

# CHEM 26200 (Thermodynamics) Notes

Steven Labalme

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**Part I**

**Statistical Mechanics**

# Week 1

## The Boltzmann Factor and Partition Functions

### 1.1 Overview of Major Results

- 1/10:
- In this course, we will review thermochemistry from intro chem, but go deeper with statistical mechanics.
  - TA: Haozhi.
    - Did his undergrad at Oxford.
    - Has already taught this class in the PME.

- **Boltzmann constant:** The following constant. *Denoted by  $k_B$ . Given by*

$$k_B = 1.381 \times 10^{-23} \text{ J/K}$$

- Equal to the quotient of the ideal gas constant and Avogadro's constant.
- **Ideal gas law:** The following relationship between the pressure  $P$ , volume  $V$ , number of moles  $n$ , and temperature  $T$  of an ideal gas, and the ideal gas constant  $R$ .

$$PV = nRT$$

- Multiplying by the quotient of Avogadro's constant with itself yields

$$PV = nN_A \frac{R}{N_A} T$$

$$PV = Nk_B T$$

where  $N$  is the number of molecules in the system.

- The unit for  $PV$  is Joules.
  - Thus, the above form states that  $PV$  is equal to the number of particles times a tiny unit of energy.
- Relating  $PV$  to the kinetic energy of gas molecules/atoms<sup>[1]</sup>.
  - Pressure originates microscopically from the collisions of particles with the walls of their container.
  - As such, we first seek to derive an expression for the number of collisions per second per area.

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<sup>1</sup>This derivation differs from that on Labalme (2021a, pp. 3–4) and Labalme (2021b, pp. 18–19), in that its approach is from a flux perspective.

- Consider the number  $N(v_x)$  particles with speed  $v_x$  in the  $x$ -direction.
- The quotient  $N(v_x)/V$  is the density in the container of particles with speed  $v_x$ .
- Thus, the flux “through”/to/at the wall is this density, times the area of the wall, times the  $x$ -velocity of the particles.
- Assume an elastic collision of each particle with the wall. Thus, when each particle of mass  $m$  collides with the wall, it transfers  $2mv_x$  of momentum.
- Therefore, since  $F = dp/dt$ , the overall force exerted on the wall by the gas particles moving with speed  $v_x$  is  $2mv_x \cdot N(v_x)/V \cdot v_x \cdot \text{Area}$  times per second.
- But, of course, we must sum over all possible  $v_x$ , so the total force

$$F = \int_{v_x > 0} 2mv_x \cdot \frac{N(v_x)}{V} \cdot v_x \cdot \text{Area} dv_x$$

- It follows that

$$\begin{aligned} P &= \frac{F}{\text{Area}} \\ &= \int_{v_x > 0} 2mv_x^2 \cdot \frac{N(v_x)}{V} dv_x \end{aligned}$$

The factor of  $1/2$  in the following line comes from the fact that we are only integrating over half of the possible  $v_x^2$ s (i.e., the positive ones).

$$\begin{aligned} &= 2m \cdot \frac{N}{V} \cdot \frac{1}{2} \langle v_x^2 \rangle \\ &= \frac{N}{V} m \langle v_x^2 \rangle \\ PV &= Nm \cdot \langle v_x^2 \rangle \end{aligned}$$

Assuming that the gas is not moving in any one direction means that  $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$ . Therefore,

$$\begin{aligned} &= Nm \cdot \frac{1}{3} \langle v^2 \rangle \\ &= \frac{2}{3} N \cdot \frac{1}{2} m \langle v^2 \rangle \\ &= \frac{2}{3} N \cdot \langle E_{KE} \rangle \\ \langle E_{KE} \rangle &= \frac{3}{2} \frac{PV}{N} \\ \langle E_{KE} \rangle &= \frac{3}{2} k_B T \end{aligned}$$

- Note that this applies to all sorts of regimes — we used no properties of the particles (e.g., atom vs. molecule) to derive this relationship.
- Getting the distribution of the gas energies or speed is the next logical step.
- First, though, we consider alternate occurrences of  $k_B T$ .
  - The activation energy of Arrhenius (1889): “To collide is to react” is inaccurate; it must collide with sufficient energy. The molecule must be “activated.”

$$k = Ae^{-E_a/RT} = Ae^{-E_a/k_B T}$$

- The first  $E_a$  is the molar energy of activation; the second is the molecular energy of activation.
  - Yields the probability distribution of a molecule reacting.
- Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q$$

- $\ln Q$  is the ratio inside vs. outside the membrane.
  - $F = N_A e$  where  $e$  is the charge of an electron.
  - Thus,
- $$\Delta E = \frac{RT}{nF} = \frac{k_B T}{ne}$$
- If the potential across the membrane is approximately  $k_B T$ , then  $\ln Q \approx 1$ , so  $Q \approx e$ .
  - Thus, at body temperature ( $T = 310 \text{ K}$ ),  $k_B T/e = 26 \text{ mV}$ .
- The speed of sound: Certainly sound cannot travel faster than the molecules. Therefore, we can derive the following approximation for the speed of sound.

$$\begin{aligned} \frac{1}{2} m \langle v^2 \rangle &= \frac{3}{2} k_B T \\ \sqrt{\langle v^2 \rangle} &= \sqrt{\frac{3 k_B T}{m}} \\ v_{\text{rms}} &= \sqrt{\frac{3 k_B T}{m}} \end{aligned}$$

- This estimate is within 20 – 30 % — take  $m$  to be the average mass of air.
- de Broglie wavelength: A molecule has a kinetic energy approximately equal to  $k_B T$ . Additionally, the quantum mechanical kinetic energy of a molecule aligns with this, as  $\hbar^2 k^2 / 2m \approx k_B T$ . Furthermore, the particle-wave duality relates the momentum to wavelength by  $p = \hbar k = h / \lambda$ . Therefore,

$$\lambda \approx \sqrt{\frac{h^2}{2m k_B T}}$$

- Thus, a gas at STP has a very small de Broglie wavelength and behaves classically.
- Only at very low temperatures with very light gasses do quantum considerations come into play.
- A  $\text{H}_2$  molecule at 300 K has de Broglie wavelength  $\lambda = 1.78 \text{ \AA}$ .
- Note that the quantum mechanical kinetic energy of a free particle is derived as follows.

$$\begin{aligned} \hat{H}\psi &= E\psi \\ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} (e^{ikx}) &= E e^{ikx} \\ \frac{\hbar^2 k^2}{2m} e^{ikx} &= E e^{ikx} \\ E &= \frac{\hbar^2 k^2}{2m} \end{aligned}$$

- **Boltzmann factor:** Gives the relative probability  $p_2/p_1$  of two states  $E_1, E_2$ , provided their respective energies  $E_1, E_2$ . Given by

$$\frac{p_2}{p_1} = e^{-(E_2 - E_1)/k_B T}$$

- Consider states  $E_1, E_2, E_3, \dots$ , denoted by their energies.

- Consistency check: Given

$$\frac{p_2}{p_1} = e^{\frac{-(E_2-E_1)}{k_B T}} \qquad \frac{p_3}{p_2} = e^{\frac{-(E_3-E_2)}{k_B T}}$$

we do indeed have

$$\frac{p_3}{p_1} = \frac{p_3}{p_2} \cdot \frac{p_2}{p_1} = e^{\frac{-(E_3-E_2)}{k_B T} + \frac{-(E_2-E_1)}{k_B T}} = e^{\frac{-(E_3-E_1)}{k_B T}}$$

- We'll take this as God-given for now. Boltzmann derived it with a very good knowledge of the thermodynamics of freshman chemistry.
- We're starting with the above exciting result, and then going back and building up to it over the next three weeks.
- We write the Boltzmann factor for degenerate states as follows.
  - Consider four states at  $E_2$  and one state at  $E_1$ .
  - The Boltzmann factor still tells us that  $p_2/p_1 = e^{-(E_2-E_1)/k_B T}$ , but we have to make the following adjustment. Indeed, the total probability of being in one of the four states at energy  $E_2$  is  $p(E_2) = 4p_2$ , while the total probability of being in the one state at energy  $E_1$  is still just  $p(E_1) = p_1$ .
  - In each state  $E_2$ ,

$$p(E_2) = \frac{N_2}{N_1} e^{-(E_2-E_1)/k_B T}$$

■ Where did  $p_1$  go in the above equation?

- The weekly quiz.
  - The first quiz will be next week.
  - A Canvas quiz – we'll have 24 hours to take it, but only 1 hour to take it.

# References

- Arrhenius, S. A. (1889). Über die dissociationswärme und den einfluß der temperatur auf den dissociationsgrad der elektrolyte. *Zeitschrift für Physikalische Chemie*, 4, 96–116. <https://doi.org/10.1515/zpch-1889-0408>
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