

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/decreases 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):

$$S_t = S_R + S_S \quad (1)$$

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:

$$\frac{dS_t}{dx} = \frac{dS_R}{dx} + \frac{dS_S}{dx} = 0. \quad (2)$$

We can use the fundamental relation:

$$dS_R = \frac{1}{T}dU_R + \frac{p}{T}dV_R. \quad (3)$$

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

$$dS_R = -\frac{1}{T}dU_S - \frac{p}{T}dV_S. \quad (4)$$

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

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

Multiplying both sides by $-T$, we get

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

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

$$\frac{dG}{dx} = 0, \quad (7)$$

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.

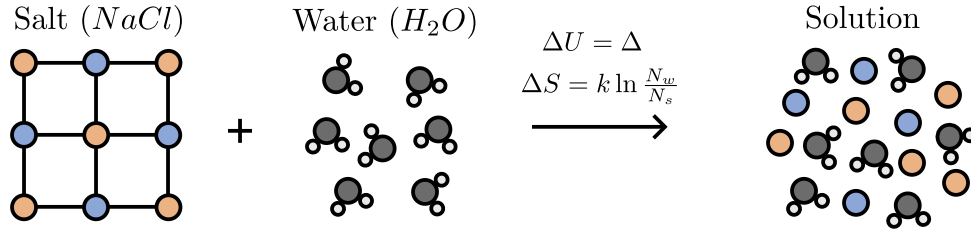


Figure 1: The model for an ideal solution

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?

$$G = U - TS + pV. \quad (8)$$

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

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

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

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

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 Ideal solutions

Let's consider the following question: in equilibrium, how much salt can be dissolved into water? The details here are very complicated; however, the general trends are very simple. Let's consider the following very simple model:

1. The **change** in total energy for moving one salt molecule from a solid to the water is Δ , which is a currently unknown parameter.
2. Once in the water, the salt molecule occupies the 'space' of one water molecule. This will change the entropy, and is called the entropy of mixing.
3. The volume of the water approximately does not change in this process. (this is good if the solution is dilute)
4. Note also that we are ignoring the fact that NaCl turns into Na^+ and Cl^- in solution. While this does matter to get everything perfectly correct, it does not change the basic behavior.

We would like to compute

$$\frac{dG_{tot}}{dN_S} = G_{tot}(N_S + 1) - G_{tot}(N_S) = 0, \quad (11)$$

where N_S is the number of salt molecules *in solution*. This equation is true from the definition of the derivative, and is accurate since there are many molecules. The derivative equals zero in equilibrium, since we are minimizing the free energy.

Since $G_{tot} = G_\ell + G_s$, where ℓ and s refer to the liquid with salt in it, and the solid salt respectively, we can reduce Eqn 11 to a quantity that only has differences in it. We reduce the equation to differences because we don't know the absolute internal energy of either the liquid or solid, nor do we know the absolute entropy. Using the fact that $G = U - TS + pV$, we then get:

$$G_{tot}(N_S + 1) - G_{tot}(N_S) = \underbrace{(U_w(N_S + 1) - U_w(N_S) + U_s(N_S - 1) - U_s(N_S))}_{\Delta} \quad (12)$$

$$- T \underbrace{(S_w(N_S + 1) - S_w(N_S) + S_s(N_S - 1) - S_s(N_S))}_{\Delta S} \quad (13)$$

$$+ p \underbrace{(V_w(N_S + 1) - V_w(N_S) + V_s(N_S - 1) - V_s(N_S))}_{\Delta V}. \quad (14)$$

This may look intimidating, but from our assumptions we already know most of these terms. The -1 in the s terms is because when we add a salt molecule from the solid to the liquid, we lose one molecule from the solid (and gain one in the liquid). From assumption 1, we know that the first term involving the internal energy we have defined as Δ . The third term involving the volume is zero from our assumption 3. That leaves us with the second term; the **entropy of mixing**.

To compute the entropy of mixing, we want to know how much entropy increases when adding a salt molecule to the water. We assume that the solid does not change its entropy very much. Then we need to compute $S_w(N_S + 1) - S_w(N_S)$. If there are N_S salt molecules in the water, and each salt molecule displaces one water molecule, then the number of ways to add them is:

$$\Omega_w(N_S) = \binom{N_w + N_S}{N_S}. \quad (15)$$

That is, we have $N_w + N_S$ possible positions and we choose N_S of them to be salt molecules. Then,

$$S_w(N_S + 1) - S_w(N_S) = k \ln \left(\frac{\Omega_w(N_S + 1)}{\Omega_w(N_S)} \right) = k \ln \left(\frac{(N_S + N_w + 1)!}{(N_S + 1)! N_w!} \frac{N_S! N_w!}{(N_S + N_w)!} \right) \quad (16)$$

Canceling out all the like terms, we get

$$S_w(N_S + 1) - S_w(N_S) = k \ln \left(\frac{N_S + N_w + 1}{N_S + 1} \right) \simeq k \ln \frac{N_w}{N_S}. \quad (17)$$

The last approximation is good because the number of water molecules is much much larger than the number of salt molecules, and both N_w and N_S are much much larger than 1.

Finally, we can put all these pieces together to get the equilibrium N_S :

$$\Delta - kT \ln \frac{N_w}{N_S} = 0. \quad (18)$$

Solving this for the concentration $\frac{N_S}{N_w}$:

$$\frac{N_S}{N_w} = e^{-\frac{\Delta}{kT}}. \quad (19)$$

In reality, we can describe most solutions by making a small modification to this equation:

$$\frac{N_S}{N_w} = n_s e^{-\frac{\Delta}{kT}}, \quad (20)$$

where n_s accounts for the fact that we might be able to fit more or less salt molecules into the solution than the number of water molecules.

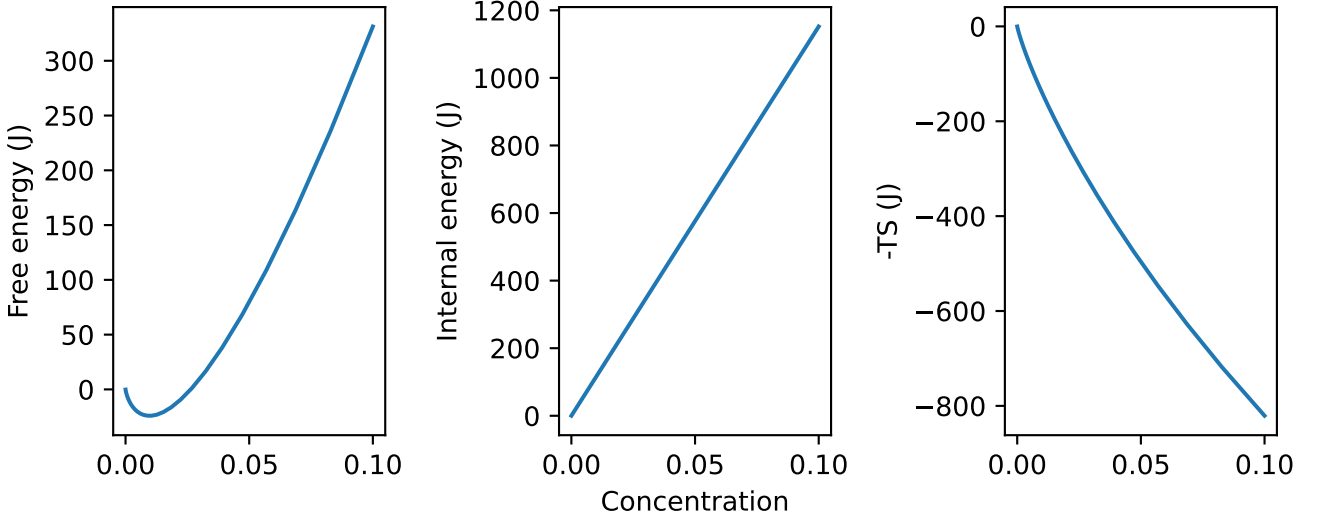


Figure 2: Free energy for $\Delta = 0.12$ eV, $T = 300$ K, and $N_w = 6 \times 10^{23}$. The minimum free energy is the equilibrium concentration, and is formed through a competition between internal energy and entropy.

8.4 Free energy versus internal energy

In Fig 2, we have the free energy, entropy and internal energy versus concentration $\frac{N_S}{N_w}$ for an ideal solution. The equilibrium concentration is the minimum in free energy. Note that the internal energy increases with the concentration, while the entropy also increases, which makes the $-TS$ term decrease. The minimum in free energy occurs as a result of competition between those two terms. Note that if you increase the temperature, the entropy term becomes more important and will push the minimum to higher concentration. On the other hand, lowering the temperature decreases the importance of the entropy and pushes the minimum to lower concentration. At zero temperature, the equilibrium concentration is zero.

The reason that higher temperature tends to favor higher entropy macrostates is that there is an environment at that temperature. The environment can increase total entropy by adding heat to the system, if it increases the entropy of the system enough. The breaking point is whether adding a given amount of heat Q increases the entropy of the system by more than Q/T , which is how much the entropy of the environment decreases when heat is transferred. As the temperature of the environment increases, the breaking point gets lower, and so the environment is more willing to give up heat to increase the entropy of the system. The free energy nicely captures all those effects!

Optional note: To compute the entropy and internal energy, you must integrate the derivatives:

$$U = \int \frac{dU}{dN_S} dN_S = \int \Delta dN_S = \Delta N_S, \quad (21)$$

and

$$S = -k \int \ln \frac{N_S}{N_w} dN_S = -k \left(N_S \ln \frac{N_S}{N_w} - N_S \right). \quad (22)$$

We assume the pV term does not change with concentration. There is an arbitrary constant in both integrals that we set to zero; only differences matter.

8.5 Arrhenius plots

A common way of analyzing systems is to take the log of Eqn 20:

$$\ln \left(\frac{N_S}{N_w} \right) = \ln n_s - \frac{\Delta}{kT}. \quad (23)$$

This equation says that if we plot the log of the concentration versus $\frac{1}{kT}$, then the slope is $-\Delta$. In this way, we can use bulk measurements to estimate the microscopic energy of a solute model. This also explains why one can dissolve more solute into a liquid when the liquid is hot. This, for example, is how sugar syrups are made.