

Potassium Line Emission from an Extended Volume Source

The **FIRES** Gang



Motivation, motivation....

- We need to understand the physical phenomena in a fire that govern the gross behavior
- We need to know what simplifications and assumptions can be made to ease calculations
- We need to be able to justify potassium detection ‘theory’ and predict the emission of narrow spectral features
- It would be great to complete the predictive loop by:
 - a. Taking the chemical and physical output of *BEHAVE* and coupling this to a line emission and blackbody model to predict the emitted spectrum
 - b. Use the spectral information obtained from (a) to provide input to *DIRSIG*

The general plan of attack....

- Describe the overall ‘picture’ and preliminary results of the study (today!)
- Describe the physical and chemical properties of a flame (soon)
 - Basic thermodynamics and atomic physics
- Present a more detailed model of line emission from a flame (less soon)
 - More detailed atomic physics
- Combine the line emission model with a multi-temperature p-LTE blackbody to produce a complete spectral rendering (later)
- Compare the complete spectral rendering with known data (AVIRIS, local data sets) (much later)



We will attempt to estimate the energy output from a fire in the potassium emission lines

- The following assumption will be made:
 - Complete thermodynamic equilibrium (CTE) or
 - Single temperature Planck distribution law describes radiation field.
 - No gradients, so no net radiative transport *within fire volume*.
 - Maxwellian distributions obtain for kinetic energy of particles.
 - Internal degrees of freedom (rotation, vibration, dissociation, excitation, ionization) populated according to Saha-Boltzmann statistics with a common T.
 - Macroscopic variables (conductivity, viscosity, enthalpy and internal energy) completely specified by a single T.
 - Detailed balancing obtained
- Local thermodynamic equilibrium (LTE)
 - Absence of a radiative field (temperature gradient and energy flow)
 - Saha-Boltzmann statistics, single T.
 - Kinetics described by Maxwellian distributions.
 - Optically thin radiation field, emitting and absorbing states known.
 - Detailed balancing not strictly required.

How good is our assumption of local thermodynamic equilibrium?

- We need CTE or LTE to enable use of a known distribution function for description of thermodynamic quantities
- LTE is useful when time scale for local movement of energy (radiation, diffusion, conduction or field interaction) are much longer than the time between (electron) collisions (collision-dominated plasma).
- Electrons have high velocity (low mass) and short mean free path, thus are mediators of energy transport.
- Electron number density (n_e) is the best single indicator of LTE.
- n_e should be higher than 10^{17} cm^{-3} for LTE to hold.
- Flames are near-neutral phenomena with $n_e < 10^8$.
- **We don't care, we'll proceed with the LTE assumption anyway!**

The LTE assumption is partially valid even for our fires

- Partial local thermodynamic equilibrium (p-LTE) may occur if energy density of the radiation field is described by Planck's formula.
- If strong spectral lines are present (e.g., K) the radiation field deviates from equilibrium.
- P-LTE may be obtained if the strong spectral lines are reabsorbed within $\sim 10^{-8}$ seconds, raising temperature of plasma.
- Even this condition is too strong. Even if there is a temperature distribution and radiation flow, a piece of the plasma may still be in LTE.
- We need this to use distribution functions to calculate the partition of energy within the plasma. Otherwise the 'ensemble' approach fails.
- We plod ahead...

What is the basic fire 'process'?

1. Combustion temperatures are reached, organic materials volatilize and burn.
2. Volatile combustible materials disassociate, raising temperature of fire further and liberating alkali compounds. There is also a single-temperature Planckian spectrum present. (~ 0.2 eV, remember room temperature is $1/40$ eV)
3. Alkali compounds disassociate into alkali + () (~ 0.75 eV)
4. Alkalies are excited and ionize. (1.7 - 4.5 eV)
5. Excited states spontaneously decay to ground state, emitting narrow spectral lines. Ionized states pass through excited states decaying to ground state, emitting narrow spectral lines. (~ 1.5 eV)

We will model the emission as a surface flux from a uniform volume source with low opacity

- The governing equation is trivial:

Power (E/s) = number of atoms (n) * atoms excited(%) * probability of de-excitation per unit time(1/s) * energy per deexcitation (E)

or in equation form:

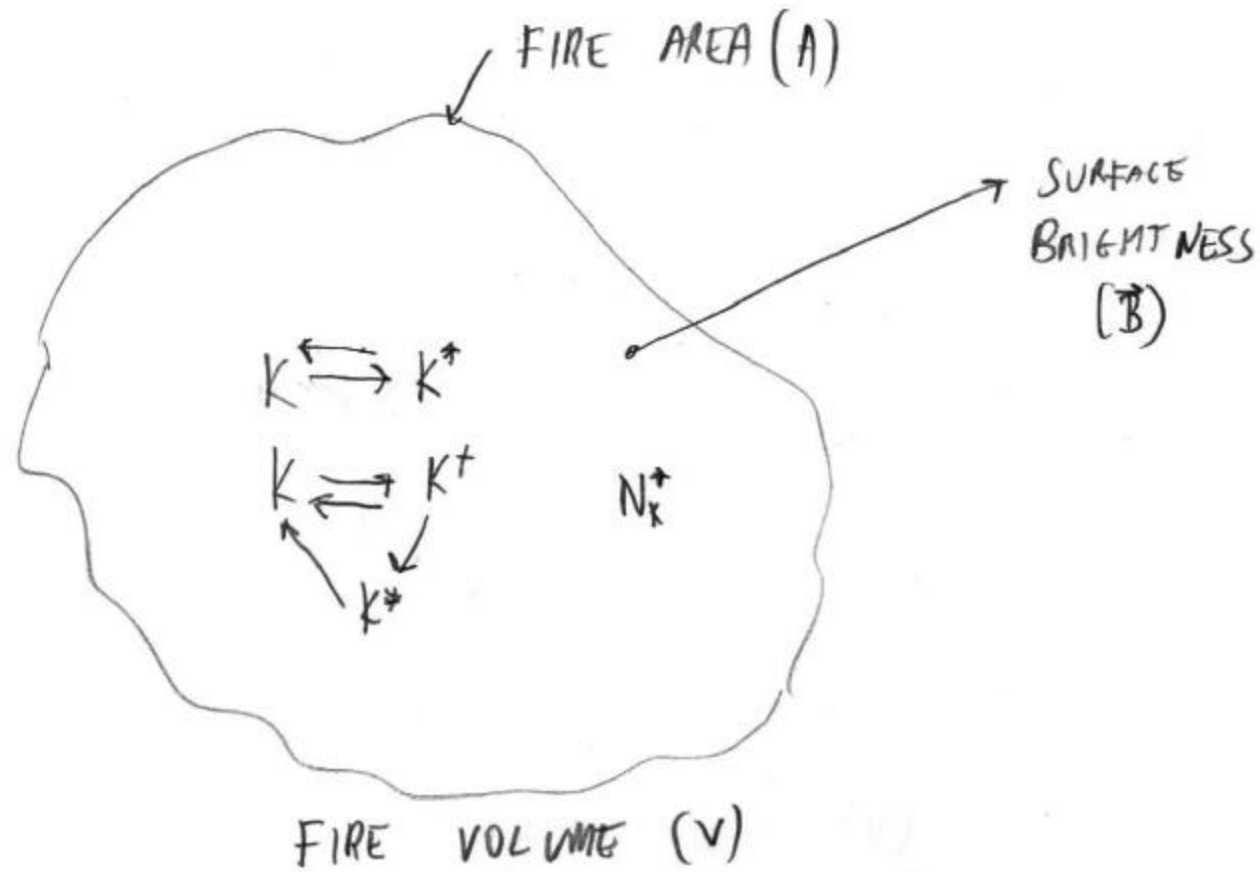
$$I = n_k f A E \quad (1)$$

- Notes:

- n_k is obtained from the elemental abundance of the species in the biomass and total amount of biomass burned.
- f is governed by Saha-Boltzmann statistics
- A is the Einstein spontaneous decay (A_{ul}) coefficient

We will model the emission as a surface flux from a uniform volume source with low opacity (2)

- The details of the geometry will be ignored. We assume spherical symmetry.



The Boltzmann distribution function governs the distribution of excited states in the system

- **Assumption of LTE allows specification of the ensemble by statistical parameters**

The probability of excited (E2) to unexcited (E1) atoms at a temperature T is determined by the ratio of the Boltzmann factors :

$$R_i := \left\{ \frac{g_2}{g_1} \right\} \cdot e^{\frac{-(E_2 - E_1)}{k \cdot T_i}} \quad \text{where } g_2 \text{ and } g_1 \text{ are the degeneracy of the states}$$

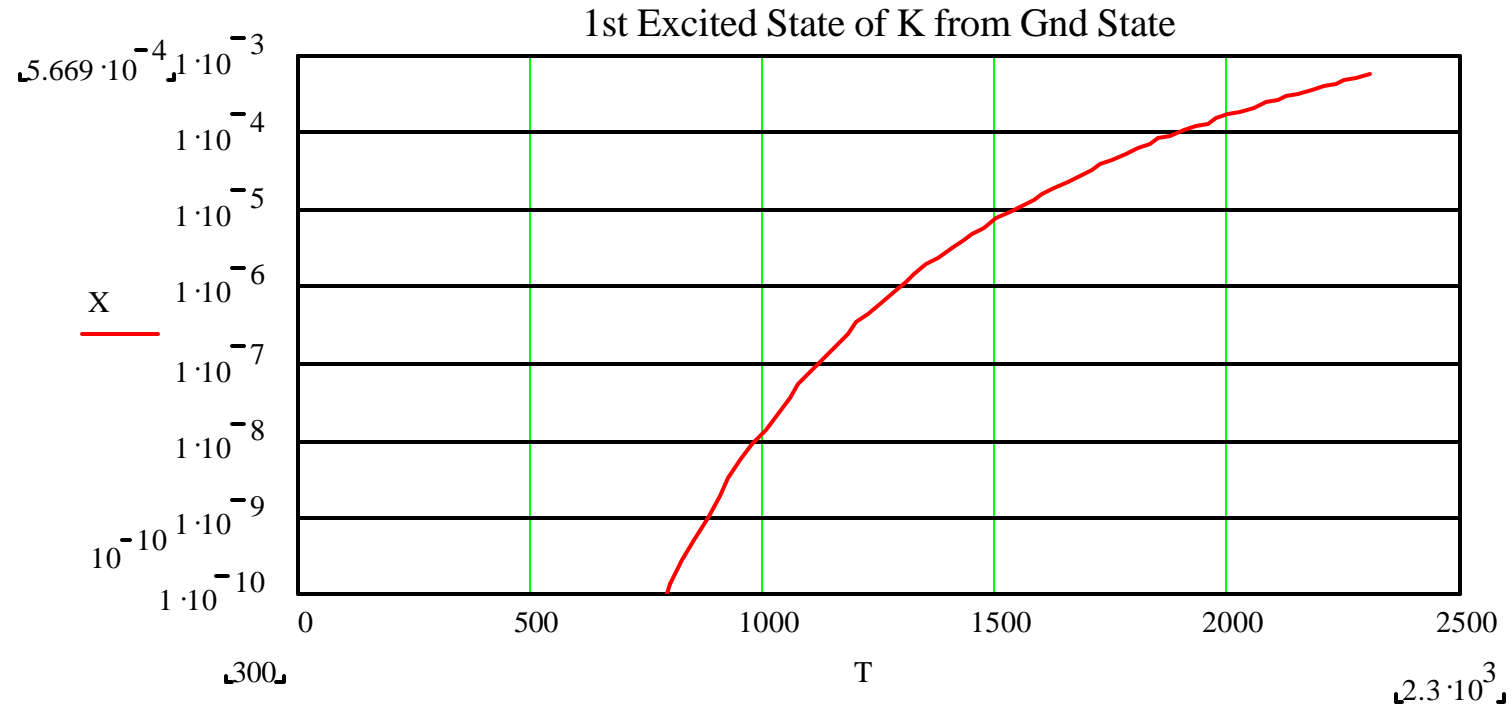
$$X = N_2 / N_{\text{total}}$$

$$X = N_2 / (N_1 + N_2) = N_2 / N_1 / (1 + N_2 / N_1)$$

$$X_i := \frac{R_i}{(1 + R_i)}$$

Even if we only consider excitation, there are a considerable number of available K atoms

- About 1 in 10 million K atoms are in the first excited state at normal fire temperatures



Let's do a back-of-the-envelope calculation of the emitted power from a 'sensible' source

- Parameters for potassium (single channel, excited state only):

- $E = \text{energy / decay} = 1.7 \text{ eV} = 2.7 \times 10^{-19} \text{ J}$
- $a = \text{decay rate} = 2.6 \times 10^{-8} / \text{s}$
- $f = \text{fraction of excited states} \sim 10^{-7} \text{ (at 1100 K)}$
- $n = \text{Total number of atoms (per Kg):}$
 - 5% potassium by weight
 - > 50 gm potassium per kg
 - > $50/40 * A_g = 7.5 \times 10^{23} \text{ K atoms per kg}$

Substituting:

$I = 5.3 \times 10^{-10} \text{ W / kg}$ burned in a spectral line $< 10 \text{ \AA}$ (10^{-3} mm) wide.

Assume that the density of wood is 0.5 (when burning?) so the volume of a 1 kg spherical mass is: $2000 \text{ cm}^3 \rightarrow 7.8 \text{ cm} \rightarrow \text{surface area} = 770 \text{ cm}^2$, $10 \text{ \AA} = 10^{-3} \text{ mm}$.

So:

$$F = 6.5 \times 10^{-6} \text{ W/m}^2\text{- mm}$$

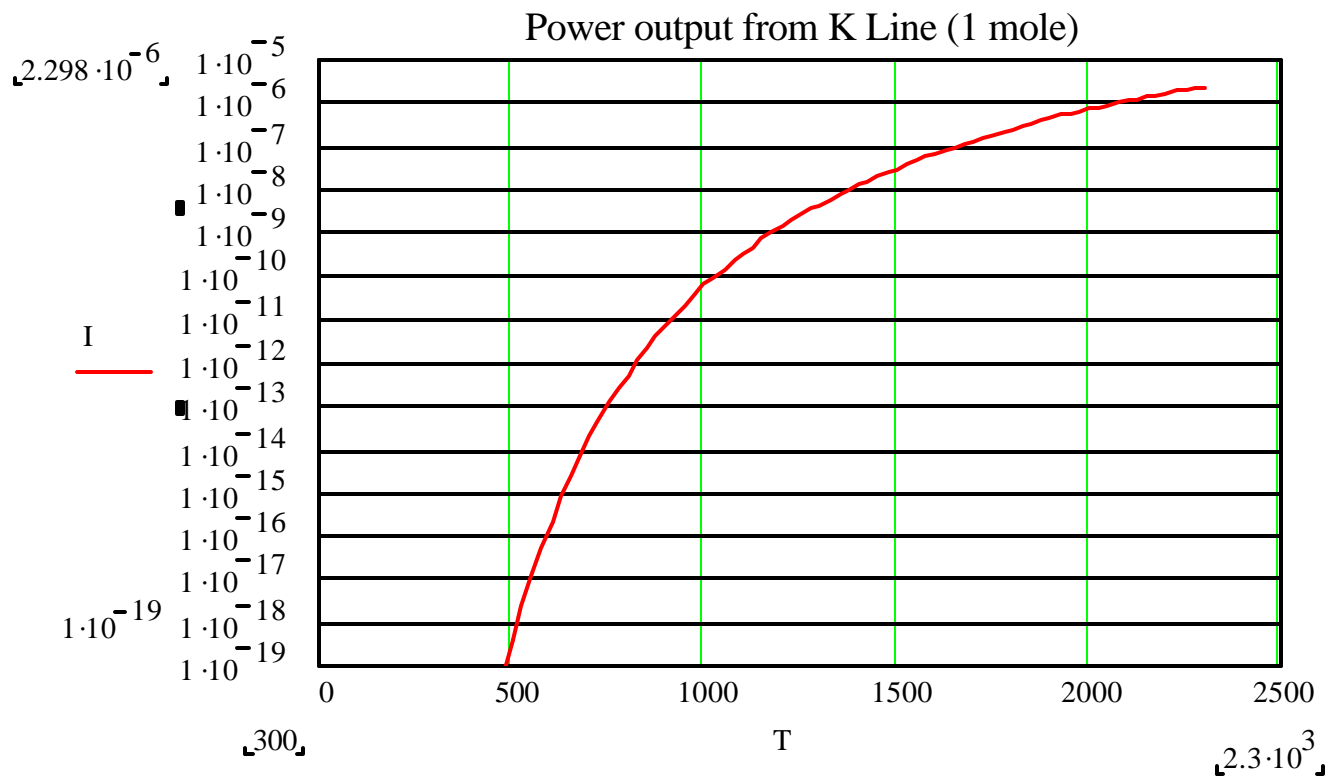


How does the thermal and line emission spectral energy densities compare?

- From A. Fordham, we get emission from a Planck-formula blackbody at 500K $\sim 8 \times 10^{-8} \text{ W/m}^2\text{-nm}$ at 766 nm (K emission line) so even for non-ionized case, *K line is significantly brighter than the Blackbody radiation from the fire.*
- The K calculation is probably *3 - 4 orders of magnitude too low in intensity* because we are ignoring all but ground state-first excited state path.

We can parameterize the energy output per unit surface area by temperature (for example)

- Direct excitation path power output increases 11 1/2 orders of magnitude between 500 and 1500 K.



Future work....

- A. Incorporate a more accurate excitation path with correct equilibrium constants.
- B. Incorporate a more exact fire model using BEHAVE output
- C. Burn something!!!
- D.