

## APPLICATIONS OF STATISTICAL MECHANICS NOTES

Statistical Mechanics links Energy-Levels (Quantum) to Macroscopic Properties (Thermodynamics).

### Partition Function

For N molecules in volume V and temperature T,

$$Q_N(V, T) = \sum_i g_i e^{-E_i / kT}$$

Measure of the number of distinguishable complexions of N-particle system.

**Helmholtz Free Energy:**

$$A_N = -kT \ln Q_N$$

(wrt lowest energy state).

Links to other thermodynamic quantities using this relation.

$$dA = -pdV - SdT$$

Therefore,

$$i) S = -\left(\frac{\partial A}{\partial T}\right)_{V, N} = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T}\right)_V$$

$$ii) U = A + TS = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V \Rightarrow S = k \ln Q + U/T$$

$$iii) P = -\left(\frac{\partial A}{\partial V}\right)_T = kT \left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$iv) \mu = \left(\frac{\partial A}{\partial N}\right)_{T, V} = -kT \left(\frac{\partial \ln Q}{\partial N}\right)_{T, V}$$

Calculating the partition function much simpler if can divide into non-interacting parts (e.g. independent molecules).

Total Energy,  $E_i = \epsilon_{i,1} + \epsilon_{i,2} + \dots + \epsilon_{i,N}$

Therefore,

$$e^{-E_i / kT} = e^{-\epsilon_{i,1} / kT} e^{-\epsilon_{i,2} / kT} \dots$$

$$\Rightarrow \sum_i e^{-E_i / kT} = \prod_{\alpha} \sum_i e^{-\epsilon_{i,\alpha} / kT} = \prod_{\alpha} q_{\alpha}$$

$\uparrow$  molecules       $\uparrow$  E-levels of molecule  $\alpha$

If molecules are identical and indistinguishable:

$$Q_N = q^N / N!$$

But  $Q_N = q^N$  if e.g. on lattice sites.

### Molecular Partition Function (Revision)

$$q = \sum_i g_i e^{-E_i / kT}$$

$$E_i = \epsilon_{i, tr} + \epsilon_{i, rot} + \epsilon_{i, vib} + \epsilon_{i, elec} \quad [\text{B-O Approx}]$$

$$\Rightarrow q = q_{tr} q_{rot} q_{vib} q_{elec} (q_{ns})$$

**Translation:**

$$q_{tr} = \left(\frac{2\pi kT}{h^2}\right)^{3/2} V = \frac{V}{\lambda^3}$$

$\uparrow$  de Broglie thermal wavelength

**Rotation:**

$$\text{Linear} \Rightarrow \epsilon_J = hcBJ(J+1)$$

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1) e^{-hcBJ(J+1)/kT}$$

$\uparrow$  can be nuclear spin restrictions

At high T: ( $kT > 2Bhc$ ) [ $\sim 15K$  for HCl where  $B \sim 10cm^{-1}$ ]  
 $q_{rot} = kT/\sigma Bhc$

where  $\sigma$  = symmetry number.

More generally for 3 moments of inertia (A,B,C):

$$q_{rot} = \frac{1}{\sigma} \left( \frac{kT}{hc} \right)^{3/2} \sqrt{\frac{\pi}{ABC}}$$

**Vibration:**

$$E_v = v h \sqrt{\frac{h}{\mu}} \quad (\text{wrt ZPE})$$

$$q_{vib} = \frac{1}{1 - e^{-h\nu/kT}}$$

At  $T \gg h\nu/k$ ,  $q_{vib} \rightarrow kT/h\nu$

**Electronic:**

$$q_{elec} = \sum_i g_i e^{-\epsilon_i/kT}$$

Important for degenerate Ground States ( $O_2$ ) or low-lying excited states (NO).

**2-Level Non-interacting System**

e.g. lattice of immobile molecules with low-lying electronic energy levels.

e.g. crystal of NO [ $\text{Ground State } ^2\Pi_{1/2}$  with low-lying  $^2\Pi_{3/2}$ ]

$$Q_N = q^N$$

Both are 2-fold degenerate,

$$q = 2 + 2e^{-\Delta\epsilon/kT}$$

$$g_0 \quad g_1$$

$$U = NkT^2 \frac{\partial \ln q}{\partial T} = \frac{N \Delta\epsilon g_1 e^{-\Delta\epsilon/kT}}{g_0 + g_1 e^{-\Delta\epsilon/kT}}$$

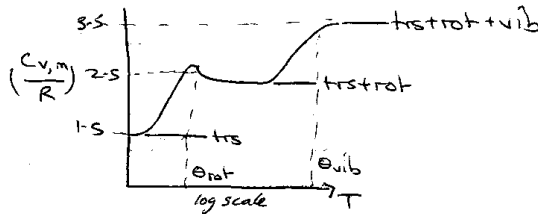
&  $S = Nk \ln q + U/T$

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v = \frac{N \left( \frac{\Delta\epsilon}{kT} \right)^2 g_0 g_1 e^{-\Delta\epsilon/kT}}{(g_0 + g_1 e^{-\Delta\epsilon/kT})^2}$$

(thermal spectroscopy)

**Heat Capacities of Gases**

Heat Capacity as a Function of T:



Little maximum present in  $C_{rot}$  due to isolation of the bottom two levels at low temperature. High T  
 → Ground → 1<sup>st</sup> → 2<sup>nd</sup> ...  
 (also degeneracies).

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v = \frac{\partial}{\partial T} \left[ kT^2 \frac{\partial \ln Q}{\partial T} \right]_v$$

$$Q_N = \frac{q^N}{N!} \quad (\text{Use Stirling's Approx}):$$

$$\ln q = \ln q_{tr} + \ln q_{rot} + \dots$$

$$\therefore C_v = C_v^{tr} + C_v^{rot} + C_v^{vib} + C_v^{elec}$$

$q_{tr}$ :

$$q_{tr} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V$$

Constant V ⇒

$$C_v^{tr} = Nk \frac{\partial}{\partial T} \ln T^{3/2} = \frac{3}{2} Nk = \frac{3}{2} R$$

$q_{rot}$ :

Diatom: high T ⇒  $\frac{kT}{\sigma Bhc} \Rightarrow C_v^{rot} = R$

Polyatomic:  $\frac{1}{\sigma} \left( \frac{kT}{hc} \right)^{3/2} \sqrt{\frac{\pi}{ABC}} \Rightarrow C_v^{rot} = \frac{3}{2} R$

Transition Regime →  $kT \sim Bhc$  -

Need full  $q_{rot}$ :

$$\sum_0 (2J+1) e^{-BhcJ(J+1)/kT}$$

$$\frac{\partial}{\partial T} \left[ kT^2 \frac{\partial}{\partial T} \ln q_{rot} \right]$$

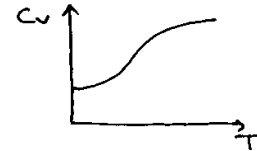
$$= \frac{\partial}{\partial T} \left[ \frac{kT^2 \frac{\partial}{\partial T} \left( \frac{Bhc}{kT^2} \right) \sum_0 (J(J+1)) (2J+1) e^{-BhcJ(J+1)/kT}}{\sum_0 (2J+1) e^{-BhcJ(J+1)/kT}} \right]$$

Let  $T^* = kT/Bhc$

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$$\frac{\partial}{\partial T^*} = k \left( \frac{Bhc}{k} \right) \frac{\partial}{\partial T} \left[ \frac{\sum_0 J(J+1)(2J+1) e^{-J(J+1)/T^*}}{\sum_0 (2J+1) e^{-J(J+1)/T^*}} \right] = k f(T^*)$$

Universal Function



i.e.  $C_v^{rot}$  for different diatomic systems is identical if plotted versus  $T^*$ , the reduced temperature.

**Nuclear Spin Effects (identical nuclei)**

$$\Psi = \Psi_{rot} \Psi_{vib} \Psi_{elec} \Psi_{ns} \quad \text{ⓐ or ⓑ w/rt exchange}$$

bosons                      fermions

$^{16}O_2$ :  $I = 0$  (boson) ⇒  $\Psi = \text{ⓐ}$

$\Psi_{ns} = 1$ ,  $\Psi_{elec} (3\Sigma_g^-) = \text{ⓐ}$

Implies only odd J allowed, i.e. half the states are missing, consistent with:

$$q_{rot}^{homo} = q_{rot}^{hetero} / 2$$

$H_2$ :

$I = 1/2$  (fermion) ⇒  $\Psi = \text{ⓑ}$

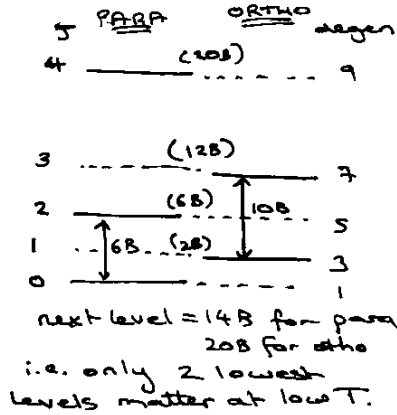
$\Psi_{ns}$  → spin 1, 3-fold degen. ⓐ

          → spin 0, 1-fold degen. ⓑ

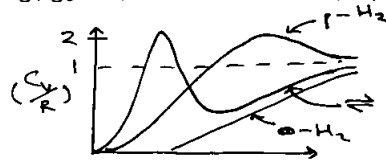
In absence of a catalyst,  $H_2$  is a mixture of spin 1 (o) - J odd, spin 0 (p) - J even.

3 times as much (o) as (p).

Can interpret the behaviour from the two-level system results:



Para:  $g_1/g_0 = 5$ , at  $kT \sim 0.3 \times 6Bhc$ ,  $C_v^{\max} \sim 1.5R$ .  
 Ortho:  $g_1/g_0 = 7/3$ , at  $kT \sim 0.35 \times 10Bhc$ ,  $C_v^{\max} \sim 0.8R$ .  
 Equilibrium,  $g_0 = 1$ ,  $g_1 = 3 \times 3$ , so  $g_1/g_0 = 9$ ,  $kT \sim 0.25 \times 2Bhc$ ,  $C_v^{\max} = 2R$ .



q<sub>vib</sub>:

$$q_{vib} = \frac{1}{1 - e^{-h\nu/kT}} \quad \text{per normal mode of vibration}$$

Since E-levels equally spaced, can't use 2-level system results.  
 At high T,  $q^{vib} \rightarrow kT/h\nu$ , i.e.  $C_v \rightarrow R \times \text{no. of normal modes}$ .

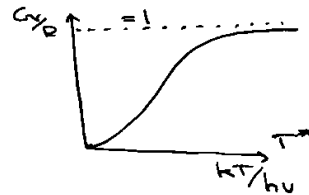
$$C_v = \frac{\partial}{\partial T} NkT^2 \frac{\partial \ln q}{\partial T}$$

$$= Nk \frac{\partial}{\partial T} \left[ \frac{T^2 (h\nu/kT)^2 e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^{-1}} \right]$$

let  $T^* = h\nu/kT$

$$C_v = Nk \frac{\partial}{\partial T^*} f(T^*) \quad \text{Universal Function of } T^*$$

Can thus measure vibration spectrum from the heat capacity.  
 The form of the Universal Function is:



EXAMPLES:

$C_v$  for  $O_2$  @ 1000K is 3.197R  
 - estimate vib<sup>n</sup> frequency.  
 $kT > Bhc \therefore C_v^{rot} + C_v^{tr} = 2.5R$   
 $\Rightarrow C_v^{vib} = 0.697R$ .  
 From graph,  $T^* = 0.48$ ,  
 $\therefore 0.48 h\nu = 1000K$   
 $\Rightarrow \nu = \frac{1.38 \times 10^{-23} \times 10^3}{6.626 \times 10^{-34}}$   
 $\approx 1550 \text{ cm}^{-1}$

### Absolute Gas-Phase Entropies

Thermodynamics:

$$S_m^\circ(T) - S_m^\circ(0) = \int_0^T \frac{C_p}{T} dT + \sum_{\text{phase transitions}} \frac{\Delta H_{tr}^\circ}{T_{tr}}$$

Calorimetric Entropy.

Area under Graph of  $C_p$  vs.  $T$ .

Statistical Mechanics:

$$S_m^\circ = k \ln Q_N + kT \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

with  $N = N_A$  &  $V = V^\circ$   
 $\Rightarrow$  do calculation at single  $T$ .  
 Spectroscopic Entropy

Difference in the calorimetric and spectroscopic entropies:  $S_{\text{resid}} = S_{\text{spec}} - S_{\text{cal}}$ .  
 $S_{\text{resid}} \neq 0 \Rightarrow$  complications!

- Undetected low temperature phase transition.
- Use of wrong low-T degeneracy.
- Disorder in the crystal at low  $T$ , such that  $S_0 > 0$ .

Gas:

$$Q_N = \frac{q^N}{N!}, \quad \ln \frac{q^N}{N!} = N \ln q - \ln N!$$

Use Stirling's Approximation:  
 $\ln N! = N \ln N - N$   
 $\therefore \ln Q_N = N \ln \left( \frac{q}{N} \right) + N$   
 $\therefore S_m^\circ = R \ln \left( \frac{q}{N_A} \right) + R + RT \left( \frac{\partial \ln q}{\partial T} \right)_V$   
 $\rightarrow$  trans, rot, vib, etc give additive contributions.

Monatomic Gas:

$$q_{tr} = \frac{V}{\Lambda^3}, \quad \Lambda = \frac{h}{\sqrt{2\pi m kT}}$$

$$\therefore S_m^\circ = R \ln \frac{V}{N_A \Lambda^3} + R + R \left( \frac{3}{2T} \right)$$

$$\text{or } S_m^\circ = R \ln \frac{e^{5/2} V}{N_A \Lambda^3} \quad \left[ \text{Sackur-Tetrode Equation} \right]$$

NOTE: Substances only distinguished by mass (at same  $T$ ), and  $S_m^\circ = \text{constant} + R \ln m^{3/2}$ .

Rotational Entropy –

Linear diatomic –  $kT > Bhc$ .

$$q_{\text{rot}} = \frac{kT}{\sigma Bhc}$$

$$S_{\text{rot}} = R \ln q_{\text{rot}} + RT \frac{\partial \ln q_{\text{rot}}}{\partial T}$$

$$= R \ln \left( \frac{kT}{\sigma Bhc} \right) + R$$

NOTE: The role of symmetry number ( $\text{CO} = 2$  while  $\text{N}_2\text{O} = 2$  despite similar  $m$  &  $I$ ).

Vibrational Entropy –

$$q_{\text{vib}} = \frac{1}{1 - e^{-hv/kT}} \quad \text{per mode of vibration}$$

If  $kT \ll hv$ ,  $q_{\text{vib}} \rightarrow 1$  and  $S_{\text{vib}} = 0$ .

Generally,

$$S_{\text{vib}} = R \ln(1 - e^{-hv/kT}) + \frac{R hv}{kT} \left( \frac{1 - e^{-hv/kT}}{1 - e^{-hv/kT}} \right)$$

Electronic Entropy -

$$q_{elec} = \sum_i g_i e^{-\epsilon_i / kT}$$

Only important for degenerate g-states, e.g. O<sub>2</sub> - g<sub>0</sub> = 3, or low-lying states, e.g. NO.

**Verification of the 3<sup>rd</sup> Law -**

Compare Calorimetric (assuming S<sub>m</sub><sup>o</sup>(0) = 0) and spectroscopic entropies.

e.g. H<sup>35</sup>Cl (1Σ<sup>+</sup>)  
 B = 10.6 cm<sup>-1</sup>  
 M = 36 g mol<sup>-1</sup>  
 ν = 2885 cm<sup>-1</sup>

@ 298K:  
 λ = 16.9 × 10<sup>-12</sup> m  
 V<sub>N<sub>A</sub></sub> = 4.11 × 10<sup>-26</sup> m<sup>3</sup>  
 q<sub>rot</sub> = 19.5  
 q<sub>vib</sub> = 1.

Statistical:

$$S_m^o = 153.4 + 33.0 = 186.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

(tr)      (rot)

Thermodynamic:

$$S_m^o - S_m(0) = 186.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

∴ S<sub>m</sub>(0) = 0.

But for N<sub>2</sub>O:

$$S_m^o(\text{stat}) = 220 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_m^o(\text{cal}) = 215.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Rightarrow S_m(0) = 4.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

If random orientations → R ln 2 (= 5.8 J K<sup>-1</sup> mol<sup>-1</sup>)

Transition to fully ordered state occurs at such low temperature (due to very small ΔH from ordering) that kinetics so slow that transition is not seen.

**Chemical Equilibrium**

$$K_p = e^{-\Delta G/RT}$$

i.e. the different of molar Gibbs Energies at T of interest where p = p<sup>o</sup>.

Link to statistical mechanics:

$$G = A + pV.$$

$$G_m = A + RT \text{ (non-interacting).}$$

$$G_m = -kT \ln (q^N/N!) + RT$$

Using Stirling's Approximation:

$$-kT [N \ln q - N \ln N + N] + RT$$

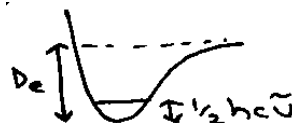
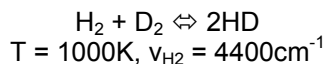
$$G_m^o = -RT \ln \frac{q^N}{N!} \text{ wrt zero of } E \text{ of system}$$

q<sub>tr</sub> calculated at V<sup>o</sup> = RT/p<sup>o</sup>.

$$K_p = \left[ \frac{(q_C^o/N)^{\nu_C}}{(q_A^o/N)^{\nu_A} (q_B^o/N)^{\nu_B}} \right] e^{-\Delta E_o/RT}$$

↳ from ΔG<sup>o</sup> = ν<sub>C</sub>G<sub>C,m}^o - ν<sub>A</sub>G<sub>A,m}^o - ν<sub>B</sub>G<sub>B,m}^o  
& ν<sub>A</sub>A + ν<sub>B</sub>B ⇌ ν<sub>C</sub>C.</sub></sub></sub>

Illustration – isotope exchange reaction –



Establish common energy zero by atomising reactants and products.

$$\begin{aligned} & \text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD} \quad (D_e \text{ same for all species}) \\ & \begin{array}{ccc} \begin{array}{l} 2D_e - \\ 2PE_{\text{H}_2} - \\ -2PE_{\text{D}_2} \end{array} & \downarrow & \begin{array}{l} 2D_e - \\ 2PE_{\text{HD}} \end{array} \\ & 2\text{H} + 2\text{D} & & \end{array} \\ \therefore \Delta E_0 &= 2(D_e - \frac{1}{2} h \nu_{\text{HD}}) - (D_e - \frac{1}{2} h \nu_{\text{H}_2}) - (D_e - \frac{1}{2} h \nu_{\text{D}_2}) \\ &= h c (\nu_{\text{HD}} - \frac{1}{2} \nu_{\text{H}_2} - \frac{1}{2} \nu_{\text{D}_2}) \\ \& \nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \leftarrow \text{same for all species} \quad \& \begin{array}{l} \mu_{\text{H}_2} = \frac{1}{2} m_{\text{H}} \\ \mu_{\text{D}_2} = m_{\text{H}} \\ \mu_{\text{HD}} = \frac{2}{3} m_{\text{H}} \end{array} \\ \Delta E_0 &= h c \nu_{\text{H}_2} \left( \sqrt{\frac{3}{4}} - \frac{1}{2} - \frac{1}{2} \sqrt{\frac{1}{2}} \right) \\ &= 54.5 \text{ cm}^{-1} \equiv 0.652 \text{ kJ mol}^{-1} \end{aligned}$$

Ratio of Partition Functions –

$q_{\text{el}} = 1$  for all.

$$\left[ \frac{(q_{\text{tr}}/N)_{\text{HD}}^2}{(q_{\text{tr}}/N)_{\text{H}_2} (q_{\text{tr}}/N)_{\text{D}_2}} \right] \left[ \frac{(q_{\text{rot}})_{\text{HD}}^2}{(q_{\text{rot}})_{\text{H}_2} (q_{\text{rot}})_{\text{D}_2}} \right] \left[ \frac{(q_{\text{vib}})_{\text{HD}}^2}{(q_{\text{vib}})_{\text{H}_2} (q_{\text{vib}})_{\text{D}_2}} \right]$$

Often high degree of cancellation when moles on left hand side of reaction equation equal the moles on the right hand side.

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

All factors cancel from this except masses.

$$\left[ \frac{(m_{\text{H}} + m_{\text{D}})^2}{(2m_{\text{H}} \times 2m_{\text{D}})} \right]^{3/2}$$

$$q_{\text{rot}} = \frac{8\pi^2 I k T}{\sigma h^2}, \quad I = \mu r^2 \quad \leftarrow \text{same for all}$$

All cancel except  $\mu$  and  $\sigma$

$$\frac{1 \left( \frac{m_{\text{H}} m_{\text{D}}}{m_{\text{H}} + m_{\text{D}}} \right)^2}{\left( \frac{1}{2} \cdot \frac{m_{\text{H}}}{2} \cdot \frac{1}{2} \cdot \frac{m_{\text{D}}}{2} \right)}$$

$$q_{\text{vib}} = \frac{1}{1 - e^{-h\nu c/kT}} = 1$$

(as  $\frac{h\nu c}{kT} \gg 1$ )

Total gives:

$$4 \left( \frac{m_{\text{H}} + m_{\text{D}}}{2m_{\text{H}} m_{\text{D}}} \right)^{1/2} = 6$$

$$\therefore K_p = 6 e^{-0.652/8.314}$$

$$= 5.5$$

(consequence of higher entropy of 2HD)

Illustration 2 – Thermal Ionisation

$$\begin{aligned}
 \text{Cs } ({}^2S_{1/2}) &\rightleftharpoons \text{Cs}^+ + e^- \quad T = 2000 \text{ K} \\
 q_{el} &= 2 \qquad \qquad \qquad q_{el} = 2 \\
 \text{I.P.} &= 3.89 \text{ eV} = 275.3 \text{ kJ mol}^{-1} \\
 K_P &= \left[ \frac{(q_{el}/N)_{\text{Cs}^+} (q_{el}/N)_e}{(q_{el}/N)_{\text{Cs}}} \right] e^{-\Delta E/RT} \\
 &\quad \uparrow \text{(same masses)} \\
 K_P &= \left( \frac{q_{el}}{N} \right)_e e^{-\text{I.P.}/RT} \quad 22.57 \\
 \frac{q_{el}}{N} &= \frac{RT}{N_p \theta} = \frac{2000}{N_A \theta} = 2.75 \times 10^{-25} \\
 \lambda_e &= \left( \frac{h^2}{2\pi m k T} \right)^{1/2} = 1.62 \text{ nm} \\
 \therefore K_P &= \frac{2.75 \times 10^{-25}}{(1.62 \times 10^{-9})^3} e^{-22.57} = 9.36 \times 10^{-9} \\
 &\quad \text{(ignoring e-e repulsions - major factor)}
 \end{aligned}$$

Fraction of ionised Cs atoms at  $p/p^0 = 10^{-4}$ .

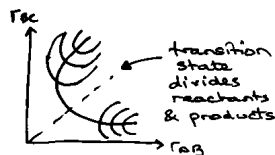
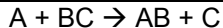
$$\begin{aligned}
 \text{Cs} &\rightleftharpoons \text{Cs}^+ + e^- \\
 \frac{p}{p^0} \left( \frac{1-\alpha}{1+\alpha} \right) &= \frac{p}{p^0} \left( \frac{\alpha}{1+\alpha} \right) \left| \frac{p}{p^0} \left( \frac{\alpha}{1+\alpha} \right) \right. \\
 \therefore K_P &= \left( \frac{\alpha^2}{1-\alpha^2} \right) \frac{p}{p^0} = 9.36 \times 10^{-9} \\
 \alpha &\ll 1 \\
 \alpha &= \sqrt{K_P / (p/p^0)} = 9.7 \times 10^{-3}
 \end{aligned}$$

Statistical Mechanics expression for  $K_C$ :

$$\begin{aligned}
 U_A + U_B &\rightleftharpoons U_C \\
 K_C &= \frac{(N_C/V)^{U_C}}{(N_A/V)^{U_A} (N_B/V)^{U_B}} = \left( \frac{N_A}{V} \right) K_P = \left( \frac{q_C^0/N^0}{} \right)^{U_C} e^{-\Delta E_0/RT} \\
 &\quad \left( \frac{q_A^0/V^0}{} \right)^{U_A} \left( \frac{q_B^0/V^0}{} \right)^{U_B} \\
 &\quad \text{where N's are \#}
 \end{aligned}$$

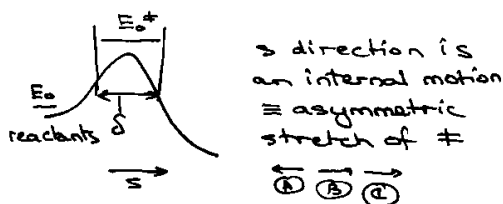
(Avogadro's Constant here)

**Transition State Theory**



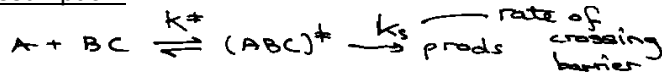
(must approach from the right orientation).

Profile:



direction is an internal motion  $\equiv$  asymmetric stretch of  $\ddagger$

Quasi-Equilibrium Assumption:



$K_C$  because equilibrium in concentration.

$$\begin{aligned}
 \frac{d[P]}{dt} &= k_s [ABC]^\ddagger = k_s K_C^\ddagger [A][BC] \\
 &= k [A][BC]
 \end{aligned}$$

$k_s$  = rate of passing through transition state = a velocity.

Alternatively, can think of vibrational motion along  $s$ .

Asymmetric stretching frequency  $\nu$  – assume transition state breaks up each time bond is stretched, i.e.  $k_s = \nu$ .

$K_C^\ddagger$  includes vibrational and rotational partition functions of  $\ddagger$ , but factor  $q_{vib}$  for asymmetric stretch. Therefore,



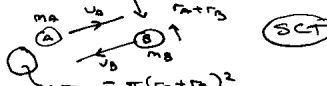
$$k = v \left( \frac{1}{1 - e^{-h\nu/kT}} \right) \overline{K_c^\ddagger}$$

Since  $v$  very low (weak bond)  $\rightarrow kT/h\nu$ . Therefore,

$$\therefore k = \frac{kT}{h} \left( \frac{q_{wv}}{V} \right)^{\ddagger} e^{-\Delta E^\ddagger/RT}$$

$\downarrow$   
 overall  
 rate  
 constant

Check that Transition State Theory gives same rate constant as Simple Collision Theory when applied to collision of structureless spheres:



area =  $\pi(r_A + r_B)^2$

rate of collision:

$$k = \left( \frac{8kT}{\pi\mu} \right)^{1/2} \pi(r_A + r_B)^2 \left( \frac{z_{AB}}{V} \right)$$

vs. TST

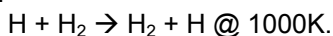
$$k = \frac{kT}{h} \left( \frac{q_{rot}^\ddagger}{V} \right) \left( \frac{q_{vib}^\ddagger}{V} \right) \left( \frac{q_{el}^\ddagger}{V} \right)$$

$$= \frac{kT}{h} \frac{((m_A + m_B)^{3/2} (8\pi^2 (\mu(r_A + r_B)^2) kT) / h^2)}{(m_A)^{3/2} (2\pi m_B kT)^{3/2} / h^2}$$

$$= \left( \frac{8kT}{\pi\mu} \right)^{1/2} \pi(r_A + r_B)^2$$

[ i.e. the same ]

Transition State Rate Constant for:



$$\begin{aligned} \nu_{H_2} &= 4400 \text{ cm}^{-1} \\ \nu_1^\ddagger &= 1943 \text{ (3 str)} \\ \nu_2^\ddagger &= 950 \text{ (2-fold degen bend)} \\ r_{AB}^\ddagger &= r_{BC}^\ddagger = 0.94 \text{ \AA} \\ r_{H_2} &= 0.74 \text{ \AA} \end{aligned}$$

Linear T.State -  $E^\ddagger = 1.02 \times 10^{-19} \text{ J}$

ZPE change:

$$\frac{hc}{\lambda} (1943 + 2 \times 950 - 4400)$$

$$= -0.05 \times 10^{-19} \text{ J}$$

$$\therefore \Delta E^\ddagger = 1.02 \times 10^{-19} \text{ J}$$

$$\frac{h\nu_1^\ddagger}{kT} \gg 1$$

$$\frac{kT}{h} \left( \frac{q_{rot}^\ddagger}{V} \right) \left( \frac{q_{vib}^\ddagger}{V} \right) \left( \frac{q_{el}^\ddagger}{V} \right) e^{-\Delta E^\ddagger/kT}$$

(bend)

$$= \frac{(3m_H)^{3/2}}{\left( \frac{2\pi m_H kT}{h^2} \right)^{3/2} (2m_H)^{3/2}} = \frac{(3/2)^{3/2} m_H}{5.9 \times 10^{30}}$$

$$\frac{q_{rot}^\ddagger}{q_{rot,H_2}} = \frac{m_H (r_{AB}^\ddagger)^2 + (r_{BC}^\ddagger)^2 \cdot 2}{m_{H_2} r_{H_2}^2 \cdot 2} = 6.4$$

degeneracy

$$q_{vib,bend}^\ddagger = (1 - e^{-h\nu_2^\ddagger/kT})^{-2} = 1.9$$

$$\frac{kT}{h} = 2.1 \times 10^{13} \text{ s}^{-1}$$

$$\therefore k = 5.0 \times 10^{-20} \text{ m}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$= 3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Experimental of  $\sim 10^9$  at these temperatures (accuracy in barrier height).

### Interacting Systems

So far, have written  $Q_N = q^N$ .

But for e.g. atomic solid cannot write  $E = \sum_{i, \text{atoms}} \epsilon_i$

Implies must effect a transformation to new variables which do not interact.  
e.g. thermal properties of an insulating crystal.

Crystal is harmonic, i.e. for small displacements  $E$  is proportional to  $(\delta r_i)^2$ .  
Transform from atomic to normal coordinates (normal modes) – phonons.

Each modes has a frequency  $\nu_i$  and is independent of degree of excitation of other modes,

$$E = \sum_{i, \text{modes}} n_i h \nu_i$$

$$Q_N^{\text{crystal}} = \prod_{i=1}^{3N-6} [1 - e^{-h\nu_i/kT}]^{-2}$$

Since  $N \sim N_A$ , spectrum is dense and continuous. Let  $P(\nu)$  be probability of finding mode

frequency  $\nu$   $[\int_0^{\infty} d\nu P(\nu) = 1]$

$$\ln Q_N = - \prod_{i=1}^{3N-6} \ln [1 - e^{-h\nu_i/kT}]$$

$$= -3N \int_0^{\infty} d\nu P(\nu) \ln (1 - e^{-h\nu/kT})$$

(ignoring the -6)

### Internal Energy (wrt ZPE) –

$$U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V = kT^2 3N \int_0^{\infty} d\nu P(\nu) \frac{\frac{h\nu}{kT} e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}$$

$$= 3Nh \int_0^{\infty} d\nu (P_\nu) \frac{\nu}{(e^{h\nu/kT} - 1)}$$

### Heat Capacity –

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 3Nh \int_0^{\infty} d\nu P(\nu) \frac{(-h\nu/kT) e^{-h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

$$= 3Nk \int_0^{\infty} d\nu \left( \frac{h\nu}{kT} \right)^2 \frac{e^{-h\nu/kT}}{(e^{h\nu/kT} - 1)^2} P(\nu)$$

If  $T \rightarrow \infty$ ,  $C_V \rightarrow 3Nk$  [Dulong & Petit's Law]

But  $C_V$  only 5.4J  $K^{-1}$  for diamond at 298K (one of "failures of classical physics").

### Einstein's Theory of Heat Capacity

$$P(\nu) = \delta(\nu - \nu_E)$$

$$C_V = 3Nk \left( \frac{\theta_E}{T} \right)^2 \frac{e^{-\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad \theta_E = \frac{h\nu_E}{k}$$

Universal Function of  $T/\theta_E$ .

Data appears to be Universal but functional form is not correct. Einstein  $\rightarrow$  exponential at low T.

### Debye Model

Improved the model of vibrational spectrum. Normal modes characterised by the wavelength  $\lambda$ .

$$\delta_i = \cos \frac{2\pi}{\lambda} x_i = \cos kx_i$$

- i) For small  $k$  (large  $\lambda$ ) behaves like a continuum ( $v = c/\lambda = ck/2\pi$ ).
- ii) Cut-off wavevector,  $k = \pi/a$  ( $\lambda = 2a$ ) – zone boundary.
- iii)  $P(\nu)$ ? Consider chain, length  $L$

$$C_V \propto 3Nk \int_0^{\pi/a} \left( \frac{h\nu}{kT} \right)^2 v^2 \frac{e^{-h\nu/kT}}{(e^{h\nu/kT} - 1)^2} dx$$

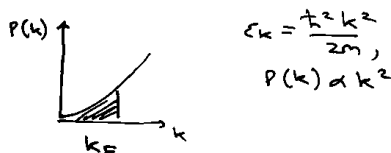
$h\nu = \hbar ck$   
 $\therefore dx = \frac{1}{\hbar c} d\nu$

$$\therefore C_V \propto T^3 \int_0^{\pi/a} dx \propto \int_0^{\infty} \frac{e^{-x}}{(e^x - 1)^2} dx$$

So for low T,  $C_v \propto T^3$ .  
 [ Integrand  $\rightarrow 0$  for  $x \ll x_{\max} \rightarrow$  integral is T-dependent ]

**Heat Capacity of Metals**

$C_v$  for metals looks Debye-like. What about free electrons?  
 Free Electron Model – e-e interactions screen e-ion interaction. Electrons move independently in a smeared out 3D particle-in-a-box like-potential.



Energy Levels are filled according to the Aufbau Principle.  
 At T = 0, highest occupied level is:

$$\epsilon_F = \frac{\hbar^2}{2m} \left( \frac{3N}{\pi V} \right)^{2/3}$$

(Fermi Energy)  
 &  $U(T=0) = \frac{3}{5} N \epsilon_F$

NB: Huge contribution to pressure balanced by electron-ion interaction.  
 Only a few electrons near to  $\epsilon_F$  can be excited thermally. Distribution described by Fermi-Dirac (not Boltzmann).

$$C_v = \frac{\pi^2}{2} N k \left( \frac{kT}{\epsilon_F} \right)$$

Therefore negligible except for very low T (all other contributions  $\rightarrow 0$ ).

**Absorption of Gas in a Porous Material**

Example of Phase Equilibrium.



Consider N immobile atoms absorbed in M sites.  
 With no 2 atoms in a single site – allows for interatomic repulsion.  
 Number of configurations =  $M(M-1) \dots (M-N-1) = M!/(M-N)!$   
 But it atoms indistinguishable =  $M!/(M-N)!N!$   
 Therefore neglect atom motion:

$$S_{\text{conf}} = k \ln [M!/(M-N)!N!]$$

Each pore is of side d. Absorption energy  $\epsilon_0$ . Model motion of absorbed atom as translation in volume  $V = d^3$ .

Partition Function =  $d^3/\Lambda^3 = q$ .

Provided box is big enough that quantum effects not important,

$$\Delta\epsilon \sim h^2/8md^2.$$

Therefore the Helmholtz Free Energy:

$$A_{\text{ad}} = N\epsilon_0 - kT \ln q^N - T S_{\text{conf}}$$

$$= N\epsilon_0 - 3NkT \ln \frac{d}{\Lambda} - kT \ln \frac{M!}{N!(M-N)!}$$

Absorbed atoms in equilibrium with gas at pressure p when  $\mu_{\text{abs}} = \mu_{\text{gas}}$ .

$$\mu = \left( \frac{\partial A_{\text{ad}}}{\partial N} \right)_{T,V}$$

$$\mu_{\text{abs}} = \epsilon_0 - 3kT \ln \frac{d}{\Lambda} + kT \ln \frac{N}{M-N}$$

For  $N_g$  gas-phase molecules,

$$A_{N_g} = -kT \ln \left( \frac{V}{\Lambda^3} \right)^{N_g} \frac{1}{N_g!}$$

$$\Rightarrow -N_g kT \ln \left( \frac{V}{\Lambda^3} \right) + kT [N_g \ln N_g - N_g]$$

$$\therefore \mu_g = \left( \frac{\partial A_{N_g}}{\partial N_g} \right)_{T,V} = -kT \ln \left( \frac{V}{\Lambda^3} \right)$$

Also,  $pV = N_g kT$ .

$$\begin{aligned} \therefore \mu_g &= -kT \ln \left( \frac{kT}{\Lambda^3} \right) + kT \ln p \\ \therefore \mu_{g,ads} &= \mu_{abs} \Rightarrow \\ \epsilon_0 - kT \ln \left( \frac{kT}{\Lambda^3} \right) + kT \ln \frac{N}{M-N} &= -kT \ln \frac{kT}{\Lambda^3 p} \\ \text{Degree of filling of pores} &\equiv \theta = N/M \\ \epsilon_0 - kT \ln \left[ \left( \frac{kT}{\Lambda^3} \right)^3 \left( \frac{1-\theta}{\theta} \right) \right] &= -kT \ln \left( \frac{kT}{\Lambda^3 p} \right) \\ \text{i.e. } \ln \left[ \frac{kT}{p \Lambda^3} \frac{\theta}{1-\theta} \right] &= -\epsilon_0/kT \\ \therefore \frac{\theta}{1-\theta} &= p \frac{d^3 e^{-\epsilon_0/kT}}{kT} \quad b \\ \Rightarrow \theta &= \frac{bp}{1+bp} \quad \text{LANGMUIR ISOTHERM} \end{aligned}$$

Provides a microscopic interpretation for the empirical parameter b.

**Classical Interacting Systems (fluid)**

For most liquids, can treat system classically, e.g. for Ar at 84K (triple point):

$$\Lambda = \left( \frac{2\pi m kT}{h^2} \right)^{-1/2} \sim 0.03 \text{ nm}$$

i.e. thermal de Broglie wavelength  $\ll$  interatomic separation, therefore classical.

How do we get a classical partition function? Expressed in terms of particle positions and momenta. A point in "phase-space" is specified by all molecular positions and momenta.

$$R, P = [r_1, r_2, \dots, r_N; p_1, p_2, \dots, p_N]$$

Expect,

$$\sum_{\text{quantum states}} \rightarrow \int \dots \int dr_1 \dots dr_N dp_1 \dots dp_N$$

Energy at R, P = H(R,P) and probability of being at R, P:

$$Q_N \propto \int \dots \int dr_1 \dots dr_N dp_1 \dots dp_N e^{-[\sum_i p_i^2/2m + V]/kT}$$

What is constant -

- i) Need 1/N! (indistinguishability)
- ii)  $\Delta x_i \Delta p_i \geq h$  (HU<sup>3</sup>P)

i.e. each point in phase-space only distinguishable from another if  $dr dp > h$ . Therefore overall need  $1/h^{3N}$  factor.

Check, do we get same value as classical limit of quantum partition function. e.g. ideal gas (quantum):

$$Q_N = \left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} V \right]^N / N!$$

Classically  $V \rightarrow 0$ :

$$\begin{aligned} &\rightarrow \frac{1}{h^{3N} N!} \int dp_1 \dots dp_N e^{-[\sum_i p_i^2/2m kT]} \int \underbrace{dr_1 \dots dr_N}_{V^N} e^0 \\ &= \frac{V^N}{h^{3N} N!} \int dp_1 e^{-p_1^2/2m kT} \int dp_2 e^{-p_2^2/2m kT} \int dp_3 \dots \int dp_N \\ &= \frac{V^N}{h^{3N} N!} \left[ \int dp_i e^{-p_i^2/2m kT} \right]^N \end{aligned}$$

Integral is:

$$\begin{aligned} &\int dp_x e^{-p_x^2/2m kT} \int dp_y e^{-p_y^2/2m kT} \int dp_z e^{-p_z^2/2m kT} \\ &\left[ \int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} \right] \\ &\rightarrow \frac{1}{N!} \left[ \left( \frac{2\pi m kT}{h^2} \right)^{3/2} V \right]^N \end{aligned}$$

Generally,

$$Q_N = \frac{(V/\lambda^3)^N}{N!} Z_N$$

$$Z_N = V^{-N} \int dr_1 \dots dr_N e^{-V/kT}$$

**Application: Low Density Interacting Gas (Virial)**

Suppose atoms of a gas interact via a pair potential:

$$V(r_1 \dots r_N) = \sum_{\substack{i,j \\ i < j}} u(r_{ij}) = \sum_{i,j} u_{ij}$$

$$e^{-V/kT} = \prod_{i,j} e^{-u_{ij}/kT} \quad [\text{let } f_{ij} = e^{-u_{ij}/kT} - 1]$$

$$\therefore e^{-V/kT} = \prod_{i,j} (1 + f_{ij})$$

$$\iint dr_1 \dots dr_N e^{-V/kT} = V^N \left( 1 + \frac{N^2}{V} B + \frac{N^3}{V^2} C \dots \right)$$

where  $B = 2\pi \int dr r^2 (e^{-u/kT} - 1)$

Consider,

$$A = -kT \ln Q_N = -kT \ln Q_N - kT \ln Z_N$$

$$\ln Z_N = \ln \left( 1 + \frac{N^2}{V} B + \frac{N^3}{V^2} C \dots \right)$$

Low densities:  $\ln Z_N = \ln \left( 1 + \frac{N^2}{V} B \right)$

[N.B:  $\ln(1+x) = x + \frac{x^2}{2} + \dots$ ]

$$\ln Z_N = \frac{N^2}{V} B + \text{other terms}$$

$$\text{pressure } p = - \left( \frac{\partial A}{\partial V} \right)_{T,N}$$

$$= \frac{NkT}{V} - kT \frac{N^2}{V^2} B + \Theta(p^3)$$

$$\therefore p = \frac{NkT}{V} [1 + pB + \Theta(p^2)]$$

i.e. Virial Expansion, B is the Virial Coefficient.