Entropy and Miscibility Gap: Tutorial for Biologists

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Main Points

- A homogeneous phase can be spontaneously decomposed into two immiscible phases.

- Concentration gradients can be spontaneously formed at the border between immiscible phases when the system reaches its equilibrium state.

- At constant temperature and pressure the entropy of system in question spontaneously decreases during the separation process.

- In the adiabatic system the increase of the entropy leads to the phase separation from a homogeneous solution.

Introduction

Recently I have written a small text Schrödinger's Order, Disorder and Entropy [1] and discussed it on the biosemiotic list. During discussion, there was a suggestion to consider a solution with a miscibility gap (see Fig 1). In this case, a homogeneous mixture spontaneously decomposes to two different solutions with different concentrations of components.

Fig 1. Miscible and Immiscible Liquids (From Youtube [2])

In this text, I will take a simple regular solution as an example and show that in an adiabatically isolated system, the increase of the entropy corresponds to the formation of two phases from a homogeneous mixture. I believe that this is a good point to think it over in what case there is more order or disorder: in a homogeneous system or in two immiscible phases.

We start with a conventional treatment at constant temperature and pressure that I will then generalize to the case of an adiabatic system. I believe that one finds a similar treatment in many thermodynamics textbooks. Yet, as I was unable quickly to find in Internet what I was looking for, I have decided to write it from the scratch. In my blog [3], you will find auxiliary files to produce all figures that you will find below.

Constant temperature and pressure

Let us consider one mole of a solution between A and B that will be denoted as L. I will use x to denote the mole fraction of B, hence the mole fraction of A will be $1 - x$. By definition, a simple regular solution is described by Eq (1)

$$\Delta_{mix} G(T, p, x) = RT(1-x)\ln(1-x) + RT x \ln x + \beta(1-x)x \qquad (1)$$

where β is the interaction parameter. In all plots in the present work, the interaction parameter is set to $\beta = 2000\, R$. The Gibbs energy of mixing is defined as the difference between the Gibbs energy of solution A-B and pure components:

$$\Delta_{mix} G(T, p, x) = G(T, p, x)_L - \{(1-x)G_A(T, p) + xG_B(T, p)\} \qquad (2)$$

The Gibbs energy in variables temperature and pressure is a master function and all other thermodynamic properties could be found from it. For example:

$$\left(\frac{\partial G}{\partial T}\right)_{p,x} = -S \qquad T^2\left(\frac{\partial(G/T)}{\partial T}\right)_{p,x} = -H \qquad \left(\frac{\partial G}{\partial p}\right)_{T,x} = V \qquad (3)$$

The application of Eq (3) to Eq (1) gives us the expression for the entropy, enthalpy, and volume of mixing of the regular solution as follows:

$$\Delta_{mix} S(T, p, x) = -\{R(1-x)\ln(1-x) + R x \ln x\} \qquad (4)$$

$$\Delta_{mix} H(T, p, x) = \beta(1-x)x \qquad (5)$$

$$\Delta_{mix} V(T, p, x) = 0 \qquad (6)$$

According to Eq (4) the entropy of mixing of the regular solution is equal to that of the ideal solution and it does not depend on temperature (see Fig 2). The entropy increases during formation of the solution and the maximum of the entropy is at the composition equal to x=0.5 when one mixes the equal amounts of A and B. The enthalpy of mixing (Eq 5) is positive provided the interaction parameter is positive (see Fig 3) and the volume of mixing is zero (the volume of the solution is equal to the sum of volumes of the components).

The Gibbs energy of mixing (Eq 1) depends on temperature (see Fig 4). At higher temperatures it has a convex form while at lower temperature it has a concave form. This tells us that at these temperatures the homogenous solution is unstable and a miscibility gap appears. In general Fig 4 shows us an interplay between the entropy and enthalpy contributions. At lower temperatures the entropy contribution is small and the enthalpy still plays a significant role. At this condition there is a miscibility gap, as the formation of the solution is not favorable energetically. At higher temperatures the contribution from the entropy increases, the enthalpy role diminishes, and there is no immiscibility any more.
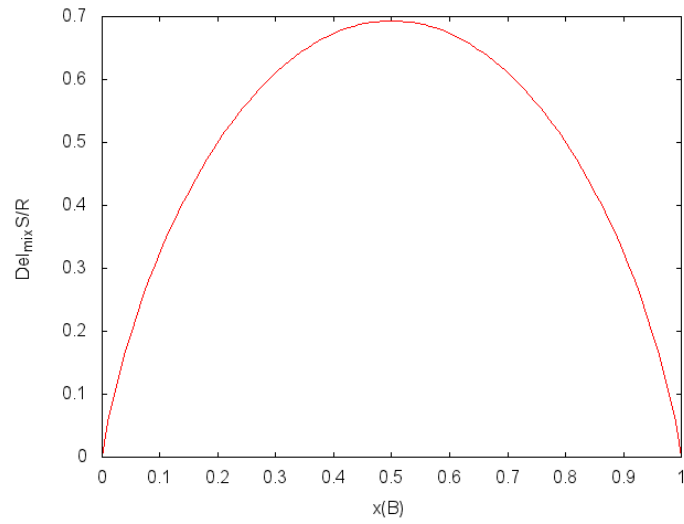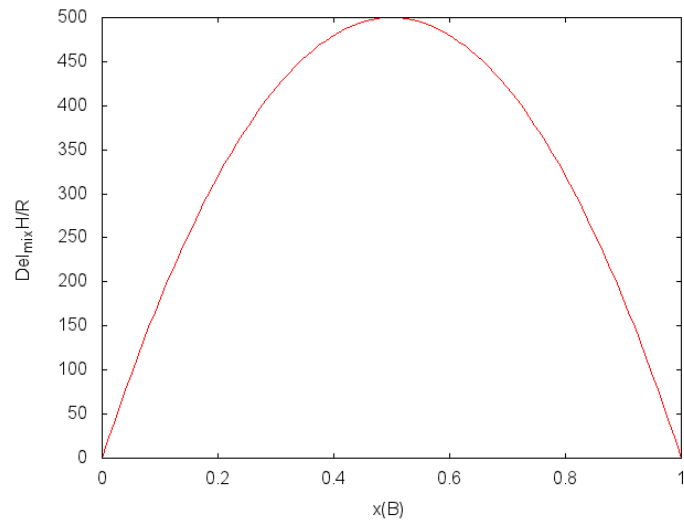
Fig 2. The entropy of mixing of the regular solution

Fig 3. The enthalpy of mixing of the regular
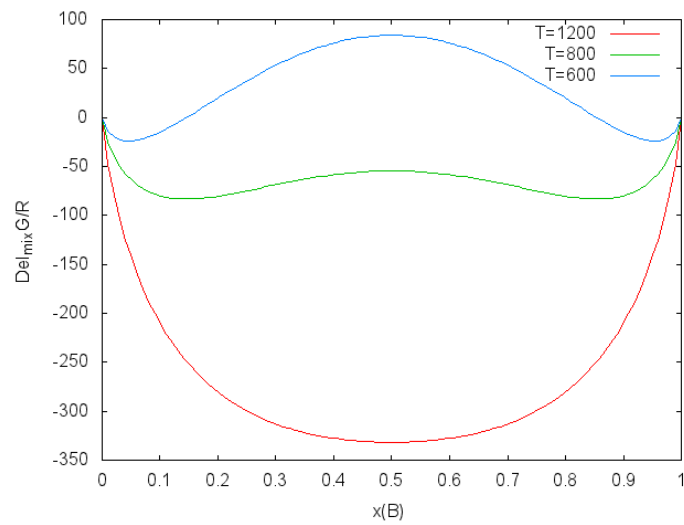solution ($\beta = 2000$ R)

Fig 4. The Gibbs energy of mixing of the regular
solution at three temperatures ($\beta = 2000$ R)

The behavior of the Gibbs energy shown in Fig 4 leads to a phase diagram with a miscibility gap shown in Fig 5. There are two regions in the phase diagram. First there is the miscibility gap where one finds two phases L1 and L2 coexisting with each other: the equilibrium state is similar to shown in Fig 1. Second there is the region with one phase only that depending on the area could be referred to as L, L1, or L2. L1 is the solution where the concentration of A is greater than that of B and L2 is vice versa. Above the critical temperature there is no immiscibility at all and the division to L1 and L2 does not make sense any more. Note that all area on the phase diagram including the miscibility gap are described by the same Gibbs energy expressed by Eq (1). Let us consider this in more detail below.
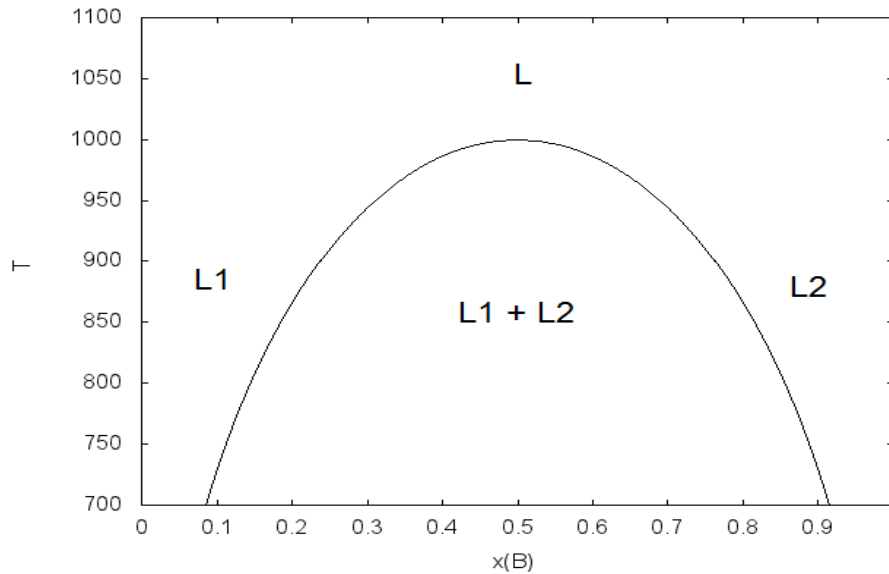

Fig 5. Miscibility gap in the regular solution

Let us consider a closed system made of 0.5 mole of A plus 0.5 mole of B. This constraints us to the vertical line in Fig 5 at mole fraction of B $x = 0.5$. There is no mass exchange with the surrounding and the system cannot escape this vertical line. Nevertheless, there are two possible states of the system, as we can have either a homogeneous solution L, or two-phase equilibrium L1 + L2. Let us explore these possibilities first from a viewpoint of material balance.

In the case of the homogeneous solution L its composition is fixed to $x = 0.5$. The phase diagram in Fig 5 says that such a solution is stable above the critical temperature and unstable below the critical temperature. In any case, the Gibbs energy of mixing is given by Eq (1) and it can be found in Fig 4 at $x = 0.5$ for all temperatures, whether the homogeneous solution is stable or not.

In the case of the two phase equilibrium, the components A and B could be transferred from one phase to another but the total number of moles must not be changed. This means that in each phase the mole fraction of B is different from 0.5 but the mass balance must be held

$$0.5 = n(A, L1) + n(A, L2)$$
$$0.5 = n(B, L1) + n(B, L2) \qquad (7)$$

The symmetricity of the Gibbs energy and hence of the phase diagram allows me to simplify mathematics. I will limit the analysis to variations expressed by one variable z only as follows

$$A_{0.5}B_{0.5} \rightarrow 0.5A_{0.5+z}B_{0.5-z} + 0.5A_{0.5-z}B_{0.5+z} \qquad (8)$$

It is easy to check that the mass balance in (7) is satisfied in (8). It is possible to say that z in Eq (8) plays a role of an order parameter. When z = 0, L1 is equivalent to L2 (and the original L) and in this case we have actually one phase only in the system. When z > 0, L1 and L2 are two different phases with different concentrations of components and hence different densities. The total Gibbs energy of the two phases L1 and L2 will be a sum G(L1) + G(L2). Now with the use of Eq (1) and (2) and the mass constraints in Eq (8), the total Gibbs energy is

$$0.5 G_A(T,p) + 0.5 G_B(T,p) + 0.5 \Delta_{mix} G(T,p,0.5-z) + 0.5 \Delta_{mix} G(T,p,0.5+z) \qquad (9)$$

as the mole fraction of B in L1 is 0.5 – z and in L2 is 0.5 + z. As I have already mentioned, the same Equation (1) can be used to describe everything in the phase diagram in Fig 5.

Eq (9) describes potential variations in the Gibbs energy of the closed system with 0.5 mole of A and 0.5 mole of B as a function of the order parameter z in accordance with the mass balance. The value of z at equilibrium can be found from the equilibrium criterion: at constant temperature and pressure, the Gibbs energy of the system at equilibrium is minimal. The straightforward mathematics gives us from Eq (9) the explicit function to minimize

$$G(T,p,z) = 0.5 G_A(T,p) + 0.5 G_B(T,p) + RT(0.5-z)\ln(0.5-z)$$
$$+ RT(0.5+z)\ln(0.5+z) + \beta(0.5-z)(0.5+z) \qquad (10)$$

and its derivative that should be at equilibrium equal to zero

$$\left(\frac{\partial G}{\partial z}\right)_{T,p} = RT \ln(0.5+z) - RT \ln(0.5-z) - 2Az = 0 \qquad (11)$$

Note that Eq (11) has always a trivial solution at z = 0. Whether this solution corresponds to a minimum or maximum will be determined by the second derivative. At the temperatures below the critical temperature, there is a nontrivial solution for which can be found numerically. In Fig 6, the derivative (11) is plotted at several temperatures to demonstrate such a behavior. The nontrivial solution will correspond to the minimum of the Gibbs energy and determine the phase diagram shown in Fig 5.
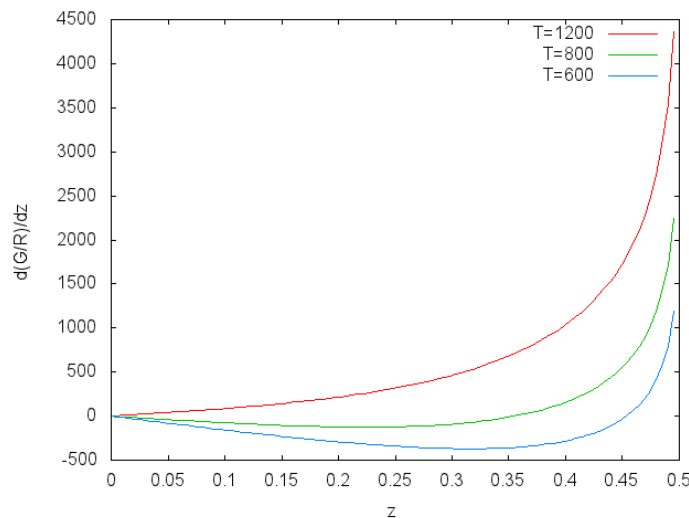

Fig 6. The derivative of the Gibbs energy at three
temperatures ($\beta = 2000$ R)

It is interesting to note that under the critical temperature, spontaneous separation of the homogeneous solution during reaction (8) at constant temperature and pressure reduces the entropy of the system. This clearly shows us that at these conditions it is not the entropy of the system but the Gibbs energy that determines the spontaneous direction of the process.

Constant enthalpy and pressure

Now I extend the treatment above to an adiabatic system. It is more convenient to consider not an isolated system but a system at constant enthalpy and pressure. In this case, I need less assumptions on the constituent equations.

At constant enthalpy and pressure, the maximum of the entropy determines the equilibrium state of the system: max $S(H, p)$. Let us check that the separation process will take place spontaneously in the adiabatic system with the regular solution under the critical temperature.

There is the important difference with the previous section. Now during the change of z in the process (8) the temperature changes. The separation reaction (8) is exothermic and the generated heat increases the temperature of the system. Eq (10) already contains temperature but now it is necessary also to write down the temperature dependence for pure components. To this end, again to keep mathematics as simple as possible, I assume that the heat mole thermal capacities of A and B are constant and equal in the considered temperature interval.

$$C_p(A) = C_p(B) = C_p = const \tag{12}$$

Now the temperature dependence of enthalpies of pure A and B is as follows

$$0.5H_A(T, p) + 0.5H_B(T, p) = H_0(p) + C_p T \tag{13}$$

were H_0 is as follows (T_0 is the reference temperature)

$$H_0(p) = 0.5H_A(T_0, p) + 0.5H_B(T_0, p) - C_p T_0 \tag{14}$$

Accordingly we obtain the expression for entropies of pure A and B

$$0.5S_A(T, p) + 0.5S_B(T, p) = S_0(p) + C_p \ln T \tag{15}$$

where

$$S_0(p) = 0.5S_A(T_0, p) + 0.5S_B(T_0, p) - C_p \ln T_0 \tag{16}$$

Now with Eqs (13) and (15) and the application of derivatives in Eq (3) to Eq (10), we get expressions for the entropy and enthalpy of L1 + L2 in the separation process (8):

$$S(T, p, z) = S_0(p) + C_p \ln T - R(0.5 - z)\ln(0.5 - z) - R(0.5 + z)\ln(0.5 + z) \tag{17}$$

$$H(T, p, z) = H_0(p) + C_p T + \beta(0.5 - z)(0.5 + z) \tag{18}$$

Finally we express the temperature from Eq (18) as a function of H and z and substitute it in Eq (17). This gives us the entropy as a function of H, p, z:

$$S(H, p, z) = S_0(p) + C_p \ln\left(\frac{H - H_o(p) - \beta(0.5-z)(0.5+z)}{C_p}\right)$$
$$- R(0.5-z)\ln(0.5-z) - R(0.5+z)\ln(0.5+z) \qquad (19)$$

The derivative of Eq (19) over z at constant enthalpy and pressure allows us to find the equilibrium value of z. Before I write a derivative down, it would be good to rewrite Eq (19) in such a way to make it more useful for practical use. During the minimization, it is necessary to keep the enthalpy H constant but the natural question is how we choose its numerical value. Provided that we define the starting point of the separation process as the homogeneous solution ($z = 0$) at given temperature T_{ini}, the enthalpy that must be constant is determined by Eq 18 as follows

$$H - H_0(p) = C_p T_{ini} + 0.25\beta \qquad (20)$$

Hence Eq (19) could be written as

$$S(H, p, z) = S_0(p) + C_p \ln\left(\frac{C_p T_{ini} + \beta(0.25 - (0.5-z)(0.5+z))}{C_p}\right)$$
$$- R(0.5-z)\ln(0.5-z) - R(0.5+z)\ln(0.5+z) \qquad (21)$$

At equilibrium the final temperature can be found from the constraint of the enthalpy being constant

$$C_p T_{ini} + 0.25\beta = C_p T_{fin} + \beta(0.5-z)(0.5+z) \qquad (22)$$

as

$$T_{fin} - T_{ini} = \beta(0.25 - (0.5-z)(0.5+z))/C_p \qquad (23)$$

Now the derivative of Eq (21):

$$\left(\frac{\partial S}{\partial z}\right)_{H,p} = \frac{2C_p \beta z}{C_p T_{ini} + \beta(0.25 - (0.5-z)(0.5+z))} + R\ln(0.5-z) - R\ln(0.5+z) = 0 \qquad (24)$$

Similar to the derivative of the Gibbs energy (11), the derivative of the entropy always has a trivial root $z = 0$. It describes the maximum of the entropy in the system above the critical temperature. Under the critical temperature it corresponds to the minimum of the entropy of the system (the homogeneous solution is thermodynamically unstable). The equilibrium composition under the critical temperature is associated with the non-trivial root of Eq (24) that can be found numerically. To this end, I have written a script in Python using SciPy to solve Eq (24) and (23). It is available in my blog [3]. For example with $T_{ini} = 800$ K, $C_p = 10$ R, $\beta = 2000$ R, the solution of Eq (24), $z = 0.338$, and from Eq (23) it follows $T_{fin} = 822.8$ K.

The treatment shows that in the adiabatically isolated system with the regular solution under critical temperature, the increase of the system entropy corresponds to the spontaneous separation of the homogeneous solution L into the two phases L1 + L2. I leave as an exercise to prove that when one starts under critical temperature in the adiabatically isolated system, the temperature of the system during the separation process will never increase the critical temperature. One can also play with my Python script to see this fact in numerical experiments.

References

[1] E. Rudnyi, Schrödinger's Order, Disorder and Entropy,
http://blog.rudnyi.ru/2013/04/schrodinger-disorder-and-entropy.html

[2] Video on Youtube, Miscible and Immiscible Liquids,
http://www.youtube.com/watch?v=NqQ_Uea9o0c

[3] http://blog.rudnyi.ru/2013/05/entropy-and-miscibility-gap.html