Thermodynamics #3

1. Pressure and volume

\[ P_a = \text{N/m}^2 \quad \text{Pascal} \]

\[ 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \]

Ideal gas: \[ \frac{P_1}{P_2} = \frac{T_1}{T_2} \quad @ \text{constant Volume} \]

\[ P_1V_1 = P_2V_2 \quad @ \text{constant } T \]

Boyle's law

Together give ideal gas law

\[ PV = nRT \quad [\text{energy}] \]

\[ n = \# \text{ moles} \]

\[ R = 8.31 \text{ J/mole/k} \]

\[ P, V, T, n \quad \text{state variables, specify thermodynamic state} \]

Ideal gas law is example of equation of state
Kinetic theory of ideal gas laws.

\[ \text{Contains well} \quad \frac{A}{V} \rightarrow x \]

\# striking area \( A \) in time \( t \) =

\[ \frac{1}{2} \left( \frac{n N_A}{V} \right) A \Delta t \]

\( \Delta = \) on average, \( \frac{1}{2} \) moving toward \( A \).

Perfectly elastic collisions (justified by quantized internal energy)

\[ F_x \Delta t = \Delta P_x = 2mV_x \quad \text{single molecule} \]

Total force: \( F_x \Delta t = (\#) 2mV_x \)

\[ = \left( \frac{n N_A}{V} \right) A \cdot m V_x^2 \Delta t \]

Pressure = \( \frac{F_x}{A} \)

\[ \rho = \frac{n N_A}{V} \cdot m V_x^2 \]
express in terms of mean translational kinetic energy of single molecule

\[ k_{tr} = \frac{1}{2} m v^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \]

\[ \bar{k}_{tr} = \frac{3}{2} m \bar{v}^2 \]

\[ pV = n N_a \cdot \frac{8}{3} \bar{k}_{tr} = n RT \]

conclude \( \bar{k}_{tr} = \frac{3}{2} \frac{R}{N_a} T \) per molecule

\[ n \bar{k}_{mol} = \frac{3}{2} RT \] per mole

**Molar Specific Heat @ Constant Volume:**

\[ \Delta V = 0, \quad \Delta U_{int} = \Delta Q \]

for monatomic ideal gas,

\[ U_{int} = n \bar{k}_{mol} = \frac{3}{2} n RT \]

\[ Q = n C_v T \]

\[ \Delta Q = \Delta U_{int} \quad \text{with} \quad C_v = \frac{3}{2} R \]

\[ C_v (He) = 12.47 \quad J/mol \cdot K \]

\[ C_v (Ar) = 12.47 \quad J/mol \cdot K \]
Equation of energy:

Energy/molecule = \( \frac{F}{2} RT \)

Energy/molecule = \( \frac{F}{2} \frac{R}{N_A} T \)

\( F \) = \# accessible degrees of freedom at normal temperature, vibrational and \( L_z \) modes are "frozen" because of quantized energy.

\[ K_{\text{rot}} = \frac{1}{2} I \omega^2 = \frac{1}{2} \frac{L^2}{I} \]

\( I_z < I_{1,2} \) therefore large excitation energy.
Vibrational is 2 degrees of freedom corresponding to kinetic and potential energy of harmonic oscillator.

For elemental solids, each atom vibrates in 3 directions,

\[ C_V = 3 \left( \frac{1}{2} R + \frac{1}{2} R \right) = 3R \]

\[ \text{kinetic potential} \]

\[ = 74.9 \text{ J/mol} \cdot \text{K} \]
Brownian Motion & Avogadro's Number

Avogadro's hypothesis: to equal volume of gas at some T, p contain equal number of molecules.

\[ \frac{pV}{T} = n \bar{R} = \left( \frac{n}{N_A} \right) \frac{R}{N_A} \]

Brown (1827, Botanist) Observed

Random motion of grains in liquid

Random walk after time \( t \)

Einstein (1905, Nobel paper): spherical particle

\[ \bar{X}^2(t) = \frac{RT}{N_A} \frac{t^2}{\alpha} = \frac{t}{N_A \bar{R}_0} \]

\( \bar{R}_0 \) & particle radius
\( \alpha \) & viscosity of liquid

Perrin (1910, Nobel experiment)

\[ N_A = 6 \times 10^{23} \]

technique to make uniform 1 mm radius balls.
\[ m_H = \frac{1 \left(10^{-3} \text{kg/mole}\right)}{6 \times 10^{23}} = 1.7 \times 10^{-27} \text{kg} \]

**Size of atom**: 1g of liquid hydrogen \( (S = 71 \text{kg/m}^3) \)

(assume close packing)

\[ V_{\text{atom}} = \frac{10^{-2} \text{kg/mole}}{S \cdot N_A} = \frac{10^{-2} \text{kg/mole}}{71 \text{kg/m}^3 \left(6 \times 10^{23}\right)} \]

\[ = 2.3 \times 10^{-29} \text{m}^3 \]

\[ d_{\text{atom}} = \sqrt[3]{V_{\text{atom}}} = 3 \times 10^{-10} \text{m} = 0.3 \text{nm} \]