

Thermodynamics of Natural Systems

Theory and Applications in Geochemistry
and Environmental Science

Third Edition
G.M. ANDERSON



CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE
UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

4843/24, 2nd Floor, Ansari Road, Daryaganj, Delhi – 110002, India

79 Anson Road, #06–04/06, Singapore 079906

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9781107175211

10.1017/9781316796856

© Greg Anderson 2017

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2017

Printed in the United Kingdom by TJ International Ltd., Padstow, Cornwall

A catalog record for this publication is available from the British Library

Library of Congress Cataloging-in-Publication Data

Names: Anderson, G. M. (Gregor Munro), 1932– author.

Title: Thermodynamics of natural systems : theory and applications in geochemistry and environmental science / G.M. Anderson.

Description: Third edition. | Cambridge, United Kingdom ; New York, NY : Cambridge University Press, 2017. | Includes bibliographical references and index.

Identifiers: LCCN 2016041118 | ISBN 9781107175211 (Hardback ; alk. paper) | ISBN 1107175216 (Hardback ; alk. paper)

Subjects: LCSH: Thermodynamics—Textbooks. | Geochemistry—Textbooks.

Classification: LCC QE515.5.T46 A53 2017 | DDC 541/.369–dc23

LC record available at <https://lccn.loc.gov/2016041118>

ISBN 978-1-107-17521-1 Hardback

Additional resources for this publication at www.cambridge.org/thermodynamics

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party Internet Web sites referred to in this publication and does not guarantee that any content on such Web sites is, or will remain, accurate or appropriate.

6

Some Simple Applications

6.1

Introduction

We now know how to determine in which direction any chemical reaction will proceed at a given temperature and pressure, at least when all the products and reactants are pure phases. When even one of the products or reactants is a solute, that is, part of a solution, we would be stuck because we haven't considered how to obtain or use such data. We will start considering this problem in the next chapter. Before going on, however, we should explore some relationships using the concepts we have defined so far, so as to make sure we fully understand them. Naturally, we will only be able to consider some simple properties of pure phases, and reactions between pure phases.

6.2

Simple Phase Diagrams

The reason we are interested in knowing $\Delta_r G$ for reactions is that we can then tell which way the reaction will go, or which side is more stable at one particular T and P . If we know how $\Delta_r G$ varies with T and P , we might find that under some conditions $\Delta_r G$ changes sign, so that the other side is more stable. This implies that there is a boundary between regions of T and P , with one side of the reaction stable on one side of the boundary, and the other side of the reaction stable on the other side of the boundary. A phase diagram shows which phases are stable as a function of T , P , composition, or other variables.

For example, calcium carbonate (CaCO_3) has two polymorphs, namely calcite and aragonite. Their properties (from Appendix B) are shown in Table 6.1. Because $\Delta_f G_{\text{calcite}}^\circ < \Delta_f G_{\text{aragonite}}^\circ$, we conclude immediately that calcite is the stable form of CaCO_3 at 25°C , 1 bar, and that aragonite is a metastable form. But what about other temperatures and pressures? Is aragonite stable at high temperature? At high pressure? How can we tell?

6.2.1

Le Chatelier's Principle

When looking at thermodynamic data, or the results of some thermodynamic calculation, it is always a good idea to ask yourself if it makes sense, if it is reasonable. To some extent this is a matter of experience, but in another way, "making sense" means obeying Le Chatelier's principle. This simply says that *if a change is made to a system, the system will respond in such a way as to absorb the force causing the change*. For example, if the pressure on a system is raised, the system will respond by lowering its volume, that is,

Table 6.1. Thermodynamic properties of calcite and aragonite, from Appendix B.

Formula	Form	$\Delta_f H^\circ$ (kJ mol ⁻¹)	$\Delta_f G^\circ$ (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	V° (cm ³ mol ⁻¹)
CaCO ₃	calcite	-1206.92	-1128.79	92.9	36.934
CaCO ₃	aragonite	-1207.13	-1127.75	88.7	34.150

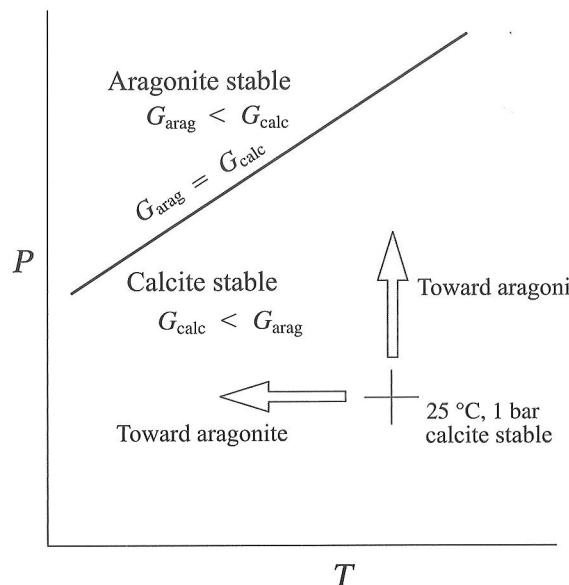


Figure 6.1 The form of the calcite–aragonite phase diagram deduced from Le Chatelier's principle.

by being compressed. Systems never expand as a result of increased pressure. The result of a change in temperature is less obvious, though equally certain. If the temperature of a system is raised, the enthalpy and the entropy of the system will both increase. This is because of Equations (3.39) and (4.32), which show that the temperature derivative of each is a simple function of C_P , the heat capacity, which is always positive for pure compounds.

Therefore, by looking at V° and $\Delta_f H^\circ$ or S° for calcite and aragonite, and assuming that the relative magnitudes of these properties do not change much with T and P , we can tell something about their relative positions on the phase diagram. We note that $V_{\text{aragonite}} < V_{\text{calcite}}$; therefore, increasing the pressure on calcite should favor the formation of aragonite. Also, $\Delta_f H^\circ$ and S° for calcite are greater than the values for aragonite, and so raising the temperature of calcite will *not* favor the formation of aragonite. In other words, *lowering* the temperature of calcite should favor the formation of aragonite. If the stability field of aragonite lies somewhere at higher pressure and lower temperature than 25 °C, 1 bar, the boundary between the two phases must have a positive slope, as shown in Figure 6.1. This is the common case for phase boundaries; it is normal for the high-pressure, lower-volume side to be the lower-enthalpy, lower-entropy side. The most common exception to this is the ice–water transition, as shown in Figure 3.1.

In Figure 6.1 we see that a phase diagram is a kind of free energy map – it shows a T – P region where calcite is stable ($G_{\text{calcite}} < G_{\text{aragonite}}$), and another where aragonite is stable ($G_{\text{aragonite}} < G_{\text{calcite}}$). These two regions are necessarily separated by a line where $G_{\text{aragonite}} = G_{\text{calcite}}$, the phase boundary. We have a lot more to say about phase diagrams in Chapter 12.

6.2.2

The Effect of Pressure on $\Delta_r G^\circ$

Having figured out the relationship between calcite and aragonite qualitatively, the next step is to define the stability field of aragonite, that is, to calculate the position of the phase boundary. This should be possible, because we know that

$$\partial G / \partial P = V \quad (4.51)$$

and thus

$$\partial \Delta G / \partial P = \Delta V$$

ΔG and ΔV refer to the difference in G and V between any two equilibrium states. In this case we are dealing with a chemical reaction between two compounds in their pure states, so we can also write

$$\partial \Delta_r G^\circ / \partial P = \Delta_r V^\circ$$

Integrating this equation between 1 bar and some higher pressure P , we have

$$\Delta_r G_P^\circ - \Delta_r G_{1\text{bar}}^\circ = \int_{1\text{bar}}^P \Delta_r V^\circ dP \quad (6.1)$$

and if we assume that $\Delta_r V^\circ$ is a constant, this becomes

$$\begin{aligned} \Delta_r G_P^\circ - \Delta_r G_{1\text{bar}}^\circ &= \Delta_r V^\circ \int_{1\text{bar}}^P dP \\ &= \Delta_r V^\circ (P - 1) \end{aligned}$$

We could use this to evaluate $\Delta_r G_P^\circ$ at any chosen value of P . However, we are particularly interested in a value of $\Delta_r G_P^\circ = \Delta_r G_{P_{\text{eqbm}}}^\circ = 0$, that is, on the phase boundary. We know the values of

$$\begin{aligned} \Delta_r G_{1\text{bar}}^\circ &= \Delta_f G_{\text{aragonite}}^\circ - \Delta_f G_{\text{calcite}}^\circ \\ &= -1127.75 - (-1128.79) \\ &= 1.04 \text{ kJ mol}^{-1} \\ &= 1040 \text{ J mol}^{-1} \end{aligned}$$

and

$$\begin{aligned} \Delta_r V^\circ &= V_{\text{aragonite}}^\circ - V_{\text{calcite}}^\circ \\ &= 34.150 - 36.934 \\ &= -2.784 \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

So we can solve the equation for P_{eqbm} , the pressure of the calcite–aragonite equilibrium at 25°C.

However, there is one little problem.

The Units of Volume

Volumes are generally measured in cubic centimeters, milliliters, liters, and so on. But if you look at an equation such as

$$w = -P \Delta V$$

you see that we have a problem with our units. Work (w) and $P \Delta V$ are obviously energy terms (J mol^{-1}), but the product of P in bars and ΔV in $\text{cm}^3 \text{mol}^{-1}$ is not joules. We must always convert our volumes to joules bar $^{-1}$, so that the product of P and V or ΔV is J mol^{-1} . The conversion factor (Appendix A) is

$$1 \text{ cm}^3 = 0.10 \text{ J bar}^{-1}$$

so now our $\Delta_r V^\circ$ is $-2.784 \times 0.1 = -0.2784 \text{ J bar}^{-1}$.

Now we can solve for pressure P_{eqbm} :

$$\Delta_r G_P^\circ_{\text{eqbm}} - \Delta_r G_1^\circ \text{ bar} = \Delta_r V^\circ (P_{\text{eqbm}} - 1)$$

$$0 - 1040 = -0.2784(P_{\text{eqbm}} - 1)$$

$$P_{\text{eqbm}} = 3737 \text{ bar}$$

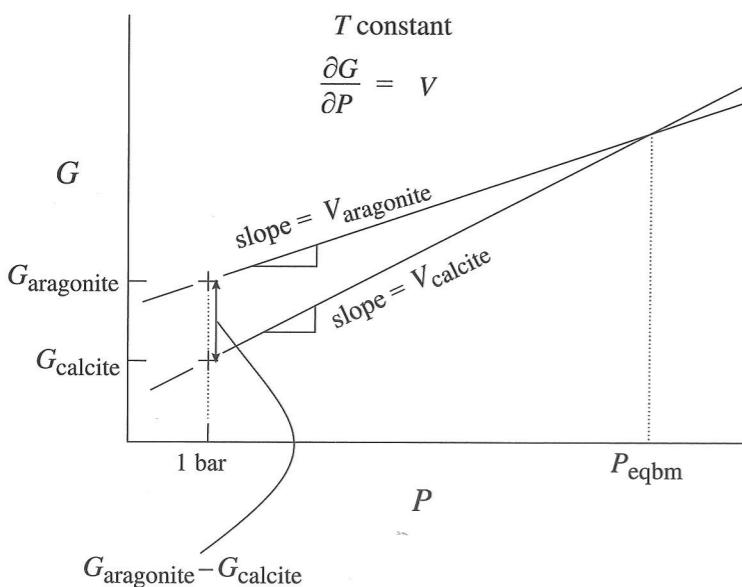


Figure 6.2 The relationship between G and P . Note that we don't know individual G values, so there are no numbers on the y -axis. We do know $G_{\text{calcite}} - G_{\text{aragonite}}$ and the slopes of the lines (the molar volumes), and this is sufficient to solve for P_{eqbm} . At P_{eqbm} , $G_{\text{calcite}} = G_{\text{aragonite}}$, the two phases can coexist, and we have a phase boundary.

6.3

The Slope of Phase Boundaries

The phase boundary is the locus of T and P conditions where $\Delta_r G = 0$, i.e., where

$$G_{\text{calcite}} = G_{\text{aragonite}} \quad (6.2)$$

It follows that on the boundary,

$$dG_{\text{calcite}} = dG_{\text{aragonite}} \quad (6.3)$$

This simply says that as you move along the boundary, the change in G_{calcite} has to be the same as the change in $G_{\text{aragonite}}$; otherwise you won't stay on the boundary. From Equation (4.48) we have

$$dG = -SdT + VdP \quad (4.48)$$

This applies to each mineral, and combining with (6.3) gives

$$-S_{\text{calcite}}dT + V_{\text{calcite}}dP = -S_{\text{aragonite}}dT + V_{\text{aragonite}}dP$$

Rearranging this gives

$$\frac{dP}{dT} = \frac{S_{\text{calcite}} - S_{\text{aragonite}}}{V_{\text{calcite}} - V_{\text{aragonite}}}$$

or, for any reaction,

$$\frac{dP}{dT} = \frac{\Delta_r S}{\Delta_r V} \quad (6.4)$$

which gives the slope of an equilibrium phase boundary in terms of the entropy and volume changes between the phases involved in the reaction. This is called the Clapeyron equation.

Equation (5.1) says

$$\Delta G_{T,P} = \Delta H - T \Delta S \quad (5.1)$$

This applies to any change between two equilibrium states at the same T and P . If those two equilibrium states have the same value of G , such as calcite and aragonite do on their phase boundary (6.2), then $\Delta G_{T,P} = 0$, and

$$\Delta H = T \Delta S \quad (6.5)$$

or

$$\frac{\Delta H}{T} = \Delta S \quad (6.6)$$

This is a useful relationship for any phase boundary,¹ which is the usual place to find $\Delta G_{T,P} = 0$. This gives an alternative form of the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad (6.7)$$

6.3.1 The Slope of the Calcite–Aragonite Boundary

We have one point on the calcite–aragonite boundary at 3737 bar, 25 °C. If we assume that the $\Delta_r S$ and the $\Delta_r V$ at this P and T are the same as those at 1 bar, 25 °C, we can calculate the slope from the data in our tables. Thus

$$\begin{aligned} \Delta_r S &= S_{\text{Aragonite}} - S_{\text{Calcite}} \\ &= 88.7 - 92.9 \\ &= -4.2 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned} \quad (6.8)$$

and

$$\begin{aligned} \Delta_r V &= V_{\text{Aragonite}} - V_{\text{Calcite}} \\ &= 34.150 - 36.934 \\ &= -2.784 \text{ cm}^3 \text{ mol}^{-1} \\ &= -0.2784 \text{ J bar}^{-1} \end{aligned}$$

Therefore

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta_r S}{\Delta_r V} \\ &= \frac{-4.2}{-0.2784} \\ &= 15.09 \text{ bar/}^\circ\text{C} \end{aligned}$$

Therefore, to get another point on the calcite–aragonite phase boundary, we simply choose an arbitrary temperature increment, say 100 °C, calculate the corresponding pressure increment, $100 \times 15.09 = 1509$ bar, and add these increments to our first point. We now have a second point at 125 °C, $3737 + 1509 = 5246$ bar, and we can plot the boundary as in Figure 6.3.

Keep in mind that we have assumed that the $\Delta_r S$ and $\Delta_r V$ from the tables are unchanged at all temperatures and pressures, that is, that they are constants. This is quite a good approximation for a reaction involving only solid phases such as this one, but you would not use it for reactions involving liquids, gases, or solutes. In general, all thermodynamic parameters do vary with T and P , so phase boundaries are in principle curved and not straight as we have assumed. However, the amount of curvature is quite small in some cases, such as this one.

¹ That is, any phase boundary in a one-component system. With two or more components, the relationship is in principle the same but becomes more complicated, and less useful.

Table 6.2. Experimental results for the system CaCO_3 from Crawford and Hoersh (1972).

Temperature (°C)	Pressure (bars)	Experimental result	Duration days
128	5180	A	21
132	5180	A	21
153	4830	C	35
76	4480	A	3
90	4140	C	28
93	4140	C	17
56	4140	A	28
70	4140	A	17
70	3690	C	8
81	3520	C	36

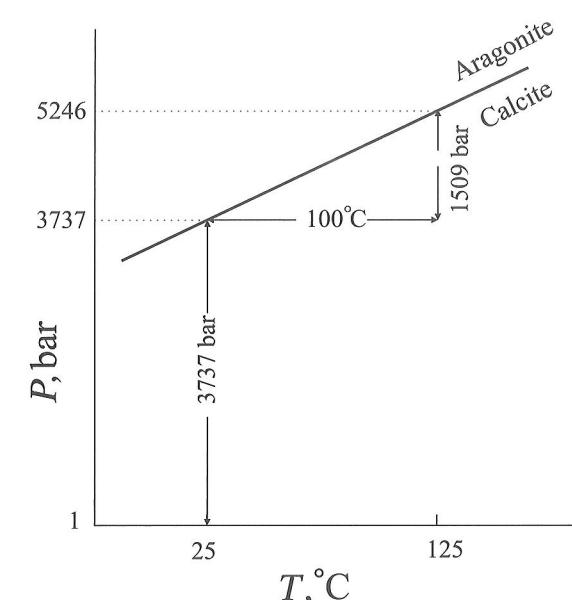


Figure 6.3 Calculation of the calcite–aragonite phase diagram.

6.3.2 Comparison with Experimental Results

Table 6.2 shows the results of some experiments on the stability of CaCO_3 at elevated temperatures and pressures. A mixture of calcite and aragonite was held at the indicated T and P for the length of time shown, then quenched and examined. The stable phase is shown as C (calcite) or A (aragonite). These points are plotted in Figure 6.4.

Also shown in this figure are the two points we have just calculated at 25 and 125 °C, plus results using data from Helgeson *et al.* (1978), and a line showing the experimenter's best estimate of the phase boundary. As you see, the calculated results using data from Appendix B are a little high, and the Helgeson *et al.* results are a bit low. Thermodynamic data have many possible sources of error, but then so do experimental data.

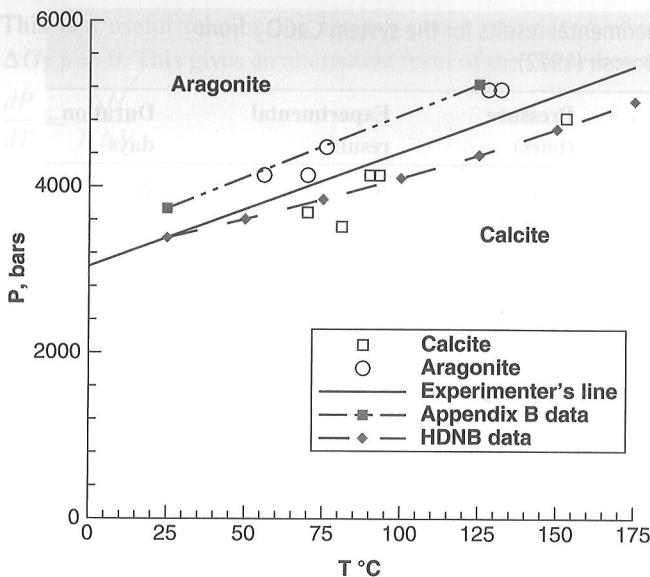


Figure 6.4 Comparison of experiment and calculation of the calcite–aragonite phase diagram.

6.4

Another Example

6.4.1

The Effect of Temperature on $\Delta_r G^\circ$

To illustrate the effect of temperature on $\Delta_r G^\circ$, we could continue with the calcite–aragonite case and try to calculate the temperature where the phase boundary crosses the 1 bar pressure line (Figure 6.3). Unfortunately, this turns out to be close to absolute zero, so it is not a very useful example. As another case let's consider the polymorphs of Al_2SiO_5 . There are three of these, kyanite, andalusite, and sillimanite. Therefore there are three two-phase boundaries, and these three boundaries meet at a single point, where $G_{\text{kyanite}} = G_{\text{andalusite}} = G_{\text{sillimanite}}$ as shown in Figure 6.5. These minerals, which form quite commonly in rocks subjected to high temperatures and pressures in the Earth's crust, are of special interest to geologists who study these rocks because the “triple point,” the point where the three phase boundaries meet, is in the middle of a rather common range of T – P conditions. If a rock contains one of these minerals, the geologist immediately has a general idea of the T and P conditions at the time the rock formed. It is only a “general idea” because it is not safe to assume that rocks reach chemical equilibrium at some P and T , and then remain unaltered as they are exhumed and are exposed at the Earth's surface. Many complications can occur, which are not within the subject of thermodynamics.

According to Figure 6.5, the kyanite–andalusite boundary crosses the 1 bar line at some elevated temperature. We should be able to calculate what this is by methods perfectly