

CHAPTER 6: Ideal Diatomic Gas

$$Q \sim \frac{[q_{rot} q_{vib} q_{tr} q_{el}]^N}{N!}$$

for N indistinguishable molecules

We will exam this more closely later

$$q_{tr} = \left[\frac{2\pi(m_1 + m_2)kT}{h^2} \right]^{3/2} V$$

Actually, we also need to consider nuclear spin and its ramifications for the rotational partition function.

Assuming a heteronuclear diatomic

$$q_{rot} = 1 + 3e^{-2\theta_r/T} + 5e^{-6\theta_r/T} + \dots$$

high T replace sum by $\int \rightarrow q_{rot} = \frac{T}{\theta_r} = \frac{8\pi^2 IkT}{h^2}$

$$q_{rot}(T) = \frac{T}{\theta_r} \left[1 + \frac{1}{3} \frac{\theta_r}{T} + \frac{1}{15} \left(\frac{\theta_r}{T} \right)^2 + \dots \right]$$

The extra terms result from doing a better sum
 \rightarrow integral transformation

$$E_{rot} = NkT + \dots$$

$$C_{V,rot} = Nk + \dots$$

homonuclear diatomic $q_{rot} = \frac{T}{2\theta_r}$ keeping only the leading term

\uparrow

symm # (# indistinguishable orientations)

The total wave function is either antisymmetric (fermions) or symmetric (bosons) wrt interchange of the nuclei

$$\Psi_{\text{tot}} = \Psi_{\text{tr}} \Psi_{\text{rot}} \Psi_{\text{vib}} \Psi_{\text{el}} \Psi_{\text{nuc}}$$

consider H₂: nuclear spins = 1/2 (fermions)

nuclear spin functions

$a\beta - \beta a$	S	
$\alpha\beta + \beta a$	}	T
$\alpha\alpha$		
$\beta\beta$		

	nuclear spin	rot	
para	S (-)	J even (+)	
ortho	T (+)	J odd (-)	← statistical weight 3

nuclei of spin $I \Rightarrow 2I + 1$ spin states per nucleus

$$q_{rot,nucl} \neq q_{rot} q_{nucl}$$

if $\theta_r \ll T$

$$\sum_{J_{even}} \approx \sum_{J_{odd}} \approx \frac{1}{2} \sum_J \approx \frac{1}{2} \int_0^\infty (2J+1) e^{-\theta_r J(J+1)/T} dJ = \frac{T}{2\theta_r}$$

$$q_{rot,nucl} \sim \frac{(2I+1)^2}{2\theta_r} = q_{rot} \uparrow (T) q_{nucl} \uparrow$$

$\frac{T}{2\theta_r}$ $(2I+1)^2$

need $\theta_r / T \lesssim 0.2$
to be valid

In the above and following discussion, we assume a $^1\Sigma_g^+$ electronic state

Half-integral spin

$I(2I+1)$ antisymm nuclear spin function – even J

$(I+1)(2I+1)$ symm nuclear spin function – odd J

Integral spin

$I(2I+1)$ antisymm nuclear spin function – odd J

$(I+1)(2I+1)$ symm nuclear spin function – even J

$$(I+1)(2I+1) + I(2I+1) = (2I+1)^2$$

Integral spin

$$q_{rot,nucl} = (I+1)(2I+1) \sum_{J_{even}} (2J+1) e^{-\theta_r J(J+1)/T} \\ + I(2I+1) \sum_{J_{odd}} (2J+1) e^{\theta_r J(J+1)/T}$$

prefactors switched for nuclei of $\frac{1}{2}$ integral spin

H_2 $\theta_r = 85.3$ (K) largest θ_r value

$$q_{rot,mol} = \underbrace{\sum_{J_{even}} (2J+1) e^{-\theta_r J(J+1)/T}}_{\text{para}} + 3 \underbrace{\sum_{J_{odd}} (2J+1) e^{-\theta_r J(J+1)/T}}_{\text{ortho}}$$

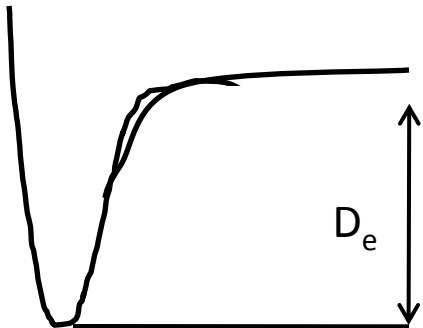
H_2 is 100% para at $T = 0$
→ 25% para at high T | If at equilibrium

Measurements of C_v vs. T : disagreement between theory and experiment

problem $O \leftrightarrow P$ interconversion slow
so high temperature distribution locked in
as sample is cooled

for most homonuclear diatomics don't have to worry
about this other than the factor of 2 symmetry #)

Due to rotational
levels being
much closer
together



$$q_e = \omega_{e1} e^{D_e/kT} + \omega_{e2} e^{-\varepsilon_2/kT} + \dots$$

↑
using free atoms as the zero of energy – generally need only retain the 1st term

$$q = \underbrace{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}}_{\text{translational}} \underbrace{V \frac{8\pi^2 IkT}{\sigma h^2}}_{\text{rotational}} e^{-\beta hv/2} (1 - e^{-\beta hv})^{-1} \omega_{e1} e^{D_e/kT} \quad \left| \quad \begin{array}{l} \text{assumes no low-lying} \\ \text{electronically states} \end{array} \right.$$

$$\frac{E}{NkT} = \frac{5}{2} + \frac{hv}{2kT} + \frac{hv/kT}{(e^{hv/kT} - 1)} - \frac{D_e}{kT} \quad \left| \quad E = \frac{5}{2} NkT + \frac{N hv}{e^{hv/kT} - 1} - \underbrace{\left(D_e - \frac{hv}{2} \right)}_{\text{does not contribute to heat capacity}} N$$

$$\frac{C_v}{Nk} = \frac{5}{2} + \left(\frac{hv}{kT}\right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2}$$

$$pV = NkT$$

$$S = \frac{\langle E \rangle}{T} + \ln Q$$

$$\frac{S}{Nk} = \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N} \right] + \ln \left(\frac{8\pi^2 I kT e}{\sigma h^2} \right) \\ + \frac{hv/kT}{e^{hv/kT} - 1} - \ln(1 - e^{-hv/kT}) + \ln \omega_{el}$$

$$\frac{\mu^0}{kT} = -\ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} kT - \ln \frac{8\pi^2 I kT}{\sigma h^2} + \frac{hv}{2kT} \\ + \ln(1 - e^{-hv/kT}) - \frac{D_e}{kT} - \ln \omega_{el}$$

For general polyatomic molecules we don't have a closed form for the rot. energy levels. So it would appear that we can't simply extend the procedure followed for diatomics.