

CHEM 26200 (Thermodynamics) Notes

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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^[1].
 - 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.

¹This 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 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 $p(E_1) = 1p_1$.
 - In each state E_2 ,

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

- 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.

1.2 Boltzmann Factor Examples / Partition Function

1/12:

- We will apply the Boltzmann factor to electronic, magnetic, translational, rotational, and vibrational molecular states.
- Example: Sodium lamp – two lines at 589.6 nm and 589.0 nm with intensity ratio 1:2.

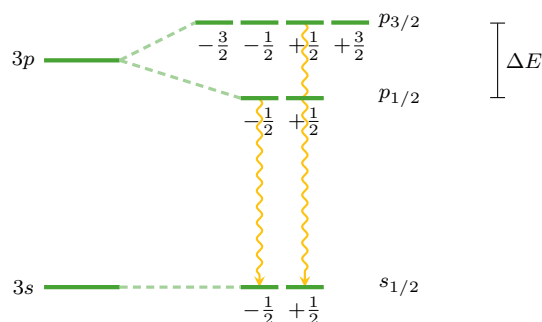


Figure 1.1: Sodium lamp energy levels.

- Street lamps use this (very efficient).
- Also used in astronomy.
- In the sodium atom, there are two energy levels (3s and 3p).
- The states have a spin-orbit coupling effect.

- $3s$ (with $S = 1/2$) splits into two degenerate states $s_{\pm 1/2}$ based on spin.
- $3p$ (with $L = 1$ and $S = 1/2$) splits into two nondegenerate states ($l = \pm 1$ [called $p_{3/2}$] and $l = 0$ [called $p_{1/2}$]), which further subdivide into four (resp. two) degenerate states ($-3/2, -1/2, 1/2, 3/2$ and $-1/2, 1/2$).
- Let ΔE be the difference in energy between the $p_{3/2}$ and $p_{1/2}$. Then

$$\frac{\Delta E}{k_B} = \frac{1}{k_B} \left(\frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} \right) = 25 \text{ K}$$

where $\lambda_1 = 589.6 \text{ nm}$ and $\lambda_2 = 589.0 \text{ nm}$.

- Thus, $e^{-\Delta E/k_B T} \approx 1$ for $T = 300 \text{ K}$ (the temperature in the sodium vapor lamp).
- Therefore,

$$\begin{aligned} \frac{p(E_2)}{p(E_1)} &= \frac{4}{2} \cdot 1 \\ p(E_2) &= 2p(E_1) \end{aligned}$$

• Example: MRI.

- The magnetic field polarizes the spins of the hydrogen protons in our body with $\Delta E = \mu_B B$.
- If we also take $B = 6 \text{ T}$ and $T = 310 \text{ K}$ (body temperature), then

$$\frac{\mu_B B}{k_B T} = 2 \times 10^{-5}$$

- Thus, very few protons actually flip, but with modern technology we can still measure this.

• **Proton magnetic moment:** The magnetic moment of a proton. *Denoted by μ_B . Given by*

$$\mu_B = 1.4 \times 10^{-26} \text{ J/T}$$

• Example: Rotational.

- The rotational energy E_J of a molecule depends on the angular momentum quantum number J and the moment of inertia of the molecule $I = \mu R^2$ via the following relation.

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

- Microwave spectroscopy can be used to find molecules out in the universe.
- At 300 K,

$$\frac{p(J=1)}{p(J=0)} = \frac{3}{1} e^{\frac{-(E_1-E_0)}{k_B T}} = 2.95$$

■ As before $J = 1$ corresponds to states $j = -1, 0, 1$.

- See Figure 18.5 in the textbook.
- There is a range of angular momenta due to the temperature that for $T = 300 \text{ K}$ peaks around $J = 5$.

• Example: Vibrational.

- Here, $\Delta E = E_n - E_{n-1} = h\nu$ for every energy level since $E_n = h\nu(n + 1/2)$.
- It follows that

$$\frac{h\nu}{k_B} = 2800 \text{ K}$$

for CO, meaning that at 300 K, CO will be largely in its ground state.

- The partition function tells us everything we wanna know about a system.

$$Q = \sum_i e^{-E_i/k_B T}$$

- All we need to know is the energy of every state in the system.
- This is impossible for an infinite system, but the Schrödinger equation gives us the energy of a system, so its a great place to start.

- Calculating the total energy from the partition function.

- To construct it, start with

$$Q = \frac{p_1}{p_1} + \frac{p_2}{p_1} + \frac{p_3}{p_1} + \dots = 1 + e^{\frac{-(E_2-E_1)}{k_B T}} + e^{\frac{-(E_3-E_1)}{k_B T}} + \dots$$

- The total energy is equal to

$$\langle E \rangle = E_1 p_1 + E_2 p_2 + E_3 p_3 + \dots$$

- Taking $E_1 = 0$ gives

$$\langle E \rangle = p_1 \left[E_2 \frac{p_2}{p_1} + E_3 \frac{p_3}{p_1} + \dots \right]$$

- Note that

$$\frac{\partial}{\partial T} \left(e^{-E_2/k_B T} \right) = \frac{E_2}{k_B T^2} e^{-E_2/k_B T} = \frac{1}{k_B T^2} (E_2 p_2)$$

- Additionally,

$$\begin{aligned} p_1 &= 1 - (p_2 + p_3 + \dots) \\ &= 1 - p_1 \left(\frac{p_2}{p_1} + \frac{p_3}{p_1} + \dots \right) \\ &= 1 - p_1 (Q - 1) \\ p_1 &= \frac{1}{Q} \end{aligned}$$

- Therefore,

$$\begin{aligned} \langle E \rangle &= p_1 k_B T^2 \frac{\partial}{\partial T} \left(E_1 \frac{p_1}{p_1} + E_2 \frac{p_2}{p_1} + \dots \right) \\ &= p_1 k_B T^2 \frac{\partial Q}{\partial T} \\ &= \frac{1}{Q} k_B T^2 \frac{\partial Q}{\partial T} \\ &= k_B T^2 \frac{\partial}{\partial T} (\ln Q) \end{aligned}$$

- Changing the origin of energy.

- We know that

$$\begin{aligned} Q(E_0) &= Q(E'_0) e^{-(E'_0 - E_0)/k_B T} \\ \ln Q(E_0) &= \ln Q(E'_0) - \frac{E'_0 - E_0}{k_B T} \end{aligned}$$

– Thus,

$$\begin{aligned}\langle E \rangle_{E_0} &= k_B T^2 \frac{\partial}{\partial T} (\ln Q(E_0)) \\ &= k_B T^2 \left(\frac{\partial}{\partial T} (\ln Q(E'_0)) - \frac{\partial}{\partial T} \left(\frac{E'_0 - E_0}{k_B T} \right) \right) \\ &= \langle E \rangle_{E'_0} + (E'_0 - E_0) \\ \langle E \rangle_{E_0} + E_0 &= \langle E \rangle_{E'_0} + E'_0\end{aligned}$$

– So the change of the energy origin does indeed change the total energy by the same amount.

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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