Chapter 0

Introduction and orientation

Exercises

0.1 Use $E = h\nu$; $h = 6.626 \times 10^{-34}$ J s; $\nu = 1/T$ [T: period]

(a) $E = (6.626 \times 10^{-34}\text{ J s})/(1.0 \times 10^{-15}\text{ s}) = \underline{6.626 \times 10^{-19}\text{ J}}$

(b) $E = h/(1.0 \times 10^{-14}\text{ s}) = \underline{6.626 \times 10^{-20}\text{ J}}$

(c) $E = h/(1.0\text{ s}) = \underline{6.626 \times 10^{-34}\text{ J}}$

0.2 Use Wien's law: $\lambda_{max}T$ = const.; const. = $hc/5k$ [Problem 0.1] = 2.878 mm K [End paper 1 of text]. Hence

$$T = (2.878\text{ mm K})/(480 \times 10^{-9}\text{ m}) \approx \underline{6 \times 10^{3}\text{ K}}$$

0.3 Use the Law of Dulong and Petit (Section 0.2):

molar heat capacity = 25 J K^{-1} $mole^{-1}$ = specific heat capacity × molar mass

The molar mass is therefore 25 J K^{-1} $mole^{-1}$/0.91 J K^{-1} g^{-1} = 27 g mol^{-1}

and the metal is <u>Al</u>.

0.4 The energy of 1.00 mol of photons is given by

$$E = (hc/\lambda) \times 6.02214 \times 10^{23}\text{ photons/mole}$$

giving **(a)** $\underline{2.3 \times 10^{5}\text{ J}}$, **(b)** $\underline{1.20 \times 10^{-3}\text{ J}}$, **(c)** $\underline{9.2 \times 10^{8}\text{ J}}$.

0.5 Use eqn 0.10: $\delta\lambda = 2\lambda_C \sin^2 \frac{1}{2}\theta$

with $\lambda_C = 2.426$ pm and $\theta = 60^0$. Hence $\delta\lambda = 1.213$ pm and the wavelength of the scattered radiation is $\lambda_f = \lambda_i + \delta\lambda = 25.878 \text{ pm} + 1.213 \text{ pm} = \underline{27.091 \text{ pm}}$.

0.6 2.3 eV corresponds to $2.3 \times (1.602 \times 10^{-19} \text{ C}) \text{ V} = 3.7 \times 10^{-19}$ J. Then use eqn 0.7 in the form

$$v = \{(2/m_e)(h\nu - \Phi)\}^{1/2} \quad \text{so long as } h\nu \geq \Phi$$

(a) $h\nu = hc/\lambda = 6.62 \times 10^{-19}$ J when $\lambda = 300$ nm:

$$v = \{[2/(9.10938 \times 10^{-31} \text{ kg})] \times (2.9 \times 10^{-19} \text{ J})\}^{1/2} = \underline{8.0 \times 10^5 \text{ m s}^{-1}}$$

(b) $h\nu = 3.31 \times 10^{-19} \text{ J} < \Phi$; hence no electrons are emitted.

Exercise: Examine the case where the ejection speed is so great that it must be treated relativistically.

0.7 Use eqn 0.11 for the Balmer series wavenumbers:

$$\tilde{\nu} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

with $R_H = 1.097 \times 10^5 \text{ cm}^{-1}$.

The highest wavenumber corresponds to $n = \infty$ and is $\underline{2.743 \times 10^4 \text{ cm}^{-1}}$, corresponding to a wavelength of $1/(2.743 \times 10^4 \text{ cm}^{-1}) = 3.646 \times 10^{-5} \text{ cm} = \underline{364.6 \text{ nm}}$.

The lowest wavenumber corresponds to $n = 3$ and is $\underline{1.524 \times 10^4 \text{ cm}^{-1}}$, corresponding to a wavelength of $1/(1.524 \times 10^4 \text{ cm}^{-1}) = 6.563 \times 10^{-5} \text{ cm} = \underline{656.3 \text{ nm}}$.

0.8 The permitted energy levels of the electron in a hydrogen atom are given by eqn 0.13:

$$E_n = -\frac{\mu e^4}{8h^2\varepsilon_0^2}\cdot\frac{1}{n^2} = -\frac{2.18\times10^{-18}\ \text{J}}{n^2} = -\frac{13.6\,\text{eV}}{n^2}$$

The two lowest levels are therefore

$n = 1$: $E_1 = \underline{-2.18 \times 10^{-18}\ \text{J}} = \underline{-13.6\ \text{eV}}$

$n = 2$: $E_2 = \underline{-5.45 \times 10^{-19}\ \text{J}} = \underline{-3.40\ \text{eV}}$

0.9 The de Broglie wavelength is given by eqn 0.14:

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{Js}}{57\text{g}\times\frac{1\ \text{kg}}{1000\text{g}}\times 80\text{km hr}^{-1}\times\frac{1000\text{m}}{1\ \text{km}}\times\frac{1\text{hr}}{3600\text{s}}}$$
$$= 5.2\times10^{-34}\,\text{m}$$

Problems

0.1

$$\rho = \left(\frac{8\pi hc}{\lambda^5}\right)\frac{e^{-hc/\lambda kT}}{1-e^{-hc/\lambda kT}} \quad \text{[eqn 0.5]}$$

$$= \frac{(8\pi hc/\lambda^5)}{e^{hc/\lambda kT}-1}$$

$$\frac{d\rho}{d\lambda} = -\frac{40\pi hc/\lambda^6}{e^{hc/\lambda kT}-1} + \frac{(8\pi hc/\lambda^5)(hc/\lambda^2 kT)e^{hc/\lambda kT}}{(e^{hc/\lambda kT}-1)^2} = 0$$

That is, at the maximum

$$\frac{5}{\lambda} = \frac{(hc/\lambda^2 kT)e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1} = \frac{(hc/\lambda^2 kT)}{1-e^{-hc/\lambda kT}}$$

and hence

$$\frac{hc}{5\lambda kT} = 1 - e^{-hc/\lambda kT}$$

At short wavelengths ($hc/\lambda kT >> 1$)

$$\frac{hc}{5\lambda kT} \approx 1, \text{ which implies that } \underline{\lambda T \approx hc/5k}$$

Exercise: Confirm that the extremum of ρ is in fact a maximum.

0.4 The Boltzmann distribution is

$$p_i = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}} \quad [\beta = 1/kT]$$

Hence

$$\langle\varepsilon\rangle = \sum_i p_i\varepsilon_i = -\frac{1}{q}\left(\frac{dq}{d\beta}\right) \quad \left[q = \sum_i e^{-\beta\varepsilon_i}\right]$$

In this case, $\varepsilon_i \rightarrow \varepsilon_v = (v + \frac{1}{2})h\nu$, so

$$q = \sum_{v=0}^{\infty} e^{-(v+\frac{1}{2})h\nu\beta} = e^{-\frac{1}{2}h\nu\beta}\sum_{v=0}^{\infty}(e^{-h\nu\beta})^v$$

$$= \frac{e^{-\frac{1}{2}h\nu\beta}}{1-e^{-h\nu\beta}} \quad \left[\sum_n x^n = (1-x)^{-1}\right]$$

Hence

$$\langle\varepsilon\rangle = \tfrac{1}{2}h\nu + \left\{\frac{h\nu e^{-h\nu\beta}}{1-e^{-h\nu\beta}}\right\} = \tfrac{1}{2}h\nu + \frac{h\nu}{e^{h\nu\beta}-1}$$

$$C_V = \frac{N\mathrm{d}\langle\varepsilon\rangle}{\mathrm{d}T} = \frac{N\mathrm{d}\langle\varepsilon\rangle}{\mathrm{d}\beta}\cdot\frac{\mathrm{d}\beta}{\mathrm{d}T} = -\frac{N}{kT^2}\frac{\mathrm{d}\langle\varepsilon\rangle}{\mathrm{d}\beta}$$

$$= \frac{N(h\nu)^2}{kT^2}\frac{e^{h\nu\beta}}{(e^{h\nu\beta}-1)^2} = \frac{Nk(\theta_E/T)^2 e^{h\nu\beta}}{(e^{h\nu\beta}-1)^2} \quad [\theta_E = h\nu/k]$$

There are three modes of oscillation for each atom in a solid, so

$$C_{V,m} = 3Rf \quad f = \frac{(\theta_E/T)^2 e^{\theta_E/T}}{(1-e^{\theta_E/T})^2}$$

as in eqn 0.6a.

Exercise: Derive an expression for the heat capacity of a two-level system, and plot it as a function of temperature.

0.7 For sodium $\theta_D/T = 0.50$; for diamond $\theta_D/T = 6.20$. If we use the Einstein formula (with $\theta_E \approx \theta_D$), then

Na(s): $f = 0.979$; hence $\underline{C_{V,m}/R = 2.94}$

C(d): $f = 0.078$; hence $\underline{C_{V,m}/R = 0.23}$

The Debye formula can be evaluated by numerical integration but it is also tabulated. See the *American Institute of Physics Handbook*, D.E. Gray (ed.), McGraw-Hill (1972), p.4.113. Then

Na(s): $f(\theta_D/T = 0.50) = 0.988$; hence $\underline{C_{V,m}/R = 2.96}$

C(d): $f(\theta_D/T = 6.20) = 0.249$; hence $\underline{C_{V,m}/R = 0.747}$

Exercise: Evaluate $C_{V,m}$ at 300 K for the Group 1 metals.

0.10 Use the experimental data at 195 nm and eqn 0.7 to compute the work function of the metal surface.

$$\Phi = h\nu - E_{\mathrm{K}} = (hc/\lambda) - \tfrac{1}{2} m_{\mathrm{e}} v^2$$

$$= (6.626 \times 10^{-34}\ \mathrm{J\ s})(3.00 \times 10^{8}\ \mathrm{m\ s^{-1}})/(195 \times 10^{-9}\ \mathrm{m}) -$$

$$\tfrac{1}{2}(9.10938 \times 10^{-31}\ \mathrm{kg})(1.23 \times 10^{6}\ \mathrm{m\ s^{-1}})^2$$

$$= 3.303 \times 10^{-19}\ \mathrm{J}$$

When light of wavelength 255 nm is used, the kinetic energy of the ejected electron is

$$E_{\mathrm{K}} = (hc/\lambda) - \Phi$$

$$= (6.626 \times 10^{-34}\ \mathrm{J\ s})(3.00 \times 10^{8}\ \mathrm{m\ s^{-1}})/(255 \times 10^{-9}\ \mathrm{m}) - 3.303 \times 10^{-19}\ \mathrm{J}$$

$$= 4.492 \times 10^{-19}\ \mathrm{J}$$

corresponding to a speed of

$$v = \left(\frac{2E_K}{m_{\mathrm{e}}}\right)^{1/2} = \underline{9.93 \times 10^{5}\ \mathrm{m\ s^{-1}}}$$

Exercise: For the above problem, what is the longest wavelength of light capable of ejecting electrons from the metal surface?

0.13 From eqn 0.11, $1/\lambda = R_{\mathrm{H}}\{(1/2^2) - (1/n^2)\}$, $n = 3, 4, \ldots$

Hence, plot $1/\lambda$ against $1/n^2$, and find R_{H} from the intercept at $n = \infty$ (since then $1/\lambda_\infty = R_{\mathrm{H}}/4$). The data extrapolate (linear regression) to

$$1/\lambda_\infty = 2.743 \times 10^{6}\ \mathrm{m^{-1}} = 2.743 \times 10^{4}\ \mathrm{cm^{-1}}$$

hence

$$R_H = 4 \times (2.743 \times 10^4 \text{ cm}^{-1}) = \underline{1.097 \times 10^5 \text{ cm}^{-1}}$$

The ionization energy (I) is the energy required for the transition $n_2 = \infty \leftarrow n_1 = 1$;

hence $\underline{I = hcR_H} = 2.179 \times 10^{-18}$ J. Because 1 eV = 1.602×10^{-19} J, I = $\underline{13.6 \text{ eV}}$.

0.16 The square of the fine structure constant is

$$\alpha^2 = \frac{e^4}{16\pi^2\hbar^2c^2\varepsilon_0^2} = \frac{e^4}{4h^2c^2\varepsilon_0^2}$$

from which it follows that (using the mass of the electron for the reduced mass in the Rydberg constant):

$$R = \frac{m_e e^4}{8h^3c\varepsilon_0^2} = \frac{m_e c\alpha^2}{2h}$$