

## Week 3

# Kinetic Theory of Gases

### 3.1 Maxwell-Boltzmann Distribution

- 1/24:
- Applying the molecular partition function to the heat capacity of a water molecule.
    - A water molecule has three vibrational modes, which we will denote by  $\nu_1, \nu_2, \nu_3$  (corresponding to symmetric stretch, antisymmetric stretch, and bend).
    - Main takeaway: Heat capacity can change with temperature.
    - After a while (at several thousand kelvin), it will level off (see Figure 18.7).
  - Considers CO<sub>2</sub>'s vibrational modes, too.
    - The infrared absorption of the bending mode is what's associated with the Greenhouse Effect.
    - The symmetric stretch is IR inactive due to its lack of change of dipole moment.
    - Raman active: Change in the polarizability of the molecule.
  - The Maxwell-Boltzmann distribution.
    - Maxwell derived it long before Boltzmann, but Boltzmann's thermodynamic derivation is much easier.
    - We know from the boltzmann factor that  $p(E) \propto e^{-E/k_B T}$ .
    - Thus, to get the probability  $p(v)$  of some speed  $v$ , we should have  $p(v) \propto e^{-mv^2/2k_B T}$  times a constant giving the number of molecules of each speed? This yields

$$p(v) = A4\pi v^2 e^{-mv^2/2k_B T}$$

where  $A$  is a normalization constant.

- The Maxwell-Boltzmann distribution is such that

$$\begin{aligned} 1 &= \int_0^\infty p(v) \, dv \\ &= A \int_0^\infty 4\pi v^2 e^{-mv^2/2k_B T} \, dv \\ &= A \int_0^\infty 4\pi \left( \frac{2k_B T}{m} \right)^{3/2} u^2 e^{-u^2} \, du \\ &= A4\pi \left( \frac{2k_B T}{m} \right)^{3/2} \int_0^\infty u^2 e^{-u^2} \, du \\ &= A4\pi \left( \frac{2k_B T}{m} \right)^{3/2} \frac{\sqrt{\pi}}{4} \end{aligned}$$

$$A = \left( \frac{m}{2\pi k_B T} \right)^{3/2}$$

– Therefore,

$$p(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

– Any distribution that doesn't look like this isn't in thermal equilibrium.

- A system with all particles having  $v = 0$  is at thermal equilibrium with  $T = 0$  K.
- A system with all particles having constant velocity in the same direction is at thermal equilibrium with  $T = 0$  K.
  - Think relativity; if you're moving with them, it looks like they're not moving and thus this case is the same as the last one because your movement doesn't affect the thermodynamics of that system.
- A system with all particles having constant velocity in different directions is not at thermal equilibrium since it does not fit the bell curve but is rather a spike.

### 3.2 The First Law of Thermodynamics

1/26:

- See Labalme (2021) for background on/content of today's lecture.
- Joule best quantified how we think about work and energy.
- **System:** Part of the world being investigated. It can contain energy, a number of particles, etc.
- The Newtonian way to change the energy into a system is to do work (mechanical, electrical, etc.) on the system. In chemistry,  $\delta w$  is positive if work is done on the system.
  - We have that

$$\delta w = -P dV$$

- A system at thermal equilibrium has a given temperature characteristic of the system. Some property of the system indicates how hot or cold it is (e.g., volume of mercury, etc.)
- Measure heat transfer using a calorimeter and a thermometer.
  - Convention: Heat put into a system  $\delta q$  is positive and this heat is transferred if the temperature is lower than another system or surroundings.
  - The heat capacity of a system times the change in temperature is equal to the heat put into the system. It is always positive as heat put into the system raises the temperature.
- Example molar heat capacities.
  - For water vapor at low pressure and 20 °C,  $\overline{C}_V = 3R = 25 \text{ J mol}^{-1} \text{ K}^{-1}$ .
  - For liquid water, it's higher (hydrogen bonding).
  - For ice, it's lower.
- **First law of thermodynamics:** The internal energy of a system changes with heat put into the system and work done on the system.

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

– Note that in engineering,  $dU = \delta q - \delta w$ .

- **State variable:** A property that describes the system.

- For example, a system of gas molecules has a state defined by the state variables  $T$ ,  $P$ ,  $V$ , and  $n$ .
- **State function:** A property that depends only upon the state of the system.
  - For example, some equations of state for an ideal gas are  $PV = nRT$  or  $PV = 2U/3$ .
  - The internal energy is a state function.
  - Heat and work are not state functions because they do not depend uniquely on the values at equilibrium.
    - They also depend on the way you do something.
- **Reversible process:** A process that can be represented as a path along state variables, e.g., a line on a  $PV$  diagram. This implies that it is also a path where all state variables are known, and is therefore a path where the system is always in quasi-equilibrium.
  - Isothermal, isochoric, isobaric, and adiabatic changes are reversible.
  - All of these processes are analyzed exactly as in Labalme (2021).
- **Irreversible process:** A process that cannot be drawn on a  $PV$  diagram.
- Experiment to measure  $\gamma$  (the ratio of specific heats):
  1. Let sit at  $P_0 T_0$ .
  2. Pump in a little gas (add  $\Delta n$ ) and let sit, measure  $P_0 + \Delta P_1, T_0$ .
  3. Open the valve to air quickly to  $P_0$ . Adiabatic expansion (cools down).
  4. Let sit to measure the new pressure  $P + \Delta P_2$  when  $T$  is back at  $T_0$ .
  5.  $\gamma$  is determined from  $\Delta P_1, \Delta P_2$  (this will be a homework problem).
  - In the second step, we add some molecules into the container. We can show that  $\Delta P_1/P_0 = \Delta N_1/n_0$ .
  - In the third step, we let out the air, and we can show that  $\Delta n_2/n_0 = \gamma \Delta P_1/P_0$ .
  - In step 4, we have in the container  $(n_0 + \Delta n_1 - \Delta n_2)RT_0 = (P_0 + \Delta P_2)V_0$ .
  - This implies that  $\Delta P_2/\Delta P_1 = 1 - 1/\gamma$ .

### 3.3 Enthalpy

- 1/28:
- Thermodynamic derivation of the formula for  $\langle P \rangle$  in terms of  $Q$ .
    - We have that

$$\begin{aligned}
 U &= \sum p_j E_j \\
 dU &= \sum (dp_j E_j + p_j dE_j) \\
 &= \underbrace{\sum dp_j E_j}_{\delta q} + \underbrace{\sum p_j \frac{\partial E_j}{\partial V} dV}_{-P}
 \end{aligned}$$

where the last part follows by analogy with  $dU = \delta q - P dV$ .

- It follows that

$$P = - \sum p_j \frac{\partial E_j}{\partial V} = - \left\langle \frac{\partial E}{\partial V} \right\rangle$$

- Thus, we have that

$$\begin{aligned}
 P &= - \sum \frac{e^{-E_j/k_B T}}{Q} \frac{\partial E_j}{\partial V} \\
 &= \frac{1}{Q} \sum k_B T \cdot - \frac{1}{k_B T} e^{-E_j/k_B T} \frac{\partial E_j}{\partial V} \\
 &= k_B T \frac{1}{Q} \sum \frac{\partial}{\partial E_j} \left( e^{-E_j/k_B T} \right) \frac{\partial E_j}{\partial V} \\
 &= k_B T \frac{1}{Q} \sum \frac{\partial}{\partial V} \left( e^{-E_j/k_B T} \right) \\
 &= k_B T \frac{1}{Q} \frac{\partial Q}{\partial V} \\
 P &= k_B T \frac{\partial \ln Q}{\partial V}
 \end{aligned}$$

- Applies the formula to an ideal gas of independent, indistinguishable particles to derive the ideal gas law.
- **Enthalpy:** A state function representign the heat put into the system at constant pressure. *Denoted by  $H$ . Given by*

$$H = U + PV$$

- We have that

$$\begin{aligned}
 dH &= dU + P dV + V dP \\
 &= \delta q - P dV + P dV + V dP \\
 &= \delta q + V dP
 \end{aligned}$$

- At constant pressure ( $dP = 0$ ), we have that  $dH = \delta q$ .
- At constant volume, we have that  $dH = \delta q$  as well?

- **Constant-volume heat capacity.** The following expression. *Denoted by  $C_V$ . Given by*

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N}$$

- **Constant-pressure heat capacity.** The following expression. *Denoted by  $C_P$ . Given by*

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P,N}$$

- For an ideal gas,

$$\begin{aligned}
 dH &= dU + d(PV) \\
 &= nC_V dT + nR dT \\
 &= n(C_V + R) dT
 \end{aligned}$$

- Recall this result from Labalme (2021).

- Considers heat diagrams.

- Recall the enthalpy of phase changes  $\Delta H_{\text{fus}}$ ,  $\Delta H_{\text{vap}}$ , and  $\Delta H_{\text{sub}}$ .
- It follows that

$$H(T) - H(T_0) = \int_{T_0}^T C_p dT + \sum \Delta H_{\text{phase changes}}$$

- **Hess's Law:**  $\Delta H = 0$  around a closed loop.
  - This is because  $H$  is a state function.
- **Standard enthalpy of formation.** Denoted by  $\Delta H_f^\circ$ . Units **kJ/mol**.
  - Calculated from the constituent elements in their standard state, 1 bar, 298.15 K.
- We have, for example, that the  $\Delta H_{\text{vap}}^\circ$  of a substance is the difference of its  $\Delta H_f^\circ$  in its gaseous state and its  $\Delta H_f^\circ$  in its liquid state.
- With the standard enthalpy of formation and the heat capacity  $C_P(T)$ , one gets the enthalpy of formation at nonstandard temperatures.
- To get the enthalpy of formation at non-standard pressures of chemical interest, most of the effect is from the gas components because solids and liquid enthalpy vary little with pressure.
- The direction of change is sometimes in the direction of *positive* enthalpy change.
  - This change is driven by the fact that in these cases, the direction of change is toward the most probable state.
- In a reversible process,  $dU = \delta q_{\text{rev}} - P dV$ . In this case

$$\delta q_{\text{rev}} = dU + P dV = nC_V dT + P dV \neq dnC_V T + PV$$

so  $\delta q_{\text{rev}}$  is not a state function.

- However,

$$\begin{aligned}\frac{\delta q_{\text{rev}}}{T} &= nC_V \frac{dT}{T} + \frac{P dV}{T} \\ &= nC_V \frac{dT}{T} + nR \frac{dV}{V} \\ &= d(nC_V \ln T + nR \ln V)\end{aligned}$$

is a state function.