Chemistry 331 **Tutorial #1**

1. In terms of the fundamental physical quantities (mass, length, time, electric charge, degree of temperature), the dimensions of energy (*e.g.*, ½ mv^2) are kg m^2 s^{-2}. What are the dimensions of:

frequency (ν)
Planck's constant (h)
Boltzmann's constant (k)
angular velocity (ω)
moment of inertia (I)
heat capacity (C_V)
force (F)
vacuum permittivity (ε_0)
velocity (v)
momentum ($p = m$v)
angular momentum ($l = I\omega$)
molar heat capacity (C_{Vm})
radiation energy density distribution function ($\rho(T, \nu)$)

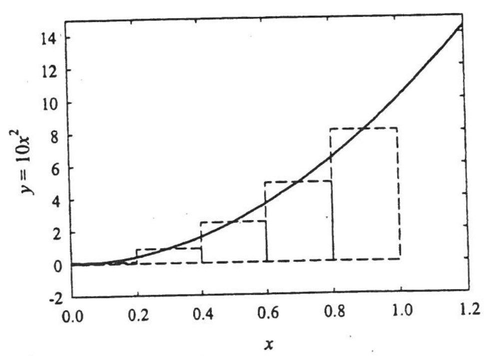
2. Use Planck's radiation law

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

for the energy density distribution of blackbody radiation to show that the frequency of maximum energy density is $\nu_{max} = 2.82kT/h$. Notice that ν_{max} is proportional to the temperature. This is *Wien's displacement law*.

3. At what frequency does the maximum in the energy density distribution function occur at temperatures of a) 4 K, b) 300 K, c) 5700 K (the surface of the sun), d) 10^7 K (the temperature at the center of a thermonuclear explosion)? In what region of the electromagnetic spectrum does each of these maxima occur?

4. Use the trapezoid rule for numerical integration to calculate the area under the curve $y = 10x^2$ from $x = 0$ to $x = 1$. Divide the area into five rectangles of equal width and add their areas. (The first rectangle extending from $x = 0.0$ to $x = 0.2$ and centered on $x = 0.1$ has width 0.2 and height 0.1^2 and therefore area $0.2 \times 0.01 = 0.02$. The second rectangle extending from $x = 0.2$ to $x = 0.4$ and centered on $x = 0.3$ has width 0.2 and height 10×0.3^2 and area $0.2 \times 0.09 = 0.18$, and so on.) Compare your answer with to the exact area evaluated by integration.



Approximate trapezoidal integration of $y = 10x^2$ from $x = 0$ to $x = 1$.

5. Use the definite integral

$$\int_0^\infty \frac{y^3}{e^y - 1}\,\mathrm{d}y = \frac{\pi^4}{15}$$

to show that the total radiation energy density at temperature T is

$$\int_0^\infty \rho(T,\nu)\,\mathrm{d}\nu = \beta T^4$$

where β is an abbreviation for the constant $8\pi^5k^4/(15h^3c^3)$.

6. In quantum chemistry (and in many other areas of science and technology), analysis of problems gives answers in terms of equations that cannot be solved analytically, so numerical methods are essential tools. Using the trapezoid rule (*and a computer!*), estimate the fraction of the total blackbody radiation energy at wavelengths of 400 nm and shorter (*i.e.*, ultraviolet and higher energy radiation) at 5700 K. For these calculations it is convenient to define the dimensionless variable $y = h\nu/kT$ which gives

$$\int_{\nu 1}^{\nu 2} \rho(T,\nu)\,\mathrm{d}\nu = \frac{15}{\pi^4}\beta T^4 \int_{y1}^{y2} \frac{y^3}{e^y - 1}\,\mathrm{d}y$$

7. Why did it take scientists until the late 1800s to discover that that energy is quantized? A contributing factor is the relatively small value of Planck's constant, which leads, in many cases, to energy levels that are so closely spaced they appear to be continuous and therefore "classical".

To illustrate this point, integrate the expression $\mathrm{d}N = (8\pi\upsilon^2/c^3)\mathrm{d}\upsilon$ for the number of blackbody energy levels per unit volume at frequencies from υ to $\upsilon + \mathrm{d}\upsilon$ to calculate the number of accessible energy levels per unit volume at frequencies from 0 to kT/h (corresponding to the average thermal energy, kT). The reciprocal of this number gives a crude measure of the energy level spacing in units of kT.

8. Infrared radiation is often expressed in "wavenumbers" ($1/\lambda$) in units of cm^{-1}. For infrared radiation of wavelength 1.00×10^{-5} m, calculate the wavenumber, frequency, and energy per photon.

9. The work function ϕ for chromium is 4.40 eV. Calculate the kinetic energy of the emitted electrons when chromium is irradiated with ultraviolet radiation of wavelength 200 nm. What is the stopping potential for these electrons?

10. Show that the Balmer series in the emission spectrum of the hydrogen atom occurs at wavelengths between 365 nm and 656 nm. Identify the spectral region of electromagnetic radiation to which Balmer radiation corresponds.

11. Derive Bohr's equation for the energy levels of an ion consisting of a single electron and a nucleus of atomic number Z (*i.e.*, $Z = 2$ for He^+, $Z = 3$ for Li^{2+}, *etc.*). Why is Bohr's equation inaccurate for ions or atoms with more than one electron?

12. Using Bohr's equation, calculate the ionization energy for a) a hydrogen atom, b) a singly charged helium ion (He^+). Express your answers in ev, J and J mol^{-1}.

13. Show that the speed of an electron in the nth Bohr orbit of a hydrogen atom is $e^2/2\varepsilon_0 nh$. Calculate the electron speed for the first Bohr orbit ($n = 1$).

14. Ignoring small relativistic effects, calculate the de Broglie wavelength of a) an electron in the first Bohr orbit of a hydrogen atom, b) an electron with a kinetic energy of 10^5 ev, c) a proton with a kinetic energy of 10^5 ev, d) a helium atom moving at a speed of 500 m s^{-1}.

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(1.) dimensional analysis:

frequency (number of "waves" per unit time, $1\ Hz = s^{-1}$) $\sim time^{-1}$

Force $\sim$ mass $\times$ acceleration $\sim$ mass $\times \frac{dv}{dt} \sim kg\ m\ s^{-2}$

Planck's constant $\sim J \cdot s \sim kg\ m^2\ s^{-2} \cdot s \sim kg\ m^2\ s^{-1}$
(same as angular momentum)

vacuum permittivity $\sim C^2\ s^2\ kg^{-1}\ m^{-3}$

force $\sim \frac{charge^2}{\varepsilon_0\ distance^2}$ $\qquad \varepsilon_0 \sim \frac{charge^2}{(force)\ distance^2} \sim \frac{C^2}{(kg\ m\ s^{-2})\ m^2}$

angular velocity $\sim$ radians(dimensionless) per unit time $\sim s^{-1}$

momentum $\sim$ mass $\times$ velocity $\sim kg\ m\ s^{-1}$

moment of inertia $\sim mr^2 \sim kg\ m^2$

angular momentum $\sim$ mass $\times$ velocity $\times$ distance $\sim kg\ m^2\ s^{-1}$
(same as Planck's constant)

heat capacity $\sim$ J per degree $\sim kg\ m^2\ s^{-2}\ K^{-1}$

molar heat capacity $\sim$ J per degree per mol $\sim kg\ m^2\ s^{-2}\ K^{-1}\ mol^{-1}$

radiation energy density distribution $\sim \left(\frac{h\nu^3}{c^3}\right) \sim \frac{(kg\ m^2\ s^{-1})\ s^{-3}}{(m\ s^{-1})^3}$

$$\sim \frac{(kg\ m^2\ s^{-1})}{m^3} \sim \frac{(kg\ m^2\ s^{-2})\ s}{m^3} \sim \frac{J}{m^3}\ s$$

(2.) $$\rho(T,\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1} = \frac{8\pi}{c^3}\left(\frac{h\nu}{kT}\right)^3 \frac{1}{e^{h\nu/kT}-1}\frac{(kT)^3}{h^2}$$

$$\rho(T,\nu) = A\frac{y^3}{e^y-1} \qquad y \equiv \frac{h\nu}{kT} \qquad A \equiv \frac{8\pi}{c^3}\frac{(kT)^3}{h^2}$$

at constant T, A is constant and y is proportional to ν

$$\frac{\partial\rho}{\partial y} = A\frac{(e^y-1)3y^2 - y^3e^y}{(e^y-1)^2} = \frac{Ay^2}{(e^y-1)^2}(3e^y-3-ye^y)$$

$$\boxed{\frac{\partial\rho}{\partial y} = 0 \text{ when } (3-y)e^y = 3}$$

y	$(3-y)e^y$
1	5.436
2	7.389
3	0
2.81	3.15
2.82	3.02 ✓
2.83	2.88

$$y_{max} = \frac{h\nu_{max}}{kT} = 2.82$$

$$\nu_{max} = 2.82\,kT/h$$

(to 3 significant figures)

(3.) $\nu_{max} = 2.82\,kT/h$

$\underline{T = 4\,K}$, $\nu_{max} = 2.82(1.381\times10^{-23}\,J\,K^{-1})\,4\,K/(6.626\times10^{-34}\,J\,s)$

$\nu_{max} = 2.35\times10^{11}\,s^{-1} = \boxed{2.35\times10^{11}\,Hz}$ (microwaves

($\lambda = 0.00128\,m = 1.28\,mm$)

$\underline{T = 300K}$ $\nu_{max} = 2.35\times10^{11}\left(\frac{300}{4}\right)Hz = \boxed{1.76\times10^{13}\,Hz}$ (microwave infrared

($\nu_{max} \propto T$)

(2. cont.)

$T = 5700\ K$ $\qquad \nu_{max} = 2.35\times 10^{11}\ Hz\left(\frac{5700}{4}\right) = \boxed{3.35\times 10^{14}\ Hz}$ (visible)

$(\lambda = 895\ nm)$

$T = 10^7\ K$ $\qquad \nu_{max} = 2.35\times10^{11}\ Hz\ \frac{10^7}{4} = \boxed{5.88\times10^{17}\ Hz}$ (X rays)

$(\lambda = 0.0510\ nm)$

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4. $\text{area} = (0.2)(10)(0.1^2 + 0.3^2 + 0.5^2 + 0.7^2 + 0.9^2)$
$= 3.300$ (1% too low)

use more trapezoids for a more accurate estimate

$$\text{exact area} = \int_0^1 10x^2\,dx = 10\left.\frac{x^3}{3}\right|_0^1 = \frac{10}{3} = 3\tfrac{1}{3}$$

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5. $y \equiv \frac{h\nu}{kT}$

$$\rho(T) = \int_0^\infty \rho(T,\nu)\,d\nu = \frac{8\pi h}{c^3}\int_0^\infty \frac{\nu^3}{e^{h\nu/kT}-1}\,d\nu$$

total radiation density

$$= \frac{8\pi h}{c^3}\left(\frac{kT}{h}\right)^4\int_0^\infty \frac{\nu^3\left(\frac{h}{kT}\right)^3}{e^{h\nu/kT}}\,d\nu\left(\frac{h}{kT}\right) = \frac{8\pi}{c^3}\frac{(kT)^4}{h^3}\int_0^\infty \frac{y^3}{e^y-1}\,dy$$

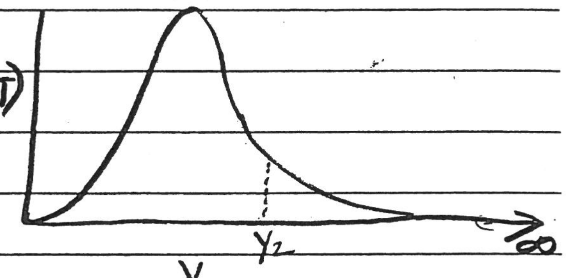
$$\rho(T) = \frac{8\pi}{c^3}\frac{(kT)^4}{h^3}\frac{\pi^4}{15} = \frac{8\pi^5 k^4}{15(ch)^3}T^4 = \beta T^4$$

$$\beta = \frac{8\pi^5 k^4}{15c^3h^3}$$

(6.) What is the fraction of radiation emitted by the sun (assumed to be a blackbody at 5700 K) at ultraviolet and higher frequencies? ($\lambda < 400\,\text{nm}$)

$$y_1 = \frac{h\nu_1}{kT} = \frac{hc}{\lambda_1 kT} = \frac{(6.626\times10^{-34}\,\text{J s})(2.9979\times10^{8}\,\text{m s}^{-1})}{(400\times10^{-9}\,\text{m})(1.381\times10^{-23}\,\text{J K}^{-1})(5700\,\text{K})}$$

$$y_1 = 6.309$$



$$y_2 = \frac{h\nu_2}{kT} = \frac{h\,\infty}{kT} = \infty$$

trapezoid rule, using $\Delta y = 0.02$ and $y = 6.319, 6.339, 6.359, \ldots$ to $y > 30$

$$\left(\begin{array}{l}\text{fraction of total radiation}\\ \text{emitted at } \lambda < 400\,\text{nm}\\ (y_1 > 6.309)\end{array}\right) = \frac{\int_{6.309}^{\infty} \frac{y^3}{e^y - 1}\,dy}{\int_0^{\infty} \frac{y^3}{e^y-1}\,dy} = \frac{\int_{6.309}^{\infty} \frac{y^3}{e^y-1}\,dy}{\pi^4/15}$$

$$= \frac{0.7546}{6.4939} = \boxed{0.1162} \qquad (11.62\,\%)$$

(7.) $$N = \int_0^{kT/h} \frac{8\pi\nu^2}{c^3}\,d\nu = \frac{8\pi}{c^3}\left(\frac{\nu^3}{3}\right)\Bigg|_0^{kT/h} = \frac{8\pi}{3c^3}\left(\frac{kT}{h}\right)^3$$

at 300K $N = 7.594\times10^{13}$ per cubic meter for photons with energies up to kT

$\therefore$ Energy level spacing $\approx \dfrac{1}{7.594\times10^{13}}\,kT \approx \boxed{1.32\times10^{-14}\,kT}$

(8.) $\lambda = 1.00 \times 10^{-5}$ m $= 10 \mu m$

$$\nu = \frac{c}{\lambda} = 2.998 \times 10^{13} \text{ Hz} \quad (\text{frequency})$$

wavenumber $\tilde{\nu} = \frac{1}{\lambda} = 1.00 \times 10^{+5} \text{ m}^{-1} \; \frac{0.01 \text{ m}}{\text{cm}} = \boxed{1000 \text{ cm}^{-1}}$

energy per photon $= h\nu = 1.986 \times 10^{-20}$ J

(9.) kinetic energy of emitted electron = photon energy − work function

$[1 \text{ eV} = (\text{electron charge})(-1 \text{ volt}) = 1.60219 \times 10^{-19} \text{ J}]$

$$\text{kinetic energy} = h\nu - 4.40 \text{ eV} = h\frac{c}{\lambda} - 4.40 \text{ eV}$$

$$= \frac{6.626 \times 10^{-34} \; 2.998 \times 10^{8}}{200 \times 10^{-9}} \text{ J} - (4.40 \text{ eV}) \frac{1.60219 \times 10^{-19} \text{ J}}{\text{eV}}$$

$$= 9.932 \times 10^{-19} \text{ J} - 7.050 \times 10^{-19} \text{ J} = 2.883 \times 10^{-19} \text{ J}$$

$$= \boxed{1.799 \text{ eV}}$$

an applied voltage of -1.799 V will stop these electrons

at the threshold frequency (when the electron kinetic energy is zero) =

$$h\nu^* = \phi \qquad \nu^* = \frac{\phi}{h} = 1.064 \times 10^{15} \text{ Hz}$$

$$\lambda^* = 282 \text{ nm}$$

10. Balmer series for the emission spectrum of H atoms: electrons drop from energy levels $n_2 = 3, 4, 5, \dots$ to $n_1 = 2$

$$\tilde{\nu} = (109677\ \text{cm}^{-1})\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$$

for $n_2 = 3$ to $n_1 = 2$ (lowest energy, lowest frequency)

$$\tilde{\nu}_{min} = 109677\left(\frac{1}{4} - \frac{1}{9}\right) = 15233\ \text{cm}^{-1} \qquad (656\ \text{nm})$$

for $n_2 = \infty$ to $n_1 = 2$ (highest energy, highest frequency)

$$\tilde{\nu}_{max} = 109677\left(\frac{1}{4} - \frac{1}{\infty}\right) = 27419\ \text{cm}^{-1} \qquad (365\ \text{nm})$$

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11. the coulombic force acting on electron is Z times larger than in a hydrogen atom

reduced mass

$$\text{I} \quad \frac{Ze^2}{4\pi\varepsilon_0 r^2} = \frac{\mu v^2}{r} \qquad \mu = \frac{m_e m_Z}{m_e + m_Z} \approx m_e$$

assuming

$$\text{II} \quad \mu v r = \frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \dots \frac{nh}{2\pi} \qquad n = 1, 2, 3, \dots$$

solve I, II for allowed radii $r = \dfrac{4\pi\varepsilon_0 (h/2\pi)^2 n^2}{me^2}$

and allowed energies $E_n = \frac{1}{2}\mu v^2 - \dfrac{Ze}{4\pi\varepsilon_0 r}$

$$\boxed{E_n = -\frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2}} \approx \frac{m_e Z^2 e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2}$$

(11. cont.)

Bohr's equation for the H atom and other one-electron atoms and molecules is inaccurate for multi-electron atoms (e.g., He) and molecules because it only includes nucleus – electron interactions, and not electron-electron interactions (difficult)

(12.) to ionize a hydrogen atom in the ground state ($n_2 = 1$) corresponds to moving an electron from $n_2 = 1$ to $n_1 = \infty$

$$\tilde{\nu} = (109677 \text{ cm}^{-1})\left(\frac{1}{1} - \frac{1}{\infty}\right) = 109677 \text{ cm}^{-1} = \frac{1}{\lambda}$$

equivalent energy $= h\nu = \dfrac{hc}{\lambda}$

$$= (6.62618 \times 10^{-34} \text{ J s})(2.997925 \times 10^{8} \text{ m s}^{-1})(109677 \text{ cm}^{-1})\, 100 \frac{\text{cm}}{\text{m}}$$

$$= 2.1787 \times 10^{-18} \text{ J} \qquad \left(13.598 \text{ eV or } 1312.0 \frac{\text{kJ}}{\text{mol}}\right)$$

for He^+, $Z = 2$, and $E_n \propto Z^2$ (four times larger energy)

$$4(2.1787 \times 10^{-18} \text{ J}) = \boxed{8.7148 \times 10^{-18} \text{ J}} \qquad \left(\begin{array}{l} 54.39 \text{ eV} \\ 5248.0 \text{ kJ mol}^{-1} \end{array}\right)$$

(13.) the Bohr condition $m v r = n h / 2\pi$ (quantized angular momentum)

and $$\frac{e^2}{4\pi\varepsilon_0 r^2} = \frac{m v^2}{r}$$ force balance

combine to give $$r = \frac{4\pi\varepsilon_0}{\mu e^2}\left(\frac{h}{2\pi}\right)^2 n^2 \qquad n = 1, 2, 3, \ldots$$

(13 cont.) reduced mass $\mu = \frac{m_e m_p}{m_e + m_p}$

$$\mu v r = \frac{nh}{2\pi} = \mu v \frac{4\pi\varepsilon_0}{\mu e^2}\frac{h^2}{4\pi^2} n^2$$

$$v = \frac{h}{\cancel{2\pi}}\frac{1}{\cancel{\mu}}\frac{\cancel{\mu} e^2 \cancel{4\pi^2}}{\cancel{4\pi}\varepsilon_0 h^2 n} = \boxed{\frac{e^2}{2\varepsilon_0 h n}}$$

for $n = 1$ $\quad v_1 = \frac{(1.60219 \times 10^{-19})^2}{2(8.854188 \times 10^{-12})(6.62618 \times 10^{-34})(1)}$

$$v_1 = 2.18769 \times 10^{6} \text{ m s}^{-1}$$ (≈ 0.7% of the speed of light)

(14.) a) for an electron in the $n=1$ orbital of a hydrogen atom

$$mvr = \frac{h}{2\pi} \qquad \lambda = \frac{h}{mv} = \frac{h}{\frac{h}{2\pi r}} = 2\pi r$$ (one circumference)

$$r = \frac{\varepsilon_0 h^2}{\mu e^2 \pi} n^2 \qquad r_{n=1} = \frac{\varepsilon_0 h^2}{\pi \mu e^2} = 0.0529466 \text{ nm}$$

$$\lambda = 2\pi r = 0.33267 \text{ nm}$$

b) $$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m}\sqrt{\frac{1}{2}mv^2}} = \frac{h}{\sqrt{2 \times 9.10953 \times 10^{-31}}\sqrt{10^5 \, 1.60219 \times 10^{-19}}} = 0.0038$$

c) $$\lambda = \frac{h}{\sqrt{(2)\, 1.67265 \times 10^{-27}}\sqrt{10^5 \, 1.60219 \times 10^{-19}}} = 0.0000905 \text{ nm}$$

d) $$\lambda = \frac{h}{\frac{4.033 \times 10^{-3}\text{ kg mol}^{-1}}{6.022 \times 10^{+23}\text{ mol}^{-1}} \, 500 \frac{\text{m}}{\text{s}}} = 0.1979 \text{ nm}$$