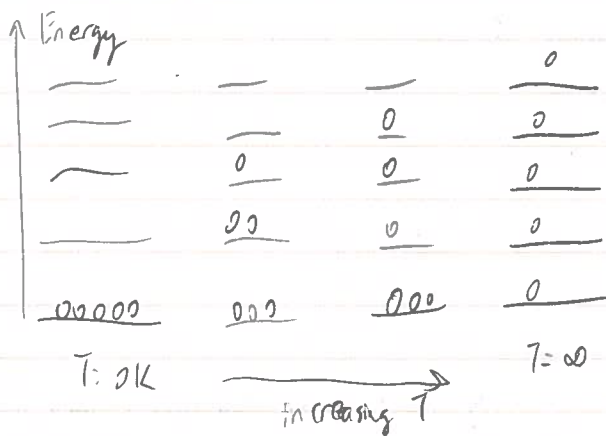


Statistical Mechanics (as from chem)

Boltzmann distribution: \Rightarrow how energy state populations differ by temp

no. of molecules (n_i) in a particular energy state (ϵ_i)
@ temp T

$$n_i \propto e^{-\frac{\epsilon_i}{kT}}$$



@ $T = 0K$

\Rightarrow all molecules occupy the lowest energy state

\downarrow increasing $T \Rightarrow$ more molecules can occupy higher states

@ $T \rightarrow \infty$

\Rightarrow all states become equally populated

removing the proportionality constant

\Rightarrow we consider relative population of the states

$$\frac{n_i}{n_j} = e^{-\frac{(\epsilon_i - \epsilon_j)}{kT}}$$

* Temperature is the only parameter that governs the population of the available energy states.

Partition function

it is not possible to know the exact values of n_i & ϵ_i

\Rightarrow instead, we know N (total no. of molecules)

\Rightarrow which is equal to the sum of the number of molecules in each energy level

$$N = n_0 + n_1 + n_2 + \dots = \sum_i n_i$$

By convention,

at lowest energy state ϵ_0 ,

there are n_0 molecules

$$\Rightarrow \frac{n_i}{n_j} = e^{-\frac{(\epsilon_i - \epsilon_j)}{kT}} \quad \left| \quad \beta = \frac{1}{kT} \right. \\ n_i = 0 \Rightarrow \epsilon_i = 0$$

$$n_i = n_0 e^{-\epsilon_i \beta}$$

$$N = \sum_i n_i = n_0 \sum_i e^{-\beta \epsilon_i}$$

$$n_0 = \frac{N}{\sum_i e^{-\beta \epsilon_i}}$$

$$n_i = n_0 e^{-\epsilon_i \beta} = \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}$$

$$\text{defining } \mathcal{Z} = \sum_i e^{-\beta \epsilon_i}$$

$$n_i = \frac{N e^{-\beta \epsilon_i}}{\mathcal{Z}}$$

where

\mathcal{Z} is the partition function

\Rightarrow an abbreviation for the sum over all energy states $e^{-\beta \epsilon_i}$

\rightarrow measures how the number of molecules is distributed/partition over available states

The partition function also contains all the info we need to calculate the bulk properties of a system,
Composed by independent molecules

Looking at Molecular energy levels

✳ does not matter what type of energy it is

↳ all possibilities for the distribution of energy are equally probable

eg if rotation/vibrational state have the same energy

↳ they have an equal probability of being occupied.

- In vibrational states: wavy SHO

$$E = \hbar \omega (v + \frac{1}{2})$$

$$\Delta E = \hbar \omega$$

$$G(v) = \omega_e (v + \frac{1}{2})$$

$$\Delta G(v) = \omega_e$$

→ does not account for anharmonicity

→ real bonds eventually break when vibrationally excited above the dissociation energy

→ in vibrational ground states, SHO is still acceptable

- In rotation energy levels, by solving the rigid rotor

$$E = \frac{\hbar^2}{2I} J(J+1)$$

$$F(J) = BJ(J+1)$$

B.E.O.T B range from 2.1 to 60 cm⁻¹

difference between

lower rotational levels : 10⁻¹ to 10⁻² cm⁻¹

✳ exists multiple degeneracy,

w/ (2J+1) states available @ each energy level

- In translation energy levels

using particle in a box model

- more practically

↳ energies for a molecule @ volume V & temp T are so close tght

↳ considered as a continuum

- translation motion of gases can be treated classically

→ except for molecules @ low T & confined volumes V

Levels & states

↳ distinguishing between energy levels & states

number of states ⇒ g_i

may be available at energy (ε_i)

↳ ∴ that energy is g_i-fold degenerate

states

— ε₂ —

— ε₁ —

— ε₀ — ← level

2-fold degenerate,

w/ 3 levels of energy

✳ summing over states

∴ accounting degeneracy

$$q = \sum_{i(\text{levels})} g_i e^{-\beta \epsilon_i}$$

Contributions to the partition functions

referring q as the molecular partition function

using the Born-Oppenheimer approximation

→ assuming an isolated molecule

i.e. no molecular interaction

→ summing contributions from different modes of energy to obtain

$$\epsilon_i = \epsilon_i^T + \epsilon_i^R + \epsilon_i^V$$

trans

rot

vib

Separating R&V is a satisfactory approximation in most cases

for the molecular partition function

$$q = \sum_{i(\text{states})} e^{-\beta \epsilon_i} = \sum_{i(\text{states})} e^{-\beta(\epsilon_i^T + \epsilon_i^R + \epsilon_i^V)}$$

$$= \sum_{i(T)} e^{-\beta \epsilon_i^T} \sum_{i(R)} e^{-\beta \epsilon_i^R} \sum_{i(V)} e^{-\beta \epsilon_i^V}$$

$$q = q^T q^R q^V$$

For a typical molecule: $q^V \ll q^T$

∴ many more translation energy levels are occupied

@ room temperature

compared to vib & rot state

Why? - ∴ trans energy levels are very close together in energy, & separation between them is \ll than thermal energy available to the molecules @ room temp

i.e.

$$\Delta \epsilon^T \ll kT$$

∴ molecules have sufficient energy to occupy

many translational states ∴ q^T is large

For vib levels

⇒ vib levels is large compared to the thermal energy available @ room temp

$$\Delta \epsilon^V \gg kT$$

∴ most molecules occupy the lowest energy level (vib ground state) @ 298K

(consistent w observations from spectroscopy)

★ Molecular partition function q , → $\frac{1}{q}$ states thermally accessible that are thermally accessible to a molecule @ the temperature of the system

Mean molecular energy $\langle \epsilon \rangle$

Assuming there are N molecules that are non-interacting / dependent independent

$$E = \sum_i N_i \epsilon_i$$

$$\langle \epsilon \rangle = \frac{E}{N} = \frac{\sum_i N_i \epsilon_i}{N}$$

remembering $N_i = \frac{N e^{-\beta \epsilon_i}}{q}$

$$\langle \epsilon \rangle = \frac{1}{q} \sum_i \epsilon_i e^{-\beta \epsilon_i}$$

⇒ eliminating ϵ_i , only involving q

$$-\frac{d}{d\beta} e^{-\beta \epsilon_i} = +\epsilon_i e^{-\beta \epsilon_i}$$

$$\langle \epsilon \rangle = -\frac{1}{q} \sum_i \frac{d}{d\beta} e^{-\beta \epsilon_i} = -\frac{1}{q} \frac{d}{d\beta} \left(\sum_i e^{-\beta \epsilon_i} \right)$$

$$\langle \epsilon \rangle = -\frac{1}{q} \frac{dq}{d\beta}$$

∴ mean molecular energy

is only in terms of q & its temperature dependence

Making further modification

1. $E_0 \neq 0$ as $E_{gs} \neq 0$, eg SHO
ground state energy

\Rightarrow true mean energy $= \langle E \rangle + E_{gs}$

2. Dependence on volume/temperature (true for q^T)

\hookrightarrow rewriting full derivative

as partial derivative

correction for

$$\langle E \rangle = E_{gs} - \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_V \quad \text{ground state} + V, T \text{ dependence}$$

Internal energy of non-interacting molecules

still continuing to assume non-interacting molecules
for a total energy of N molecules, E_N :

$$E_N = N \langle E \rangle$$

for $E_N = U$, U = internal energy:

$$U = U(0) - \frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V$$

$$U - U(0) = -\frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V \quad \left| \quad \frac{d(\ln x)}{dx} = \frac{1}{x} \right.$$

$$= -\frac{N}{q} q \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad \left| \quad d\ln = x d\ln x \right.$$

$$U - U(0) = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V$$

$$\left[\frac{\partial \ln q}{\partial \beta} \right]_V = \left[\frac{\partial \beta}{\partial T} \times \frac{\partial \ln q}{\partial \beta} \right]_V = \left[\frac{\partial}{\partial T} \left(\frac{1}{kT} \right) \times \frac{\partial \ln q}{\partial \beta} \right]_V$$

$$= -\frac{1}{kT^2} \left(\frac{\partial \ln q}{\partial \beta} \right)_V$$

$$\Rightarrow \left(\frac{\partial \ln q}{\partial \beta} \right)_V = -kT^2 \left[\frac{\partial \ln q}{\partial T} \right]$$

$$\therefore U - U(0) = NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

Canonical ensemble & canonical partition function

- accounting for interacting molecules

Additional energy terms arise

when bonding is considered

\hookrightarrow which may not scale linearly
with number of molecules present

\rightarrow Now imagine a closed collection of
 N interacting molecules @ temp T & Volume V

\hookrightarrow molecules can be distributed across
a set of energy states

\hookrightarrow each molecule has total energy E_i

\hookrightarrow energy states can adjust to

any intermolecular interactions that exist

replicating this system
multiple times

$\&$
consider the behavior of
this collection

Canonical ensemble

\hookrightarrow defining how molecules are partitioned
among the available system
energy states as the

canonical partition function Q

$$Q = \sum_i e^{-\beta E_i} \quad \begin{array}{l} \text{energy of } i \text{ member of} \\ \text{the ensemble} \end{array}$$

\nwarrow summing all members
of the ensemble

same T, N, V

Molecular interactions are already taken in to the definition of Q ,
 \therefore can be applied to condensed phases & real gases

$$U = U(0) - \left(\frac{\partial \ln Q}{\partial \beta} \right)_V$$

* scaling factor of N is not required

Q already considers the partitioning of the N molecules as a whole

\Rightarrow not as the product of N separate molecular contributions

Relationship between canonical molecular partition functions

(considering non-interacting molecules)

if independent + distinguishable (solids \therefore they have well defined position in a crystal lattice)

$$Q = q^N$$

[solids]

if independent + indistinguishable (liquids/gases \therefore molecules are in constant motion)

$$Q = \frac{q^N}{N!}$$

* Does not matter which to use when calculating internal energy U

$$U - U(0) = - \left(\frac{\partial \ln \left(\frac{q^N}{N!} \right)}{\partial \beta} \right)_V = -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V$$

$\langle \epsilon \rangle$ of a gas composed of N indistinguishable molecules is N -times the mean energy of a single molecule

* Matters which to use when calculating entropy

See 8) derive thermodynamic functions in notes ($S, A, p, H(T), G(T)$)

Translational partition function, q^T

factorising into 3-D

$$q^T = \sum_i e^{-\beta \epsilon_i^T} = \sum_{n(x)} e^{-\beta \epsilon_{n(x)}^T} \sum_{n(y)} e^{-\beta \epsilon_{n(y)}^T} \sum_{n(z)} e^{-\beta \epsilon_{n(z)}^T}$$

$$\epsilon_n = \frac{n^2 h^2}{8m x^2} = q_x^T q_y^T q_z^T$$

\Rightarrow considering subsequent energy levels relative to the $n=1$ level

$$\epsilon_n = \epsilon_n - \epsilon_{n=1} = \frac{n^2 h^2}{8m x^2} - \frac{h^2}{8m x^2} = (n^2 - 1) \frac{h^2}{8m x^2}$$

$$q_x^T = \sum_{n=1}^{\infty} e^{-\beta(n^2-1)\epsilon} = (n^2-1) \sum_{n=1}^{\infty} e^{-\beta n^2 \epsilon}$$

- translational energy levels are so close together \hookrightarrow replacing sum to integral

[continuum approximation]

$$q_x^T = \int_0^{\infty} e^{-\beta n^2 \epsilon} dn = e^{\beta \epsilon} \int_1^{\infty} e^{-\beta n^2 \epsilon} dn$$

introducing negligible error $= \int_0^{\infty} e^{-n^2 \beta \epsilon} dn$

$$q_x^T = \left(\frac{2\pi m}{h^2 \beta} \right)^{1/2} x$$

$$q^T = q_x^T q_y^T q_z^T = \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} x y z = \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} V$$

$$q^T = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V$$

$$q^T = \frac{V}{\Lambda^3} \rightarrow \Lambda = \frac{h}{(2\pi m k T)^{1/2}}$$

* $V \gg \Lambda$

$\therefore q^T$ should be v. large

\uparrow thermal wavelength of a molecule

Mean molecular $\bar{\epsilon}$
internal energy of monoatomic
perfect gas

- using q^T to determine thermodynamic quantities
- considering only translational motion (no vib/rot)
- assuming atoms are independent & non-interacting (from perfect gas)

$$\langle \epsilon \rangle = \langle \epsilon^T \rangle = \epsilon_{gs} - \frac{1}{q^T} \left(\frac{\partial q^T}{\partial \beta} \right)_V$$

neglected

$$\langle \epsilon \rangle = \frac{3}{2} kT$$

$$U - U(0) = \frac{3}{2} RT$$

For pressure:

$$p = kT \left(\frac{\partial \ln Q}{\partial V} \right)_T$$

$$p = \frac{NkT}{q} \left(\frac{\partial q}{\partial V} \right)_T$$

using $q = q^T = \frac{V}{\Lambda^3}$

$$p = \frac{NkT(\Lambda^3)}{V} \left(\frac{\partial \frac{V}{\Lambda^3}}{\partial V} \right)_T = \frac{NkT}{V} = \frac{nRT}{V}$$

$$\Rightarrow PV = nRT = NkT$$

For Gibbs's free energy:

$$dG = Vdp - SdT$$

↓ integrating?

$$G(T) = G(0) - kT \ln Q + \underbrace{V kT \left(\frac{\partial \ln Q}{\partial V} \right)_T}_P$$

$= nRT$

$$pV = nRT$$

$$\Rightarrow G(T) = G(0) - kT \ln Q + nRT$$

Subbing in $Q = \frac{q^N}{N!}$

using Stirling's approximation

$$\ln N! \approx N \ln N - N$$

$$G(T) = G(0) - nRT \ln \left[\frac{q}{N} \right] \rightarrow \text{average number of thermally accessible states per molecule}$$

$$G(T) - G(0) = -nRT \ln \frac{q}{N}$$

By $\uparrow q$, you increase the average number of accessible states

$$\hookrightarrow \frac{q}{N} \uparrow \rightarrow -nRT \ln \frac{q}{N} \text{ becomes more -ve}$$

$$\hookrightarrow \Delta G \downarrow$$

\therefore the thermodynamic tendency to lower Gibbs's energy is driven by the tendency to maximize the number of thermally accessible states

Rotational Partition Function q^R

$$q^R = \sum_i e^{-\beta \epsilon_i^R} = \sum_J (2J+1) e^{-\beta B h c J(J+1)}$$

if large $B \Rightarrow$ large gap between energy levels

\hookrightarrow less thermally accessible

$\hookrightarrow q^R$ is gonna be smaller on lower

$$q^T \gg q^R$$

\hookrightarrow a considerable number of rotational states are occupied at 298K for most molecules

\rightarrow many rotational states are occupied

$\rightarrow kT \gg \epsilon^R$, separation between rotational levels

assumption

\Rightarrow using the continuum approximation

$$q^R = \int_0^\infty (2J+1) e^{-\beta B h c J(J+1)} dJ$$

$$q^R = \frac{kT}{hcB}$$

\Rightarrow valid only for linear non-symmetrical

* check validity of diatomic molecules

q^R for molecules most likely to be "borderline" for assuming $kT \gg \epsilon^R$

[e.g. Molecule with large B , small μ]

To assess the temp above

which $q^R = \frac{kT}{hcB}$ is valid:

\hookrightarrow using θ^R

[the characteristic rotational temp of a molecule]

$$\theta^R = \frac{hcB}{k}$$

\leftarrow where does this come from

$$\hookrightarrow q^R = \frac{T}{\theta^R}$$

\leftarrow why

if:

$$\hookrightarrow T/\theta^R > 100$$

\hookrightarrow continuum approximation is fully justified

$$\text{else if: } T/\theta^R = 10$$

\hookrightarrow 0.5% error, continuum approx is still acceptable

$$\text{else if: } T/\theta^R \approx 1$$

\hookrightarrow Large error

\hookrightarrow summation should be considered

q^R for homonuclear
diatomic molecules (A-A)
or
symmetrical linear
molecules (CO_2 , ethyne)

→ T , rot rotation results
in an indistinguishable
state of molecule
↳ \therefore # of thermally accessible
rotational states for a
symmetrical linear molecule
is only half the # of
available states to
an asymmetric linear molecule
[using Pauli principle]

$$q^R = \frac{kT}{2hcB} = \frac{T}{2\theta^R}$$

⇒ combining the expressions

$$q^R = \frac{kT}{\sigma hcB} = \frac{T}{\sigma \theta^R}$$

$$\sigma = 1$$

↳ heteronuclear diatomic molecule

$$\sigma = 2$$

↳ homonuclear or linear symmetrical
molecule

Nuclear spin statistics & rotational states

[half-integer nuclear spin]

exchanging two identical fermions

$$\hookrightarrow \psi(2,1) = -\psi(1,2)$$

[integer / zero spin]

exchanging two identical bosons:

$$\hookrightarrow \psi(1,2) = \psi(2,1)$$

for ψ_{rot} :

only this satisfy
for a boson

$$\psi_{\text{rot}}(2,1) = \psi_{\text{rot}}(1,2) \text{ (even } J)$$

$$\psi_{\text{rot}}(2,1) = -\psi_{\text{rot}}(1,2) \text{ (odd } J)$$

↳ only half of the thermally available
rot states are allowed to be occupied
for the latter case (CO_2)

$\therefore q^R \Rightarrow \frac{1}{2}$ value obtained

$$\hookrightarrow \sigma = 2$$

what does it represent
↑

The electronic partition function q^E

$$q^E = \sum_i g_i e^{-\beta \epsilon_i}$$

most cases: $q^E = 1$

for diatomic molecules

↳ energy gaps between ground & excited electronic states are of the order $> 10^4 \text{ cm}^{-1}$

⇒ 10 times than that of the gap between vibrational

ground & first excited state

[$q^V \approx 1$ for diatomic molecules @ room temp
∴ vibrational ground state is appreciably occupied]

↳ same for electronic levels

unless: - molecule/ion has particularly low lying electronic states

- temp is much higher than room temp ($> 1000 \text{ K}$)

✱ for most cases, only need to consider occupancy of the electronic ground state: $q^E = g_0 = 1$

$q^E = 1$ ∴ the ground electronic state of simple diatomic molecules is non-degenerate

✱ does not contribute to the overall partition function of the molecule

determining degeneracy: $\beta \sum g_i e^{-\beta \epsilon_i}$

✱ q^E for atomic species!

✱ degeneracy is determined by the total angular momentum $q.R.N.J$

eg. $1. \quad 2S_{1/2} \Rightarrow J = \frac{1}{2}$

degeneracy = $2J + 1$

⇒ ∴ $g_0 = 2$

if no excited electronic states are occupied, $q^E = 2$

✱ see w.r. 6.1 for calc

Two-level systems:

two non-degenerate energy levels separated by an energy difference $\epsilon_1 - \epsilon_0 = \epsilon$

eg. - two conformations of a molecule w/ a diff energy

- e⁻/spin in B-field

- protons in B-field

- atoms/molecules w/ a single low-lying electronic excited state

general temp dependence of $q_{2l} = 1$

$$q_{2l} = 1 + e^{-\beta \epsilon}$$

energy of a sample size N :

$$N\langle \epsilon \rangle = N\epsilon_{ss} - \frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V = \frac{N\epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}}$$

$$= \frac{N\epsilon}{1 + e^{\beta \epsilon}}$$

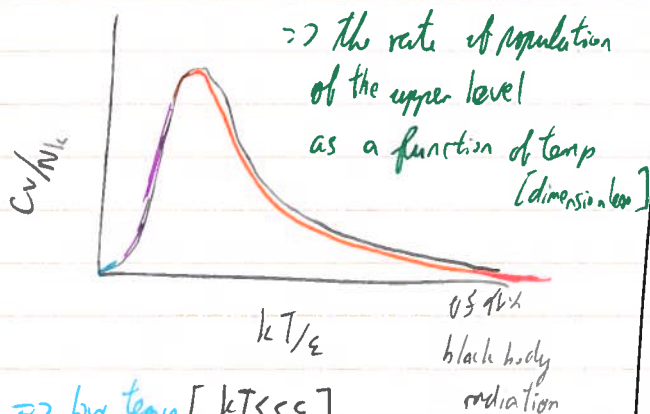
$T = 0 \text{ K} \Rightarrow N\langle \epsilon \rangle = 0$

$T \rightarrow \infty, N\langle \epsilon \rangle \rightarrow N \frac{\epsilon}{2}$

Heat Capacity C_v for 2-level systems
[Schottky Anomaly]
for C_v :

$$C_v = \left(\frac{dU}{dT} \right)_v = \frac{W \epsilon^2}{k T^2} \left[\frac{e^{\beta \epsilon}}{(1 + e^{\beta \epsilon})^2} \right]$$

↳ representing the change of internal energy w/ T
for a 2L system:



\Rightarrow low temp [$kT \ll \epsilon$]

C_v is small \because promotion to the higher level is not possible

$\Rightarrow T \uparrow \uparrow \rightarrow$ sufficient thermal energy available to start populating the upper level
 \rightarrow which is when $C_v \uparrow \uparrow$ rapidly
 $\rightarrow U(T) \uparrow \uparrow$

$\Rightarrow C_v$ hits a maximum

↳ drops to lower values

\because not possible for the upper state to become more populated than the lower state

↳ once populations are equal,
 $U \rightarrow W \epsilon / 2$ [const]

$\rightarrow C_v \downarrow 0 \because$ no further change in internal energy no matter how much higher the temp is raised.

Example:

- $C_2H_5SO_2$

\rightarrow max $C_v \approx 3K$

\because existence of low-lying $Ce(III)$ excited electronic states

- NO same as above

\rightarrow max $C_v \approx 10K$

See W.P.5

Weights & configurations

Instantaneous configuration

↳ population of a state at a given time

- eg. 3 molecules ($N=3$)
each one can occupy
one of three degenerate states $\{s_0, s_1, s_2\}$

* assume all of the states available
to the molecules have
exactly the same energy
↳ no restriction on the number of
molecules that occupy each state

- each molecule can occupy
one of three degenerate states $\{s_0, s_1, s_2\}$
- instantaneous configuration: $\{n_0, n_1, n_2\}$

⇒ 3 types of configurations

1. $\{3, 0, 0\}$ all molecules occupy s_0
* only one way

2. $\{2, 1, 0\}$ two molecules remain in s_0
1 molecule remains in s_1

s_0 A B	s_1 C
s_0 A C	s_1 B
s_0 B C	s_1 A

* if distinguishable

3. $\{1, 1, 1\}$ one molecule in
each state

s_0 A	s_1 B	s_2 C
s_0 A	s_1 C	s_2 B
s_0 B	s_1 A	s_2 C
s_0 B	s_1 C	s_2 A
s_0 C	s_1 A	s_2 B
s_0 C	s_1 B	s_2 A

* statistically:

$$III : II : I$$

$$\Rightarrow 6 : 3 : 1$$

↳ these are some configurations
that will be observed more often
than others

↳ more ways in which
it can be achieved

Weights & most probable configuration

$$W = \frac{N!}{n_0! n_1! n_2! \dots}$$

Finding dominating configuration:

↳ levels

$dW=0$: if distinct, why can
we differentiate it,
if not differentiable

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \epsilon_i = E$$

n_i for the dominating configuration
(most probable)

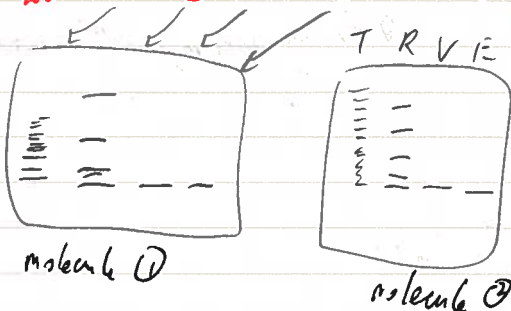
$$n_i = \frac{N e^{-\beta \epsilon_i}}{\sum_i e^{-\beta \epsilon_i}}$$

(see derivation
in stat of mols
& therm)

More on: Canonical Ensemble

Consider first: non-interacting molecules:

$$\epsilon_{tot} = \epsilon^T + \epsilon^R + \epsilon^V + \epsilon^{IE} \Rightarrow q_{tot} = q^T q^R q^V q^{IE}$$



$$E_N = \epsilon_{1,1}^0 + \epsilon_{1,2}^0 + \epsilon_{2,1}^0 + \dots + \epsilon_{N,1}^0 = \sum_{i=1}^N \epsilon_{i,1}^0 = N \langle \epsilon_{tot} \rangle$$

$$q_N = q^0 q^0 q^0 \dots q^0 = \prod_{i=1}^N q^0 = q^N = Q$$

Canonical partition function
for non-interacting molecules

$$Q = q^N \quad [\text{distinguishable}]$$

$$Q = \frac{q^N}{N!} \quad \text{if } [\text{indistinguishable}]$$

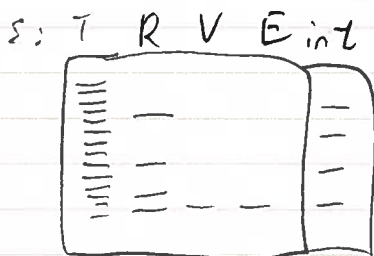
For INTERACTING molecules

for molecule one:

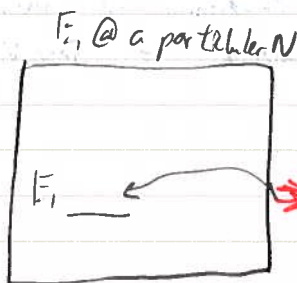
$$\epsilon_{tot}^0 = \epsilon_i^T + \epsilon_i^R + \epsilon_i^V + \epsilon_i^{IE} + \epsilon^{int}(N)$$

fixed energy
independent of N

changes w/ N, not linearly dependent



=>



$$E_1 = \epsilon^T + \epsilon^R + \epsilon^V + \epsilon^{IE} + \epsilon^{int}(N)$$

$$E^0 = E_1$$

$$E^0 = E_2$$

$$E^0 = E_N$$

Now changing N ($N_{\text{initial}} \rightarrow N_{\text{final}}$)

N_{initial}



as Σ^{int}
changes

N_{final}



* Energy spacings will change

$$\bar{E}^0 = E_1(N_{\text{initial}})$$

$$\bar{E}^0 = E_1(N_{\text{final}})$$

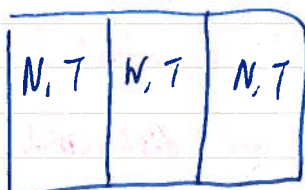
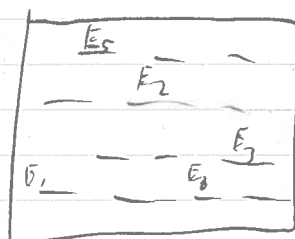
For multiple molecules

$$E_N = E_1 + E_2 + E_3 + \dots + E_N = N E_1(N)$$

$$Q = \sum_i e^{-\beta E_i} \quad \left[\begin{array}{l} i: \text{label for the molecule,} \\ \text{not the level} \end{array} \right]$$

Canonical

Ensemble: (fixed N) \Rightarrow level spacing fixed.



ensemble \Rightarrow as many "boxes" of molecules as you like

f

Ensemble: Large number of ^{virtual} copies of a system, considered all at once, each of which has certain identical properties

Microcanonical \Rightarrow same \bar{E}, V, N

Canonical \Rightarrow same V, T, N

Worked problems

1.1:

$$\epsilon_1 = 1 \times 10^{-21} \text{ J}$$

$$\epsilon_2 = 0$$

$$q = \sum_i e^{-\beta \epsilon_i} \quad \beta = \frac{1}{kT}$$

$$q = e^{-\beta \cdot 0} + e^{-\beta \epsilon_1}$$

$$q = 1 + e^{-\frac{1 \times 10^{-21}}{1.3806 \times 10^{-23} \times T}}$$

$$q_{100} = 1 + 0.79 = 1.79$$

$$q_{500} = 1 + 0.97 = 1.97$$

$$q_{1000} = 1 + 0.97 = 1.93$$

$q \uparrow$ as $T \uparrow$

as ϵ_1 becomes more thermally accessible

\Rightarrow tends to a more even distribution across ϵ_2 & ϵ_1

as $T \rightarrow \infty$

$$\hookrightarrow q \rightarrow 2$$

\Rightarrow equal contribution of 2 energy levels

$$\text{for } \epsilon_1 = 1 \times 10^{-21} \text{ J}$$

$$q_{300K} = 1 + 0.05 = 1.05$$

$$q_{500K} = 1 + 0.21 = 1.21$$

$$q_{1000K} = 1 + 0.48 = 1.48$$

for $\epsilon_1 = 1 \times 10^{-19} \text{ J} \Rightarrow$ larger energy separation

$$q_{300K} = 1 + 0 \approx 1$$

$$q_{500K} = 1 + 0 = 1$$

$$q_{1000K} = 1 + 0 \approx 1$$

$q \uparrow$ as $T \uparrow$ (as above)
partition of molecules into ϵ_1 is less than above

$\rightarrow \therefore$ energy gap between ϵ_2 & ϵ_1 is larger $\Delta \epsilon$ is larger

More ~~energy~~ thermal energy is required to populate ϵ_1

for large energy separation

negligible molecules in ϵ_1

\rightarrow Not enough thermal energy to populate upper state, as $\Delta \epsilon$ is too large

1.2

$$\epsilon_4 = 8 \times 10^{-22} \text{ J}$$

$$\epsilon_3 = 6 \times 10^{-22} \text{ J}$$

$$\epsilon_2 = 4 \times 10^{-22} \text{ J}$$

$$\epsilon_1 = 2 \times 10^{-22} \text{ J}$$

$$\epsilon_0 = 0$$

$$q = \sum_i e^{-\beta \epsilon_i}$$

$$= e^{-\beta \epsilon_0} + e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + e^{-\beta \epsilon_3} + e^{-\beta \epsilon_4}$$

$$q_{300K} = 1 + 0.008 + 0.001$$

$$+ 5 \times 10^{-7} + 4 \times 10^{-9} = 1.0081$$

$$q_{600K} = 1 + 0.2349 + 0.2552$$

$$+ 0.0137 + 0.0020 = 1.3061$$

$$q_{8000K} = 1 + 0.8344 + 0.6962$$

$$+ 0.5809 + 0.4847 = 3.5962$$

As before, $q \uparrow$ as $T \uparrow$

\Rightarrow as state become more thermally accessible

At 300K, only ground state (ϵ_0) has appreciable contribution to q

At 800K, all state are contributing to q

As $T \rightarrow \infty$, expect $q \rightarrow 5$
 \Rightarrow reflecting how many states are available

\hookrightarrow expect even distribution of molecules in all 5 states

② q tends to total number of states as $T \rightarrow \infty$

$q = 1$ at $T = 0K$ (only 1 state (ϵ_0) is thermally accessible)

1.3

$$q = \sum_{i=0}^{\infty} e^{-\beta \epsilon_i} = e^{-\beta \epsilon_0} + e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \dots$$

if $\epsilon_0 = 0, \epsilon_1 = \epsilon, \epsilon_2 = 2\epsilon, \epsilon_3 = 3\epsilon$

$$q = e^{-\beta \epsilon_0} + e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + e^{-\beta \epsilon_3} + \dots$$

$$= 1 + (e^{-\beta \epsilon}) + (e^{-\beta \epsilon})^2 + (e^{-\beta \epsilon})^3 + \dots$$

using geometric series,

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$q = \left(\frac{1}{1 - e^{-\beta \epsilon}} \right) \text{ as required}$$

$$q_{300K} = \frac{1}{1 - e^{-2 \times 10^{-22} / 300K}} = 1.008$$

(same as (1.2) $\because \Delta \epsilon$ between ϵ_0 & ϵ_1 is the same)

$$q_{8000K} = 6.038$$

(higher than in (1.2) as more states are available)

$T \rightarrow \infty, q \rightarrow \infty$
 \Rightarrow number of state available

2.1

$$q^v = \sum_v e^{-\beta \epsilon_v} \quad \epsilon_0 = 0 \quad \epsilon_1 = h\nu_e \quad \epsilon_2 = 2h\nu_e$$

[by definition]

$$q^v = e^{-\beta \epsilon_0} + e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \dots$$

$$= 1 + 5 \times 10^{-7} + \dots$$

$$= 1.0000005$$

2.2.

$$q^R = \sum_J \underbrace{(2J+1)}_{g(J)} e^{-\beta \epsilon_J}$$

$$\epsilon_J = h c B J(J+1)$$

$$\left. \begin{array}{l} \epsilon_0 = 0, g_0 = 1 \\ \epsilon_1 = 4.21 \times 10^{-21} \text{ J}, g_1 = 3 \\ \epsilon_2 = 1.26 \times 10^{-20} \text{ J}, g_2 = 5 \end{array} \right\} \begin{array}{l} \text{enter in} \\ \text{my spreadsheet} \\ 19.9196 \\ f_{\text{rot}} = 19.9196 \end{array}$$

↓
etc

2.3

$$E(n_1, n_2, n_3) = \left[\left(\frac{n_1}{L} \right)^2 + \left(\frac{n_2}{L} \right)^2 + \left(\frac{n_3}{L} \right)^2 \right] \frac{h^2}{2m}$$

$$= E(n_1) + E(n_2) + E(n_3)$$

$$q^T = \sum_{n_1, n_2, n_3} e^{-\beta E(n_1, n_2, n_3)}$$

$$= \sum_{n_1, n_2, n_3} e^{-\beta [(E(n_1) + E(n_2) + E(n_3))]}$$

$$= \underbrace{\sum_{n_1} e^{-\beta E_{n_1}}}_{q_x^T} \underbrace{\sum_{n_2} e^{-\beta E_{n_2}}}_{q_y^T} \underbrace{\sum_{n_3} e^{-\beta E_{n_3}}}_{q_z^T}$$

$$q^T = q_x^T q_y^T q_z^T$$

3.1

$$\langle \epsilon \rangle = \overbrace{\epsilon_{gs}}^{\text{20}} - \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_v$$

$$q = \frac{1}{1 - e^{-\beta \epsilon}}$$

Deriving an expression for $\langle \epsilon \rangle$

$$\langle \epsilon \rangle = - \frac{1}{q} \left(\frac{\partial q}{\partial \beta} \right)_v$$

$$\left(\frac{\partial}{\partial \beta} (1 - e^{-\beta \epsilon})^{-1} \right) = -(1 - e^{-\beta \epsilon})^{-2} \cdot \epsilon e^{-\beta \epsilon}$$

$$= -\epsilon e^{-\beta \epsilon}$$

$$\langle \epsilon \rangle = - \frac{(1 - e^{-\beta \epsilon})}{\epsilon e^{-\beta \epsilon} \times e^{\beta \epsilon}} \left(- \frac{\epsilon e^{-\beta \epsilon}}{(1 - e^{-\beta \epsilon})^2} \right)$$

$$= \frac{\epsilon e^{-\beta \epsilon} \times e^{\beta \epsilon}}{(1 - e^{-\beta \epsilon})} e^{\beta \epsilon}$$

$$\langle \epsilon \rangle = \frac{\epsilon}{e^{\beta \epsilon} - 1}$$

$$\epsilon = \text{separation in space energy level}$$

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

3.2

$$U - U(0) = -\frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V$$

$$\frac{d}{dn}(\ln n) = \frac{1}{n}$$

$$dn = n d(\ln n)$$

$$\Rightarrow dq = q d \ln q$$

$$\begin{aligned} \therefore U - U(0) &= -\frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V \\ &= -\frac{Nq}{q} \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad \text{by subst.} \\ &= -N \left(\frac{\partial \ln q}{\partial \beta} \right)_V \quad \text{as required} \end{aligned}$$

$$\begin{aligned} \left[\frac{\partial \ln q}{\partial \beta} \right]_V &= \left[\frac{\partial \beta}{\partial T} \right]_V \left[\frac{\partial \ln q}{\partial \beta} \right]_V \\ &= \left(\frac{\partial}{\partial T} \left(\frac{1}{kT} \right) \right)_V \left[\frac{\partial \ln q}{\partial \beta} \right]_V \\ &= -\frac{1}{kT^2} \left[\frac{\partial \ln q}{\partial \beta} \right]_V \end{aligned}$$

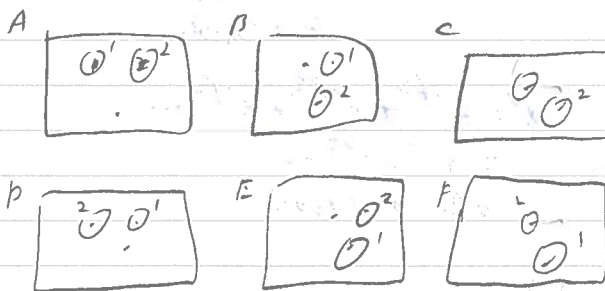
$$\left[\frac{\partial \ln q}{\partial \beta} \right]_V = -kT^2 \left[\frac{\partial \ln q}{\partial T} \right]_V$$

$$\Rightarrow U - U(0) = NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

3.3

NB: assume only 1 molecule on each site

(a) distinguishable - molecules labelled 1 & 2



Distinguishable \Rightarrow 6 arrangements

(a). Indistinguishable \Rightarrow lose labels 1 & 2

\Rightarrow A: D B: E C: F

Only 3 unique arrangements

\rightarrow relates to why we use $Q = \frac{q^N}{N!}$ for distinguishable

$Q = \frac{q^N}{N!}$ when indistinguishable

account for overcounting

4.1

$$q_x^T = \sum_n e^{-\beta \epsilon_n}$$

from lecture: $\epsilon_n = (n^2 - 1) \epsilon$
where $\epsilon = \frac{h^2}{8mL^2}$

$$\therefore q_x^T = \sum_{n=1}^{\infty} e^{-\beta (n^2 - 1) \epsilon}$$

using continuum approximation

$$q_x^T = \int_1^{\infty} e^{-\beta (n^2 - 1) \epsilon} dn$$

$$\sim \int_0^{\infty} e^{-\beta n^2 \epsilon} dn$$

$$q_x^T = \int_0^{\infty} \frac{\pi}{4\beta\epsilon} = \left[\frac{8m \times \pi^2}{\rho h^2 4} \right]^{\frac{1}{2}}$$

$$= \left[\frac{2m\epsilon}{\rho h^2} \right]^{\frac{1}{2}} \times$$

4.2

$$q^T = \left[\frac{2\pi m kT}{h^2} \right]^{\frac{3}{2}} V$$

$$= \left[\frac{2\pi (3.6 \times 1.66 \times 10^{-27}) (1.38 \times 10^{-11}) (298)}{(6.63 \times 10^{-34})^2} \right]^{\frac{3}{2}}$$

$\times 1$

$$= 2 \times 10^{32}$$

$$\Lambda = \left(\frac{h}{2\pi m kT} \right)^{\frac{1}{2}} = 17 \text{ pm}$$

$$c. q^T = \frac{V}{\Lambda^3} = \frac{(0.5 \times 10^{-9})^3}{(1.7 \times 10^{-11})^3} = 26065$$

even in this confined volume q^T is still v. large

\therefore continuum approx is still valid.

NB: Dimension of pore

$$L = 0.5 \times 10^{-9} \text{ m}$$

$$\gg \Lambda = 1.7 \times 10^{-11} \text{ m}$$

4.3.

Showing for perfect monatomic gas

$$G(T) = G(0) - nRT \ln$$

$$G(T) - G(0) = -kT \ln Q + kT \ln \left[\frac{\partial \ln Q}{\partial V} \right]_{T, nRT}$$

In lecture:

$$G(T) - G(0) = -kT \ln Q + nRT$$

for a gas: particles are

indistinguishable

$$Q = \frac{q^N}{N!}$$

$$G(T) - G(0) = -kT \ln \left(\frac{q^N}{N!} \right) + nRT$$

$$= -kT \ln q + kT \ln N! + nRT$$

$$\ln N! = N \ln N - N \rightarrow \text{Stirling's approx}$$

$$G(T) - G(0) = -kT \ln q + kT (N \ln N - N) + nRT$$

$$= -kT \ln q + kT N \ln N - kTN + nRT$$

$$G(T) - G(0) = -nRT \ln \left(\frac{q}{N} \right) + \text{require}$$

W.P 8.2

$$S_m = R \left\{ \frac{\beta \epsilon}{1 + e^{\beta \epsilon}} + \ln(1 + e^{-\beta \epsilon}) \right\}$$

2L System (Topic 6)

for distinguishable state: $S = \frac{U - U_0}{T} + Nk \ln q$

$$q = 1 + e^{-\beta \epsilon}$$

$$\begin{aligned} \langle \epsilon \rangle &= \frac{\epsilon}{1 + e^{\beta \epsilon}} \Rightarrow U - U_0 = N \langle \epsilon \rangle \\ &= \frac{N \epsilon}{1 + e^{\beta \epsilon}} \\ &= \frac{n N_A \epsilon}{1 + e^{\beta \epsilon}} \end{aligned}$$

$$S = \frac{n N_A \epsilon}{T (1 + e^{\beta \epsilon})} + N_A n k \ln(1 + e^{-\beta \epsilon})$$

$$= N_A k \left(\frac{\epsilon}{kT(1 + e^{\beta \epsilon})} + \ln(1 + e^{-\beta \epsilon}) \right) \quad \left| \quad S_m = \frac{S}{n} \right.$$

$$S = R \left(\frac{\epsilon \beta}{1 + e^{-\beta \epsilon}} + \ln(1 + e^{-\beta \epsilon}) \right)$$

$$\begin{aligned} T \rightarrow \infty \\ &= R \left(\underbrace{\frac{\epsilon \frac{1}{kT}}{1 + e^{-\frac{\epsilon}{kT}}}}_{\rightarrow 0} + \underbrace{\ln(1 + e^{-\frac{\epsilon}{kT}})}_2 \right) \end{aligned}$$

$$\rightarrow R \ln 2$$

W.P. 5.1

$$q^R = \int_0^{\infty} (2J+1) e^{-\beta B h c J(J+1)} dJ$$

$$q^R = \frac{kT}{hcB}$$

$$q^R = \int_0^{\infty} (2J+1) e^{-\beta B h c J(J+1)} dJ$$

$$x = -\beta B h c J(J+1)$$

$$x = -\beta B h c (J^2 + J)$$

$$\frac{dx}{dJ} = -\beta B h c (2J+1) dJ$$

$$dJ = \frac{dx}{-\beta B h c (2J+1)}$$

$$q^R = - \int_0^{\infty} \frac{(2J+1)}{\beta B h c (2J+1)} e^x \frac{1}{\beta B h c (2J+1)} dx$$

$$= \frac{kT}{hcB} \int_0^{\infty} e^x dx$$

$$= \frac{kT}{hcB} \quad \underbrace{\quad}_{=1}$$

5.2

Any sample of ^1H have $11 \left(\frac{3}{4} \right)$
 $11 \left(\frac{1}{4} \right)$

ortho $\text{H} \quad \uparrow \uparrow \quad \psi_{\text{nuc}}(2,1) = \psi_{\text{nuc}}(1,2) \quad \text{sym to exchange}$

para $\text{H} \quad \uparrow \downarrow \quad \psi_{\text{nuc}}(2,1) = -\psi_{\text{nuc}}(1,2) \quad \text{anti sym}$

^1H has $I = \frac{1}{2} \Rightarrow \therefore$ is a fermion

using Pauli principle: $\psi_{\text{total}}(2,1) = -\psi_{\text{total}}(1,2)$

$$\psi_{\text{total}} = \underbrace{\psi_{\text{ele}} \psi_{\text{vib}}}_{\text{sym}} \underbrace{\psi_{\text{rot}} \psi_{\text{nuc}}}_{\text{antisym w.r.t exchange}}$$

$$\begin{aligned} \psi_{\text{rot}}(2,1) &= \psi_{\text{rot}}(1,2) \text{ even } J \xrightarrow{\text{sym}} \text{pair up w/ para H} \left[\frac{3}{4} \right] \\ \psi_{\text{rot}}(2,1) &= -\psi_{\text{rot}}(1,2) \text{ odd } J \xrightarrow{\text{anti sym}} \text{pair up w/ ortho H} \left[\frac{1}{4} \right] \end{aligned}$$

\therefore ortho H only odd J allowed $\left(\frac{3}{4} \right)$
 para H only even J allowed $\left(\frac{1}{4} \right)$

$$q^R = \underbrace{\frac{3}{4} \sum_{\text{odd } J} (2J+1) e^{-\beta B h c J(J+1)}}_{\text{ortho}} + \underbrace{\frac{1}{4} \sum_{\text{even } J} (2J+1) e^{-\beta B h c J(J+1)}}_{\text{para}}$$

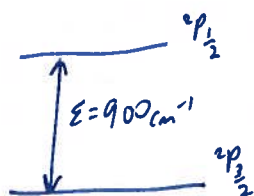
if many levels ~~are~~ occupied $\Rightarrow kT \gg B h c J(J+1)$
 rotational

\Rightarrow average averages out per molecule

$$q^R = \left(\frac{1}{2} \sum_J (2J+1) e^{-\beta B h c J(J+1)} \right)$$

$\sigma = 2$

W.P. 6.1



$$q^E = \sum_i g_i e^{-\beta \epsilon_i}$$

$$= g_0 + g_1 e^{-\beta \epsilon}$$

$$g = 2J+1 \Rightarrow g_0 = 2 \times \frac{3}{2} + 1 = 4$$

$$g_1 = 2 \times \frac{1}{2} + 1 = 2$$

$$q^E(300\text{K}) = 4 + 2 e^{-\frac{900 \times h \times c}{k \times 300}} = 4 + 0.03 = 4.03$$

$$q^E(1000\text{K}) = 4 + 0.55 = 4.55$$

$$q^E(2000\text{K}) = 4 + 1.05 = 5.05$$

$$\frac{n_1}{N}(300\text{K}) = \frac{2e^{-\beta \epsilon}}{q} = \frac{0.03}{4.03} = 0.007$$

$$\frac{n_1}{N}(1000\text{K}) = \frac{0.55}{4.55} = 0.12$$

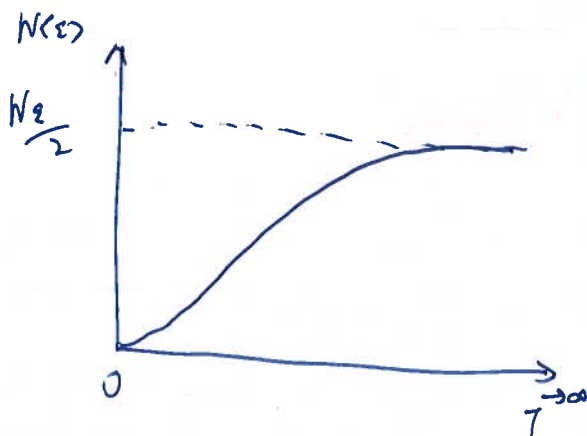
$$\frac{n_1}{N}(2000\text{K}) = \frac{1.05}{5.05} = 0.21$$

W.P. 6.2

$$N(\epsilon) = \frac{N\epsilon}{1 + e^{\beta \epsilon}}$$

$$\text{As } T \rightarrow 0 \quad \frac{1}{kT} = \beta \rightarrow \infty, N(\epsilon) \rightarrow 0$$

$$\text{As } T \rightarrow \infty \quad \frac{1}{kT} = \beta \rightarrow 0 \quad N(\epsilon) = \frac{N\epsilon}{1+1} = \frac{N\epsilon}{2}$$



W.P.

7.1

$$A \{ 2, 2, 0, 5, 4 \}$$

$$B \{ 6, 6, 0, 0, 0 \}$$

$$C \{ 2, 3, 2, 2, 3 \}$$

$N=12$ for all cases

$$A: W_A = \frac{N!}{n_0! n_1! n_2! n_3! n_4!} = \frac{12!}{2! 1! 0! 5! 4!} = 83160$$

$$W_B = 924$$

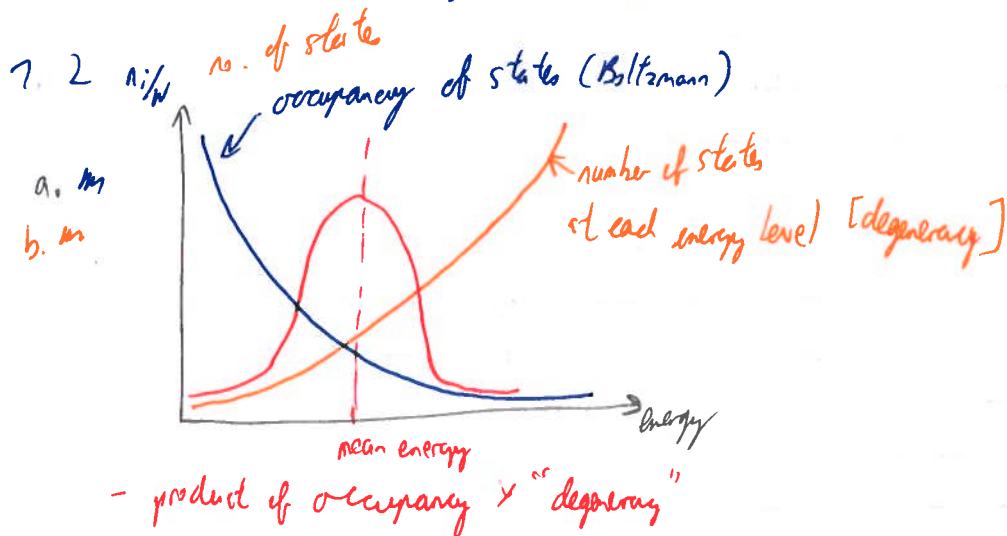
$$W_C = 1663200$$

Class C has the greatest weight

\therefore this is the dominating configuration

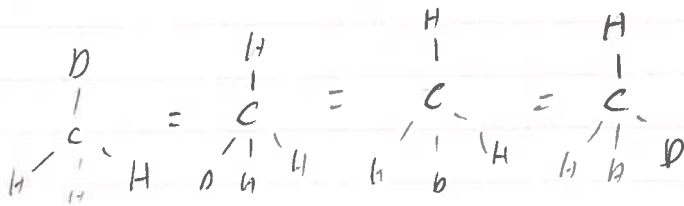
System will have characteristics of configuration C

if only ABC are possible



W.R. 83

why CH_3D has a residual entropy of $11.5 \text{ J K}^{-1} \text{ mol}^{-1}$



4 possible equivalent arrangement of CH_3D of the same energy

$$S_{\text{res}} = k \ln W$$

$$W = (\text{no. of equivalent orientations})^{\# \text{ of molecules}}$$

$$= 4^N$$

$$S_{\text{res}} = k \ln 4^N$$

$$= Nk \ln 4$$

$$= n N_A k \ln 4$$

$$= R \ln 4 \text{ for 1 mol (n=1)}$$

$$= 11.52 \text{ J K}^{-1} \text{ mol}^{-1}$$

quest was to find the "Baptist" in the "Bible"

Quaker Love

Quaker's "Baptism" for 1818

Quaker's "Baptism"

Quaker's "Baptism"

Quaker's "Baptism"

Quaker's "Baptism"

Canonical ensemble

$$\epsilon_{tot} = \epsilon^T + \epsilon^R + \epsilon^V + \epsilon^E$$

$$E_{tot} = N \langle \epsilon_{tot} \rangle$$

different for interacting molecules:

$$\epsilon_{tot}^{int} = E_i(N) = \epsilon^T + \epsilon^R + \epsilon^V + \epsilon^E + \epsilon^{int}(N)$$

does not scale linearly with N

an energy state, encompassing all forms of energy that can be occupied by a molecule in the

canonical ensemble defined more on dominating configuration

- if states are equally thermally accessible

↳ dom- config will be much more likely than any other

∴ it can be achieved in more ways

↳ config is much more probable & hence dominates all thermodynamic properties of the ensemble

Statistical entropy:

Boltzmann formula:

$$S = k \ln W \quad (\text{See derivation!})$$

↳ statistical entropy

$$\Delta S = n R \frac{V_f}{V_i}$$

for independent, distinguishable molecules

$$W = \frac{N!}{n_1! n_2! \dots} = \frac{N!}{n! (N-n)!}$$

$$\ln W = \frac{\ln N!}{\ln n_1! n_2! \dots}$$

$$= \ln N! - \ln n_1! - \ln n_2! - \dots$$

$$\ln W = \ln N! - \sum_i n_i! \quad \left| \begin{array}{l} \text{using} \\ \text{Stirling's Approx} \\ \ln n! = n \ln n - n \end{array} \right.$$

$$\ln W = N \ln N - N - \sum_i (n_i \ln n_i - n_i)$$

$$= N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i$$

$$= N \ln N - N - \sum_i n_i \ln n_i + N$$

$$= N \ln N - \sum_i n_i \ln n_i \quad \left| \begin{array}{l} N = \sum_i n_i \\ \ln N = \end{array} \right.$$

$$\ln W = \sum_i n_i \ln N - \sum_i n_i \ln n_i$$

$$= \sum_i n_i \ln N - \ln n_i$$

$$\ln W = - \sum_i n_i \ln \frac{n_i}{N}$$

$$\hookrightarrow S = -k \sum_i n_i \ln \frac{n_i}{N} \quad \left| \begin{array}{l} \frac{e^{-\beta \epsilon_i}}{q} \end{array} \right.$$

$$S = -k \sum_i n_i \ln \frac{e^{-\beta \epsilon_i}}{q}$$

$$S = -k \sum_i n_i \ln \frac{e^{-\beta \epsilon_i}}{q}$$

$$S = -k \sum_i n_i \ln e^{-\beta \epsilon_i} - \ln q$$

$$= -k \sum_i n_i (-\beta \epsilon_i) + k \sum_i n_i \ln q$$

$$= k\beta \sum_i n_i \epsilon_i + k \sum_i n_i \ln q$$

$$= N\langle \epsilon \rangle \quad N$$

$$S = k\beta N\langle \epsilon \rangle + kN \ln q$$

Inserting the canonical partition func instead of / not part func.

$$S = \frac{U - U(0)}{T} + Nk \ln q$$

$$S = \frac{U - U(0)}{T} + Nk \ln q \quad S = \frac{U - U(0)}{T} + k \ln Q$$

For independent, indistinguishable molecules

→ W is reduced by $N!$

∴ $N!$ permutations among the energy states that would result in the same system

$$S = \frac{U - U(0)}{T} + Nk \ln q - k \ln N!$$

$$= \frac{U - U(0)}{T} + Nk \ln q - k[N \ln N - N]$$

$$= \frac{U - U(0)}{T} + Nk \ln q - Nk \ln N + Nk$$

$$= \frac{U - U(0)}{T} + Nk \ln \frac{q}{N} + Nk \ln \frac{e^1}{1}$$

$$= \frac{U - U(0)}{T} + Nk \ln \frac{q e^1}{N}$$

$$S = \frac{U - U(0)}{T} + Nk \ln \frac{q e^1}{N}$$

Residual entropy:

entropy @ $T = 0K$ is > 0

due to disorder present in the solid

Thermodynamics (mixing)

Mixtures: material system made up of 2 or more diff substances that are mixed, but not chemically combined

Solutions: 2 or more components mixed homogeneously to form a single phase

Gibbs energy:

$$dG = dH - TdS = Vdp - SdT$$

criterion of spontaneous change:

$$dG \leq 0 \quad (p, T = \text{constant})$$

eqⁿ of a system @ fixed p, T corresponds to the min Gibb's free energy

[pure substance]
for a one-component system:
molar Gibbs energy = chemical potential

(state function) $\mu = G_m = \frac{G}{n}$

See also phase diagrams in T1