# 8 Equilibrium in contact with a bath: Gibbs free energy

- $G = U - TS + pV$

- $G$ is minimized in equilibrium (is there a good example?)

- Concept of 'fixed' variables.

In this section, we are changing our consideration to the computation of equilibrium when a thermodynamic system is connected to a bath, reservoir, or environment. (In thermodynamics, these terms are generally used roughly interchangeably.) The most common situation in our everyday life is that we are in a fixed (or specified) pressure and temperature environment, as opposed to a fixed energy and volume environment. That is to say, energy flows in or out of objects until the temperature is in equilibrium with the environment, and the volume increases/decrease until the pressure is equilibrated. We see this occur in our daily life–water freezes when the outside temperature goes below 0 C, for example. The phases of matter are predicted by finding the state that maximizes the entropy of **both** the environment and the system under consideration.

## 8.1 Minimization of the free energy is maximization of total entropy

Let's consider maximizing the total entropy of a system ($S$ subscripts for system) + reservoir ($R$ subscripts for reservoir):

$$S_t = S_R + S_S \tag{1}$$

with respect to some macrostate variable $x$. ($x$ could be the internal energy, volume, etc of the system) Then we maximize the entropy by setting the derivative to zero:

$$\frac{dS_t}{dx} = \frac{dS_R}{dx} + \frac{dS_S}{dx} = 0. \tag{2}$$

We can use the fundamental relation:

$$dS_R = \frac{1}{T}dU_R + \frac{p}{T}dV_R. \tag{3}$$

We'd like to get the equation in terms of just system variables. We do this by noting that if the reservoir internal energy increases, then it must have come from the system, so $dU_R = -dU_S$, and the same for volume, $dV_R = -dV_S$. So

$$dS_R = -\frac{1}{T}dU_S - \frac{p}{T}dV_S. \tag{4}$$

Finally, plugging everything back in, we get the following equation for the maximization of total entropy:

$$\frac{dS_R}{dx} + \frac{dS_S}{dx} = \frac{dS_S}{dx} - \frac{1}{T}\frac{dU_S}{dx} - \frac{p}{T}\frac{dV_S}{dx} = 0. \tag{5}$$

Multiplying both sides by $-T$, we get

$$\frac{dU_S}{dx} - T\frac{dS_S}{dx} + p\frac{dV_S}{dx} = 0. \tag{6}$$

For convenience, we define the **free energy** $G = U - TS + pV$. Then the equilibrium condition is

$$\frac{dG}{dx} = 0, \tag{7}$$

where $T$ and $p$ are understood to be the temperature and pressure of the reservoir, which don't change when the system changes. This is a minimum because we multiplied by $-T$ above, which is a negative number.

From the above, we have a new concept: the free energy, which is minimized in equilibrium, and includes the effects of the reservoir. For fixed pressure and temperatures, this is called the Gibbs free energy and is defined as $G = U - TS + pV$. Note that the Gibbs free energy is only minimized when both pressure and temperature are fixed. In another situation, such as a fixed volume, the Gibbs free energy is not minimized.
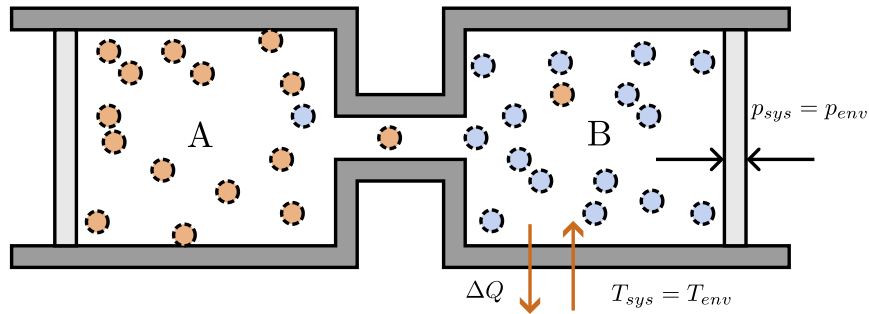
Figure 1: Two systems A and B that can exchange particles in the presence of an environment at a given pressure and temperature. Particles will flow between the systems until $\mu_A = \mu_B$, where $\mu_A = \frac{\partial G_A}{\partial N_A}$

## 8.2 Example: finding the equilibrium volume of an ideal gas in an environment

Consider an ideal gas with $N$ atoms at a fixed pressure and temperature $p, T$. What is the equilibrium volume?

$$G = U - TS + pV. \tag{8}$$

We'd like to find the value of $V$ such that

$$\frac{dG}{dV} = \frac{dU}{dV} - T\frac{dS}{dV} + p\frac{dV}{dV} = 0 \tag{9}$$

Using the fact that for an ideal gas, $S = Nk \ln V + f(U, N)$ and that $U$ does not depend on $V$,

$$\frac{dG}{dV} = -NkT/V + p = 0, \tag{10}$$

which results in the familiar by now ideal gas law. Note that $p$ and $T$ do not have a derivative because they refer to the pressure and temperature of the environment/reservoir. The important thing here is that as long as we can write down the entropy and internal energy of a system, we can find the equilibrium volume in an environment with a given pressure and temperature by taking the derivative of the Gibbs free energy, even if it's not an ideal gas.

## 8.3 Definition of chemical potential

In the last section, we found that the quantity $\frac{\partial G}{\partial V}$ is useful for finding equilibrium when the volume can change. When particles can move between systems, such as in Fig 1, $\frac{\partial G}{\partial N}$ is very useful. In fact, this is such a useful quantity that it gets a special name:

$$\mu = \frac{\partial G}{\partial N} \tag{11}$$

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:

$$\frac{G_{tot}}{dN_A} = \frac{dG_A}{dN_A} + \frac{dG_B}{dN_B}\frac{dN_B}{dN_A} = 0. \tag{12}$$

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

$$\frac{dG_A}{dN_A} = \frac{dG_B}{dN_B},\tag{13}$$

or

$$\mu_A = \mu_B.\tag{14}$$

## 8.4 $\quad G = \mu(T,p)N$

Now let's consider 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,

$$G(T,p,\alpha N) = \alpha G(T,p,N).\tag{15}$$

Immediately from this perspective we can see that

$$\frac{\partial G(T,p,\alpha N)}{\partial(\alpha N)} = \frac{\partial G(T,p,N)}{\partial N} = \mu(T,p,N),\tag{16}$$

which means that $\mu$ does not depend at all on $\alpha$, and therefore does not depend on $N$. Therefore,

$$G(T,p,N) = \mu(T,p)N.\tag{17}$$

There are a few intuitive ways to understand Eqn 17. 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 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 $N_1$, $N_2$, ..., which is $G = \mu_1 N_1 + \mu_2 N_2 + ...$. The simple arguments we make later for the stability of phases need to be extended when there are multiple components.

## 8.5 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]

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

$$G_{tot} = \mu_\ell(p,T)N_\ell + \mu_g(p,T)N_g,\tag{18}$$

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:

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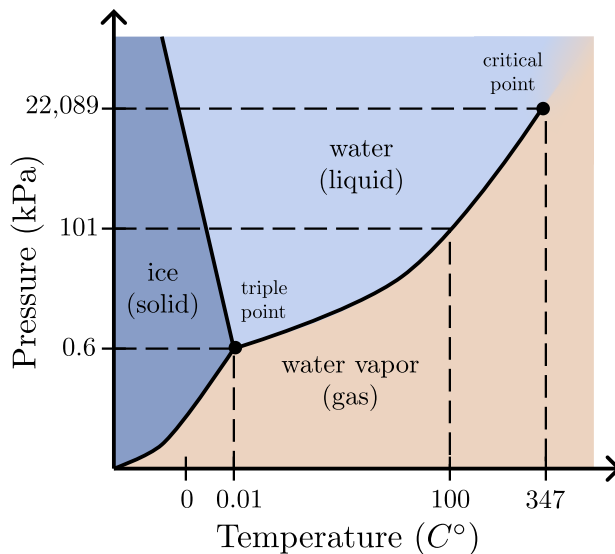
Figure 2: The phase diagram of water, taken from [https://openstax.org/books/chemistry-2e/pages/10-4-phase-diagrams], and used under the Creative Commons License.

- 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 $N_\ell$ 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.