

# STATISTICAL MOLECULAR THERMODYNAMICS

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Video 4.9

Review of Week 4

# CRITICAL CONCEPTS FROM WEEK 4

- The partition function for an atom is the product of its translational and electronic partition functions
- The translational partition function for an atom (and for *all* ideal gas molecules) comes from solution of the particle-in-a-box Schrödinger equation and depends on the gas' atomic (molecular) weight and a box volume that is chosen by convention
- The electronic partition function for an atom at “normal” temperatures typically involves at most two states (and their degeneracies)
- In the absence of a populated excited electronic state, a monatomic ideal gas has a molar internal energy of  $(3/2)RT$  and a molar heat capacity at constant volume of  $(3/2)R$

# CRITICAL CONCEPTS FROM WEEK 4

- The monatomic ideal gas partition function is consistent with the ideal gas equation of state. As *all* ideal gases depend on volume in the same way (through their common translational partition functions), the same equation of state applies to ideal diatomic and polyatomic ideal gases as well
- The partition function for the diatomic ideal gas is the product of translational, rotational, vibrational, and electronic partition functions
- Although for an atom one conventionally takes the zero of energy to be the ground electronic state, for a diatomic molecule one instead takes minus  $D_e$  (the sum of the bond dissociation energy and zero-point vibrational energy); excited electronic states can generally be ignored

# CRITICAL CONCEPTS FROM WEEK 4

- The vibrational partition function for a diatomic is a convergent sum that takes the ground state vibrational energy to be equal to the zero-point vibrational energy
- The vibrational temperature is Planck's constant times the vibrational frequency divided by Boltzmann's constant
- At temperatures well *below*  $\Theta_{\text{vib}}$ , a vibration contributes its *zero-point energy* to  $\bar{U}$  and *zero* to  $\bar{C}_V$ ; at temperatures well *above*  $\Theta_{\text{vib}}$ , it adds an additional  $RT$  and  $R$  to these two quantities, respectively
- The rotational temperature for a rigid rotator is  $\Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_{\text{B}}}$

# CRITICAL CONCEPTS FROM WEEK 4

- For temperatures well above  $\Theta_{\text{rot}}$ , the rotational partition function can be solved as an integral owing to the density of rotational energy levels
- Diatomic rotation contributes  $RT$  and  $R$  to  $\bar{U}$  and  $\bar{C}_V$ , respectively.
- Increasing degeneracy together with dense energy levels cause many rotational states above the ground state to be populated at “normal” temperatures
- In the absence of populated electronic or vibrational excited states, a diatomic ideal gas has a molar internal energy of  $(5/2)RT$  and a molar heat capacity at constant volume of  $(5/2)R$

# CRITICAL CONCEPTS FROM WEEK 4

- Rotation for polyatomic ideal gases involves an equivalent partition function to a diatomic if the polyatomic is linear (using the proper moment of inertia), while for a non-linear polyatomic, spherical, symmetric, or asymmetric top rotational partition functions depend on up to 3 potentially different moments of inertia
- Polyatomic rotation contributes  $RT$  and  $R$  to  $\bar{U}$  and  $\bar{C}_V$ , respectively, *for a linear polyatomic*, and  $(3/2)RT$  and  $(3/2)R$ , respectively, *for a non-linear polyatomic*.
- A polyatomic vibrational partition function is the product of the vibrational partition functions for each of the individual normal modes; each mode contributes to a polyatomic molecule's properties as does the single vibration in a diatomic molecule

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



*Next: First Law of Thermodynamics*