutorial 4.

①

Q.1) for one dimensional oscillator, $q_{\text{vib}} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$

for 3D oscillator $q_1 q_2 q_3 = \left[\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right]^3$

$q_{\text{sub}} = e^{-\beta U_0/N}$ where U_0 is the sublimation energy and $N = \text{no. of atoms/oscillators}$

$$E = E_{\text{vib}} + E_{\text{sub}}$$

$$\therefore q = q_{\text{vib}}^3 q_{\text{sub}} = e^{-\beta U_0/N} \left[\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right]^3$$

these are distinguishable oscillators.

$$\therefore \Omega(N, V, T) = [q(V, T)]^N$$

$$\text{or } \Omega = q^N = e^{-\beta U_0} \left[\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right]^{3N}$$

$$\text{Now, } \langle E \rangle = - \frac{\partial \ln \Omega}{\partial \beta}$$

$$- \ln \Omega = \beta U_0 + 3N \frac{\beta h\nu}{2} + 3N \ln(1 - e^{-\beta h\nu})$$

$$\therefore \langle E \rangle = U_0 + 3N \frac{h\nu}{2} + 3N h\nu \left(\frac{1}{e^{\beta h\nu} - 1} \right)$$

$$C_v = \left(\frac{\partial E}{\partial T} \right) = 3N h\nu \left(\frac{1}{e^{h\nu/kT} - 1} \right)^2 e^{h\nu/kT} \left(\frac{h\nu}{kT^2} \right)$$

(2)

$$\bar{C}_V = 3R \left(\frac{h\nu}{k_B T} \right)^2 \frac{e^{-h\nu/k_B T}}{(1 - e^{-h\nu/k_B T})^2}$$

(Use $N = N_A$)

$$Q.2) \quad Q = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N/2} (V - Nb)^N e^{\beta a N^2 / V}$$

$$\ln Q = N \ln(V - Nb) + \frac{\beta a N^2}{V} + \text{terms in } N \text{ and } \beta \text{ only}$$

$$\left(\frac{\partial \ln Q}{\partial V} \right)_{N, \beta} = \frac{N}{V - Nb} - \frac{\beta a N^2}{V^2}$$

$$\therefore P = \frac{N k_B T}{V - Nb} - \frac{a N^2}{V^2}$$

$$\text{or } \left(P + \frac{a N^2}{V^2} \right) (V - Nb) = N k_B T$$

i.e. Van der Waals equation.

Volume ~~of~~ of molecules is not zero \therefore available volume is less.

applied pressure + an attractive term that increases the pressure appears.

(3)

$$U = - \frac{\partial \ln \Omega}{\partial \beta} = - \frac{\partial}{\partial \beta} \left[- \ln N! + \frac{3}{2} N \ln \left(\frac{2\pi m}{h^2 \beta} \right) + N \ln (V - Nb) + \frac{\beta a N^2}{V} \right]$$

$$= \frac{3N}{2\beta} - \frac{aN^2}{V} = \frac{3}{2} N k_B T - \frac{aN^2}{V} + \text{terms that go to zero } \because \text{ } \partial_{\beta} \text{ independent}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} N k_B = \frac{3}{2} R \quad (\text{for one mole})$$

~~Q.3~~

Q.3)

total energies $Q(3, V, T) = \sum_{ijk=1}^3 e^{-\beta(\epsilon_i + \epsilon_j + \epsilon_k)}$

9

$\epsilon_1 + \epsilon_1 + \epsilon_1$		
$\epsilon_1 + \epsilon_1 + \epsilon_2$	$\epsilon_1 + \epsilon_2 + \epsilon_1$	$\epsilon_1 + \epsilon_2 + \epsilon_2$
		$\epsilon_1 + \epsilon_2 + \epsilon_3$
$\epsilon_1 + \epsilon_1 + \epsilon_3$	$\epsilon_1 + \epsilon_3 + \epsilon_1$	$\epsilon_1 + \epsilon_3 + \epsilon_2$
		$\epsilon_1 + \epsilon_3 + \epsilon_3$

+ 9 with ϵ_2 in the first place

+ 9 with ϵ_3 in the first place.

i.e. 27 for unrestricted evaluation.

for fermions \rightarrow no two fermions in same energy.
and these are identical (indistinguishable)

\therefore only $\epsilon_1 + \epsilon_2 + \epsilon_3$

Six possibilities divided by $3! = 1$.

for bosons \rightarrow as many bosons in a state.
but these are also identical.

Out of the nine possibilities we have

$\epsilon_1 + \epsilon_1 + \epsilon_1$ (111)	$\epsilon_1 + \epsilon_2 + \epsilon_1$ (121)	$\epsilon_1 + \epsilon_2 + \epsilon_2$ (22)	$\epsilon_1 + \epsilon_2 + \epsilon_3$ (123)
$\epsilon_1 + \epsilon_1 + \epsilon_2$ (112)	$\epsilon_1 + \epsilon_3 + \epsilon_1$ (131)	$\epsilon_1 + \epsilon_3 + \epsilon_2$ (132)	$\epsilon_1 + \epsilon_3 + \epsilon_3$ (133)
$\epsilon_1 + \epsilon_1 + \epsilon_3$ (113)			

next 9

$\epsilon_2 + \epsilon_1 + \epsilon_1$ (211)	$\epsilon_2 + \epsilon_2 + \epsilon_1$ (221)	$\epsilon_2 + \epsilon_3 + \epsilon_1$ (231)	$\epsilon_2 + \epsilon_3 + \epsilon_2$ (232)	$\epsilon_2 + \epsilon_3 + \epsilon_3$ (233)
$\epsilon_2 + \epsilon_2 + \epsilon_2$ (222)	$\epsilon_2 + \epsilon_2 + \epsilon_3$ (223)	$\epsilon_2 + \epsilon_3 + \epsilon_3$ (233)		

Crossed out repeats

next 9

311	312	313	321	322	323	331	332	333
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total 10

5

8.4)

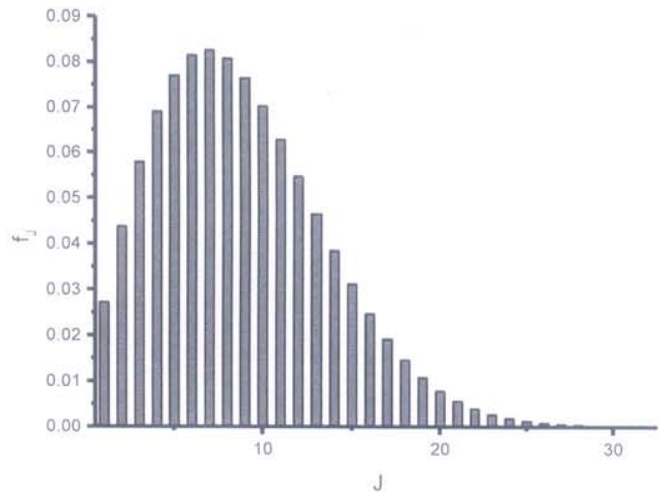
$$f_J = (2J+1) e^{-\theta_{rot} J(J+1)/T} (\theta_{rot}/T)$$

$$\theta_{rot} = 2.77 \text{ K}$$

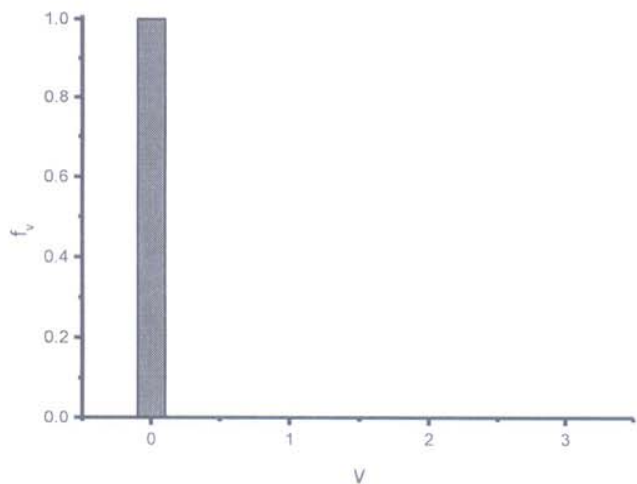
$$f_v = (1 - e^{-\theta_{vib}/T}) e^{-v \theta_{vib}/T}$$

$$\theta_{vib} = 3103 \text{ K}$$

J	f _J
1	0.02719
2	0.04368
3	0.05785
4	0.06909
5	0.07699
6	0.08145
7	0.08258
8	0.08074
9	0.07642
10	0.07022
11	0.06277
12	0.05467
13	0.04644
14	0.03852
15	0.03121
16	0.02473
17	0.01916
18	0.01453
19	0.01078
20	0.00783



v	f _v
0	0.99997
1	3.22058E-5
2	1.03724E-9
3	3.34063E-14



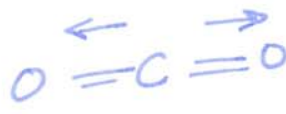
Q5) linear molecule, $M=3$

Vib. degrees of freedom = $3N - 5 = 4$

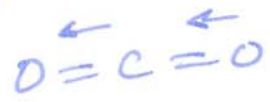
$$\bar{C}_v = R \sum_{j=1}^4 \left[\left(\frac{\theta_{vib,j}}{T} \right)^2 \frac{e^{-\theta_{vib,j}/T}}{(1 - e^{-\theta_{vib,j}/T})^2} \right]$$

The 4 modes are

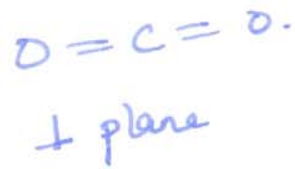
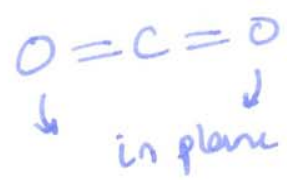
1) symmetric stretch



2) asymmetric stretch



3) bend
(doubly degenerate)



1) $\bar{C}_{v,1} = R \left(\frac{3360}{300} \right)^2 \frac{e^{-3360/300}}{(1 - e^{-3360/300})^2} = 0.0017 R$

2) $\bar{C}_{v,2} = R \left(\frac{1890}{300} \right)^2 \frac{e^{-1890/300}}{(1 - e^{-1890/300})^2} = 0.0731 R$

3) $\bar{C}_{v,3/4} = R \left(\frac{954}{300} \right)^2 \frac{e^{-954/300}}{(1 - e^{-954/300})^2} = 0.4578 R$

$\bar{C}_v = [0.0017 + 0.0731 + 2 \times 0.4578] R$
for 2 modes

$= 0.9905 R$

8.6)

⑦

$$W = \frac{A!}{a_1! (A-a_1)!}$$

$$\begin{aligned} \ln W &= \ln A! - (\ln a_1! + \ln (A-a_1)!) \\ &= A \ln A - A - \left[a_1 \ln a_1 - a_1 + (A-a_1) \ln (A-a_1) - (A-a_1) \right] \\ &= A \ln A - a_1 \ln a_1 - (A-a_1) \ln (A-a_1) \end{aligned}$$

$$\frac{\partial \ln W}{\partial a_1} = 0 = -1 - \ln a_1 + 1 + \ln (A-a_1) = 0$$

$$\Rightarrow a_1 = A - a_1 \quad \text{or} \quad a_1 = A/2 = a_2$$

for 3 states, $a_1 + a_2 + a_3 = A$, 2 independent values are there, say a_1 and a_2 . $W = \frac{A!}{a_1! a_2! (A-a_1-a_2)!}$

$$\begin{aligned} \ln W &= A \ln A - A - \left[a_1 \ln a_1 - a_1 + a_2 \ln a_2 - a_2 \right. \\ &\quad \left. + (A-a_1-a_2) \ln (A-a_1-a_2) - (A-a_1-a_2) \right] \end{aligned}$$

$$= A \ln A - a_1 \ln a_1 - a_2 \ln a_2 - (A-a_1-a_2) \ln (A-a_1-a_2)$$

$$\frac{\partial \ln W}{\partial a_1} = 0 = -1 - \ln a_1 + 1 + \ln (A-a_1-a_2) \Rightarrow a_1 = A - a_1 - a_2$$

$$\frac{\partial \ln W}{\partial a_2} = 0 = -1 - \ln a_2 + 1 + \ln (A-a_1-a_2) \Rightarrow a_2 = A - a_1 - a_2$$

$$\Rightarrow a_1 = a_2 \quad \text{and} \quad a_1 = A/3 \Rightarrow a_1 = a_2 = a_3 = A/3$$

8

87) Given $U(S, V)$

$$dU = TdS - PdV \quad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

We identify $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -P$

Differentiating twice $\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S$

and $\frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$

Since U is a state function, $\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$

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

$$H = U + PV$$

$$dH = dU + d(PV) = dU + PdV + VdP$$

$$= TdS - PdV + PdV + VdP = TdS + VdP$$

$$\therefore H = H(S, P)$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Differentiating twice and equating,

$$\frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$A = U - TS$$

$$dA = dU - TdS - SdT = -PdV - SdT$$

$$A = A(T, V)$$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

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

$$G = H - TS$$

$$dG = dH - TdS - SdT = VdP - SdT$$

$$G = G(P, T)$$

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

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

The four Maxwell relations are squared in red.

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

$H = U + pV$

$dH = du + p dv + v dp$

$\left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial T} \right)_p$ ————— ①

$U = U(T, p) \leftarrow$ possible to write as $v = v(T, p)$

$du = \left(\frac{\partial u}{\partial T} \right)_p dT + \left(\frac{\partial u}{\partial p} \right)_T dp$

$\left(\frac{\partial u}{\partial T} \right)_v = \left(\frac{\partial u}{\partial T} \right)_p + \left(\frac{\partial u}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v$

substitute in ①

$\left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial u}{\partial T} \right)_v - \left(\frac{\partial u}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v + p \left(\frac{\partial v}{\partial T} \right)_p$ — ②

Now, $du = T ds - p dv$

$\therefore \left(\frac{\partial u}{\partial p} \right)_T = T \left(\frac{\partial s}{\partial p} \right)_T - p \left(\frac{\partial v}{\partial p} \right)_T$ ~~use it~~

Use this in ②,

$C_p = C_v - \left[T \left(\frac{\partial s}{\partial p} \right)_T - p \left(\frac{\partial v}{\partial p} \right)_T \right] \left(\frac{\partial p}{\partial T} \right)_v + p \left(\frac{\partial v}{\partial T} \right)_p$

\therefore cyclic $\left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p = -1$

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

we used Maxwell relation ④ from Q-7.

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

$$\begin{aligned} \text{KHS} &= -\frac{1}{V^2} \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial T}\right)_P \cdot T \cdot V^2 \cdot \left(\frac{\partial P}{\partial V}\right)_T \\ &= -T \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T\right] \\ &= T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \\ &= C_p - C_v \quad \text{from previous Q. 8. i)} \end{aligned}$$

(iii) $dH = dU + PdV + VdP$

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

$$\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = V \left(\frac{\partial T}{\partial H}\right)_P \left[\frac{1}{V} \left(\frac{\partial U}{\partial P}\right)_T + \frac{P}{V} \left(\frac{\partial V}{\partial P}\right)_T + 1\right]$$

$$-\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_p} \left[\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + P \left(\frac{\partial V}{\partial P}\right)_T + 1\right]$$

$$= \frac{V}{C_p} \left[\frac{1}{V} \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + P \left(\frac{\partial V}{\partial P}\right)_T + 1\right]$$

$$= \frac{V}{C_p} \left[-\beta \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U - \beta P + 1\right]$$

$$= -\frac{V}{C_p} \left[\beta C_v \mu_J - \beta P + 1\right]$$

$$iv) \left(\frac{\partial H}{\partial v}\right)_s = -\frac{\gamma}{\beta}$$

$$dH = v dp + T ds$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p$$

$$dU = -p dv + T ds$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$$

$$\left(\frac{\partial H}{\partial v}\right)_s = v \left(\frac{\partial p}{\partial v}\right)_s = -v \left(\frac{\partial s}{\partial v}\right)_p \left(\frac{\partial p}{\partial s}\right)_v \quad (\text{cyclic})$$

$$= -v \left(\frac{\partial s}{\partial T}\right)_p \left(\frac{\partial T}{\partial v}\right)_p \frac{1}{T} \frac{1}{T} \left(\frac{\partial T}{\partial s}\right)_v \left(\frac{\partial p}{\partial T}\right)_v$$

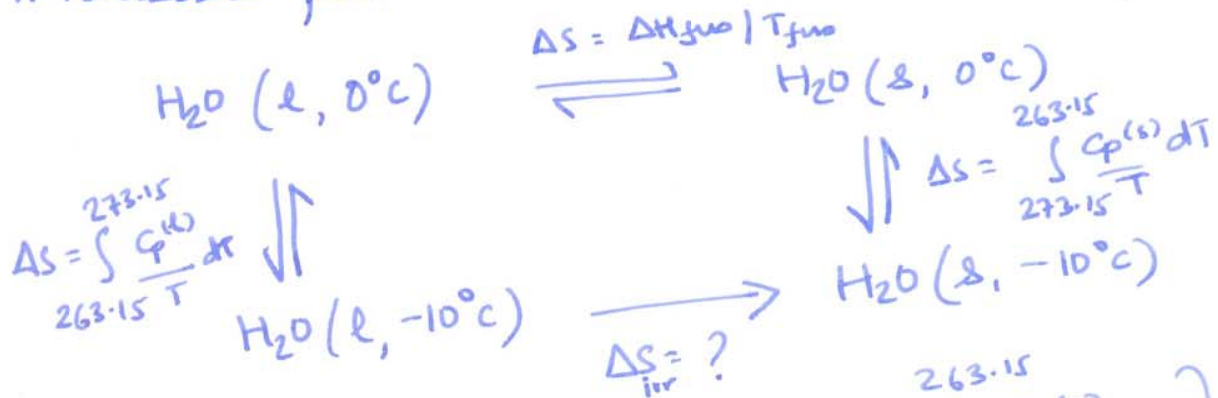
$$= -v \frac{C_p}{C_v} \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial p}{\partial T}\right)_v = v (C_p/C_v) \left(\frac{\partial p}{\partial v}\right)_T$$

$$= -\gamma/\beta$$

$$v) \beta/\alpha = \left(\frac{\partial v}{\partial p}\right)_T \cdot \left(\frac{\partial T}{\partial v}\right)_p = -\left(\frac{\partial T}{\partial p}\right)_v$$

putting this it equals 8.8.i)

Q.9) A reversible path needs to be constructed



$$\Delta S_{irr} = \left[\int_{263.15}^{273.15} \frac{C_p^{(l)}}{T} dT + \frac{\Delta H_{fus}}{273.15} + \int_{273.15}^{263.15} \frac{C_p^{(s)}}{T} dT \right] \times 1000$$

$$= \left[4.185 \ln \frac{273.15}{263.15} + \left(\frac{-334}{273.15} \right) + 2.092 \ln \frac{263.15}{273.15} \right] \times 1000$$

$$= -1144.71 \text{ J K}^{-1}$$

Entropy decreases but heat is released to the surroundings which increases the entropy of surroundings.

$$\begin{aligned}
 \text{heat released} &= 1000 \times [4.185 \times 10 - 334 - 2.092 \times 10] \\
 &= -313070 \text{ J}
 \end{aligned}$$

$$\Delta S_{surr} = \frac{313070}{263.15} = 1189.70 \text{ J K}^{-1}$$

∴ net inc. of entropy.

However, here we have an insulated vessel and ∴ this heat will warm the H₂O (s, -10°C). To warm 1 kg H₂O from -10°C to 0°C, 2.092 × 10 × 1000 = 20920 J heat is required. 313070 - 20920 = 292150 J is still available.

$$\frac{292150}{334} = 874.7 \text{ g will get converted to liquid state}$$

$$125.3 \text{ g will remain solid.}$$

Q.10)

This is similar to Q.9. for ΔS

Calculate ΔS using the reversible path.

Use ΔH as temperature independent

$$\text{Get } \Delta U = \Delta H - P\Delta V$$

$$\Delta A = \Delta U - T\Delta S = W_{\text{max}}$$

$$\Delta G = \Delta H - T\Delta S = W_{\text{add,max}}$$