

# CHEM 26100 (Quantum Mechanics) Notes

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# Chapter 1

## From Classical to Quantum Mechanics

### 1.1 Blackbody Radiation

9/27: • The surface of a hot body emits energy in the form of EM radiation.

• Changes that occur with temperature:

- If less than 500 °C, we have IR Radiation (heat).
- If 500 °C to 600 °C, we have visible radiation (a glowing body).
- If 5 000 °C, we have a “white hot” body (short wavelength).

• As a body gets hotter, it emits shorter wavelength radiation.

• **Stefan-Boltzmann law:** The the total emissive power  $R$  (recall that power is en / time) of a blackbody (BB) is given by

$$R(T) = \sigma T^4$$

where  $\sigma \approx 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$  is **Stefan’s constant**.

- Work done by Stefan and Boltzmann (c. 1870 / 1884, respectively).

• **Wien’s 1st Law:** The wavelength for maximum emissive power obeys the equation

$$\lambda_{\text{max}} T = b$$

where  $b = 2.898 \times 10^{-3} \text{ m K}$  is **Wein’s displacement constant**. *Also known as Wien’s displacement law.*

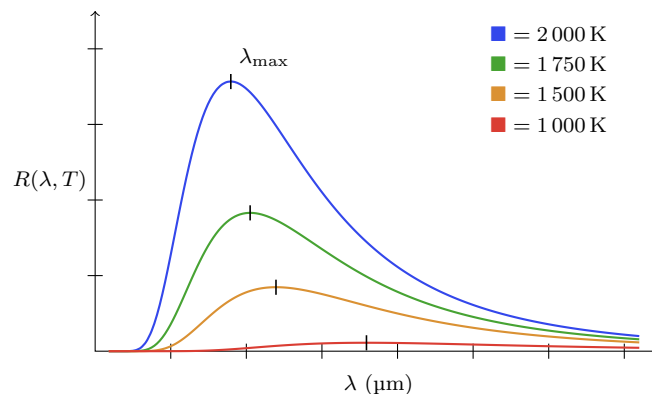


Figure 1.1: Wein’s 1st Law.

- Area under the curve (found with integration) is the total emissive power.
- We now change variables from emissive power  $R$  to energy density  $\rho$  in the BB cavity.

$$\rho(\lambda, T) = \frac{4}{c} R(\lambda, T)$$

- Wien's 2nd Law (1893): The energy density must have a functional relationship with the following form.

$$\rho(\lambda, T) = \frac{f(\lambda T)}{\lambda^5}$$

–  $f(\lambda T)$  cannot be determined from thermodynamics. Thus, something else is needed!

- Lord Rayleigh and his graduate student Jeans (1899) propose a solution.
  - EM: The thermal radiation within a cavity must exist in the form of standing waves.
  - RJ showed that the number  $n$  of standing waves per unit volume, per wavelength has the following form.

$$n(\lambda) = \frac{8\pi}{\lambda^4}$$

– If  $\bar{\epsilon}$  is the average energy in the mode with wavelength  $\lambda$ , then

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4} \bar{\epsilon}$$

- Waves come from atoms in the walls of the BB cavity, which act as linear harmonic oscillators at a frequency  $\nu = c/\lambda$ .
- Assuming thermal equilibrium, we obtain

$$\begin{aligned} \bar{\epsilon} &= \frac{\int_0^\infty \epsilon e^{-\epsilon/kT} d\epsilon}{\int_0^\infty e^{-\epsilon/kT} d\epsilon} \\ &= -\frac{\partial}{\partial \beta} \ln \left( \int_0^\infty e^{-\beta \epsilon} d\epsilon \right) \\ &= \frac{1}{\beta} \\ &= kT \end{aligned}$$

where  $k$  is the Boltzmann constant.

- Basically, we sum all energies  $\epsilon$ , weighted by the probability  $e^{-\epsilon/kT}$  of the energy existing, and divided by the total energy.
- The first equation is equivalent to the second with  $\beta = 1/kT$ .
- Therefore,

$$\rho(\lambda, T) = \frac{8\pi kT}{\lambda^4}$$

- UV catastrophe: Rayleigh's formula diverges from the experimental data for short wavelength.
  - The above formula diverges to  $+\infty$ , driven by the  $\lambda^4$  term in the denominator, as  $\lambda \rightarrow 0$ . However, the amount of radiation of shorter wavelengths should decrease past a point, as seen in Figure 1.1.
- Max Planck comes in, proposes an idea to the German academy that's so radical, they think he's insane, but he's actually right and it lays a key idea for quantum mechanics.
- Planck's key insight: The energy levels of the oscillators are not continuous, but are quantized.

- So we can't actually take an integral as Rayleigh did; we have to take an infinite series.
- In reality,

$$\begin{aligned}\bar{\epsilon} &= \frac{\sum_{n=0}^{\infty} n\epsilon_0 e^{-\beta n\epsilon_0}}{\sum_{n=0}^{\infty} e^{-\beta n\epsilon_0}} \\ &= \frac{\epsilon_0}{e^{\beta\epsilon_0} - 1}\end{aligned}$$

- Thus,

$$\rho(\lambda, T) = \frac{8\pi\epsilon_0}{\lambda^4(e^{hc/\lambda kT} - 1)}$$

- But to satisfy Wien's 2nd law, we must let  $\epsilon_0 \propto 1/\lambda$ . More specifically,  $\epsilon_0 = hc/\lambda = h\nu$ , where  $h$  is Planck's constant.
  - This setup allowed us to get an accurate value for Planck's constant for the first time in history.
- Planck's theory predicts the data of Figure 1.
- A perfect blackbody absorbs and emits radiation at all frequencies.
  - A star is pretty close to a blackbody. The graphite in a pencil is 97% a blackbody. We are all blackbodies.
  - The entire universe can be viewed as a blackbody.
- Princeton and Bell Labs telescopes find **Cosmic Background Radiation** (A. A. Penzias and R. W. Wilson, 1964).
  - Background radiation from the universe itself.
  - $\lambda_{\text{max}} = 7.35 \text{ cm}$ .
  - Isotropic radio signal, that comes from everywhere.
  - From this, you can work out the temperature of the universe from Wein's first law.
  - Thus, the whole universe is a blackbody with a temperature of approximately 3 K.

## 1.2 Chapter 1: The Dawn of the Quantum Theory

*From McQuarrie and Simon (1997).*

- 9/28:
- **Blackbody:** A body which absorbs and emits all frequencies. *Also known as ideal body.*
  - “Many theoretical physicists tried to derive expressions consistent with these experimental curves of intensity versus frequency [see Figure 1.1], but they were all unsuccessful. In fact, the expression that is derived according to the laws of nineteenth century physics is” as follows (McQuarrie & Simon, 1997, p. 3).
  - **Rayleigh-Jeans law:** The equation

$$d\rho(\nu, T) = \rho_\nu(T) d\nu = \frac{8\pi k_B T}{c^3} \nu^2 d\nu$$

where  $\rho_\nu(T) d\nu$  is the “radiant energy density between the frequencies  $\nu$  and  $\nu + d\nu$ ” (McQuarrie & Simon, 1997, p. 3).

- The ultraviolet catastrophe is so named because the frequency increases as the radiation enters the ultraviolet region.
- Planck's solution:

- Rayleigh and Jeans assumed (as does classical physics) that the energies of the electronic oscillators responsible for the emission of the radiation could have any value whatsoever.
- However, Planck assumed discrete oscillator energies proportional to an integral multiple of the frequency:  $E = nh\nu$ , where  $n \in \mathbb{Z}$ .
- Using this quantization energy and ideas from statistical thermodynamics (see Chapter 17), Planck derived the **Planck distribution law for blackbody radiation**.
- The only undetermined constant in the above equation was  $h$ , and Planck showed that if we let  $h = 6.626 \times 10^{-34}$  J s, then this equation gives excellent agreement with the experimental data for all frequencies and temperatures.

- **Planck distribution law for blackbody radiation:** The equation

$$d\rho(\nu, T) = \rho_\nu(T) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1}$$

- Note that for small frequencies, the Planck distribution law and Rayleigh-Jeans law converge, but they diverge for large frequencies, as expected.
- Because  $\nu$  and  $\lambda$  are related by  $\lambda\nu = c$  (and subsequently by  $d\nu = -c/\lambda^2 d\lambda$ ), we can write the Planck distribution law in terms of wavelength, as well.

$$d\rho(\lambda, T) = \rho_\lambda(T) d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda k_B T} - 1}$$

- Differentiating  $\rho_\lambda(T)$  with respect to  $\lambda$  gives an alternate formulation for  $b$ :

$$\lambda_{\max} T = \frac{hc}{4.965 k_B}$$

- Astronomers use the theory of blackbody radiation to estimate the surface temperatures of stars.
  - We can measure the electromagnetic spectrum of a star (which will follow a curve similar to one of the ones in Figure 1.1).
  - Then we can find  $\lambda_{\max}$ . From here, all that's necessary is to plug into Wien's displacement law:

$$T = \frac{b}{\lambda_{\max}}$$

# References

McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach*. University Science Books.