Statistical Molecular Thermodynamics

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Video 1.8

Review of Week 1

Critical Concepts from Week 1

- At the microscopic level, energy levels are discrete (quantized)
- Planck's constant relates the energy of radiation to its frequency
- Solution of the Schrödinger equation is the quantum mechanical technique that determines allowed wave functions and energies for systems defined by potentials and boundary conditions
- The energy levels in atoms are associated with electronic and translational energy
- For one-electron atoms (like H) exact energy levels are very simply computed and depend on quantum number $n = 1,2,3\ldots$

Critical Concepts from Week 1

- For many electron atoms, energy levels are generally available from experiment
- Translational energy can be computed by solving the Schrödinger equation for a particle in a box
- Allowed translational energy levels depend on box side lengths, mass, and quantum numbers $n_q = 1,2,3\ldots$ where q is a spatial dimension
- In more than one dimension, translational energy levels have degeneracy
- There is zero-point energy associated with translation

Critical Concepts from Week 1

- Diatomic molecules have rotational and vibrational energy levels in addition to electronic and translational
- Rotational energy can be computed by solving the Schrödinger equation for a rigid rotator
- Allowed rotational energy levels for a diatomic depend on its moment of intertia and quantum number $J = 0,1,2,\ldots$
- Diatomic rotational energy levels have degeneracy $2J+1$
- There is no zero-point energy associated with rotation
- Vibrational energy can be computed by solving the Schrödinger equation for a harmonic oscillator

Critical Concepts from Week 1

- Allowed vibrational energy levels depend on vibrational frequency and quantum number $v = 0,1,2,\ldots$
- Vibrational energy levels are not degenerate
- There is zero-point energy associated with vibration equal to $(1/2)$ $h\nu$
- For a diatomic the difference between the ground-state electronic energy and the negative of the bond dissociation energy is the zero-point vibrational energy
- Molecule have $3n$ degrees of freedom where n is the number atoms; 3 are translational, 2 (linear molecules) or 3 (non-linear molecules) are rotational, and the remainder are vibrational

Critical Concepts from Week 1

- Rotational energy levels for polyatomic molecules are determined similarly to diatomics when they are linear, and otherwise depend on multiple moments of inertia
- Vibrational energy levels for polyatomic molecules are associated with the normal modes (vibrational degrees of freedom) and their characteristic vibrational frequencies
- Total atomic or molecular energy is equal to the sum of the energies associated with each level, indexed by its respective quantum number
- The spacing of energy levels is usually electronic >> vibrational > rotational >> translational