


# Understanding Chemical Equilibrium: The Role of Gas Phases and Mixing Contributions in the Minimum of Free Energy Plots

J. Pablo Tomba\*

Department of Chemical Engineering, National University of Mar del Plata, Juan B. Justo 4302, 7600 Mar del Plata, Argentina

## Supporting Information

**ABSTRACT:** The use of free energy plots to understand the concept of thermodynamic equilibrium has been shown to be of great pedagogical value in materials science. Although chemical equilibrium is also amenable to this kind of analysis, it is not part of the agenda of materials science textbooks. Something similar is found in chemistry branches, where free energy plots in the context of chemical equilibrium are occasionally addressed, in qualitative fashion, and with a main focus on gas phase reactions. With the aim of providing a more complete perspective on the topic, free energy plots in several reactive systems that include condensed and gas phase components are analyzed. Free energy functions of the reactive systems are assembled using expressions of chemical potentials as building blocks, a useful approach to articulate several layers of concepts (fugacity coefficients, activity coefficients, solution thermodynamics) developed in earlier stages of thermodynamic courses. The examples presented highlight the influence of two factors on chemical equilibrium: mixing contributions and the presence of gas phases. A single gas phase reaction is first addressed to show a case where mixing contributions have direct impact on the minimum of free energy curves. The second example is a reaction involving a gas and two solid phases, formally similar to those represented in Ellingham charts, where despite the presence of a gas phase, mixing does not occur. A third example illustrates the case of a reaction between solid phases to generate a third solid, where neither mixing nor gas phases are present. The examples highlight the role played by entropic contributions in the minimum of free energy curves, providing a deeper understanding of chemical equilibrium in systems of interest to chemistry and material science.

**KEYWORDS:** Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, Chemical Engineering, Materials Science, Thermodynamics

The visualization of free energy functions is a useful ingredient to introduce the idea of thermodynamic equilibrium. Textbooks in materials science devote particular attention to the topic.<sup>1,2</sup> For instance, in one-component systems, the representation of free energy versus temperature allows the visualization of driving forces for phase transformation or the influence of surfaces in phase equilibrium. In multicomponent systems, the representation of free energy versus mixture composition is useful to identify the driving forces for phase separation whereas the application of the common tangency rule allows the characterization of two- and three-phase equilibria, a useful support to explain the shape of the resulting phase diagrams.

The analysis of free energy curves is also very useful in the context of chemical thermodynamics. The representation of free energy as a function of reaction progress allows visualization of the driving forces for chemical reaction or the several factors that determine chemical equilibrium.<sup>3,4</sup> On the other hand, the understanding of concepts of spontaneity or the differences between  $G$  and  $\Delta_r G^\circ$ , issues particularly problematic for students, are remarkably facilitated with this representation.<sup>4,5</sup> Despite its importance, the quantitative development of this topic is usually not part of the agenda of thermodynamic textbooks used in branches of material science.<sup>1,2</sup> The same happens in chemistry branches,<sup>6–10</sup> with some exceptions.<sup>11,12</sup> At this point, we have found that the methodological approach based on detailed construction of free energy functions is very effective, not only as a direct tool of visualization of the several

factors that operate in chemical equilibrium, but also as an integration element where several key concepts developed in earlier stages of the course (fugacity coefficients, activity coefficients, chemical potentials, solution thermodynamics) naturally converge.

Chemical reactions in the gas phase have been the typical showcase for the analysis of equilibrium via free energy curves.<sup>3,4,13</sup> It has been shown that the minimum in free energy that leads the reactive system to equilibrium is solely produced by the upward curvature resulting from mixing contributions to free energy terms. In fact, one may conclude that mixing between components is a necessary condition for the existence of a minimum in free energy and, so, for the chemical equilibrium. However, chemical equilibrium is also predicted in systems where mixing between phases does not occur. One example can be found in the formation of metallic oxides from neat metals in the presence of oxygen, where the three phases involved (gas, metal, and oxide) do not significantly mix with each other. These reactions are the base of Ellingham charts used in several branches of materials science to predict ranges of stability of metals and their oxides. Another example includes reactions in the solid phase to form intermediate compounds, of common occurrence in ceramics solid-state chemistry. In those situations, the question that arises is the following: If

**Received:** September 27, 2016

**Revised:** January 17, 2017

**Published:** February 2, 2017

there are no mixing contributions, which other factors produce a minimum in the free energy curve of the reactive system and the eventual equilibrium state?

The examples presented below attempt to clarify that issue and, at the same time, to present the construction of free energy plots in a general way. The basic equations needed to assemble free energy functions, including specific expressions for chemical potentials, are first presented. Then, an example of a reaction in the gas phase is revisited, to establish a base for the different contributions to free energy of the reactive system. The second example presented is the decomposition of a solid salt in a gas compound and a new solid phase, where, despite the presence of a gas phase, mixing does not occur. Finally, the reaction between two solid oxides to yield a third solid compound is introduced as a case where neither mixing nor gas phases are present. In each example, the factors that determine the minimum in free energy functions are discussed.

### BRIEF SUMMARY OF FUNDAMENTAL EQUATIONS

The total Gibbs or Helmholtz free energy functions ( $G$ ,  $A$ ) of a given phase can be assembled from the additivity rule in terms of the respective partial molar properties ( $\bar{G}_i$ ,  $\bar{A}_i$ ):

$$G = \sum n_i \bar{G}_i = \sum n_i \mu_i \quad (1)$$

where the summation extends over all the chemical species contained in the phase, whereas  $\mu_i$  represents the chemical potential of the  $i$  species. Similarly

$$A = \sum n_i \bar{A}_i \quad (2)$$

An expression for  $\bar{A}_i$  in terms of  $\mu_i$  can be derived from the relationship between  $G$  and  $A$ . As  $G = H - TS$  and  $A = U - TS$ , it follows that  $G - A = H - U = PV$ , or that  $A = G - PV$ . If written in terms of partial molar properties

$$\bar{A}_i = \mu_i - P\bar{V}_i \quad (3)$$

Analytical expressions for free energy functions can be developed from eq 1 or 3, after choosing appropriate expressions for  $\mu_i$  and  $\bar{V}_i$ . Appendix I in Supporting Information presents a detailed derivation of expressions of  $\mu_i$  for relevant aggregation states, whereas those for  $\bar{V}_i$ , the partial molar volume, will be discussed in each example.

The combination of the first and second laws of thermodynamics yields fundamental relationships that dictate the evolution of any process:  $dG - V dP + S dT \leq 0$  and  $dA + P dV + S dT \leq 0$ ; in both cases, only  $P$ - $V$  work is considered. These expressions are typically developed in earlier stages of the course, and the reader can find them in any text covering thermodynamics or physical chemistry.<sup>1,6,8</sup> In transformations occurring at constant temperature and pressure, with only  $P$ - $V$  work involved, the condition  $dG|_{P,T} \leq 0$  has to be met, where the equality  $dG|_{P,T} = 0$  is satisfied at the equilibrium state. The  $A$  function behaves similarly but for processes produced at constant volume and temperature. These principles explain the evolution of chemical reactions. The representation of  $G$  or  $A$  as a function of the progress or evolution of the chemical reaction, under specific  $P$ ,  $T$  or  $V$ ,  $T$  conditions, should yield a curve with a negative slope ( $dG$ ,  $dA < 0$ ) that eventually reaches a minimum at equilibrium ( $dG$ ,  $dA = 0$ ), see Figure 1. Excellent discussions about the use of these graphs to introduce concepts of spontaneity in chemical reactions can be found in earlier publications of this Journal.<sup>4,5,14</sup>

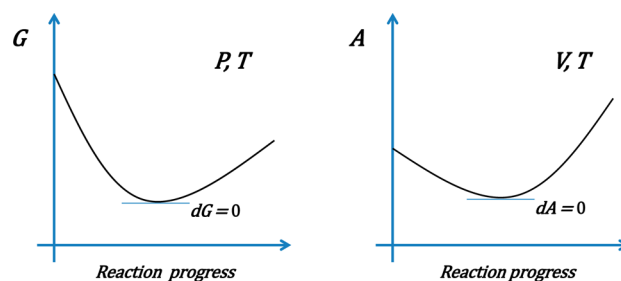


Figure 1. Schematic representation of the evolution of  $G$  and  $A$  in chemical reactions.

### HOMOGENEOUS GAS PHASE REACTIONS

Let us revise the decomposition of  $N_2O_4$  into  $NO_2$ , a classic example of a single gas phase reaction. The reactive system is considered to be enclosed in a chamber, for instance, a cylinder-piston type that operates at constant pressure. The system is surrounded by a thermostatic bath to maintain constant temperature. It is further assumed that the only possible reaction is  $N_2O_4(g) \rightarrow 2NO_2(g)$  and that it is produced at 1 bar and 298 K. The reactive mixture is initially composed of the reactants, for instance, 1 mol of  $N_2O_4$ , that eventually will form  $NO_2$ . The number of moles of each of the species at any reaction stage can be expressed in terms of a single variable, the extent of reaction  $\xi$

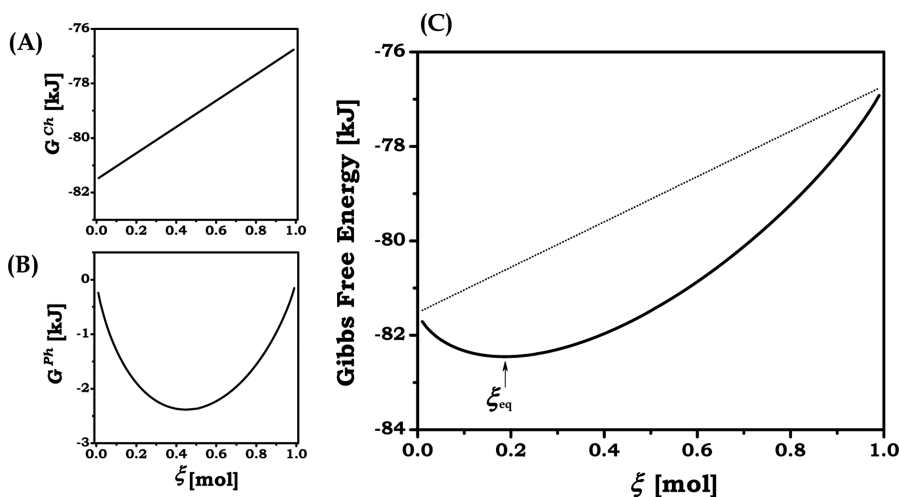
$$n_{N_2O_4} = 1 - \nu_{N_2O_4}\xi = 1 - \xi \quad n_{NO_2} = \nu_{NO_2}\xi = 2\xi \quad (4)$$

where  $\nu_i$  are the stoichiometric coefficients,  $-1$  and  $2$  for  $N_2O_4$  and  $NO_2$ , respectively. The  $\xi$  represents our progress or evolution variable for the chemical transformation, assuming that  $P$  and  $T$  remain constant. In the present example,  $\xi$  has limiting values between 0 (no reaction) and 1 (complete reaction).

We pursue the development of an expression for the  $G$  function for the reactive system as a function of  $P$ ,  $T$ , and our progress variable, the extent of reaction  $\xi$ . From eq 1, that function for the gas phase is given by

$$G(P, T, \xi) = n_{N_2O_4}\mu_{N_2O_4} + n_{NO_2}\mu_{NO_2} \quad (5)$$

where each  $n_i$  term, including those implicitly contained in  $\mu_i$ , depend on  $\xi$  via eq 4. Equation 5 can be further elaborated making expressions for the chemical potential explicit. At this point, any type of gas phase is feasible to be described as long as we chose appropriate expressions for  $\mu_i$ , see Supporting Information. If a real gas mixture is considered, partial fugacity coefficients ( $\hat{\phi}_i$ ) need to be introduced. The virial equation of state for gas mixtures, typical content of chemical engineering thermodynamics curricula, yields detailed expressions for  $\hat{\phi}_i$  as a function of  $P$ ,  $T$ , and mixture composition, which can be readily adapted to this development. The assumption of an ideal mixture further simplifies the treatment as  $\hat{\phi}_i$  equals that of the pure components,  $\phi_i$ , that only depends on  $P$  and  $T$  but not on properties of the mixture. In this case,  $\phi_i$  values appear as constant factors in the expressions of  $\mu_i$ , assuming  $P$  and  $T$  are fixed. At the low pressure of this example (1 bar), ideal gas behavior can be assumed ( $\hat{\phi}_i = 1$ ) and  $\mu_i = G_i^\circ + RT \ln(Py_i/P^\circ)$  (see eq A4, Supporting Information), where  $G_i^\circ$  represents the free energy of the component in the standard state (pure ideal gas at  $T$  and  $P^\circ = 1$  bar) and  $y_i$  the molar fraction of the  $i$  species. One can replace



**Figure 2.** Variation of the Gibbs free energy function with the extent of reaction for  $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$  at 298 K and 1 bar: (A) chemical contribution, (B) physical contribution, and (C) global function (solid line) and chemical contribution (dotted line).

$$G = n_{\text{N}_2\text{O}_4} G_{\text{N}_2\text{O}_4}^\circ + n_{\text{N}_2\text{O}_4} RT \ln\left(\frac{P y_{\text{N}_2\text{O}_4}}{P^\circ}\right) + n_{\text{NO}_2} G_{\text{NO}_2}^\circ + n_{\text{NO}_2} RT \ln\left(\frac{P y_{\text{NO}_2}}{P^\circ}\right) \quad (6)$$

which can be reorganized as

$$G = n_{\text{N}_2\text{O}_4} \left[ G_{\text{N}_2\text{O}_4}^\circ + RT \ln\left(\frac{P}{P^\circ}\right) \right] + n_{\text{NO}_2} \left[ G_{\text{NO}_2}^\circ + RT \ln\left(\frac{P}{P^\circ}\right) \right] + RT (n_{\text{N}_2\text{O}_4} \ln y_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} \ln y_{\text{NO}_2}) \quad (7)$$

Molar fractions and mole numbers can be expressed in terms of  $\xi$  to yield:

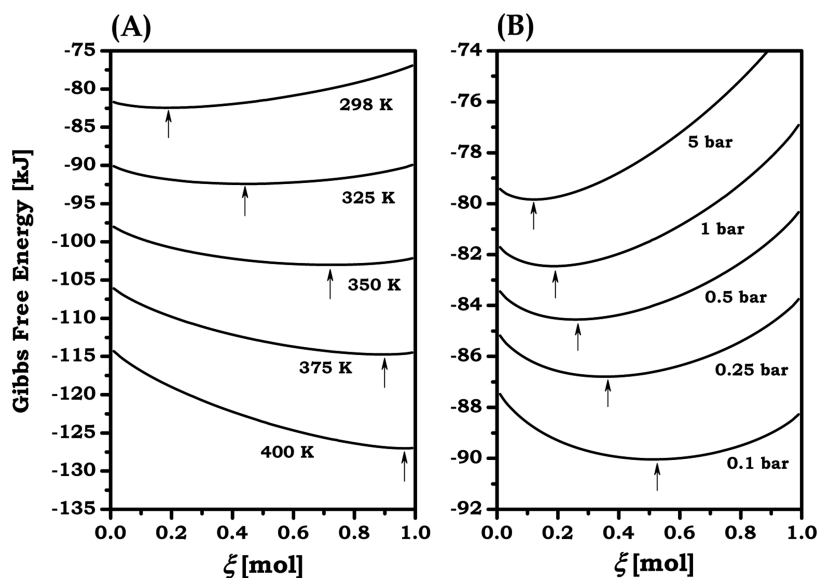
$$G(P, T, \xi) = \underbrace{(1 - \xi) \left[ G_{\text{N}_2\text{O}_4}^\circ + RT \ln\left(\frac{P}{P^\circ}\right) \right] + 2\xi \left[ G_{\text{NO}_2}^\circ + RT \ln\left(\frac{P}{P^\circ}\right) \right]}_{G^{\text{Ch}}} + \underbrace{RT \left[ 2\xi \ln\left(\frac{2\xi}{1 + \xi}\right) + (1 - \xi) \ln\left(\frac{1 - \xi}{1 + \xi}\right) \right]}_{G^{\text{Ph}}} \quad (8)$$

Equation 8 quantitatively describes the behavior of total Gibbs free energy of the gas phase as a function of the extent of reaction  $\xi$ . Values of  $G_i^\circ$  are evaluated at 1 bar so they only depend on  $T$ ; details on how the values are established are given in Appendix II of Supporting Information. For convenience, the terms have been grouped into two contributions. The first two terms, that we will call  $G^{\text{Ch}}$ , contain the chemical contribution to the problem, represented by the  $G_i^\circ$  values. Somewhat arbitrarily,  $G^{\text{Ch}}$  also contains a physical contribution, the  $RT \ln(P/P^\circ)$  terms that might as well have been left aside in a separate group. However, for a pure ideal gas, the integration of the expression  $dG_{i,T} = RT d \ln P$  between  $P$  and  $P^\circ$  yields  $G_i = G_i^\circ + RT \ln(P/P^\circ)$ , and so, the  $RT \ln(P/P^\circ)$  terms can be seen well as corrections for pressure to  $G_i^\circ$  terms at  $T$ . At fixed  $P, T$ , the group of factors  $G_i = G_i^\circ + RT \ln(P/P^\circ)$  is constant; therefore, a representation of  $G^{\text{Ch}}$  versus  $\xi$

is linear, as is seen in Figure 2A. The line starts at  $[G_{\text{N}_2\text{O}_4}^\circ + RT \ln(P/P^\circ)]$  and ends at  $2[G_{\text{NO}_2}^\circ + RT \ln(P/P^\circ)]$ . These two extremes represent the Gibbs free energy of the reactive system at the initial ( $\xi = 0$ ) and final ( $\xi = 1$ ) states. Notice that stoichiometry as well as  $G_i^\circ$  values determine the slope of the line.

The contribution containing the last two terms in eq 8 has been called  $G^{\text{Ph}}$ . It should be familiar to the students as they represent contributions of mixing entropy to free energy, developed in the treatment of solution thermodynamics. The meaning of that contribution is more explicit in eq 7, where the terms have exactly the same form as those developed for ideal solutions. As in that case, the arguments of the logarithmic terms contain molar fractions less than 1 (see eq 7), which leads to an increase of entropy in the state of mixing (or decrease in free energy), compared with that of the pure state. This increase of entropy is actually produced by the increase in accessible volume experienced by each component in the mixture compared with that in the pure state, a purely volumetric effect.<sup>15–17</sup> The concept is not only applicable to gas mixtures but also extensive to liquid or solid mixtures.<sup>16</sup> With this consideration, we will refer to any term containing molar fractions, such as those found in  $G^{\text{Ph}}$ , as mixing contributions, but also taking into account a volumetric effect as ultimately responsible for the increase in entropy. Figure 2B shows a plot of the  $G^{\text{Ph}}(\xi)$  function where it is seen that it has an upward concavity that tends to zero at the boundaries. Notice, however, that the curve is not symmetrical with respect to 0.5, as was seen in solution thermodynamics, as we are plotting against  $\xi$  instead of versus  $y_i$ .

Figure 2C shows the resulting behavior of the total  $G$  function for the mixture, whose minimum corresponds to the equilibrium state. Overall, the representation shows that the minimum of the curve is produced by a combination of the so-called chemical contribution, embodied in the first two terms, and the physical part containing the mixing contributions, where the latter is actually responsible for the existence of the minimum. The  $G^{\text{Ch}}$  contribution has also been represented in Figure 2C with a dotted line. Notice that, in the eventual absence of mixing terms, the conversion of  $\text{N}_2\text{O}_4$  to  $\text{NO}_2$  at 298 K and 1 bar would be forbidden as free energy at the initial state is below that for complete reaction, and it would imply



**Figure 3.** Variation of the Gibbs free energy function with the extent of reaction for  $N_2O_4$  decomposition at (A) 1 bar for the temperature range 298–400 K and (B) 298 K for a range of pressures between 0.1 and 5 bar.

$dG|_{p,T} > 0$ . The students can verify the correspondence between the equilibrium state obtained from this graphical representation and that from the standard analytical condition  $K_{eq} = \prod a_{i,eq}^{\nu_i}$ . For instance, the value of  $\xi$  at equilibrium obtained from the plot (about 0.18) is identical to that obtained from the value of  $K_{eq}$  at 298 K for the system (0.144), calculated from the expression  $\ln K_{eq} = -\Delta_r G^\circ / RT$  and values of  $\Delta_r G^\circ$  (298).

The influence of changes of  $P$  and  $T$  on the equilibrium position can be readily assessed. It is shown in Figure 3. The effect of  $T$  is explicit in each  $RT$  term but implicit in  $G_i^\circ$ . At this point, we can remind the students of another important representation, in this case,  $G_i$  versus  $T$  at constant  $P$ , whose slope is minus the entropy of the phase. As  $T$  increases, the extremes of the plots decrease but at different rates depending on stoichiometry and on calorimetric properties of individual components. A rigorous development of the effect of temperature on  $K_{eq}$  (van't Hoff equation) will allow the students to crosscheck those results. On the other hand, the dependence on  $P$  is explicit in the first two terms (logarithmic arguments), the corrections for pressure of  $G$  of an ideal gas. As pressure increases with respect to  $P^\circ$ , the extremes of the plots move upward but at different rates, depending on the stoichiometric coefficients, which are larger for products than for reactants in our example. As a consequence, the minimum in  $G$  shifts toward the left, as predicted by Le Châtelier's principles learned in introductory courses. Other influences such as number of moles of reactants and the presence of inert solid or gaseous compounds can also be analyzed with this representation.

### ■ HETEROGENEOUS GAS PHASE REACTIONS

The second example presented is the decomposition of solid calcium carbonate in carbon dioxide and calcium oxide,  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ , where two aggregation states (gas and solid) are involved. The formation of oxides from the reaction of oxygen with neat metals, the base of the Ellingham charts used by metallurgists, is comparable to the example presented, so all the arguments and features to be discussed also apply to those systems. Ellingham charts represent

equilibrium constants as a function of temperature and are used to assess stability of metals against potential oxidation. In the example presented here, it is considered that a certain amount of calcium carbonate is placed in a sealed rigid vessel, previously evacuated from gases, which is then heated to promote decomposition. The pressure of the container will vary in the course of the reaction as a gas phase is generated. Assuming that the container initially has 1 mol of solid  $CaCO_3$ , the number of moles of each of the species is given by

$$\begin{aligned} n_{CaCO_3} &= 1 + \nu_{CaCO_3}\xi = 1 - \xi & n_{CaO} &= \nu_{CaO}\xi = \xi \\ n_{CO_2} &= \nu_{CO_2}\xi = \xi \end{aligned} \quad (9)$$

Formally, the situation corresponds to a chemical reaction conducted at constant  $T$  and  $V$  so the evolution of the system should be described in terms of the Helmholtz free energy. As the crystalline structures of  $CaCO_3$  and  $CaO$  are different (cubic and trigonal, respectively), it is assumed that each solid crystallizes in its own lattice, forming two separated phases. The free energy function for the reactive system is then composed by three different contributions, those of the two solids ( $s, s'$ ) and that of the gas phase ( $g$ ):

$$A(V, T, \xi) = A^s + A^{s'} + A^g \quad (10)$$

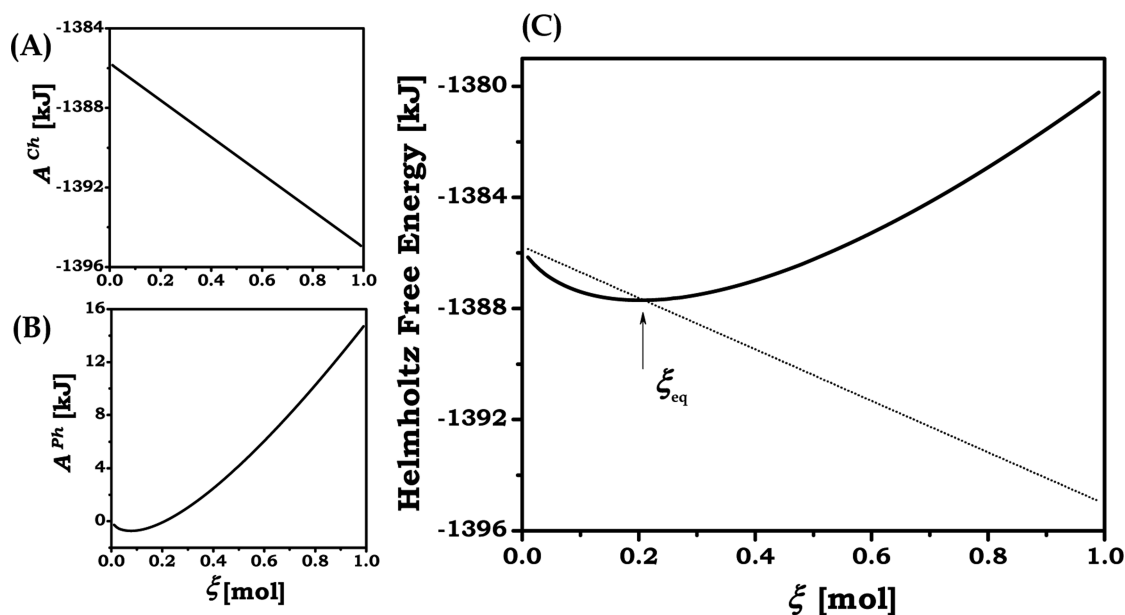
Applying eq 2 leads to

$$A(V, T, \xi) = \sum n_i \bar{A}_i^s + \sum n_i \bar{A}_i^{s'} + \sum n_i \bar{A}_i^g \quad (11)$$

where summations compute all the chemical species present in each phase. Common considerations for these systems follow: (i) vapor pressures of solids are sufficiently low to neglect their presence in the gas phase; (ii) solubility of  $CO_2$  in any solid phase is negligible; (iii) as supposed earlier, solids are immiscible. Essentially, we are neglecting any phase equilibrium between components, that is, any kind of mixing effects. Therefore, eq 11 is written as

$$A(V, T, \xi) = n_{CaCO_3} \bar{A}_{CaCO_3}^s + n_{CaO} \bar{A}_{CaO}^{s'} + n_{CO_2} \bar{A}_{CO_2}^g \quad (12)$$





**Figure 4.** Variation of the Helmholtz free energy function with the extent of reaction for  $\text{CaCO}_3$  decomposition carried out in a 20 l reservoir maintained at 1150 K: (A) chemical contribution, (B) physical contribution, and (C) global function (solid line) and chemical contribution (dotted line).

Expressions for  $\bar{A}_i$  as a function of  $\mu_i$  are given by eq 3. As in the examples presented the equilibrium pressure is never above 4 bar, any gas phase can be considered ideal, so, for  $\text{CO}_2$

$$\bar{A}_{\text{CO}_2} = \mu_{\text{CO}_2} - RT = G_{\text{CO}_2}^\circ + RT \ln\left(\frac{P}{P^\circ}\right) - RT \quad (13)$$

where  $\bar{V}_i = RT/P$  has been assumed and  $G_{\text{CO}_2}^\circ$  corresponds to the free energy of pure  $\text{CO}_2$  in the ideal gas state at  $T$  and  $P^\circ$ . For condensed phases, eq A8, Supporting Information, combined with eq 3 yields

$$\bar{A}_i = \mu_i - P\bar{V}_i = G_i^\circ + RT \ln a_i - V_i P^\circ = G_i^\circ \quad (14)$$

where  $a_i$  values have been assumed to equal 1,  $\bar{V}_i = V_i$ , and the term  $V_i P^\circ$  is neglected (see arguments after eq A8). Replacing terms in eq 11 yields

$$A(V, T, \xi) = n_{\text{CaCO}_3} G_{\text{CaCO}_3}^\circ + n_{\text{CaO}} G_{\text{CaO}}^\circ + n_{\text{CO}_2} \left[ G_{\text{CO}_2}^\circ + RT \ln\left(\frac{P}{P^\circ}\right) - RT \right] \quad (15)$$

We will assume that the volumes of the condensed phases are negligible compared with that of the gas phase so  $P = n_{\text{CO}_2} RT/V$ . With placement of each  $n_i$  term as a function of  $\xi$ , the following is obtained:

$$A(V, T, \xi) = \underbrace{(1 - \xi)G_{\text{CaCO}_3}^\circ + \xi G_{\text{CaO}}^\circ + \xi(G_{\text{CO}_2}^\circ - RT)}_{A^{\text{Ch}}} + \underbrace{\xi RT \ln\left(\frac{\xi RT}{VP^\circ}\right)}_{A^{\text{Ph}}} \quad (16)$$

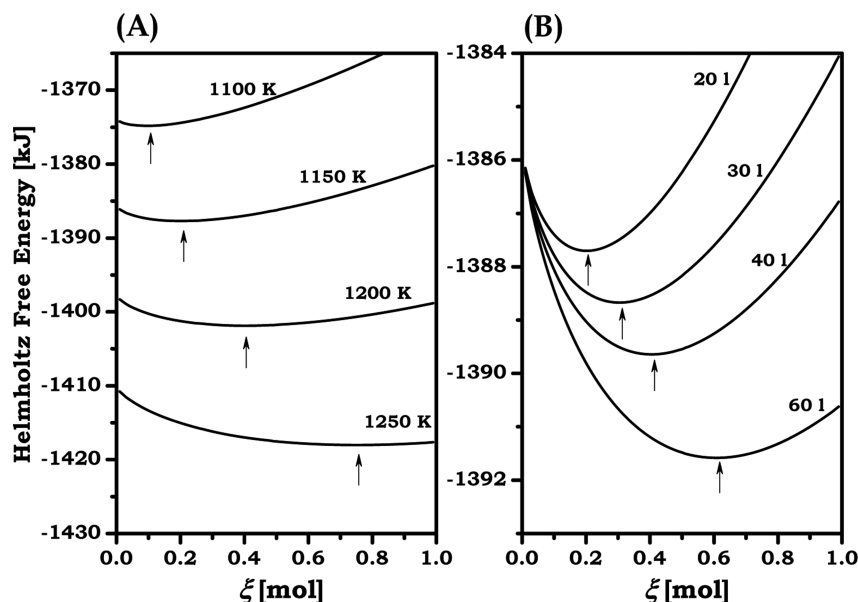
The earlier form is the quantitative expression for the Helmholtz free energy of the reactive system, where the temperature-dependent  $G_i^\circ$  terms can be established as explained in Appendix II of Supporting Information. As in

the previous example, the terms containing  $G_i^\circ$  are referred to as the chemical contribution ( $A^{\text{Ch}}$ ), and they have been grouped separately. Arbitrarily, the  $RT$  factor has also been included in that group. With the assumption that  $T$  and  $V$  are fixed, it is seen that the three terms included in  $A^{\text{Ch}}$  are linear with  $\xi$ . They have been represented in Figure 4A, for a reservoir volume of 20 L and  $T = 1150$  K. The linear plot starts at  $G_{\text{CaCO}_3}^\circ$  and ends at  $(G_{\text{CaO}}^\circ + G_{\text{CO}_2}^\circ - RT)$ .

The last term of eq 16 arises from the pressure correction of free energy of the pure  $\text{CO}_2$  gas phase [ $RT \ln(P/P^\circ)$ ], see eq 15. Notice that these types of terms were constants in the first example of the reaction conducted at  $P, T$  fixed, but in this case, it depends on  $\xi$ , as shown by eq 16. As the first three terms are linear with  $\xi$ , it should be this last one term, represented as  $A^{\text{Ph}}$ , that is responsible for the eventual curvature in the free energy curve. Figure 4B shows a plot of  $A^{\text{Ph}}$  versus  $\xi$ . The curve shows a minimum, as a result of a combination between linear and logarithmic functions.  $A^{\text{Ph}}$  does not tend to zero at both extremes, as in the case of  $G^{\text{Ph}}$  of the gas phase reaction, but it is only zero at the left boundary, when  $\xi = 0$ .

The combination of  $A^{\text{Ch}} + A^{\text{Ph}}$  has been represented in Figure 4C. The plot shows a minimum at  $\xi$  about 0.2, corresponding to the equilibrium state of the reactive mixture. The linear  $A^{\text{Ch}}$  contribution (Figure 4A) has also been represented in Figure 4C. Notice that  $A^{\text{Ch}}$  is not a secant line between end points in Figure 4C as in the case shown in Figure 2C. The reason for that is that  $A^{\text{Ph}}$  does not tend to zero at both function boundaries (Figure 4B) as does  $G^{\text{Ph}}$  (Figure 2B). The students can verify that the equilibrium state obtained from the minimum of the free energy curve is in excellent agreement with that calculated from the analytical equilibrium condition at 1150 K (0.203). For this calculation, the student will need the value of  $K_{\text{eq}}$  at 1150 K for the problem (0.97), which can be in turn calculated from thermodynamic tables.

Let us now interpret the  $A^{\text{Ph}}$  contribution. It certainly does not arise from mixing terms as that possibility has been ruled out from the problem statement.  $A^{\text{Ph}}$  originates in the gas



**Figure 5.** Variation of the Gibbs free energy function with the extent of reaction for  $\text{CaCO}_3$  decomposition. (A) Temperature was varied between 1100 and 1250 K for a reservoir of 20 L. (B) Reservoir volume was varied between 20 and 60 L for  $T = 1150$  K.

phase, as shown in the logarithm term in eq 13, as a contribution that accounts for the change in entropy of  $\text{CO}_2$  with pressure. While the increase in the number of  $\text{CO}_2$  molecules in the gas phase increases entropy ( $\xi$  term), it also increases pressure ( $\xi RT/V$  term), which reduces entropy. The competition between these two opposite factors produces a maximum in entropy, or minimum in free energy. In some way, the effect has the same root as the mixing contributions analyzed in the earlier example: the presence of a component that changes its entropy by either changes in volume or pressure, guaranteeing the existence of an equilibrium state of the reactive system. We also may anticipate that, in systems lacking mixing and a gas phase, there will not be a minimum in the free energy and an equilibrium state with appreciable amounts of all the components, as will be shown in the forthcoming example.

Effects of temperature and volume on equilibrium position of  $\text{CaCO}_3$  decomposition are examined in Figure 5. Temperatures operate explicitly in  $RT$  terms and implicitly in  $G_i^\circ$  whereas volume only appears in the arguments of logarithmic term. The effect of temperature on equilibrium position shown in Figure 5A can be rationalized with the same arguments used to analyze the homogeneous gas phase reaction, with function boundaries moving downward with increasing temperature. On the other hand, the effect of volume change illustrated in Figure 5B only shifts the right-hand boundary that contains the highly compressible gas phase. The left-hand boundary of the plot remains invariant, reflecting the incompressibility of the solid  $\text{CaCO}_3$  phase (see eq A8, Supporting Information).

## REACTIONS IN SOLID PHASE

The final example addresses the reaction of formation of magnesium aluminate from alumina and magnesium oxide,  $\text{MgO}(s) + \text{Al}_2\text{O}_3(s) \rightarrow \text{MgAl}_2\text{O}_4(s)$ , where all the components are solids. The reaction is a showcase for solid-state chemistry and can be used to represent the formation of intermediate compounds, a situation frequently found in materials science. It will be assumed that the components mutually exclude each other upon crystallization so mixing between them is neglected.

The system is then composed by three distinct solid phases, each of which contains one specific component. It is usual to perform these reactions at constant  $T$  and  $P$ ; therefore, the free energy function for the reactive system is written as

$$G(P, T, \xi) = n_{\text{MgO}}\mu_{\text{MgO}} + n_{\text{Al}_2\text{O}_3}\mu_{\text{Al}_2\text{O}_3} + n_{\text{MgAl}_2\text{O}_4}\mu_{\text{MgAl}_2\text{O}_4} \quad (17)$$

whereas the number of moles for each of the species, assuming 1 mol of each reactant in the initial condition, is given by

$$\begin{aligned} n_{\text{MgO}} &= 1 - \nu_{\text{MgO}}\xi = 1 - \xi \\ n_{\text{Al}_2\text{O}_3} &= 1 - \nu_{\text{Al}_2\text{O}_3}\xi = 1 - \xi \quad n_{\text{MgAl}_2\text{O}_4} = \nu_{\text{MgAl}_2\text{O}_4}\xi = \xi \end{aligned} \quad (18)$$

Expressions for the chemical potentials are given by eq A9, Supporting Information. Assuming  $a_i$  equals 1 (each phase is pure),  $\mu_i = G_i^\circ$  for each solid-state component. Replacing expressions for  $n_i$  and  $\mu_i$  in eq 17 gives

$$G(P, T, \xi) = (1 - \xi)G_{\text{MgO}}^\circ + (1 - \xi)G_{\text{Al}_2\text{O}_3}^\circ + \xi G_{\text{MgAl}_2\text{O}_4}^\circ \quad (19)$$

Equation 19 represents the free energy function for the solid-state reactive system, where  $G_i^\circ$  values are only temperature-dependent and can be evaluated as detailed in Appendix II of Supporting Information. The function is linear with  $\xi$ , without nonlinear contributions that could produce a curvature in the plot. Free energy is then entirely dominated by the chemical contribution represented by the  $G_i^\circ$  terms. Figure 6 shows a graph of that function at three different temperatures. As the minor value of free energy occurs at  $\xi = 1$ , thermodynamics predicts in this case a complete transformation of reactants to products, and an equilibrium state characterized by pure  $\text{MgAl}_2\text{O}_4(s)$ . The same can be concluded at any of the temperatures represented. Actually, the reaction is not practical at room temperature, despite it being thermodynamically favorable, due to kinetic constraints (slow diffusion in the solid state), but it is feasible at temperatures above 750 K, where diffusion barriers are overcome.

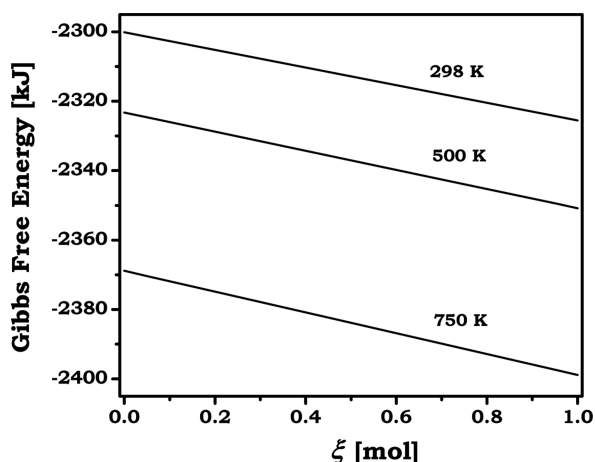


Figure 6. Variation of the Gibbs free energy function with the extent of reaction for the formation of  $\text{MgAl}_2\text{O}_4$  from  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  in the solid state, at three different temperatures.

It is instructive to calculate the equilibrium state from the analytical equilibrium condition  $K_{\text{eq}} = \prod a_{i,\text{eq}}^{\nu_i}$ , as we did in earlier examples. Although the left-hand term,  $K_{\text{eq}}$ , can be formally calculated from a value of  $\Delta_r G^\circ$ , the right-hand term equals 1, as each phase is in the pure state; in fact, that term is independent of  $\xi$ . The student should remember that the analytical equilibrium corresponds to the minimum condition for free energy and that the minimum does not exist in the interval  $0 < \xi < 1$ ; this explains the lack of a meaningful solution for  $\xi$ .

Finally, let us analyze what would be predicted for this reactive system if the components were miscible at the degree to form a solid solution. In that situation, the expressions for chemical potentials (see eq A9, Supporting Information) include molar fractions (and activity coefficients), which would lead to the appearance of mixing contributions in the free energy function, of the type shown by gas phase reactions. As in that case, these terms predict an increase in entropy (or decrease in free energy) in the mixing state, which is explained by the increase in accessible volume that perceives each individual component in the mixture, compared with that of the pure state.<sup>16</sup> Those mixing terms would produce a minimum in the free energy curve and an equilibrium state characterized by the presence of appreciable amounts of the three components in a single solid phase.

## CONCLUSIONS

In these examples, free energy curves in reactive systems that include gas and solid phases have been analyzed. These examples are helpful to develop a better appreciation of the factors that determine the shape of free energy curves. The role of entropy either through the so-called mixing contributions or the presence of a compressible phase, both related with changes in the accessible volume upon mixing or pressure, is highlighted as a physical contribution that produces a minimum in free energy. In systems lacking this mechanism, equilibrium is mostly determined by chemical effects, where the final state entirely corresponds to the species with minor free energy. These concepts are useful to rationalize chemical equilibrium in several systems involving condensed phases, such as the formation of oxides by contact of oxygen with metals or the generation of intermediate compounds in phase diagrams, topics of relevance in materials science programs.

We have also found that the assembly of free energy functions from expressions of chemical potentials and the additivity rule is a simple but general approach that the students follow very well. It reinforces the importance of this fundamental property that allows a natural integration of several layers of concepts (fugacity coefficients, activity coefficients, solution thermodynamics) developed in early stages of a thermodynamics course. Finally, we reaffirm here that key concepts such as spontaneity or the correct interpretation of  $\Delta_r G^\circ$  are remarkably facilitated with the quantitative representation, highly rewarding the time invested in developing the topic.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00726.

Expressions for the chemical potentials in specific aggregation states (Appendix I) and thermodynamic data necessary for the calculations (Appendix II) (PDF, DOCX)

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: jptomba@fi.mdp.edu.ar.

### ORCID

J. Pablo Tomba: 0000-0003-2112-4953

### Notes

The author declares no competing financial interest.

## ACKNOWLEDGMENTS

The author acknowledges Dr. Pablo Botta for the suggestion of the example of a solid phase reaction.

## REFERENCES

- (1) DeHoff, R. *Thermodynamics in Materials Science*, 2nd ed.; Taylor and Francis Group: Boca Raton, FL, 2006.
- (2) Gaskell, D. R. *Introduction to the Thermodynamics of Materials*, 4th ed.; Taylor and Francis Group: New York, NY, 2003.
- (3) Cohen, R. W.; Whitmer, J. C. The Gibbs function versus degree of advancement. *J. Chem. Educ.* **1981**, *58*, 21–24.
- (4) Raff, L. M. Spontaneity and equilibrium: why “ $\Delta G < 0$  denotes a spontaneous process” and “ $\Delta G = 0$  means the system is at equilibrium” are incorrect. *J. Chem. Educ.* **2014**, *91*, 386–395.
- (5) Quílez, J. First-Year University Chemistry Textbooks’ Misrepresentation of Gibbs Energy. *J. Chem. Educ.* **2012**, *89*, 87–93.
- (6) Smith, J. M.; Van Ness, H. C.; Abbot, M. N. *Introduction of Chemical Engineering Thermodynamics*, 7th ed.; McGraw-Hill: New York, NY, 2005.
- (7) Elliot, J. R.; Lira, C. T. *Introductory Chemical Engineering Thermodynamics*; Prentice Hall: Upper Saddle River, NJ, 2008.
- (8) Levine, I. N. *Physical Chemistry*, 5th ed.; McGraw-Hill: New York, NY, 2002.
- (9) Sandler, S. I. *Chemical, Biochemical, and Engineering Thermodynamics*, 4th ed.; John Wiley & Sons: Hoboken, NJ, 2006.
- (10) Dahm, K. D.; Visco, D. P. *Fundamentals of Chemical Engineering Thermodynamics*; Cengage Learning: Stamford, CT, 2015.
- (11) Pitzer, K. S. *Thermodynamics*, 3rd ed.; McGraw Hill: New York, NY, 1995.
- (12) Rock, P. *Chemical Thermodynamics*; University Science Books: Sausalito, CA, 1983.
- (13) Shultz, M. J. Why equilibrium? Understanding the role of entropy of mixing. *J. Chem. Educ.* **1999**, *76*, 1391–1393.

- (14) Ochs, R. S. Thermodynamics and spontaneity. *J. Chem. Educ.* **1996**, *73*, 952–954.
- (15) Ben-Naim, A. Entropy: Order or information. *J. Chem. Educ.* **2011**, *88*, 594–596.
- (16) Tomba, J. P. Teaching Thermodynamics of Ideal Solutions: An Entropy-based Approach To Help Students Better Understand and Appreciate the Subtleties of Solution Models. *J. Chem. Educ.* **2015**, *92*, 2100–2105.
- (17) Meyer, E. F. Thermodynamics of mixing of ideal gases. *J. Chem. Educ.* **1987**, *64*, 676.