

# STATISTICAL MOLECULAR THERMODYNAMICS

*Christopher J. Cramer*

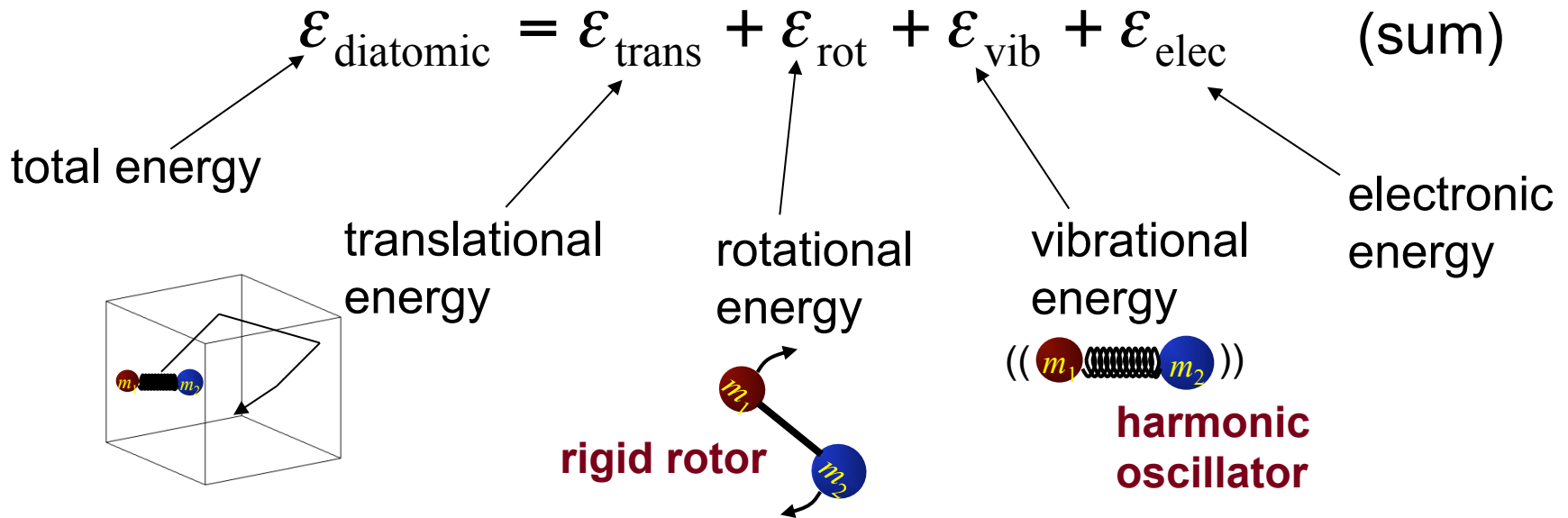
Video 4.6

Ideal Diatomic Gas:  $Q$

# ENERGY OF AN IDEAL DIATOMIC GAS

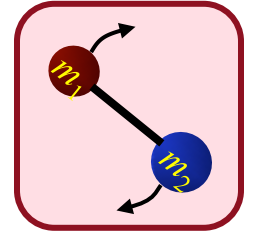
In addition to translational and electronic degrees of freedom, a diatomic also can rotate and vibrate. These motions can be treated within the *rigid rotator* and *harmonic oscillator* approximations, respectively (*exactly solvable QM problems*)

## The Energy:



# ONE WRINKLE

Due to quantum mechanical boundary conditions associated with the indistinguishability of particles, we need to add a *symmetry number* to the rotational partition function,



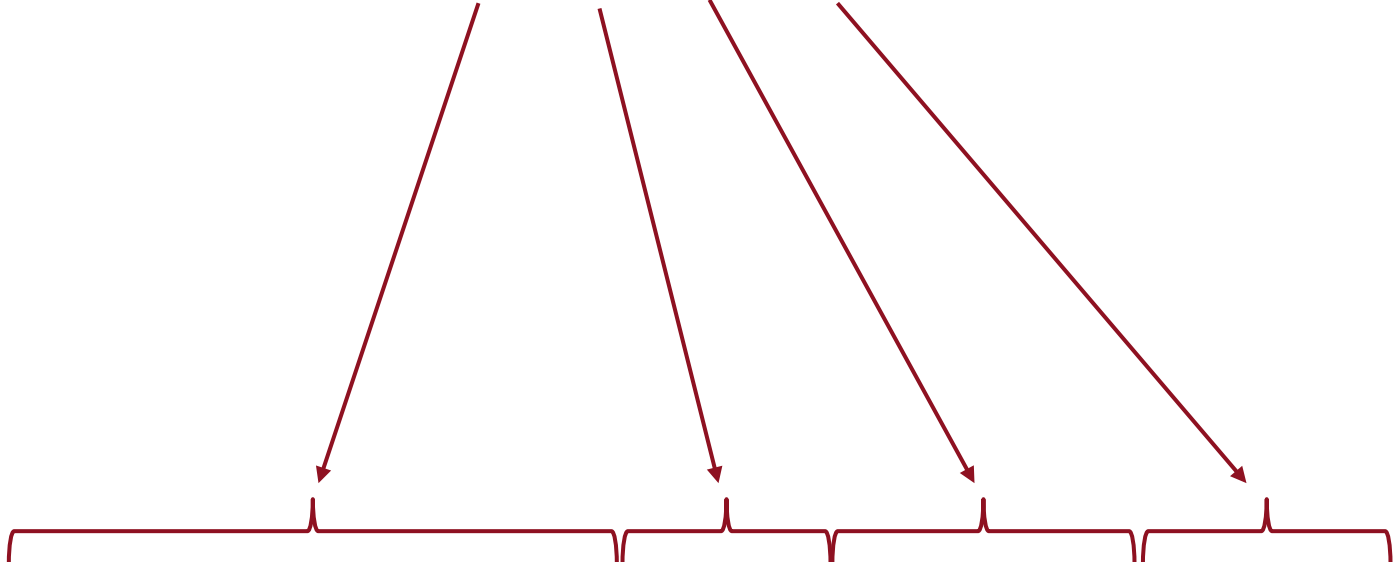
$$q_{\text{rot}} = \frac{T}{\sigma \Theta_{\text{rot}}}, \quad \begin{array}{ll} \sigma = 1 & \text{heteronuclear diatomic} \\ \sigma = 2 & \text{homonuclear diatomic} \end{array}$$

*symmetry number*

So, last lecture our derivation was valid only for *heteronuclear diatomic rotation*,  $\sigma = 1$ .

# THE FULL DIATOMIC PARTITION FUNCTION

$$q(V, T) = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$


$$q(V, T) = \left( \frac{2\pi(m_1 + m_2)k_B T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{\text{rot}}} \cdot \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} \cdot g_1 e^{D_e/k_B T}$$

# THE FULL DIATOMIC IDEAL GAS $\bar{U}$ AND $\bar{C}_V$

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$

with  $q(V, T) = \left( \frac{2\pi(m_1 + m_2)k_B T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{\text{rot}}} \cdot \frac{e^{-\Theta_{\text{vib}}/2T}}{1 - e^{-\Theta_{\text{vib}}/T}} \cdot g_1 e^{D_e/k_B T}$

From  $Q$

translations

rotations

zero-point  
vib energy

vib energy above  
zero point

electronic

• Energy

$$\bar{U} = \frac{3}{2}RT + RT + R \frac{\Theta_{\text{vib}}}{2} + R \frac{\Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1} - N_A D_e$$

• Heat Capacity

$$\bar{C}_V = \frac{5}{2}R + R \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$

# Self assessment insert here

- Andy's Week 4 question 9.

# VIBRATIONAL HEAT CAPACITY: EXAMPLE

$$\bar{C}_{V,\text{vib}} = R \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left( 1 - e^{-\Theta_{\text{vib}}/T} \right)^2}$$

$$^{14}\text{N}_2 \text{ has } \nu_{\text{vib}} = 2330 \text{ cm}^{-1}$$

$$^{79}\text{Br}_2 \text{ has } \nu_{\text{vib}} = 323 \text{ cm}^{-1}$$

Recalling  $\Theta_{\text{vib}} = \frac{h\nu}{k_{\text{B}}}$

Noting  $h\nu$  is in wavenumbers here, we use  $k_{\text{B}} = 0.695 \text{ cm}^{-1} \cdot \text{K}^{-1}$  to determine:

$$^{14}\text{N}_2 \text{ has } \Theta_{\text{vib}} = 3353 \text{ K}$$

$$^{79}\text{Br}_2 \text{ has } \Theta_{\text{vib}} = 465 \text{ K}$$

At 500 K:

$$\bar{C}_{V,\text{vib}}(^{14}\text{N}_2) = (8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \left( \frac{3353}{500} \right)^2 \frac{e^{-3353/500}}{\left( 1 - e^{-3353/500} \right)^2}$$

$$= 0.459 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$= 0.06 R$$

# Self assessment insert here

- Given  $\bar{C}_{V,\text{vib}} = R \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left(1 - e^{-\Theta_{\text{vib}}/T}\right)^2}$  and a vibrational temperature

for  $^{79}\text{Br}_2$  of 465 K, what is the vibrational heat capacity of bromine gas at 500 K expressed as a multiple of  $R$ ?

Answers can be 0.06, 0.42, 0.61, and 0.93 (final answer correct)



# VIBRATIONAL HEAT CAPACITY: EXAMPLE

$$\bar{C}_{V,\text{vib}} = R \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{\left( 1 - e^{-\Theta_{\text{vib}}/T} \right)^2}$$

At 500 K:

$$^{14}\text{N}_2 \text{ has } \bar{C}_{V,\text{vib}} = 0.06 R$$

$$^{79}\text{Br}_2 \text{ has } \bar{C}_{V,\text{vib}} = 0.93 R$$

$$^{14}\text{N}_2 \text{ has } \nu_{\text{vib}} = 2330 \text{ cm}^{-1}$$

$$^{79}\text{Br}_2 \text{ has } \nu_{\text{vib}} = 323 \text{ cm}^{-1}$$

$$^{14}\text{N}_2 \text{ has } \Theta_{\text{vib}} = 3353 \text{ K}$$

$$^{79}\text{Br}_2 \text{ has } \Theta_{\text{vib}} = 465 \text{ K}$$

As the temperature of a diatomic ideal gas goes from below to above its vibrational temperature, the molar heat capacity goes from  $\sim(5/2)R$  to  $\sim(7/2)R$   
(cf. Video 1.4 last slide!)

$$dU = \delta q + \delta w$$



*Next: Ideal Polyatomic Gases: Part 1*

# Call Out Demo Here

- Energy Partition