CHEM 226

Analytical Spectroscopy

EXAM #1

February 22, 2000

Name:___________________________

Date:____________________________

Start Time:______________________

End Time:_______________________

INSTRUCTIONS: Answer **all** of the questions that follow in this exam. You must show **all** of your work in order to receive full credit. You might find the following physical constants and conversion factors useful:

$k = 1.381 \times 10^{-16}$ erg/K

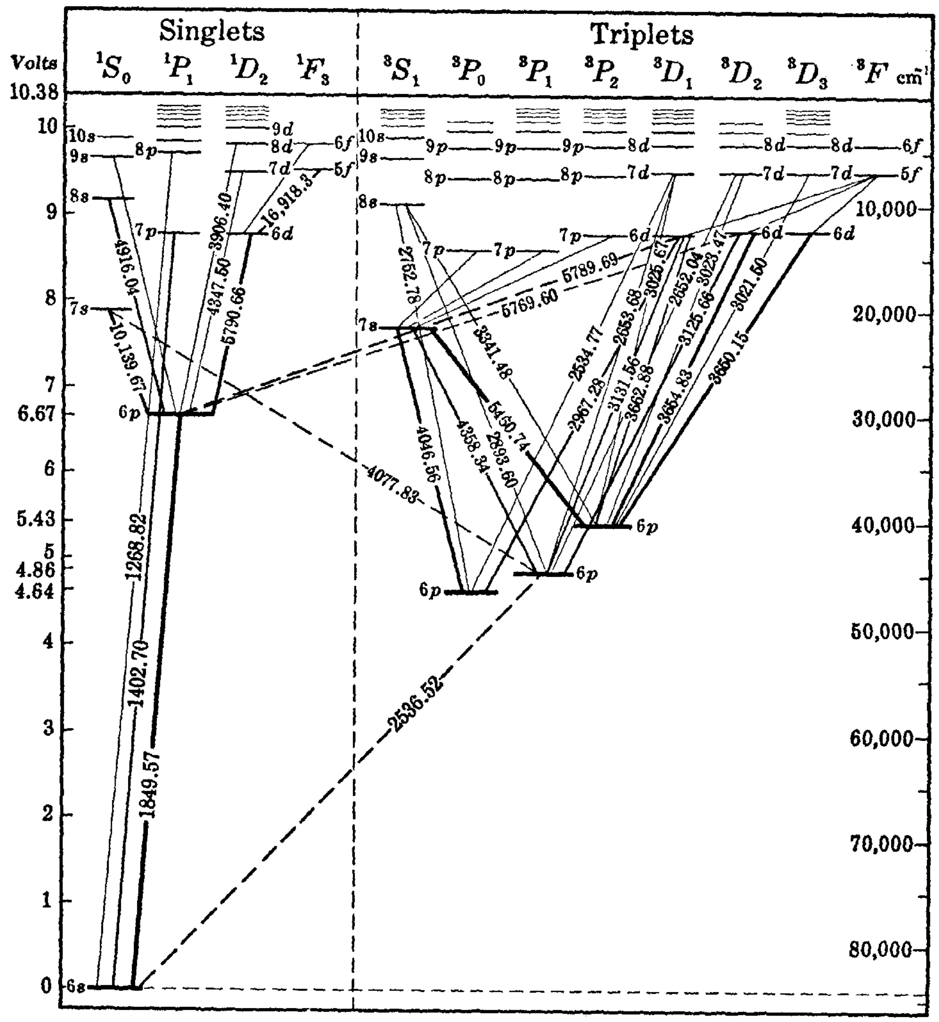
$1 \text{ eV} = 8067.5 \text{ cm}^{-1} = 1.60 \times 10^{-12}$ erg

$h = 6.626 \times 10^{-27}$ erg-sec $= 6.626 \times 10^{-34}$ Joule-sec

$c = 3.00 \times 10^{10}$cm/sec

"I love hearing that lonesome wail of the train whistle as the magnitude of the frequency of the wave changes due to the Doppler effect."

1. The following is an energy level diagram (Grotrian diagram) for Mercury:



Energy Level Diagram of Hg I [Grotrian (8)].

From this diagram, identify (*using correct notation!)* the following:

a. *(15 pts)* A spectral line resulting from a "forbidden" transition. Why is this transition considered to be "forbidden"?

b. *(10 pts)* The most intense resonance line.

c. *(15 pts)* A metastable state.

d. *(15 pts)* What is the *longest* wavelength (Å) of the continuum radiation band originating from an e^-/Hg^+ recombination producing Hg in the ground state?

e. *(10 pts)* Describe one other process which can result in the emission of continuum radiation.

2. **a.** *(15 pts)* Calculate the excitation energy *in eV* for the 3944.03 Å Al(I) resonance line.

b. *(20 pts)* Compute the doppler linewidth (in Å) for the Al(I) 3944.03 Å resonance line in a dc Arc (temperature = 5000 K). How does this compare with the *natural* linewidth (assuming $A_{qp} \approx 10^8$ sec^{-1})?

c. *(10 pts)* Briefly describe which broadening processes would predominate in an atmospheric pressure plasma source, such as an arc or spark – order of magnitude values for linewidths would be especially helpful.

3. **a.** *(40 pts)* A radiation source at 3000 K contains 1.0 x 10^{20} Na atoms per cm^3. Compute the number of 5889.963 Å photons per second from a resonance transition which pass through a 10.0 μm x 50.0 μm aperture located 1.0 m from the source (assume that the source can be considered as a point source). The statistical weight of the excited state is 4; assume that the partition function at 3000 K is 4.3 and the transition probability is 1.25 x 10^8 sec^{-1}. Lastly, assume that the ionization of Na is insignificant.

b. *(30 pts)* Assuming an electron partial pressure equal to 4.0 x 10^{-8} atm and that $Z_{Na+} = Z_{Na}$, calculate the percent ionization for the Na in the source described in *part a* if the ionization potential for Na is 5.14 eV. Describe in a semi-quantitative fashion how this changes the results obtained in *part a*.

4. *(35 pts)* The sampling processes in an atomic emission source often have a profound impact on its analytical properties; this is especially evident with sources used for the analysis of solid samples. Select *two* sources that are typically used for solids analysis that have different sampling mechanisms. Contrast the sampling processes operative with each of these emission sources and describe how that impacts on their analytical properties (e.g., matrix effects, precision, etc.).

5. *(35 pts)* Glow discharge sources are often viewed as being nearly ideal excitation sources for atomic emission spectroscopy. Describe the excitation processes operative in glow discharges and explain why they produce nearly ideal emission spectra. What is it, then, about glow discharges that limits its popularity as a more routine source for atomic emission spectrochemical analysis?