Section 6: Ionization

AE435

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1 Equilibrium Ionization

Here we derive the ionization fraction for an equilibrium gas. This results in what is called the Saha Equation.

Contents

1.1 Detailed Balancing

Assume **detailed balancing**, where every process is balanced by the reverse process:

Examples of the sort of reactions involved in detailed balancing:

1. a
2. a

The overall reaction can be described by an equilibrium constant

Can show from statistical mechanics that at equilibrium:

State of Plasma

$$a$$

Where

a is the total population within the control volume
a is the population within the CV at a given state, i
a is the energy state ij
a k is Boltzmann constant.

This determines the distribution among individual energy states at equilibrium.

1.2 Partition Functions

We can define a **total partition function** for a given species that is the product of a series of individual partial partition functions,

Where for each energy mode of a given species:

- Translational
- Electronic
- Rotational
- Vibrational

We have a **partial partition function**

Jahn defines f as the sum of accessible energy states, appropriately weighted by degeneracies and by the Boltzmann factors in the relative energies of those states.

Other ways of writing f include:

where is the ground-state energy. (Note: this is a more general form as it indicates that energy is relative)

includes the degeneracy , making it useful for electronic states.

The partition function is a link between classical thermo and the microscopic behavior of gases (statistical kinetic theory). It is fairly easy to show that the total energy for N particles is:

For instance, the **translational partial partition function** is given on quantum mechanics basis, as (6.9) for atoms of mass MA:

Using (6.9), we can take

So that

The total translational energy is then:

which is the result we had before in section IV. A. 2. when we discussed Kinetic Theory and Internal Translational Energy.

Thus...

electronic partial partition function

a

Where

a degeneracy for state j

a represents the ground state

a is the highest bound state

Note that this series converges rapidly, so we may need to only take a few terms at low to moderate temperature. In hot plasmas, may need to take many terms for an accurate solution.

The **total atomic partition function** for species with negligible rotational and vibrational modes is:

Substituting in the partial partition functions,

Likewise, the **total ionic partition function**

becomes

We need to make sure that we have consistent assumptions about the energy reference state. Doesn't matter what it is, but it has to be the same for all.

For atoms, we use the ground state,

For ions, we need to add the ionization energy to reference back to atomic ground, thus

where the following terms express an electronic energy level in the ion:

is referenced to the ionic ground state

is referenced to the atomic ground state

is the ionization energy (referenced to the atomic ground state)

The total electron partition function (for free electrons) is

where is the spin degeneracy (the only internal degree of freedom); substituting and using (6.9),

1.3 Saha Equation

The equilibrium constant for ionization

can be expressed as the ratio of total partition functions,

Substituting in, using (6.20), (6.15), (6.17) and (6.18),

where

is the electronic partial partition function for ions, and

is the electronic partial partition function for atoms. This is the classic form of the Saha Equation from astrophysics (6.23).

An alternative form used often in gas dynamics started by defining the ionization fraction

Ionization Fraction

$$a$$

Where

a is the ion density

a is the neutral density

a is the total density of heavy particles

If we assume quasineutrality

We can write

So the pressure from all 3 species (ions, atoms, electrons) is:

Substituting into the equilibrium constant equation (6.21)

where

SAHA Equation

$$a$$

Can plot for argon:

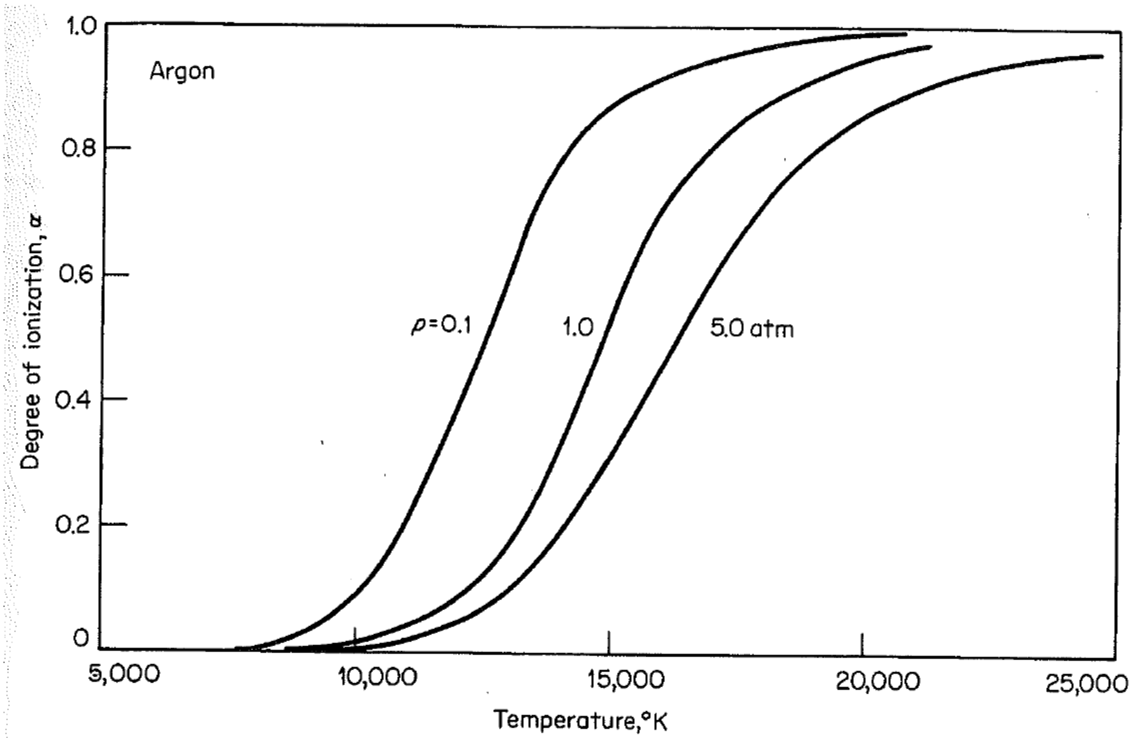


Fig. 3-4 Dependence of ionization of argon on temperature and pressure, from Saha equation. *(From K. S. Drellishak, C. K. Knopp, and A. B. Cambel, Partition Functions and Thermodynamic Properties of Argon Plasma, Phys. Fluids, ser. 6, vol. 9, p. 1280, 1963.)*

Note that collisional recombination drives the ionization fraction down at higher pressures.

Jahn gives a more complex analysis, required for multiple species and internal degrees of freedom. Main points:

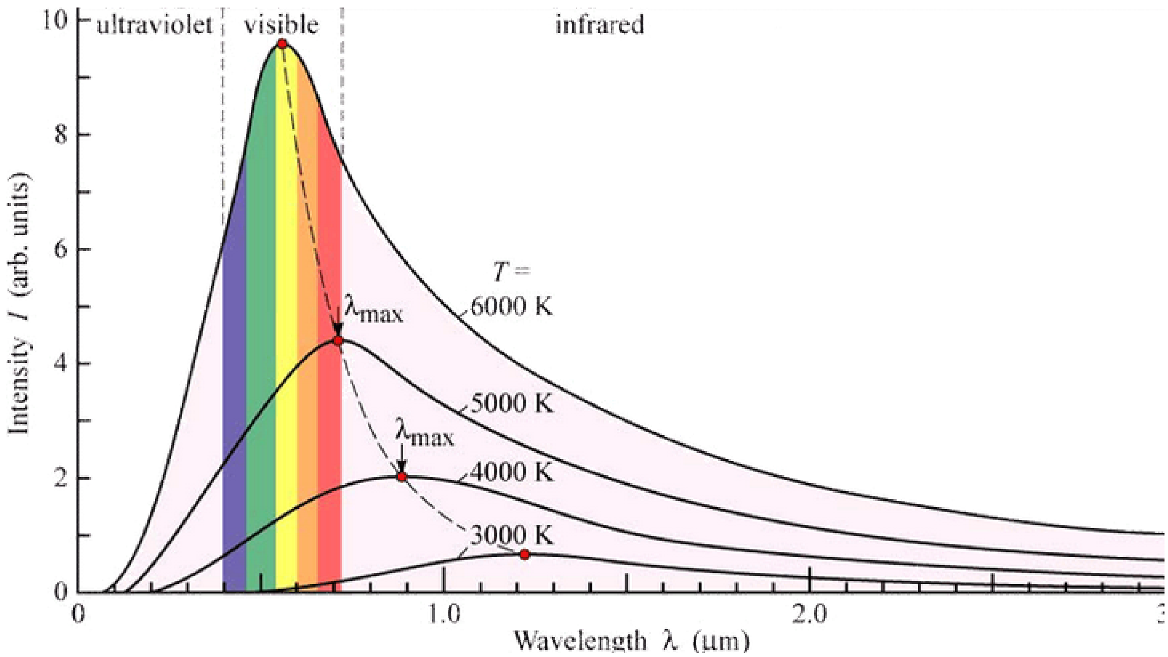
- Vibration and rotation require their associated partition functions
- Additional reactions (dissociation, etc) can be handled the same way
- Multiple ionization (high temp, low density) adds partition function and number of reactions

1.4 Conditions for Equilibrium

Above analysis assumes **complete thermodynamic equilibrium (CTE)**:

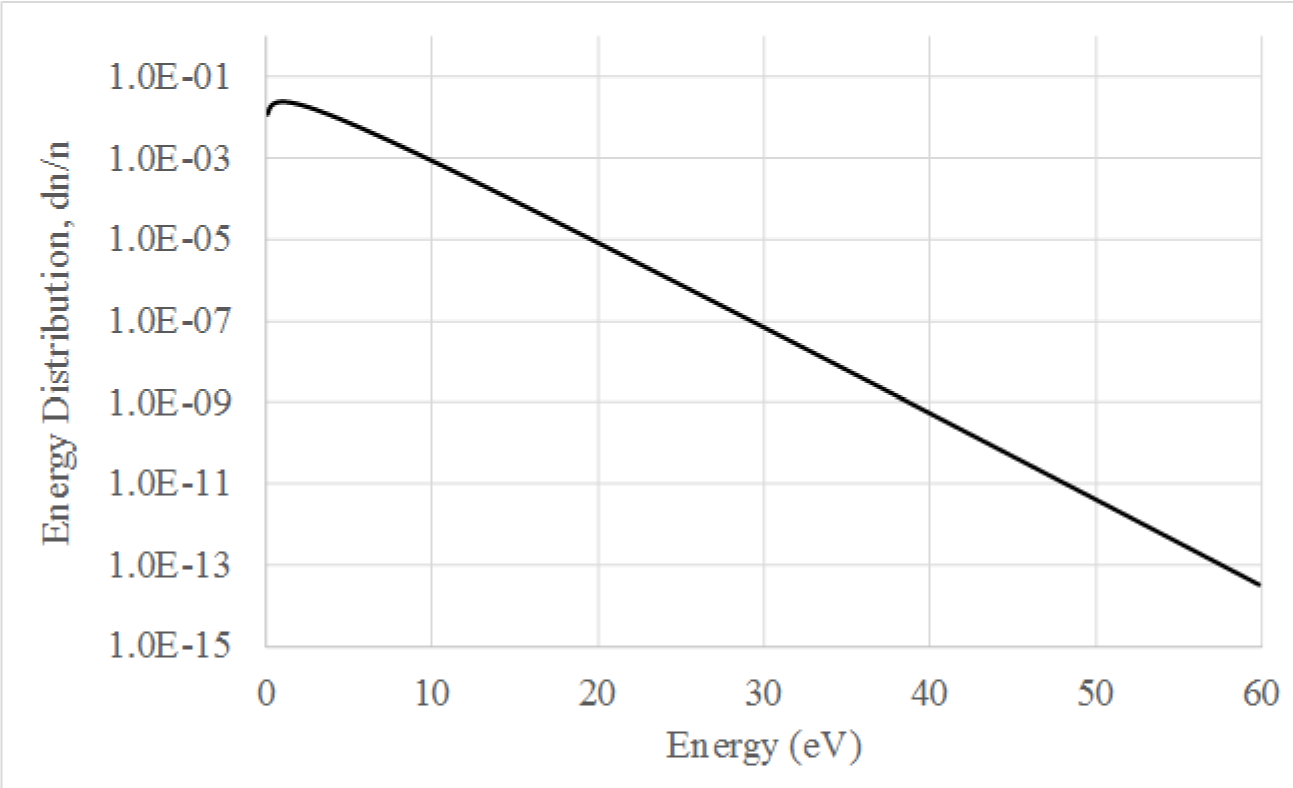
1. Single temperature
2. Homogeneous plasma
3. Radiation field follows blackbody distribution

   where is the radiation intensity (energy per unit time per u nit area per unit solid angle) and is the vacuum speed of light. Note that this requires an optically thick plasma, where all radiation is absorbed and re-radiated multiple times (as in Sun's interior).



4. Maxwellian-Boltzmann energy distribution. Which follows from the Maxwellian velocity (speed) distribution (4.30).

For Te = 2eV electrons



Note that the slope varies inversely with the temperature, we use this in several diagnostics (Langmuir probes, atomic Boltzmann method in optical emission spectroscopy) to measure plasma temperature. In terms of speed,

And, again, the mean speed for a Maxwellian is:

In CTE,

- All ionization follows the Saha equation
- All excitation follows the Boltzmann equation

1.4.1 Deviations from Equilibrium

1. Local thermodynamic equilibrium (LTE), where plasma is
   - Sufficiently dense that collisions are dominant populating mechanism
   - Optically thin, so radiation field is nonequilibrium, can't use Planck's law
   - Radiative processes do not follow detailed balancing, assume we can ignore radiation processes, plasma is collision determined.

   In LTE, radiative emission dominates over absorption and photoionization, depleting the number of free electrons and excited states. LTE is frequently encountered in lab plasmas.

2. Partial local thermodynamic equilibrium (PLTE), where plasma is lower density:

- Collisions are in detailed balance for upper energy levels
- Collisions are not in detailed balance for transitions to the ground state
- Often Ti ¡ Te

As a result, upper energy levels follow Boltzmann distribution, but the ground state is overpopulated. Again, depletes the free electron density.

3. Non-equilibrium Plasma

   - Multi-thermal ”equilibrium”

     where we have a two-temperature plasma. Typically:

     The reason for this is electron-impact collisions are an efficient method to transfer energy to gas, but a poor method of transferring momentum. So atoms get energy from electron to become ionized (takes ionization energy), but they don’t get momentum, so their translational energy (temperature) doesn’t change.

     Fluorescent lights work by electron-impact excitation of mercury atoms. (The dominant lines are in the UV, but coatings in the tube walls downconvert to visible light). Temperatures:

     - Gas, 300 K 1/40 eV
     - Electrons, 3.5 eV 35,000 K

     Collisional processes are often dominated by electrons, so we can get LTE or PLTE where the relevant temperature is Te.

   - Corona ”equilibrium”

     Note really a true equilibrium, as there is no detailed balancing. Characteristics:

     - Very low density plasmas
     - Radiative decay rates ¿¿ collisional decay rates
     - Optically thin
     - Radiative excitation and ionization ¡¡ collisional excitation and ionization

     In this case we can balance

     Energy in by collisions = energy out by radiation

     For charge states Z and Z+1, the ionization balance is then:

     where

     is the radiative recombination rate [s-1]

     is the electron-impact ionization rate [s-1]

     Rearranging we get a simple relation for the corona model,

     which you’ll note is independent of ne.