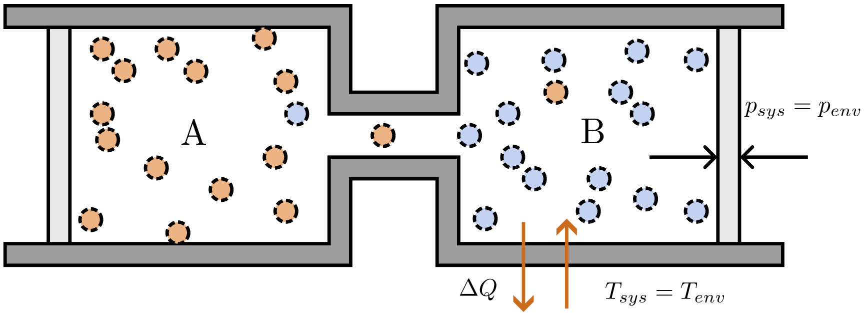

Figure 1: Two systems A and B that can exchange particles in the presence of an environment at a given pressure and temperature. Particles will flow between the systems until $\mu_A = \mu_B$, where $\mu_A = \frac{\partial G_A}{\partial N_A}$

9 Chemical potential and phases

9.1 Definition of chemical potential

In the last section, we found that the quantity $\frac{\partial G}{\partial N}$ is useful for finding equilibrium. In fact, this is such a useful quantity that it gets a special name:

$$\mu = \frac{\partial G}{\partial N} \tag{1}$$

is called the chemical potential. The chemical potential is to the number of particles in a system as temperature is to internal energy. Just like heat flows from high temperature to low temperature until the temperatures are equilibrated, particles flow from high chemical potential to low chemical potential until the chemical potentials are equilibrated.

The reason that particles spontaneously flow from high chemical potential to low chemical potential is the same as spontaneous heat flow! This spontaneous flow maximizes the entropy or equivalently minimizes the free energy. To see the reason, consider the minimization of free energy:

$$\frac{G_{tot}}{dN_A} = \frac{dG_A}{dN_A} + \frac{dG_B}{dN_B}\frac{dN_B}{dN_A} = 0. \tag{2}$$

$\frac{dN_B}{dN_A}$ is simply -1 because any increase in N_B must be taken from system A. So therefore, our equilibrium condition is simply

$$\frac{dG_A}{dN_A} = \frac{dG_B}{dN_B}, \tag{3}$$

or

$$\mu_A = \mu_B. \tag{4}$$

9.2 $G = \mu(T,p)N$

Now let's consider a pure substance (our ideal solution example from before was not a pure substance), for example, water in a gas phase, kept at fixed temperature and pressure. A general principle is that if we double the number of particles, then G also doubles. That is,

$$G(T,p,\alpha N) = \alpha G(T,p,N). \tag{5}$$

Immediately from this perspective we can see that

$$\frac{\partial G(T,p,\alpha N)}{\partial \alpha N} = \frac{\partial G(T,p,N)}{\partial N} = \mu(T,p,N), \tag{6}$$

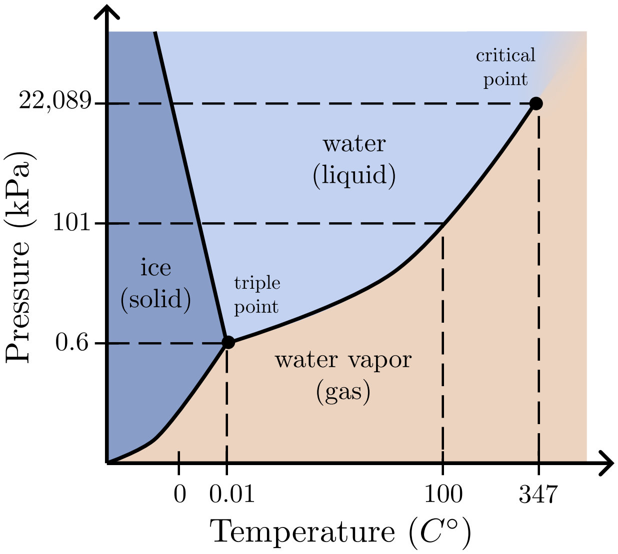

Figure 2: The phase diagram of water, taken from [https://openstax.org/books/chemistry-2e/pages/10-4-phase-diagrams], and used under the Creative Commons License.

which means that μ does not depend at all on α, and therefore does not depend on N. Therefore,

$$G(T, p, N) = \mu(T, p)N. \tag{7}$$

There are a few intuitive ways to understand Eqn 7. One way to think of it is that if the pressure and temperature are fixed, then the density (number of particles per volume) is also fixed, and since the chemical potential can only depend on the local environment of a molecule, it cannot depend on the total number of particles. The reason that the density is only dependent on temperature and pressure is that if we increase the number of particles, then the volume will just increase. You can see that quite clearly for an ideal gas; if $pV = NkT$, then for a given pressure and temperature, increasing the number of particles just increases the volume by an equivalent amount, and therefore N/V (the density) is the constant p/kT. We know that there will be no net particle flow between two containers of gas at the same temperature and pressure, and so therefore their chemical potentials are the same, even if one of the containers is much larger than the other one.

Note on multicomponent systems. A similar relation exists for systems with multiple components labeled N_1, N_2, $\ldots$, which is $G = \mu_1 N_1 + \mu_2 N_2 + \ldots$. The simple arguments we make later for the stability of phases need to be extended when there are multiple components.

9.3 Phases

To understand why $G = \mu(T, p)N$ is useful, let's consider the following situation. We have N molecules of water in an environment with a given pressure p and temperature T. From our everyday experience, we know that if we wait long enough at atomospheric pressure (101 kPa) and temperature below 0°C then all the water will eventually freeze and become ice. On the other hand, between 0°C and 100°C it will be liquid, and above 100°C a gas (water vapor). These observations are typically summarized in a *phase diagram* as in Fig 2. Note that for this situation, the only way we can have coexistence of two phases in equilibrium is to have the temperature and pressure exactly at one of the phase transition lines.[1]

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[1] The reason that we do often see coexistence of water vapor and liquid water, and liquid water and solid ice can vary. One is that most of the time, things are not really in equilibrium. The other is that we are considering a fixed pressure situation, which implies that the volume can vary without bound. That is rarely exactly true.

Since pressure and temperature are fixed by the environment, we expect our observations from above to be reproduced by minimizing the free energy G. Let's consider just liquid and gas phases for concreteness. The free energy is simply

$$G_{tot} = \mu_\ell(p,T)N_\ell + \mu_g(p,T)N_g, \tag{8}$$

with the constraint that $N_\ell + N_g = N_w$, where N_w is the total number of water molecules. For a given pressure and temperature, $\mu_\ell(p,T)$ and $\mu_g(p,T)$ are just constants. The number of water molecules in the liquid phase can change, if they evaporate and enter the gas, and vice versa. Minimizing G_{tot} is achieved by:

- If $\mu_\ell < \mu_g$, $N_\ell = N_w$, $N_g = 0$
- If $\mu_\ell > \mu_g$, $N_g = N_w$, $N_\ell = 0$
- If $\mu_\ell = \mu_g$, then N_ℓ and N_g are free to change and G_{tot} remains at a minimum.

The conditions to minimize G exactly predict what we observed in the phase diagram. Evidently, the liquid phase occurs when $\mu_\ell < \mu_g$ and $\mu_\ell < \mu_s$ (the solid), and the same for each of the phases. The phase areas represent the values of p and T such that that particular phase has the lowest chemical potential. The lines indicate values of p and T such that two chemical potentials are equal. The triple point is a particular value of p and T such that *three* chemical potentials are equal.

We thus have a mechanism to determine phase diagrams: if we can compute the difference between chemical potentials (or free energies) for all the phases, we can determine the equilibrium phases by taking the lowest chemical potential, and the phase transition temperature and pressures by finding the values of T and p such that the chemical potentials are equal.