Chem 524 – Homework #1 Answers 2013
plus some old ones

(2-4) a. Flux is 3.18×10^{15} ph/s $\lambda = 632.8$ nm

~~(sort of like 2-12 – attached)~~ $E_p = h\nu = hc/\lambda$

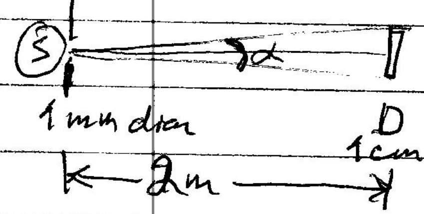
$= 3.14 \times 10^{-19}$ J

$\Phi = 3.18 \times 10^{15} \times 3.14 \times 10^{-19} = \underline{9.98 \times 10^{-4}\ W} \sim 1$ mW

b. $E = \Phi/A = 9.98 \times 10^{-4}\ W / 5\ mm^2 \cdot (10^{-2}\ cm^2/mm^2) = 2 \times 10^{-2}\ W/cm^2$

c. "E" $= 3.18 \times 10^{15} / 0.05\ cm^2 = \underline{6.36 \times 10^{16}\ phot\ s^{-1}\ cm^{-2}}$

(2-7) – basically same idea as 2-3, 2-16 attached



$\Omega = A/d^2 = 1\ cm^2/(200\ cm)^2 = 2.5 \times 10^{-5}$

$B = 2\ W\ cm^{-2}\ sr^{-1}\ nm^{-1} \cdot 2.5 \times 10^{-5}\ sr \cdot (0.05)^2 \pi\ cm^2$

$= 3.93 \times 10^{-7}\ W\ nm^{-1}$

$E = 10\ nm\ (6.6 \times 10^{-19}\ J/ph)^{-1} (3.93 \times 10^{-7}\ W\ nm^{-1})$ $E_p = \frac{hc}{\lambda} = 6.6 \times 10^{-19}$

$= 5.9 \times 10^{12}$ phot/sec

(2-15) if transmit 90% ⇒ absorb 10% $= \boxed{0.1\ \mu W}$

= luminescence would be zero Stokes shift

(i.e. lum at same λ as abs – not happen)

and 100% quantum yield (no loss)

new (a) population – do relative pop $v=0$ and $v=1$

$P_{01}^{1000} = (n_1/n_0) = e^{-\Delta E/kT} = \exp\left(\frac{-3600}{1000 \cdot 2/3}\right)$ $\Delta E_{10} = 3600\ cm^{-1}$

$= 0.0045$ $= 1650\ cm^{-1}$

$P_{01}^{300} = \exp\left(\frac{-3600}{300 \cdot 2/3}\right) = e^{-18} = 1.5 \times 10^{-8}$ $kT \sim 2/3\ cm^{-1}/K$

$P_{01}^{1000} = \exp(-1650/1000 \cdot 2/3) = 8.4 \times 10^{-2}$

$P_{01}^{300} = \exp\left(\frac{-1650}{200}\right) = e^{-8.25} = 2.6 \times 10^{-4}$

extra!

Chem 524—~~2009~~ 2011 Homework Set #1, Some answers

Part I INTRODUCTION

Chapter 2

2-3 #3 An extended source is spherical in shape with a radius of 2.00 cm and emits 12.57 W from 399.5 to 400.5 nm. Determine the spectral radiant emittance, the spectral radiant intensity, and the spectral radiance at 400nm.

Answer:

Radiant emittance: $M = \Phi / A = 12.57W/[4\times\pi\times(2.00cm)^2] = 12.57W/(4\times12.57cm^2) = 0.25\ Wcm^{-2}$

Radiant intensity: $I = \Phi / \Omega = 12.57W/12.57sr = 1.00\ Wsr^{-1}$

Radiance: $B = \Phi / (\Omega A) = 12.57W/[12.57sr\times4\times\pi\times(2.00cm)^2] = 2.00\times10^{-2}\ Wsr^{-1}cm^{-2}$

15 A sample is illuminated with 1.0 μ W of radiation and transmits 90% of the incident radiatio[n]. Calculate the maximum value of the luminescence radiant power that could be observed.

Answer:

$\Phi_L = k(\Phi_0 - \Phi)$

When k=1, $\Phi_{L\max} = \Phi_0 - \Phi = 1.0\ \mu W - 90\%\times1.0\ \mu W = 0.1\ \mu W$

2-16 # 16 The irradiance on a receptor 50cm from a source with a projected area of $0.010cm^2$ is 2.0 μ W cm^{-2}. Calculate the radiance of the source.

& Calculate population of molecular state for vibrations at 100, 600 cm^{-1} and $3000cm^{-1}$ f[or] T=300K.

Answer:

$\Phi_i = B\Omega A_1' = B(A_2/d^2)A_1'$

$2.0\ \mu W\ cm^{-2} = B[0.010cm^2/(50cm)^2]\times0.010cm^2$

Source radiance: $B = 5\times10^7\ \mu W\ cm^{-2}\ sr^{-1}$

plus! 9 Slightly different variation of question a, note energies are 100, 600, 3000 cm^{-1}

$n_i = [n_t g_i e^{-Ei/kT}]/Z(T)$

$n_i / n_0 = e^{[(-Ei-E0)/kT]} = e^{(-h\nu/kT)} = e^{(-hc/\lambda kT)}$

population of molecular state for vibrations at 100 cm^{-1}:

$n_i / n_0 = e^{(-hc/\lambda kT)} = e[(-6.626\times10^{-34}Js\times3.00\times10^8ms^{-1}\times100cm^{-1})/ 1.38\times10^{-23}JK^{-1}\times300K]$

$= e[(-6.626\times10^{-34}Js\times3.00\times10^8ms^{-1}\times10000m^{-1})/ 1.38\times10^{-23}JK^{-1}\times300K]$

$= 0.6188$

population of molecular state for vibrations at 600 cm^{-1}:

$n_i / n_0 = e^{(-hc/\lambda kT)} = e[(-6.626\times10^{-34}Js\times3.00\times10^8ms^{-1}\times600cm^{-1})/ 1.38\times10^{-23}JK^{-1}\times300K]$

$= 0.0561$

population of molecular state for vibrations at 3000 cm^{-1}:

$n_i / n_0 = e^{(-hc/\lambda kT)} = e[(-6.626\times10^{-34}Js\times3.00\times10^8ms^{-1}\times3000cm^{-1})/ 1.38\times10^{-23}JK^{-1}\times300K]$

$= 5.574\times10^{-7}$

2-11

power consumed / output

$3V * 0.25A = 0.75W * 0.01 = 7.5\times10^{-3}W$ light

a. Photons/sec: $550\ nm = 18{,}200\ cm^{-1}$

photon need conversion to energy units compatible with W

$E = h\nu = hc\tilde{\nu} = (6.63\times10^{-34}\ J\cdot s)(3.0\times10^{10}\ cm/s)(1.82\times10^{4}\ cm^{-1})$

$= 3.61\times10^{-19}\ J$

photon rate: $(N/t) = 7.5\times10^{-3}W / 3.61\times10^{-19}J$

$= 2.08\times10^{16}$ phot/sec

b. Cross section $10\ cm^2 \rightarrow$ flux $= \phi_p = 2.08\times10^{15}$ phot/cm²·sec

Vol: $1\ m^3 = (100)^3 cm^3 = 10^6 cm^3$

length of cylinder $10\ cm^2 = A \Rightarrow 10^5\ cm = l$

time to fill cylinder w/ photons: $t = 10^5 cm / 3\times10^{10} cm/s$

$c = l/t \quad t = l/c$

$= 0.33\times10^{-5}\ s$

total photons in volume: $\phi_p \cdot t \cdot A = 2.08\times10^{15} \frac{ph}{cm^2 se} \cdot 0.33\times10^{-5}\ s \cdot 10$

$= 6.86\times10^{9}$ photons/cm²·10

$= 6.86\times10^{10}$ photons in vol.

Jon did much nicer: $\frac{n}{V} = \frac{\phi \cdot dt}{A \cdot dl} = \frac{\phi}{Ac} = \frac{2.08\times10^{16}}{10^{-3}m^2 \cdot 3\times10^{8} m/s}$

$= 6.86\times10^{10}$ ph/m³

c. Assume leaves at $10\ cm^2 = A$

complex: $\phi_p = 2.08\times10^{15}$ ph/cm²·sec

$\phi_p \cdot (hc\tilde{\nu}) = 2.08\times10^{15} \frac{ph}{cm^2 \cdot s} (6.6\times10^{-34} J\cdot s)(3.0\times10^{10} \frac{cm}{s})(1.82\times10^{4} cm^{-1})$

$= 7.52\times10^{-4}\ W\ cm^{-2}$

simpler: power $= 7.5\times10^{-3}\ W/A$

$\phi = 7.5\times10^{-3} W / 10\ cm^2 = 7.5\times10^{-4}\ W/cm^2$

(2-8) Thermal equilibrium $n_1 = n_0 e^{-\Delta E/kT}$

$T = 3000°C = 3273°K$ $kT = 1.38\times10^{-23}\,J/K \cdot 3273K = 4.5\times10^{-20}\,J$

$\Delta E = h\nu = h\frac{c}{\lambda} = 6.63\times10^{-34}\,Js \cdot 3\times10^{8}\,m/s \,/\, 400\times10^{-9}\,m$

~~Fraction~~ excited: $= 4.97\times10^{-19}\,J$

$(n_1/n_0) = \exp\left(-4.97\times10^{-19}/4.5\times10^{-20}\right) = \underline{1.69\times10^{-5}}$

(2-12) $\Phi = 1.0\times10^{-3}\,W$ $d = 2\times10^{-3}\,m = 0.2\,cm$

$A = \pi r^2 = \pi d^2/4 = 3.14\cdot4\times10^{-6}\,m^2/4 = 3.14\times10^{-6}\,m^2$

$= 3.14\times10^{-2}\,cm^2$

Energy density is question but I thought I asked for Irradiance

$E = \partial\Phi/\partial A \simeq \Phi/A = 1.0\times10^{-3}\,W / 3.14\times10^{-2}\,cm^2 = 3.2\times10^{-2}\,W/cm^2$

Energy density is $U = \partial Q/\partial V \sim Q/V$

in a volume → cylinder of diam 2 mm

in 1 s → 1 mJ ⇒ $h = 3\times10^{10}$ cm long

$V = 3\cdot3.14\times10^{8}\,cm^3 = 9.4\times10^{8}\,cm^3$

$U = \dfrac{1.0\times10^{-3}\,J}{9.4\times10^{8}\,cm^3} = 1.06\times10^{-12}\,J/cm^3$

old problem same method

plus 9. CO_2 population — not written well — example p.l does this for 3 vibs as ratios to ground state n_1/n_0, n_2/n_0 ...

ask for 3 temps — just change T in formula

3 vibs — just change $h\nu$ in formula

but population is: $n = n_{000} + n_{100} + n_{010} + n_{001} + n_{200}$ etc

easier if use $k \sim 2/3\,(cm^{-1}/K)$ and assume negligible error

Consider $\nu = 1380\,cm^{-1}$: $n_{010}/n_{000} = \exp\left[-1680/0.67\times1000\right] = 0.081$

$= \exp\left[-1680/0.67\times300\right] = 2.3\times10^{-4}$

$= \exp\left[-1680/0.67\times77\right] = 7.2\times10^{-15}$

etc.

(plus) (b) Again not well-written problem

Lamp: 1 mm × 5 mm filament ⇒ $A = 5\,mm^2$

50 W   Color Temp: 2000 K

old problem

Wien: $\lambda_{max} = \cancel{C_2/4.96T} = \frac{2.897\times10^6}{T} = 1.448\times10^3$ nm

or 1448 nm

(near IR)   or $\underline{1.45\ \mu m}$

Same method

Stefan-Boltzman: $M^b = \pi B^b = \pi \int_0^\infty B^b_\lambda\, d\lambda = \sigma T^4 = 5.67\times10^{-12}\ W cm^{-2} K^{-4} \times T^4$

~~if 90% is light~~: Total radiant emittance of bb:

$5.67\times10^{-12}\cdot(2\times10^3)^4 = \underline{90.7\ W cm^{-2}}$

Area: $5\times10^{-2}\ cm^2$ — problem – emit all direction

so $A \sim 3.14\times5\times10^{-2} \sim 16.7\times10^{-2}$

radiant flux — $90.7\ W\,cm^{-2}\times16.7\times10^{-2}\ cm^2 \sim \underline{15\ W}$

(then correct 90% ~ $\underline{13.5\ W}$)

new (b) – color temp 1500 K

$\lambda_{max} = C_2/4.96\,T = \frac{2.897\times10^6}{T} = \underline{1931\ nm}$

total power: $M = \sigma T^4 = 5.67\times10^{-12}\ W cm^{-2} K^{-4}$

$= 28.7\ W cm^{-2}$

area: $3\times5\ mm^2 = 0.15\ cm^2$ but get 70%

$\underline{I = 3\ W}$ – radiance (intensity)

Part II INCOHERENT LIGHT SOURCES

Chapter 4

(4-1) #1 Usually when one buys a radiation source, the manufacturer will supply spectral radiance data so that one can judge if the intensity is sufficient for a given application. For tungsten lamps, the spectral radiance can be estimated from blackbody parameters.

(a) Calculate the spectral radiance of a tungsten lamp at 500 nm with a color temperature of 2700 K, $\varepsilon_\lambda = 0.40$, and $T_w = 0.92$ in W sr^{-1} cm^{-2} nm^{-1} and photons s^{-1} cm^{-2} sr^{-1} nm^{-1}.

(b) Apply propagation of error mathematics to the blackbody equation to determine how the uncertainty in temperature relates to an uncertainty in radiance. Evaluate the standard deviation and RSD in radiance at 500 nm caused by a 5℃ temperature standard deviation under the conditions in part (a).

Answer:

(a) Radiance of tungsten lamp:

$B_\lambda = \varepsilon(\lambda)T_w(\lambda)B^b_\lambda$

$= \varepsilon(\lambda)T_w(\lambda)\, c_1\lambda^{-5}/(e^{c2/\lambda T}-1)$

$= 0.40\times0.92\times1.190\times10^{16}\ \mathrm{W\ nm^4cm^{-2}sr^{-1}}\times(500\mathrm{nm})^{-5} / (e^{1.438E7\ \mathrm{nm\ K}/(500\mathrm{nm}\times2700\mathrm{K})}-1)$

$= 4.3792\times10^{15}\times(500)^{-5}/ 42271.8\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

$= 3.315\times10^{-3}\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

The energy of a photon: $E = hc/\lambda = (6.63\times10^{-34}\mathrm{Js}\times3.00\times10^{8}\mathrm{ms^{-1}})/(500\times10^{-9}\mathrm{m}) = 3.978\times10^{-19}$ J

$B_\lambda = 3.315\times10^{-3}\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}/3.978\times10^{-19}\ \mathrm{Jphoton^{-1}}$

$= 3.315\times10^{-3}\ \mathrm{Js^{-1}\ sr^{-1}\ cm^{-2}\ nm^{-1}}/3.978\times10^{-19}\ \mathrm{Jphoton^{-1}}$

$= 8.33\times10^{15}$ photons s^{-1} cm^{-2} sr^{-1} nm^{-1}

(b) $B_\lambda(2700K) = 3.315\times10^{-3}\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

$B_\lambda(2695K) = \varepsilon(\lambda)T_w(\lambda)B^b_\lambda$

$= \varepsilon(\lambda)T_w(\lambda)\, c_1\lambda^{-5}/(e^{c2/\lambda T}-1)$

$= 0.40\times0.92\times1.190\times10^{16}\ \mathrm{W\ nm^4cm^{-2}sr^{-1}}\times(500\mathrm{nm})^{-5} / (e^{1.438E7\ \mathrm{nm\ K}/(500\mathrm{nm}\times2695\mathrm{K})}-1)$

$= 4.3792\times10^{15}\times(500)^{-5}/ 43112.87\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

$= 3.250\times10^{-3}\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

$B_\lambda(2705K) = \varepsilon(\lambda)T_w(\lambda)B^b_\lambda$

$= \varepsilon(\lambda)T_w(\lambda)\, c_1\lambda^{-5}/(e^{c2/\lambda T}-1)$

$= 0.40\times0.92\times1.190\times10^{16}\ \mathrm{W\ nm^4cm^{-2}sr^{-1}}\times(500\mathrm{nm})^{-5} / (e^{1.438E7\ \mathrm{nm\ K}/(500\mathrm{nm}\times2705\mathrm{K})}-1)$

$= 4.3792\times10^{15}\times(500)^{-5}/ 41445.55\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

$= 3.381\times10^{-3}\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

Average $B_\lambda(2695K, 2700K, 2705K) = [B_\lambda(2695K) + B_\lambda(2700K) + B_\lambda(2705K)]/3$

$= [3.250\times10^{-3} + 3.315\times10^{-3} + 3.381\times10^{-3}]/3$

$= 3.315\times10^{-3}\ \mathrm{W\ sr^{-1}\ cm^{-2}\ nm^{-1}}$

Standard Deviation: $\sigma = \sqrt{\Sigma(B_\lambda - B_{\lambda average})^2/(n-1)} = 6.550\times10^{-5}$

$RSD = \sigma / B_{\lambda average} = 6.550\times10^{-5}/3.315\times10^{-3} \times 100\% = 1.976\%$

4-2 Ruby 10 cm long
1.58×10^{19} cm^{-3} conc
1.27×10^{-20} cm^{+2} crossection 694 nm

a. (p35) defines $A = 0.434\,\sigma b n$ or $\alpha = \sigma b n$

$$T = e^{-\alpha} = \exp[-(1.27\times10^{-20}\,cm^2)(10\,cm)(1.58\times10^{19}\,cm^{-3})]$$

$$= e^{-(2.0066)} = \cancel{\quad} \; \underline{0.134}$$

b. Threshold population inversion and number density upper need

$$(n_j - n_i)_{th} = \frac{\ln(1/\rho_1\rho_2)}{2\sigma b}$$ eqn 4-18 derived from gain

$\rho_1 = 0.99$, $\rho_2 = 0.74$; $b = 10\,cm$

but σ is problem - can assume σ = groundstate value but that would be a two level system so not very realistic

$$(n_j - n_i)_{th} = \frac{\ln(1/(0.99)(0.74))}{2(1.27\times10^{-20}\,cm^2)(10\,cm)}$$

$$= \underline{1.23 \times 10^{18}\ cm^{-3}}$$

This implies

$$n_j - n_i = \Delta n$$
$$n_j + n_i = n_T$$
$$2n_j = \Delta n + n_T$$
$$n_j = (1.23\times10^{18} + 1.58\times10^{19})/2\ cm^{-3}$$
$$= \underline{0.85 \times 10^{19}\ cm^{-3}}$$

Note not physically reasonable
problem is a bit defective

Part III LASER LIGHT SOURCES

Chapter 4

4-14 #14 Calculate the longitudinal mode separation for a 0.25 m laser in Hz and nm for lasing wavelength of 488 nm.

Answer:

Longitudinal mode are separated by frequency difference $\Delta\nu_n = c/2d = 3.00\times10^8\ ms^{-1}/(2\times0.25m)$
$= 6.00\times10^8$ Hz

1.4

1.4 If two levels at 300K are in thermal equilibrium with n2/n1 = 1/e, calculate the frequency of the transition from 1→2. In what part of the spectrum does this occur?

Answer:

modify values method OK

$n_2/n_1 = e^{(-h\Delta\nu/kT)} = 1/e$

$e^{(-h\Delta\nu/kT)} = e^{-1} \rightarrow -h\Delta\nu/kT = -1$

$\Delta\nu = kT/h = (1.38\times10^{-23}\ Jk^{-1}\times300K)/6.63\times10^{-34}Js = 6.24\times10^{12}Hz$

$\lambda = c/\Delta\nu = 3.00\times10^8 mS^{-1}/6.24\times10^{12}Hz = 48.08\ \mu m$ (middle IR) ~ 200 cm⁻¹ (far-IR)

2.0

2.0 Calculate the number of longitudinal modes that occur in $\Delta\lambda$ = 1nm at $\lambda^0 = 1.06\ \mu$ for a 1 m long laser cavity.

Answer:

modify values method OK

$\lambda^1 = \lambda^0 - 1 = 1.06\mu - 1\times10^{-3}\mu = 1.059\mu = 1059nm$

$\nu^0 = c/\lambda^0 = 3.00\times10^8 mS^{-1}/1.06\ \mu = 3.00\times10^8 mS^{-1}/1.06\times10^{-6}m = 2.8301887\times10^{14}Hz$

$\nu^1 = c/\lambda^1 = 3.00\times10^8 mS^{-1}/1.059\ \mu = 3.00\times10^8 mS^{-1}/1.059\times10^{-6}m = 2.8328612\times10^{14}Hz$

$\nu_n = \nu^1 - \nu^0 = 2.8328612\times10^{14}Hz - 2.8301887\times10^{14}Hz = 2.6725\times10^{11}Hz$

$\nu_n = nc/2d \rightarrow n = 2\nu_n d/c = (2\times2.6725\times10^{11}Hz\times1m)/(3.00\times10^8 mS^{-1})$
$= 1.78\times10^3$

4.4 Question 4.4: Ar+ Ion laser (from Kansas State site)

The difference between adjacent modes in Ar+ Ion laser is 100MHz. The mirrors are at the end of the laser tube.

Calculate: 1. The length of the laser cavity.

2. The mode number of the wavelength 488[nm].

3. The change in difference between adjacent modes when the tube is shortened to half its length.

Answer:

1. $\Delta\nu_n = c/2d \rightarrow d = c/2\Delta\nu_n = 1.50$ m

2. $\nu_n = c/\lambda = 3.00\times10^8 ms^{-1}/488nm = 6.15\times10^{14}Hz$

$m = 2\nu_n d/c = (2\times6.15\times10^{14}Hz\times1.50m)/3.00\times10^8 ms^{-1} = 6.15\times10^6$

3. $m = 2\nu_n d'/c = (2\times6.15\times10^{14}Hz\times0.75m)/3.00\times10^8 ms^{-1} = 3.075\times10^6$

Thanks to Ling Wu for answers