
Minerals

Their Constitution and Origin

Hans-Rudolf Wenk

University of California, Berkeley, USA

and

Andrei Bulakh

St Petersburg State University, Russia



PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS

The Edinburgh Building, Cambridge CB2 2RU, UK
40 West 20th Street, New York, NY 10011-4211, USA
477 Williamstown Road, Port Melbourne, VIC 3207, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain
Dock House, The Waterfront, Cape Town 8001, South Africa
<http://www.cambridge.org>

© Hans-Rudolf Wenk & Andrei Bulakh 2004

This book 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 2004

Printed in the United Kingdom at the University Press, Cambridge

Typefaces Swift 9/12.25 pt. and Gill Sans System L^AT_EX 2_E [TB]

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

Library of Congress Cataloging in Publication data

Wenk, Hans-Rudolf, 1941-

Minerals: their constitution and origin / Hans-Rudolf Wenk and Andrei Bulakh.

p. cm.

Includes bibliographical references and index.

ISBN 0 521 82238 6 (hardback) - ISBN 0 521 52958 1 (paperback)

1. Mineralogy. I. Bulakh, A. G. (Andrei Glebovich) II. Title

QE363.2 .W46 2003

549 - dc21 2002031558

ISBN 0 521 82238 6 hardback

ISBN 0 521 52958 1 paperback

(SG)

QE363

2

W46

2004

The publisher has used its best endeavors to ensure that the URLs for external websites referred to in this book are correct and active at the time of going to press. However, the publisher has no responsibility for the websites and can make no guarantee that a site will remain live or that the content is or will remain appropriate.

Chapter 17

Stability of minerals. Principles of thermodynamics

Introduction

Minerals form by chemical reactions over a wide range of conditions, with temperature, pressure and chemical potentials of all components being the most important variables. The principles of thermodynamics, developed in chemistry to quantify chemical transformations, are directly applicable to these reactions. The formal derivation of thermodynamic relationships will not be covered here and it is assumed that the reader has some background in elementary chemistry. Many of the quantitative derivations are not necessary to follow the rest of this book. Yet, at the end of this chapter, a student should be familiar with phase diagrams, and how they are related to the chemical properties of minerals.

We introduce some basic concepts and illustrate them with mineral examples. There are three main laws of thermodynamics that were formulated in the nineteenth century. The first law, based on the recognition by Robert Mayer in 1840 that heat (ΔQ) is equivalent to mechanical work (ΔW), states that a change in the total internal energy of a system (ΔE) is equivalent to the heat transferred into the system minus the work performed by the system; that is, $\Delta E = \Delta Q - \Delta W$. The total value of internal energy (E) cannot be readily quantified, and in most cases we need to know only how E changes during a process or reaction.

The second law of thermodynamics, proposed by Rudolf Clausius in 1850, can be formulated in several different ways. Unlike in an ideal (reversible) process, the heat absorbed by a system under

going an irreversible process is not equal to the work performed on the system. Part of the energy is always lost in the process and cannot be retrieved. "Irreversibility" is reflected through changes in the value of entropy S , which is a measure of the degree of disorder in the system. Thus, for all irreversible processes, the second law of thermodynamics can be formulated as $\Delta S > Q/T$, and for reversible processes, it can be stated as $\Delta S = Q/T$, where T stands for absolute temperature. For example, two bodies at different temperatures will exchange heat, such that heat flows from the hotter to the colder body.

Both internal energy and entropy characterize the state of a system, and they are independent of how that state has been reached. If C is the heat capacity, a scalar property that specifies the heat maintained by a substance, then for any given compound whose entropy is known at a temperature T_1 , an absolute value of S at T_2 can be found by integrating its heat capacity over the T_1-T_2 interval. It has been proved experimentally that all pure and perfectly ordered crystalline substances (i.e., all substances excluding solid solutions, glasses, and crystals with defects) have the same entropy at absolute zero temperature. This statement, known as the *third law of thermodynamics*, provides a useful reference frame. These fundamental laws of thermodynamics have profound implications for geological processes of all magnitudes.

It should be emphasized, however, that kinetics (i.e., the rate at which reactions take place) is also important for mineral reactions. Many minerals do not crystallize in their stability field

and are not in chemical equilibrium. On cooling, reaction rates slow down, often to immeasurable rates at low temperature, and minerals that are stable at high temperature are preserved at room temperature. For example: cristobalite and tridymite, high-temperature SiO_2 phases, precipitate in seawater; sanidine, the disordered K feldspar in volcanic rocks, forms in sediments; and aragonite, the high-pressure polymorph of CaCO_3 is the main constituent of seashells. At higher temperatures, as during the crystallization of many metamorphic and igneous rocks, a closer approximation to equilibrium exists. However, most minerals collected in the field or analyzed in the laboratory are presently not in chemical equilibrium and this is used by petrologists to establish the conditions present during rock formation.

Minerals are products of chemical reactions or polymorphic transformations. These always involve an assemblage (*system*) of *phases* and chemical components (such as elements, oxides, etc.). There are open and closed systems, depending on whether matter can or cannot enter or leave the system. Thermodynamic principles allow us to analyze real or imaginary phases and chemical transformations within the system. A *phase* is a homogeneous and physically distinct part of the thermodynamic system that may be isolated mechanically from the system. It may be a solid, a liquid or a gas. Figure 17.1 shows a pressure versus temperature phase diagram for H₂O. Ice, vapor, and water are three coexisting phases at T = 298.16 K (0.01 °C) and P = 0.61 Pa, which is the invariant point, or triple point, for water. There are several high-pressure polymorphs of ice. Each mineral in a solidifying magma is a separate phase; the melt itself is a separate phase as long as it is homogeneous. A homogeneous gas mixture that has separated from the melt is another phase.

Thermodynamic *components* are chemical constituents that can be used to describe completely the chemical compositions of the phases of a system. In principle we could use individual elements as chemical components, but it is simpler to use compounds. For example, the system containing the three phases ice, vapor, and water has one component, namely H_2O . The system

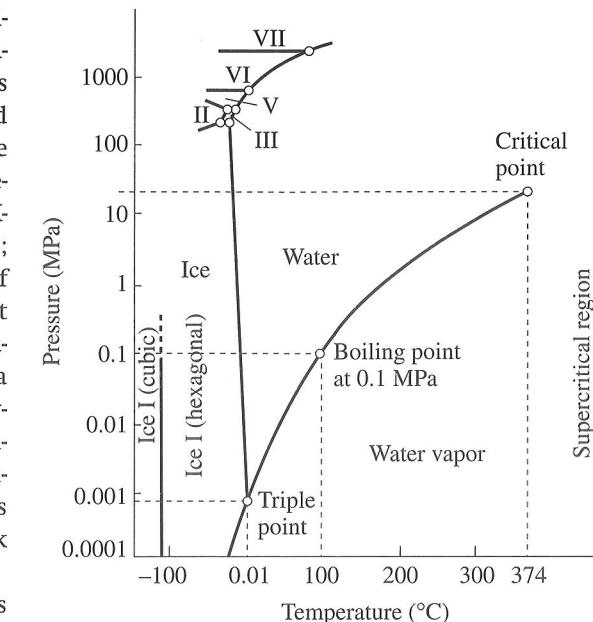
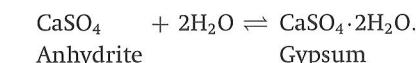
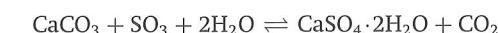


Fig. 17.1 $P-T$ phase diagram of H_2O illustrating stability fields of ice, liquid, and gas. All three phases coexist at the triple point. The different polymorphs of ice are indicated by roman numerals.

gypsum plus anhydrite (as in some sedimentary rocks) can be regarded as having two components, CaSO_4 and H_2O . These components may be connected in the following manner by a chemical reaction:



In the system calcite + gypsum (which is found in corroded marbles of old statues and buildings) the following reaction can proceed:



CaO, CO₂, SO₃, and H₂O can be chosen as thermodynamic components of this system. The number of components ($c = 4$) is the number of phases ($p = 5$) minus the number of chemical reactions between the phases ($n = 1$), i.e.,

$$c = p - n \quad (17.1)$$

The stable state of a mineral is determined by the energy minimum rule. The maximum

Table 17.1 | Definition of some thermodynamic potentials

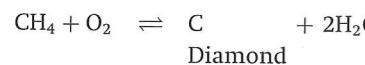
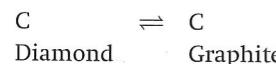
	General relationships (equilibrium state)	Equilibrium restrictions	Spontaneous process		Equilibrium states
			Possible	Impossible	
Entropy, S	$dS = dQ/T$	$dE = 0; dV = 0$	$dS > 0$	$dS < 0$	$dS = 0$
Internal energy, E	$dE = TdS - PdV$	$dS = 0; dV = 0$	$dE < 0$	$dE > 0$	$dE = 0$
Enthalpy, H	$dH = dE + PdV$	$dS = 0; dP = 0$	$dH < 0$	$dH > 0$	$dH = 0$
Helmholtz potential, F	$F = E - TS,$ $dF = -SdT - PdV$	$dV = 0; dT = 0$	$dF < 0$	$dF > 0$	$dF = 0$
Gibbs potential, G	$G = E + PV - TS;$ $G = H - TS;$ $dG = -SdT + VdP$	$dT = 0; dP = 0$	$dG < 0$	$dG > 0$	$dG = 0$

Notes: Q , heat; P , pressure; V , volume; T , temperature.

number of minerals that could coexist in equilibrium is determined by the phase rule. Both will be discussed in the following sections.

Energy minimum in a system

A mineral is stable when it coexists in equilibrium with other minerals and chemical compounds. The symbol \rightleftharpoons indicates the state of equilibrium. For example,



In the first example, diamond coexists in equilibrium with graphite. In the second, it coexists with a mixture of methane, oxygen, and water. These two very different thermodynamic systems reach equilibrium at some energy minimum that is different in the two cases. The mineral's stability is not determined by the minimum of the mineral's own energy, but by that of the system as a whole.

Under different conditions the same thermodynamic system will spontaneously reach its stable (equilibrium) state at a different energy minimum. The values of these minima may be defined by using thermodynamic potentials or internal energies (Table 17.1). These chemical

potentials – such as entropy, enthalpy, and Helmholtz or Gibbs potentials – are material constants, similar to the physical properties discussed in Chapter 8. They depend on chemical composition, bonding, and crystal structure, as well as on temperature and pressure. Values for these potentials are listed for standard conditions in handbooks (e.g., Wagman *et al.*, 1982; Robie and Hemingway, 1995). Standard conditions usually refer to a temperature of 25 °C (298.15 K) and a pressure of 1 bar (0.1 MPa). In the following discussion we will sometimes use absolute values. Often relative values are important, for example energy differences between reactants and reaction products. If potentials change, for example with temperature and pressure, differential expressions are useful. In Box 17.1 notations, constants, and conversion factors used in thermodynamic calculations are summarized.

The simplest thermodynamic calculations and diagrams

Dolomite–quartz–diopside reaction, enthalpy, and entropy

The variation of enthalpy H in a system corresponds to the heat exchange of an isobaric process or reaction. Enthalpy can be considered as thermal or kinetic energy due to atomic

Box 17.1 | Notation, constants, and conversion factors used in thermodynamic calculations

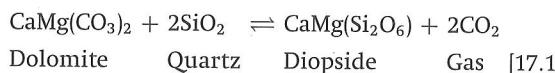
Symbol	Explanation
T	Absolute temperature in Kelvin, 25 °C = 298.15 K
K	Kelvin, the unit of absolute temperature
mol	mole, the amount of a substance corresponding to a gram formula weight
P	pressure in Pascals. The standard atmosphere is equal to 1.013 25 × 10 ⁵ Pa; 1 kg/cm ² is equal to 0.980 655 × 10 ⁵ Pa.
p_{CO_2}	partial pressure of CO ₂
$p_{\text{H}_2\text{O}}$	partial pressure of H ₂ O
V	volume (in cm ³)
V_{298}^0	molar volume of 1 mole of a substance at 1 bar pressure and 298.15 K (cm ³ /mol = J/(MPa mol))
0	superscript here and in the following expressions indicates standard state
ΔV_{298}^0	change of total molar volume of a substance as a result of a process (in cm ³)
$C_{P,298}^0$	heat capacity at constant pressure P 1 bar and temperature 25 °C (in J/(mol degree), or in cal/(mol degree))
$\Delta C_{P,298}^0$	change of a total heat capacity of a substance as result of a process (in J/degree, or in cal/degree)
S_f^0	entropy of formation of a substance from the elements in their reference state (in J/(mol degree), or in cal/(mol degree))
ΔS^0	change of entropy as a result of a process (in J/degree, or in cal/degree)
S_T^0	entropy at temperature T (in J/mol, or in cal/mol)
$\Delta_f H^0$	enthalpy of formation of a substance from the elements in their reference states (in J/mol, or in kcal/mol)
ΔH^0	change of enthalpy as a result of a process (in J, or in kcal)
ΔH_T^0	change of enthalpy as a result of a process, at temperature T (in J, or in kcal)
$\Delta_f G^0$	Gibbs free energy of formation of a substance from the elements in their reference states (in J/(mol degree), or in kcal/(mol degree))
ΔG^0	change of Gibbs free energy as a result of a process (in J, or in kcal)
ΔG_T^0	change of Gibbs free energy as a result of a process, at temperature T (in J, or in kcal)
$\Delta G_{T,P}^0$	change of Gibbs free energy as a result of a process, at temperature T and pressure P (in J, or in kcal)
k	equilibrium constant
k_{red}	equilibrium constant, reduced to standard conditions

n	number of moles
a	activity
f	fugacity
E^0	electromotoric force (emf) for an electro-chemical cell at standard conditions (in V)
E_h	emf between electrode in any state and H ₂ electrode in standard state (in V)
pH	logarithm of the activity of hydrogen ions in a solution
R	gas constant, 8.3145 J/(degree mol), or 0.848 kg/(degree mol) (or 1.9872 cal/(degree mol))
F	Faraday constant, 96.485 J/(V mol) (or 23.062 kcal/(V mol))
$\ln x$	2.302585 log x
$R \ln x$	4.57567 log x (in cal/(degree mol))
1 bar	10 ⁵ Pa = 0.1 MPa (1 kbar = 100 MPa)
1 J	2.390 10 ⁻⁴ kcal (1 MPa cm ³ /mol)
1 cal	4.18 MPa cm ³ /mol = 4.184 J

vibrations. If the temperature is 25 °C and the pressure 0.1 MPa, then

$$\Delta H^0 = \sum n_i \Delta H_j^0 \text{ (products)} - \sum n_i \Delta H_j^0 \text{ (reactants)} \quad (17.2)$$

where ΔH_j^0 are the standard enthalpy values for individual substances, and n_i are the molar fractions of the components in a balanced chemical reaction. Enthalpy is measured in J/mol (or in kcal/mol) units, and, because calculations are in multiples of moles, the results are in J (or in kcal) units. Let us calculate ΔH^0 for a process at 25 °C and 0.1 MPa for the reaction between dolomite and quartz, which is a typical reaction for metamorphism of limestones at high temperature and pressure:



The thermodynamic data for these substances are as follows:

	Enthalpy, $\Delta_f H^0$ (kJ/mol)
Diopside	-3210.68
CO ₂	-393.51
Dolomite	-2325.97
Quartz	-910.69

$$\begin{aligned} \Delta H^0 &= [(-3210.68 \text{ kJ/mol}) \times 1 \text{ mol} \\ &\quad + (-393.51 \text{ kJ/mol}) \times 2 \text{ mol}] \\ &\quad - [(-2325.97 \text{ kJ/mol}) \times 1 \text{ mol} \\ &\quad + (-910.69 \text{ kJ/mol}) \times 2 \text{ mol}] \\ &= (-3997.70 \text{ kJ}) - (-4147 \text{ kJ}) = +149.65 \text{ kJ} \end{aligned} \quad (17.3)$$

This reaction [17.1] (left to right) is *endothermic*, which means that heat is absorbed.

When heat is added to a substance (dQ), the temperature increases (dT). The scalar property that specifies the heat maintained is called the *heat capacity C* and described with the expression

$$dQ = C dT \quad (17.4)$$

Heat capacities are measured in J/(mol degree), and for the substances discussed above they have the following values:

	Heat capacity, $C_{P,298}$ (J/(mol degree))
Diopside	166.36
CO ₂	37.11
Dolomite	157.78
Quartz	46.64

It is easy to calculate that for the reaction described above the change in heat capacity of the system $\Delta C_{P,298}^0$ is -6.49 kJ/degree (i.e., $1 \times 157.78 + 2 \times 46.64 - 1 \times 166.36 - 2 \times 37.11$).

Heat capacities vary slightly with temperature. It makes a difference if heat is added at constant pressure or constant volume, and usually the heat capacity at constant pressure C_P is specified. If we add heat Q to a closed system during a reversible change in its state at constant pressure, we increase the enthalpy correspondingly. Therefore we can write

$$dH = C_P dT \quad (17.5)$$

The most common form of *mechanical work W* of a thermodynamic system is to expand against the constant pressure P of the surroundings. Mathematically, this is written as $\Delta W = P\Delta V$, where ΔV is the volume change. The first law of thermodynamics can then be expressed as

$$dE = dQ - P dV \quad (17.6)$$

i.e., the change of internal energy E is the difference between thermal energy Q and the expansion against pressure.

The *entropy S* is involved in all thermodynamic potentials. It is measured in J/(degree mol) (or in cal/(degree mol)). Entropy is not easily defined, but it can be viewed as a measure of internal disorder. It increases, for example, if a substance transforms from a highly ordered crystalline state to a liquid or a gaseous state. But it can also vary within the solid state. For example, going from fully ordered microcline to sanidine with a disordered Si-Al distribution, and finally to a feldspar glass with no long-range order in a regular lattice, S changes from 995.83 to 1100.94 to 1206.75 J/(degree mol). Among the Al₂SiO₅ polymorphs, kyanite has the lowest entropy (92.17 J/(degree mol)). It is higher for andalusite (93.22 J/(degree mol)), and sillimanite (96.19 J/(degree mol)), but the differences are much smaller than for K-feldspar, since all three of these polymorphs are ordered crystal structures.

The change of entropy in a system (ΔS^0) is used in many thermodynamic calculations. The system entropy is equal to the weighted sum of

entropies of formation (S_f^0) for the reaction products minus that for the reactants

$$\Delta S^0 = \sum n_i S_f^0 \text{ (products)} - \sum n_i S_f^0 \text{ (reactants)} \quad (17.7)$$

where n_i are the molar fractions of the components.

The second law of thermodynamics stipulates that in any reversible process the change in entropy of the system (dS) is equal to the heat received by the system (dQ) divided by the absolute temperature T :

$$dS = dQ/T \quad (17.8a)$$

In an irreversible process, the change in entropy of the system is larger than the heat received by the system divided by the absolute temperature T :

$$dS > dQ/T \quad (17.8b)$$

If we substitute the expression for dQ from equation 17.4 into equation 17.8a we obtain

$$dS = C(dT/T) \quad (17.9)$$

At an arbitrary temperature and pressure, enthalpy $\Delta H_{T,P}$ values may be calculated from the following equation:

$$\begin{aligned} dH &= T dS \text{ (change in heat)} \\ &\quad + V dP \text{ (mechanical work)} \end{aligned} \quad (17.10)$$

For a constant pressure (e.g., $P = 0.1$ MPa) and temperature T a simplified equation may be used (equation 17.5):

$$\Delta H_T = \Delta H^0 + \Delta C_{P,298}^0(T - 298) \quad (17.11)$$

where ΔH^0 and $\Delta C_{P,298}^0$ are, respectively, enthalpy and heat capacity at 298 K.

Let us now return to the dolomite-quartz reaction forming diopside and CO₂ but at a temperature of 500 °C (773 K). Using equation 17.11 and values of +149.65 for ΔH^0 and -6.49 for $\Delta C_{P,298}^0$ from above, we obtain

$$\begin{aligned} \Delta H_{773} &= +149.65 \text{ kJ} + [(-6.49 \text{ J/degree}) \\ &\quad \times (773 - 298) \text{ degree}] \\ &= +149.65 \text{ kJ} - 3.08 \text{ kJ} = +146.57 \text{ kJ} \end{aligned} \quad (17.12)$$

Again, the value is positive and the reaction is endothermic.

Table 17.1 gives equilibrium restrictions for enthalpy: $dS = 0$ and $dP = 0$. In the example above, P is constant and therefore $dP = 0$, whereas the entropy of the system greatly increases because a gas phase forms. Thus $dS \neq 0$, and the equilibrium restriction for using S is not satisfied. At this point in our discussion, we can draw no conclusions as to whether this reaction is possible or not, at either 25 or 500 °C. We will explore this question in the next section.

Calcite–aragonite transformation: Gibbs free energy

In order to account for changes in both entropy and enthalpy, J. Willard Gibbs defined a new function, which we now call the Gibbs free energy (Gibbs potential) G . This function is independent of variations in pressure and temperature and can be stated as

$$G = H - TS \quad (17.13)$$

where H is enthalpy and S is entropy.

The Gibbs free energy depends only on the state of a system, not on how this state has been attained. The change in free energy associated with the formation of a compound from its constituent elements under standard conditions (25 °C and 0.1 MPa) is termed the standard Gibbs free energy of formation (ΔG_f^0) and measured in J/mol (or in kcal/mol). Gibbs potentials for elements are by definition zero. The change of Gibbs free energy of a chemical reaction in the standard state (25 °C and 0.1 MPa) is

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (17.14)$$

From Table 17.1, a spontaneously occurring reaction requires that $dG < 0$; hence changes in entropy and enthalpy work together to define whether or not the process may occur spontaneously. Reactions that result in more order ($dS < 0$) will occur spontaneously if the heat expelled during the process is greater than the increase in G due to the decrease in entropy. And, vice versa, reactions absorbing heat ($dH > 0$) will occur if the decrease in the Gibbs potential due

to the increase in entropy outweighs the increase in G due to the heat absorption.

Indeed, in comparison with H (Table 17.1), the conditions necessary for the application of the Gibbs potential (namely pressure and temperature invariability) are most easily understood and most readily measured. Therefore evaluations of the Gibbs potential are frequently used to analyze the formation processes of various substances, both by chemists and mineralogists. A change of G in a system during some process (ΔG^0 of the process) at 25 °C (≈ 298 K) and 0.1 MPa pressure (standard conditions) is equal to

$$\Delta G^0 = \sum n_i \Delta G_f^0 \text{ (products)} - \sum n_i \Delta G_f^0 \text{ (reactants)} \quad (17.15)$$

The ΔG_f^0 values (free energy to form compounds from elements in the reference state) for different substances are listed in many reference books on thermodynamics. Here we apply the concept of Gibbs free energy to the polymorphic reaction



Values for S_f^0 , ΔG_f^0 , and molar volume V for aragonite and calcite are as follows:

	S_f^0 (J/(degree mol))	ΔG_f^0 (kJ/mol)	V_{298}^0 (cm ³ /mol)
Aragonite	88.62	-1128.33	34.15
Calcite	92.68	-1129.30	36.93

Using equation 17.15, ΔG^0 for the phase transition of one mole of calcite to aragonite at standard conditions (25 °C and 0.1 Pa) is:

$$\Delta G^0 = (-1128 \text{ kJ/mol}) \times 1 \text{ mol} \\ \text{Aragonite (final composition)} \\ -(-1129.30 \text{ kJ/mol}) \times 1 \text{ mol} = +0.970 \text{ kJ} \\ \text{Calcite (initial composition)} \quad (17.16)$$

Since the ΔG^0 value is larger than zero, the reaction must proceed in the direction opposite to that indicated by the arrow in [17.2]. In other

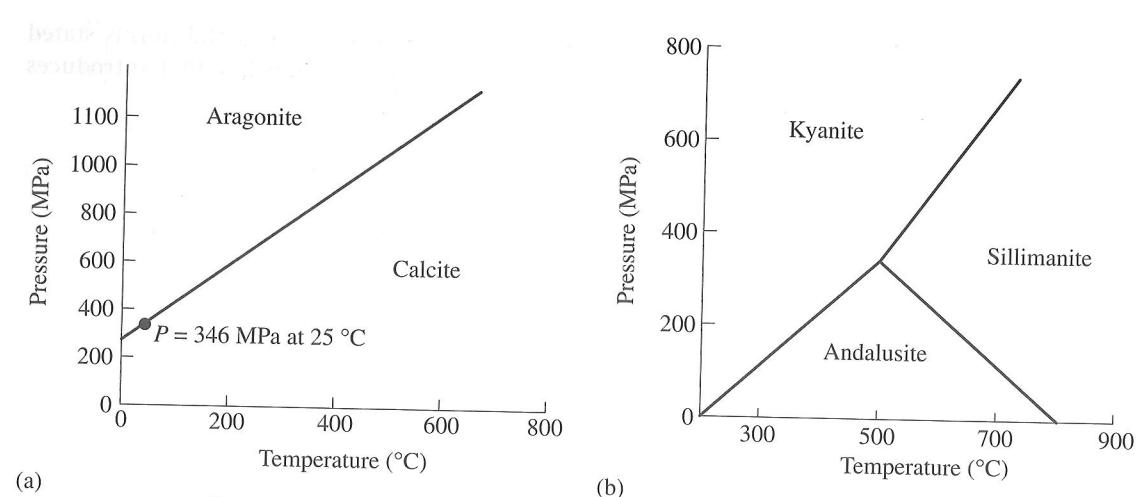


Fig. 17.2 P-T phase diagrams. (a) System CaCO_3 , illustrating stability fields of aragonite and calcite. (b) System Al_2SiO_5 , showing stability fields of polymorphs kyanite, andalusite, and sillimanite.

words, calcite is stable at standard conditions, whereas aragonite is not. At equilibrium ΔG^0 , the free energy of the reaction, is zero. This can be used to determine the pressure at which calcite and aragonite are in equilibrium at 25 °C.

To answer this question, we first consider the difference in molar volume V^0 at 298 K between aragonite and calcite, which is

$$\Delta V_{298}^0 = 1 \text{ mol} \times 34.15 \text{ cm}^3/\text{mol}$$

$$\begin{aligned} &\text{Aragonite (final composition)} \\ &-1 \text{ mol} \times 36.93 \text{ cm}^3/\text{mol} = -2.78 \text{ cm}^3 \\ &\text{Calcite (initial composition)} \end{aligned} \quad (17.17)$$

Since aragonite has the smaller molar volume, it is favored at high pressure. Using this value, we can then calculate the pressure P at which aragonite and calcite are in equilibrium at 25 °C, i.e., the pressure at which the free energy of the reaction $\Delta G_{p,T}^0 = 0$. To obtain the Gibbs free energy ΔG_p^0 at pressure P we have to add, to the Gibbs free energy at standard conditions ΔG_T^0 obtained in equation 17.17, the mechanical work due to volume change:

$$\Delta G_{p,T}^0 = \Delta G_T^0 + P \Delta V_{298}^0 \quad (17.18)$$

Because at equilibrium $\Delta G_{p,T}^0 = 0$, we can write: $0 = +0.970 \text{ kJ} + P(-2.78 \text{ cm}^3)$. Correspondingly, we obtain $P = (0.970 \text{ kJ}/2.78 \text{ cm}^3) = 349 \text{ J/cm}^3 = 349 \text{ MPa}$ equilibrium pressure for the transformation from calcite to aragonite at 25 °C, where 1.00 MPa cm^3 is a conversion factor from joules to MPa cm^3 units (see Box 17.1). This gives us one point on the line that separates the stability fields of calcite and aragonite in the temperature-pressure phase diagram (Figure 17.2a).

For differential temperature and pressure changes during a reaction we can use the following expression of the first law (see Table 17.1):

$$\Delta G_{T,P}^0 = \Delta V dP - \Delta S^0 dT \quad (17.19)$$

At equilibrium, $\Delta G_{T,P}^0 = 0$ and, correspondingly (using equation 17.4),

$$dP/dT = \Delta S^0/\Delta V = \Delta H_T^0/(T \Delta V) \quad (17.20)$$

This relationship, known as the Clausius-Clapeyron equation, defines the slope of the equilibrium line on the pressure-temperature phase diagram at the position of the point calculated above. Because only one variable (P or T) can be assigned arbitrarily along this line, it is said to be univariant.

From the thermodynamic data for calcite and aragonite we can calculate that $\Delta S^0 = 4.06 \text{ J/degree}$, and we have obtained that $\Delta V_{298}^0 = 2.78 \text{ cm}^3$ (equation 17.17). Now, assuming that ΔS and ΔV are unaffected by temperature and

pressure, we can write

$$\begin{aligned} dP/dT &= (4.06 \text{ J/degree})/2.78 \text{ cm}^3 \\ &= 1.46 \text{ MPa/degree} \end{aligned} \quad (17.21)$$

again using the joules to MPa cm³ conversion (Table 17.1). From this we can finish constructing the *P-T* phase diagram shown in Figure 17.2a. Note that in this diagram the line along which the two minerals coexist is more or less straight because in solids the volume difference between two polymorphs is roughly constant and does not change much with pressure and temperature. Figure 17.2b gives a phase diagram for the aluminosilicate polymorphs andalusite, kyanite, and sillimanite (Al_2SiO_5), which are important components of metamorphic rocks and whose presence can be used to estimate *P-T* formation conditions. Also in this diagram phase boundaries are straight because we are dealing with solids, but the Clausius–Clapeyron slopes between the phases are very different. The boundary kyanite/sillimanite has a positive slope whereas the boundary andalusite/sillimanite has a negative slope. The Clausius–Clapeyron slope is significant because it determines the change of stability of a mineral with pressure.

Stability of malachite and azurite: mass action law and partial gas pressure phase diagrams

The thermodynamic potentials and phase diagrams, such as those shown in Figure 17.2, refer only to the ultimate results of a process; they do not provide any information on how easy (or difficult) it is for a system to reach equilibrium. In other words, a system may be far from equilibrium, but it is prevented from attaining equilibrium by the sluggishness of the process. There are countless examples of such sluggish processes in the geological environment, including devitrification of volcanic glasses and the metastable existence of high-pressure and high-temperature minerals (e.g., diamond and coesite).

To a first approximation, the rate of a reaction such as $aA + bB \rightleftharpoons cC + dD$ depends on the concentrations a, b, c, d of the components A, B, C, D that are involved. At equilibrium, the rates of the forward (left side) and backward (right side) reac-

tions are the same, and this condition is stated in the general mass action law that introduces the equilibrium constant k :

$$\frac{a_C^c a_D^d}{a_A^a a_B^b} = k \quad (17.22)$$

where a_x are activities of the components. Activities are used if the components are dissolved in a solution, or if a mixture of gases is present. The pressure of air, for example, is the sum of the partial pressures of its individual components such as nitrogen, oxygen, and water vapor. The sum of all partial pressures is the total pressure, and the sum of activities adds to 1.0. The activities for solids and liquids involved in the reaction are 1.0.

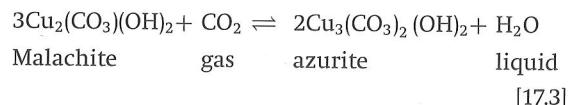
For ideal gases ($VP = RT$ for one mole of gas, where R is the gas constant; see Box 17.1), there is a simple correspondence between the Gibbs free energy G and the chemical reaction equilibrium constant k :

$$\begin{aligned} \Delta G_{T,P}^0 - \Delta G^0 &= RT \ln k \\ &= 2.303 RT \log k \end{aligned} \quad (17.23a)$$

where $\Delta G_{T,P}^0$ is the free energy change of the reaction at any state and ΔG^0 is the free energy change in the standard state (logarithms to base 10 are generally preferred for such calculations). At standard conditions ($T = 298 \text{ K}$ and $\Delta G_{T,P}^0 = 0$), then, we have (for ΔG^0 in kJ)

$$\log k^0 = -0.1750 \Delta G^0 \quad (17.23b)$$

In the oxidation zone of copper ores, some malachite and azurite may form. Can we predict which of them is more stable? Garrels and Christ (1990) considered the transformation of one to the other with the reaction



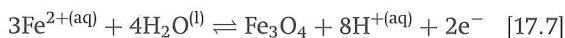
This reaction is shown in the phase diagram of partial pressures p_{O_2} – p_{CO_2} (Figure 17.3a).

The equilibrium constant of this reaction [17.3], for a partial CO_2 pressure p_{CO_2} , is

$$k = \frac{a_{\text{azurite}}^2 a_{\text{water}}^1}{a_{\text{malachite}}^3 p_{\text{CO}_2}} \quad (17.24)$$

This line is also shown in Figure 17.5. As we would expect, magnetite is more stable at lower pH and Eh than hematite.

Magnetite and hematite are slightly soluble in water. For magnetite we can write the reaction



In this case,

$$\begin{aligned}\Delta G &= (1 \text{ mol} \times 1014.2 \text{ kJ/mol}) \\ &\quad - (3 \text{ mol} \times 84.94 \text{ kJ/mol}) \\ &\quad + 4 \text{ mol} \times 237.23 \text{ kJ/mol) } \\ &= 189.54 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\text{Eh} &= [189.54/(2 \times 96.485)] \\ &\quad + (0.059/2) \left(\log a_{\text{H}^+}^8 / a_{\text{Fe}^{2+}}^3 \right) \\ &= 0.98 - 0.236\text{pH} - 0.089 \log a_{\text{Fe}^{2+}} \quad (17.38)\end{aligned}$$

This is again a straight line but of a different (steeper) slope, and the position of the line (but not its slope) depends on the activity of Fe^{2+} . In Figure 17.5 the line for reaction [17.7] is drawn for an activity of 10^{-6} mol ions/liter, and a similar line is added for the equilibrium of hematite with Fe^{2+} .

Such Eh-pH diagrams are widely used in investigations of mineral equilibria, where aqueous solutions are present and oxidation-reduction reactions occur. Note that the condition $\text{Eh} = E^0$ is not a statement of equilibrium, but rather implies that the activities of all products and all reactants in a solution are unitary. The true equilibrium is achieved only when $\text{Eh} = 0$, $\Delta G_r = 0$, and pressure and temperature remain constant. Eh-pH diagrams help us to understand the equilibrium of minerals and ions in seawater, in weathering oxidation processes, and in hydrothermal transformations.

Phase rule

The phase rule relates the number of minerals (phases) to the number of components in a system, and the number of possible reactions. It can be proven that in any thermodynamic system the number of phases p , the number of components c , and the number of degrees of freedom f are

related in the following manner:

$$p = c + m - f \quad (17.39)$$

where the number m denotes the external parameters that have an effect on the state of the system. The number of degrees of freedom f corresponds to a number of thermodynamic parameters that are allowed to change without affecting the state of the system and its phase composition. In mineralogical systems such parameters are usually represented by external pressure, temperature, and chemical potentials.

The more complex the chemical composition of a geological system, and the more external factors affecting it, the greater the number of minerals expected to occur in this system. For those geological systems, where the formation of minerals is only temperature and pressure dependent ($m = 2$):

$$p = c + 2 - f \quad (17.40)$$

The cooling of a magmatic melt is an example. Such a system ideally has an invariable bulk chemical composition. The external factors are largely temperature and pressure changes that cause crystallization processes in the melt. It is obvious that both pressure and temperature may be arbitrary in value, i.e., $f = 2$. Therefore:

$$p = c \quad (17.41)$$

This equality, introduced by V. Goldschmidt as the mineralogical phase rule, states that in geological systems, where temperature and pressure are the only external factors that may vary arbitrarily, the maximum number of minerals that may coexist in equilibrium is equal to the number of chemical components.

In a $P-T$ phase diagram (e.g., Figure 17.2a,b) the stability fields of minerals have two degrees of freedom, since both pressure and temperature change independently. The lines separating stability fields correspond to one degree of freedom because only one parameter (either temperature or pressure) can vary independently. Junctions of lines (triple points) have no degrees of freedom. The equilibrium conditions described above are correspondingly called divariant, univariant, and invariant, respectively.

For example, in Figure 17.2b the triple point corresponds to the invariant conditions of kyanite, sillimanite, and andalusite coexistence. The lines indicate the univariant coexistence conditions of mineral pairs ($\text{kyanite} \rightleftharpoons \text{andalusite}$; $\text{kyanite} \rightleftharpoons \text{sillimanite}$; $\text{sillimanite} \rightleftharpoons \text{andalusite}$). The fields between the lines correspond to the bivariant stability conditions of one mineral. There are three phases (three minerals) and one component (Al_2SiO_5) in the andalusite–kyanite–sillimanite system. At the invariant point, f is zero. Thus, the highest possible number of coexisting phases p is 3 ($p = 1 + 2 - 0 = 3$). Similarly, anywhere on the line of univariant equilibrium $f = 1$. Thus p is equal to 2 ($p = 1 + 2 - 1 = 2$). Finally, within any field between the lines, $f = 2$. Therefore, p is equal to 1 ($p = 1 + 2 - 2 = 1$).

One of the major drawbacks of equation 17.40 is that many geological systems behave as open systems that are capable of exchanging volatile components with their surroundings, and hence c becomes a variable. Dmitriy Korzhinsky (1959) suggested that the phase rule had to be modified to account for the number of components that migrate in or out of the system, i.e., that behave as the mobile components M :

$$p = c + 2 - f - M \quad (17.42)$$

In this modified form, the mineralogical phase rule states that, in geological systems, the maximum number of minerals that may coexist in equilibrium is equal to the number of inert components.

Phase diagrams

Mineral (phase) equilibrium diagrams show the limits of stable existence of minerals at different conditions. They are plotted either on the basis of thermodynamic calculations and the phase rule, as illustrated in the previous sections, or as a graphic representation of experimental results.

Phase diagrams, as a rule, are plotted as a function of two variables such as:

- temperature T versus total pressure P (Figure 17.2);
- temperature T versus partial pressure p (Figure 17.3b) (or fugacity f , activity a , pH);

- partial pressure p_x versus partial pressure p_y (or activity versus activity, etc.);
- oxidation-reduction potential Eh versus pH (Figure 17.5);
- temperature T versus composition of system X .

More rarely three variables are used, for example activity versus pH versus composition or temperature versus pressure versus composition.

The principles of interpretation of such diagrams are quite simple. They allow us to determine, for example, which phase is in equilibrium at a certain temperature and pressure. Temperature-composition phase diagrams, however, which describe crystallization of a magma and subsolidus exsolution processes in minerals, deserve further elaboration.

Diagrams for crystallization from a melt

The binary system diopside ($\text{CaMgSi}_2\text{O}_6$)-anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) (Figure 17.6) is a classical example and has direct application to our understanding of crystallization processes in basaltic magmas. There are two components ($\text{CaMgSi}_2\text{O}_6$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$) and one free parameter (temperature, $m = 1$) in this system. The solid lines correspond to the univariant equilibrium between two phases ($p = c + 1 - f = 2 + 1 - 1 = 2$ for equation 17.39), which are a mineral (anorthite or diopside) and a melt.

At the E-point, where the two univariant lines meet, the number of degrees of freedom is zero, while the number of coexisting phases is three ($p = c + 1 - f = 2 + 1 - 0 = 3$): diopside, anorthite, and melt. E is called the eutectic point and corresponds to the lowest temperature at which the melt and solid phases can coexist. The two univariant lines marking the onset of crystallization constitute the *liquidus* curve, whereas the horizontal line that meets the liquidus at E is called the *solidus*. The solidus line marks the temperature limit below which only the solid phases are stably present.

For a composition X (in weight%) and a temperature above T_1 the melt is homogeneous and consists of 25% of the $\text{CaMgSi}_2\text{O}_6$ component and 75% of the $\text{CaAl}_2\text{Si}_2\text{O}_8$ component. When the

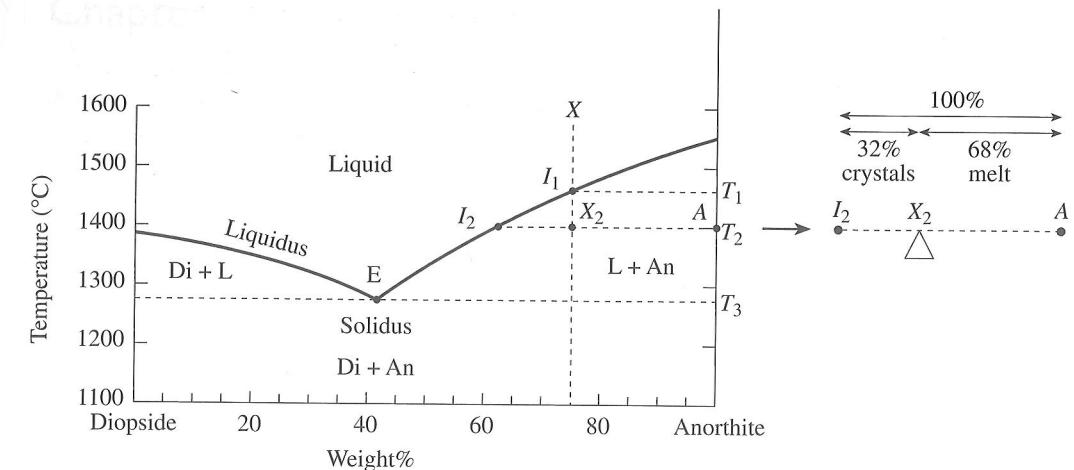


Fig. 17.6 Eutectic melting in the system diopside ($\text{CaMgSi}_2\text{O}_6$)-anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Di, diopside; An, anorthite; L, liquid. For other symbols, see the text.

temperature decreases and becomes less than T_1 (1490 °C at point I_1), anorthite begins to crystallize. With further cooling, the composition of the melt shifts to the left, since anorthite has been extracted as crystals. The relative amounts of crystals and remaining melt can be derived with the help of the lever rule shown with the diagram on the right-hand side (Figure 17.6). (It is called lever rule because it balances crystals and liquid according to their relative amounts.) For example, at temperature T_2 the distance $T_2 - A$ is divided into $T_2 - X_2$ (crystals) and $X_2 - A$ (melt). At temperature T_2 (1400 °C) the crystals of anorthite comprise 32% while the melt comprises 68%. The composition of the melt corresponds to that at point I_2 (40% $\text{CaMgSi}_2\text{O}_6$ and 60% $\text{CaAl}_2\text{Si}_2\text{O}_8$). As the temperature decreases, more anorthite crystallizes, the volume of the melt decreases, and its composition changes towards $\text{CaMgSi}_2\text{O}_6$. At temperature T_3 (1270 °C) the anorthite crystals comprise 52%, and the melt 48%, again applying the lever rule. The composition of the remaining melt is 42% $\text{CaAl}_2\text{Si}_2\text{O}_8$ and 58% $\text{CaMgSi}_2\text{O}_6$.

At the eutectic temperature T_3 diopside may coexist with anorthite and melt in equilibrium, but the slightest loss of heat causes the simultaneous crystallization of the two minerals. The temperature remains constant until both minerals are fully crystallized. Only at this point does the system continue to cool.

The resultant rock has a microstructure with euhedral anorthite crystals (which crystallized freely in the melt as *phenocrysts*) within a mass of intergrown anorthite and diopside that crystallized at the same time (the *groundmass*) (cf. Figure 12.1a). The ratio of total diopside and anorthite in the aggregate is the same as the initial ratio between the corresponding components in the melt X , i.e., 75% anorthite and 25% diopside. However, within the groundmass the proportion is different and corresponds to the composition of the melt at the eutectic E-point (58% diopside and 42% anorthite). Melting of this gabbroic rock will follow the same route in reverse.

Eutectic crystallization can result in a groundmass microstructure if many nucleation sites exist. If nucleation is limited, unusual intergrowths of the two minerals form that have a worm-like or cuneiform appearance.

Many mineral pairs are known to crystallize eutectically and some are listed in Table 17.4. We will discuss some more complex melting diagrams in Chapter 26.

Table 17.4 Eutectic points for some mineral pairs (percentages of the phases in the groundmass are given in parentheses, and the eutectic temperature is indicated)

Orthoclase (75.5)–quartz (24.5)	990 °C
Albite (96.5)–diopside (3.5)	1085 °C
Anorthite (42)–diopside (58)	1270 °C
Diopside (88)–forsterite (12)	1387 °C
Spinel (29)–forsterite (71)	1725 °C

Test your knowledge

1. Review with a mineral example the two basic laws of thermodynamics.
2. What are thermodynamic phases and components in geological systems?
3. Which potential is the most useful in geological contexts? Illustrate it with a mineral system.
4. What is the difference between E^0 and Eh?
5. Describe the phase rule with an example.

Important concepts

Entropy
Enthalpy
Gibbs free energy
 $P-T$ mineral phase diagram
Redox reactions and Eh-pH diagrams
Phase rule
Eutectic system

Further reading

- Bulakh, A. G., Krivovitchev V. G. and Zolotariov A. A. (1995). *Mineral Formulas. Thermodynamics of Mineral Equilibria. Manuals and Handbook.* (In Russian.) St Petersburg Univ. Press, St Petersburg, 169pp.
- Faure, G. (1998). *Principles and Applications of Geochemistry*, 2nd edn. Prentice Hall, Englewood Cliffs, NJ, 600pp.
- Gill, R. (1996). *Chemical Fundamentals of Geology*, 2nd edn. Chapman & Hall, London, 291pp.
- Gottshalk M. (1997). Internally consistent thermodynamic data for rock forming minerals. *Eur. J. Mineral.*, 9, 175–223.
- Nordstrom, N. D. and Munoz, J. L. (1994). *Geochemical Thermodynamics*, 2nd edn. Blackwell Scientific Publications, Boston, Oxford and London, 493pp.
- Wood, B. J. and Fraser, D. G. (1976). *Elementary Thermodynamics for Geologists*. Oxford Univ. Press, Oxford, 303pp.