**Radiative Process (Absorption/Emission)**

- **Bound-Bound** (discrete energies)
  - excitation = photon absorbed, energy deposited as increased internal energy in atom/molecule
  - de-excitation = photon released into radiation field resulting atom in a lower internal energy state

- **Bound-Free** (continuum energies)
  - photoionization = photon with $E_\gamma > X_i$ absorbed, ejecting an electron into the gas; electron quickly "thermalized" in gas.
  - recombination = electron captured to bound excitation level in atom; emits photon into radiation field, $E_\gamma = \frac{1}{2}mv^2 + X_i$

"The continuum and though free electrons are not bound in discrete excitation levels, the quantum mechanical treatment is to employ complex quantum number (which can take on any rational value—not just integers). The "orbits" of unbound states are hyperbolic in this formalism.

![Figure 12.4: Schematic of three primary atomic absorption transitions and the principle quantum numbers employed to quantitatively describe the processes.](image)

(a) b-b absorption
(b) b-f absorption
(c) f-f absorption

**Free-Free Absorption/Emission**

must take place near an atom/molecule to conserve angular momentum.

 photon $L = h$
Radiative Processes (cont)

**Free-Free**

(continuum energies)

- absorption = photon absorbed by free electron + atom/ion system; electron elevated to higher energy hyperbolic "orbit"

- emission = (also known as Bremsstrahlung)
  photon emitted by free electron + atom/ion system; electron moves to lower energy hyperbolic "orbit".

**Line Scattering**

(discrete energies)

bound-bound absorption followed by bound-bound emission between the same excitation levels. The photon energy is essentially unchanged but its direction is altered. Technically photon is not absorbed, but is scattered.

- the complication of line scattering
  if original bound-bound absorption is to a high excitation state then spontaneous decay to lower levels can cascade to lower excitation states as the electron "steps" its way down to the ground state.

  results in several photons of lower energies than the original absorbed photon. These photons are emitted in random directions. Technically, this is not scattering, but it is technically not absorption either because the original photon energy is not converted into the gas but redistributed into the radiative field.

**Note on Line Scattering**

* the energy can be slightly change for two reasons. damping constant
  (1) atom energy levels have small energy spreads, \( \Delta E = 10^{-4} \text{eV} \)
  (2) Doppler shift due to motion of atom/ion relative to incident and emitted photon
Boltzmann Relations (Excitation Levels)

- If collisional equilibrium holds, then Boltzmann Equation holds and these conditions do hold well in stellar atmospheres. ($\chi > 0.1$)

- Condition required:

\[
\begin{bmatrix}
\text{number of excitations and deexcitations out of excitation level } i \\
\text{per unit time per unit volume}
\end{bmatrix}
\begin{bmatrix}
\text{number of excitations and deexcitations in to excitation level } i \\
\text{per unit time per unit volume}
\end{bmatrix}
\]

Excitation levels: ionized atom $j$ of species $k$

\[\chi_{ijk}, g_{ijk}\]

Excited: $i$

Ground: $l$

\[\chi_{ijk} = 0, g_{ijk}\]

Boltzmann (relative to ground state)

\[
\frac{N_{ijk}}{N_{ij}} = \frac{g_{ijk}}{g_{ij}} \exp\left\{ - \frac{\chi_{ijk}}{kT} \right\}
\]

Boltzmann (between two states, $i$ and $i'$)

\[
\frac{N_{ijk}}{N_{ij}} = \frac{g_{ijk}}{g_{ij}} \exp\left\{ - \frac{(\chi_{ijk} - \chi_{ij})}{kT} \right\}
\]

Applies when collisional processes dominate over radiative processes (high densities)
defining
\[ \eta_{jk} = \sum_{i=1}^{\infty} \eta_{ijk} = \text{number density of species } k \text{ in ionization level } j \]

we obtain:
\[ \frac{\eta_{ijk}}{\eta_{jk}} = \frac{\sum_{i=1}^{\infty} \eta_{ijk}}{\eta_{jk}} = \frac{\left( \frac{g_{ijk}}{g_{jk}} \right) \exp \left\{ -\frac{\chi_{ijk}}{kT} \right\} \sum_{i=1}^{\infty} \left( \frac{g_{ijk}}{g_{jk}} \right) \exp \left\{ -\frac{\chi_{ik}}{kT} \right\}}{\sum_{i=1}^{\infty} \frac{g_{ijk}}{g_{jk}} \exp \left\{ -\frac{\chi_{ijk}}{kT} \right\}} = \frac{g_{ijk} \exp \left\{ -\frac{\chi_{ijk}}{kT} \right\}}{\sum_{i=1}^{\infty} \frac{g_{ijk}}{g_{jk}} \exp \left\{ -\frac{\chi_{ijk}}{kT} \right\}} \]

which defines the partition function
\[ U_{jk}(T) = \sum_{i=1}^{\infty} \frac{g_{ijk}}{g_{jk}} \exp \left\{ -\frac{\chi_{ijk}}{kT} \right\} \]

depends only on \( T \)
values are tabulated as function of \( \theta = \frac{5040}{T} \) in Grey App. D.

yielding
\[ \frac{\eta_{ijk}}{\eta_{jk}} = \frac{g_{ijk}}{U_{jk}(T)} \exp \left\{ -\frac{\chi_{ijk}}{kT} \right\} \]

does not depend upon pressure or density.

**NOTE:** Since \( kT \) is usually in [ergs] and \( \chi_{ijk} \) in [eV]
it is convenient to write
\[ \exp \left\{ -\frac{\chi_{ijk}}{kT} \right\} = 10^{-\theta \chi_{ijk}} \]

where \( \theta = \frac{5040}{T} \) and \( \chi_{ijk} \) is in [eV] \( \theta \) in units [eV⁻¹]

thus
\[ \frac{\eta_{ijk}}{\eta_{jk}} = \frac{g_{ijk}}{g_{jk}} 10^{-\theta \left[ \chi_{ijk} - \chi_{jk} \right]} \quad \text{and} \quad \frac{\eta_{ijk}}{\eta_{jk}} = \frac{g_{ijk}}{U_{jk}(T)} 10^{-\theta \chi_{ijk}} \]

etc.

alternate forms
Saha Equation (ionization levels)

- As with Boltzmann's Equations, the Saha Equations require equilibrium collisional balancing such that all ionizations out of a given ionized atom must equal all recombination into a given ionized atom.

- This requires that the electron pool is thermalized with the atoms, a condition which holds in stellar atmospheres \( \text{for } \gamma \geq 0.1 \). Need non-LTE for \( \gamma \leq 0.1 \).

- Grand state to ground state ionization

Define \( n_{i,j,k} = \text{density of species } k \text{ ionized } j \text{ time with remaining electrons in the ground state } (i=1) \)

Then, for electrons in the velocity interval \( v \rightarrow v + dv \), the Boltzmann Equation is

\[
\frac{N_{i,j,k} dv}{n_{i,j,k}} = \frac{g(v) dv}{q_{i,j,k}} \exp\left\{ -\frac{h v}{k T} \right\}
\]

\( g(v) dv = g_{i,j,k} \cdot g_e(v) dv \) = statistical weight of combined ground level ion state and electron with \( v \rightarrow v + dv \)

\[
q_{e}(v) dv = \frac{8\pi}{\hbar^2} \frac{1}{n_e} m_e^3 v^2 dv
\]

Ionization potential of \( jk \)

And applying conservation of energy \( h v = \chi_{ijk} + \frac{1}{2} m_e v^2 \) we have

\[
\frac{N_{i,j,k} dv}{n_{i,j,k}} = \frac{8\pi}{n_e} \left( \frac{m_e}{h} \right)^3 \frac{g_{i,j,k}^{(3)}}{q_{i,j,k}} \exp\left\{ -\frac{(\chi_{ijk} + \frac{1}{2} m_e v^2)}{k T} \right\} v^2 dv
\]

\{ ratio of ground state ions \}
this last equation must be integrated over all electron velocities

let \( x = \left( \frac{m v^2}{2kT} \right)^{1/2} \) then the integral takes the form

\[
\int_0^\infty x^2 e^{-x^2} \, dx = \frac{\sqrt{\pi}}{4}
\]

and we obtain (ground states only)

\[
\frac{n_{ij,lk}}{n_{ijk}} = \frac{2}{n_e} \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \frac{9_{ijk,lk}}{g_{ijk}} \exp \left\{ -\frac{x_{ijk}}{kT} \right\}
\]

i=1 ground state

- clearly, i=1 in the denominator can be generalized to any excitation level

\[
(n_{ijk} \rightarrow n_{ij,lk}) \quad (g_{ijk} \rightarrow g_{ij,lk}) \quad (x_{ijk} \rightarrow x_{ij,lk} - x_{ijk})
\]

with the above substitutions. [what if both j+1, and j are generalized?]

- substituting the partition functions yields

\[
\frac{n_{ij,lk}}{n_{jk}} = \frac{2}{n_e} \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} \frac{U_{ij,lk}(T)}{U_{jk}(T)} \exp \left\{ -\frac{x_{ijk}}{kT} \right\}
\]

this provides the ratio of adjacent ionization stages for species k, accounting for all excitation levels

which follows from \( n_{jk} = \sum_{i=1}^\infty n_{ijk} \)

- some convenient notations

\[
\frac{n_{jk,k}}{n_{j,lk}} = n_e^{-1} \Phi_j(T) \quad \Phi_j(T) = C_{\Phi}^{3/4} \frac{U_{jk,lk}(T)}{U_{jk}(T)} \exp \left\{ -\frac{x_{ijk}}{kT} \right\}
\]

\[
\Phi_j(T) = C_{\Phi}^{3/4} \frac{U_{jk,lk}(T)}{U_{jk}(T)} \exp \left\{ -\frac{x_{ijk}}{kT} \right\}
\]

\[
C_{\Phi} = 2 \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} = 4.83 \times 10^{16} \text{ cm}^{-3} K^{-3/2}
\]
SAHA - in terms of electron pressure $P_e = n_e kT$

$$n_e = \frac{P_e}{kT}$$

so, changes power of $kT$ from $\frac{3}{2}$ to $\frac{5}{2}$ in previous equations: $(kT)^{3/2} \rightarrow (kT)^{5/2}$

and if we use notation $\Theta = \frac{5040}{T}$ for $\frac{1}{kT}$ in [eV$^{-1}$]

we have the alternate form:

$$\frac{n_{\text{IJK}}}{n_{\text{JK}}} = \frac{2}{P_e} \left( \frac{2\pi \hbar^2}{m_e} \right)^{3/2} \frac{(kT)^{5/2}}{U_{\text{IJK}}(T)} \frac{U_{\text{JK}}(T)}{10^{-\Theta \chi_{\text{IJK}}}}$$

in terms of pressure (electron) and $\Theta$

in log$_{10}$ format:

$$\log \left( \frac{n_{\text{IJK}}}{n_{\text{JK}}} \right) = \log C_\Phi - \log n_e + \frac{3}{2} \log T + \log \left( \frac{U_{\text{IJK}}(T)}{U_{\text{JK}}(T)} \right) - \frac{5040}{T} \chi_{\text{IJK}}$$

w/ $\log C_\Phi = 15.68$ electron density

or:

$$\log \left( \frac{n_{\text{IJK}}}{n_{\text{JK}}} \right) = \log C'_\Phi - \log P_e + \frac{5}{2} \log T + \log \left( \frac{U_{\text{IJK}}(T)}{U_{\text{JK}}(T)} \right) - \frac{5040}{T} \chi_{\text{IJK}}$$

w/ $\log C'_\Phi = -0.1761$ electron pressure

these forms can be computationally convenient...
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* Source: National Institute of Standards and Technology (NIST) (http://www.nist.gov/)
All data quoted to the accuracy given by NIST
these metals dominate neon gases until H ionizes
Applying Saha to obtain ionization fractions

- Saha provides ratio of densities of adjacent ionization stages, \( \frac{n_{n+1}}{n_n} \), but we require ionization fractions

\[
f_{jk} = \frac{n_{j(k)}}{n_k} \quad \text{where} \quad n_k = \sum_{j=1}^{k+1} n_{j(k)}
\]

- Consider neutral hydrogen \( f_{11} \)

\[
f_{11} = \frac{n_{11}}{n_{11} + n_{21}} = \frac{1}{1 + \frac{n_{21}}{n_{11}}} = \frac{1}{1 + n_e \Phi_{11}(T)}
\]

- Consider ionized hydrogen \( f_{21} \)

\[
f_{21} = \frac{n_{21}}{n_{11} + n_{21}} = \frac{n_{21}/n_{11}}{1 + n_{21}/n_{11}} = \frac{n_{21} \Phi_{21}(T)}{1 + n_e \Phi_{11}(T)} = f_{11} \cdot \frac{n_{21} \Phi_{21}(T)}{1 + n_e \Phi_{11}(T)}
\]

where

\[
\Phi_{n}(T) = C_n T^{3/2} \frac{U_{n}(T)}{U_1(T)} \exp \left\{ - \frac{X_{n}}{kT} \right\}
\]

- For helium \( f_{12}, f_{22}, f_{23} \) (neutral, once ionized, twice ionized)

\[
f_{12} = \frac{n_{12}}{n_{12} + n_{22} + n_{32}} = \frac{1}{1 + \frac{n_{32}/n_{12}}{n_{12} + n_{32}/n_{12}}} = \frac{1}{1 + \frac{n_{22}/n_{12}}{1 + \left( \frac{n_{32}/n_{22}}{n_{22}/n_{12}} \right)}}
\]

\[
f_{12} = \frac{1}{1 + n_e \Phi_{12}(T) + n_e \Phi_{22}(T) \Phi_{12}(T)}
\]

where

\[
\Phi_{12}(T) = C_\Phi T^{3/2} \frac{U_{22}(T)}{U_{12}(T)} \exp \left\{ - \frac{X_{12}}{kT} \right\}
\]

\[
\Phi_{22}(T) = C_\Phi T^{3/2} \frac{U_{32}(T)}{U_{22}(T)} \exp \left\{ - \frac{X_{22}}{kT} \right\}
\]
\[ f_{zz} = \frac{n_{zz}}{n_{zz} + n_{z2} + n_{z3}} = \frac{n_{zz}/n_{1z}}{1 + n_{1z}/n_{zz} + (n_{zz}/n_{xx})(n_{zz}/n_{1z})} = f_{12} n_{z}^{-1} \Phi_{zz}(T) \]

\[ f_{z2} = \frac{n_{z2}}{n_{1z} + n_{z2} + n_{z3}} = \frac{(n_{zz}/n_{x2})(n_{zz}/n_{1z})}{1 + n_{1z}/n_{zz} + (n_{zz}/n_{xx})(n_{zz}/n_{1z})} = f_{22} n_{z}^{-1} \Phi_{z2}(T) \]

\[ f_{z3} = \frac{n_{z3}}{n_{1z} + n_{z2} + n_{z3}} = \frac{(n_{zz}/n_{x3})(n_{zz}/n_{1z})}{1 + n_{1z}/n_{zz} + (n_{zz}/n_{xx})(n_{zz}/n_{1z})} = f_{23} n_{z}^{-1} \Phi_{z3}(T) \]

**Recursive Pattern Emerges**

let \[ Y_{jk} = \frac{n_{j+1,k}}{n_{j,k}} = n_{z}^{-1} \Phi_{jk}(T) \] as new variable.

then for hydrogen

\[ f_{11} = \frac{1}{1 + Y_{11}} \quad f_{21} = f_{11}, Y_{11} \]

for helium

\[ f_{12} = \frac{1}{1 + Y_{12} + Y_{12} Y_{z2}} \quad f_{22} = f_{12} \cdot Y_{12} \quad f_{32} = f_{22} \cdot Y_{z2} \]

for lithium

\[ f_{13} = \frac{1}{1 + Y_{13} + Y_{13} Y_{z3} + Y_{13} Y_{z2} Y_{z3}} \quad f_{23} = f_{13} \cdot Y_{13} \quad f_{33} = f_{23} \cdot Y_{z3} \quad f_{33} = f_{33} \cdot Y_{z3} \]

**IN GENERAL**

\[ f_{jk} = \frac{P_{jk}}{S_{k}} \quad \text{where } P_{1k} = 1 \quad \text{and} \quad P_{jk} = P_{j+1,k} Y_{j+1,k} (j > 1) \]

\[ S_{k} = \Sigma_{j=1}^{k-1} P_{jk} \]

and where

\[ T_{\text{recursion formula}}. \]
Figure 6.3. (a) Fractional ionization of hydrogen versus temperature (solid curve is electron pressure $P_e = 10$ dynes/cm$^2$, dashed curve is $P_e = 1$ dynes/cm$^2$). (b) Fractional ionization of He (for $P_e = 1$ and $P_e = 10$ dynes/cm$^2$).

$Y_{1k} = n_e^{-1} f_{jk}(T)$

HI: $f_{11} = \frac{1}{1 + Y_h}$

HII: $f_{21} = f_{11} Y_{11} = \frac{Y_{11}}{1 + Y_{11}}$

HeI: $f_{12} = \frac{1}{1 + Y_{12} + Y_{12} Y_{22}}$

HeII: $f_{22} = f_{12} Y_{12} = \frac{Y_{12}}{1 + Y_{12} + Y_{12} Y_{22}}$

HeIII: $f_{32} = f_{22} Y_{22} = \frac{Y_{12} Y_{22}}{1 + Y_{12} + Y_{12} Y_{22}}$

Recursive Saha used to get ionization fractions $f_{jk}(n_e, T)$

Figure 2.13 Behavior of the hydrogen lines with temperature.

$\frac{n_{211}}{n_{111}} = \frac{n_{211}/n_{111}}{1 + n_{21}/n_{11}}$

Boltzmann

Saha

$\frac{n_{211}}{n_{111}} = \frac{g_{211}}{U_{11}(T)} \exp \left\{ \frac{-\chi_{211}}{kT} \right\}$

$\chi_{211} = R_{11} (1 - \frac{1}{2})$ excitation potential $n = 2$

$\frac{n_{2}}{n_{11}} = n_e^{-1} \phi(T) = Y_{11}$
Fig. 13.4. Typical metal lines show strong changes in strength as a function of temperature. The cases discussed in the text are shown.

- **Case 1:** weak line of neutral species with element mostly neutral.
- **Case 2:** weak line of neutral species with element mostly ionized.
- **Case 3:** weak line of an ion with element mostly neutral.
- **Case 4:** weak line of an ion with element mostly ionized.

Temperature affects on EW due to occupation of states - in this case ground state neutral Na dominant effect ⇒ ionized w/ increasing T (Saha Equation).

Fig. 13.5. The sodium D lines weaken with increasing temperature. These measurements were made at the Elginfield Observatory with a spectral-line scanner having a resolution of ≈0.27Å.
Single macroscopic variable describing thermal conditions of components of gas

TEMPERATURES

radiation

\( T_R \)

excitation levels

\( T_e \)

electron pool

\( T_e \)

kinetic (atoms/molecules)

\( T_k \)

\( T_e = T_k \) in stellar atmospheres

In T.E.'s

\( T = T_R = T_e = T_{ex} = T_k \)

\( B_x (T) = \frac{2hc}{\lambda^2} \frac{1}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \)

\( f(v) = \left\{ \begin{array}{ll}
\frac{m}{2\pi kT}^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) & \text{for radiation} \\
9_{ij} \exp\left(-\frac{X_{ij}}{kT_k}\right) & \text{for electrons} \\
9_{ii} \exp\left(-\frac{X_{ii}}{kT_k}\right) & \text{for excited states}
\end{array} \right. 
\)

\( \frac{n_{ij}}{n_j} = \frac{g_{ij} \exp\left(-\frac{X_{ij}}{kT_k}\right)}{U_i (T_k)} \)

\( \frac{n_{ii}}{n_j} = \frac{2}{n_e} \frac{U_{ii}(T_k)}{U_i (T_k)} \left(\frac{2\pi m k T_k}{\hbar^3}\right)^{3/2} \exp\left(-\frac{X_{ii}}{kT_k}\right) \)

but... what if not T.E.? then we define the various appropriate temperatures ...
Relationships between various "Temperatures"

0. **Radiation Temperature** - is wavelength dependent. It is temperature inserted in Planck function that yields \( B_\lambda (T_R) = S_\lambda \) where \( S_\lambda \) is the source function describing the actual value of the radiation intensity at wavelength \( \lambda \), as measured.

\[
S_\lambda = B_\lambda (T_R) = \frac{2hc}{\lambda^5} \frac{1}{\exp(hc/\lambda k T_R)-1}
\]

0. **Electron Temperature** - temperature that describes \( f(v) \) of the electron pool. Electrons rapidly thermalize and thus \( T_e \) is a robust macroscopic parameter describing the gas thermal conditions.

\[
f(v) = \frac{(m_e / 2\pi k T_e)^{3/2}}{\exp(-mv^2 / 2k T_e)}
\]

0. **Excitation Temperature** - the temperature inserted into the Boltzmann Eq. \( n_j \) that provides the actual value measured.

\[
\left( \frac{n_{j+1}}{n_j} \right)_{\text{measured}} = \frac{g_{j+1} \exp \left(-\frac{\chi_{j+1}}{k T_{ex}} \right)}{g_j U_j(T_{ex})}
\]

Tex measures combination of photo and collisional excitation processes.

0. **Saha is both excitation and electron**

\[
\left( \frac{n_{j+1}}{n_j} \right)_{\text{measured}} = \frac{Z}{N_e} \frac{U_{j+1}(T_{ex})}{U_j(T_{ex})} \left( \frac{2 \pi m_e k T_e}{h^3} \right)^{3/2} \exp \left(-\frac{\chi_{j+1}}{k T_{Te}} \right)
\]

Tex measures combination of photo and collisional excitation processes.

\* In reality, none of these temperatures are real, nor should they be viewed as being physical; for our purposes, their definitions serve to illustrate that the above TE equations strictly apply only when all processes are characterized by a single temperature.
Figure 7-25
Temperature distribution for LTE and non-LTE models with $T_{\text{eff}} = 15,000$°K and $\log g = 4$. The atmosphere is composed of hydrogen, which is represented by a schematic model atom with three bound levels and continuum. This model atom accounts for the Lyman, Balmer, Paschen, and free-free continua, and the $H\alpha$ line. From (41), by permission.

When $\chi < 10^{-2}$, LTE breaks down because radiation becomes non-local.

Figure 7-19
Non-LTE departure coefficients in the first two states of hydrogen for a model with $T_{\text{eff}} = 15,000$°K and $\log g = 4$. Dashed curves: Lyman, Balmer and free-free continua only; solid curves: Ly line included. The optical depth scale in the abscissa is measured just longward of the Balmer jump. From (40), by permission.

Departure from LTE, measured using departure coefficients, $b_i = \frac{n_i}{n_i^{\text{LTE}}}$.

$\text{Hydrogen departure coefficients}$

Figure 7-20
Non-LTE departure coefficients in the second and third level of hydrogen in a model with $T_{\text{eff}} = 15,000$°K and $\log g = 4$. Dotted curves: Lyman, Balmer, Paschen, and free-free continua only; solid curves: $H\alpha$ included. Optical depth scale as in Figure 7-19. From (41), by permission.