# Stellar/Planetary Atmospheres

## Part 10: EOS

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# LTE equation of state

- TE = thermodynamic equilibrium
  - state completely described by 2 thermodyn. quantities ($T, P_{\rm gas}$)
  - detailed balance for *all* processes
- local thermodynamic equilibrium (LTE)
  - assume TE holds locally even though there are gradients

# LTE equation of state

- LTE assumes that non-local effects (radiation!) are unimportant
- material is driven toward LTE, e.g., by collisional processes
- non-local process tend to destroy LTE
- in many cases, radiation can easily invalidate LTE

# LTE is OK if . . .

- collisions dominate radiation
- radiation field is Planckian
- no scattering of radiation

# LTE is nonsense if . . .

- radiation dominates collisions
    - chromospheres, coronae
    - optically thin regions of all stars
- scattering is important
    - hot stars (electron scattering, line scattering)
    - novae/SNe
    - lines of some elements (Lyman series of H)

# Maxwell velocity distribution

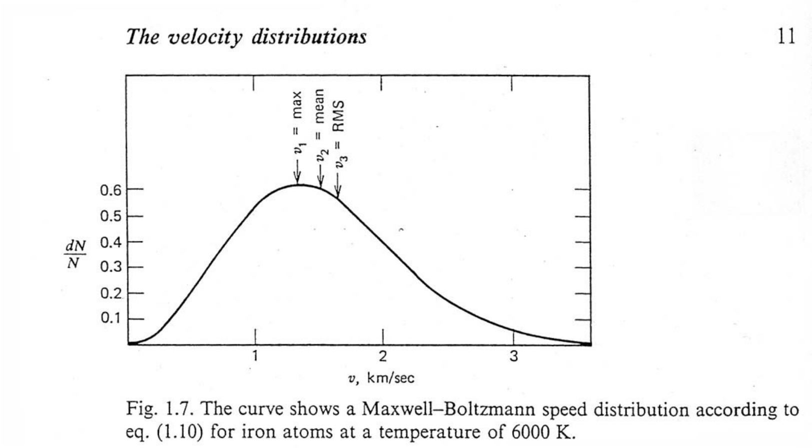
- holds in TE
- in stars, it basically always holds to very good approximation

$$f(\vec{v})\,d\vec{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{1/2mv^2}{kT}\right)\,d\vec{v}$$

or for $v = |\vec{v}|$

$$f(v)\,dv = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{1/2mv^2}{kT}\right) 4\pi v^2\,dv$$

# Maxwell velocity distribution



*The velocity distributions* 11

Fig. 1.7. The curve shows a Maxwell–Boltzmann speed distribution according to eq. (1.10) for iron atoms at a temperature of 6000 K.

# Maxwell velocity distribution

- most probable velocity: $v_1 = \sqrt{2kT/m}$
- average velocity: $v_2 = \sqrt{8kT/\pi m}$
- rms velocity: $v_3 = \sqrt{3kT/m}$

# Boltzmann excitation formula

- describes the relative populations between 2 energy levels
- holds only in TE (or LTE)

$$\frac{n_i}{n_1} = \frac{g_i}{g_1} \exp\left(-\frac{\chi_i}{kT}\right)$$

- $n_i$: population density (particles $/\mathrm{cm}^3$)
- $g_i$: statistical weights (number of degenerate quantum states)
- $\chi_i$: excitation energy ($\chi_1 \equiv 0$)

# Boltzmann excitation formula

- set

  $$N = \sum n_i$$

  so that

  $$N = \frac{n_1}{g_1} \sum g_i \exp\left(-\frac{\chi_i}{kT}\right) \equiv \frac{n_1}{g_1} Q(T)$$

- $Q$: partition function (*Zustandssumme*, sometimes $Z$)

# Boltzmann excitation formula

- with $Q$ we have

$$\frac{n_i}{N} = \frac{g_i}{Q} \exp\left(-\frac{\chi_i}{kT}\right)$$

- → with given $Q$ and $N$ we can calculate the population of any/all level

# Properties of $Q$

$$Q = \sum g_i \exp\left(-\frac{\chi_i}{kT}\right)$$

- it is divergent!

$$\lim_{n\to\infty} \sum_{i=0}^{n} g_i \exp\left(-\frac{\chi_i}{kT}\right) = \infty$$

because $g_i \geq 1$ and $\chi_i \leq \chi_{\mathrm{ion}}$

# Properties of $Q$

- this is only a problem for a single atom with infinite space!
- in reality:
  - last bound state Bohr radius $\leq$ average distance between atoms

    $$r_n = n^2 a_0 \leq r_v = (3/4\pi N)^{1/3}$$

    so that

    $$n^2 \leq (3/4\pi N)^{1/3} / a_0$$

  - $a_0$: Bohr radius of ground state (e.g., H I)
  - $N$: particle density ($1/cm^3$)
- $N = 10^{15} \rightarrow n_{\mathrm{H\ I}} \approx 30$

# The Saha Equation

- how to describe ionization/recombination?
- in general: rate equations!
- in LTE: Saha equation
- describes distribution of nuclei over all ionization stages
- considers chemical equilibrium

$$n_k \rightleftharpoons n_{k+1} n_{\mathrm{e}}$$

- it is basically an extension of the Boltzmann formula to "continuum" states

# The Saha Equation

$$n_k = n_{k+1} n_{\mathrm{e}} \frac{Q_k}{Q_{k+1} Q_{\mathrm{e}}} \left( \frac{h^2}{2\pi m_e k T} \right)^{3/2} \exp\left( \frac{\chi_{k\to k+1}}{kT} \right)$$

- $n_k$: number density of ionization stage $k$ (summed over all energy levels)
- $n_{\mathrm{e}}$: electron density
- $Q_k$: partition function of state $k$
- $Q_{\mathrm{e}} = 2$
- $\chi_{k\to k+1}$: ionization energy (ground state to ground state)

# The Saha Equation

- combination with Boltzmann formula is easily possible
- for *given* $(T, n_{\rm e})$:
  Saha-Boltzmann formula → explanation of Harvard sequence
- compute

$$f_{ij} \equiv \frac{n_{ij}}{n_i}$$

- $n_{ij}$: number density of element $i$ in ionization stage $j$
- $n_i = \sum_j n_{ij}$

# The Saha Equation

$$f_{ij} = \frac{n_{ij}/n_{i0}}{n_i/n_{i0}} = \frac{(n_{i1}/n_{i0})(n_{i2}/n_{i1})\cdots(n_{ij}/n_{ij-1})}{1+(n_{i1}/n_{i0})+(n_{i1}/n_{i0})(n_{i2}/n_{i1})+\cdots}$$

- $f_{ij} = f_{ij}(T, n_\mathrm{e}, P_\mathrm{gas})$

# Harvard sequence

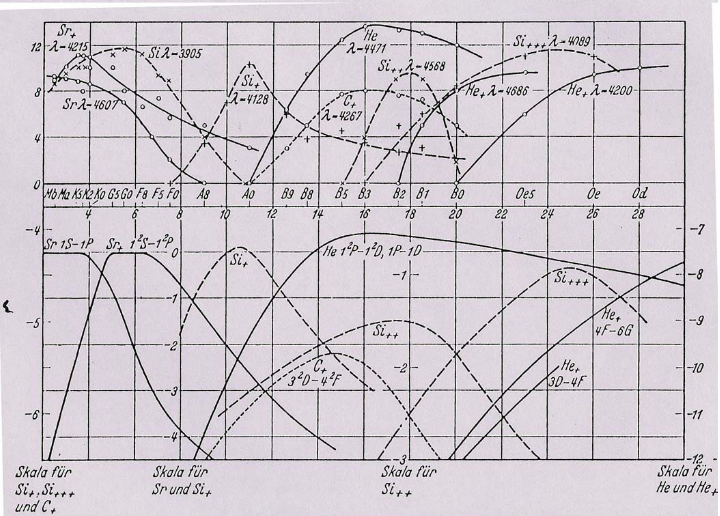


Abb. 48. [Nach C. H. Payne [407] und Harvard Circ. 256, (1924).] Oberer Teil der Abbildung: Beobachtete Linienintensitäten. Unterer Teil der Abbildung: Nach Fowler und Milne für $P_e = 132$ bar berechnete Konzentrationen (in logarithmischem Maßstab). Die Skala der Spektraltypen ist der Temperaturskala (Abszissen = $T \cdot 10^{-3}$) so angepaßt, daß die beobachteten und berechneten Maxima zusammenfallen: Vorläufige Ionisations-Temperaturskala.

# The Saha Equation

- need equations to close the system
- → particle conservation

$$n_i = \epsilon_i \left( P_{\mathrm{gas}}/kT - n_{\mathrm{e}} \right)$$

- $\epsilon_i$: normalized abundance (by number) of this element
- charge conservation:

$$n_{\mathrm{e}} = \sum_i \sum_j q_{ij} n_{ij}$$

# The Saha Equation

- problem: need to know $n_{\rm e}$ for $(T, P_{\rm gas})$!
- insert $f_{ij}$ into charge conservation $\rightarrow$

$$n_{\rm e} = \sum_i n_i \sum_j q_{ij} f_{ij} = (P_{\rm gas}/kT - n_{\rm e}) \sum_i \epsilon_i \sum_j q_{ij} f_{ij}$$

so that

$$P_{\rm gas}/kT = n_{\rm e} \left[ 1 + \frac{1}{\sum_i \epsilon_i \sum_j q_{ij} f_{ij}} \right]$$

- one non-linear ($f_{ij}$!) equation for $n_{\rm e}$
- can be solved by any suitable root-finding method!

# The Equation of State

- high temperatures: only ions
- → solve Saha equations for $n_\mathrm{e}$
- → know all partial pressures!
- → done.

# The Equation of State

- low temperatures: consider molecules!
- mass action law for molecule $AB$ and atoms $A$ and $B$

$$\frac{P_A P_B}{P_{AB}} = K_{AB}(T)$$

or

$$\frac{P_A P_B P_C \cdots P_n}{P_{ABC\ldots n}} = (kT)^{n-2} K_{ABC\ldots n}(T)$$

for molecules with $> 2$ nuclei

- *non-linear!*

# The Equation of State

- dissociation constant $K(T)$:

$$K_{AB}(T) = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} kT \, \frac{Q_A Q_B}{Q_{AB}} \, e^{-D_0^0/kT}$$

  where $m = m_A m_B / m_{AB}$
- $D_0^0$: dissociation energy

# The Equation of State

- molecules, atoms, ions, electrons contribute to $P_{\mathrm{gas}}$

$$P_{\mathrm{gas}} = P_{\mathrm{atom}} + P_{\mathrm{ions}} + P_{\mathrm{elec}} + P_{\mathrm{molec}}$$

- must solve set of chemical equilibria to compute each $P_i$
- in terms of number densities:

$$N_i = N_i^{\mathrm{at}} + \sum_j N_{ij}^{\mathrm{ion}} + \sum_k \alpha_{ik} N_k^{\mathrm{mol}}$$

- $N_{ij}$: number density of atom $i$ in ionization state $j$
- $\alpha_{ik}$: number of nuclei of element $i$ in molecule $k$

# The Equation of State

- particle conservation:

$$N_T = \sum_{i=1}^{n_{\rm at}} N_i = \frac{1}{kT}\left[P_g - P_e + \sum_{k=1}^{n_{\rm mol}} (\alpha_k - 1) P_k^{\rm mol}\right]$$

- conservation of nuclei:

$$\varepsilon_i = \frac{N_i}{\sum_{i=1}^{n_{\rm at}} N_i} = \frac{N_i \cdot kT}{P_g - P_e + \sum_{k=1}^{n_{\rm mol}} (\alpha_k - 1) P_k^{\rm mol}}$$

- $\varepsilon_i$: fraction of atoms of element $i$ relative to $N_T$

# The Equation of State

- from this we obtain:

$$
\begin{aligned}
0 \;=\; & \varepsilon_i \cdot \left[ P_g - P_e + \sum_{k=1}^{n_{\mathrm{mol}}} (\alpha_k - 1) P_k^{\mathrm{mol}} \right] \\
& - P_i^{\mathrm{at}} - \sum_{j=1}^{n_{\mathrm{ion}}} P_{ij}^{\mathrm{ion}} - \sum_{k=1}^{n_{\mathrm{mol}}} \alpha_{ik} P_k^{\mathrm{mol}}
\end{aligned}
$$

- set of linear equations?
- however, system is non-linear via Saha equation and mass-action law!

# The Equation of State

- add charge conservation:

$$P_e = \sum_{i=1}^{n_{\mathrm{at}}} \sum_{j=1}^{n_{\mathrm{ion}}} Z_j \cdot P_{ij}^{\mathrm{ion}}$$

  where $Z_j$ is here the electric charge associated with ionization state $j$

- $\rightarrow$ close the system

# The Equation of State

- molecular EOS can be solved by 'any' method
- Problem: large number of molecules!

# Molecules

Selected molecules considered in the EOS

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| NH | $C_2$ | CN | CO | MgH | CaH | SiH | TiO | $H_2O$ | $H_2$ |
| $N_2$ | NO | $CO_2$ | $O_2$ | ZrO | VO | MgS | SiO | AlH | HCl |
| HF | HS | TiH | AlO | BO | CrO | LaO | MgO | ScO | YO |
| SiF | NaCl | CaOH | HCN | $C_2H_2$ | $CH_4$ | $CH_2$ | $C_2H$ | HCO | $NH_2$ |
| LiOH | $C_2O$ | AlOF | NaOH | MgOH | $AlO_2$ | $Al_2O$ | AlOH | $SiH_2$ | $SiO_2$ |
| $H_2S$ | OCS | KOH | $TiO_2$ | TiOCl | $VO_2$ | $FeF_2$ | $YO_2$ | $ZrO_2$ | BaOH |
| $LaO_2$ | $C_2H_4$ | $C_3$ | $SiC_2$ | $CH_3$ | $C_3H$ | $NH_3$ | $C_2N_2$ | $C_2N$ | $CaF_2$ |
| AlOCl | $Si_2C$ | $CS_2$ | $CaCl_2$ | AlF | CaF | $Si_2$ | SiS | CS | AlCl |
| KCl | CaCl | TiS | TiCl | SiN | AlS | $AL_2$ | FeO | SiC | $TiF_2$ |
| FeH | LiCl | NS | NaH | SO | $S_2$ | $AlBO_2$ | AlClF | $AlCl_2$ | $AlF_2$ |
| $AlOF_2$ | $AlO_2H$ | $Al_2O_2$ | $BeBO_2$ | OBF | HBO | $HBO_2$ | HBS | $BH_2$ | $BO_2H_2$ |
| $BH_3$ | $H_3BO_3$ | $KBO_2$ | $LiBO_2$ | $NaBO_2$ | $BO_2$ | $BaCl_2$ | $BaF_2$ | $BaO_2H_2$ | BaClF |
| $BeCl_2$ | $BeF_2$ | BeOH | $BeH_2$ | $BeH_2O_2$ | $Be_2O$ | $Be_3O_3$ | ClCN | CHCl | CHF |
| CHP | $CH_3Cl$ | KCN | NaCN | $BeC_2$ | $C_2HCl$ | $C_2HF$ | $(NaCN)_2$ | $C_4$ | $C_5$ |
| $CaO_2H_2$ | MgClF | $SiH_3Cl$ | $FeCl_2$ | $K_2Cl_2$ | $MgCl_2$ | $Na_2Cl_2$ | $TiOCl_2$ | $SrCl_2$ | $TiCl_2$ |
| $ZrCl_2$ | $TiCl_3$ | $ZrCl_3$ | $ZrCl_4$ | $CrO_2$ | $SiH_3F$ | OTiF | $SiH_2F_2$ | $MgF_2$ | $SrF_2$ |
| $ZrF_2$ | $TiF_3$ | $ZrF_4$ | $FeO_2H_2$ | SrOH | $(KOH)_2$ | $(LiOH)_2$ | $MgO_2H_2$ | $(NaOH)_2$ | $SrO_2H_2$ |
| $PH_2$ | $PH_3$ | $SiH_4$ | $Si_2N$ | $PO_2$ | $SO_2$ | $P_4$ | $Si_3$ | $NO_2$ | $NO_3$ |
| $C_3N$ | $C_2H_3$ | $C_4H$ | $HC_3N$ | $C_4H_2$ | $CH_3CN$ | $HC_5N$ | $C_6H$ | $C_4H_4$ | $C_6H_2$ |
| $HC_7N$ | $C_4H_4S$ | $C_4H_4O$ | $C_4H_6$ | $C_6H_4$ | $HC_9N$ | $C_5H_5N$ | $C_6H_5O$ | $C_6H_6$ | $C_6H_6O$ |
| $HC_{11}N$ | $OH^-$ | $CH^-$ | $C_2^-$ | OH | CH | $CN^-$ | $SiH^-$ | $H_2^-$ | $HS^-$ |
| $CS^-$ | $FeO^-$ | $BO^-$ | $AlCl_2{}^-$ | $AlF_2{}^-$ | $AlOF_2{}^-$ | $AlOH^-$ | $CO_2{}^-$ | $NO^+$ | $H_2{}^+$ |
| $TiO^+$ | $ZrO^+$ | $AlOH^+$ | $BaOH^+$ | $HCO^+$ | $CaOH^+$ | $SrOH^+$ | $H_3O^+$ | $H_3^+$ | |

# The Equation of State

- very low temperatures ($< 2000\,\mathrm{K}$)
- $\rightarrow$ need to consider condensation!!

# Liquids & Solids

Selected liquid/dust species considered in the EOS

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Al/l | B/l | Ba/l | Be/l | Ca/l | Cr/l | Cu/l | Fe/l | K/l |
| Li/l | Mg/l | Mn/l | Na/l | Nb/l | Ni/l | P/l | S/l | Si/l |
| Sr/l | Ti/l | V/l | Zn/l | Zr/l | BeO/l | ClK/l | NbO/l | OSr/l |
| ClNa/l | VO/l | $B_2Ti$/l | $BaCl_2$/l | $CaCl_2$/l | $Cl_2Fe$/l | $Cl_2Sr$/l | $O_2Si$/l | $Li_2O$/l |
| $Mg_2Si$/l | $Cu_2O$/l | $Cl_3Fe$/l | $Cr_2O_3$/l | $NiS_2$/l | $BLiO_2$/l | $Cl_2S_2$/l | $Ni_3S_2$/l | $Al_2O_3$/l |
| $O_3V_2$/l | $Cl_5Nb$/l | $Nb_2O_5$/l | $B_4K_2O_7$ | $B_4Na_2O_7$ | $Li_2O_3Si$ | $B_4Li_2O_7$ | $Mg_3O_8P_2$ | $Al_3F_{14}N$ |
| $B_5H_9$/l | $H_{10}O_8S$ | $B_8K_2O_{13}$ | $B_{10}H_{14}$ | Al | B | Ba | Be | C |
| Ca | Co | Cr | Cu | Fe | Li | Mg | Mn | Na |
| Nb | Ni | P | S | Si | Sr | Ti | V | Zn |
| Zr | MgO | FeS | CaO | CaS | MgS | TiN | AlN | NiS |
| MnS | TiO | VO | CuO | FeO | TiC | SiC | ZrC | $H_2O$ |
| $TiO_2$ | $ZrO_2$ | $SiO_2$ | $FeS_2$ | $NiS_2$ | $Mg_3N_2$ | $Ni_3S_2$ | $Ti_2O_3$ | $Ti_3O_5$ |
| $Ti_4O_7$ | $V_2O_3$ | $Al_2O_3$ | $Al_2O_3$ | $Al_2O_3$ | $Al_2O_3$ | $Al_2S_3$ | $Cr_2O_3$ | $CaTiO_3$ |
| $MgTiO_3$ | $MgSiO_3$ | $CaSiO_3$ | $MnSiO_3$ | $Na_2SiO_3$ | $K_2SiO_3$ | $Fe_2SiO_4$ | $Ca_2SiO_4$ | $Mg_2SiO_4$ |
| $ZrSiO_4$ | $Fe_2O_3$ | $Fe_3O_4$ | $MgAl_2O_4$ | $MgTi_2O_5$ | $Al_2SiO_5$ | $CaMgSi_2$ | $Ca_2MgSi$ | $Ca_2Al_2S$ |
| $CaAl_2Si$ | $KAlSi_3O$ | $NaAlSi_3$ | $Al_6Si_2O$ | $MgC_2$ | $Cr_3C_2$ | $Mg_2C_3$ | $Al_4C_3$ | $Cr_7C_3$ |
| $Cr_{23}C_6$ | | | | | | | | |