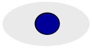
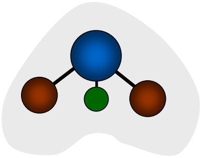
Diatomic Molecules



- So for monatomic gas $Q = Q_{tr}Q_{int}$
  $= Q_{tr}Q_{el}$
- What happens when we add more nuclei

$$Q = Q_{tr}Q_{int} = Q_{tr}\underbrace{\boxed{Q_{el}}\boxed{Q_{rot,vib}}}$$

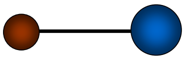
Born-Oppenheimer Approximation
separating electron from nuclear motion,
e^- move so fast that E field they experience
is from “fixed” position nuclei



$$Q = Q_{tr}Q_{el}Q_{rot}Q_{vib}$$

and assuming rotation and vibration modes (motions) independent

- Simplest multiatom molecules?
  - diatomics
    - Q_{tr} – no change
    - Q_{el} – similar to atoms



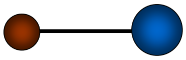
Electronic States of Diatomics

- Naming nomenclature similar to multielectron atoms

$${}^{2s+1}\ell_J \longrightarrow {}^{2S+1}\Lambda_\Omega$$

describes e^- orbitals around nucleus

describes e^- orbitals about internuclear axis



$$J = \ell+s,\ \ell+s-1, \ldots \ell-s \geq 0 \qquad \Omega = \Lambda+S,\ \Lambda+S-1, \ldots \Lambda-S \geq 0$$

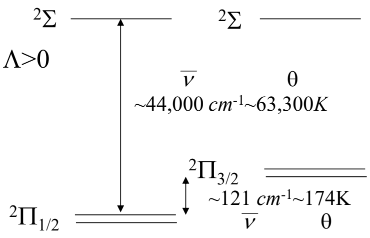
(*except for* Λ=0, *then not defined*)

	0	**1**	**2**
ℓ	S	P	D
Λ	Σ	Π	Δ

$$g_{el,i} \neq 2\Omega + 1$$

Q_{el} Example: NO

- Ground (lowest energy) electronic levels of NO have a $^2\Pi$ configuration $\Rightarrow \Lambda=1, S=½$
  - so we get 2 spin(-split) states: $\Omega= {}^1/_2, {}^3/_2$
  - and 2 "lambda-doubled" states
    - lambda-doubling occurs for all $\Lambda>0$
- Next excited electronic state is a $^2\Sigma \Rightarrow \Lambda=0, S=½$
- If we count each spin-split state as different (non-degenerate)



$$g_{el} = \begin{cases} 1 & \Lambda = 0 \\ 2 & \Lambda \neq 0 \end{cases}$$

- So $Q_{el,NO} \cong 2 + 2e^{-174K/T} + 2e^{-63{,}300K/T}$
  - and $Q_{el,NO} \cong 4$ for $174K \ll T \ll 63{,}300K$

Rotational Partition Function: Q_{rot}

- Recall for rigid rotor model
  - B is rotational constant (typical units of cm^{-1})
  - and

$$\varepsilon_{rot} = \frac{\hbar^2}{2I} J(J+1) \equiv hcBJ(J+1)$$

quantum number for angular momentum

$$g_{rot} = 2J+1$$

- So $$Q_{rot} = \sum_J (2J+1) e^{-\theta_r J(J+1)/T}$$ with $\theta_r \equiv hcB/k$

characteristic rotational temperature

- For $T \gg \theta_r$, summation can be approximated by continuous integral

$$Q_{rot} \cong \int_0^\infty (2J+1) e^{-\theta_r J(J+1)/T} dJ = \int_0^\infty e^{-z\theta_r/T} dz$$ with $z=J(J+1)$

$$\int_0^\infty e^{-ax} dx = 1/a$$

$$\boxed{Q_{rot} \cong \frac{T}{\theta_r}}$$

closer approximation for $T/\theta_r \gtrsim 1/4$
less than 1% difference for $T/\theta_r > 33.6$

$$Q_{rot} \cong \frac{T}{\theta_r}\left(1 + \frac{\theta_r/T}{3} + \frac{(\theta_r/T)^2}{15} + \dots\right)$$

see McQuarrie p. 99

Rotational Energy

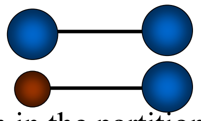
- Rotational energy (**for $T >> \theta_r$**)

$$\hat{e}_{rot} = \bar{R}T^2 \left.\frac{\partial \ln Q_{rot}}{\partial T}\right|_V \cong \bar{R}T^2 \frac{d\ln T/\theta_r}{dT} = \bar{R}T^2 \frac{1}{T}$$

$$\boxed{\begin{array}{l}\hat{e}_{rot} = \bar{R}T \\ \hat{c}_{v,rot} = \bar{R}\end{array}}$$

  - and specific heat $\hat{c}_{v,rot} = d\hat{e}_{rot}/dT$
  - so rotational mode calorically perfect
    - $c_{v,rot}$=constant=2/2 R
    - *same result as Equipartition of Energy* for rotational mode with 2 degrees of freedom (linear molecule has 2 moments of inertia)
      - **when rotational mode is fully-excited** (i.e., for T/θ_r>>1)

Homonuclear vs Heteronuclear



- Diatomics can have 2 nuclei that are the same (homonuclear) or different (heteronuclear)
- This leads to a symmetry consideration in the partition function, so actually

$$\boxed{Q_{rot} \cong \frac{T}{\sigma\theta_r}}$$

Symmetry factor

$$\sigma = \begin{cases} 1 & \text{heteronuclear} \\ 2 & \text{homonuclear} \end{cases}$$

  - if 2 nuclei are identical, 180° rotation can't be distinguished from original configuration ⇒ have overcounted number of distinguishable states by 2×
- Does not effect e_{rot} or $c_{v,rot}$ since they depend on $\partial\ln Q=(\partial Q)/Q$

More accurate explanation based on nuclear spin and symmetry requirements

Wave function requires specific type of symmetry for Boson/Fermion (determined by nuclear spins)

Symmetry type flips for odd vs even J, so half the rotational states are missing for homonuclear diatomics

Vibrational Partition Function: Q_{vib}

- Assuming harmonic oscillator $\varepsilon_{vib} = h\nu\left(\mathrm{v}+\frac{1}{2}\right)$
  - which also has $g_{vib}=1$ (no degeneracy)

vibrational quantum number

frequency of oscillation

- So $Q_{vib} = \sum_{\mathrm{v}=0}^{\infty} e^{-\theta_\mathrm{v}\left(\mathrm{v}+\frac{1}{2}\right)/T}$ with $\theta_\mathrm{v} \equiv h\nu/k$

characteristic vibrational temp.

$$= e^{-\theta_\mathrm{v}/2T}\sum_{\mathrm{v}=0}^{\infty} e^{-\mathrm{v}\theta_\mathrm{v}/T} \quad = e^{-\theta_\mathrm{v}/2T}\left(1+\sum_{\mathrm{v}=1}^{\infty} e^{-\mathrm{v}\theta_\mathrm{v}/T}\right)$$

- From Taylor series expansion for $\frac{1}{1-x} = 1+\sum_{n=1}^{\infty} x^n$
  - we can see if we let $x=e^{-\theta_\mathrm{v}/T}$

$$\boxed{Q_{vib} = \frac{e^{-\theta_\mathrm{v}/2T}}{1-e^{-\theta_\mathrm{v}/T}}}$$

valid for for all θ_v/T
(not approximation,
for harmonic oscillator)

if we let lowest vibration level have zero energy (remove $\frac{1}{2}k\theta_\mathrm{v}$ energy)

$$Q_{vib} = \frac{1}{1-e^{-\theta_\mathrm{v}/T}}$$

Vibrational Energy

- Get macroscopic energy from $\hat{e}_{vib} = \bar{R}T^2 \left.\frac{\partial \ln Q_{vib}}{\partial T}\right|_V = \bar{R}T^2\left(\frac{d\ln e^{-\theta_\mathrm{v}/2T}}{dT} + \frac{d\ln \frac{1}{1-e^{-\theta_\mathrm{v}/T}}}{dT}\right)$

$$= \bar{R}T^2\left(\frac{\theta_\mathrm{v}}{2T^2} + \frac{\frac{\theta_\mathrm{v}}{T^2}e^{-\theta_\mathrm{v}/T}}{1-e^{-\theta_\mathrm{v}/T}}\right) \quad = \bar{R}\theta_\mathrm{v}\left(\frac{1}{2}+\frac{e^{-\theta_\mathrm{v}/T}}{1-e^{-\theta_\mathrm{v}/T}}\right)$$

$$\boxed{\hat{e}_{vib} = \bar{R}\theta_\mathrm{v}\left(\frac{1}{2}+\frac{1}{e^{\theta_\mathrm{v}/T}-1}\right)}$$

if we let lowest vibration level have zero energy (remove $\frac{1}{2}k\theta_\mathrm{v}$ energy)

$$\hat{e}_{vib} = \bar{R}\theta_\mathrm{v}\frac{1}{e^{\theta_\mathrm{v}/T}-1}$$

- Also $\hat{c}_{v,vib} = d\hat{e}_{vib}/dT = \bar{R}\theta_\mathrm{v}\left(0+\frac{\theta_\mathrm{v}}{T^2}\frac{e^{\theta_\mathrm{v}/T}}{\left(e^{\theta_\mathrm{v}/T}-1\right)^2}\right) = \bar{R}\left(\frac{\theta_\mathrm{v}}{T}\right)^2\frac{e^{\theta_\mathrm{v}/T}}{\left(e^{\theta_\mathrm{v}/T}-1\right)^2}$

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Vibrational Energy

- Normalizing expressions

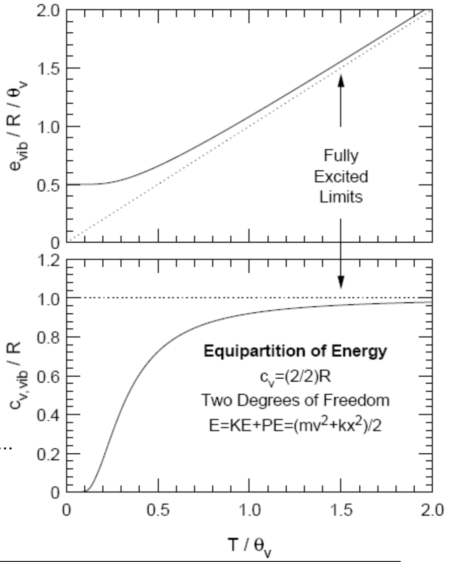
$$\frac{e_{vib}}{R\theta_v} = \frac{1}{2} + \frac{1}{e^{\theta_v/T} - 1}$$

$$\frac{c_{v_{vib}}}{R} = \left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2}$$

- Limits
  - for $\theta_v/T >> 1$, $e^{\theta_v/T} \to \infty$
    - $e_{vib} \to \frac{1}{2} R\theta_v$
    - $c_{v,vib} \to 0$
  - for $\theta_v/T << 1$

$$e^{\theta_v/T} = 1 + \frac{\theta_v}{T} + \frac{1}{2!}\left(\frac{\theta_v}{T}\right)^2 + \ldots$$

    - $e_{vib} \to R\theta_v (\frac{1}{2} + T/\theta_v)$
    - $c_{v,vib} \to R$



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Typical Values for Diatomic Molecules

Gas	θ_r(K)	θ_v(K)	Q_{el}
H_2	85	6300	$1 + e^{-132{,}000/T}$
NH	24	4496	$3 + 2e^{-18{,}250/T} + 2e^{-30{,}490/T}$
OH	27	5370	$2 + 2e^{-125/T} + 2e^{-47{,}000/T}$
N_2	2.88	3390	$1 + 2e^{-99{,}600/T}$
CO	2.8	3120	$1 + 2e^{-93{,}500/T}$
NO	2.44	2740	$2 + 2e^{-174/T} + 2e^{-63{,}300/T}$
O_2	2.08	2270	$3 + 2e^{-11{,}400/T}$

m

- For typical conditions $\theta_r << T \lesssim \theta_v << \theta_{el,1}$

except H_2 at low T

except for some radicals like NO, OH

but then often $Q_{el} \sim g_0 + g_1$

except at very high T

→ NH and OH nearly the same mass, O has higher electronegativity than N ⇒ OH has much stronger bond thus: 1) lower r_e (and moment of inertia) so higher θ_r; and 2) higher k_{spring} (and vibrational frequency) so higher θ_v

Overall Diatomic Properties

- Combining all modes, i.e., $Q=Q_{tr}Q_{rot}Q_{vib}Q_{el}$, can write
- Specific heat $\hat{c}_v = \overline{R}\left[\frac{5}{2}+\left(\frac{\theta_v}{T}\right)^2 \frac{e^{\theta_v/T}}{\left(e^{\theta_v/T}-1\right)^2}\right]+\hat{c}_{v,elec}$
- Pressure $p = \overline{R}T\left.\frac{\partial \ln Q}{\partial V}\right|_T = \overline{R}T\left.\frac{\partial \ln Q_{tr}}{\partial V}\right|_T \Rightarrow pV = n\overline{R}T$

  all other modes $Q\neq Q(V)$
- Entropy

$$\hat{s} = \hat{s}_{tr} + \hat{s}_{int} = \hat{s}_{tr} + \hat{s}_{rot} + \hat{s}_{vib} + \hat{s}_{el}$$

Already showed

$$\frac{\hat{s}_{tr}}{\overline{R}} = \frac{5}{2}\ln T - \ln p + \left(\frac{5}{2}+\ln\underbrace{\left\{\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right\}}_{\equiv bk}\right)$$

constant

$$\frac{\hat{s}_{int}}{\overline{R}} = \ln Q_{int} + T\left.\frac{\partial \ln Q_{int}}{\partial T}\right|_V$$

for $T>>\theta_r$ $\hat{s}_{rot}/\overline{R} \cong \ln T + (1-\ln(\sigma\theta_r))$ constant

$$\hat{s}_{vib}/\overline{R} = -\ln\left(1-e^{-\theta_v/T}\right)+\frac{\theta_v/T}{e^{\theta_v/T}-1}$$

$=\ln T+(1-\ln\theta_v)$ when $T>>\theta_v$

constant

for $T<<\theta_{el,1}$ $\hat{s}_{el}/\overline{R} \cong \ln g_o$ constant

$$\boxed{\frac{\hat{s}}{\overline{R}} = \frac{7}{2}\ln T - \ln\left(1-e^{-\theta_v/T}\right)+\frac{\theta_v/T}{e^{\theta_v/T}-1} - \ln p + \text{constant}}$$

$=(c_p/R)\ln T - \ln p + \text{constant}$ when c_p const.

Overall Diatomic Properties

- Similarly for the chemical potential

$$\mu = \mu_{tr} + \underset{\downarrow \atop = -\overline{R}T\ln Q_{\text{int}}}{\mu_{int}} = \overline{R}T\ln p + \underbrace{\overline{R}T\left[fn\left(T,b,\theta_r,\theta_v,g_{el,i},\theta_{el,i}\right)\right]}_{\mu^o(T)}$$

$b \equiv (2\pi mk/h^2)^{3/2}$

$$\cong \overline{R}T\ln p - \overline{R}T\left[\begin{array}{ll} \frac{5}{2}\ln T + & \ln(bk) \\ +\ln T - & \ln(\sigma\theta_r) \\ -\ln\left(1-e^{-\theta_v/T}\right)-\frac{\theta_v}{2T} & \\ + & \ln g_o \\ +\frac{\theta_D}{T} & \end{array}\right]$$

tran.

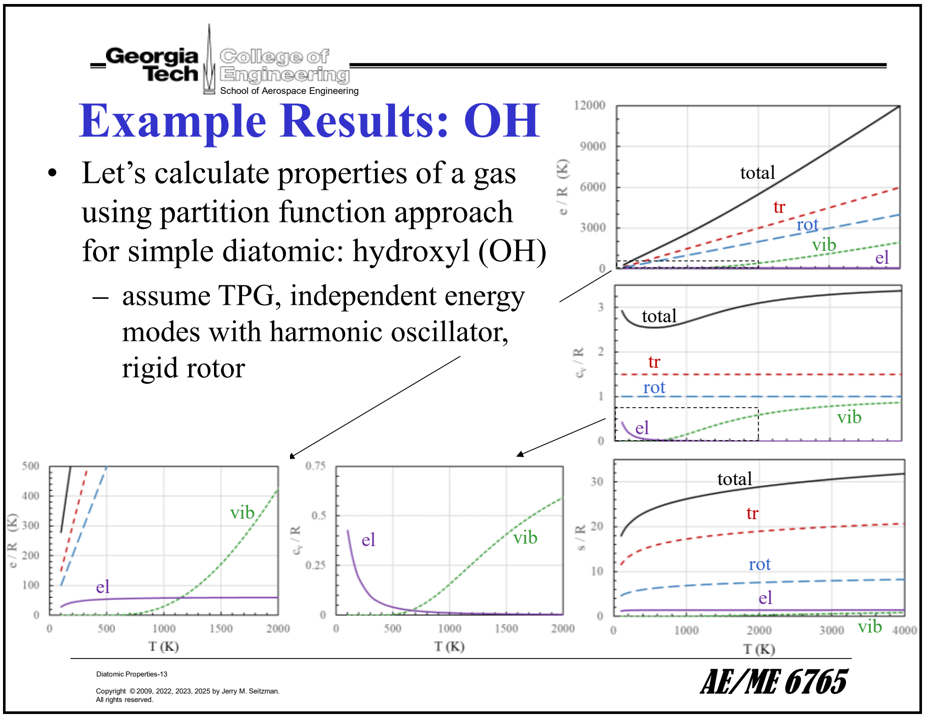
rot. for $T>>\theta_r$

vib.

elec. for $T<<\theta_{el,1}$

chemical *for atoms as the "elements"*

$\theta_D \equiv \varepsilon_D/k$ *with ε_D=energy required to dissociate molecule's ground state into atoms*



Example Results: OH

- Let's calculate properties of a gas using partition function approach for simple diatomic: hydroxyl (OH)
  - assume TPG, independent energy modes with harmonic oscillator, rigid rotor

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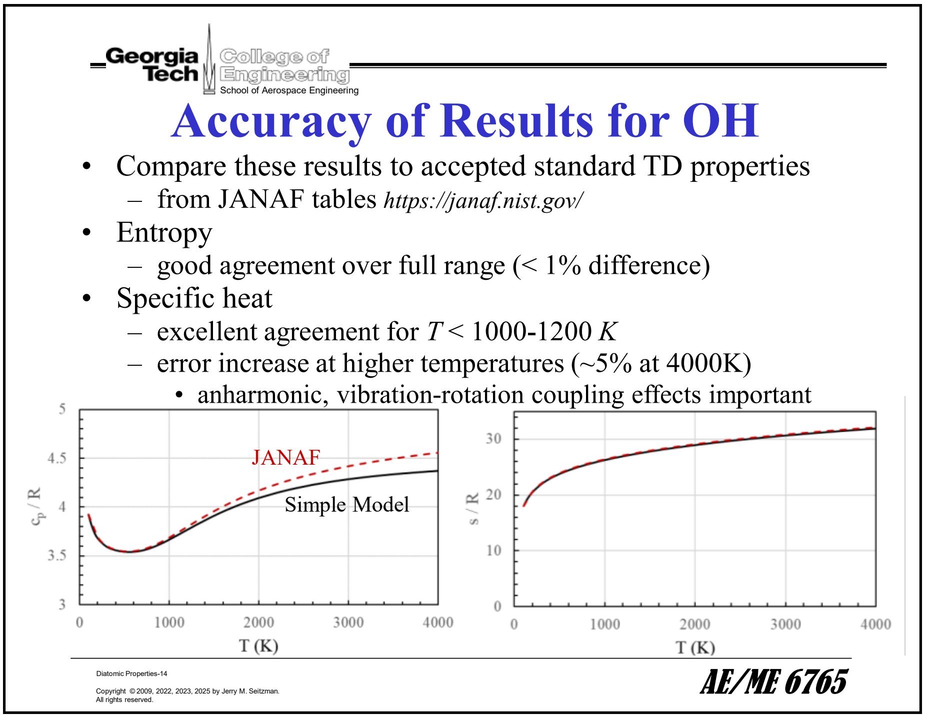

Accuracy of Results for OH

- Compare these results to accepted standard TD properties
  - from JANAF tables *https://janaf.nist.gov/*
- Entropy
  - good agreement over full range (< 1% difference)
- Specific heat
  - excellent agreement for $T < 1000\text{-}1200\ K$
  - error increase at higher temperatures (~5% at 4000K)
    - anharmonic, vibration-rotation coupling effects important