The Gibbs Free Energy of a Chemical Reaction System as a Function of the Extent of Reaction and the Prediction of Spontaneity

by

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Abstract

Students often have a very simplistic idea of the relationship between the value of $\Delta G°$ for a reaction and the reaction's spontaneity: if $\Delta G°$ is negative, the reaction is spontaneous; if it is positive, the reaction is not spontaneous and in fact is anti spontaneous, going spontaneously in the reverse direction. This exercise is designed to help students develop a more nuanced understanding of the relationship between $\Delta G°_{rxn}$ and spontaneity through the creation of a graph of G for a reaction mixture vs. the extent of reaction, ζ, and an exploration of how the shape of that graph is affected by the value of $\Delta G°_{rxn}$.

Goal

The goal of this exercise is to help the user to discover

1. The shape of the graph of G for a reaction mixture vs. extent of reaction and the effect of the value of $\Delta G°_{rxn}$ on the shape of that graph
2. The fact that the value of $\Delta G°_{rxn}$ determines how far the reaction will proceed before reaching equilibrium, not whether or not the reaction is initially spontaneous.

This exercise will use the graphical power of Mathcad to help the user make these discoveries in a clear, visual, concrete way.

Performance Objectives

After completing this exercise the user should be able to

1. Draw a qualitative, generalized, graph of G for a reaction mixture vs. extent of reaction and, for a reaction of the type A + B <--> C + D, predict from the value of $\Delta G°_{rxn}$ roughly where the minimum of the graph will be
2. Label the region of the graph in which the reaction is spontaneous (goes in the forward direction), the region in which it is anti spontaneous (goes in the reverse direction), and the point at which it is at equilibrium, and explain the reasons for the labeling decisions
3. For a reaction of the type A + B <--> C + D estimate the values of $\Delta G°_{rxn}$ that will result in essentially complete reaction or essentially no reaction.

References and Suggestions for Further Reading

1. Atkins, Peter; de Paula, Julio *Physical Chemistry*, 7th ed.; W.H. Freeman: New York, 2002

2. Ball, David W. *Physical Chemistry;* Brooks/Cole: Pacific Grove, CA, 2003; Section 5.3

3. Sibley, Robert J.; Alberty, Robert A *Physical Chemistry*, 3rd ed.; John Wiley & Sons: New York, 2001; Sections 5.1 and 5.2

4. Deumié, M.; Boulil, B.; Henri-Rousseau, O *J. Chem. Educ.* **1987,** 64, 201-204

Introduction

In this exercise we are going to examine how the Gibbs free energy of a system undergoing a chemical reaction changes during the course of the reaction and relate that behavior to the spontaneity of the reaction. A number of questions will be asked and tasks assigned in this color font. Answer the questions and complete the tasks in the spaces provided below the questions and task assignments. Use the **Enter** key to create additional space there as needed.

For convenience we will use the imaginary reversible reaction

A(g) + B(g) <--> C(g) + D(g)

where A, B, C, and D are all ideal gases. Assume that the molar Gibbs free energy of formation values for these substances at 298 K are: -15.36, -10.69, -5.51, and -21.93 kJ/mole respectively.

$$kJ := 10^3 \cdot J$$

$$\Delta G°_{f,A} := -15.36 \cdot \frac{kJ}{mol} \quad \Delta G°_{f,B} := -10.69 \cdot \frac{kJ}{mol} \quad \Delta G°_{f,C} := -5.51 \cdot \frac{kJ}{mol} \quad \Delta G°_{f,D} := -21.93 \cdot \frac{kJ}{mol}$$

From these values we can calculate that ΔG° for the reaction at 298 K is

$$\Delta G°_{rxn} := \left[(1 \cdot mol)\Delta G°_{f,C} + (1 \cdot mol)\Delta G°_{f,D}\right] - \left[(1 \cdot mol)\Delta G°_{f,A} + (1 \cdot mol)\Delta G°_{f,B}\right]$$

$$\Delta G°_{rxn} = -1.39 \times 10^3 \, J$$

From the negative value of $\Delta G°_{rxn}$ we might conclude that this reaction is spontaneous; but is it always? We will explore that question by looking at how the Gibbs free energy value of the system changes during the reaction starting with 1 mole each of A and B in their standard states (pressure of 1 bar) at 298 K and the reaction and ending with 1 mole each of C and D in their standard states at 298 K. The value of any extensive property of a system is the sum, taken over all of the components of the system, of the number of moles of each component times the partial molar value of the property with respect to that component. Applying this to the Gibbs free energy of our reaction mixture and remembering that the partial molar Gibbs free energy is the chemical potential, μ, we have

$$G_{system} = Moles_A\mu_A + Moles_B\mu_B + Moles_C\mu_C + Moles_D\mu_D \quad (1)$$

We can express the number of moles of each component during the course of the reaction in terms of the extent of reaction, ξ. ξ is a parameter that runs from 0 at the beginning of the reaction, when the system consists of 1 mole of A and 1 mole of B, to 1 at the end, when the system consists of 1 mole of C and 1 mole of D. When ξ increases by Δξ, Δξ moles of A and Δξ moles of B are converted to Δξ moles of C and Δξ moles of D. Therefore, we can see that $Moles_A = 1 - \xi$, $Moles_B = 1 - \xi$, $Moles_C = \xi$, and $Moles_D = \xi$. We will represent ξ as a vector whose elements increase from 0 to 1 in increments of 0.01.

$$i := 0 .. 100 \qquad \xi_i := \frac{i}{100}$$

$$Moles_A := (1 - \xi) \cdot mol \quad Moles_B := (1 - \xi) \cdot mol \quad Moles_C := \xi \cdot mol \quad Moles_D := \xi \cdot mol \quad (2)$$

(In the page to the right type Moles.A =. Notice that $Moles_A$ has automatically been created as a vector.)

For an ideal gas

$$\mu = \mu° + RT \ln (P/1 \text{ bar}) \qquad (3)$$

where μ° is the molar Gibbs free energy for the pure gas. For quantities such as energy, enthalpy, and Gibbs free energy classical thermodynamics does not let us determine actual values; it only lets us determine **changes** in value resulting from various processes. Therefore, within the framework of classical thermodynamics we have no way of determining the values of μ° for the components of our reaction.

However, we can get around this problem by arbitrarily setting the values of μ° for the reactants and products equal to their $\Delta G°_f$ values. The equation for the molar Gibbs free energy of formation of a compound can be written

$$\Delta G^o_f(\text{compound}) = \mu^o(\text{compound}) - \Sigma(\text{moles of element})\mu^o(\text{element})$$

where the sum is taken over the elements making up the compound and "moles of element" refers to the number of moles of a given element contained in one mole of the compound. From this we can see that setting the μ° values for the reactants and products equal to their $\Delta G°_f$ values amounts to ignoring the μ° values for the elements from which they are made.

This is clearly not conceptually correct. However, for our purposes we can justify doing so as follows. The effect of including the μ° values for the elements on G_{system} calculated from Equation 1 is simply to add a constant that is independent of the extent of reaction, ξ. (You may want to demonstrate this for yourself using a sample reaction such as $CH_4(g) + F_2(g) \rightarrow CH_3F(g) + HF(g)$.) Therefore, ignoring the μ° values for the elements removes that constant from the value of G_{system}. This in turn shifts the graphs of G_{system} vs. ξ that we are going to create up or down on the y axis but does not affect their shape and so does not affect the results we are trying to achieve.

Substituting ΔG^o_f for μ° in Equation 3 we can write for each component of our reaction $\mu = \Delta G°_f + RT \ln(P/1 \text{ bar})$. P, the partial pressure of a component, can be calculated from the usual ideal gas equation P = nRT/V, where the value of V will be 24.777 liters, the value that will result in partial pressures of 1 bar for A and B at the beginning of the reaction and for C and D if the reaction has gone to completion. Translating all of this into Mathcad constant and variable definitions, we have

$$\text{bar} := \frac{\text{atm}}{1.01325} \qquad V := 24.777\cdot\text{liter} \qquad R1 := 0.083145\cdot\frac{\text{liter}\cdot\text{bar}}{\text{mol}\cdot\text{K}} \qquad T := 298\cdot\text{K}$$

$$P_A := \frac{\text{Moles}_A\cdot R1\cdot T}{V} \qquad P_B := \frac{\text{Moles}_B\cdot R1\cdot T}{V} \qquad P_C := \frac{\text{Moles}_C\cdot R1\cdot T}{V} \qquad P_D := \frac{\text{Moles}_D\cdot R1\cdot T}{V} \qquad (4)$$

$$j := 1 .. 99 \qquad R2 := 0.0083145\cdot\frac{\text{kJ}}{\text{mol}\cdot\text{K}}$$

$$\mu_{A_j} := \Delta G°_{f,A} + R2\cdot T\cdot\ln\left(\frac{P_{A_j}}{1\cdot\text{bar}}\right) \qquad \mu_{B_j} := \Delta G°_{f,B} + R2\cdot T\cdot\ln\left(\frac{P_{B_j}}{1\cdot\text{bar}}\right)$$

$$\mu_{C_j} := \Delta G^\circ_{f,C} + R2 \cdot T \cdot \ln\left(\frac{P_{C_j}}{1 \cdot bar}\right) \qquad \mu_{D_j} := \Delta G^\circ_{f,D} + R2 \cdot T \cdot \ln\left(\frac{P_{D_j}}{1 \cdot bar}\right)$$

$$G_{system_j} := Moles_{A_j} \cdot \mu_{A_j} + Moles_{B_j} \cdot \mu_{B_j} + Moles_{C_j} \cdot \mu_{C_j} + Moles_{D_j} \cdot \mu_{D_j}$$

a. In the space below create a graph of G_{system} vs. extent of reaction, ξ.

Create the graph by typing @. Put ξ[j in the placeholder for the horizontal axis and G_{system}[j in the placeholder for the vertical axis. Note: the subscript here is j, not i.

b. Is the reaction spontaneous, anti spontaneous, or neither after it has gone 20% to completion (ξ = 0.2)?

Explain the reasoning behind your answer. (What is the effect on G_{system} of the reaction proceeding a tiny increment beyond 20% completion?)

c. Is the reaction spontaneous, anti spontaneous, or neither after it has gone 80% to completion? Explain the reasoning behind your answer.

d. Can you find a value of ξ from the graph at which the reaction is neither spontaneous nor anti spontaneous? Estimate that value as closely as you can. What can you say about the reaction at that value of ξ?

Expanding the graph to fill the space made available for it, increasing the number of grid markers on the horizontal axis, and adding grid lines on the horizontal axis may improve the accuracy of your estimation of the value of ξ.

The reaction quotient for this reaction is $(P_C P_D)/(P_A P_B)$. When the reaction is at equilibrium, the value of the reaction quotient is equal to the equilibrium constant K_P, whose value can be calculated from the equation

$$K_P = e^{\frac{-\Delta G^\circ_{rxn}}{R \cdot T}}$$

e. Use the value of ξ estimated in part d along with Equations 2 and 4 to calculate P_A, P_B, P_C, and P_D at that value of ξ. Then use those pressure values to calculate the reaction quotient at that value of ξ. Compare this reaction quotient to the value of K_P calculated from ΔG°_{rxn}. Does this confirm what you said in part d about the reaction at that value of ξ?

Now let us examine the case of positive $\Delta G^\circ_{rxn.}$ The equations for ΔG°_{rxn}, the μ values, and G_{system} are copied below along with a new value for $\Delta G^\circ_{f,D}$. The effect of this new value of $\Delta G^\circ_{f,D}$ is to change the sign of ΔG°_{rxn} from negative (-1.39 kJ) to positive (3.74 kJ).

$$\Delta G°_{f,D} := -16.8 \cdot \frac{kJ}{mol}$$

$$\Delta G°_{rxn} := \left[(1 \cdot mol)\Delta G°_{f,C} + (1 \cdot mol)\Delta G°_{f,D}\right] - \left[(1 \cdot mol)\Delta G°_{f,A} + (1 \cdot mol)\Delta G°_{f,B}\right]$$

$$\Delta G°_{rxn} = 3.74 \times 10^{3}\,J$$

$$\mu_{A_j} := \Delta G°_{f,A} + R2 \cdot T \cdot \ln\left(\frac{P_{A_j}}{1 \cdot bar}\right) \qquad \mu_{B_j} := \Delta G°_{f,B} + R2 \cdot T \cdot \ln\left(\frac{P_{B_j}}{1 \cdot bar}\right)$$

$$\mu_{C_j} := \Delta G°_{f,C} + R2 \cdot T \cdot \ln\left(\frac{P_{C_j}}{1 \cdot bar}\right) \qquad \mu_{D_j} := \Delta G°_{f,D} + R2 \cdot T \cdot \ln\left(\frac{P_{D_j}}{1 \cdot bar}\right)$$

$$G_{system_j} := Moles_{A_j} \cdot \mu_{A_j} + Moles_{B_j} \cdot \mu_{B_j} + Moles_{C_j} \cdot \mu_{C_j} + Moles_{D_j} \cdot \mu_{D_j}$$

How does the change in the sign of $\Delta G°_{rxn}$ affect the spontaneity of the reaction? Does it change it from spontaneous to anti spontaneous? Investigate this question by repeating parts a-e with this new value of $\Delta G°_{f,D}$ and the resultant positive value of $\Delta G°_{rxn}$. Use **Enter** to create space for doing this.

f. Comment on the validity of the statement "If $\Delta G°_{rxn}$ is negative, the reaction is spontaneous; if it is positive, the reaction is anti spontaneous." How *does* the sign and magnitude of $\Delta G°_{rxn}$ affect the spontaneity of a reaction and how far it will go toward completion before it reaches equilibrium? Can you come up with a more valid statement of the role of $\Delta G°_{rxn}$?

g. Further study: to gain further insights into the role of the sign and magnitude of $\Delta G°_{rxn}$ on the spontaneity of reactions and the location of the equilibrium point, copy the equations for the $\Delta G°_f$ values, $\Delta G°_{rxn}$, the μ values, and G_{system} in the space below text box (using the Enter key as needed to clear additional space)**, create the graph of G_{system} vs. ξ, and explore how that graph is affected if you play around with the $\Delta G°_f$ values and the $\Delta G°_{rxn}$ values that result.** Expanding the graph so that it fills the whole screen will make the effects stand out better. **On the basis of your explorations answer the following questions:**

1. For what values of $\Delta G°_{rxn}$ is the extent to which the reaction proceeds before reaching equilibrium so small that the reaction may be considered not to occur at all?

2. For what values of $\Delta G°_{rxn}$ is the extent to which the reaction proceeds before reaching equilibrium so great that the reaction may be considered to go to completion?

Support your answers to both questions with appropriate graphs.

One thing that should be very clear from this exercise is that, regardless of the value of ΔG^o_{rxn}, a graph of G_{system} vs. ξ is a curve that dips to a minimum. This indeed is what causes the reaction to reach an equilibrium somewhere between the system consisting of only reactants in their standard states and the system consisting only of products in their standard states. Why should this be the case? What causes this minimum?

As discussed on pages 226 and 227 of Reference 1, the fact that the graph of G_{system} vs. ξ is U-shaped is due to to effect of the mixing of the reactants and products in the reaction vessel. If the reaction could transform pure separate reactants into pure separate products without any mixing occurring, the graph of G_{system} vs. ξ would be a straight line running from G^o of the reactants to G^o of the products (See Fig. 9.2 of Reference 1).

The effect of mixing on G_{system} can be expressed in terms of a ΔG of mixing. However, if we look into this a bit more deeply, we see that the effect is really due to the ΔS of mixing. This is can be demonstrated by noting that, by definition, $G = H - TS$. Therefore, at constant temperature, $\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing}$. Since for ideal gases H depends only on temperature, it will be unaffected by the changes in pressure and volume resulting from the mixing of the gases. Moreover, if the gases are ideal, there is no interaction between their molecules that might cause a change in H on mixing. Therefore, $\Delta H_{mixing} = 0$, and $\Delta G_{mixing} = -T\Delta S_{mixing}$. A comparison of the equations for ΔG_{mixing} and ΔS_{mixing} in physical chemistry textbooks, such as Equations 7.18 and 7.19 of Reference 1, confirms this.