Solutions to **Homework #3** Chemistry 524 by Gomez Yoder
(Suicide assignment)

Solutions for $\boxed{HW\ 3-13}$ cobbled from old ones

Some missing problems

#4-3) 1P28 photomultiplier
$1.0\times10^{7}\ \Omega$ feedback resistor
$V = 800\ V$
collection efficiency = 1.00
$\lambda = 500\ nm$
$\Phi = 1.0\times10^{-11}\ W$

a) from figure D-1 b
measured gain (m) $= 6\times10^{5}$

b) from figure D-1 a
$K(\lambda) = 0.063$ $\quad I_p = \Phi/h\nu = \frac{\Phi\lambda}{hc}$

$$i_{cp} = \frac{eK(\lambda)\Phi\lambda}{hc} = \frac{(1.6\times10^{-19}C)(0.063)(1.0\times10^{-11}W)(500\times10^{-9}m)}{(6.626\times10^{-34}J\cdot s)(3.00\times10^{8}m/s)} = 2.5\times10^{-13}A$$

One could have also used the abs. sens. $\times\ \Phi$ for this one.

c) $i_{ap} = m\, i_{cp} = (6\times10^{5})(2.5\times10^{-13}A) = 1.5\times10^{-7}A$

d) $i_{cp} = e\, r_{cp}$

$$\Rightarrow r_{cp} = \frac{i_{cp}}{e} = \frac{2.5\times10^{-13}A\ (C/s)}{1.6\times10^{-19}C} = 1.6\times10^{6}\ s^{-1}$$

e) from fig D-2 a $\quad i_{ad} = 2\times10^{-9}A$

f) $i_{cd} = i_{th} \Rightarrow i_{ad} = m\, i_{cd}$

$$\Rightarrow i_{cd} = \frac{i_{ad}}{m} = \frac{2\times10^{-9}A}{6\times10^{5}} = 3.3\times10^{-15}A$$

g) $E_o = i_{ap}\times R_L = (1.5\times10^{-7}A)(1.0\times10^{7}\Omega) = 1.5\ V$

h) $E_d = i_{ad}\times R_L = (2\times10^{-9}A)(1.0\times10^{7}\Omega) = 0.02\ V$

Extra

4-7 - a) $0.08\ AW^{-1}$ $\quad 400nm \Rightarrow E = h\nu = hc/\lambda = \frac{6.6\times10^{-34}J\cdot s\cdot 2.99\times10^{8}m/s}{4\times10^{-7}m} = 4.9\times10^{-19}J/ph$

$A = C/s$ $\not\equiv$ photoelect $[1.6\times10^{-19}C/4.9\times10^{-19}J]^{-1} = 3.06$
if 1:1

$0.08\ AW^{-1} = 0.08\ C/J$ observed but should be $3.06 \Rightarrow$ 2.6% quantum eff

b) $2.75\times10^{5}\ ph/s \times 2.6\% \times \cancel{0.9} = 6.43\times10^{3}$ pulse/sec
(only 2.6% of photons make electron which ~~each~~ makes pulse)

Current: no multiplication $- 6.43\times10^{3}\cdot 1.6\times10^{-19}\ C/s = 1.03\times10^{-18}$ Amp

4-15

$$D^* = D\, A^{1/2}\, (\Delta f)^{1/2}$$

$$D = D^*/[A^{1/2}(\Delta f)^{1/2}] = \frac{1.0\times10^9 \text{ cm Hz}^{1/2}\text{ W}^{-1}}{(0.1\text{ cm}^2)^{1/2}\ (1\text{ Hz})^{1/2}}$$

$$= 3.16\times10^9 \text{ W}^{-1}$$

$$\Phi_n = 1/D = 3.16\times10^{-10}\text{ W} \qquad (1/D \equiv NEP)$$

4-16

$$3.6\text{ pC} = 12\text{ pA }\mu\text{W}^{-1}\text{ cm}^2 \times 1.0\ \mu\text{W cm}^{-2}\times t\,(s)$$

$$t\,(s) = \frac{3.6\text{ pC}}{12\text{ pA}\times 1.0} = \underline{0.3\ (s)}$$

Electron-holes pairs

$$= \frac{3.6\text{ pC}}{1.6\times10^{-19}\text{ C}} = \frac{3.6\times10^{-12}\text{ C}}{1.6\times10^{-19}\text{ C}} = \underline{2.25\times10^7}$$

4-17

$$r' = r(1 - r\tau) \qquad r' = 0.99\,r$$

$$0.99\,r = r\,(1 - r\times 2\text{ ns})$$

$$0.99 = 1 - 2r$$

$$r = 5\times10^{-3}\ (\text{ns})^{-1} \Rightarrow \underline{5\times10^6\ \text{s}^{-1}}$$

5-2

* a).

$$\Delta f = (2t)^{-1} = (2 \times 0.5\ s)^{-1} = 1\ Hz$$

$$K = 2e\Delta f(1+\alpha)$$
$$= 2 \times 1.6 \times 10^{-19}\ (C) \times 1\ (Hz) \times (1+0.3)$$
$$= 4.2 \times 10^{-19}\ \cancel{As^{-1}}\ A \qquad (Cs^{-1})$$

?— $mG = E_{fs}/i_r = \frac{1.00\ V}{1.0 \times 10^{-11} A} = 1.0 \times 10^{11}\ V \cdot A^{-1}$

$mGK = 4.6 \times 10^{-8}\ Vs^{-1}$

b) When $A = 1$ $\quad T = 10\%$

$$\sigma_A = \frac{0.43}{E_r}\left[KmGE_rT^{-1} + (\xi E_r)^2 + \left(\frac{\sigma_{dt}}{T}\right)^2\right]^{1/2}$$

$$E_r = E_{fs} = 1.00\ V$$

$$KmGE_rT^{-1} = 4.2 \times 10^{-7}$$

$$(\xi E_r)^2 = (2.0 \times 10^{-4} \times 1.0)^2 = 4.0 \times 10^{-8}$$

$$\left(\frac{\sigma_{dt}}{T}\right)^2 = \left(\frac{4.0 \times 10^{-5}}{0.1}\right)^2 = 1.6 \times 10^{-7}$$

$$\frac{\sigma_A}{A} = 3.4 \times 10^{-4}$$

When $A = 2$ $\quad T = 1\%$

Similarly

$$\sigma_A = \frac{0.43}{E_r}\left[4.2 \times 10^{-6} + 4.0 \times 10^{-8} + 1.6 \times 10^{-5}\right]^{1/2}$$

$$= 1.9 \times 10^{-3}$$

$$\frac{\sigma_A}{A} = 9.5 \times 10^{-4}$$

When $A=0$. No signal Still have noise

$$\frac{\sigma_A}{A} = \infty \qquad \sigma_A = \frac{0.43}{E_r}\left[4.2\times10^{-8} + 4.3\times10^{-8} + 1.6\times10^{-9}\right]^{1/2}$$

c). $A = 1$ Signal shot noise limiting

$A = 2$ 0% T noise limiting

$A = 0$ Signal shot and flicker noise limiting

? d). Increase E_{fs} and decrease in makes mG bigger. and thus increase signal shot noise ~~and~~ ~~reference~~ ~~flicker~~ ~~shot~~ noise. ~~Therefore for A = 2, signal shot and flicker noise may become dominantant~~ poor phrase

5-4.

$$\sigma_J = (4kTR\Delta f)^{1/2} \qquad (5\text{-}15)$$
$$= (1.6\times10^{-20} R\,\Delta f)^{1/2} \qquad \text{at } 25°C$$
$$= (1.6\times10^{-20}\times10^{8}\times1)^{1/2}$$
$$= 1.3\times10^{-6} \quad V s^{1/2}$$

(5)

5-10)

(a) Signal flicker noise limited → signal is proportional to noise.

(b) Signal shot noise limited

(c) Blank noise limited. → noise is independant of signal.

5-17)

for signal shot noise limited,
S/N enhancement of the multichannel spectrometer

$$= n^{1/2}$$
$$= \left(\frac{100s}{10s}\right)^{1/2}$$
$$= 10^{1/2}$$
$$= 3.16$$

single scan takes 10x longer to scan once

for background shot noise limited,
S/N enhancement $= n^{1/2}$
$= 3.16$

for signal flicker noise limited, no S/N enhancement.

R

6

6-3

a)

	A			
0 ng.mL^{-1}	4.32×10^{-3}	-8.69×10^{-3}	4.36×10^{-3}	-4.70×10^{-3}
10 ng.ml^{-1}	0.0980	0.103	0.0925	
unknown	0.0472	0.0414	0.0461	

Means for 0 ng $\bar{A} = -4.71 \times 10^{-3} \times \frac{1}{4} = -1.18 \times 10^{-3}$

10 ng $\bar{A} = 0.0978$

unknown $\bar{A} = 0.0449$

b). $$S_A = \left(\frac{\sum_i (A_i - \bar{A})^2}{N-1} \right)^{1/2}$$

$= 6.58 \times 10^{-3}$ for 0 ng·mL^{-1}

5.25×10^{-3} for 10 ng·ml^{-1}

3.08×10^{-3} for unknown

c). $$m = \frac{\Delta A}{\Delta C} = \frac{0.0978 - (-1.18 \times 10^{-3})}{10 \text{ ng} \cdot \text{ml}^{-1}}$$

$= 9.90 \times 10^{-3}$ ng^{-1}. ml

d). $$\gamma = \frac{m}{S} = \frac{9.90 \times 10^{-3} \text{ ng}^{-1} \cdot \text{ml}}{5.25 \times 10^{-3}} = 1.89 \text{ ng}^{-1} \cdot \text{ml}$$

f) for 98% level of confidence, $k=3$

$$\mu_E = \bar{E}_E \pm \frac{t_\alpha S_s}{n^{1/2}}$$

$\alpha = 0.01$, $t_{0.01} = 6.965$, $n=3$

$$\therefore \mu_E = 1.083 \pm \frac{6.965 \times 0.018}{\sqrt{3}}$$

$$= 1.083 \pm 0.072 \text{ V}$$

(g) $\mu_c = 5.20$ ng mL^{-1} , mean analyte signal = 0.487 V

$$\therefore \bar{c} = 0.487 / 0.1003 = 4.86 \text{ ng mL}^{-1}$$

$$\mu_c = \bar{c} \pm \frac{t_\alpha S_c}{n^{1/2}} , \quad t = \left| \frac{\bar{c} - \mu_c}{S_c / n^{1/2}} \right|$$

$$S_c = S_s / m = \frac{0.019}{0.1003} = 0.1894 \text{ ng mL}^{-1}$$

for $n=3$, 98% confidence level.

$t_{0.01} = 6.965$, $n=3$.

$$\therefore t = \left| \frac{4.86 - 5.20}{0.1894/\sqrt{3}} \right| = 3.159$$

$t < t_{0.01}$

$\therefore$ there is no systematic error.

Set # 3 continued 3013

8

Problem ~~Set #4~~ — Additional answers by TAK + old keys

7.5 — 422.7 nm — 3000 K — Ca, $m = 40.08\ \text{g/mol}^{-1}$

$$\Delta\nu_D = 2\left[\frac{2\ln 2\, k_B T}{m}\right]^{1/2}\frac{\nu_m}{c}$$

$$\frac{\Delta\lambda_D}{\lambda} = 7.16\times10^{-7}\sqrt{T}/\sqrt{M}$$

$$\Delta\lambda_D = 7.16\times10^{-7}\frac{\sqrt{3000}}{\sqrt{40}}\,422.7 = 2.62\times10^{-3}\ \text{nm}$$

7.7. Na

$2P_{3/2}\ (g=4) - g_j$

$2S_{1/2}\ (g=2) - g_i$

$\lambda = 589$ nm absorbance $gf = 1.3$

g – lower level deg

f – emission f_{ji}

$\boxed{gf = g_i f_{ji}}$

$f_{ij} \sim B_{ij}$

$g_j f_{ji} = g_i f_{ij} \sim g_i B_{ij} = g_j B_{ji}$ (F-4)

f_{ij} – absorp. oscill strength

A_{ji} – spont. emission

$$A_{ji} = \frac{6.67\times10^{-5}\, g_i f_{ij}}{g_j\ \lambda_m^2}$$

$f_{ij} = (\cancel{gf}/g_i)\, f_{ji} = \cancel{g}\, f_{ji}$ (problem states f is emission oscillator strength)

$gf = g_i f_{ji}$

$1.3 = g_i f_{ji} = 2f$

$f_{ji} = f_{ij}\ \frac{g_i}{g_j}$ (F-14) emission oscillator strength

$gf = g_i f_{ji} = g_j f_{ij}$ (F 15)

~~note~~ these are inconsistent

$\boxed{\text{F-15 must be incorrect}}$!!!

$$A_{ji} = \frac{6.67\times10^{-5}\,\cancel{(g_i f)}\ 2\cdot(1.3/2)}{g_j\ \lambda_m^2}\quad \lambda_m \text{ in nm}$$

$$= \frac{6.67\times10^{-5}\,(1.3)}{4\cdot(\cancel{.}589\cancel{\times10})^2}$$

$6.25\times10^{7}\ \text{s}^{-1}$

~~$2.5\times10^{8}\ \text{s}^{-1}$~~

~~F15~~

$\tau_r = (A_{ji})^{-1} = \cancel{4\times10^{-9}\text{ s}}\ 0.16\times10^{-7}\ \text{s}$

This problem is a bad one because ~~Appendix~~ E is not self consistent

7.10 a) Hg allowed $\Delta S = 0,\ \Delta L = \pm1,\ \Delta J = 0, \pm1\ (\Delta l = \pm1)$

$(6s)^2\,(^1S_0) \rightarrow 6s6p\,(^1P_0) \rightarrow 6s7s\,(^1P_0)$

$\cancel{6s6p(^3P_{1})} \leftrightarrow 6s7s\,(^3S_1)$

b) cold (room temp) only populate $(6s)^2\,(^1S_0)$

so $(6s)^2\ ^1S_0 \rightarrow (6s6p)\ ^1P_0$ & only transition

? 7.11

6 6)

x (c_s')	S (mV)
0	18
2.997×10^{-3}	24
5.989×10^{-3}	30
8.973×10^{-3}	36
1.1952×10^{-2}	42
1.492×10^{-2}	48

conc = 3.00 g/L = 3 mg/ml

ex 1 ml → $\frac{3\text{ mg Sr}}{1000\text{ ml}+1\text{ ml}} = 2.997\times10^{-3}$ mg/ml

need the <u>absolute value</u> of x-intercept

eq. for line (according to my calculator);

$y = 2010.5x + 17.98$

set y to zero

$2010.5x = 17.98$

$x = 8.94\times10^{-3}$ mg/ml = 8.94 g/L

For single addition of <u>2 ml</u>.

$$c_x = \frac{S_x V_s C_s}{S_{x+s}(V_x+V_s) - S_x V_x} = \frac{18_{mV}(2\text{ ml})(3\text{ mg/ml})}{30\text{ mV}(1002\text{ ml}) - 18\text{ v}(1000\text{ ml})} = 8.96\times10^{-3}\text{ mg/ml} = 8.96\text{ g/}$$

Exam

6-9) $k = 2$; $G = 1.0\times10^{6}\ VA^{-1}$ (sig. processor) ; $m = 1.0\times10^{6}$ (PMT)

$\Delta f = 1.0$ Hz ; $\alpha = 0.30$; cal. curve slope = $1.0\text{ mV}\cdot\text{nM}^{-1}$; $E_B = 0.1$

<u>limited by background luminescence</u>

Find DL

$$D_L = \frac{k S_{b,K}}{m}$$

$$S_b = (mGKE)^{1/2} = [2e\Delta f(1+\alpha)mGE]^{1/2} = [2(1.6\times10^{-19})(1.0)(1+0.3)(1.0\times10^{6})(0$$

$= 2.0\times10^{-7}$ V

$= 2(2.0\times10^{-10}\text{ mV}) = 4.0\times10^{-10}$ nM

19

12-1 $k_F = 10^9 \quad k_{nr} = 9\times10^9\ s^{-1}$

$\phi_F = k_F/k_F+k_{nr} = 10^9/(9+1)\times10^9 = 0.1$

$\tau_F = (k_F)^{-1} = 10^{-9}s$

12.4

Integrated molar absorptivity

$$\bar{\varepsilon} = 1.065\ \varepsilon_m \cdot \Delta\nu$$

This assumes band is equivalent to triangle

$$= 1.065 \times \underbrace{15\ L\ mol^{-1}\ cm^{-1}}_{\varepsilon_m} \times \underbrace{600\ cm^{-1} \times 3\times10^{10}\ cm\cdot s^{-1}}_{\Delta\nu}$$

$$= 2.88\times10^{14}\ L\ mol^{-1}\ cm^{-1}\ Hz$$

some people tried to use $\frac{1.06\ \varepsilon c\Delta\lambda}{\lambda^2}$

but recall $\Delta\lambda \neq \frac{1}{\Delta}$

Oscillator strength

$$f_{ij} = 1.53\times10^{-19}\ \varepsilon_m\ \Delta\nu$$

$$= 4.13\times10^{-5}\ \cancel{L\ mol^{-1}\ cm^{-1}\ Hz}$$

simplest the integral but easy to do

Transition probability

$$R^2 = 9.46\times10^{-24}\ a^2 \qquad a \approx 3\text{Å} = 3\times10^{-10}\ m$$

$$\approx 9\times10^{-43}\ J\ cm^3$$

This is actually the "Dipole Strength" and is proportional to transition probability

Einstein A_{ji} is value I would have looked for but book clearly favors R^2

$$A_{ji} = \frac{64\pi^4 R^2}{3h\lambda_m^3 g_i}$$

11[redacted]

12.9

a). Neglect K_{ic} . $K_{nr} = K_{ec} + K_{isc}$

$$\phi_F = \frac{K_F}{K_F + K_{ec} + K_{isc}} = \frac{2.0 \times 10^{+8}}{2.0 \times 10^{+8} + 5 \times 10^{7} + 2 \times 10^{8}}$$

$$= 0.44$$

$$\tau_F = \frac{1}{K_F + K_{nr}} = 2.2\,[redacted] \times 10^{-9}\ \text{s} = 2.2\,[redacted]\ \text{ns}$$

b).

$$\phi_P = \left(\frac{K_P}{K_P + K'_{nr}}\right)\left(\frac{K_{isc}}{K_F + K_{nr}}\right)$$

$$= \left(\frac{K_P}{K_P + K'_{ec}}\right)\left(\frac{K_{isc}}{K_F + K_{ec} + K_{isc}}\right)$$

$$= \left(\frac{0.70}{0.70 + 0.20}\right)\left(\frac{2 \times 10^{8}}{2 \times 10^{8} + 5 \times 10^{7} + 2 \times 10^{8}}\right)$$

$$= 0.35$$

$$\tau_P = \frac{1}{K_P + K'_{nr}} = [redacted]\ \text{s}$$