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5.62 Physical Chemistry II
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5.62 Lecture #11: INTERNAL DEGREES OF FREEDOM FOR ATOMS AND DIATOMIC MOLECULES

Readings: Hill, pp. 147-159;
Maczek pp. 42-53

Pages 11-1, 11-2 and 11-3 are a review of Lecture #10.

ATOMS — have one internal degree of freedom
ELECTRONIC degree of freedom

MOLECULES — have other degrees of freedom

ELECTRONIC, VIBRATION, AND ROTATION which each contribute to total energy and to other macroscopic properties.

Nuclear hyperfine? [Nuclear spin degeneracy factors. LATER.]

Internal energy adds to translational energy to get total energy

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{int}}$$

quantum #'s
internal quantum #'s
N,M,L

where ϵ_{int} = energy from internal degrees of freedom

$$q = \sum_i e^{-\epsilon_i/kT} = \sum_{\epsilon} g(\epsilon) e^{-(\epsilon_{\text{trans}} + \epsilon_{\text{int}})/kT}$$

all molecular
all molecular
states
energies

We do not have to start from the beginning. q_{trans} and q_{int} appear as separate multiplicative factors.

$$q = \sum_{\text{translational states}} e^{-\epsilon_{\text{trans}}/kT} \sum_{\text{internal states}} e^{-\epsilon_{\text{int}}/kT}$$

$$q = q_{\text{trans}} \cdot q_{\text{int}} \quad \leftarrow \quad \text{INTERNAL MOLECULAR PARTITION FUNCTION}$$

$$Q = \frac{(q_{\text{trans}} q_{\text{int}})^N}{N!} = \left(\frac{q_{\text{trans}}}{N!} \right) q_{\text{int}}^N$$

NOTE: $N!$ is included with q_{trans} . This is because it's the translational motion that causes the positions of identical particles to be interchanged (thus rendering them indistinguishable), requiring the factor of $N!$. The internal motions do not interchange particles.

$Q = Q_{\text{trans}} Q_{\text{int}}$	CANONICAL PARTITION FUNCTION
$Q_{\text{trans}} = \frac{q_{\text{trans}}^N}{N!}$	CANONICAL TRANSLATIONAL PARTITION FUNCTION
$Q_{\text{int}} = q_{\text{int}}^N$	CANONICAL INTERNAL PARTITION FUNCTION

Classically

$Q_{\text{cl}} = Q_{\text{trans,cl}} Q_{\text{int,cl}}$
$Q_{\text{trans,cl}} = \frac{q_{\text{trans,cl}}^N}{N!} = \frac{[\int e^{-\epsilon_{\text{trans}}/kT} d\mathbf{p}^3 d\mathbf{q}^3]^N}{N! h^{3N}}$
$Q_{\text{int,cl}} = q_{\text{int}}^N = \int dp^{3N} dq^{3N} e^{-\epsilon_{\text{int}}/kT}$

CONTRIBUTION OF INTERNAL DEGREES OF FREEDOM TO MACROSCOPIC PROPERTIES

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = kT^2 \left(\frac{\partial \ln Q_{\text{trans}} Q_{\text{int}}}{\partial T} \right)_{N,V}$$

$$E = kT^2 \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_{N,V} + kT^2 \left(\frac{\partial \ln Q_{\text{int}}}{\partial T} \right)_{N,V}$$

$$E = E_{\text{trans}} + E_{\text{int}}$$

$$\begin{aligned}
 A &= -kT \ln Q = -kT \ln Q_{\text{trans}} Q_{\text{int}} \\
 &= -kT \ln Q_{\text{trans}} + -kT \ln Q_{\text{int}} \\
 &= A_{\text{trans}} + A_{\text{int}}
 \end{aligned}$$

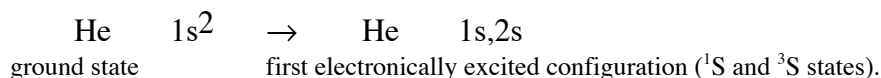
Likewise: $S = S_{\text{trans}} + S_{\text{int}}$

because $A = \bar{E} - TS$
 $S = \bar{E}/T - A/T = \bar{E}/T - kT \ln Q/T$

But: $p = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} = p_{\text{trans}} + p_{\text{int}} = p_{\text{trans}}$ no V dependence
for internal coordinates

INTERNAL DEGREE OF FREEDOM OF AN ATOM

Electronic Excitation: promotion of an electron to a higher energy orbital.



Goal: Derive electronic molecular partition function

$$q_{\text{elec}} = \sum_i e^{-\varepsilon_i/kT} = \sum_{\varepsilon_j} g(\varepsilon_j) e^{-\varepsilon_j/kT}$$

electronic states allowed energies

$\varepsilon_j \equiv$ energy of j^{th} electronic energy level

$g(\varepsilon_j) \equiv$ degeneracy — number of isolated-atom states with electronic energy ε_j

Electronic energies and degeneracies are determined by atomic spectroscopy experiments. Tabulated in tables such as NBS circular #467 by Charlotte Moore.

$q_{\text{elec}} = g(\varepsilon_0) e^{-\varepsilon_0/kT} + g(\varepsilon_1) e^{-\varepsilon_1/kT} + g(\varepsilon_2) e^{-\varepsilon_2/kT} + \dots$

electronic molecular partition function

no simple energy level

formula except for $1e^-$
atoms H, He^+ , Li^{2+} , etc.

$\varepsilon_0 \equiv$ ground electronic state — zero of energy (arbitrarily) set at $\varepsilon_0 = 0$

$\epsilon_1 \gg kT$ usually. Contribution from first excited state and higher energy states usually very, very small (except when $L \neq 0$ and $S \neq 0$, get spin-orbit splittings).

$$q_{\text{int}} = q_{\text{elec}} = g(\epsilon_0) \quad \text{FOR ATOMS}$$

Example: Electronic Excitation of a Hydrogen Atom – Rydberg States

$$\epsilon_n = R_y \left(1 - \frac{1}{n^2} \right) \quad n \equiv \text{principal quantum number } (\epsilon_1 = 0, \epsilon_\infty = R_y)$$

$$R_y \equiv \text{Rydberg constant} = 2.180 \times 10^{-18} \text{ J/molecule} = 313.76 \text{ kcal/mol} = hc(109737 \text{ cm}^{-1})$$

When $n = \infty$ $\epsilon_\infty = 313.76 \text{ kcal/mol} = 13.60 \text{ eV}$
 ionization potential of H atom

$$\text{Units: } 350 \text{ cm}^{-1} = 1 \text{ kcal/mol, } k = 0.695 \text{ cm}^{-1}/\text{K}$$

Degeneracy of a Rydberg energy level is $g(\epsilon_n) = 2n^2$ e.g. $n = 4$: 4s, 4p, 4d, 4f
 [L-S terms: $g(L,S) = (2L+1)(2S+1)$] give 2L states, each with
 degeneracy $2 \times (2L + 1)$

Calculate q_{elec} for H atom ...

$$\text{At } T = 1000\text{K, } kT = 1.987 \text{ kcal mol}^{-1} = 8.315 \text{ kJ mol}^{-1}$$

n	ϵ_n (kcal mol ⁻¹)	$g(\epsilon_n)$	$g(\epsilon_n)e^{-\epsilon_n/kT}$
1	0	2	2
2	235.3	8	2.98×10^{-51}
3	278.9	18	1.98×10^{-60}
⋮			
n	313.8	$2n^2$	$2n^2(2.58 \times 10^{-69})$
$q_{\text{elec}} = 2 + 2.98 \times 10^{-51} + 1.98 \times 10^{-60} + \dots = 2$			

Ratio of population of molecules with energy ϵ_2 to energy ϵ_1 .

$$\frac{\bar{n}_{\epsilon_2}}{\bar{n}_{\epsilon_1}} = \frac{g(\epsilon_2)}{g(\epsilon_1)} e^{-(\epsilon_2 - \epsilon_1)/kT} = \frac{2.98 \times 10^{-51}}{2} = 1.5 \times 10^{-51}$$

Only ground state contributes significantly to q_{elec} and only ground state is populated significantly. But sum includes ∞ # of nonzero terms! How do we justify neglect of infinite number of positive, non-zero terms in q_{elect} ? Hint: $\langle r \rangle_n = a_0 n^2$.

What about the nuclear partition function q_{nuc} ? $2I + 1$. Nuclear spin degeneracy? Excited states of nucleus?

Changing the nuclear state generally requires huge energies, so as for the electronic case there is only one nuclear energy level that must be considered at normal temperatures.

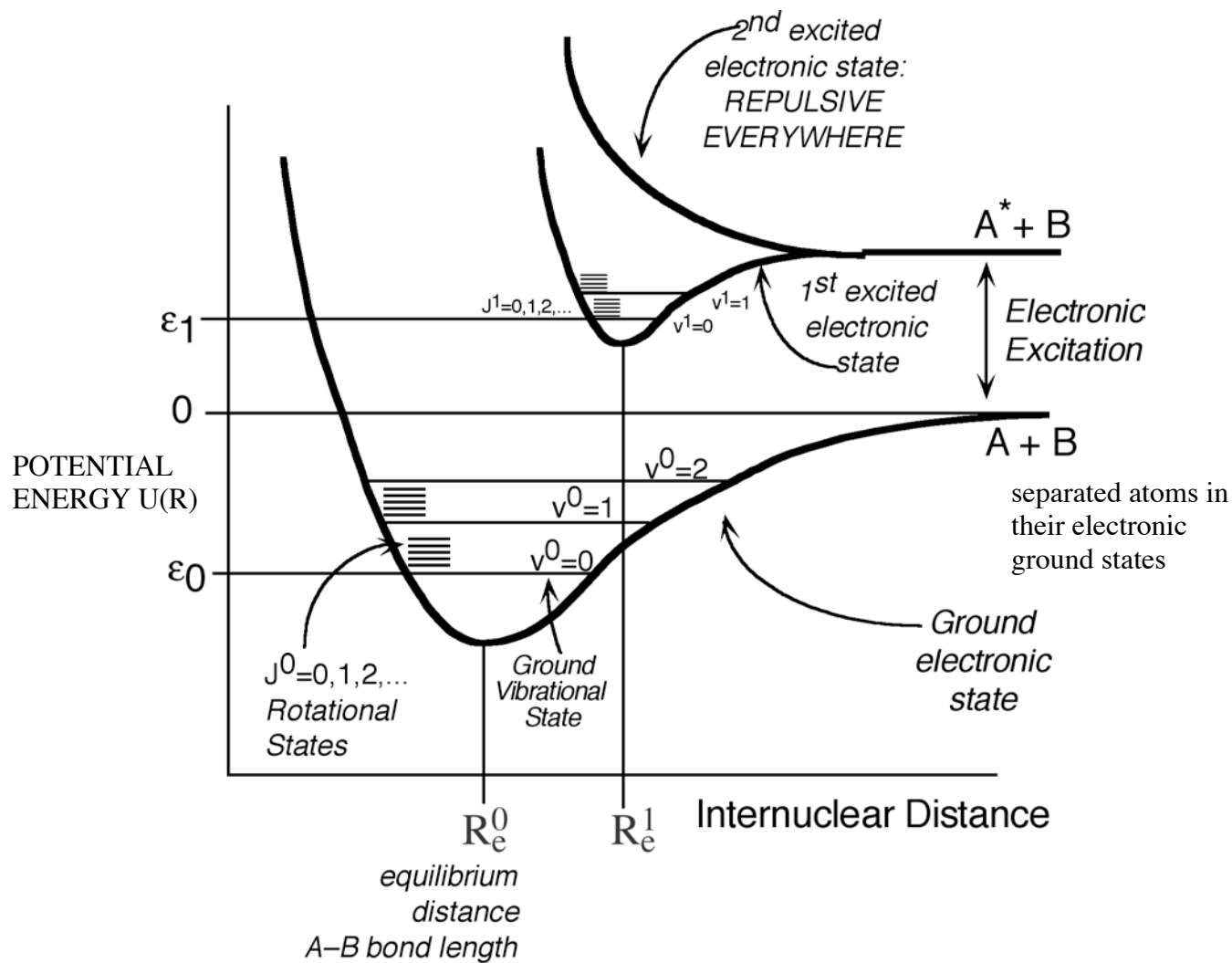
However, the nuclear ground state has an associated spin angular momentum denoted by nuclear spin quantum number I . There is a degeneracy

$$\begin{aligned} g(I) &= 2I + 1 = q_{\text{nuc}}. \\ \text{e.g. for H}(I = 1/2) \text{ } ^2\text{P} \quad J = 3/2 &\rightarrow F = 2, 1 \quad g = 5 + 3 \\ &\quad J = 1/2 \rightarrow F = 1, 0 \quad g = 3 + 1 \\ \text{total } g &= 12 = 2 \times 2 \times 3 \\ &\quad \uparrow \quad \uparrow \quad \uparrow \\ &\quad \text{S} \quad \text{I} \quad \text{L} \end{aligned}$$

This should affect the entropy for $I \geq 1/2$ and $L \neq 0$ or $S \neq 0$ since there are several available nuclear states at the lowest energy level. However, this contribution is not generally included in q_{nuc} because all hyperfine levels are equally populated except at *extremely* low T . Thus there is no nuclear spin contribution to S except at *extremely* low T . In the case of thermonuclear reactions, I may change and q_{nuc} must be accounted for.

INTERNAL DEGREES OF FREEDOM — DIATOMIC MOLECULES

INTRAMOLECULAR POTENTIAL OF A DIATOMIC AB MOLECULE



Note: The 0 in J^0, v^0 , etc. denotes ground electronic state

[Spectroscopists use X,A,B... a,b,c... instead of 0, 1, 2...]

INTERNAL ENERGY LEVELS OF DIATOMIC MOLECULES

ELECTRONIC ENERGIES — same situation as for atoms — no analytical expression — consult tables in which these energies, as measured in a spectroscopy experiment, are tabulated — denoted as $\epsilon_0, \epsilon_1, \epsilon_2 \dots$ Degeneracy: $(2S + 1)(2-\delta_{0,\Lambda})$.

Notation: $^{2S+1}\Lambda_{\Omega}$

VIBRATIONAL ENERGIES — **harmonic oscillator** model used to approximate intramolecular potential in solution of Schrödinger equation.

vibrational energy levels given by ...

$$\epsilon_{\text{vib}}(v) = \left(v + \frac{1}{2}\right) h\nu = \left(v + \frac{1}{2}\right) hc\omega_e \quad (\omega_e \text{ in cm}^{-1} \text{ units})$$

where $v = 0, 1, 2 \dots$ vibrational quantum number

$$v \text{ (sec}^{-1}\text{)} = c/\lambda = \text{frequency } [3 \times 10^{13} \text{ s}^{-1} \text{ typical}] \quad (\omega_e = 1000 \text{ cm}^{-1})$$

$$v = c\omega_e$$

$$\omega_e = 1/\lambda \text{ (cm}^{-1}\text{)} \equiv \text{wavenumber [all spectroscopists use cm}^{-1} \text{ units synonymously with Energy and Frequency!]}$$

- need ω_e or v to calculate $\epsilon_{\text{vib}}(v)$ — get from IR spectroscopy expt.
- vibrational frequencies have different values in each electronic state because force constants are different (e.g. consider bonding \leftrightarrow antibonding orbital excitation in N_2)

$$v^0 \equiv c\omega_e^0 \equiv \text{vibrational frequency in ground electronic state}$$

$$v^1 \equiv c\omega_e^1 \equiv \text{vibrational frequency in 1}^{\text{st}} \text{ electronically excited state}$$

- degeneracy of each vibrational level = 1.

$$g_{\text{vib}} = 1$$

- note that lowest energy is $\frac{1}{2} h\nu$ or “zero point energy”.

[There are two common choices of the zero of vibrational energy, at $v = 0$ or at $v = -1/2$. We will return to this when we consider isotope effects on reaction equilibrium constants.]

ROTATIONAL ENERGIES — use **rigid rotor** approximation; bond length does not change with rotational excitation.

rotational energy levels given by ...

$$\epsilon_{\text{rot}}(J) = J(J+1)hcB_e = J(J+1)\frac{h^2}{8\pi^2\mu R_e^2}$$

(B_e in cm^{-1} units,
 $B = 1 \text{ cm}^{-1}$ typical)
 [to get from cm^{-1} to E units,
 multiply by hc]

where $J = 0, 1, 2 \dots$ rotational quantum number [J can be 1/2 integer or integer depending on whether there is an odd or even # of e^- .]

$B_e \equiv$ rotational constant — property of molecule [always given in cm^{-1} units.]

$$B_e = \frac{h}{8\pi^2\mu R_e^2 c} = \frac{h}{8\pi^2 I c} [\text{cm}^{-1}]$$

$I =$ moment of inertia = μR_e^2 for diatomics

$$\mu = \frac{m_A m_B}{m_A + m_B} \text{ reduced mass}$$

- degeneracy of each rotational level = $2J + 1$

$$g_J = 2J + 1$$

- rotational constants B_e have different values in each electronic state

B_e^0 rotational constant in ground electronic state

B_e^1 rotational constant in first electronically excited state

INTERNAL MOLECULAR PARTITION FUNCTION — q_{int} — DIATOMICS

GOAL: Obtain an expression for q_{int} including all degrees of freedom

$$q_{\text{int}} = \sum_{\epsilon(n, v^n, J^n)} g(n, v^n, J^n) e^{-\epsilon(n, v^n, J^n)/kT} \quad (\text{n here refers to electronic state, not principal quantum number})$$

sum over all internal energy levels

Assume internal energies are separable and additive (not quite true):

$$\epsilon_{\text{int}}(n, v^n, J^n) = \epsilon_{\text{el}}(n) + \epsilon_{\text{vib}}(v^n) + \epsilon_{\text{rot}}(J^n)$$

This approximation (Born-Oppenheimer) is okay for separation of electronic from internal degrees of freedom, but ω_e and B_e both depend on electronic state. But it is OK here because only the lowest electronic state usually contributes (except rare earths). Separability of vibration from rotation okay for low vibrational energies.

Because energies are additive, q_{int} factors into terms for each electronic state

$$q_{\text{int}} = g_0 e^{-\epsilon_0/kT} \sum_{v^0} e^{-\epsilon_{0,\text{vib}}/kT} \sum_{J^0} g(\epsilon_{J^0}) e^{-\epsilon_{0,\text{rot}}/kT} \\ + g_1 e^{-\epsilon_1/kT} \sum_{v^1} e^{-\epsilon_{1,\text{vib}}/kT} \sum_{J^1} g(\epsilon_{J^1}) e^{-\epsilon_{1,\text{rot}}/kT} + \dots$$

$$q_{\text{int}} = q_{0,\text{el}} q_{0,\text{vib}} q_{0,\text{rot}} + q_{1,\text{el}} q_{1,\text{vib}} q_{1,\text{rot}} + q_{2,\text{el}} q_{2,\text{vib}} q_{2,\text{rot}} + \dots$$

$$q_{\text{int}} = g_0 e^{-\epsilon_0/kT} q_{0,\text{vib}} q_{0,\text{rot}} + g_1 e^{-\epsilon_1/kT} q_{1,\text{vib}} q_{1,\text{rot}} + g_2 e^{-\epsilon_2/kT} q_{2,\text{vib}} q_{2,\text{rot}} + \dots$$

usually only 1st term contributes significantly

because $g_1 e^{-\epsilon_1/kT} \ll g_0 e^{-\epsilon_0/kT}$

Only the ground electronic state contributes significantly except at extremely high temperature or when electronic ground state has $S \neq 0$. ("Multiplet states" have low-lying Ω -components. Ω is projection of \vec{J} on body axis.)

Need to find q_{rot} and q_{vib} !!! But usually only for the lowest electronic state.