March 14, 2005

- It's Pi Day! (3.14 at 1:59)
- <u>Office hours:</u>
  - Today
  - Until 2:15 pm
  - A223 Cook
- <u>Exam #2:</u> Wednesday at 7 pm!

AAS versus AES?

- **AAS:** Absorbance $\propto N_p$
- **AES:** Emission Int. $\propto N_q$

But: *concentration* $\propto N_T$

For a *thermal* population distribution, we use the Boltzmann Equation to relate N_p and N_q to N_T:

$$\frac{N_q}{N_T} = \frac{g_q e^{-(E_q/kT)}}{\Sigma(g_i e^{-(E_i/kT)})}$$

Where: T = absolute temp., k = Boltzmann's constant, and g_i = statistical weight of state i

Impact of Boltzmann

- Population of *any state* is ***temperature dependent***
- <u>**BUT:**</u> even at high temperatures, N_q/N_T is usually very small (~10^{-3} - 10^{-7} @ 3000 K)
- <u>***So:***</u> N_p (ground state population) $\approx N_T$
  (99+% of atoms are in the ground state)

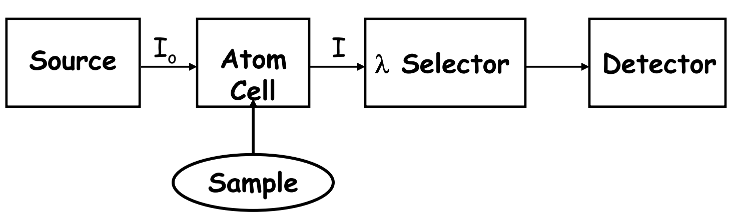
  -**So:** absorbance $\propto N_T$
  -**And:** absorbance is relatively temp indep

- <u>***Also:***</u> N_q/N_T is very temperature sensitive, but *at constant temperature:*

$$\mathbf{N_q = N_T K} \propto \text{conc} (\propto I)$$

Instrumentation

- <u>Let's start with AAS:</u>



-lets first look at Atom Cells and how a sample is converted to <u>*gas phase atoms*</u>

Obtaining Gas Phase Atoms

- From an *aqueous solution*:

$$MX_{(aq)} \xrightarrow{1} MX_{(s)} \xrightarrow{2} MX_{(g)} \xrightarrow{3} M_{(g)} + X_{(g)}$$

1. **Desolvation**
   -conversion of analyte to solid crystals
2. **Vaporization**
   -conversion of solid to molecular vapor
3. **Atomization**
   -dissociation of molecular vapor into atomic vapor

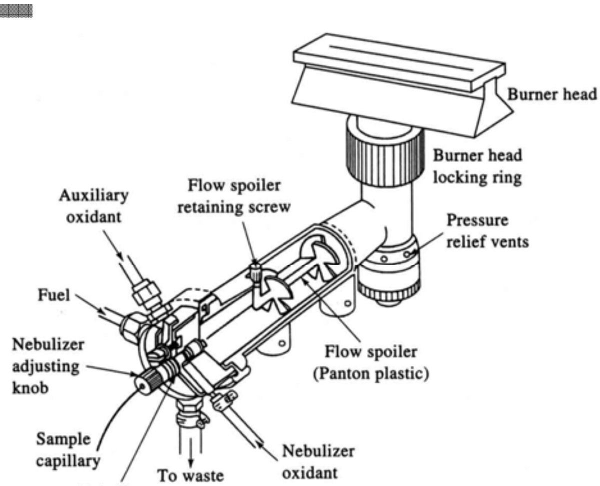
Flame Atom Cells:
Laminar Flow Pre-mix Spray Chamber Burner

- **Requirements:**
stable, quiet, long path-length, "cool"

(H_2/air: 2000°C,
C_2H_2/air - 2300 °C)

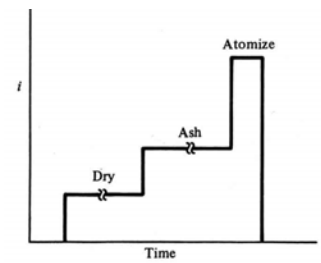
•**Limitations:**

- *flashback!*
- inefficient

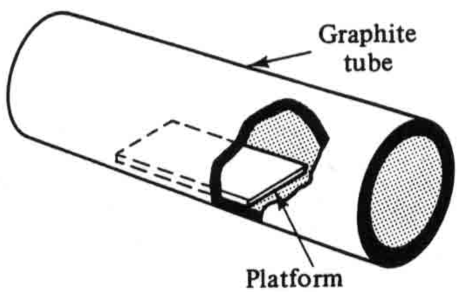


Electrothermal Atomizers:
The Graphite Furnace

3-stage heating cycle:



■ Resistively heated carbon tube:



•Sample micropipetted (5-50 μL) onto platform in tube

•Dry (~120°C) - *desolvation*

•Ash (~500 - 1000°C)
-*atomize matrix*

•Atomize (~1000 - 3000°C)
-*atomize analyte*

Graphite Furnace Atomization:
Why Use a Platform?

■ Ideally, atomize into an *isothermal* environment: