March 14, 2005

- **It's Pi Day! (3.14 at 1:59)**
- **Office hours:**
  - **Today**
  - **Until 2:15 pm**
  - **A223 Cook**
- **Exam #2: 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

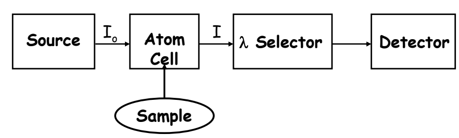
- Population of *any state* is ***temperature dependent***
- **BUT:** even at high temperatures, N_q/N_T is usually very small (~10^{-3} - 10^{-7} @ 3000 K)
- ***So:*** N_p (ground state population) $\approx N_T$ (99+% of atoms are in the ground state)

  -**So**: absorbance $\propto N_T$
  -**And**: absorbance is relatively temp indep
- ***Also:*** N_q/N_T is very temperature sensitive, but *at constant temperature:*

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

Instrumentation

- Let's start with AAS:



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

Obtaining Gas Phase Atoms

- From an *aqueous solution*:

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

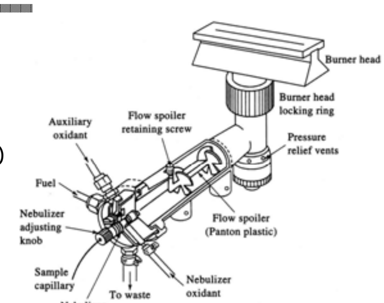
1. **Desolvation**
   -conversion of analyte to solid crystals
2. **Vaporization**
   -conversion of solid to molecular vapor
3. **Atomization**
   -dissociation of molecular vapor into atomic vapor

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

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

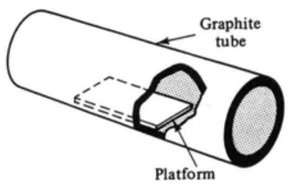
(H_2/air: 2000°C, C_2H_2/air - 2300 °C)

- **Limitations:**
  - *flashback!*
  - inefficient



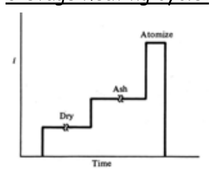
Electrothermal Atomizers:
The Graphite Furnace

- Resistively heated carbon tube:



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

<u>3-stage heating cycle:</u>



•<u>Dry</u> (~120°C) - *desolvation*

•<u>Ash</u> (~500 - 1000°C)
  -*atomize matrix*

•<u>Atomize</u> (~1000 - 3000°C)
  -*atomize analyte*

Graphite Furnace Atomization:
Why Use a Platform?

- Ideally, atomize into an *isothermal* environment: