STATISTICAL MECHANICS NOTES

Boltzmann Factor

Physical quantity $\propto \exp[-\frac{f_E(E)}{const \times f_T(T)}]$

$f_E(T)$ is a function of energy only, while $f_T(T)$ is a function of temperature only. The constant makes the expression dimensionless (E/T)

Boltzmann Law:

$$\frac{n_i}{n_j} = e^{-(\varepsilon_i - \varepsilon_j)/kT}$$

Distinct, Independent Particles –

Distinct ➔ can tell which is which (labels) a,b,c…
Independent ➔ minimal interaction (can exchange energy in collision).
Hence, E = $\varepsilon^a + \varepsilon^b + \varepsilon^c + \ldots = \sum_i \varepsilon^i$

Configurations –

Sharing energy amongst particles from a manifold of energy states, ε_o, ε_1, ε_2 … etc ($\varepsilon_0 = 0$).
At any instant, there are:

- n_o particles with ε_o.
- n_1 particles with ε_1, etc.

This is the configuration. (Same Total Energy).

Statistical Weights –

Number of ways of reaching a given configuration, Ω. Represents the probability that the configuration can be reached.

$$\Omega = \frac{N!}{n_0!n_1!n_2!\ldots}$$, where x! = x(x-1)(x-2)(x-3)…3,2,1 and 0! = 1.

Equal Probability of Configurations –

No bias to any configuration. This is the Principle of equal *a priori* probabilities.

Conservation of Number and Energy –

$$N = \sum_i n_i \quad \& \quad E = \sum_i \varepsilon_i n_i$$

Predominant Configuration –

Configuration with the largest statistical weight.
For very large number of configurations, the average peak of the distribution completely dominates so that everything else is negligible.

Maximisation Subject to Constraints –

Find maximum in distribution (Ω) subject to constraints of Conservation.
Predominant configuration amongst N particles is found to have energy states populated as:

$\frac{n_i}{N} e^{\alpha - \beta \mathbf{e}_i}$, where α and β are constants under fixed temperature.

Identify α:

$$\frac{n_o}{N} = e^{\alpha}$$

ε_o = 0, n_o = 0 – Ground State

$$\therefore \frac{n_o}{N} = e^{\alpha} e^{-\beta\varepsilon_i} = \frac{n_o}{N} = e^{-\beta\varepsilon}$$

$$\therefore \frac{n_i}{n_o} = e^{-\beta\varepsilon_i}$$

This is the T dependent ratio.

β = $^1/_{kT}$ [can be proven, see later]

Molecular Partition Function

Derived from Boltzmann Law.

$$n_i = n_o e^{-\beta \varepsilon_i}$$

Eliminate n_o (generally not known):

$N = n_o + n_1 + n_2 + \ldots = \sum_{\text{all states}} n_i$

Hence,

$$\therefore\ N = n_o + n_o e^{-\beta\varepsilon_1} + n_o e^{-\beta\varepsilon_2} + \ldots = n_o \sum_{\substack{\text{all}\\ \text{states}}} e^{-\beta\varepsilon_i}$$

From this,

$$n_i = \frac{N e^{-\beta\varepsilon_i}}{\underbrace{\sum_{\substack{\text{all}\\ \text{states}}} e^{-\beta\varepsilon_i}}_{\underline{\underline{q}}}}$$

$$q = \sum_{\substack{\text{all}\\ \text{st}}} e^{-\beta\varepsilon_i} = 1 + e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \ldots \quad (\varepsilon_0 = 1,\ \beta = \tfrac{1}{kT})$$

Shows how particles distribute (partition) over accessible quantum states.

- Infinite series that converges more rapidly for increasing ε_i and increasing β.
- Can be evaluated as soon as $\beta_\varepsilon >> 0$, so that $e^{-\beta\varepsilon} \rightarrow 0$.
- If $\varepsilon_1 >> kT$, $q \rightarrow 1$.
- For successive energy gap $\Delta\varepsilon$, $q >> 1$ if $\Delta\varepsilon < kT$.

Degeneracy –

$$q = \sum_{\substack{\text{all}\\ \text{levels}}} g_j e^{-\beta\varepsilon_j} \qquad g_j = \#\text{ states sharing same energy (energy level)}$$

NOTES:

$$L = \sum_{\substack{\text{all}\\ \text{states}}} n_i = \sum_{\substack{\text{all}\\ \text{levels}}} g_j n_j = n_o q$$

$$\therefore\ q = \frac{L}{n_o}$$

Measure extent of particles escaping ground state.

T = 0K, q =1 (n_o = L).

Increasing T, q → ∞ (fewer particles in Ground State; infinite number of accessible states).

Applications –

Total Energy, $E = n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots = \sum_{\text{states}} n_i \varepsilon_i$

From q:

$$E = \frac{\varepsilon_1 N e^{-\beta\varepsilon_1}}{\sum e^{-\beta\varepsilon_i}} + \frac{\varepsilon_2 N e^{-\beta\varepsilon_2}}{\sum e^{-\beta\varepsilon_i}} + \ldots = \frac{N \sum \varepsilon_i e^{-\beta\varepsilon_i}}{\sum e^{-\beta\varepsilon_i}}$$

Note that:

$$\frac{d}{d\beta}\left(e^{-\beta\varepsilon_i}\right) = -\varepsilon_i e^{-\beta\varepsilon_i}$$

Thus,

$$E = -\frac{N}{q}\frac{dq}{d\beta} = -N\left(\frac{d \ln q}{d\beta}\right)$$

Internal Energy –

$$U = U(0) + E$$

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

Also, q depends on V (which depends on T) so must specify constant volume:

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

This can be combined with the only temperature-dependent term in q for translational energy (see later):

$$\ln q = {}^{-3}/_{2} \ln \beta$$

Such that:

$$U = U(0) + \frac{3}{2}N\left(\frac{\partial \ln \beta}{\partial \beta}\right)_V = U(0) + \frac{3N}{2\beta}$$

This can be compared to N atoms in a perfect gas:

$$\mathbf{U = U(0) + {}^{3}/_{2}NkT}$$

And hence we see that $\beta = {}^{1}/_{kT}$ [as used earlier]

Entropy –

$$\mathbf{S = k \ln \Omega.}$$

$$U = U(0) + E = U(0) + \sum_{states} n_i \varepsilon_i$$

$$dU = \underbrace{\sum n_i d\varepsilon_i}_{heat} + \underbrace{\sum \varepsilon_i dn_i}_{work}$$

At constant V (as for internal energy) the spacing of successive energy states does not change on heating. Thus, $d\varepsilon_i = 0$,

$$dU = \sum_{states} \varepsilon_i dn_i$$

From here, $dU = dq_{rev} = T\,dS$ [classical thermodynamics]

$$dS = \frac{dU}{T} = k\sum \beta\varepsilon_i dn_i$$

Condition for max Ω (predominant configuration):

$$\frac{\partial \ln \Omega}{\partial n_i}) = \beta\varepsilon_i - \alpha$$

$$dS = k\sum_i \left(\frac{\partial \ln \Omega}{\partial n_i}\right) dn_i + k\alpha \sum_i dn_i$$

Number of particles is constant: $\sum_{states} dn_i = 0$

Therefore,

$$dS = k\, d(\ln \Omega)$$

$$\mathbf{S = k \ln \Omega.}$$

Molecule → Mole (Canonical Partition Function)

$$E = -N\left(\frac{d \ln q}{d\beta}\right) \Rightarrow \langle \varepsilon \rangle = \frac{E}{N} = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

Molar E, E_m: $E_m = -L\left(\frac{\partial \ln q}{\partial \beta}\right)_V$

Reasonable when assuming non-interacting, and does not apply to other properties, e.g. S. Allow possibility of interactions by invoking the idea that every system has a set of system energy states which molecules can populate.

Canonical Partition Function, Q_N :

$$Q_N = \sum_{\substack{system\\states}} e^{-\beta\varepsilon_i}$$

Canonical – according to a rule. Applies to states of constant amount, volume and temperature

Hence,

$$E_m = \langle E_i \rangle = -\left(\frac{\partial \ln Q_N}{\partial \beta}\right)_V$$

Compare to:

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

scaling factor implied. Not so in Q_N (N particles already considered)

Can continue to develop a statistical toolkit of functions, e.g. Entropy:

$$dS = C_V \frac{dT}{T}$$

$$C_V = \left(\frac{\partial(U - U(0))}{\partial T}\right)_V = \left[\frac{\partial}{\partial V}\left(kT^2\left(\frac{\partial \ln Q}{\partial T}\right)\right)_V\right]_V$$

$$= 2kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + kT^2\left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_V$$

$$\therefore \; S = k \ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + S_0$$

Third Law ➔ $S_0 = 0$, on integrating:

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

Compare to $\quad A = U - TS$

$$A - A(0) = U - U(0) - TS$$

$$\therefore \; S = \frac{(U - U(0))}{T} - \frac{(A - A(0))}{T}$$

i.e.

$$A - A(0) = -kT \ln Q$$

Massieu Function

$$\mathbf{J = -{}^{A}/_{T}}$$

This gives:

$$J = -\frac{(A - A(0))}{T} = k \ln Q \quad \text{(MASSIEU BRIDGE)}$$

Links Statistical and Classical Thermodynamics.

$$U = T^2\left(\frac{\partial(A/T)}{\partial T}\right)_V = \left(\frac{\partial(A/T)}{\partial(1/T)}\right)_V$$

$$U - U(0) = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V \quad \text{(as shown earlier)}$$

$$\text{Also} \quad = -k\left(\frac{\partial \ln Q}{\partial(1/T)}\right)_V = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V$$

Also, **Pressure**:

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

Heat Capacity,

$$C_V = \left.\frac{\partial U}{\partial T}\right)_V$$

i.e.

$$C_V = \left[\frac{\partial}{\partial T}\left[T^2\left(\frac{\partial(A/T)}{\partial T}\right)_V\right]\right]_V = 2kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + kT^2\left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_V$$

Entropy:

$$S = \left.\frac{\partial A}{\partial T}\right)_V = k \ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_V$$

$$= \frac{E}{T} + k \ln Q$$

Enthalpy:

$$H = U + pV$$

$$\therefore \quad H = T^2\left(\frac{\partial(A/T)}{\partial T}\right)_V - \left(\frac{\partial A}{\partial V}\right)_T$$

$$\Rightarrow H - H(0) = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$H(0) = U(0) = A(0)\,[= G(0)]$$

$pV = nkT \Rightarrow$ (perfect gas) $\Rightarrow$

$$H - H(0) = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V + NkT$$

Gibbs Free Energy:

$$G = A + pV$$

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

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

Perfect Gas ➔

$$\mathbf{G - G(0) = -kT\ln Q + nkT.}$$

Chemical Potential:

$$dA = -pdV - SdT + \mu\, dn$$

& $n = \frac{N}{N_{AV}}$ = # moles:

$$\mu = \frac{dA}{dn}\Big)_{V,T} = N_{AV}\left(\frac{\partial A}{\partial N}\right)_{V,T}$$

$$= -RT\frac{\partial \ln Q}{\partial N}\Big)_{V,T}$$

Independent Systems:

$$Q = \begin{cases} \dfrac{q^N}{N!} & \text{— ind. + INDISTINGUISHABLE} \\ q^N & \text{— ind. + DISTINGUISHABLE} \end{cases}$$

Use Stirling's Approximation:

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

e.g.

$$-kT\ln Q = -NkT\ln q + NkT\ln N - NkT$$

Thus,

G – G(0) = -NkT ln (q/N) [For INDISTINGUISHABLE]

G – G(0) = -NkT ln q [For DISTINGUISHABLE]

Translational Partition Function, q_{trs}

Consider particle in a box:

$$\varepsilon_x = \frac{{n_x}^2 h^2}{8m{l_x}^2}$$

Sum over all accessible states:

$$q_{trs,x} = \sum_{\substack{\text{all} \\ n}} e^{-\beta n_x^2 h^2/8ml_x^2}$$

But practically all energy levels densely packed, so becomes an integral:

$$q_{trs,x} = \int_0^\infty e^{-\beta n_x^2 h^2 / 8m L_x^2}\, dn_x$$

$$q_{trs,x} = \left(\frac{2\pi m}{\beta}\right)^{1/2} \frac{L_x}{h}$$

$$q_{trs,x,y,z} = \left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{L_x L_y L_z}{h^3} \quad (\text{i.e. } 3d \Rightarrow \text{cubed})$$

$$q_{trs} \therefore = \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} V$$

Canonically,

$$Q_{trs} = \frac{q_{trs}^N}{N!} = \frac{1}{N!}\left[\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V\right]^N$$

Collecting constants,

$$q_{trs} = \left(\frac{2\pi k}{h^2 L}\right)^{3/2} (MT)^{3/2} V$$

Thermodynamic Functions for an Ideal Monatomic Gas

$$\ln Q_{trs} = \frac{3}{2} N \ln(2\pi m) + \frac{3}{2} N \ln \underbrace{T + N \ln V}_{\text{variables}} - 3N \ln h - \ln N!$$

Thus, derivatives simple:

$$\left(\frac{\partial \ln Q_{trs}}{\partial T}\right)_V = \frac{3N}{2T} \qquad \left(\frac{\partial^2 \ln Q_{trs}}{\partial T^2}\right)_V = -\frac{3N}{2T^2}$$

$$\left(\frac{\partial \ln Q_{trs}}{\partial V}\right)_T = \frac{N}{V}$$

These can then be used in the functions found earlier. Hence,

$$E_{trs} = \frac{3}{2} NkT$$

$$p = \frac{NkT}{V} \qquad C_V = 3Nk - \frac{3}{2} Nk$$

$$\therefore C_{v,m} = \frac{3R}{2}$$

Entropy more complex, since ln Q_{trs} appears. It proceeds as:

$$S = k \ln Q_{trs} + kT\left(\frac{\partial \ln Q_{trs}}{\partial T}\right)_V$$

$$k \ln Q_{trs} = k \ln \frac{1}{N!} q^N$$
$$= k\left(\ln \frac{1}{N!} + \ln q^N\right) = k(N \ln q - \ln N!)$$

Use Stirling's Approximation: ln N! ≈ N ln N – N

$$k \ln Q_{trs} = k(N \ln q - N \ln N + N)$$
$$= Nk\left(1 + \ln \frac{q}{N}\right)$$

Thus,

$$S = Nk\left(1 + \ln \frac{q}{N}\right) + \frac{3}{2} Nk$$

$$S = Nk\left(\frac{5}{2} + \ln \frac{q}{N}\right)$$

Overall,

$$S = Nk\left[\frac{5}{2} + \ln\left[\left(\frac{2\pi m kT}{h^2}\right)^{3/2} \frac{V}{N}\right]\right]$$

One mole of Ideal Gas ➔

$$N = L,\ Lk = R,\ Lm = M \ \& \ V_r = \frac{RT}{p}$$

gives:

$$S_m = R\underbrace{\left[\ln\left(\frac{M^{3/2}T^{5/2}}{p}\right)\right]}_{\text{VARIABLES}} + R\underbrace{\left[\ln\left(\left(\frac{2\pi}{Lh^2}\right)^{3/2}(ek)^{5/2}\right)\right]}_{\text{CONSTANTS}}$$

This is the **Sackur-Tetrode Equation**. The constants add up to 172.29 J K^{-1} mol^{-1} [20.723R]

$$\frac{1}{p} = \frac{V}{RT} \Rightarrow \ln p^{-1} = \ln V - \ln R - \ln T$$

$$\therefore\ S_m = R\ln V + \tfrac{3}{2}R\ln T + \tfrac{3}{2}R\ln M + \underset{(\hookrightarrow 18.605R)}{\text{constant}}$$

Note that:

$$\left.\begin{aligned} \Delta S_T &= R\ln\frac{V_2}{V_1} \\ \Delta S_V &= \tfrac{3}{2}R\ln\frac{T_2}{T_1} = C_V\ln\frac{T_2}{T_1} \end{aligned}\right\}\text{known classically}$$

$$\left(\tfrac{3}{2}R\ln M + \text{constant}\right) - \text{not known classically}$$

Ideal Diatomic Gas – Rotational Partition Function.

For a rigid rotor:

$$\varepsilon_J = J(J+1)\frac{h^2}{8\pi^2 I} = hcBJ(J+1) \qquad I = \mu r^2$$

$$B = \frac{h}{8\pi^2 Ic}$$

$$\varepsilon_J = J(J+1)k\Theta_r \quad \Theta_r = \frac{h^2}{8\pi^2 Ik} = \frac{hcB}{k}$$

$$\text{Degeneracy} \Rightarrow g_J = (2J+1)$$

$$q_{rot} = \sum g_J e^{-\varepsilon_J/kT} = \sum (2J+1)e^{-J(J+1)\Theta_r/T}$$

θ_r may equal B/k (depends on units)

If I is not too small and T not too low, then appreciable number of rotational states are occupied, and there is a virtual continuum as for q_{trs}:

$$q_{rot} = \int_0^\infty (2J+1)\,e^{-J(J+1)\Theta_r/T}\,dJ$$

$$\text{This gives} \quad q_{rot} = \frac{T}{\Theta_r} = \frac{8\pi^2 IkT}{h^2}$$

Problems tend to arise when T is nearly 0K and the molecule contains Hydrogen.

This expression otherwise works for all heteronuclear diatomics. Special considerations required for homonuclear diatomics. This is due to over-counting of rotational states by a factor of 2. This is because 180° rotation of X-X gives a result indistinguishable from 360°.
There $q_{rot}/2$ required for all linear symmetric molecules.
Or,

$$\mathbf{q_{rot} = T/\sigma\theta_r}$$

Where:
σ = symmetry factor (= 2 for homonuclear diatomic, = 1 for heteronuclear diatomic).
σ = 2 for H_2O and σ = 3 for NH_3, for example.

Quantum Mechanically,
Interchange of identical nuclei may leave ψ unchanged, i.e. symmetric, or $\psi \rightarrow -\psi \Rightarrow$ antisymmetric.
Symmetric ➔ boson (integral), while antisymmetric ➔ fermion (half-integral).

$$\psi_{tot} = \psi_{trs} \cdot \psi_{rot} \cdot \psi_{vib} \cdot \psi_{el} \cdot \psi_{ns}$$

$\psi_{\mathbf{ns}}$ = nuclear spin wavefunction. Symmetric or antisymmetric depending on whether 2 nuclear spin states are parallel / antiparallel.
$\psi_{\mathbf{rot}}$ = antisymmetric or symmetric. For even J it is symmetric, for odd J it is antisymmetric.
$\psi_{\mathbf{el}}$ = antisymmetric or symmetric. Homonuclear diatomic is usually ${}^1\Sigma_g^+$ = symmetric. Only O_2 is common exception, ${}^3\Sigma_g^-$ is antisymmetric.
$\psi_{\mathbf{trs}}$ = only motion of centre of mass, so no effect on symmetry (symmetric).
$\psi_{\mathbf{vib}}$ = only depends on internuclear distance (symmetric).

Thus, in hydrogen I = ½ and the nucleus is a fermion so the ψ_{tot} is antisymmetric.
This requires odd J to give symmetric nuclear spin and even J to give antisymmetryic.

In Deuterium, I = 1 (boson) ➔ ψ_{tot} is symmetric. Thus,
Odd J ➔ paired nuclear spin.
Even J ➔ parallel nuclear spin.

Thermodynamic Functions with q_{rot}:

$$\ln Q_{rot} = N \ln T + N \ln\left[\frac{8\pi^2 I k}{\sigma h^2}\right]$$

$$\therefore U_{rot} = kT^2\left(\frac{\partial \ln Q_{rot}}{\partial T}\right)_V = NkT^2\left(\frac{\partial}{\partial T}\ln T\right)$$

$$= NkT \quad (\text{for diatomics})$$

Applies to all linear molecules with only two degrees of freedom in rotation.

Molar ➔ $U_{rot} = RT$, $C_{rot,m} = R$.

For entropy,

$$S_{rot} = kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + k \ln Q = \frac{U_{rot}}{T} + k \ln Q$$

$$= \frac{NkT}{T} + k \ln\left[\frac{8\pi^2 IkT}{\sigma h^2}\right]^N$$

$$S_{rot} = Nk\left[1 + \underbrace{\ln\frac{IT}{\sigma}}_{\text{dependence on } \mu.} + \ln\left(\frac{8\pi^2 k}{h^2}\right)\right]$$

Extending to polyatomic, non-linear molecules – must consider 3 independent motions of inertia:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left[\left(\frac{T}{\Theta_{r,x}}\right)\left(\frac{T}{\Theta_{r,y}}\right)\left(\frac{T}{\Theta_{r,z}}\right)\right]^{1/2}$$

<u>Ortho and Para Spin States</u>

In general, for homonuclear diatomic with nuclear spin I, each nucleus have p (=2I+1) spin states, and a total of p^2 nuclear spin wavefunctions to include in ψ_{rot}.
Of these p^2,

½ p(p+1) = symmetric [ORTHO]
½ p(p-1) = antisymmetric [PARA]

This is true whether they are bosons or fermions.

Proton, I = ½ , ψ_{tot} = antisymmetric.
2 spin states, ↑ or ↓, therefore 4 ψ_{ns} (p^2)
Thus,
3 ortho (symmetric) = ODD J [o-Hydrogen]
1 para (antisymmetric) = EVEN J [p-Hydrogen]

Deuteron, I = 1, ψ_{tot} = symmetric.
3 spin states per nucleus, so 9 per molecule (p^2)

6 x ortho (symmetric) =	EVEN J	[o-Deuterium]
3 x para (antisymmetric)=	ODD J	[p-Deuterium]

Therefore ortho-Hydrogen ➔ Odd J, 3:1 ratio with odd predominating (due to statistical weight).
Similarly, ortho-Deuterium ➔ Even J, 6:3 ratio with even predominating.
Ratios apply to e.g. rotational Raman Spectrum.
At high temperatures, hydrogen exists in an equilibrium mixture of spin states favouring o-Hydrogen by 3:1.
At low temperatures, there is an increased tendency for J = 0. Even ➔ switch to p-Hydrogen. This conversion is slow.
Normal Hydrogen (n-H_2) = 3:1 mixture.

Nuclei with zero spin –
Some nuclei are I=0 (e.g. ^{16}O).
8 protons and 8 neutrons occupy their own energy manifolds (closed shell configurations – all spins paired). Also true for ^{12}C.
p = 2I + 1 ➔ O_2 or CO_2 have only 1 spin state.
I = 0 ➔ integral, therefore boson, so ψ_{tot} = symmetric.
Hence,

CO_2 ➔ only even J.
O_2 ➔ only odd J.

Reason now is that ground electronic state is $^3\Sigma_g^-$ (i.e. antisymmetric), therefore rotation must also be antisymmetric (odd), unlike CO_2.

Vibrations in an Ideal Diatomic, q_{vib}

Orders of magnitude: $q_{vib} > q_{rot} > q_{trs}$ are usually in the ratio 1:10:250-300 orders of magnitude. Thus, cannot use the continuum approximation for q_{vib}.
q_{vib} @ 300K ≈ 1.

Simple Harmonic –

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \& \quad \varepsilon_{vib} = (v+\tfrac{1}{2})h\nu$$

Always non-degenerate in diatomics. Not so for polyatomics – linear ➔ (3N-5) normal vibrational modes, while non-linear ➔ (3N-6).
$\varepsilon_o = 0$, $\varepsilon_1 = h\nu$, $\varepsilon_2 = 2h\nu$, etc, due to reference against ground state of ½hν. Thus,

$$q_{vib} = \sum e^{-\beta\varepsilon_{vib}} = 1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + e^{-3\beta h\nu} + \ldots$$

This gives a geometric series:

$$q_{vib} = \frac{1}{1-e^{-\beta h\nu}} = \frac{1}{1-e^{-\Theta_{vib}/T}} \quad \left(\Theta_{vib} = \frac{h\nu}{k}\right)$$

This is true for diatomics only. For polyatomics, just consider each normal mode of vibration separately.

Vibrational Energy spacings are much larger than Rotational, therefore $\theta_{vib} \approx 10^2$-$10^3$, $\theta_{rot} \approx 10^1$-$10^2$.

Polyatomics –

$$q_{vib}^{tot} = \prod (q_{vib}^{(n)}) = q_{vib}^{(1)} \times q_{vib}^{(2)} \times q_{vib}^{(3)} \times \ldots$$

$$(1),(2),(3)\ldots \Rightarrow \text{normal modes } 1,2,3\ldots$$

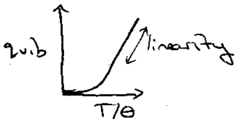
Independent and factorisable, therefore ignore anharmonicity (except at high T).

High Temperature Limit –
At high T, linear in q_{vib} against T.

Expand $1-e^{-\theta_{vib}/T}$:

$$q_{vib} \approx \frac{1}{1-1+(\theta_{vib}/T)+\ldots} = \frac{T}{\theta_{vib}} \quad \text{(high T limit)}$$

$\Rightarrow$



Thermodynamic Functions –

$$U_{vib} = kT^2\left(\frac{\partial \ln Q_{vib}}{\partial T}\right)_V = \frac{Nk\theta_{vib}}{(e^{\theta_{vib}/T}-1)}$$

Note: far less simple than U_{trs} and U_{rot}.

At high T: $U_{vib,m}$ = RT (for each normal mode)

At 300 K: $U_{vib,m} = \dfrac{3000R}{(e^{10}-1)} \approx \dfrac{R}{7}$

Also note that if ε_0 is set to ½hv instead, then must add this to the result.

Heat Capacity –

$$C_{vib,m} = \left(\frac{\partial U}{\partial T}\right)_V = R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{(e^{\theta_{vib}/T}-1)^2} \qquad \text{EINSTEIN EQUATION}$$

$$C_{vib,m} = R\mathcal{F}_E\left(\frac{\theta_{vib}}{T}\right) \qquad \mathcal{F}_E = \frac{u^2e^u}{(e^u-1)^2} \quad u = \frac{\theta_{vib}}{T}$$

(Einstein Function)

Entropy –

$$S_{vib} = \frac{U_{vib}-U_{vib}(0)}{T} - \frac{A_{vib}-A_{vib}(0)}{T} = \frac{U_{vib}-U_{vib}(0)}{T} + k \ln Q_{vib}$$

$$\ln Q_{vib,m} = Lk \ln q_{vib} = R \ln q_{vib}$$

$$\frac{S_{vib,m}}{R} = \frac{\theta_{vib}/T}{(e^{\theta_{vib}/T}-1)} - \ln(1-e^{-\theta_{vib}/T})$$

Electronic Partition Function

$$q_{el} = \sum_i g_{\neq i}\, e^{-\varepsilon_{el,i}/kT} = g_0 e^{-0} + 0 \text{ (higher terms)} = g_0$$

Ground States are commonly degenerate (not O_2 though, $g_1 = 1$).

For Atoms, use ${}^{(2S+1)}\Gamma_J$ and $g_o = 2J+1$.
For molecules, use ${}^{(2S+1)}\Gamma$ and $g_o = 2S+1$.

Excited States can be approached in a similar manner.

Usually, the energy gap from ground state to 1st excited state is large and the above applies. If the gap is not negligible compared to kT (i.e. $\theta_{el}/T << 1$) then:

$$q_{el} = g_0 + g_1 e^{-\theta_{el}/T}$$

(Higher states than the 1st are rarely occupied).