

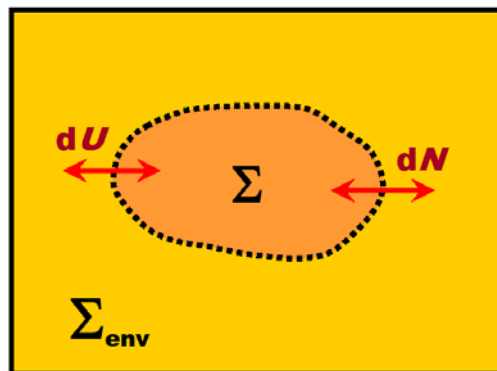
5. The GRAND CANONICAL DISTRIBUTION

GOAL: To derive the grand canonical partition function, and to use it to analyze problems in which the chemical potential and/or particle transfer are important.

This section generalizes the whole notion of a partition function to include particle exchange – it is therefore connected directly to the Gibbs free energy and the grand canonical potential (see Chapter 1, part 1(c)), which you should look at again.

5(a) Grand Canonical Partition Function

We will consider a “sub-system” or central system Σ , coupled to a bath or reservoir Σ_{env} at temperature T and chemical potential μ , such that both particles and energy can be exchanged between the two. Thus the reservoir is now not only a thermal reservoir but also a particle reservoir. In the figure the central system is not yet in equilibrium – neither the temperature nor the particle concentrations are the same in system and reservoir, and flows still exist.



We are going to derive the grand partition function for this system – we will do this using 2 different methods, which exactly parallel those used for the derivation of the canonical partition function in the last chapter.

Argument 1: We know that the total energy E_0 , of the combined central system plus bath, is conserved. We also know that the total number N_0 of particles in this total system is conserved. We will again expand about the maximum probability state for the bath, as we did before.

To do this, let us again define the set of energies $\{ \mathcal{E}_k \}$ referring to the bath Σ_{env} , and the set $\{ \mathcal{E}_j \}$ for the central system Σ . We will also define the set $\{ N_\alpha \}$ of particle numbers for the bath, and $\{ n_\beta \}$ for the central system. We then have the constraints

$$E_0 = \mathcal{E}_k + \mathcal{E}_j = \text{const} \quad (\text{for all allowed pairs } k, j) \quad (1)$$

$$N_0 = N_\alpha + n_\beta = \text{const} \quad (\text{for all allowed pairs } \alpha, \beta) \quad (2)$$

where now we must include in our analysis all possible energy eigenstates states j, k of the system and bath respectively that obey eqtn. (1), as well as all possible number eigenstates that obey (2).

Again, the bath is by hypothesis very large compared to the central system, and so for any given values of E_0 and N_0 we expect that almost all of the energy and of the particles will be in the bath Σ_{env} . We therefore assume that

$$\mathcal{E}_j/E_0 \ll 1 \quad \text{and} \quad n_\beta/N_0 \ll 1 \quad (3)$$

for any of the relevant central system states. The description of the central system will then reside in the probabilities of occupation of the combined set of “pair states” labelled by $\{ j, \beta \}$.

Let us now count the number of microstates $\Omega_0(\mathcal{E}_j, n_\beta; \mathcal{E}_k, N_\alpha)$ corresponding to the macroscopic state of the combined system plus bath having these fixed number of particles and energy. We now get

$$\begin{aligned} \Omega_0(\mathcal{E}_j, n_\beta; \mathcal{E}_k, N_\alpha) &= \Omega(\mathcal{E}_j, n_\beta) \Omega_{\text{env}}(\mathcal{E}_k, N_\alpha) \\ &\times \delta(E_0 - (\mathcal{E}_j + \mathcal{E}_k)) \delta(N_0 - (n_\beta + N_\alpha)) \end{aligned} \quad (4)$$

with any sums over j, k, α, β , having to satisfy the constraints imposed by the two delta-functions.

From this point the argument goes along as before; the multiplicity $\Omega_{\text{env}}(\mathcal{E}_k, N_\alpha)$ for the bath states is far larger than that of the central system, and increases with both energy and particle number incredibly fast. Thus we can immediately see that the most probable energy for the bath is just its maximum possible value E_0 , and the most probable particle number for the bath is $N_\alpha = N_0$.

Again, as before, we want to find out how the probabilities vary as we move away from the maximum probability at $(\mathcal{E}_k, N_\alpha) = (E_0, N_0)$. To find this we expand around this maximum, now by varying the two variables (energy and particle number). We then get, in place of eqtns (4.4) and (4.5) in Chapter 4, the result

$$\begin{aligned}
\ln \Omega_{\text{env}}(E, N) &= \ln \Omega_{\text{env}}(E_0, N_0) + (d \ln \Omega_{\text{env}} / d E) \Big|_{E=E_0} (E_0 - E) \\
&\quad + (d \ln \Omega_{\text{env}} / d N) \Big|_{N=N_0} (N_0 - N) + \dots \\
&= \ln \Omega_{\text{env}}(E_0) - \beta \epsilon + \mu \beta n \dots
\end{aligned} \tag{5}$$

Where we use the fact that the energy of the central sub-system here is just $\epsilon = E_0 - E$, if the bath energy is E , and the number of particles in the sub-system is $n = N_0 - N$, if the bath number is N . As before, $\beta = 1/k_B T$, the inverse temperature. We identify the second coefficient here with $-\mu\beta = -\mu/k_B T$ using the same kind of thermodynamic arguments as we used in deriving the canonical partition function. In this case we can compare with, eg., eqn (41) for the variation dU of the energy with N ; we see that at constant p , one has $dS/dN = -\mu/T$, so that using Boltzmann's usual relation that $S = k \ln W$, we get $d \ln \Omega / d N = -\mu/k_B T$.

From this it follows, again by just exponentiating the result back, that we can write the probability function and partition function for this system in the form

$$P(\epsilon_j, n_\beta) = \exp[-\beta(\epsilon_j - \mu n_\beta)] / \Xi \tag{6}$$

$$\Xi(\beta, \mu) = \sum_{j, \beta} \exp[-\beta(\epsilon_j - \mu n_\beta)] \tag{7}$$

where $\Xi(\beta, \mu)$ is usually called the grand canonical partition function, and we note that in (7), we sum over both particle number index β and energy level index j .

Finally, let us emphasize that the energy ϵ_j in all these expressions denotes the eigenenergies of the whole central system, which may itself contain many particles. Later on we will, in the case where the central system is made up of independent particles, write $\epsilon_j = n \epsilon_j$, where the ϵ_j are the "1-particle" energies, ie., the energy per particle, and n is the number of particles (dropping the index β for brevity).

Argument 2: Our 2nd argument parallels the 2nd derivation of the canonical distribution in the preceding chapter. Assume Σ has a single quantum state only – the simplest system we can imagine - with energy E if it is occupied, or energy 0 if it is unoccupied. Thus the entropy in Σ depends entirely on whether it is occupied or not. As an example, consider a H atom in free space, which we imagine can either be in its ground state or in an ionized state (we ignore here all the excited states). In this case $E = -13.6eV$. A model which only has a single possible occupied state is actually a good description of certain impurity ions in solids.

Now suppose E is positive. The reservoir, and thus the total system, will have a smaller entropy when the state in Σ is occupied; indeed it will be reduced by an amount

$$\Delta S = \left(\frac{\partial S_0}{\partial N_0} \right)_U (-1) + \left(\frac{\partial S_0}{\partial U_0} \right)_N (-E) = \frac{\mu - E}{T} \quad (8)$$

where the second equal sign accords with our the definitions for μ and T . Now we recall that

$$\left(\frac{\partial S_0}{\partial N_0} \right)_U \equiv -\frac{\mu}{T} \quad \text{and} \quad \left(\frac{\partial S_0}{\partial U_0} \right)_N \equiv \frac{1}{T} \quad (9)$$

Thus when a particle leaves the reservoir the change in entropy has two contributions: one from the decrease in the particle number from $N_0 \rightarrow N_0 - 1$, and a second from the decrease in the energy in the reservoir by an amount E .

Generalizing to a state that can hold n particles, we get

$$\Delta S = \frac{n\mu - E(n)}{T} \quad (10)$$

where the intensive variables μ and T for the large reservoir are independent of n , but $E(n)$ is extensive, and is in general a non-trivial function of n ; only if the particles are non-interacting do we have $E(n) = nE$.

The probability that the state is occupied by n particles, with energy $E(n)$ can now be compared with the probability that the state is unoccupied. We get

$$\frac{\Omega_{occ}}{\Omega_{unocc}} = \frac{\exp[S_{occ}/k_B]}{\exp[S_{unocc}/k_B]} = \exp[\Delta S/k_B] = \exp\left[\frac{n\mu - E(n)}{k_B T}\right] = \exp[\beta(n\mu - E(n))] \quad (11)$$

and, just as in the canonical distribution, this must hold true for a microsystem with multiple energy levels and occupancies. The only way for this to hold true is if the probability for the system to contain n particles in microstate i with energy E_i is proportional to the *Gibb's factor* $\equiv \exp[\beta(n\mu - E_i)]$, so that we can write

$$P(n, E_i) = \Xi^{-1} \exp[\beta(n\mu - E_i)] \quad (12)$$

As in (60) above; and the normalization constant Ξ , ie., the grand canonical partition function, is just given by (7) as before.

Properties of Grand Canonical Partition Function: There are various useful things we can say about Ξ . Let us first just find the probability that the system has n

particles - this is clearly just obtained by summing over all microstates E_i with n particles, so that we get

$$P(n) = \Xi^{-1} \sum_i \exp[\beta(n\mu - E_i)] = \Xi^{-1} \exp[\beta n\mu] \sum_i \exp[-\beta E_i] \quad (13)$$

$$P(n) = \Xi^{-1} \alpha^n Z_n$$

where Z_n is the partition function for n particles, and we define the function

$$\alpha \equiv \exp[\beta\mu] \quad (14)$$

This function $\alpha(\beta\mu)$ is usually called the *activity*. From the result in (13) we can now find the expectation value $\langle n \rangle$ of n , and we get:

$$\langle n \rangle = \Xi^{-1} \sum_{n,i} n \exp[\beta(n\mu - E_i)] = k_B T \Xi^{-1} \left(\frac{\partial \Xi}{\partial \mu} \right)_T = \left(\frac{\partial \ln \Xi}{\partial \ln \alpha} \right)_T = \frac{\alpha}{\Xi} \left(\frac{\partial \Xi}{\partial \alpha} \right)_T \quad (15)$$

which should be compared with the analogous relation in the canonical ensemble for the mean energy.

Fluctuations in n : In the canonical ensemble, the energy could fluctuate but not the particle number. In the grand canonical ensemble n fluctuates as well. The mean squared fluctuation in occupancy, defined by

$$\langle \Delta n^2 \rangle \equiv \langle n^2 \rangle - \langle n \rangle^2 \quad (16)$$

is then given by computing these 2 quantities, to get

$$\langle n^2 \rangle = \Xi^{-1} \sum_{n,i} n^2 \exp[\beta(n\mu - E_i)] = \beta^{-2} \Xi^{-1} \left(\frac{\partial^2 \Xi}{\partial \mu^2} \right)_T \quad (17)$$

$$\langle n \rangle^2 = \left[\beta^{-1} \Xi^{-1} \left(\frac{\partial \Xi}{\partial \mu} \right)_T \right]^2 \quad (18)$$

Thus we finally obtain

$$\langle \Delta n^2 \rangle = \beta^{-2} \frac{\partial}{\partial \mu} \left(\Xi^{-1} \frac{\partial \Xi}{\partial \mu} \right)_T = \beta^{-1} \left(\frac{\partial \langle n \rangle}{\partial \mu} \right)_T = \beta^{-1} \left(\frac{\partial \mu}{\partial \langle n \rangle} \right)^{-1} \quad (19)$$

And we see that if μ is insensitive to $\langle n \rangle$ then fluctuations in $\langle n \rangle$ will be large. In the same we we can calculate the mean value of the energy, as:

$$\langle E \rangle = \Xi^{-1} \sum_{n,i} E_i \exp[\beta(n\mu - E_i)] = -\Xi^{-1} \left(\frac{\partial \Xi}{\partial \beta} \right)_T + \mu \langle n \rangle \quad (20)$$

and if we wish we could also calculate fluctuation in the energy E in the same way as for the canonical distribution.

Influence of an External Potential: We have seen above that the chemical potential μ is the same for two systems Σ_a and Σ_b which are in thermal and diffusive equilibrium.

However, suppose there is some external potential V (gravitational, electrical etc) which changes the potential energy of each particle in Σ_a by an amount E_a , but which changes the potential energy of each particle in system Σ_b by a *different* energy E_b .

In this case, for the two systems to be in equilibrium we require that the two chemical potentials be related by

$$\mu'_a = \mu_a + E_a = \mu_b + E_b = \mu'_b. \quad (21)$$

To show this consider the free energy in Σ_a including E_a ; we then have

$$F_a = U_a - TS_a + NE_a \quad (22)$$

and

$$dF_a = -S_a dT - p_a dV + \mu_a dN_a + E_a dN_a \quad (23)$$

so that

$$\mu'_a = \left(\frac{\partial F_a}{\partial N_a} \right)_{T,V} = \mu_a + E_a \quad (24)$$

Similarly for the other system we get

$$\mu'_b = \left(\frac{\partial F_b}{\partial N_b} \right)_{T,V} = \mu_b + E_b \quad (25)$$

In thermal and diffusive equilibrium we must have $\mu'_a = \mu'_b$ and thus we get

$\mu_a + E_a = \mu_b + E_b$ as given in (21). Note that in many texts and papers the effect of V is already included in the definition of the potential.

There are many ways that we can get a variation of chemical potential in this way. As we discuss below, in many cases they vary continuously across a large system, where the gradient of change in potential corresponds to some field. If an electric field is responsible, then μ' is referred to as the *electrochemical potential*. If a gravitational field is responsible, then we refer to the gravitational contribution to μ , or to the “*gravimetric*” potential. In all these cases, we can then define a spatially varying chemical potential by

$$\mu'(\mathbf{r}) = \mu + U(\mathbf{r}) \quad (26)$$

where \mathbf{r} is the spatial coordinate, and $U(\mathbf{r})$ the spatially varying external potential.

5(b) Some Examples

We will give only a few examples here because a lot more will appear in subsequent chapters. Note that by far the most common use of the chemical potential and the grand partition function is in theoretical chemistry, to deal with chemical reactions and/or equilibrium between different chemical species.

Example 1: Electrochemical Potential Consider two metals A and B, separated in space. We define *work functions* ϕ_A and ϕ_B respectively, where ϕ is the energy required to remove an electron from one or other metal to the outside reference vacuum. Thus we have $\phi_A = \mu_v - \mu_A$ and $\phi_B = \mu_v - \mu_B$, where μ_v is the potential of the electron in the vacuum.

Let us assume that $\phi_A > \phi_B$ to be definite. Imagine that we now bring the two metals into contact. Electrons will then flow from B to A (ie., from higher chemical potential to lower potential). In equilibrium a contact voltage $V_c \equiv V_B - V_A$ must then develop between A and B, in order that the electrochemical potential be equal on both sides of the interface. Taking into account the charge of the electron is negative (ie., writing it as $-q$ where q is positive), we have

$$\mu_A + (-q)V_A = \mu_B + (-q)V_B$$

or

$$q(V_B - V_A) = \mu_B - \mu_A = \phi_A - \phi_B$$

so that finally

$$V_c = \frac{\phi_A - \phi_B}{q} \quad (27)$$

which is what we might have guessed in the first place.

Example 2: Earth's Atmosphere In the atmosphere, as is in the sea, the gravitational potential varies with height. Consider, eg., a single particle in the earth's atmosphere, for which the gravitational potential energy is

$$E = mgz \quad (28)$$

where z is height above sea level. We will assume here for simplicity that the other contributions to the energy, such as the temperature, are independent of height this of course is not true – precisely *because* the gravitational potential varies with height).

Notice immediately that this is not a quantum-mechanical problem, and we don't have discrete states. However we can still use the usual SM tools. Suppose, eg., we try to analyze this using the ordinary canonical distribution. Even though we don't have discrete states, we can still define a probability distribution $P(z)$ for the particle to be found at height z ; this means that in an interval dz , the probability of finding the particle is $P(z) dz$. In the canonical distribution, where the probability goes like $\exp[-\beta E]$, we then have

$$P(z)dz = Z^{-1} \exp[-\beta mgz]dz \quad (29)$$

where the partition function $Z(\beta)$ is just the integral of $\exp[-\beta mgz]$ over z from zero to infinity, so as to properly normalize the distribution, ie., we have

$$Z(\beta) = 1/\beta mg \quad (30)$$

Now the particle density $\rho(z)$ is just proportional to $P(z)$, so we have

$$\rho(z) = \rho_0 \exp[-\beta mgz] \quad \text{ie.,} \quad mgz = -k_B T \ln \frac{\rho(z)}{\rho_0} \quad (31)$$

where ρ_0 is the particle density at sea level.

Note that so far we have not used the grand canonical ensemble at all, even though particle exchange is involved between different levels of the atmosphere. In order to use it, we first have to determine how the chemical potential varies with z . From the discussion given above, we actually already know this – we expect it vary linearly with z , according to equations (26), since the energy $U(z)$ in this equation varies linearly according to (28).

To see this explicitly, using what we have already found, we start off by letting μ_0 be the chemical potential at sea level. Then in equilibrium the total gravitational+chemical potential – the gravipotential – is independent of height, and just given according to (26) by

$$\mu' = \mu(z) + mgz = \mu_0 \quad (31)$$

which, according to (31), gives

$$\mu(z) = \mu_0 + k_B T \ln \frac{\rho(z)}{\rho_0} \quad (32)$$

We have thus established, in this simplified model, that not only does the chemical potential drop linearly and the gravitational potential rise linearly as a function of z to keep the gravi-chemical potential constant, but that the density drops exponentially.

Notice a curious feature of (32); as the density $\rho(z) \rightarrow 0$, the chemical potential $\mu(z) \rightarrow -\infty$ logarithmically. This result is actually misleading – we do not expect the linear increase in potential given by (28) to persist indefinitely (otherwise we on earth would be in an infinitely deep potential well!), and so the calculation needs to be re-

worked to take account of the real $1/r$ potential of the earth's field. However, we will see in a later chapter that μ must always be negative for an ideal gas.

The physics here, which is adequately captured by the canonical distribution, is one of a competition between the gravitational potential which tends to concentrate at the gas at sea level and the entropy, which tried to maximize itself by distributing the gas over a larger volume. If we now want to go further with this calculation – for example, to calculate the fluctuations in density, or to look at what happens when we have multiple species of gas atom – then it becomes advantageous to use the grand canonical potential to analyze the problem.

Example 3: Partially Ionized Gas: Consider an atom with ionization energy I in contact with a reservoir of electrons at temperature T and chemical potential μ . Here we choose the zero of energy of the atom to be when it is in the ionized state (ie., the energy of the vacuum plus one free electron), so that when the electron is on the atom $E = -I$.

If we ignore electron spin and excited state there are only two possible microstates of the system, viz., the state $n = 0, E = 0$ (ie., the ionized atom), and the bound atomic state $n = 1, E = -I$. The grand canonical partition function for the system of a single atom and its ionic counterpart is then very simple, since there are only 2 states involved; we have

$$\Xi = 1 + \alpha \exp[\beta I] \quad (33)$$

where α is again the activity (see eqtn (14)); here the first term refers to the ionized state (so that $\beta\mu n = 0$, and $E = 0$), and the second term to the atomic state).

The mean occupancy in the bound atomic state is then given by

$$\langle n \rangle = \frac{\alpha \partial \Xi}{\Xi \partial \alpha} = \frac{\alpha \exp[\beta I]}{1 + \alpha \exp[\beta I]} = \frac{1}{\exp[-\beta(\mu + I)] + 1} \quad (34)$$

Here we see explicitly how the chemical potential μ and the number expectation value are connected, and both depend on temperature. Notice that the occupied atomic state will have a 50% occupancy, ie. $\langle n \rangle = 1/2$, when $\mu = -I$.

Now this calculation equally applies to a set of non-interacting atoms and ions, ie., a gas in which a set of neutral atoms of density $\rho = N\langle n \rangle$ coexists with a *plasma* of positive ions and negative electrons, each with density $N(1-\langle n \rangle)$; here N is the number of atoms per unit volume when there is no ionization at all. We assume still tha the electrons constitute the particle and thermal reservoir – in reality there will be many different chemical species, and the density of electrons will predominate over that of all the other species. The chemical potential is then a function of the density ρ and temperature.

The reason that we can take over the results in (33) and (34) directly to the gas is that if the different species (ions and atoms) do not interact, then the grand partition function for the mixed gas/plasma is just the product over all the different atoms, i.e., we have

$$\Xi_N = \Xi_1^N \quad (35)$$

where Ξ_1 refers to the partition function in (33) above, for a single H atoms and its ionic counterpart, and Ξ_N to the partition function for a set of N atoms and their ionic counterparts.

Because we can use these results to describe this mixed system, we see it has real practical application - we can use it to describe, eg., a gas of H atoms in interstellar space, far from any star – some of these will be ionized, even at low T , because the density is so low. It can equally well be used to describe the same gas inside a star – here far more of the atoms will be ionized, because now T is very high!

Let's see how this goes in practice.

It is convenient to express things in terms of the “quantum concentration” ρ_q (the inverse of the quantum volume V_q defined in eqtns (4.64) and (4.66) of the last chapter), and given here by

$$\rho_q \equiv \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} (2S+1) \quad (36)$$

where we have generalized eqtns (4.64) and (4.66) to include the effect of spin, which multiplies the single particle partition function by a factor of $2S+1$.

Now as it happens, the behavior of the chemical potential for a low-density gas, in the limit $\rho \ll \rho_q$ takes a very simple form. One finds that the activity is simply $\alpha = \rho / \rho_q$; or equivalently we have

$$\mu = k_B T \ln \left[\frac{\rho}{\rho_q} \right] \quad (37)$$

We have not yet shown this - will show this is true in the next chapter. Note however that it is consistent with the density variation we found for a gas in a gravitational field where we saw that:

$$\mu(z) = \mu_0 + k_B T \ln \frac{\rho(z)}{\rho_0} = k_B T \ln \alpha_0 + k_B T \ln \frac{\rho(z)}{\rho_0} = k_B T \ln \frac{\alpha_0 \rho(z)}{\rho_0} \quad (38)$$

(compare eqtn. (32) above).

Actually, formulas like (33) and (34), and their generalization to multiple species, are of crucial importance to astrophysics. In astrophysical systems one arrives at an equilibrium between different species of atoms, molecules, and ions, depending on the temperature and the densities of the species. Consider, eg., a simple problem involving the equilibrium between photons, protons, the electron bath, and the neutral H atoms. Obviously at very high T , as in a star, most of the H atoms will ionize, and come equilibrium with the free photons, electrons, and protons (with photon emission accompanying any recombination processes, and absorption any ionization of the H atoms) .

However one can also have almost complete ionization if the gas density is very low, even at moderate temperatures – this is because for very low densities, one an atom ionizes it is very hard for a proton and electron to find each other again and recombine. The physics of this is described by the “Saha equation”, which is described simply at, eg.,

https://en.wikipedia.org/wiki/Saha_ionization_equation

for this sort of problem.

We can see how this might work by considering a simple example. At the surface of the sun, the electron density $\rho = 6 \times 10^{19} m^{-3}$ and $T = 6400K$ or $k_B T = 0.55eV$. At this temperature, and ignoring electron spin, we have $\rho_q = 1.25 \times 10^{27} m^{-3}$, from (36), for the electron system (using the electron mass in (36)). It then follows that

$$\mu = k_B T \ln \alpha = 0.55eV \ln \frac{6 \times 10^{19}}{1.25 \times 10^{27}} = 0.55eV \ln [4.8 \times 10^{-8}] = -9.3eV \quad (38)$$

Note μ is negative for non-degenerate gases where $\rho \ll \rho_q$, but increases with number density. We can now consider 2 cases.

(i) Consider first the case of Li where $I = 5.4eV$ which is considerably less than $|\mu|$. From eqtn. (34) we have the atomic occupation probability

$$\langle n \rangle \approx \frac{1}{\exp[(9.3 - 5.4)/0.55]} = 8 \times 10^{-4} \quad (\text{Li}) \quad (39)$$

so that even though $k_B T \ll I$ ionization is nearly complete. This is because the electron density, even at the surface of the sun, is not that high – if we were in interstellar space the degree of ionization would be even higher at this temperature, and indeed for much lower temperatures as well.

(ii) Now consider the case of H, where the ionization energy is $I = 13.6 eV$ (ie., just over 150,000K). We then find from eqtn. (34) that

$$\langle n \rangle \sim 0.9996 \quad (\text{H}) \quad (40)$$

ie., there is almost no ionization of the H atoms at all. The key point here is that it is much harder to ionize the H atoms at the same density as the Li atoms, because they are more tightly bound. Another way to see what is going on is to notice the when the chemical potential $\mu = -9.3 \text{ eV}$, the bound H state has much lower energy than μ , but the bound Li state has much higher energy. Thus the Li it is energetically advantageous for the Li atoms to ionize.

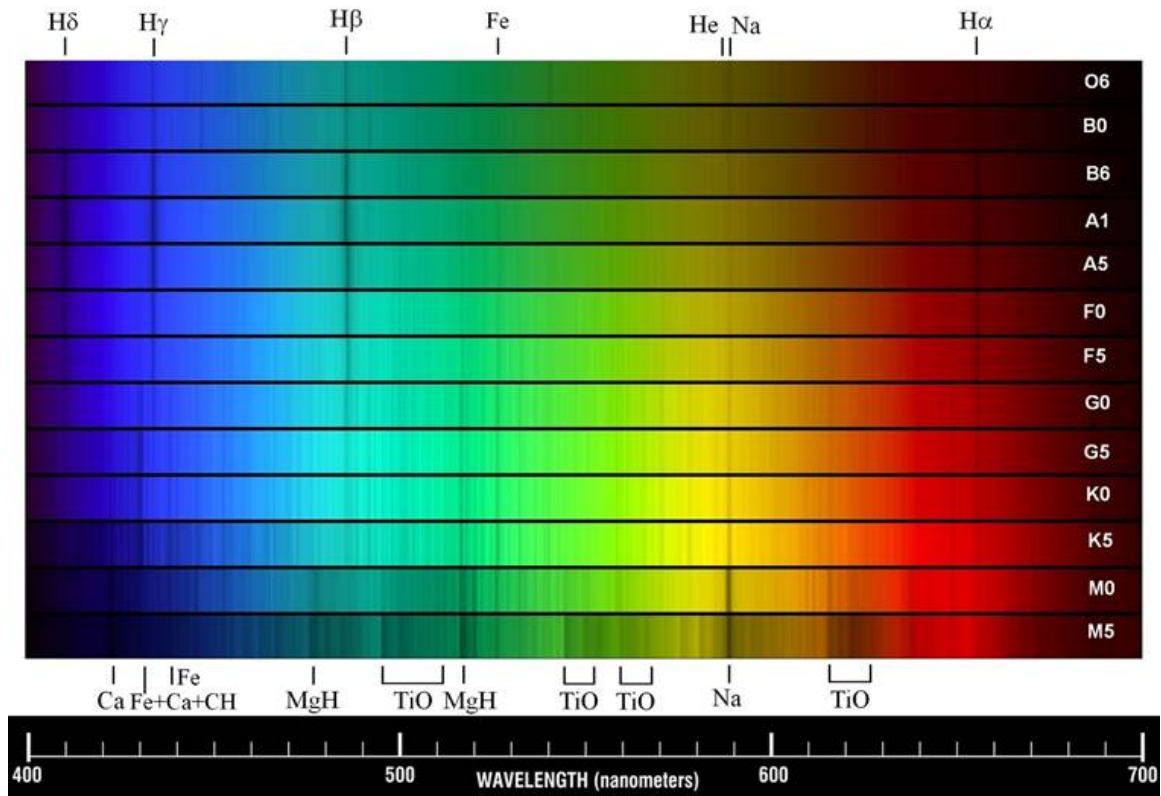


FIG: shows characteristic spectra for stars in classes from O6 to M5.

In real stars there are many species and one has to look at the equilibrium between all of them. The results allow us to compute their concentration, and thereby predict the intensity of their contribution to the various spectral lines of a stellar spectrum (or indeed the spectrum of any other celestial object). This is what makes spectroscopy such a powerful tool in astronomy.

The figure above shows spectra for stars ranging from very hot (O6 stars have surface temperatures $\sim 45,000\text{K}$), to very cool (M5 stars have surface temperatures $\sim 3,100\text{K}$). We notice how lines appear and disappear according to spectral type.

Actually we can get lots more information from stellar spectra. The exact lineshape of a given line can tell us a great deal, because the line broadening comes from the random velocities of the relevant ions or atoms (via the Doppler effect), which is governed both by the temperature and the density; the lineshape is also influenced by a magnetic field

(by its action on different spin states), and so on. Thus detailed analysis of a stellar spectrum can give a fantastically detailed picture of the star.