Lecture 21 (2-4), Mar 6, 2023

Discrepancy in Heat Capacity – Effect of Quantum Mechanics

- Based on quantum mechanics, can we estimate the energy where molecules have enough energy to excite rotations?
- Consider a hydrogen molecule: interatomic distance of $0.7 \times 10^{-10}\,\mathrm{m}$ and mass of $1 \times 10^{-27}\,\mathrm{kg}$
  - The momentum is $L = I\dot{\phi}$ classically, rotational energy is $\frac{1}{2}I\dot{\phi}^2 = \frac{L^2}{2I}$
  - Moment of inertial is given by $I \sim mr^2$
  - Angular momentum is quantized, we can consider it as either $L = 0$ for no rotation or $L \geq \hbar^2$ for some rotation
  - Therefore the minimum energy of rotation is $E \sim \frac{\hbar^2}{I}$
  - $I \sim 1 \times 10^{-27}\,\mathrm{kg}(0.7 \times 10^{-10}\,\mathrm{m})^2 = 1 \times 10^{-48}\,\mathrm{kg\,m^2}$
  - This gives the minimum energy on the order of $1 \times 10^{-20}\,\mathrm{J}$
  - If we compare this to kT, we get that a temperature on the order of 1000K is needed to have enough energy to excite rotations

First Law of Thermodynamics

- $\Delta U = Q + W$, where Q is the heat absorbed and W is the work done on the system
- Consider a piston of area A being pushed against a gas with pressure p, volume V for length $\mathrm{d}x$
  - $\mathrm{d}x$ is positive of the gas expands, negative if it contracts
  - The force is pA, therefore the work done by the gas is $pA\,\mathrm{d}x = p\,\mathrm{d}V$
  - Let $\mathrm{d}U = \delta Q - p\,\mathrm{d}V$, where δQ is some small amount of heat resulting from this
    - * Note the sign on $p\,\mathrm{d}V$ since here it's the work done on the gas, not by the gas
  - This is the first law expressed in terms of infinitesimal changes

Isothermal Processes

Definition

A *quasistatic* process is one where the process is slow enough such that the system is in thermodynamic equilibrium for every moment of the process

- How do finite changes of V affect the state of the system?
  - We need to make assumptions about the nature of the change
  - This question is easy to answer if the process is *quasistatic*
    - * In a non-quasistatic expansion we'll get a depletion of gas density near the piston as it moves, so the force it experiences will be less
    - * Therefore the work done in a quasistatic expansion is strictly larger than the work in a non-quasistatic expansion
  - For such processes we can find the work done by $W = \int_{V_i}^{V_f} p(V,T)\,\mathrm{d}V$
    - * If the temperature is constant (*isothermal* process), then $W = \int_{V_i}^{V_f} \frac{NkT}{V}\,\mathrm{d}V = NkT\ln\left(\frac{V_f}{V_i}\right)$
    - * To keep the process as isothermal we need to keep it in contact with a thermal reservoir, and now the process must be slow enough that we get both pressure and temperature equilibrium
  - For an isothermal process $\Delta U = Q - NkT\ln\left(\frac{V_f}{V_i}\right)$, but since U is dependent only on T for an ideal gas, we must have $Q = NkT\ln\left(\frac{V_f}{V_i}\right)$
- For an isothermal process $pV = \mathit{const}$ so on a P-V diagram this shows up as a curve $P = \frac{C}{V}$

- The area under this curve is the work done by the process