



GEOLOGICAL SURVEY OF CANADA
COMMISSION GÉOLOGIQUE DU CANADA

PAPER 75-43

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**APPLICATIONS OF THERMODYNAMICS
IN METAMORPHIC PETROLOGY**

EDGAR FROESE





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1976

Minister of Supply and Services Canada 1976

Printing and Publishing
Supply and Services Canada,
Ottawa, Canada K1A 0S9,

from the Geological Survey of Canada
601 Booth St., Ottawa, K1A 0E8

or through your bookseller.

Catalogue No. M44-75-43
ISBN - 0-660-00846-7

Price: Canada: \$3.00
Other Countries: \$3.60

Price subject to change without notice

Reprinted 1977

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Abstract

This paper summarizes the principles of chemical thermodynamics in a form which is convenient for dealing with problems encountered in metamorphic petrology. Particular effort has been made to illustrate thermodynamic concepts by means of graphical representation. The concept of the equilibrium constant and the choice of standard states are discussed in detail. A brief introduction to nonideal solutions deals with relatively simple binary solution models based on the method of Margules. Various applications of thermodynamics and guides for specific calculations are presented, with some emphasis on oxidation and sulphidation reactions.

Résumé

Cette étude rappelle les principes de la thermodynamique chimique sous une forme applicable aux problèmes de pétrologie des roches métamorphiques. L'auteur insiste particulièrement sur l'importance de la représentation graphique pour illustrer les concepts de la thermodynamique. La notion de constante d'équilibre et le choix d'états standards y sont étudiés en détail. Une courte introduction au problème des solutions non idéales traite de modèles relativement simples de solutions binaires, basés sur la méthode de Margules. Diverses applications de la thermodynamique et des marches à suivre pour des calculs spécifiques, particulièrement en ce qui concerne les réactions d'oxydation et de sulfuration, y sont présentées.

Introduction

This paper is based on a series of lectures given at the University of Göttingen in October 1973. Professor H. Winkler kindly invited me to spend three weeks at the Mineralogical-Petrological Institute. I am particularly grateful to the Sonderforschungsbereich Göttingen of the Deutsche Forschungsgemeinschaft for financial support, which made this visit possible.

As indicated by the title, applied aspects of thermodynamics are stressed. Recent years have seen a beneficial integration of field work and experimental investigations in metamorphic petrology. These two approaches have, of course, a common goal and, in the study of certain aspects of metamorphism, they share a common theoretical framework, i. e. the principles of chemical equilibrium. The theoretical framework constitutes a unifying element for the results obtained in field work and experiments and provides a firm footing for a part of metamorphic petrology. Although thermodynamics can be applied only to some aspects of metamorphism, it is gratifying that these can be studied with some degree of rigour.

The treatment of various topics is uneven. The theoretical analysis is biased towards an understanding of the thermodynamics of a chemical reaction with particular emphasis on the equilibrium constant. No attempt is made to deduce complete phase relations in a chemical system; there is no discussion of Schreinemaker's rules. The selection of examples reflects my own interest and background.

Contact with various persons has significantly shaped my interest and thinking. D. R. E. Whitmore introduced me to the study of metamorphosed sulphide deposits. During a previous stay at Prof. H. Winkler's

Institute, I was introduced to experimental petrology and had many discussions concerning phase equilibria with P. Metz and G. Hoschek. My early attempts in thermodynamic analysis were guided by T. N. Irvine. In more recent years, I have particularly benefitted from an association with T. M. Gordon and G. B. Skippen.

I am much obliged to Prof. H. Winkler for arrangements to have most of the figures drafted at his Institute. His constant encouragement provided the decisive impetus in writing this paper. N. D. Chatterjee critically read an earlier manuscript.

NOTATION

a	activity of a component in a solution
C	heat capacity
f	fugacity of a gas
G	Gibbs free energy
H	enthalpy
K	equilibrium constant
P	pressure
q	heat absorbed by a system
R	gas constant
S	entropy
T	temperature
U	internal energy
V	volume
w	work done by a system

X	mole fraction
γ	activity coefficient
ϕ	fugacity coefficient
If M	designates a molar property of a substance
M°	molar property in its standard state at a specified temperature (solids and liquids – pure substance at 1 atm; gases – hypothetical perfect gas at 1 atm)
M^*	molar property of the pure substance at a specified pressure and temperature
\bar{M}	partial molar property
\bar{M}^{id}	partial molar property in a solution following Raoult's Law ($\bar{M}^{\text{id}} = M^* + RT \ln X$)
\bar{M}^{ex}	excess partial molar property ($\bar{M}^{\text{ex}} = \bar{M} - \bar{M}^{\text{id}}$)
$\bar{M}_\infty^{\text{ex}}$	excess partial molar property at infinite dilution

THE THERMODYNAMIC APPROACH

In the study of metamorphic rocks, many aspects confront the observer at the same time. These are no doubt interrelated in the evolution of the rocks but this relationship is complex and difficult to grasp. For this reason, there is a tendency to group aspects according to methods employed in their study. This is not a natural subdivision with regard to the origin of the rocks and may, at times, be a hindrance in an integrated view of the metamorphic process and its geological setting. However, this approach is dictated to some extent by the theoretical tools available in the study of metamorphic rocks. Before proceeding with the analysis of selected aspects, it is advisable to realize that such studies are by themselves "out of context" geologically and provide at best fragmentary answers. Nevertheless, there is some justification for this approach.

The complex nature of metamorphic rocks makes it very difficult to state precisely the question one is asking, yet a problem cannot be solved unless it is logically defined. Consequently, there is a tendency, if not necessity, to make an attempt of understanding the rocks in terms of a model based largely on plausibility. One might assign to an association of metamorphic rocks a geological history which "makes sense", based on imprecise reasoning involving elements of intuition, imagination, analogy, and "gap-filling" to provide continuity. This reasoning is not necessarily wrong but it cannot be proven right because it lacks sufficient factual and logical checks. Nevertheless, these models are essential in geology. They provide direction and inspiration in geological studies. Intuitive insight might eventually even be proven right in some instances; it certainly suggests lines of attack. Limiting attention strictly to the few facts which can be rigorously established would make any coherent view impossible and overshadow unifying elements

among the diversity of observations. This then is the fundamental compromise in any geological study. However, in order to make such models closer approximations to reality, it is advisable to include as many factual and logical restrictions as possible in any aspect of theoretical model building. There is no reason to stop model building but such enterprise should be made as difficult as possible. It is in this spirit that specialized investigations are undertaken: They provide restrictions, not complete understanding. No present theory suggests that metamorphic rocks are precipitates from a primordial ocean. This restriction has not laid bare all secrets of metamorphic rocks but has led to a more probable model.

Having made this declaration about the unity of nature, a fragmentation will be allowed in the interest of methodology, contrasting two groups of aspects in metamorphic rocks:

1. Features reflecting the past history of the rocks. These include deformation paths, sequences of mineral assemblages reflected by textural disequilibrium, and mechanisms of recrystallization. Problems of kinetics and reaction rates loom large in such a list.
2. Features characterizing the quenched state of the rocks.

For geological reasons, we are very interested in the first group. But the fact that a theoretical tool, thermodynamics, is available in the study of the second group leads to an emphasis of these aspects in many investigations.

The repetition of the same mineral assemblages in rocks of different ages and orogenic belts suggests equilibration of minerals over short distances. This encourages the application of thermodynamics to metamorphic rocks. The usefulness of thermodynamics lies in the fact that it provides a relationship among variables at equilibrium; one of its limitations is that it presupposes equilibrium. Thermodynamics cannot be used to prove or disprove equilibrium. If equilibrium is conceded, the rocks are subject to the laws of thermodynamics and geological models should not violate them any more than the law of gravity.

It is readily accepted that a portion of matter is characterized not only by its mass but also by its energy content. It turns out that the energy may be stored in forms of different stability. Spontaneous changes strive to reach an arrangement of maximum stability. Thermodynamics defines a function, entropy, which is maximized for a given amount of mass and energy content. From this function many relationships among variables may be deduced. Some of these variables can be measured and others may then be calculated.

For a chemical reaction a very convenient relationship among variables is given by the equilibrium constant, deduced from thermodynamics. It is an expression involving partial pressures and/or chemical compositions of reactants and products at equilibrium and is itself a function of pressure and temperature. It provides for each equilibrium a link between

measurable variables, i. e., compositions of minerals and non-measurable variables, i. e., pressure, temperature and partial pressure of volatiles.

For a solid-solid reaction, the equilibrium constant can be measured. This gives a relationship between P and T but not both variables. For a reaction involving gases, only a portion of the equilibrium constant can be measured, leaving more unknowns. The key to determining as many unknowns as possible is the simultaneous solution of equations based on several equilibrium constants.

One of the goals of metamorphic petrology is mapping the distribution of non-measured variables. Then it may become apparent whether, for example, P_{H_2O} is imposed by the environment, i. e. uniform over a large area, or controlled by the mineral assemblages, i. e. variable from rock to rock. Having established the variables of the environment, it is possible to characterize types of metamorphism according to the relationship among these variables, e. g. paths traced out in a P-T diagram. Also, it will be possible to test various models proposed for the environment, e. g. $P_{H_2O} = P_{total}$, $P_{H_2O} + P_{CO_2} = P_{total}$, or $P_{H_2O} \ll P_{total}$.

In order to do quantitative work, equilibrium constants must be calibrated either directly or from free energy changes (a thermodynamic function involving entropy) of reactions. Such data may be obtained from calorimetric, electrochemical, and spectroscopic measurements or from addition of various reactions. The free energy change, like the heat of reaction, is an additive property.

The application of thermodynamics, e. g. the interpretation of natural mineral assemblages in terms of equilibrium constants, is logically independent of the method of calibration. Even in the absence of quantitative data, the relationship among variables is qualitatively correct and in itself useful.

Some methods are more convenient and accurate than others, but in applying thermodynamics, it does not matter how thermochemical properties are obtained. Calibrations based on experimental reactions are valid even if such reactions do not occur in nature. A good experiment provides thermochemical data; it is not meant to model a natural process. In fact, frequently geologically insignificant reactions are experimentally investigated, for reasons of convenience or kinetics, and then combined to give equilibrium constants of more useful reactions. The thermodynamic approach cannot be criticized because some experimental calibrations are not "close to nature".

The validity of the thermodynamic approach may be questioned on the basis of its inherent limitations. Two problems are encountered:

1. Lack of equilibration over distances greater than a few centimeters and other disequilibrium features, i. e. zoning and reaction rims.
2. Difficulty of determining compatible mineral assemblages in some rocks.

Because all thermodynamic relationships and derivations presuppose the concept of equilibrium, thermodynamics does not provide criteria of equilibrium; it describes features of equilibrium, e. g. relationships among variables. In order to apply thermodynamics, this assumption must be conceded.

BASIC CONCEPTS OF THERMODYNAMICS

Introduction

Thermodynamics is concerned with the relationship among properties of macroscopic bodies. Although the fundamental relationships are set out in numerous texts, it is advantageous to list the concepts and present them in a form which is most convenient for the present purpose. In the development of ideas, as well as in notation, mainly the book by Denbigh (1966) will be followed.

Essential to thermodynamic analysis is the concept of a system. This is a portion of matter or a given volume which is separated from its surroundings by boundaries having definite properties. A closed system refers to a fixed amount of matter. An open system commonly refers to a solution. Transfer of matter changes the concentration and, thereby, the properties of the constituents.

A given amount of a homogeneous substance is characterized by a set of macroscopic properties; these define the thermodynamic state. Furthermore, if this state is altered by changing some of the variables, it is possible to return the substance to its original state without leaving any traces of such a process in the state variables, i. e. the state variables are not affected by the past history. If a particular thermodynamic state persists with time, the substance is in a state of equilibrium. It has been observed that at equilibrium, two variables are sufficient to specify the thermodynamic state of a given mass of a homogeneous substance; there are only two independent variables. Thus at fixed P and V, all other properties like refractive index, viscosity etc. are specified.

Accepting P and V as state variables familiar from mechanics, thermodynamics leads to the recognition of three new state variables: temperature T, internal energy U, and entropy S. The principles of chemical equilibrium are based on the interrelationship of these five variables. In this chapter, the symbols for the extensive properties, e. g. V, U, and S, refer to the whole system. In some cases, this will be emphasized by a subscript.

Temperature

Since two variables determine the state of a pure substance at equilibrium, temperature may be defined as a function of P and V

$$T = f(P, V)$$

For example if we want to use the functional relationship of PV of a substance and T, it is necessary to assign temperatures to two PV values. If the same procedure is adopted for another substance, a different

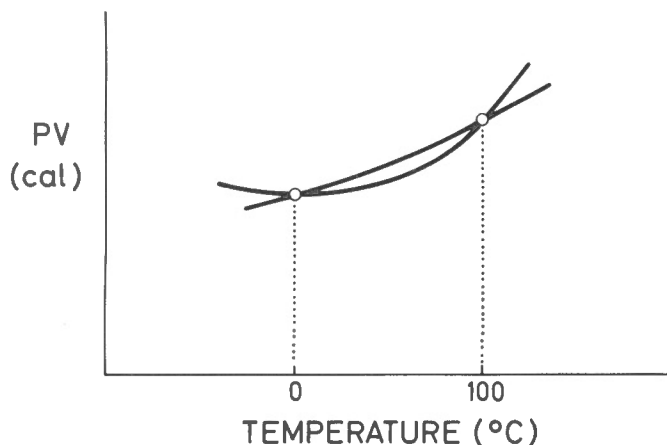


Figure 1. Thermometers based on real substances.

functional relationship exists and at temperatures other than the two fixed points, the two thermometers give a different reading (Fig. 1).

However, as $P \rightarrow 0$ different gases give very nearly the same temperature readings, i. e. a linear relationship between PV and T is approached. The PV product at zero pressure can be obtained by extrapolating measured PV products to zero pressure. It is then possible to plot $\lim (PV)_{P \rightarrow 0} = 0$ vs. T (Fig. 2). Assigning 0°K to the value of $\lim (PV)_{P \rightarrow 0} = 0$ and 273.16°K to the triple point of water, temperature is defined as

$$T = 273.16 \frac{\lim (PV)_{P \rightarrow 0}}{\lim (PV)_{P \rightarrow 0} \text{ at triple point}}$$

Since $\lim (PV)_{P \rightarrow 0}$ at the triple point for one mole of a gas is 542.815 cal

$$T = \frac{\lim (PV)_{P \rightarrow 0}}{R}$$

where $R = 542.815/273.16 = 1.98717 \text{ cal/deg}$

On this scale, the normal freezing point of water is 273.15°K and the normal boiling point is 373.15°K . A particularly good discussion of the definition of temperature is given by Rossini (1950).

The First Law

The first law of thermodynamics develops a relationship between the work performed and the heat received by a system. This treatment will be concerned only with work due to expansion or compression, given by

$$\delta w = PdV$$

Commonly such slow expansions will be considered that P of the system is equal to the external pressure on the system. Work is taken as positive if the system expands ($dV = \text{positive}$), i. e. the system performs work.

In order to develop the concept of heat, it is advantageous to define two types of walls or boundaries between a substance (the system) under consideration and the surroundings. A boundary which allows the

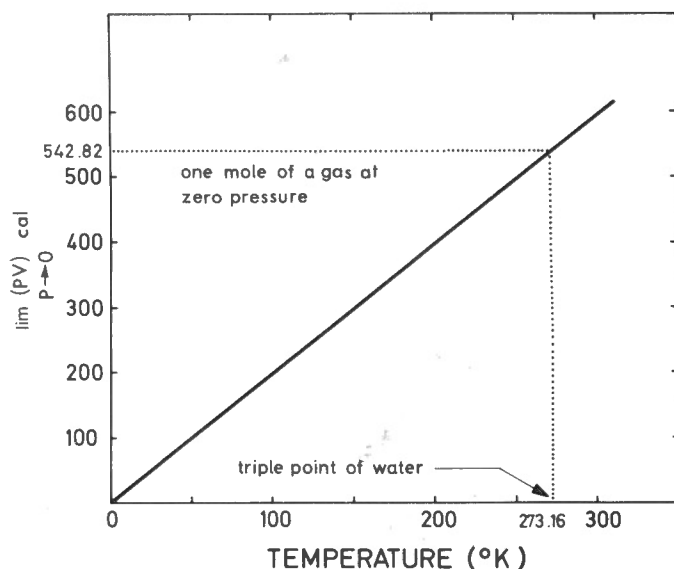


Figure 2. Zero pressure gas thermometer.

establishment of thermal equilibrium is called diathermal, whereas a boundary with very high insulating qualities is known as adiabatic. A perfect adiabatic boundary, conceivable as a limiting case of a real boundary, would allow the maintenance of a temperature difference between the system and the surroundings indefinitely.

The experiments of Joule showed that the expenditure of a certain amount of work on a given amount of substance in an adiabatic container resulted in a definite temperature increase. The temperature was raised by transferring energy to the body in the form of work. The same change can be accomplished by putting the substance into a diathermal container, keeping the volume constant, and bringing it into contact with a body of higher temperature. Energy again is transferred to the substance, this time in response to a temperature difference. Energy transferred in this manner is defined as heat. Heat is taken as positive if absorbed by the system.

The state of a homogeneous substance in a closed system is specified by any two variables. It can be adequately represented e. g. in a P-V diagram (Fig. 3). If the state is changed from A to B, the amount of work performed by the system, given by the area under the curve, depends on the path in the P-V diagram, i. e. on the nature of the process. Similarly, the heat absorbed by the system varies. However, it has been found that the difference ($q-w$) is the same for any path. It depends only on the initial and final state and, therefore, is a state variable. Thus, although neither work nor heat are state variables, their difference is and may be used to define a new state variable known as the internal energy U

$$U_B - U_A = \Delta U = q-w$$

or in differential form

$$dU = \delta q - \delta w$$

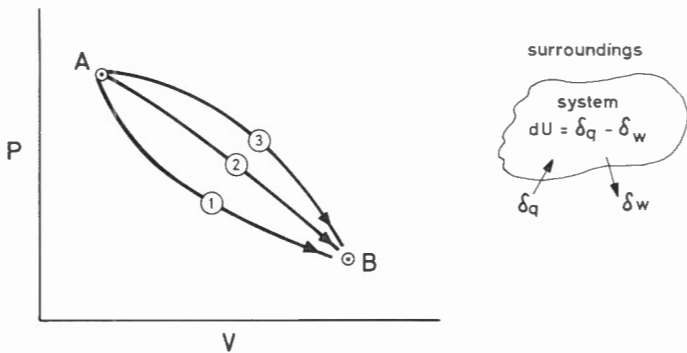


Figure 3. Illustration of the first law.

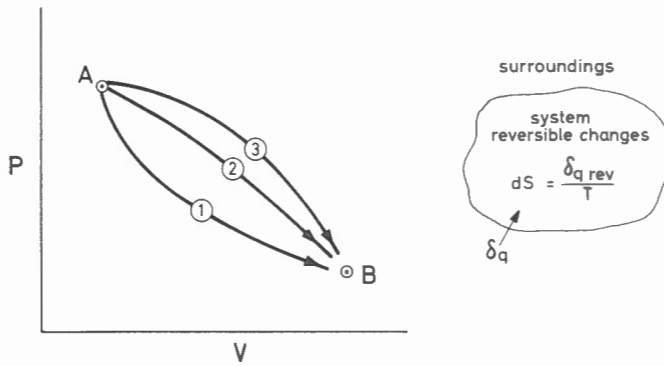


Figure 4. Illustration of the second law.

The differential dU is exact and its integral is independent of path; the differentials δq and δw are inexact and their integrals are path-dependent. Thus for a cyclic process

$$\oint dU = 0$$

This is not true of δq and δw .

For some particular paths, work and heat are state variables. Because $\delta q = 0$ for an adiabatic system

$$dU = -dw$$

If expansion is very slow, so that the external pressure differs infinitesimally only from the pressure of the system

$$dw = PdV$$

If a process takes place at constant volume, dV is zero and

$$dq_V = dU$$

and if it takes place at constant pressure

$$dq_P = dU + PdV$$

$$dq_P = d(U + PV)$$

The combination $(U + PV)$ is a new function of state called the enthalpy or heat content.

The heat capacity of a substance is defined as

$$C = \frac{\delta q}{dT}$$

It is convenient to recognize heat capacities for two specified paths of heat transfer, at constant volume and at constant pressure

$$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_P = \frac{dq_P}{dT} = \left(\frac{\partial H}{\partial T} \right)_P$$

The Second Law

Changes taking place within a system have direction and proceed towards equilibrium. The conditions at equilibrium are governed by the substances in the system and by the nature of its boundaries. As equilibrium is approached as a limit, the changes become reversible,

i. e. they occur at an infinitesimal rate at conditions only infinitesimally removed from equilibrium. Thus a reversible change represents a succession of equilibrium states. At each stage of the change, all state variables are defined.

If a system is brought from state A to state B, the heat absorbed is, in general, dependent on the path. However, it has been observed that if inside the system only reversible changes occur, the ratio q_{rev} / T is the same for any path (Fig. 4). It depends only on the initial and final state and defines a new state variable known as entropy S

$$S_B - S_A = \Delta S = \frac{q_{rev}}{T}$$

or in differential form

$$dS = \frac{\delta q_{rev}}{T}$$

Thus the differential dS is exact, its integral is independent of path and

$$\oint dS = 0$$

The nature of the First and Second Law has been expressed by Nash (1962) in a particularly lucid paragraph:

"For the purposes of classical thermodynamics we need say no more than that the internal energy U is a function of state defined by the equation $dU = q - w$, and this is a statement of the first principle. And for the purposes of classical thermodynamics we need say no more than that the entropy S is a function of state defined by the equation $dS = q_{rev}/T$, and this is a statement of the second principle. Some have argued that the urgency of our quest for a "something constant" in all change leads us to invent the concept of energy and to enforce it as a convention. But the fact that, however q and w may vary individually, the difference $(q - w)$ is a constant for any given change of state – that is a discovery, providing a firm empirical footing for the first principle. Conceivably one might equally argue that the urgency of our quest for a "something pointing" the direction of all spontaneous change drives us to invent the concept of entropy. But the fact that, however q_{rev} and T may vary individually, the

quotient q_{rev}/T is a constant for a given change of state – that is a discovery, providing a firm empirical footing for the second principle."

Changes in a Closed System

Changes inside a system must conform to the first and second law. By combining the two laws, useful relationships among the five fundamental state variables are obtained. This derivation will be carried out by considering the same change brought about in three different paths (Fig. 5).

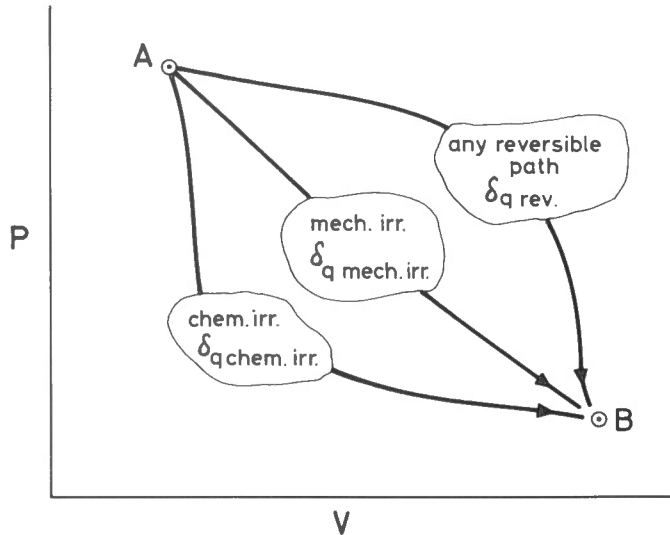


Figure 5. Changes in a closed system.

1. All changes are reversible, including PV work.

In this case

$$dU = \delta q_{rev} - \delta w_{rev}$$

$$dU = TdS - PdV$$

2. There is some irreversibility in the PV work of expansion or compression, here designated as mechanical irreversibility

Therefore,

$$\delta q_{mech. irr.} \neq TdS$$

$$\delta w_{mech. irr.} \neq PdV$$

and

$$dU = \delta q_{mech. irr.} - \delta w_{mech. irr.}$$

However, dU must be the same in both cases since the change in state from A to B is identical. Therefore,

$$dU = TdS - PdV = \delta q_{mech. irr.} - \delta w_{mech. irr.}$$

$$\delta q_{mech. irr.} = TdS - PdV + \delta w_{mech. irr.}$$

3. There is irreversibility due to changes like elimination of reversibility gradients, diffusion, mixing, and chemical reactions, here designated collectively as chemical irreversibility. Hence one can distinguish two possibilities a) and b)

- a) With mechanical irreversibility. For such changes it is always observed that

$$\delta q_{chem. irr.} < TdS - PdV + \delta w_{mech. irr.}$$

The first law in this case is

$$dU = \delta q_{chem. irr.} - \delta w_{mech. irr.}$$

Equating

$$\delta q_{chem. irr.} = dU + \delta w_{mech. irr.}$$

$$< TdS - PdV + \delta w_{mech. irr.}$$

$$dU < TdS - PdV$$

- b) Without mechanical irreversibility. For such changes it is always observed that

$$\delta q_{chem. irr.} < TdS$$

The first law in this case is

$$dU = \delta q_{chem. irr.} - PdV$$

Equating

$$\delta q_{chem. irr.} = dU + PdV < TdS$$

$$dU < TdS - PdV$$

We thus obtain in both cases $(dU + PdV - TdS) < 0$

The equation

$$(dU + PdV - TdS) \leq 0$$

is the most general thermodynamic description of changes in a closed system. Since the derivation presupposes the concept of equilibrium, the equation codifies features of equilibrium rather than constituting a criterion of equilibrium (Reiss, 1965). The equal sign refers to reversible changes and those involving mechanical irreversibility. The inequality refers to irreversible chemical changes with or without mechanical irreversibility.

If P and T can be imposed on the system by the surroundings and maintained constant, the relationship among the five fundamental thermodynamic variables becomes more restricted

$$d(U + PV - TS) \leq 0$$

for a closed system at constant P, T . The combination of variables $(U + PV - TS)$ is known as the Gibbs free energy G .

The Variation of the Gibbs Free Energy

The Gibbs free energy defined by

$$G = U + PV - TS$$

is a state variable. For a fixed amount of a homogeneous substance of specified composition it is a function of any two state variables. We are particularly interested in its variation with P and T . This is obtained by differentiating G .

$$dG = dU + PdV + VdP - TdS - SdT$$

and since $dU = TdS - PdV$

$$dG = VdP - SdT$$

$$\text{or } \left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S$$

These equations apply to either a pure substance or to a solution of fixed composition. Commonly the properties of a pure substance are of particular concern. Even in case of a solution it is desirable to "divide" the state properties of the system among the components and thus assign definite properties to particular substances even if they occur in a solution. Although there is no physical significance to this, it is a convenient procedure. It is accomplished by defining the partial molar free energy \bar{G} (or chemical potential)

$$\left(\frac{\partial G_{\text{system}}}{\partial n_i}\right)_{P, T, n_j} = \bar{G}_i$$

where G refers to the free energy of the system, n_i to the number of moles of component i , and n_j to the number of moles of all other components. This definition may be represented as the tangent on plot of G vs. n_i (Fig. 6).

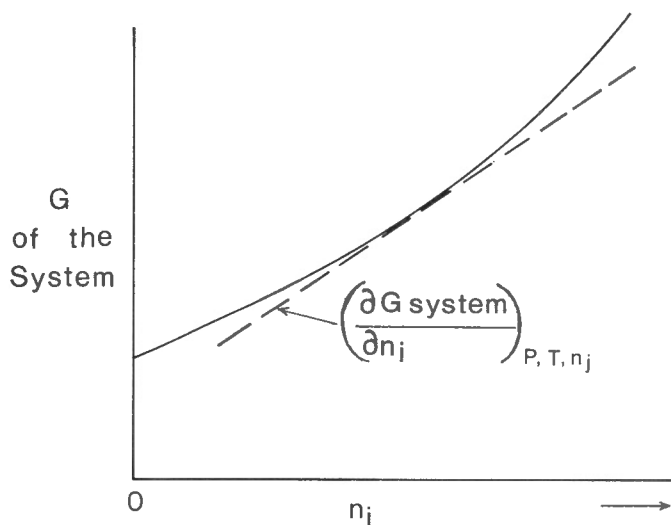


Figure 6. Definition of the partial molar free energy.

The partial molar free energy may be thought of as the free energy of one mole of substance i in a solution of particular composition. Since \bar{G}_i varies with composition, it would be of interest to know the relationship

$$\left(\frac{\partial \bar{G}_i}{\partial X_i}\right)_{P, T}$$

Thermodynamics, however, does not provide an answer in this case.

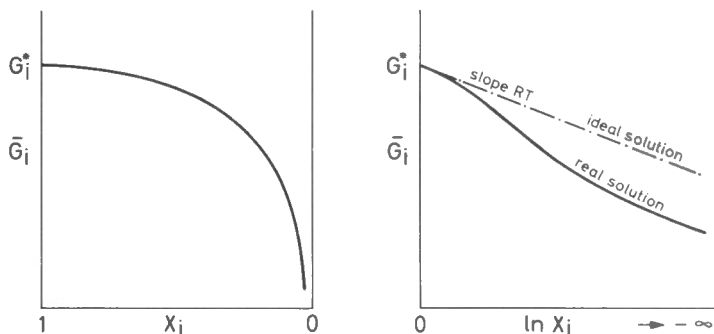


Figure 7. The partial molar free energy of a component in a solution.

In some instances it is possible to measure \bar{G}_i at various concentration. Plotting \bar{G}_i vs. X_i suggests a logarithmic variation. Plotting \bar{G}_i vs. $\ln X$ shows that many solutions plot close to a straight line and become tangential to a straight line with slope RT at $X_i = 1$, even if the mole fractions X_j are varying (Fig. 7). This suggests the model of an ideal solution defined by the equation

$$\left(\frac{\partial \bar{G}_i}{\partial \ln X_i}\right)_{P, T} = RT$$

THERMODYNAMICS OF REACTION EQUILIBRIA

Introduction

A state of equilibrium in a closed system is characterized by thermodynamic functions derived from a combination of the first and second law. A chemical equilibrium is stated in the form of a mass balance equation and the mass involved in the reaction is considered as a closed system. Thermodynamics provides an energy balance based on the mass balance. In case of a chemical reaction it enables the comparison of two energy states of an isochemical aggregate.

The Gibbs free energy of a substance is determined if three parameters are stated: Pressure P , temperature T , and composition state X , i. e. pure substance or mole fraction in a solution of fixed composition. If these parameters are given for each reactant, the energy of the left side of the reaction equation is specified ($G_{\text{reactants}}$). The energy of the right side may be similarly specified (G_{products}). If P , T , and X are fixed for each reactant and product, then at equilibrium

$$\Delta G_{\text{reaction}} = G_{\text{products}} - G_{\text{reactants}} = 0$$

Because it is physically impossible to equilibrate reactants and products at different temperatures, only cases with a uniform temperature are considered. It is common, however, to have various reactants and products in different composition states at equilibrium and the pressure of the gas species generally is not the same as that of liquids and solids. If the P - T - X conditions of any reactant or product are changed, the equilibrium is shifted. Therefore, the variation of G with P , T , and X will be considered next.

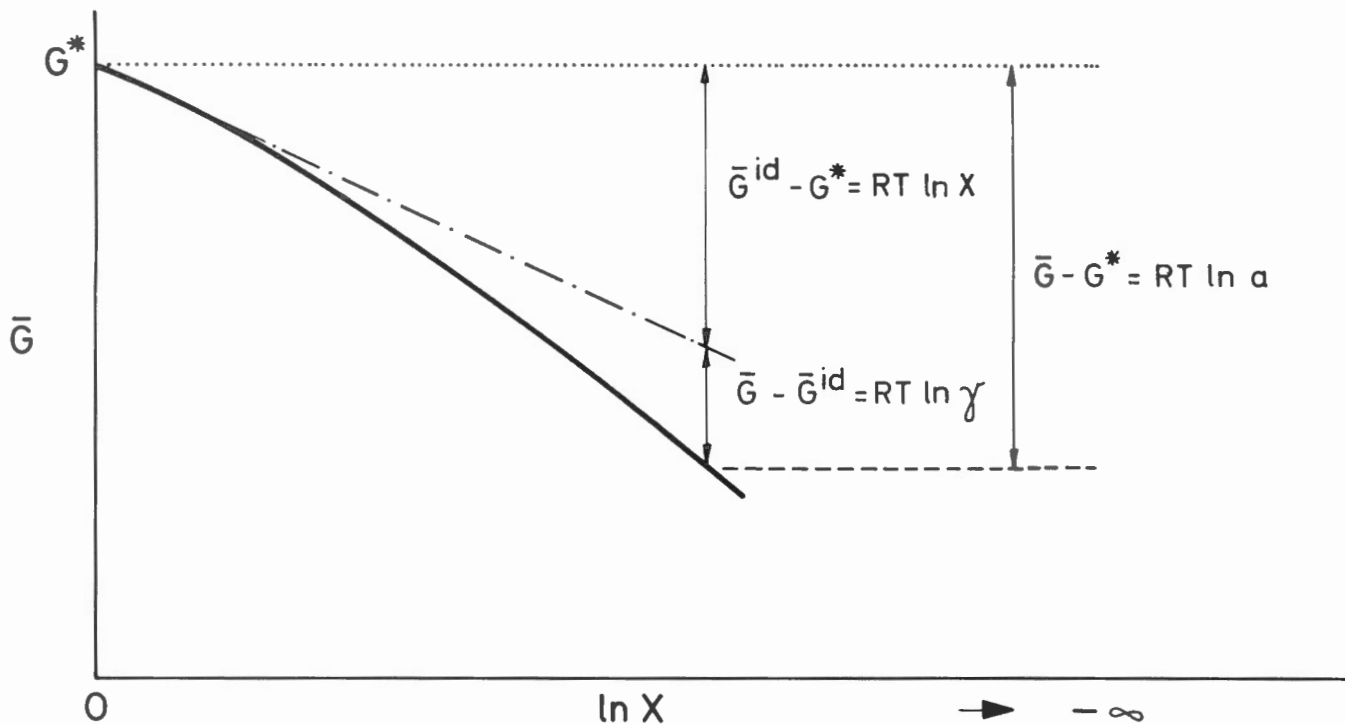


Figure 8. The definition of activity and activity coefficient.

From here on, the symbols for the extensive properties refer to one mole of a substance, unless specifically stated otherwise. However, if preceded by the symbol Δ , the property change refers to a reaction.

The Variation of G of Liquids and Solids with P

The equation

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

may be integrated between two states

$$G_P - G_{P'} = \int_{P'}^P V dP$$

In order to evaluate this integral precisely, the isothermal compressibility must be known. For liquids and solids, the lower limit of the integral is generally taken at a standard state pressure of one atm. In this paper, the equation will be applied to pure substances only. Thus

$$G^* - G^\circ = \int_1^P V dP$$

where G° and G^* refer to the Gibbs free energy of the pure substance at one atm and specified pressure P, respectively.

The Variation of G with X

The defining equation of an ideal solution

$$\left(\frac{\partial \bar{G}}{\partial \ln X}\right)_{P,T} = RT$$

may be integrated between any two compositions. A convenient lower limit for many purposes is $X = 1$

$$\bar{G} - G^* = \int_{X=1}^X RT d \ln X$$

$$\bar{G} - G^* = RT \ln X$$

where \bar{G} is the Gibbs free energy of one mole of the component in solution at any given P and T, G^* is the molar free energy of the pure substance at the same P and T, and X is the mole fraction. For real solutions, the $RT \ln X$ term is not equal to $\bar{G} - G^*$. The deviation may be expressed by a term $RT \ln \gamma$. Thus

$$\bar{G} - G^* = RT \ln X + RT \ln \gamma = RT \ln \gamma X$$

The product γX is known as the activity and γ as the activity coefficient. Both are defined by appropriate energy differences (Fig. 8).

The complex nature of many solid solutions found in minerals presents some special problems. The equation valid for an ideal solution

$$\bar{G} - G^* = RT \ln X = RT \ln a$$

refers to one mole of a component in a solution. For instance, if Fe and Mg are the mixing units in olivine,

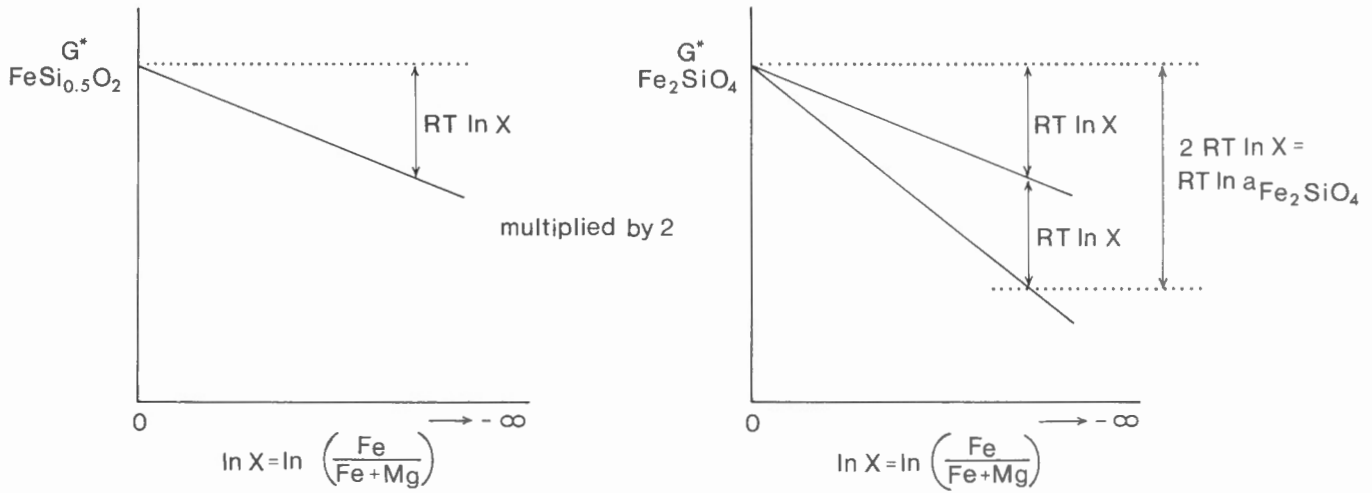


Figure 9. The activity in a solution with multiple mixing units.

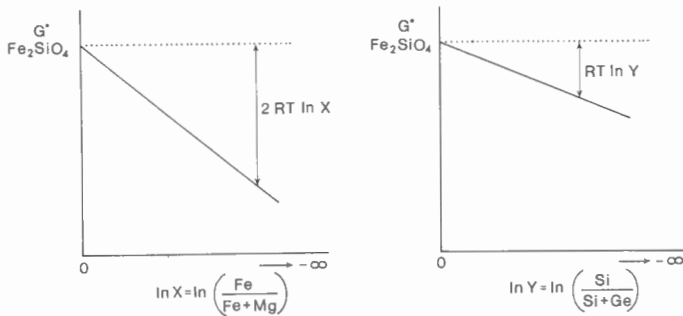


Figure 10. The activity of fayalite in olivine.

the equation refers to one mole of $\text{FeSi}_{0.5}\text{O}_2$. If the formula is doubled, the energy difference between Fe_2SiO_4 in solution and pure Fe_2SiO_4 is twice the energy difference between $\text{FeSi}_{0.5}\text{O}_2$ in solution and pure $\text{FeSi}_{0.5}\text{O}_2$. It is often convenient to define an activity on the basis of the energy difference for the unit Fe_2SiO_4 in solution and pure Fe_2SiO_4 (Fig. 9). Thus

$$a_{\text{FeSi}_{0.5}\text{O}_2} = \left(X_{\text{FeSi}_{0.5}\text{O}_2} \right) = \left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}} \right)$$

but

$$a_{\text{Fe}_2\text{SiO}_4} = \left(X_{\text{FeSi}_{0.5}\text{O}_2} \right)^2 = \left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}} \right)^2$$

in a binary solution. If the mixing unit is multiplied by some number, the activity is equal to the mole fraction raised to a power equal to that number.

In many solid solutions, mixing takes place on more than one lattice site. For example, if Si and Ge occupy the tetrahedral position of olivine, this contributes a further energy drop with respect to an end member. It is now convenient to define an activity on the basis of the total energy drop (Fig. 10):

$$\begin{aligned} \bar{G}_{\text{Fe}_2\text{SiO}_4} - G_{\text{Fe}_2\text{SiO}_4}^* &= RT \ln a_{\text{Fe}_2\text{SiO}_4} \\ &= 2 RT \ln \frac{\text{Fe}}{\text{Fe} + \text{Mg}} + RT \ln \frac{\text{Si}}{\text{Si} + \text{Ge}} \end{aligned}$$

Therefore,

$$a_{\text{Fe}_2\text{SiO}_4} = \left(\frac{\text{Fe}}{\text{Fe} + \text{Mg}} \right)^2 \left(\frac{\text{Si}}{\text{Si} + \text{Ge}} \right)$$

This type of model involving ideal solution in more than one lattice site was first discussed by Temkin (1945) and introduced into the geological literature by Ringwood (1958).

The components (Fe, Mg) and (Si, Ge) were treated as separate solutions and the equation of an ideal solution

$$\left(\frac{\partial \bar{G}}{\partial \ln X} \right)_{P, T} = RT$$

was integrated for each constituent, from $\frac{\text{Fe}}{\text{Fe} + \text{Mg}} = 1$ and from $\frac{\text{Si}}{\text{Si} + \text{Ge}} = 1$. This is appropriate because

these atomic fractions are unity in Fe_2SiO_4 . In biotite, mixing of atoms also takes place in the octahedral and tetrahedral positions. However, in the end member annite $\text{K Fe}_3 (\text{Si}_3\text{Al}) \text{O}_{10} (\text{OH})_2$, not all atomic fractions of concern are unity. Therefore, the following lower integration boundaries are used:

$$\begin{aligned} X &= \frac{\text{Fe}}{\text{Fe} + \text{Mg} + \text{Al}} = 1 && \text{in the octahedral position} \\ Y &= \frac{\text{Si}}{\text{Si} + \text{Al}} = 0.75 && \text{in the tetrahedral position} \\ Z &= \frac{\text{Al}}{\text{Si} + \text{Al}} = 0.25 && \text{in the tetrahedral position} \end{aligned}$$

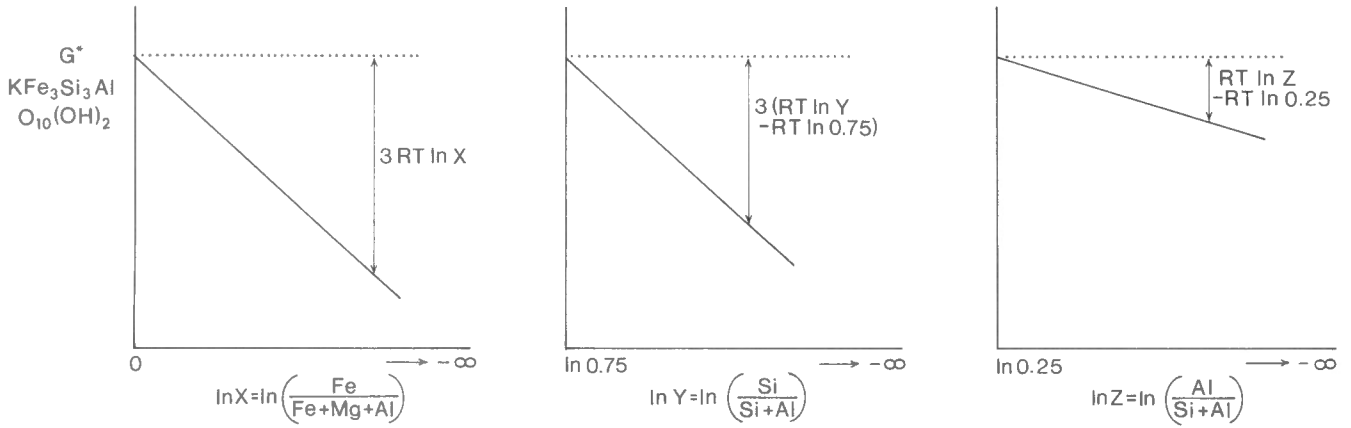


Figure 11. The activity of annite in biotite.

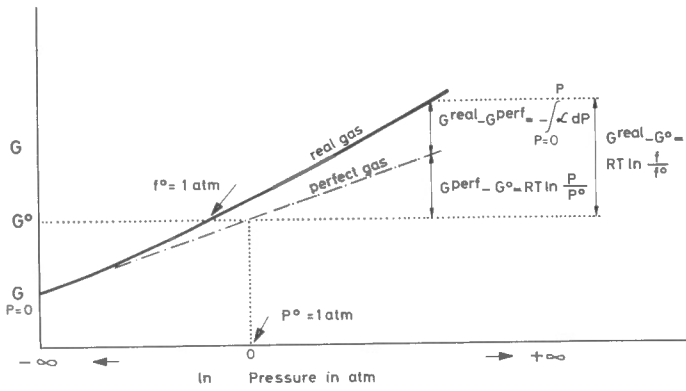


Figure 12. The definition of fugacity.

The activity again is defined on the basis of the total energy difference (Fig. 11):

$$\bar{G}_{\text{KFe}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2} - G^*_{\text{KFe}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2} =$$

$$RT \ln a_{\text{KFe}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2} = 3 RT \ln X +$$

$$3 (RT \ln Y - RT \ln 0.75) + (RT \ln Z - RT \ln 0.25)$$

Therefore

$$a_{\text{K}_2\text{Fe}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2} =$$

$$\left(\frac{\text{Fe}}{\text{Fe} + \text{Mg} + \text{Al}} \right)^3 \left(\frac{\text{Si}}{\text{Si} + \text{Al}} / 0.75 \right)^3 \left(\frac{\text{Al}}{\text{Al} + \text{Si}} / 0.25 \right)$$

Variation of G of a Gas with P and X

For a perfect gas, the general equation

$$\left(\frac{\partial G}{\partial P} \right)_T = V$$

may be integrated as follows

$$G - G^{\circ} = \int_{P^{\circ}}^P V dP = \int_{P^{\circ}}^P RT d \ln P = RT \ln \frac{P}{P^{\circ}}$$

At a standard state pressure of $P^{\circ} = 1$ atm, G° is the molar Gibbs free energy at one atm.

For a real gas, the energy difference $G - G^{\circ}$ may be used to define the fugacity. This concept will be introduced following essentially the treatment of Rossini (1950). It can be shown (see e.g. Beattie and Stockmayer, 1951) that a real gas at zero pressure has the same internal energy and entropy as a perfect gas. Furthermore, the PV product of a real gas at zero pressure is equal to RT. Therefore, also the enthalpy and Gibbs free energy of a gas at zero pressure are those of a perfect gas. However, the difference in volume between a real and a perfect gas does not become zero at zero pressure; it has a finite limiting value (Van Ness, 1964). Defining $Z = PV/RT$, the volume of a real gas is $V^{\text{real}} = ZRT/P$. Thus

$$\alpha = V^{\text{perf}} - V^{\text{real}} = \frac{RT}{P} - \frac{ZRT}{P} = \frac{RT}{P} (1-Z)$$

As P approaches 0, (1-Z) also approaches 0. In order to evaluate the limit, the numerator and denominator are differentiated with respect to P (L'Hôpital's rule). Therefore, α at zero pressure = $-RT (\partial Z / \partial P)_T$. It is customary to express the properties of a real gas in terms of deviations from perfect behaviour. It would be desirable, therefore, to use $G_{P=0}$ as the lower boundary of integration in both cases. Thus

$$G^{\text{real}} - G_{P=0}^{\text{real}} = \int_{P=0}^P V^{\text{real}} dP$$

and

$$G^{\text{perf}} - G_{P=0}^{\text{perf}} = \int_{P=0}^P V^{\text{perf}} dP$$

Since

$$G_{P=0}^{\text{real}} = G_{P=0}^{\text{perf}}$$

$$G^{\text{real}} - G^{\text{perf}} = \int_{P=0}^P V^{\text{real}} dP - \int_{P=0}^P V^{\text{perf}} dP$$

These integrals cannot be evaluated because $V \rightarrow \infty$ as $P \rightarrow 0$. However, although both $V^{\text{real}} \rightarrow \infty$ and $V^{\text{perf}} \rightarrow \infty$ as $P \rightarrow 0$, it has been shown that the difference $V^{\text{real}} - V^{\text{perf}} = -\alpha$ approaches a constant. Therefore, the following integral may be evaluated

$$G^{\text{real}} - G^{\text{perf}} = \int_{P=0}^P -\alpha dP$$

If the molar free energy of the perfect gas at 1 atm, G° , is taken as the standard state, the molar free energy of a real gas may be expressed by two energy terms

$$G^{\text{real}} - G^\circ = (G^{\text{perf}} - G^\circ) + (G^{\text{real}} - G^{\text{perf}})$$

$$= RT \ln \frac{P}{P^\circ} - \int_{P=0}^P \alpha dP$$

This energy difference may be used to define the fugacity (in atm) of a real gas at pressure P (Fig. 12), if the fugacity in the standard state f° is taken as 1 atm. The standard state for this purpose is the perfect gas at $P^\circ = 1$ atm and having an energy G° ; the real gas has the same energy G° but its pressure is such that its fugacity is one atm, i. e. $f^\circ = 1$ atm. Thus

$$G^{\text{real}} - G^\circ = RT \ln \frac{f}{f^\circ} = RT \ln \frac{P}{P^\circ} - \int_{P=0}^P \alpha dP$$

Since both P° and f° are 1 atm

$$RT \ln \frac{f}{P} = - \int_{P=0}^P \alpha dP$$

The ratio f/P , designated by ϕ (commonly also χ , γ , or ν) is known as the fugacity coefficient and may be evaluated from PV measurements by plotting

$$-\alpha = V^{\text{real}} - V^{\text{perf}} = V^{\text{real}} - \frac{RT}{P}$$

against P and measuring the area under the curve.

The variation of the Gibbs free energy of a constituent in a gaseous solution is given by the same formula as that of a solid solution

$$\bar{G} - G^* = RT \ln X + RT \ln \gamma$$

However, in the case of a gaseous component, it is convenient to measure the energy in solution \bar{G} from G° rather than from G^* . This is easily obtained by adding two energy differences, one due to the variation of G with pressure and one due to the variation of \bar{G} with composition (Fig. 13):

$$G^* - G^\circ = RT \ln P + RT \ln \phi$$

$$\bar{G} - G^* = RT \ln X + RT \ln \gamma$$

$$\bar{G} - G^\circ = RT \ln P + RT \ln \phi + RT \ln X + RT \ln \gamma$$

This energy difference is used to define the fugacity of a component in a gaseous solution

$$\bar{G} - G^\circ = RT \ln f$$

For a perfect gas species ($\phi = 1$) in an ideal solution ($\gamma = 1$)

$$\bar{G} - G^\circ = RT \ln f = RT \ln P + RT \ln X = RT \ln P_{\text{partial}}$$

For a real gas in an ideal solution ($\gamma = 1$)

$$\bar{G} - G^\circ = RT \ln f = RT \ln P_{\text{partial}} + RT \ln \phi$$

Thus $f = P_{\text{partial}} \cdot \phi$, where ϕ is the fugacity coefficient of the species at the total pressure P of the solution. This is known as the Lewis and Randall rule. It is a useful approximation for many gaseous solutions. (The rule may also be stated as $f = f^\circ X$; where f° is the fugacity of the pure gas at the same pressure as that of the solution).

It is generally difficult to obtain activity coefficient of gaseous solutions. Shaw (1967) imposed a known fugacity of hydrogen on a solution of H_2 and H_2O by using platinum as a membrane permeable to hydrogen. Knowing also the total pressure of the solution, the fugacity coefficient of pure hydrogen at this pressure, and the composition of the solution, it is possible to calculate γ from the relationship

$$f = P \phi X \gamma$$

More commonly activity coefficients are obtained by measuring partial molar volumes. It is generally assumed that at zero pressure gases mix ideally. Therefore the following relationship may be integrated at constant composition

$$RT \ln \gamma = \bar{G} - \bar{G}^{\text{id}} = \int_{P=0}^P (\bar{V} - V) dP$$

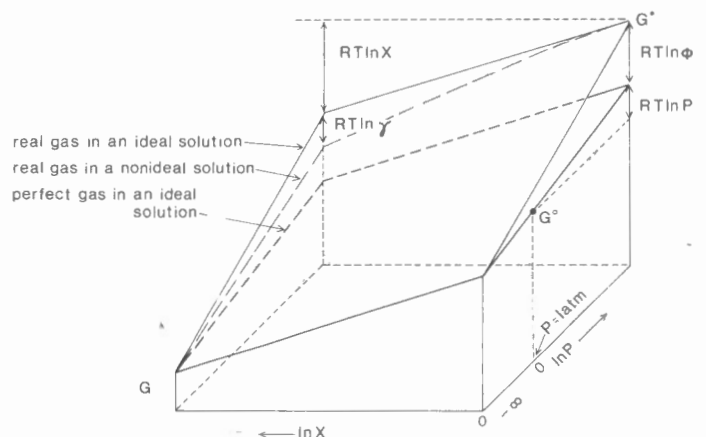


Figure 13. The fugacity of a component in a gas mixture.

The Variation of G with Temperature

The formula

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

is valid for each reactant and product. It will be more convenient, however, to apply an equivalent formula to the energy change of a reaction, particularly with all substances in their standard states. Thus

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_P = -\Delta S^\circ$$

The Equilibrium Constant

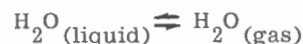
At constant temperature, the variation of G with pressure and composition is given by the relationships shown in Table 1.

Table 1 The variation of the Gibbs free energy

	Solids and liquids	Gases
Pressure P	$G^* - G^\circ = \int_1^P VdP$	$\bar{G} - G^\circ = RT \ln f/f^\circ$
Composition X	$\bar{G} - G^* = RT \ln a$	

It is important to remember that in this paper G° always refers to the molar free energy of a pure substance at standard pressure, i. e. one atmosphere for solids and liquids and a pressure making the fugacity equal to one atmosphere for gases. G^* refers to the molar free energy of the pure substance at any particular stated pressure. In gases the variation of G with pressure and composition is accounted for by the expression $RT \ln f/f^\circ$.

Now it is possible to compare the energy levels of the two sides of a reaction equation (i. e. consider the difference $\Delta G_{\text{reaction}} = G_{\text{products}} - G_{\text{reactants}}$) at different values of P and X for various reactants and products. This will be done with the example of a simple reaction



The variation of G_{gas} with P and X is accounted for by the fugacity and may be plotted on a diagram of G vs. $\ln f$. The variation of G_{liquid} may be shown by contours of activities of H_2O on a diagram of G vs. P (Fig. 14). In order to relate these two energy levels it is necessary to know ΔG of reaction in one case, with P and X for both substances specified. These conditions need not be the same for both substances. In tabulations of thermochemical data it is convenient

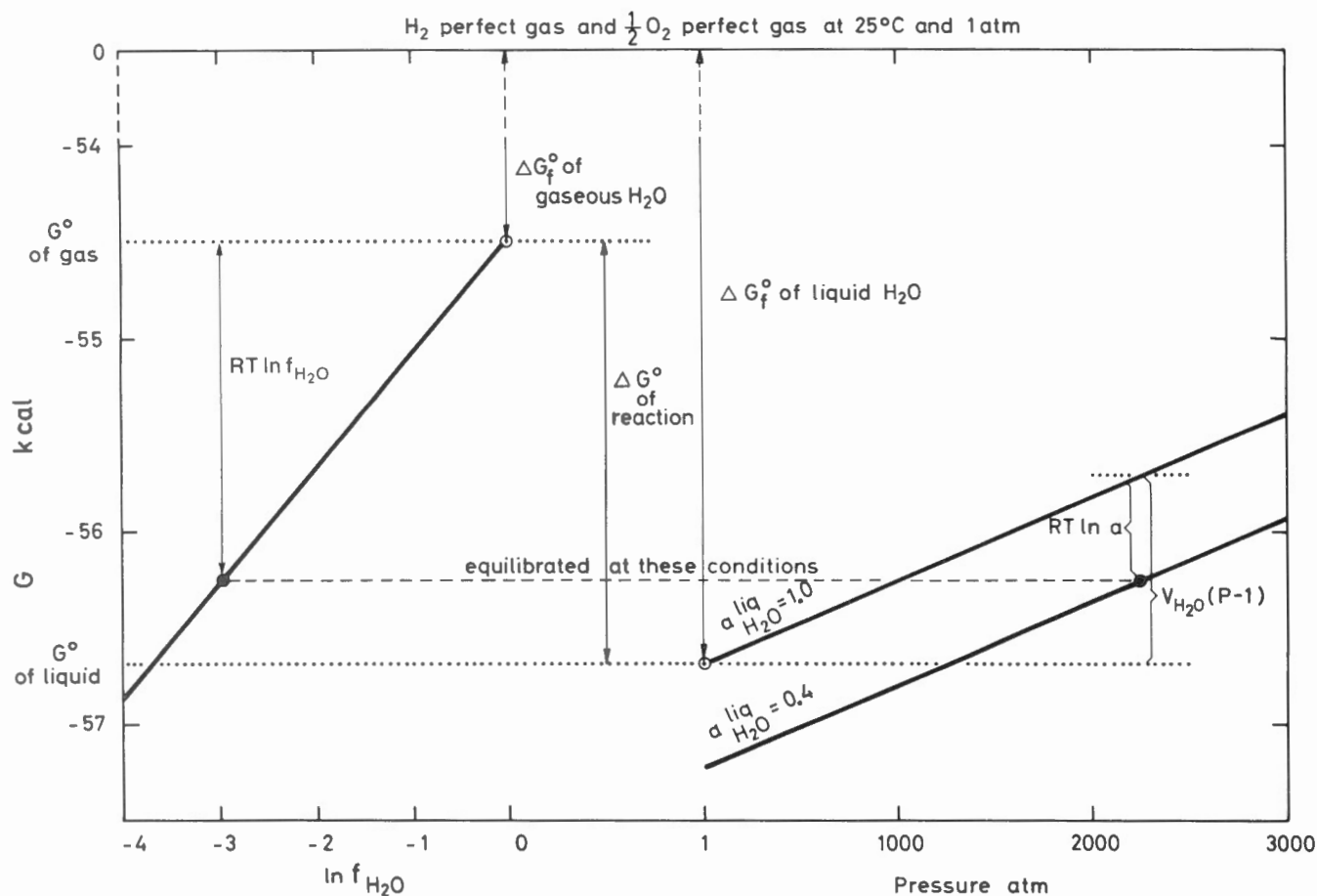


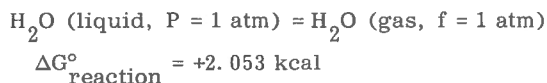
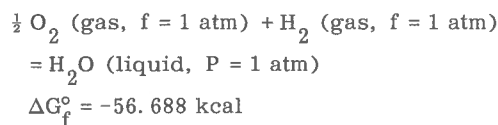
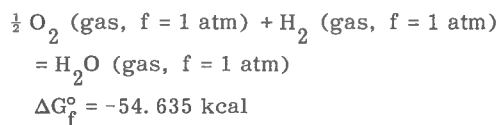
Figure 14. The equilibrium between liquid and gaseous H_2O .

Table 2

The equilibrium between liquid and gaseous H₂O

H ₂ O (liquid) = H ₂ O (gas)	
left side $G_{\text{reactant}} = \Delta G_f^\circ \text{ of liquid H}_2\text{O}$ $+ \int_{P=1}^P V_{\text{H}_2\text{O}} dP$ $+ RT \ln a_{\text{H}_2\text{O}}^{\text{liq}}$	right side $G_{\text{product}} = \Delta G_f^\circ \text{ of steam}$ $+ RT \ln f_{\text{H}_2\text{O}}$
At equilibrium $\Delta G = G_{\text{product}} - G_{\text{reactant}} = 0$	

to state this energy difference with each substance in its standard state, i. e. for liquids and solids the pure substance at $P = 1$ atm and for gases the pure substance at $f = 1$ atm. This energy difference is known as the standard free energy change, designated by ΔG° . In some books (e. g. Kubaschewski *et al.*, 1967), ΔG° of various reactions is given. More often the standard free energy of formation from the elements is given (Robie and Waldbaum, 1968; JANAF Tables) and ΔG° of reaction is obtained by difference. At 25°C



The molar volume of water is 18.069 cm³ or

$$\frac{18.069 \text{ cm}^3}{41.292 \text{ cm}^3 - \text{atm/cal}} = 0.43759 \text{ cal/atm}$$

(from Robie *et al.*, 1967)

It is convenient to assign zero energy to the elements in their standard state (at any temperature) and "build up" the energy content of both sides of a reaction from this datum. Thus G at given values of P and X , is obtained as shown in Table 2.

It follows that at equilibrium

$$\begin{aligned} \Delta G^\circ = (\Delta G_f^\circ \text{ of steam} - \Delta G_f^\circ \text{ of liquid H}_2\text{O}) = \\ -RT \ln \frac{f_{\text{H}_2\text{O}}}{a_{\text{H}_2\text{O}}^{\text{liq}}} - \int_{P=1}^P \Delta V_{\text{liq}} dP \end{aligned}$$

[Note: ΔV liquid of the reaction is $-V_{\text{H}_2\text{O}}$ of liq. H₂O; assumed to be constant in Fig. 14]. In metamorphic processes reactions commonly involve solids and gases. For such reactions the last relationship may be generalized

$$\Delta G^\circ = -RT \ln K - \int_{P=1}^P \Delta V_s dP$$

where K is the equilibrium constant in terms of activities and fugacities. From the first and second law $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; therefore

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K - \int_{P=1}^P \Delta V_s dP$$

Now two approximations will be discussed which are appropriate in many circumstances. The heat capacities of reactants and products often are sufficiently similar so that very nearly $\Delta C_P^\circ = 0$ over a limited temperature range ($\sim 400^\circ\text{C}$). This implies that ΔH° and ΔS° are constant because

$$\left(\frac{\partial \Delta S^\circ}{\partial T}\right)_P = \frac{\Delta C_P^\circ}{T} \text{ and } \left(\frac{\partial \Delta H^\circ}{\partial T}\right)_P = \Delta C_P^\circ$$

ΔS° and ΔH° are independent of pressure because the standard state specifies the pressure.

The isothermal compressibility and the isobaric expansion of solids usually are sufficiently similar so that ΔV_{solids} is constant over a limited range of P and T ($\sim 10 \text{ kb}$, $\sim 400^\circ\text{C}$).

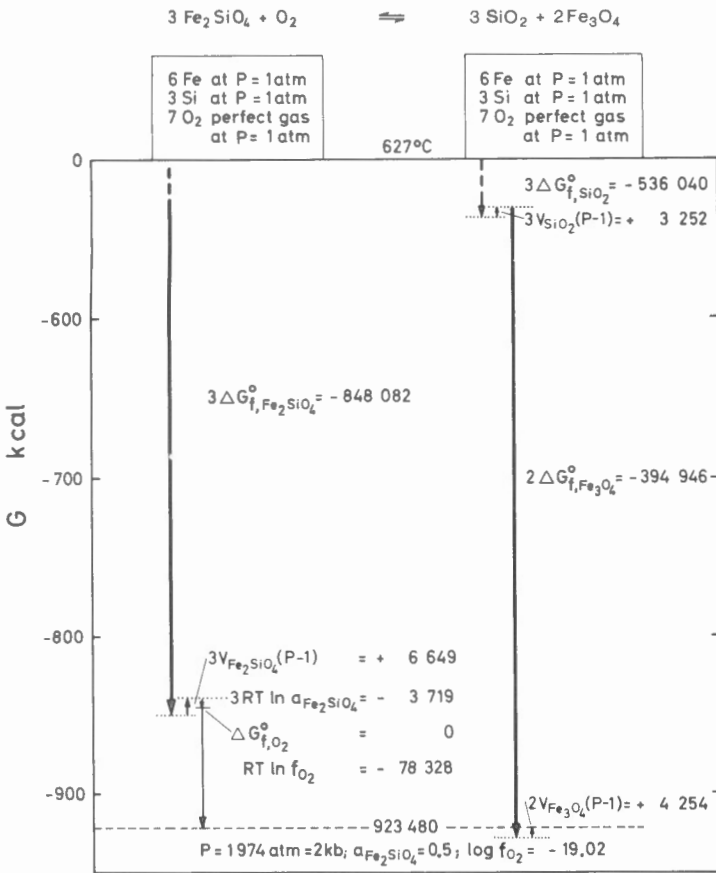


Figure 15. The oxidation of fayalite.

With these two approximations one can write

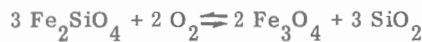
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K - \Delta V_S (P-1)$$

And plotting $\Delta G^\circ = -RT \ln K - \Delta V_S (P-1)$ vs. T will yield a straight line with slope $-\Delta S^\circ$.
Or, rearranging and dividing by RT

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} - \frac{\Delta V_S}{RT} (P-1)$$

Plotting $\ln K + \frac{\Delta V_S}{RT} (P-1)$ vs. $1/T$ yields a straight line with slope $-\Delta H^\circ/R$. It is significant to retain the term involving ΔV_S .

Another illustration of a chemical equilibrium



is shown in Fig. 15. The thermochemical data are taken from Robie and Waldbaum (1968). It is important to note that equilibrium may be established at various combination of total pressure, activities, and fugacities as long as the relationship

$$\Delta G^\circ = -RT \ln K - \Delta V_S (P-1)$$

is satisfied. In the chosen example the equilibrium constant is

$$K = \frac{1}{(a_{\text{Fe}_2\text{SiO}_4})^3 (f_{\text{O}_2})^2}$$

Thermochemical properties are listed for substances in their standard states. For solids and liquids the standard state for G , H , and S , is the pure substance at a pressure of one atm. For gases the standard state for G , H , and S is the hypothetical perfect gas at a pressure of one atm. If the perfect gas has a standard free energy G° at one atm, the real gas has the same energy at a different pressure where $f^\circ = 1$ atm. At this pressure G (real) = G° (perf) but H (real) \neq H° (perf) and S (real) \neq S° (perf).

The enthalpy of a perfect gas is independent of pressure. This can be seen from the following relationships. Substituting

$$G = G^\circ + RT \ln P$$

and
$$-S = \left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{dG^\circ}{dT}\right) + R \ln P$$

into the formula

$$H = G + TS$$

one obtains

$$H = G^\circ - T \left(\frac{dG^\circ}{dT}\right)$$

Therefore, the enthalpy of a real gas can be equal to that of the perfect gas only at zero pressure.

The entropy of a real gas is equal to that of a perfect gas at some pressure which is different from the pressure where the free energies are equal. These relations are shown in Fig. 16. Thus, although the standard state of a gas for G is the real gas at $f^\circ = 1$, this is not true for H and S .

The experimental determination of the heat capacity of a substance makes it possible to integrate the equations

$$\left(\frac{\partial H^\circ}{\partial T}\right)_P = C_P^\circ \quad \text{and} \quad \left(\frac{\partial S^\circ}{\partial T}\right)_P = \frac{C_P^\circ}{T}$$

The lower limits of integration are H_{298}° and S_{zero}° . According to the third law of thermodynamics the entropy of a pure crystalline substance is zero at absolute zero. Thus results are listed as $(H_T^\circ - H_{298}^\circ)$ and S_T° . For each substance

$$G_T^\circ = H_T^\circ - TS_T^\circ$$

Subtracting H_{298}° from each side

$$(G_T^\circ - H_{298}^\circ) = (H_T^\circ - H_{298}^\circ) - TS_T^\circ$$

This function for a substance or combination of substances (one side of a reaction equation) is easily plotted, e. g. $\text{H}_2 + \frac{1}{2} \text{O}_2$, each a perfect gas at 1 atm, and H_2O steam perfect gas at 1 atm). Tables commonly list the function $(G_T^\circ - H_{298}^\circ)/T$ called the Gibbs free energy function, a somewhat misleading name.

In order to relate the two $(G_T^\circ - H_{298}^\circ)$ curves for two sides of a reaction equation it is necessary to know either ΔH° or ΔG° at some temperature. ΔH_T° is obtained

from calorimetric measurements. ΔG° may be obtained from determining the equilibrium constant or from reactions in galvanic cells.

If ΔH_T° is known, ΔG_T° may be calculated from the relationship

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$$

For instance, consider the following example (Fig. 17 and Table 3):

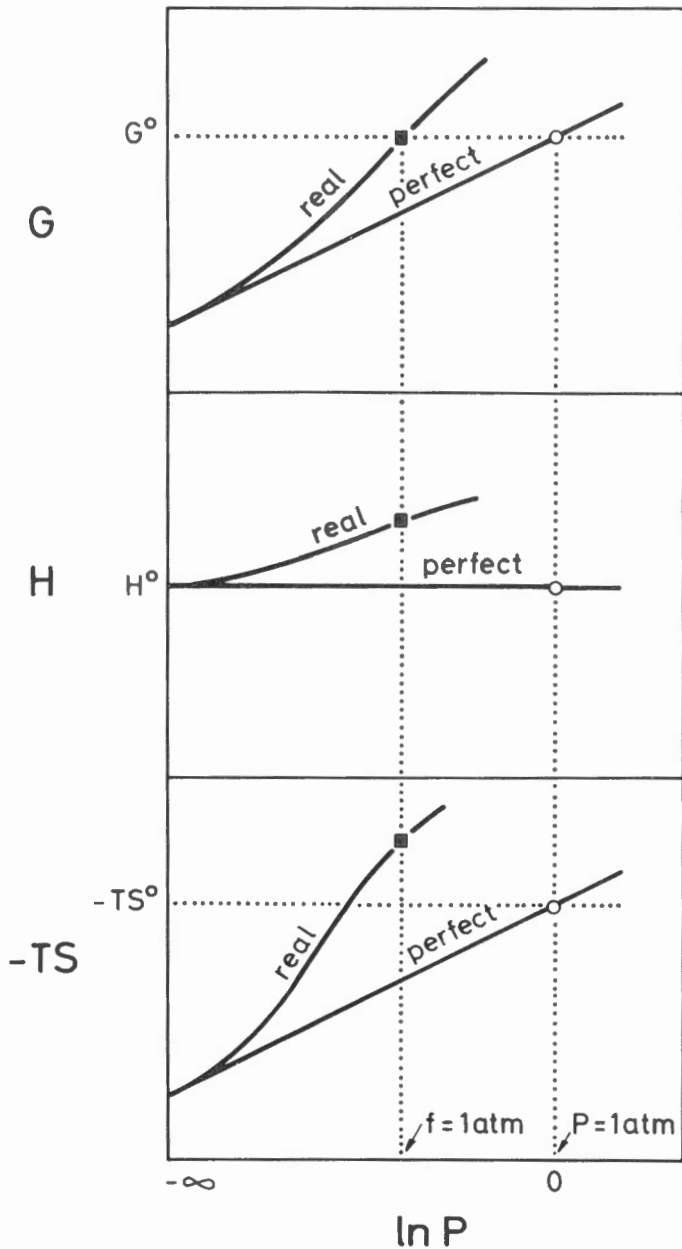
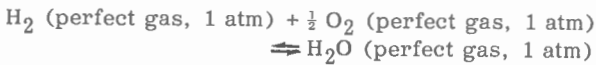


Figure 16. The standard state of a gas.

At 500°K

$$\begin{aligned} \Delta G_{500}^\circ &= \Delta H_{500}^\circ - 500 (\Delta S_{500}^\circ) \\ &= -58275 - 500 (49.33 - 34.806 - 26.357) \\ &= -52359 \text{ cal} \end{aligned}$$

ΔG° of this reaction is the standard free energy of formation of steam. The reactants are the elements in their standard state; the product is in its standard state. Therefore it is designated by $\Delta G_{f, 500}^\circ$.

Commonly the standard enthalpies of formation at 298.15°K are listed as $(\Delta H_{f, 298}^\circ)$. The following relationships exist:

$$\begin{aligned} \Delta H_{f, T}^\circ &= [\text{H}_{298}^\circ + (\text{H}_T^\circ - \text{H}_{298}^\circ)] - [\text{H}_{298}^\circ + (\text{H}_T^\circ - \text{H}_{298}^\circ)] \\ &\quad \text{products} \qquad \qquad \qquad \text{reactants} \\ &= \Delta H_{f, 298}^\circ + \Delta (\text{H}_T^\circ - \text{H}_{298}^\circ) \end{aligned}$$

Thus at 500°K

$$\Delta H_{f, 500}^\circ = -57796 + (1654 - 2133) = -58275 \text{ cal}$$

$$\begin{aligned} \Delta G_{f, T}^\circ &= [\text{H}_{298}^\circ + (\text{G}_T^\circ - \text{H}_{298}^\circ)] - [\text{H}_{298}^\circ + (\text{G}_T^\circ - \text{H}_{298}^\circ)] \\ &\quad \text{products} \qquad \qquad \qquad \text{reactants} \\ &= \Delta H_{f, 298}^\circ + \Delta (\text{G}_T^\circ - \text{H}_{298}^\circ) \end{aligned}$$

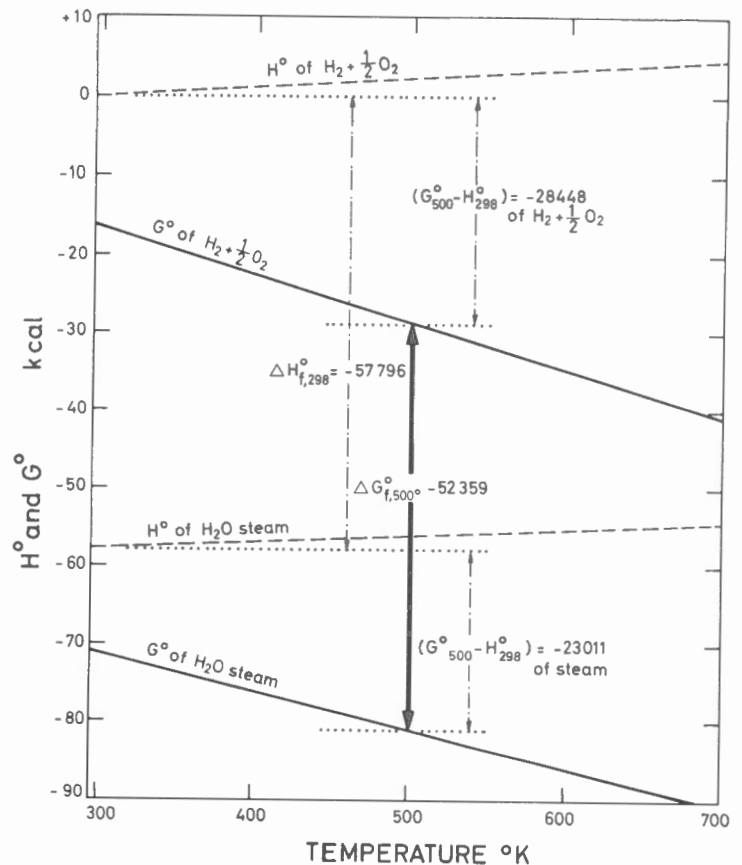


Figure 17. Thermochemical properties of steam.

Thus at 500°K

$$\Delta G_{f, T}^{\circ} = -57796 + (23011 + 28448) = -52359$$

SOLID-SOLID REACTIONS

Garnet - Cordierite Equilibria

The assemblage quartz-sillimanite-garnet-cordierite is common in high-grade pelitic rocks (e. g. Reinhardt, 1968). These minerals are related by the equilibria



It is commonly possible to express ΔG° as a linear function of T:

$$\Delta G^{\circ} = A + BT \quad (T \text{ in } ^{\circ}\text{K})$$

where $A = \Delta H^{\circ}$ and $B = -\Delta S^{\circ}$. Thus for the two reactions one can write

$$A_{(1)} + B_{(1)}T = -RT \ln K_{(1)} - \Delta V_{(1)}(P-1)$$

$$A_{(2)} + B_{(2)}T = -RT \ln K_{(2)} - \Delta V_{(2)}(P-1)$$

$$T(B_{(1)} + R \ln K_{(1)}) = -\Delta V_{(1)}P + \Delta V_{(1)} - A_{(1)}$$

$$T(B_{(2)} + R \ln K_{(2)}) = -\Delta V_{(2)}P + \Delta V_{(2)} - A_{(2)}$$

Solving for P

$$T(B_{(1)} + R \ln K_{(1)})(B_{(2)} + R \ln K_{(2)}) =$$

$$(B_{(2)} + R \ln K_{(2)})(\Delta V_{(1)} - A_{(1)})$$

$$- P\Delta V_{(1)}(B_{(2)} + R \ln K_{(2)})$$

$$T(B_{(1)} + R \ln K_{(1)})(B_{(2)} + R \ln K_{(2)}) =$$

$$(B_{(1)} + R \ln K_{(1)})(\Delta V_{(2)} - A_{(2)})$$

$$- P\Delta V_{(2)}(B_{(1)} + R \ln K_{(1)})$$

$$(B_{(2)} + R \ln K_{(2)})(\Delta V_{(1)} - A_{(1)})$$

$$- P\Delta V_{(1)}(B_{(2)} + R \ln K_{(2)})$$

$$= (B_{(1)} + R \ln K_{(1)})(\Delta V_{(2)} - A_{(2)})$$

$$- P\Delta V_{(2)}(B_{(1)} + R \ln K_{(1)})$$

$$(B_{(1)} + R \ln K_{(1)})(\Delta V_{(2)} - A_{(2)})$$

$$- (B_{(2)} + R \ln K_{(2)})(\Delta V_{(1)} - A_{(1)})$$

$$P = \frac{(B_{(1)} + R \ln K_{(1)})(\Delta V_{(2)} - A_{(2)}) - (B_{(2)} + R \ln K_{(2)})(\Delta V_{(1)} - A_{(1)})}{\Delta V_{(2)}(B_{(1)} + R \ln K_{(1)}) - \Delta V_{(1)}(B_{(2)} + R \ln K_{(2)})}$$

Solving for T

$$T\Delta V_{(2)}(B_{(1)} + R \ln K_{(1)}) =$$

$$-\Delta V_{(1)}\Delta V_{(2)}P + \Delta V_{(1)}\Delta V_{(2)} - A_{(1)}\Delta V_{(2)}$$

$$T\Delta V_{(1)}(B_{(2)} + R \ln K_{(2)}) =$$

$$-\Delta V_{(1)}\Delta V_{(2)}P + \Delta V_{(1)}\Delta V_{(2)} - A_{(2)}\Delta V_{(1)}$$

$$T^{\circ}\text{K} = \frac{A_{(2)}\Delta V_{(1)} - A_{(1)}\Delta V_{(2)}}{\Delta V_{(2)}(B_{(1)} + R \ln K_{(1)}) - \Delta V_{(1)}(B_{(2)} + R \ln K_{(2)})}$$

Assuming ideal ionic solution in garnet and cordierite

$$a_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}+\text{Mn}+\text{Ca}} \right)^3;$$

$$a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} = \left(\frac{\text{Mg}}{\text{Fe}+\text{Mg}+\text{Mn}+\text{Ca}} \right)^3$$

and

$$a_{\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}}^{\text{cor}} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}+\text{Mn}} \right)^2;$$

$$a_{\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}}^{\text{cor}} = \left(\frac{\text{Mg}}{\text{Fe}+\text{Mg}+\text{Mn}} \right)^2$$

It is now possible to write the equilibrium constants in the form of atomic fractions:

$$K_{(1)} = \frac{\left(a_{\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}}^{\text{cor}} \right)^3 \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}+\text{Mn}} \right)_{\text{cor}}^6}{\left(a_{\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} \right)^3 \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}+\text{Mn}+\text{Ca}} \right)_{\text{gar}}^6}$$

$$K_{(2)} = \frac{\left(a_{\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}}^{\text{cor}} \right)^3 \left(\frac{\text{Mg}}{\text{Fe}+\text{Mg}+\text{Mn}} \right)_{\text{cor}}^6}{\left(a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{gar}} \right)^2 \left(\frac{\text{Mg}}{\text{Fe}+\text{Mg}+\text{Mn}+\text{Ca}} \right)_{\text{gar}}^6}$$

Thus the two equilibrium constants may be calculated for each pair of analyzed garnet and cordierite. The volume changes of the reactions may be obtained from Robie *et al.* (1967). And if the standard free energy changes for both reactions are known, it is possible to solve for P and T.

Hutcheon *et al.* (1974) have used the following values of ΔG° to estimate P and T of some rocks from the Daly Bay Complex, N. W. T.:

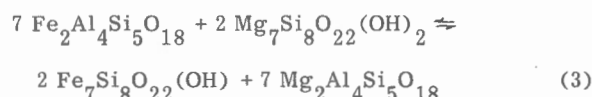
$$\Delta G^\circ_{(1)} = 6590 - 18.0 T; \Delta V_{(1)} = 3.6480 \text{ cal/bar}$$

$$\Delta G^\circ_{(2)} = -9030 - 22.95 T; \Delta V_{(2)} = 3.8252 \text{ cal/bar}$$

Froese (1973) calculated the free energy change of reaction (1) with the pure solids at 2 kb. In the present notation this corresponds to $\Delta G^\circ + \Delta V$ (2000-1); therefore $\Delta G^\circ = \Delta G$ at 2kb - ΔV (2000-1). The standard free energy change of reaction (2) was estimated by Hutcheon *et al.* (1974).

Exchange Reactions

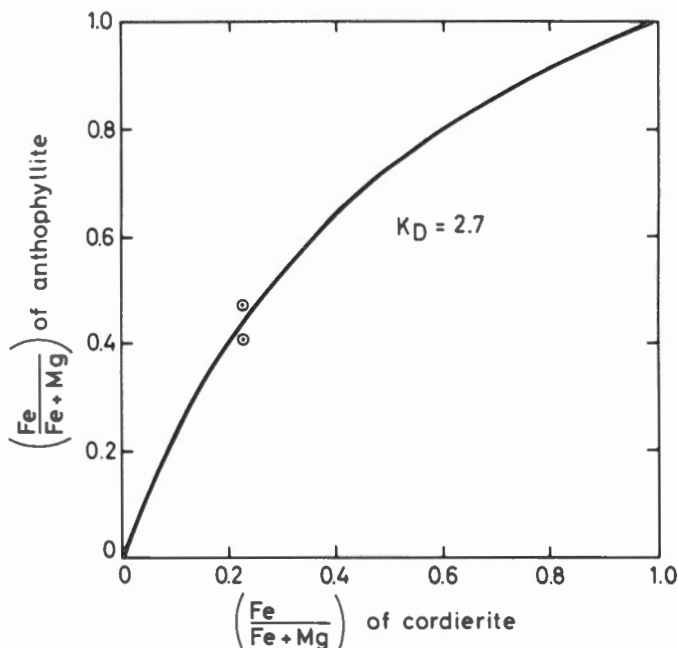
Exchange reactions are important examples of solid-solid reactions. For instance, the distribution of iron and magnesium between cordierite and anthophyllite may be represented by the following equilibrium:



$$K_{(3)} = \frac{\left(\frac{\text{anth}}{\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2}\right)^2 \left(\frac{\text{cor}}{\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}}\right)^7}{\left(\frac{\text{anth}}{\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2}\right)^2 \left(\frac{\text{cor}}{\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}}\right)^7}$$

Assuming ideal ionic solution

$$\frac{\text{anth}}{\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}+\text{Al}}\right)^7_{\text{octahedral position}} \left(\frac{\text{Si}}{\text{Si}+\text{Al}}\right)^8_{\text{tetrahedral position}}$$



$$\frac{\text{cor}}{\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}}\right)^2$$

Analogous relations hold for the Mg end members. If anthophyllite contains no Al

$$\frac{\text{anth}}{\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}}\right)^7$$

and

$$K_{(3)}^{14} = \frac{\left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}}\right)_{\text{anth}} \left(\frac{\text{Mg}}{\text{Fe}+\text{Mg}}\right)_{\text{cor}}}{\left(\frac{\text{Mg}}{\text{Fe}+\text{Mg}}\right)_{\text{anth}} \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}}\right)_{\text{cor}}}$$

The expression on the right side of the equation is known as the distribution coefficient K_D . A common method of representing K_D , introduced into the geological literature by Kretz (1961), is plotting Fe/(Fe+Mg) in anthophyllite vs. Fe/(Fe+Mg) in cordierite.

If anthophyllite contains some aluminum, e. g. 2.5 atoms per formula unit (Fe, Mg)_{5.75} Al_{1.25} Si_{6.75} Al_{1.25} O₂₂(OH)₂,

$$\frac{\text{anth}}{\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}+\text{Al}}\right)^{5.75} \left(\frac{6.75}{\text{Si}+\text{Al}}\right)^8$$

but, because of cancellation, K_D remains the same.

Figure 18 shows the distribution of Fe and Mg between anthophyllite and cordierite based on two analyses reported by Lal and Moorhouse (1969). The distribution curve corresponds to tie lines in a conventional phase diagram, also shown in Figure 18.

The iron-magnesium distribution among silicates commonly is not very temperature-sensitive and subtle variations may be obscured by uncertainties in the analyses.

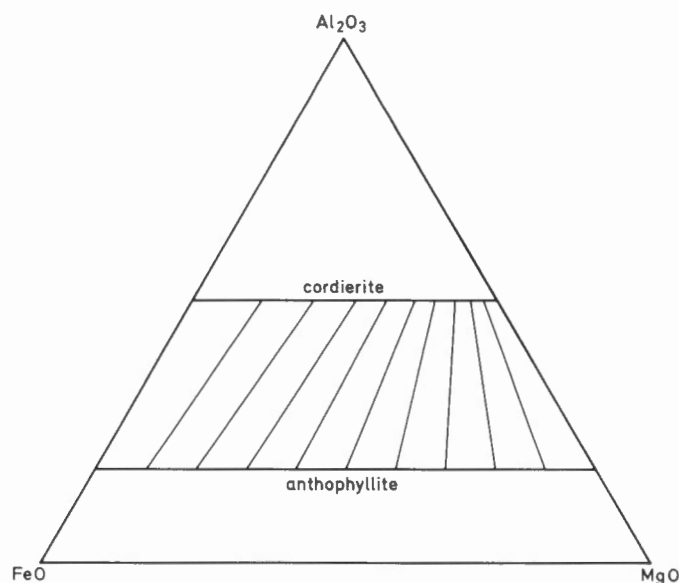
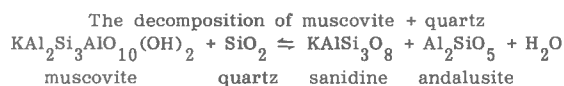


Figure 18. The distribution of iron and magnesium between cordierite and anthophyllite.

Table 4



$P_{H_2O} = P_{total}$ kb	T°C	P_{H_2O} atm	ϕ_{H_2O}	f_{H_2O} atm	$\Delta V_s (P-1)$ cal	ΔG° cal
0.5	520	493	0.681	336	-37	-9131
0.5	560	493	0.739	365	-37	-9731
1	550	987	0.551	544	-74	-10229
1	570	987	0.585	577	-74	-10578
2	590	1974	0.507	1001	-149	-11701
2	605	1974	0.531	1048	-149	-11987
3	620	2961	0.543	1608	-224	-12879
3	640	2961	0.575	1702	-224	-13276
4	660	3948	0.638	2519	-298	-14224
4	670	3948	0.653	2578	-298	-14423
5	690	4935	0.745	3676	-373	-15340
5	705	4935	0.770	3800	-373	-15649

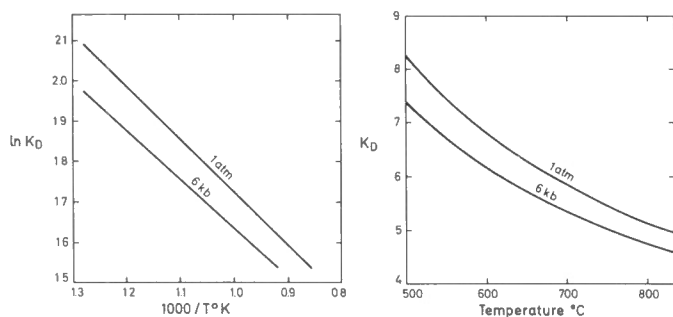
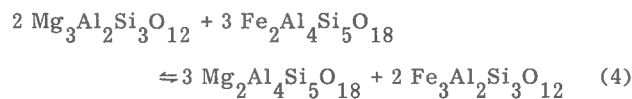


Figure 19. Variation of the distribution coefficient with temperature and pressure.

For example, by subtracting reaction (1) from reaction (2), the following exchange reaction is obtained



$$K_{(4)} = \frac{\left(\frac{Fe}{Fe+Mg}\right)_{gar} \left(\frac{Mg}{Fe+Mg}\right)_{cor}}{\left(\frac{Mg}{Fe+Mg}\right)_{gar} \left(\frac{Fe}{Fe+Mg}\right)_{cor}}$$

$$\Delta G^\circ = -15620 - 4.95 T; \Delta V_s = 0.1772 \text{ cal/bar}$$

$$\Delta G^\circ = -6 RT \ln K_D - \Delta V_s (P-1)$$

In Figure 19, the variation of K_D with temperature and pressure is shown.

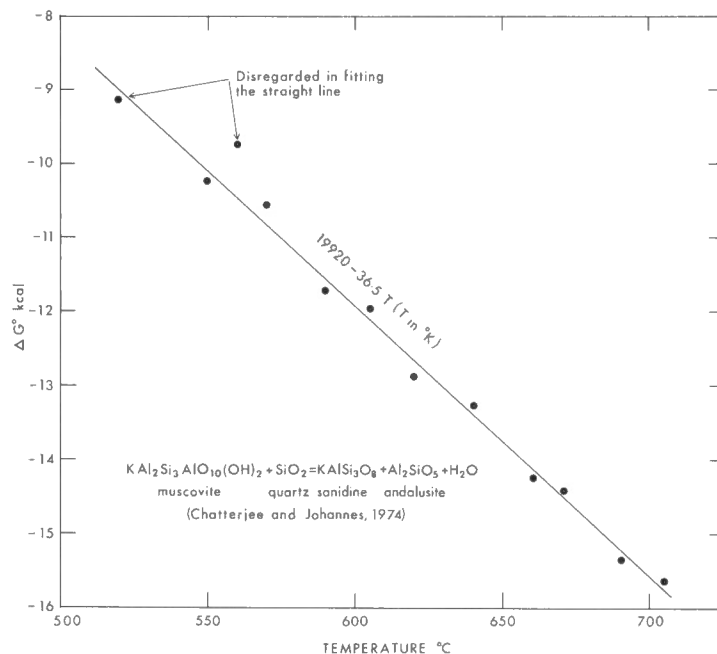
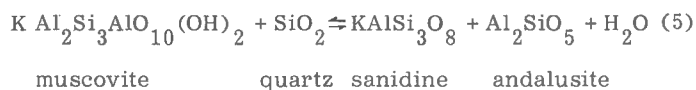


Figure 20. The decomposition of muscovite + quartz.

DEHYDRATION REACTIONS

The Decomposition of Muscovite + Quartz

A very important reaction during metamorphism is the dehydration of muscovite in the presence of quartz:



The most recent experimental determination of this reaction is that of Chatterjee and Johannes (1974). For each experimental bracket (Table 4) it is possible to calculate

$$\Delta G^\circ_{(5)} = -RT \ln f_{H_2O} - \Delta V_s (P-1)$$

The pressure was converted to atmospheres to be strictly consistent with the standard state used in this paper. The fugacity coefficients of H_2O at each P and T were taken from Burnham *et al.* (1969) and the molar volume of the solids from Robie *et al.* (1967). On a plot of ΔG° vs. T (Fig. 20) a straight line may be passed through all brackets. Disregarding the large bracket at 0.5 kb, the deviations in ΔG° have been minimized. The equation of the straight line is

$$\Delta G^\circ_{(5)} = 19920 - 36.5 T \quad (T \text{ in } ^\circ K)$$

It follows that ΔS° is 36.5 cal/deg and ΔH° is 19920 cal.

It is now possible to calculate the equilibrium surface of the reaction in $P - P_{H_2O} - T$ space (Fig. 21). The surface may be shown by contours in various projections.

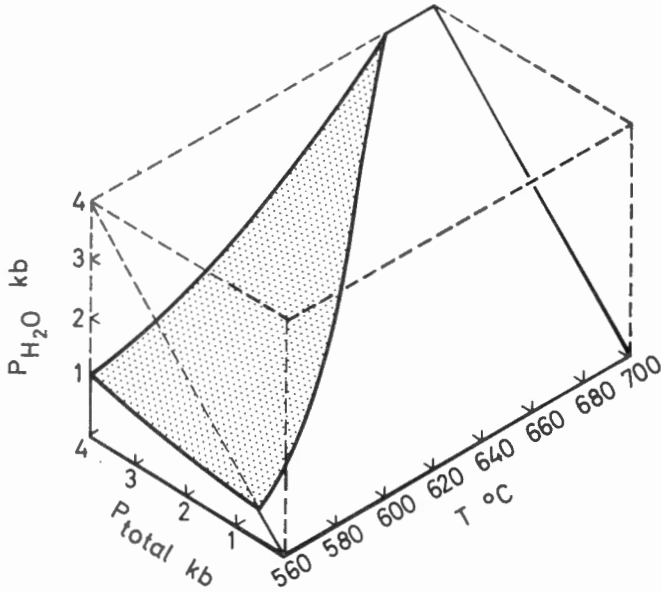
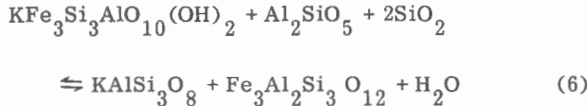


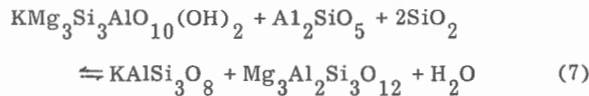
Figure 21. The stability of muscovite + quartz.

Biotite-Garnet Equilibria

A very common mineral assemblages in high-grade pelitic rocks is quartz-K feldspar-biotite-garnet-sillimanite. This assemblage is easily represented on a triangular diagram with corners $A = Al_2O_3 - K_2O$, $F = FeO$ and $M = MgO$ (e.g. Froese, 1963). The assemblage plots as a subtriangle in such a diagram. This subtriangle will shift in response to changes of P , P_{H_2O} , and T . In order to express this variation quantitatively the following procedure may be used. The minerals are related by the equilibria



$$K_{(6)} = f_{H_2O} \left(\frac{a_{Fe_3Al_2Si_3O_{12}}^{gar}}{a_{KFe_3Si_3AlO_{10}(OH)_2}^{bio}} \right)$$



$$K_{(7)} = f_{H_2O} \left(\frac{a_{Mg_3Al_2Si_3O_{12}}^{gar}}{a_{KMg_3Si_3AlO_{10}(OH)_2}^{bio}} \right)$$

The following relationships hold

$$\Delta G^\circ_{(6)} = A_{(6)} + B_{(6)} T = -RT \ln f_{H_2O} - RT \ln \frac{a_{Fe_3Al_2Si_3O_{12}}^{gar}}{a_{KFe_3Si_3AlO_{10}(OH)_2}^{bio}} - \Delta V_{s(6)} (P-1)$$

$$\Delta G^\circ_{(7)} = A_{(7)} + B_{(7)} T = -RT \ln f_{H_2O} - RT \ln \frac{a_{Mg_3Al_2Si_3O_{12}}^{gar}}{a_{KMg_3Si_3AlO_{10}(OH)_2}^{bio}} - \Delta V_{s(7)} (P-1)$$

or, abbreviating the activity ratio part of the equilibrium constant by L

$$A_{(6)} + B_{(6)} T + RT \ln f_{H_2O} + RT \ln L_{(6)} + \Delta V_{s(6)} (P-1) = 0$$

$$A_{(7)} + B_{(7)} T + RT \ln f_{H_2O} + RT \ln L_{(7)} + \Delta V_{s(7)} (P-1) = 0$$

Subtracting

$$\begin{aligned} & A_{(6)} - A_{(7)} \\ & + T [(B_{(6)} + R \ln L_{(6)}) - (B_{(7)} + R \ln L_{(7)})] \\ & + (P-1) (\Delta V_{s(6)} - \Delta V_{s(7)}) = 0 \\ T = & \frac{(A_{(7)} - A_{(6)}) - (P-1) (\Delta V_{s(6)} - \Delta V_{s(7)})}{(B_{(6)} + R \ln L_{(6)}) - (B_{(7)} + R \ln L_{(7)})} \end{aligned}$$

For any given rock, T may be calculated at an assumed P . Then $\ln f_{H_2O}$ is given by

$$\ln f_{H_2O} = - \left(\frac{A_{(6)} + B_{(6)} T + RT \ln L_{(6)} + \Delta V_{s(6)} (P-1)}{RT} \right)$$

The volume change ΔV_s for both reactions may be obtained from Robie *et al.* (1967).

Froese (1970, 1973b) studied rocks with this assemblage from the Thor-Odin gneiss dome and reported analyses of coexisting pairs of garnet and biotite. The geological setting of the area is given by Reesor (1970) and Reesor and Moore (1971). Most samples came from unmigmatized gneisses mantling a migmatitic core. The activity ratio parts of the equilibrium constants may be calculated from the chemical analyses by assuming ideal ionic solution in biotite and garnet.

The free energy changes of reactions (6) and (7) are not known. In order to assess differences in metamorphic conditions from rock to rock, these were

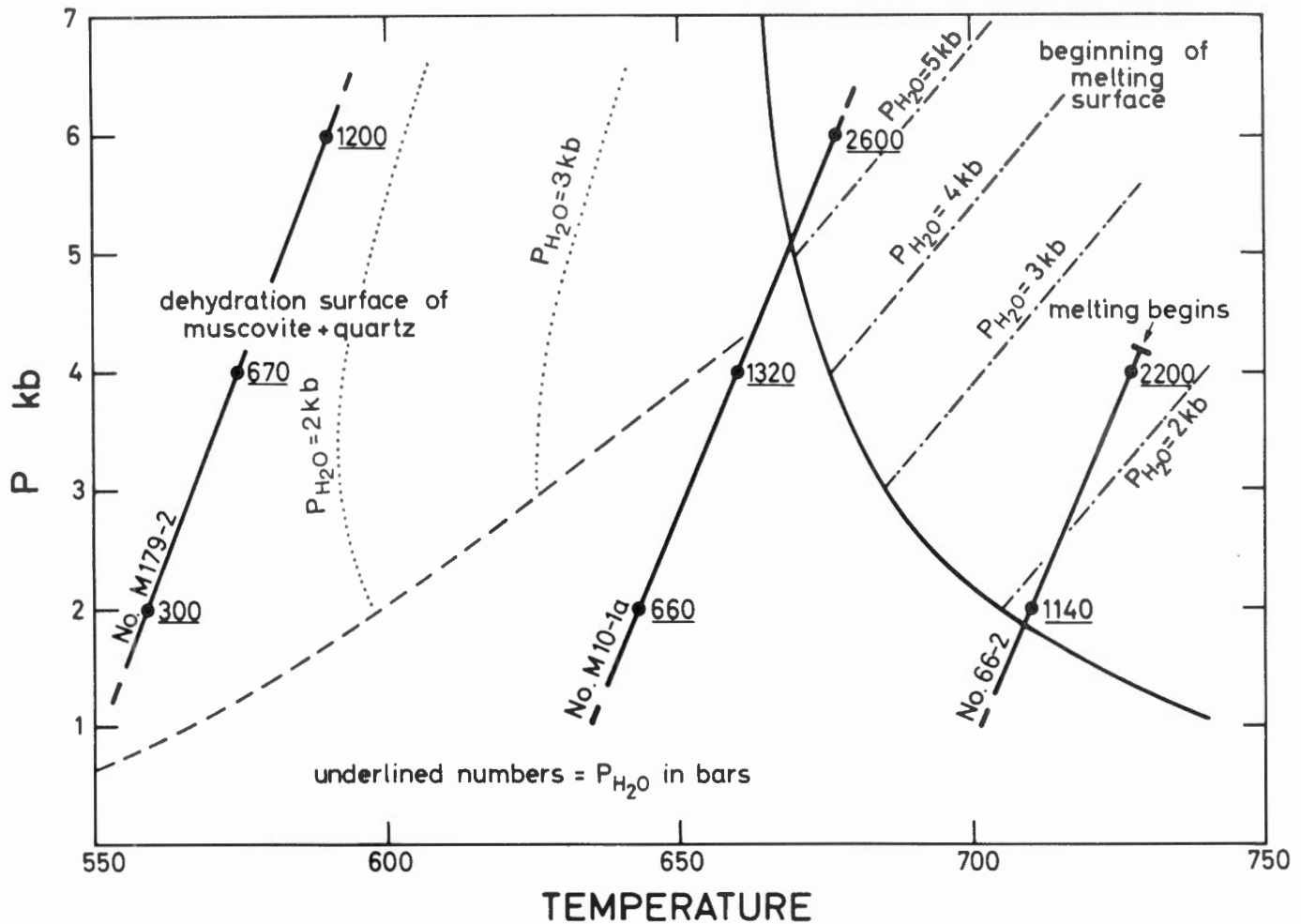


Figure 22. Metamorphic conditions for some rocks from the Thor-Odin gneiss dome.

assumed for one sample (No. 279-3): $T = 550^{\circ}\text{C}$,
 $P = 3 \text{ kb}$, $P_{\text{H}_2\text{O}} = 1 \text{ kb}$. On this basis ΔG° may be
 calculated:

$$\Delta G^{\circ}_{(6)} = -RT \ln K_{(6)} - \Delta V_{s(6)} (P-1) = -10200 \text{ cal}$$

$$\Delta G^{\circ}_{(7)} = -RT \ln K_{(7)} - \Delta V_{s(7)} (P-1) = -4245 \text{ cal}$$

Assuming a dehydration entropy of 32 cal/deg mole

$$\Delta G^{\circ}_{(6)} = 16140 - 32.0 T$$

$$\Delta G^{\circ}_{(7)} = 22100 - 32.0 T$$

For each particular rock, the activity ratio parts of the equilibrium constants can be regarded as given. For biotite and garnet of that particular composition, the equilibrium surface of reaction (6) and of reaction (7) plots as a surface in $P - P_{\text{H}_2\text{O}} - T$ space. The intersection of the two surfaces, corresponding to the simultaneous solution of the two equations, gives a line (Table 5). The rock with this particular biotite and garnet composition is stable only along this line. The line may be terminated by

1. The intersection with the muscovite equilibrium surface. At $P_{\text{H}_2\text{O}}$ greater than this point, muscovite forms and the mineral assemblage becomes unstable.
2. The intersection with the surface of the beginning of melting.

The stability line of the mineral assemblage of reactions (6) and (7) may be projected onto any convenient surface. Three rocks from the Thor-Odin gneiss dome are shown projected onto the P - T plane (Fig. 22).

NONIDEAL SOLUTIONS

Introduction

The molar free energy of a component in solution \bar{G}_i is defined by

$$\bar{G}_i = \left(\frac{\partial G_{\text{system}}}{\partial n_i} \right)_{P, T, n_j}$$

Table 5

P - P_{H₂O} - T conditions of quartz - sillimanite - K feldspar -
garnet-biotite rocks from the Thor-Odin gneiss dome, B. C.

No	ln L ₍₃₎	ln L ₍₄₎	P _{total}	T°C	f _{H₂O} bars	φ _{H₂O}	P _{H₂O} bars
M 179-2	2.137	-1.537	2 kb	559	139	.461	300
			4 kb	57	337	.500	670
			6 kb	590	782	.650	1 200
M 10-1a	1.918	-1.418	2 kb	643	396	.600	660
			4 kb	660	882	.638	1 320
			6 kb	677	2 111	.813	2 600
66-2	1.800	-1.313	2 kb	710	779	.684	1 140
			4 kb	727	1 629	.770	2 200

It represents the energy change when one mole of substance *i* is added to an infinite reservoir of solution, thus the other moles *n_j* remaining constant. Since it is a partial derivative, it is commonly called the partial molar free energy. It is helpful to remember, however, that it refers to one mole of a substance in a solution of fixed composition, and not to a fraction of a mole.

Although thermodynamics provides no relationship for the variation of \bar{G}_i with composition, the variations of \bar{G} of the components of a solution are related by the Gibbs-Duhem equation. It will be derived for binary solutions following some definitions. In a binary solution, there may be a systematic variation of \bar{G}_A and \bar{G}_B with composition, which permits adequate representation by a solution model. Solution models facilitate various calculations (see e.g. Chatterjee and Froese, 1975) and make it possible to derive activity coefficients from phase diagrams.

Definitions

An ideal solution may be defined by the relationship

$$\left(\frac{\partial \bar{G}}{\partial \ln X} \right)_{P, T} = RT$$

If the molar free energy of a component in a solution is plotted against $\ln X$, it is found that the solution becomes ideal as $X \rightarrow 1$ and as $X \rightarrow 0$ (Fig. 8). For the present purposes, we will use $X = 1$ as the lower limit for integrating the ideal solution equation

$$\int_{G^*}^{\bar{G}^{id}} d\bar{G} = \int_{X=1}^X d \ln X$$

$$\bar{G}^{id} - G^* = RT \ln X$$

where G^* is the molar free energy of the pure component. The behaviour of the real solution will now be compared with this type of ideal solution. In real solutions, the $RT \ln X$ term is not sufficient to account for the energy difference $\bar{G} - G^*$. Instead, it consists of an ideal term and an excess term. However, it is convenient to define a new function, the activity *a*, on the basis of this energy difference:

$$\bar{G} - G^* = RT \ln a$$

Thus the following relationships exist (Fig. 8):

$$(\bar{G} - G^*) = (\bar{G}^{id} - G^*) + (\bar{G} - \bar{G}^{id})$$

$$RT \ln a = RT \ln X + RT \ln \gamma$$

The departure from ideal behaviour is expressed by an energy difference $\bar{G} - \bar{G}^{id}$, the excess free energy of one mole of component in the solution and the activity coefficient γ is defined by it. It follows that $\gamma = a/X$.

The energy difference $\bar{G} - \bar{G}^{id}$ will be abbreviated by \bar{G}^{ex} . It may be expressed by an enthalpy and entropy term. Thus

$$\bar{G}^{ex} = \bar{H}^{ex} - T\bar{S}^{ex} = RT \ln \gamma$$

Similarly one can write for an ideal solution

$$(\bar{G}^{id} - G^*) = (\bar{H}^{id} - H^*) - T(\bar{S}^{id} - S^*) = RT \ln X$$

Differentiating

$$(\bar{G}^{id} - G^*) = RT \ln X$$

with respect to T we obtain

$$\left(\frac{\partial \bar{G}^{\text{id}}}{\partial T}\right)_{P, X} - \left(\frac{\partial G^*}{\partial T}\right)_{P, X} = \left(\frac{\partial RT \ln X}{\partial T}\right)_{P, X}$$

or $-\bar{S}^{\text{id}} + S^* = R \ln X$

Substituting this, it follows that

$$\bar{H}^{\text{id}} = H^*$$

Differentiating

$$(\bar{G}^{\text{id}} - G^*) = RT \ln X$$

with respect to P

$$\left(\frac{\partial \bar{G}^{\text{id}}}{\partial P}\right)_{T, X} - \left(\frac{\partial G^*}{\partial P}\right)_{T, X} = 0; \bar{V}^{\text{id}} = V^*$$

The Gibbs-Duhem Equation

At constant pressure and temperature, the Gibbs free energy of a binary solution is a function of the two mole numbers:

$$G_{\text{system}} = f(n_A, n_B)$$

General differentiation of this function gives

$$dG_{\text{system}} = \bar{G}_A dn_A + \bar{G}_B dn_B$$

However, G_{system} is a homogeneous function of the first degree (see Klotz, 1950) and, according to Euler's theorem,

$$G_{\text{system}} = \bar{G}_A n_A + \bar{G}_B n_B$$

This equation again may be differentiated to give

$$dG_{\text{system}} = \bar{G}_A dn_A + n_A d\bar{G}_A + \bar{G}_B dn_B + n_B d\bar{G}_B$$

Equating the two expressions for dG_{system} we obtain

$$n_A d\bar{G}_A = -n_B d\bar{G}_B$$

This is the Gibbs-Duhem equation. Division by $(n_A + n_B)$ produces a more convenient form:

$$X_A d\bar{G}_A = -X_B d\bar{G}_B$$

Since

$$\bar{G} = G^* + RT \ln a, \text{ where } G^* \text{ is a constant,}$$

$$X_A d \ln a_A = -X_B d \ln a_B$$

or since $a = X\gamma$

$$X_A d \ln X_A + X_A d \ln \gamma_A = -X_B d \ln X_B - X_B d \ln \gamma_B$$

Also for a binary system

$$X_A = 1 - X_B$$

$$\text{or } dX_A = -dX_B$$

or

$$X_A \left(\frac{dX_A}{X_A}\right) = -X_B \left(\frac{dX_B}{X_B}\right)$$

or

$$X_A d \ln X_A = -X_B d \ln X_B$$

Substituting this into the previous form of the Gibbs-Duhem equation we obtain

$$X_A d \ln \gamma_A = -X_B d \ln \gamma_B$$

If the variation of $\ln a$ with X_B is known, the equation may be integrated between appropriate limits (Fig. 23). As a lower limit of integration both activities at one composition (X_B initial) must be known

$$\ln a_A \text{ at } X_B \quad \ln a_B \text{ at } X_B$$

$$\int d \ln a_A = - \int \frac{X_B}{X_A} d \ln a_B$$

$$\ln a_A \text{ at } X_B \text{ initial} \quad \ln a_B \text{ at } X_B \text{ initial}$$

$\ln a_A \text{ at } X_B - \ln a_A \text{ at } X_B \text{ initial} = \text{area under the curve}$

Since at $X_B = 0$, $\ln a_A = 0$, it would be desirable to use this as the lower boundary. However, then $\ln a_B \rightarrow -\infty$ and because of a "tail to infinity" the integral becomes imprecise.

It is better, therefore, to integrate the Gibbs-Duhem equation in the form involving activity coefficients. At $X_B = 0$, $\ln \gamma_A = 0$ and $\ln \gamma_B = a$ constant.

$$\ln \gamma_A \text{ at } X_B \quad \ln \gamma_B \text{ at } X_B$$

$$\int d \ln \gamma_A = - \int \frac{X_B}{X_A} d \ln \gamma_B$$

$$\ln \gamma_A = 0 \text{ at } X_B = 0 \quad \ln \gamma_B \text{ at } X_B = 0$$

The activity coefficient $\ln \gamma_A$ at any value of X_B is given by the area under the curve (Fig. 23).

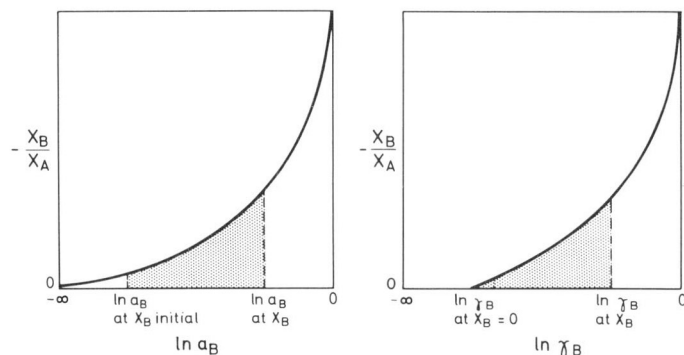


Figure 23. Integration of the Gibbs-Duhem equation.

Determination of Activity Coefficients

- By measuring the energy difference $\bar{G} - G^*$. This determines $RT \ln a$. By subtracting $RT \ln X$, $RT \ln \gamma$ is obtained.

A. In many cases it is possible to measure the fugacity of a component in the saturated vapour over a solution.

For the pure liquid

$$G^* (\text{liquid}) = G (\text{vapour}) = G^\circ + RT \ln f^\circ$$

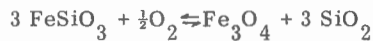
For the solution

$$\bar{G} (\text{solution}) = \bar{G}(\text{vapour}) = G^\circ + RT \ln f$$

where G° is the molar free energy of the gaseous component at unit fugacity and f° is the fugacity in the vapour equilibrated with the pure liquid component. Subtracting we obtain

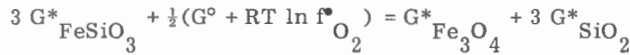
$$\begin{aligned} \bar{G} - G^* &= RT \ln \frac{f}{f^\circ} = RT \ln a \\ a &= \frac{f}{f^\circ} \end{aligned}$$

B. In many cases, it is impossible to measure the fugacity, but the energy difference $\bar{G} - G^*$ may be obtained by performing a reaction involving the pure component and then repeating the reaction involving the component in solution. This method is often useful in oxidation reactions, e. g.

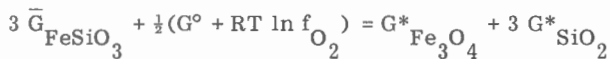


It is essential that Fe_3O_4 and SiO_2 remain pure phases, even when FeSiO_3 occurs in solution.

For the reaction involving pure FeSiO_3



For the reaction involving the solution



Subtracting

$$\bar{G}_{\text{FeSiO}_3} - G^*_{\text{FeSiO}_3} = -\frac{1}{6} RT \ln \frac{f_{\text{O}_2}}{f^\circ_{\text{O}_2}}$$

C. The energy difference may be obtained from galvanic cells if the cell reaction consists of a transfer of a component from the pure phase to a solution and does not involve the electrolyte.

- If the activity coefficients of one component in a binary solution are known, the activity coefficients of the other component may be determined by integrating the Gibbs-Duhem equation.
- Activity coefficients may be obtained from phase diagrams if solution models are assumed. The experimental data required are either a solvus in a two-component system or a set of tie lines between two binary solutions.

The Variation of $RT \ln \gamma$ in Binary Solutions

The excess molar free energy of a component in solution

$$\bar{G}^{\text{ex}} = \bar{G} - \bar{G}^{\text{id}} = RT \ln \gamma$$

is a complicated function of temperature, pressure, and composition. In multi-component solutions, γ of a component varies not only with its own mole fraction but also with the ratio among other mole fractions. In binary solutions there is only one composition variable and the variation of γ is less complicated. Nonideal solution models are based on regularities in the variation of $RT \ln \gamma$ with composition and temperature, at constant pressure.

At constant temperature, the logarithms of the activity coefficients in many solutions fall along relatively simple curves. (Fig. 24).

The two curves are subject to two restrictions

- Raoult's Law. It has been observed that real solutions become ideal as $X \rightarrow 1$. Thus at $X = 1$

$$\left(\frac{\partial \bar{G}}{\partial \ln X} \right)_{P, T} = RT$$

$$\bar{G} - G^* = RT \ln X = RT \ln a$$

$$a = X \text{ and } \gamma = 1$$

Raoult's Law cannot be derived from thermodynamics but represents an independent empirical observation.

- The Gibbs-Duhem equation for a binary solution.

$$X_A d \ln \gamma_A = -X_B d \ln \gamma_B$$

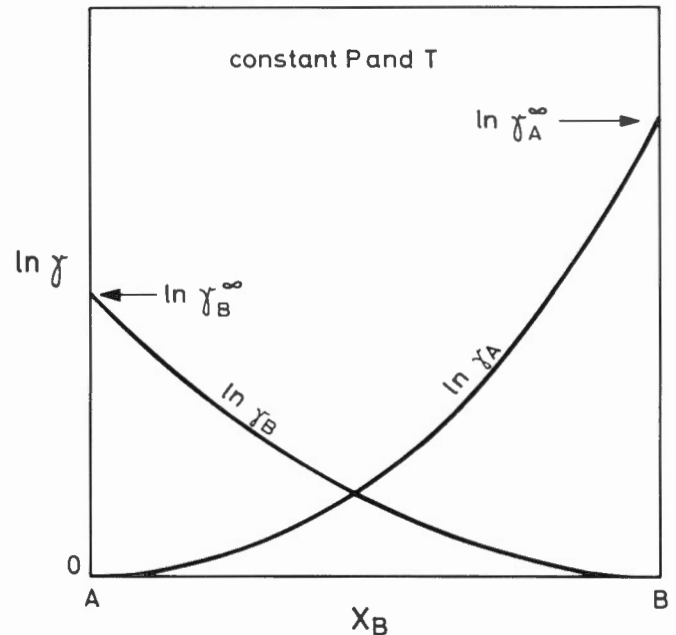


Figure 24. Variation of activity coefficients in a binary solution.

This relates the slopes of the curves but does not determine their shape. At each mole fraction, the slopes must be opposite. This is best seen by dividing both sides by dX_B

$$X_A \left(\frac{\partial \ln \gamma_A}{\partial X_B} \right)_{P, T} = -X_B \left(\frac{\partial \ln \gamma_B}{\partial X_B} \right)_{P, T}$$

The two curves must also be consistent with Henry's Law, which can be derived from Raoult's Law and the Gibbs-Duhem equation. According to Henry's Law, a solution again becomes ideal as $X \rightarrow 0$. A solution following Henry's Law has the same slope $\partial \bar{G}/\partial \ln X$ as one following Raoult's Law.

Therefore, the difference in \bar{G} of a component in a solution following Henry's Law and one following Raoult's Law must be constant.

Thus

$$(\bar{G} - \bar{G}^{id}) \text{ at infinite dilution} = \bar{G}^{ex} = RT \ln \gamma^\infty$$

where γ^∞ is a constant. Since $a = X\gamma$, at infinite dilution $a = X \cdot \text{constant}$.

The derivation is as follows:

The Gibbs-Duhem equation may be written as

$$X_A d \ln a_A = -X_B d \ln a_B$$

For component A following Raoult's Law

$$\ln a_A = \ln X_A$$

$$d \ln a_A = d \ln X_A = \left(\frac{dX_A}{X_A} \right)$$

Substituting this into the Gibbs-Duhem equation

$$dX_A = -X_B d \ln a_B$$

Also for a binary solution

$$dX_A = -dX_B$$

Therefore

$$\left(\frac{-dX_B}{X_B} \right) = -d \ln a_B$$

$$d \ln a_B = d \ln X_B$$

On general integration

$$\ln a_B = \ln X_B + \text{an integration constant}$$

$$a_B = X_B \cdot \text{constant}$$

Thus each activity curve must start at

$$\ln \gamma = 0 \text{ and } X = 1$$

and intersect the $\ln \gamma$ axis (cannot become tangential) at

$$\ln \gamma = \ln \gamma^\infty \text{ and } X = 0$$

For many solutions the variation of $\ln \gamma$ with composition may be empirically expressed by a power series, as suggested by Margules (1895)

$$\ln \gamma_A = \lambda_A (1-X_A) + \alpha_A (1-X_A)^2 + \beta_A (1-X_A)^3 + \dots$$

$$\ln \gamma_B = \lambda_B (1-X_B) + \alpha_B (1-X_B)^2 + \beta_B (1-X_B)^3 + \dots$$

These expressions are consistent with Raoult's and Henry's Laws. Furthermore, the two activity coefficients must conform to the Gibbs-Duhem equation:

$$X_A \left(\frac{\partial \ln \gamma_A}{\partial X_B} \right)_{P, T} + X_B \left(\frac{\partial \ln \gamma_B}{\partial X_B} \right)_{P, T} = 0$$

Therefore, the constants in the two power series are not independent. If the power series are limited to three terms, the following relationship exists.

Differentiating both series we obtain

$$\left(\frac{d \ln \gamma_A}{d X_B} \right) = \lambda_A + 2\alpha_A X_B + 3\beta_A X_B^2$$

$$\left(\frac{d \ln \gamma_B}{d X_A} \right) = \lambda_B + 2\alpha_B X_A + 3\beta_B X_A^2$$

or since $dX_A = -dX_B$

$$\left(\frac{d \ln \gamma_B}{d X_B} \right) = -\lambda_B - 2\alpha_B X_A - 3\beta_B X_A^2$$

These two expressions are substituted into the Gibbs-Duhem equation and $(1-X_B)$ is substituted for X_A

$$(1-X_B) (\lambda_A + 2\alpha_A X_B + 3\beta_A X_B^2)$$

$$- X_B (\lambda_B + 2\alpha_B \{1-X_B\} + 3\beta_B \{1-X_B\}^2) = 0$$

$$\lambda_A + 2\alpha_A X_B + 3\beta_A X_B^2 - \lambda_B X_B - 2\alpha_B X_B^2 - 3\beta_B X_B^3$$

$$- \lambda_B X_B - 2\alpha_B X_B + 2\alpha_B X_B^2 - 3\beta_B X_B + 6\beta_B X_B^2$$

$$- 3\beta_B X_B^3 = 0$$

Collecting terms for each power of X

$$\left. \begin{aligned} X_B^0 (\lambda_A) \\ + X_B (2\alpha_A - \lambda_A - \lambda_B - 2\alpha_B - 3\beta_B) \\ + X_B^2 (3\beta_A - 2\alpha_A + 6\beta_B + 2\alpha_B) \\ + X_B^3 (-3\beta_A - 3\beta_B) \end{aligned} \right\} = 0$$

This equation can only be equal to 0 if the coefficients of each power of X are equal to zero. This requires

$$\begin{aligned} \lambda_B \text{ and } \lambda_A &= 0 \\ \alpha_B &= \alpha_A + \frac{3}{2} \beta_A \\ \beta_B &= -\beta_A \end{aligned}$$

Now the following relationships are obtained:

$$\begin{aligned} \ln \gamma_A^\infty &= \alpha_A + \beta_A \\ \ln \gamma_B^\infty &= \alpha_B + \beta_B = \alpha_A + \frac{1}{2} \beta_A \end{aligned}$$

In view of these relationships, Carlson and Colburn (1942) expressed the constants in the two power series in terms of the activity coefficients at infinite dilution

$$\begin{aligned} \ln \gamma_A &= (2 \ln \gamma_B^\infty - \ln \gamma_A^\infty) (1-X_A)^2 \\ &+ 2(\ln \gamma_A^\infty - \ln \gamma_B^\infty) (1-X_A)^3 \\ \ln \gamma_B &= (2 \ln \gamma_A^\infty - \ln \gamma_B^\infty) (1-X_B)^2 \\ &+ 2(\ln \gamma_B^\infty - \ln \gamma_A^\infty) (1-X_B)^3 \end{aligned}$$

The excess free energy of a component in a solution is given by

$$\bar{G}^{\text{ex}} = \bar{G} - \bar{G}^{\text{id}} = RT \ln \gamma$$

At infinite dilution

$$\bar{G}_\infty^{\text{ex}} = RT \ln \gamma^\infty$$

The equations proposed by Carlson and Colburn may be multiplied by RT giving

$$\begin{aligned} RT \ln \gamma_A &= (2 \bar{G}_B^{\text{ex}} - \bar{G}_A^{\text{ex}}) (1-X_A)^2 \\ &+ 2(\bar{G}_A^{\text{ex}} - \bar{G}_B^{\text{ex}}) (1-X_A)^3 \\ RT \ln \gamma_B &= (2 \bar{G}_A^{\text{ex}} - \bar{G}_B^{\text{ex}}) (1-X_B)^2 \\ &+ 2(\bar{G}_B^{\text{ex}} - \bar{G}_A^{\text{ex}}) (1-X_B)^3 \end{aligned}$$

These may be rearranged to give a form used by Thompson (1967)

$$\begin{aligned} RT \ln \gamma_A &= X_B^2 [\bar{G}_A^{\text{ex}} + 2X_A (\bar{G}_B^{\text{ex}} - \bar{G}_A^{\text{ex}})] \\ RT \ln \gamma_B &= X_A^2 [\bar{G}_B^{\text{ex}} + 2X_B (\bar{G}_A^{\text{ex}} - \bar{G}_B^{\text{ex}})] \end{aligned}$$

In Thompson's notation $\bar{G}_\infty^{\text{ex}} = W_G$.

If the power series are terminated after the second power term, the variation of RT ln γ is symmetrical and $\bar{G}_A^{\text{ex}} = \bar{G}_B^{\text{ex}}$

$$RT \ln \gamma_A = \bar{G}_\infty^{\text{ex}} (1-X_A)^2$$

$$RT \ln \gamma_B = \bar{G}_\infty^{\text{ex}} (1-X_B)^2$$

Thus solutions may be classified according to the number of constants required to describe the variation of RT ln γ with composition. The one-constant Margules model is called a simple mixture by Guggenheim (1967) and often referred to as a "regular" solution in the literature. The term "sub-regular" has been proposed by Hardy (1958) for the two-constant Margules model.

Next, the variation of RT ln γ with temperature at constant composition will be considered. It is convenient to specify ln γ^∞ , the activity coefficient at infinite dilution. The relationship

$$\bar{G}_\infty^{\text{ex}} = RT \ln \gamma^\infty$$

may be expressed by corresponding enthalpy and entropy terms

$$\bar{H}_\infty^{\text{ex}} - T\bar{S}_\infty^{\text{ex}} = RT \ln \gamma^\infty$$

Over a limited temperature range (about 300-400°C) it has been observed that $\bar{H}_\infty^{\text{ex}}$ and $\bar{S}_\infty^{\text{ex}}$ are approximately constant. This implies that \bar{C}_P^{ex} is very small. The assumption that $\bar{H}_\infty^{\text{ex}}$ and $\bar{S}_\infty^{\text{ex}}$ are constant (i. e. that $\bar{C}_P^{\text{ex}} = 0$) is so commonly made that no special name has been given to a solution conforming to this. It follows that in this case ln γ^∞ will vary linearly with 1/T.

It has been found that for some solutions $\bar{S}_\infty^{\text{ex}}$ is very small and one can recognize as a limiting behaviour that $\bar{S}_\infty^{\text{ex}}$ is zero. These are known as regular solutions. Again ln γ^∞ will vary linearly with 1/T.

As another limiting type of solution one could think of the case of $\bar{H}_\infty^{\text{ex}}$ being zero. Such solutions have been called athermal. There are only very few examples of this behaviour among real solutions.

The variation of RT ln γ with composition and with temperature may be combined to give various solution models (Table 6).

The excess molar free energy of a component at infinite dilution also varies with pressure. This is seen from the relationship

$$\bar{G}_\infty^{\text{ex}} = \bar{U}_\infty^{\text{ex}} + P\bar{V}_\infty^{\text{ex}} - T\bar{S}_\infty^{\text{ex}}$$

The excess molar volume of a component at infinite dilution commonly is approximately constant over a limited P-T range.

Table 6

Nonideal binary solution models

<p>Variation of $\bar{G}^{ex} = RT \ln \gamma$ with composition at constant T</p> <p>Variation of $\bar{G}^{ex} = RT \ln \gamma^\infty$ with T</p>	<p>One-constant Margules model "Regular" solution "Simple mixture"</p>	<p>Two-constant Margules model "Sub-regular" solution</p>
	$RT \ln \gamma_A = \bar{G}_A^{ex} (1-X_A)^2$ $RT \ln \gamma_B = \bar{G}_B^{ex} (1-X_B)^2$ $\bar{G}_A^{ex} = \bar{G}_B^{ex} = \bar{G}^{ex}$	$RT \ln \gamma_A = (2\bar{G}_B^{ex} - \bar{G}_A^{ex}) (1-X_A)^2$ $+ 2(\bar{G}_A^{ex} - \bar{G}_B^{ex}) (1-X_A)^3$ $RT \ln \gamma_B = (2\bar{G}_A^{ex} - \bar{G}_B^{ex}) (1-X_B)^2$ $+ 2(\bar{G}_B^{ex} - \bar{G}_A^{ex}) (1-X_B)^3$
$\bar{C}_P^{ex} = 0$ \bar{H}^{ex} and \bar{S}^{ex} are constant	$RT \ln \gamma_A = (\bar{H}^{ex} - T\bar{S}^{ex}) (1-X_A)^2$ $RT \ln \gamma_B = (\bar{H}^{ex} - T\bar{S}^{ex}) (1-X_B)^2$	Substitute $\bar{G}_A^{ex} = (\bar{H}_A^{ex} - T\bar{S}_A^{ex})$ $\bar{G}_B^{ex} = (\bar{H}_B^{ex} - T\bar{S}_B^{ex})$
$\bar{S}^{ex} = 0$; $\bar{G}^{ex} = \bar{H}^{ex}$ Regular solution	$RT \ln \gamma_A = (\bar{H}^{ex}) (1-X_A)^2$ $RT \ln \gamma_B = (\bar{H}^{ex}) (1-X_B)^2$	Substitute $\bar{G}_A^{ex} = \bar{H}_A^{ex}$ and $\bar{G}_B^{ex} = \bar{H}_B^{ex}$
$\bar{H}^{ex} = 0$; $\bar{G}^{ex} = -T\bar{S}^{ex}$ Athermal solution	$RT \ln \gamma_A = (-T\bar{S}^{ex}) (1-X_A)^2$ $RT \ln \gamma_B = (-T\bar{S}^{ex}) (1-X_B)^2$	Substitute $\bar{G}_A^{ex} = -T\bar{S}_A^{ex}$ and $\bar{G}_B^{ex} = -T\bar{S}_B^{ex}$

Activity Coefficients from Exchange Reactions

In some experiments it is possible to measure the compositions of two coexisting binary solutions. Similar data may be obtained from rocks. Davidson (1968) reported the analyses of coexisting orthopyroxene and clinopyroxene from granulites, which he considered to have crystallized at the same temperature. Treating these minerals as binary solutions, it is possible to derive activity coefficients (Froese and Gordon, 1974).

It is possible to write the following exchange reaction



The equilibrium constant in terms of mole fractions (X's) and activity coefficients (γ 's) is given by

$$K_{(8)} = \left(\frac{X_{\text{FeSiO}_3}^{\text{opx}} X_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}}}{X_{\text{MgSiO}_3}^{\text{opx}} X_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}}} \right) \left(\frac{\gamma_{\text{FeSiO}_3}^{\text{opx}} \gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}}}{\gamma_{\text{MgSiO}_3}^{\text{opx}} \gamma_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}}} \right)$$

The term comprising the mole fractions is the distribution coefficient K_D ; therefore,

$$\ln K = \ln K_D + \ln \gamma_{\text{FeSiO}_3}^{\text{opx}} - \ln \gamma_{\text{MgSiO}_3}^{\text{opx}} + \ln \gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}} - \ln \gamma_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}}$$

Using a one-constant solution model for both pyroxenes, the activity coefficients are given by

$$\ln \gamma_{\text{FeSiO}_3}^{\text{opx}} = \ln \gamma^{\infty, \text{opx}} (1-X_{\text{FeSiO}_3}^{\text{opx}})^2$$

$$\ln \gamma_{\text{MgSiO}_3}^{\text{opx}} = \ln \gamma^{\infty, \text{opx}} (X_{\text{FeSiO}_3}^{\text{opx}})^2$$

$$\ln \gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}} = \ln \gamma^{\infty, \text{cpx}} (X_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}})^2$$

$$\ln \gamma_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}} = \ln \gamma^{\infty, \text{cpx}} (1-X_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}})^2$$

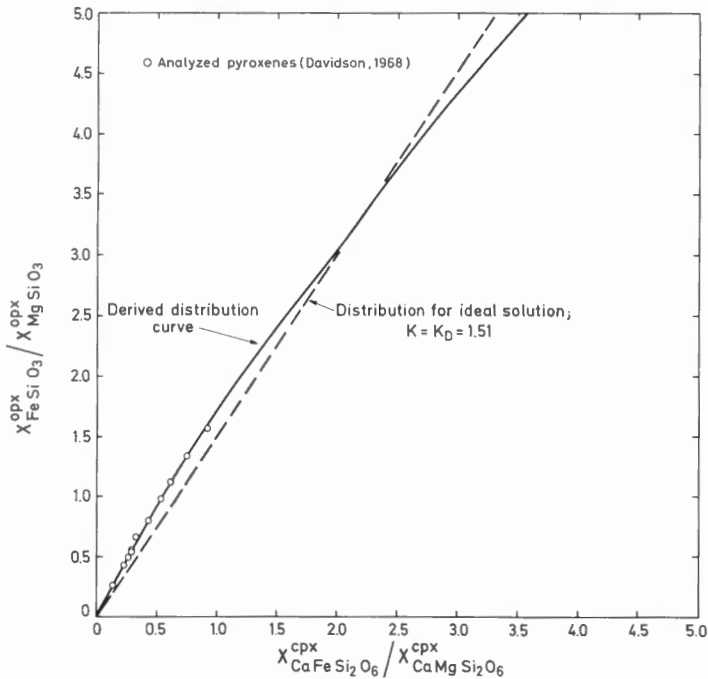


Figure 25. Iron-magnesium distribution between pyroxenes.

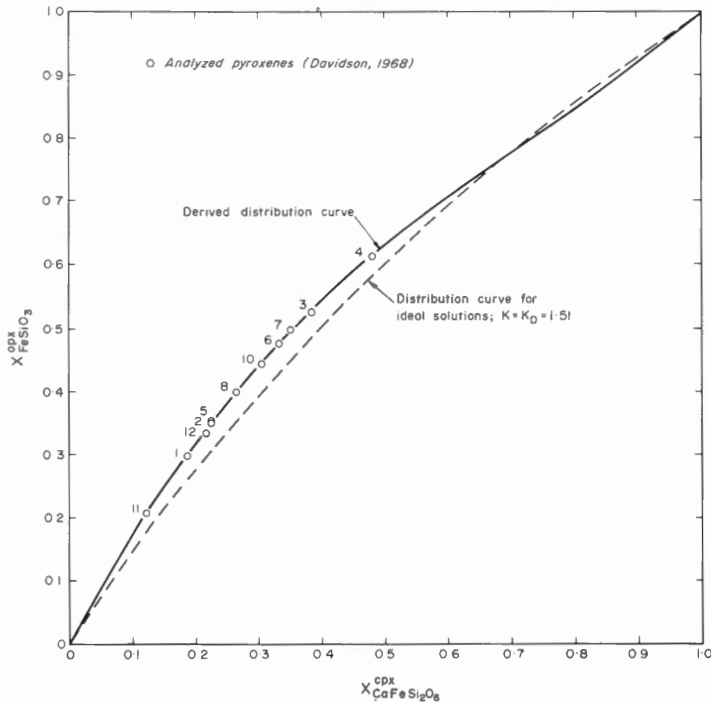


Figure 26. Iron-magnesium distribution between pyroxenes.

Substituting these expressions for the activity coefficients, the following relationship, previously derived by Mueller (1964), is obtained

$$\ln K = \ln K_D + \ln \gamma^{\infty, \text{opx}} (1 - 2X_{\text{FeSiO}_3}^{\text{opx}}) - \ln \gamma^{\infty, \text{cpx}} (1 - 2X_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}})$$

It is seen that the distribution coefficient is dependent on composition if either one or both pyroxenes are nonideal solutions. Davidson (1968) demonstrated such dependence for pyroxenes from Quairading, Australia (Figs. 25 and 26).

For each pair of coexisting pyroxenes, $X_{\text{FeSiO}_3}^{\text{opx}}$, $X_{\text{CaFeSi}_2\text{O}_6}^{\text{cpx}}$, and in K_D are known; thus there is an equation in three unknowns $\ln K$, $\ln \gamma^{\infty, \text{opx}}$, and $\ln \gamma^{\infty, \text{cpx}}$. The compositions of at least three pairs of coexisting pyroxenes must be known to solve for the unknowns. Davidson (1968) reports analyses of 11 pairs, neglecting one sample which shows signs of textural disequilibrium. The three unknowns obtained from a least-squares fit to the available data are:

$$\ln K = 0.412 \quad (K = 1.51); \quad \ln \gamma^{\infty, \text{opx}} = 0.447; \\ \ln \gamma^{\infty, \text{cpx}} = 0.625$$

It is possible to substitute a more complicated solution model and solve for more unknowns but commonly the data are not sufficiently accurate to warrant this. For instance, in applying this method to the distribution of Fe and Mg between olivine and aqueous solution, Saxena (1972) found that only the one-constant model gave consistent results.

It is more common to use at least a two-constant model if the activity coefficients of one solution are known. As an example, the exchange of K and Na between aqueous solution and sanidine will be considered (Orville, 1963; Thompson and Waldbaum, 1968):



Aqueous solutions and KCl and NaCl at 2 kb and high temperatures are practically ideal and one can write at constant P, T and Cl concentration

$$K_{(9)} = \left(\frac{X_{\text{Or}} X_{\text{Na}}^{\text{sol}}}{X_{\text{Ab}} X_{\text{K}}^{\text{sol}}} \right) \left(\frac{\gamma_{\text{Or}}}{\gamma_{\text{Ab}}} \right)$$

where the term comprising the mole fractions is the distribution coefficient K_D . Therefore:

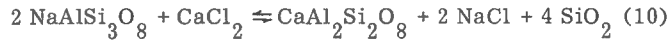
$$\ln K = \ln K_D + \ln \gamma_{\text{Or}} - \ln \gamma_{\text{Ab}}$$

Into this equation one can substitute

$$\begin{aligned} \ln \gamma_{Or} &= (2 \ln \gamma_{Ab}^{\infty} - \ln \gamma_{Or}^{\infty}) (1 - X_{Or})^2 \\ &+ 2(\ln \gamma_{Or}^{\infty} - \ln \gamma_{Ab}^{\infty}) (1 - X_{Or})^3 \\ \ln \gamma_{Ab} &= (2 \ln \gamma_{Or}^{\infty} - \ln \gamma_{Ab}^{\infty}) (1 - X_{Ab})^2 \\ &+ 2(\ln \gamma_{Ab}^{\infty} - \ln \gamma_{Or}^{\infty}) (1 - X_{Ab})^3 \end{aligned}$$

There now is an equation in three unknowns $\ln K$, $\ln \gamma_{Or}^{\infty}$, and $\ln \gamma_{Ab}^{\infty}$ for each pair of analyzed sanidine and solution. If more than three pairs are available, the unknowns may be determined by a least-squares method.

This method was used by Saxena and Ribbe (1972) to derive activity coefficients in plagioclase, based on Orville's (1972) experiments. The exchange reaction in this case is



At constant P, T and Cl concentration

$$K_{(10)} = \left(\frac{X_{An} X_{Na}^2}{X_{Ab}^2 X_{Ca}} \right) \left(\frac{\gamma_{An}}{\gamma_{Ab}^2} \right)$$

where X_{An} and X_{Ab} are the mole fractions $\text{An}/(\text{Ab} + \text{An})$ and $\text{Ab}/(\text{Ab} + \text{An})$ and X_{Na} and X_{Ca} are the atomic fractions $\text{Na}/(\text{Na} + \text{Ca})$ and $\text{Ca}/(\text{Na} + \text{Ca})$ in solution. Designating the term comprising the X's as K_D

$$\ln K = \ln K_D + \ln \gamma_{An} - 2 \ln \gamma_{Ab}$$

Again, a two-constant solution model for plagioclase may be substituted into this equation resulting in the unknowns $\ln K$, $\ln \gamma_{An}^{\infty}$, and $\ln \gamma_{Ab}^{\infty}$.

Activity Coefficients from the Solvus

Exchange reactions involve two binary solutions in a three-component system. Therefore, there is a bundle of tie lines at one temperature. In contrast, if a two-component system exhibits a solvus, there is only one tie line at each temperature.

But, at each temperature there are two equilibria



$$K_{(11a)} = \frac{a_A^{\text{II}}}{a_A^{\text{I}}} = \frac{X_A^{\text{II}} \gamma_A^{\text{II}}}{X_A^{\text{I}} \gamma_A^{\text{I}}} \quad K_{(11b)} = \frac{a_B^{\text{II}}}{a_B^{\text{I}}} = \frac{X_B^{\text{II}} \gamma_B^{\text{II}}}{X_B^{\text{I}} \gamma_B^{\text{I}}}$$

However, the standard state of A in both phases is the same, i. e. the solid phase of pure A. For this reason

$\Delta G^{\circ} = 0$ and since $\Delta G^{\circ} = -RT \ln K$, $K = 1$ and

$$a_A^{\text{I}} = a_A^{\text{II}}$$

For the same reason

$$a_B^{\text{I}} = a_B^{\text{II}}$$

Or, in logarithmic form

$$\ln X_A^{\text{I}} + \ln \gamma_A^{\text{I}} = \ln X_A^{\text{II}} + \ln \gamma_A^{\text{II}}$$

$$\ln X_B^{\text{I}} + \ln \gamma_B^{\text{I}} = \ln X_B^{\text{II}} + \ln \gamma_B^{\text{II}}$$

Substituting a two-constant solution model for the logarithms of the activity coefficients it is possible to solve two equations for two unknowns, $\ln \gamma_A^{\infty}$ and $\ln \gamma_B^{\infty}$, at each temperature.

Activity coefficients have been derived for sanidine-albite (Thompson and Waldbaum, 1969 a; Luth and Fenn, 1973) halite-sylvite (Thompson and Waldbaum, 1969 b; Green, 1970), muscovite-paragonite (Eugster *et al.*, 1972); and magnetite-hercynite (Froese, 1973a).

OXIDATION AND SULPHIDATION REACTIONS

Stability of Iron Sulphides and Magnetite

Toulmin and Barton (1964) measured f_{S_2} at various temperatures over pyrrhotites of known composition. They expressed the composition of pyrrhotite by the mole fraction N_{FeS} in the system $\text{FeS} - S_2$ and calculated the activity of FeS in pyrrhotite by applying the Gibbs-Duhem equation to this system.

This choice of components for the purpose of integrating the Gibbs-Duhem equation is not strictly correct because FeS is an intermediate compound in the system $\text{Fe} - S$. The Gibbs-Duhem equation for the Gibbs free energy is valid only if $\bar{G} \rightarrow -\infty$ as $X \rightarrow 0$. Therefore, the fugacity in the vapour equilibrated with the solution must approach zero. However, in analogy with other intermediate compounds, it is probable that f_{S_2} over stoichiometric FeS remains finite. But as the stoichiometric composition is approached there is a very rapid decrease in f_{S_2} and the approximation that $f_{S_2} \rightarrow 0$ as $N_{S_2} \rightarrow 0$, inherent in applying the Gibbs-Duhem equation to the system $\text{FeS} - S_2$, probably is reasonable. In order to be consistent, it is appropriate to use a hypothetical component FeS having the property that $\log f_{S_2} \rightarrow -\infty$ as $N_{FeS} \rightarrow 1$. However, for practical purposes, the properties of hypothetical FeS and stoichiometric FeS may be regarded as being the same.

The activities of S_2 and hypothetical FeS in pyrrhotite are related by the Gibbs-Duhem equation:

$$N_{FeS} d \log a_{FeS} = (N_{FeS} - 1) d \log a_{S_2}$$

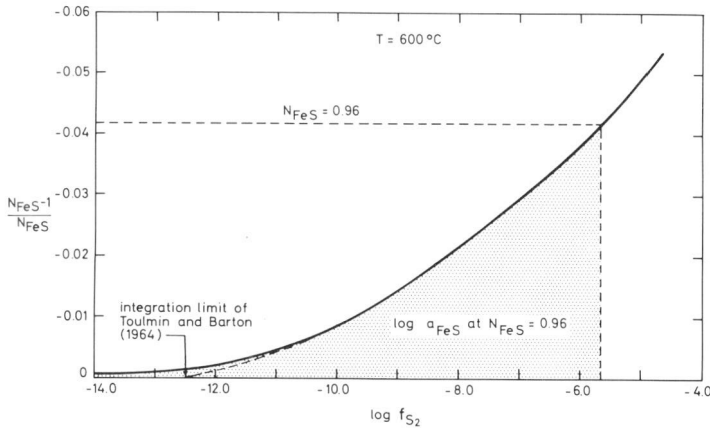


Figure 27. Integration of the Gibbs-Duhem equation for pyrrhotite in terms of activities.

The activity of S_2 in pyrrhotite is given by

$$a_{S_2} = \frac{f_{S_2} \text{ over pyrrhotite}}{f^{\bullet}_{S_2} \text{ over } S_2 \text{ with pyrrhotite structure}}$$

or

$$\log a_{S_2} = \log f_{S_2} - \log f^{\bullet}_{S_2}$$

Since $f^{\bullet}_{S_2}$ over S_2 "pyrrhotite" is constant at fixed P and T

$$d \log a_{S_2} = d \log f_{S_2}$$

and the Gibbs-Duhem equation may be written as

$$N_{FeS} d \log a_{FeS} = (N_{FeS} - 1) d \log f_{S_2}$$

This equation may be integrated, in principle, from the boundary condition $a_{FeS} = 1$ at $N_{FeS} = 1$ and $f_{S_2} = 0$ at $N_{FeS} = 1$. Thus

$$\int_{\log a_{FeS} = 0}^{\log a_{FeS}} d \log a_{FeS} = \int_{\log f_{S_2} = -\infty}^{\log f_{S_2}} \left(\frac{N_{FeS} - 1}{N_{FeS}} \right) d \log f_{S_2}$$

This integration poses a problem because $\log f_{S_2} = -\infty$

at $N_{FeS} = 1$. Toulmin and Barton (1964), therefore,

used f_{S_2} corresponding to the coexistence of pyrrhotite and iron as the lower integration limit (Fig. 27). This is known from the reaction

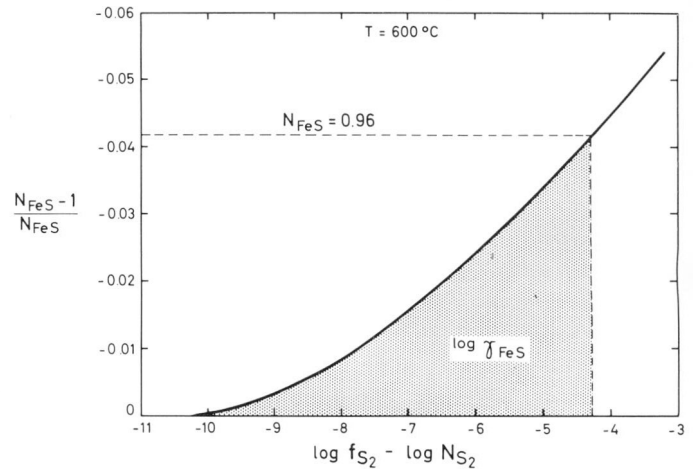
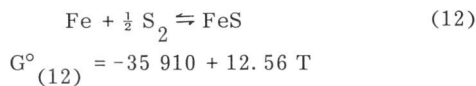


Figure 28. Integration of the Gibbs-Duhem equation for pyrrhotite in terms of activity coefficients.

The value for the standard free energy change is taken from Richardson and Jeffes (1952). At $600^{\circ}C$, $\log f_{S_2} = -12.49$. Neglecting the area at very low f_{S_2} turns out to be a satisfactory approximation.

Because of the "tail to infinity" problem, the Gibbs-Duhem equation is more commonly integrated in the form

$$N_{FeS} d \log \gamma_{FeS} = (N_{FeS} - 1) d \log \gamma_{S_2}$$

The activity coefficient of S_2 is given by

$$\gamma_{S_2} = \frac{a_{S_2}}{N_{S_2}} = \frac{f_{S_2}}{f^{\bullet}_{S_2} N_{S_2}}$$

This activity cannot be obtained, because $f^{\bullet}_{S_2}$ the fugacity over pure S_2 "pyrrhotite" cannot be measured. However

$$\log \gamma_{S_2} = \log f_{S_2} - \log N_{S_2} - \log f^{\bullet}_{S_2}$$

And since $f^{\bullet}_{S_2}$ is a constant

$$d \log \gamma_{S_2} = d(\log f_{S_2} - \log N_{S_2})$$

Now it is possible to integrate from the boundary condition $\gamma_{FeS} = 1$ at $N_{FeS} = 1$ and $(f_{S_2}/N_{S_2}) = \text{constant}$ at $N_{FeS} = 1$ (Fig. 28).

$$\int d \log \gamma_{FeS} = \int \left(\frac{N_{FeS} - 1}{N_{FeS}} \right) d(\log f_{S_2} - \log N_{S_2})$$

$$\log \gamma_{FeS} = 0 \quad (\log f_{S_2} - \log N_{S_2}) = \text{constant}$$

Table 7

The pyrrhotite-vapour equilibrium at 600°C and 1 atm

N_{FeS}	X_{FeS}	a_{FeS}	$\log f_{\text{S}_2}$
1.0000	1.0000	1.000	$-\infty$
*0.9988	0.9977	0.998	- 12.49
0.9900	0.9802	0.969	- 9.68
0.9800	0.9608	0.917	- 8.10
0.9700	0.9417	0.850	- 6.81
0.9600	0.9231	0.774	- 5.68
0.9500	0.9048	0.692	- 4.65
0.9400	0.8868	0.609	- 3.69
0.9300	0.8692	0.528	- 2.80
**0.9202	0.8522	0.453	- 1.98

* Coexisting with iron

** Coexisting with pyrite

Table 8

The pyrrhotite-vapour equilibrium at 600°C and 2 kb

N_{FeS}	X_{FeS}	a_{FeS}	$\log f_{\text{S}_2}$	$\log f_{\text{O}_2}$
1.0000	1.0000	1.000	$-\infty$	
*0.9989	0.9979	0.998	-12.22	-24.38
0.9900	0.9802	0.969	- 9.33	-22.19
0.9800	0.9608	0.917	- 7.75	-20.97
0.9700	0.9417	0.850	- 6.46	-19.96
0.9600	0.9231	0.774	- 5.33	-19.05
0.9500	0.9048	0.692	- 4.30	-18.20
0.9400	0.8868	0.609	- 3.34	-17.40
0.9300	0.8692	0.528	- 2.45	-16.64
**0.9233	0.8576	0.476	- 1.89	-16.15

*Coexisting with iron

**Coexisting with pyrite

Instead of graphical integration, a more convenient analytical procedure may be used. From now on, the composition of pyrrhotite will be expressed by the mole fraction X_{FeS} in the system $\text{FeS} - \square\text{S}$. This corresponds to the solution mechanism, i. e. the omission of iron atoms. The composition of pyrrhotite is often stated in terms of atomic fractions. The following relationships hold:

$$N_{\text{FeS}} = \left(\frac{\text{FeS}}{\text{FeS} + \text{S}_2} \right) = 2 \left(\frac{\text{Fe}}{\text{Fe} + \text{S}} \right)$$

$$X_{\text{FeS}} = \left(\frac{\text{FeS}}{\text{FeS} + \square\text{S}} \right) = \left(\frac{\text{Fe}}{\text{S}} \right)$$

The excess partial molar free energy of the two components in pyrrhotite may be expressed by a two-constant Margules model:

$$RT \ln \gamma_{\square\text{S}} = (2 \bar{G}_{\text{FeS}}^{\text{ex}} - \bar{G}_{\square\text{S}}^{\text{ex}}) X_{\text{FeS}}^2 + 2 (\bar{G}_{\square\text{S}}^{\text{ex}} - \bar{G}_{\text{FeS}}^{\text{ex}}) X_{\text{FeS}}^3$$

$$RT \ln \gamma_{\text{FeS}} = (2 \bar{G}_{\square\text{S}}^{\text{ex}} - \bar{G}_{\text{FeS}}^{\text{ex}}) (1 - X_{\text{FeS}})^2 + 2 (\bar{G}_{\text{FeS}}^{\text{ex}} - \bar{G}_{\square\text{S}}^{\text{ex}}) (1 - X_{\text{FeS}})^3$$

The coexistence of pyrrhotite and sulphur vapour implies the following equilibrium



$$\ln K = \frac{1}{2} \ln f_{\text{S}_2} - \ln (1 - X_{\text{FeS}}) - \ln \gamma_{\square\text{S}}$$

or

$$RT \ln K = -\Delta G^\circ (13) = \frac{1}{2} RT \ln f_{\text{S}_2} - RT \ln (1 - X_{\text{FeS}}) - RT \ln \gamma_{\square\text{S}} \quad (13a)$$

By substituting the solution model for $RT \ln \gamma_{\square\text{S}}$ at any given T , $\log f_{\text{S}_2}$, and X_{FeS} , an equation in three unknowns is obtained, i. e. $\Delta G^\circ (13)$, $\bar{G}_{\text{FeS}}^{\text{ex}}$, and $\bar{G}_{\square\text{S}}^{\text{ex}}$. By assuming a linear temperature dependence for the three unknowns, each may be expressed by a slope and intercept. Thus the relationship (13a) at any given T , $\log f_{\text{S}_2}$, and X_{FeS} becomes a linear equation in six unknowns. The author and A. Gunter picked 30 combinations of pyrrhotite composition and temperature within the experimental range of Toulmin and Barton (1964). For each composition, $\log f_{\text{S}_2}$ was calculated according to their equation (8). Treating T , $\log f_{\text{S}_2}$, and X_{FeS} as given in each case, a linear equation in six unknowns, i. e. slope and intercept of $\Delta G^\circ (13)$, $\bar{G}_{\text{FeS}}^{\text{ex}}$, and $\bar{G}_{\square\text{S}}^{\text{ex}}$, was calculated. Solving for the unknowns by the method of least-squares, the following results were obtained:

$$\Delta G^\circ (13) = - 57 966 + 34.824 T$$

$$\bar{G}_{\text{FeS}}^{\text{ex}} = - 141 563 + 126.825 T$$

$$\bar{G}_{\square\text{S}}^{\text{ex}} = - 93 911 + 59.250 T$$

It is now possible to calculate a_{FeS} and $a_{\text{□S}}$ at any FeS and, therefore, plot reactions (12) and (13) on a diagram of $\log f_{\text{S}_2}$ vs. X_{FeS} (Fig. 29, Table 7).

Now consider the reaction



$$K_{(14)} = \frac{1}{\left(f_{\text{S}_2}\right)^{\frac{1}{2}} \left(a_{\text{FeS}}\right)}$$

The composition of pyrrhotite coexisting with pyrite is known (Toulmin and Barton, 1964). The activity coefficients of FeS and □S may be calculated at the appropriate temperature and composition. According to reaction (13) this determines f_{S_2} . Knowing both a_{FeS} and f_{S_2} , it is possible to calculate $\Delta G^\circ_{(14)}$. In the temperature range 599 – 743°C, $\Delta G_{(14)}$ may be expressed by the following equation

$$\Delta G_{(14)} = -36\,774 + 36.006 T$$

Reaction (14) is also plotted in Figure 29. The intersection of reaction (13) with reaction (12) and (14) gives the composition of pyrrhotite coexisting with iron and pyrite, respectively.

All reactions so far have been considered at 1 atm. If the molar volumes of pyrrhotite (Fleet, 1968) are plotted against X_{FeS} , an approximately linear relationship is obtained (Fig. 30). This means that there is no excess volume of mixing. Since

$$\left(\frac{\partial \bar{G}^{\text{ex}}}{\partial P}\right)_T = \left(\frac{\partial RT \ln \gamma}{\partial P}\right)_T = \bar{V}^{\text{ex}}$$

it follows that the activity coefficients are independent of pressure.

In order to solve for $\log f_{\text{S}_2}$ at any composition at a pressure other than 1 atm, the following formula is used

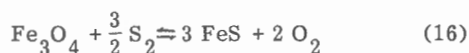
$$\Delta G^\circ = -RT \ln K - \Delta V_s (P-1)$$

The molar volume of the solids is given by Robie *et al.* (1967) except that of □S in the pyrrhotite structure. This is obtained by extrapolating the molar volumes (Fleet, 1968) to $X_{\text{□S}} = 1$ ($X_{\text{FeS}} = 0$). The three reactions discussed so far have been plotted at 2 kb (Fig. 29, Table 8).

Following Holland (1959), it is convenient to plot the stability of the iron oxides and sulphides on a diagram of $\log f_{\text{O}_2}$ vs. $\log f_{\text{S}_2}$ (Fig. 31). First, the following reaction is required



The standard free energy change of this reaction may be obtained from Eugster and Wones (1962). The pyrrhotite-magnetite boundary is given by the reaction



This is obtained by combining reactions (12) and (15). For reaction (16) there is the relationship

$$\Delta G^\circ_{(16)} = -RT \ln \frac{\left(f_{\text{O}_2}\right)^2 \left(a_{\text{FeS}}\right)^3}{\left(f_{\text{S}_2}\right)^{3/2}} - \Delta V_s (P-1)$$

At any pyrrhotite composition, γ_{FeS} and $\gamma_{\text{□S}}$ are known. From reaction (13) $\log f_{\text{S}_2}$ is obtained. Now the above equation may be solved for $\log f_{\text{O}_2}$ (Table 8). In this way, the pyrrhotite-magnetite boundary is plotted at any given pressure and temperature. Thermochemical data for reactions (12) to (16), used in the construction of Fig. 31, are listed in Table 9.

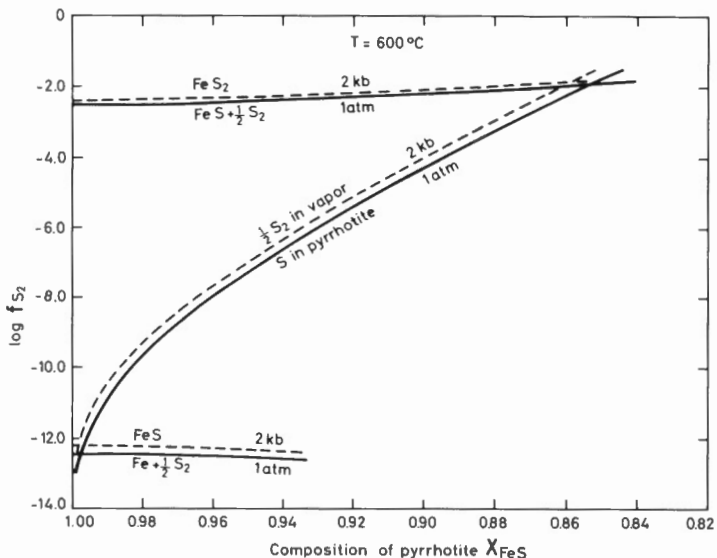


Figure 29. Reactions in the system iron-sulphur.

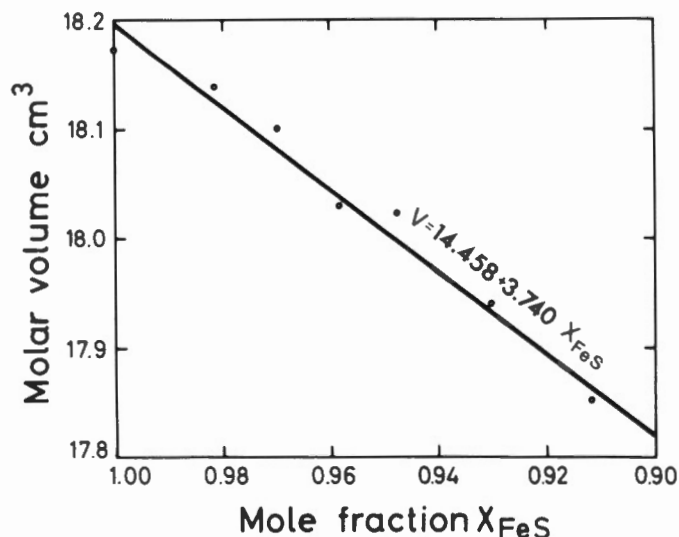


Figure 30. Molar volume of pyrrhotite.

Table 9

Equilibria in the system Fe-S-O

Reaction	ΔG° at 600°C	$\Delta V \frac{\text{cal}}{\text{sbar}}$	1999 ΔV_s
(12) $\text{Fe} + \frac{1}{2} \text{S}_2 \rightleftharpoons \text{FeS}$	- 24 943	. 2655	531
(13) $\square\text{S in po} \rightleftharpoons \frac{1}{2} \text{S}_2 \text{ in vapour}$	- 27 559	-. 3455	-691
(14) $\text{FeS} + \frac{1}{2} \text{S}_2 \rightleftharpoons \text{FeS}_2$	- 5 335	. 1372	274
(15) $3 \text{Fe} + 2 \text{O}_2 \rightleftharpoons \text{Fe}_3\text{O}_4$	-195 932	. 5556	1111
(16) $\text{Fe}_3\text{O}_4 + \frac{3}{2} \text{S}_2 \rightleftharpoons 3\text{FeS} + 2\text{O}_2$	121 103	. 2408	481

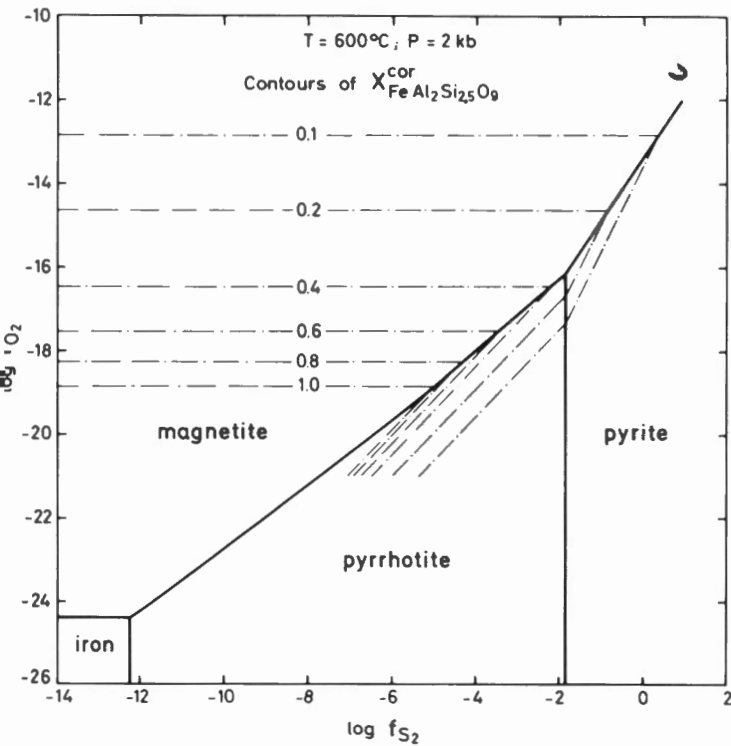


Figure 31. Stability of iron sulphides and magnetite.

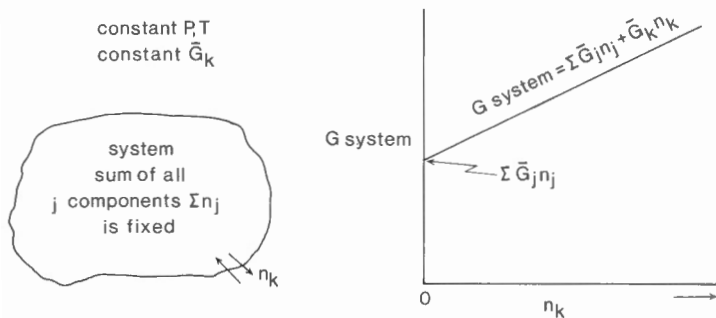


Figure 32. Equilibrium in an open system.

Beyond the triple point pyrrhotite-magnetite-pyrite, there is the reaction



The slope of this reaction is obtained from the reaction equation

$$K_{(17)} = \frac{(f_{\text{O}_2})^2}{(f_{\text{S}_2})^3}$$

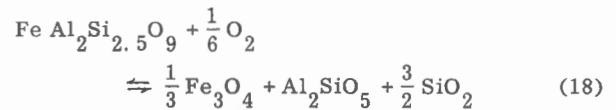
$$\log K = 2 \log f_{\text{O}_2} - 3 \log f_{\text{S}_2}$$

$$\log f_{\text{O}_2} = \frac{3}{2} \log f_{\text{S}_2} + \frac{\log K}{2}$$

The slope on the $\log f_{\text{O}_2}$ vs. $\log f_{\text{S}_2}$ diagram is 3/2.

The Oxidation and Sulphidation of Cordierite

Froese (1973) derived the free energy change of the reaction



The designation ΔG° in that paper is, according to the present notation, $\Delta G^\circ + \Delta V_s$ (2000 - 1). At 600°C

$$\Delta G^\circ + 1999 (\Delta V_s) = -12 530 = -RT \ln \frac{1}{(f_{\text{O}_2})^{1/6} (a_{\text{Fe cor}}^{\text{cor}})}$$

Writing the formula of cordierite with one iron atom and assuming ideal solution

$$a_{\text{FeAl}_2\text{Si}_{2.5}\text{O}_9}^{\text{cor}} = X_{\text{FeAl}_2\text{Si}_{2.5}\text{O}_9}^{\text{cor}}$$

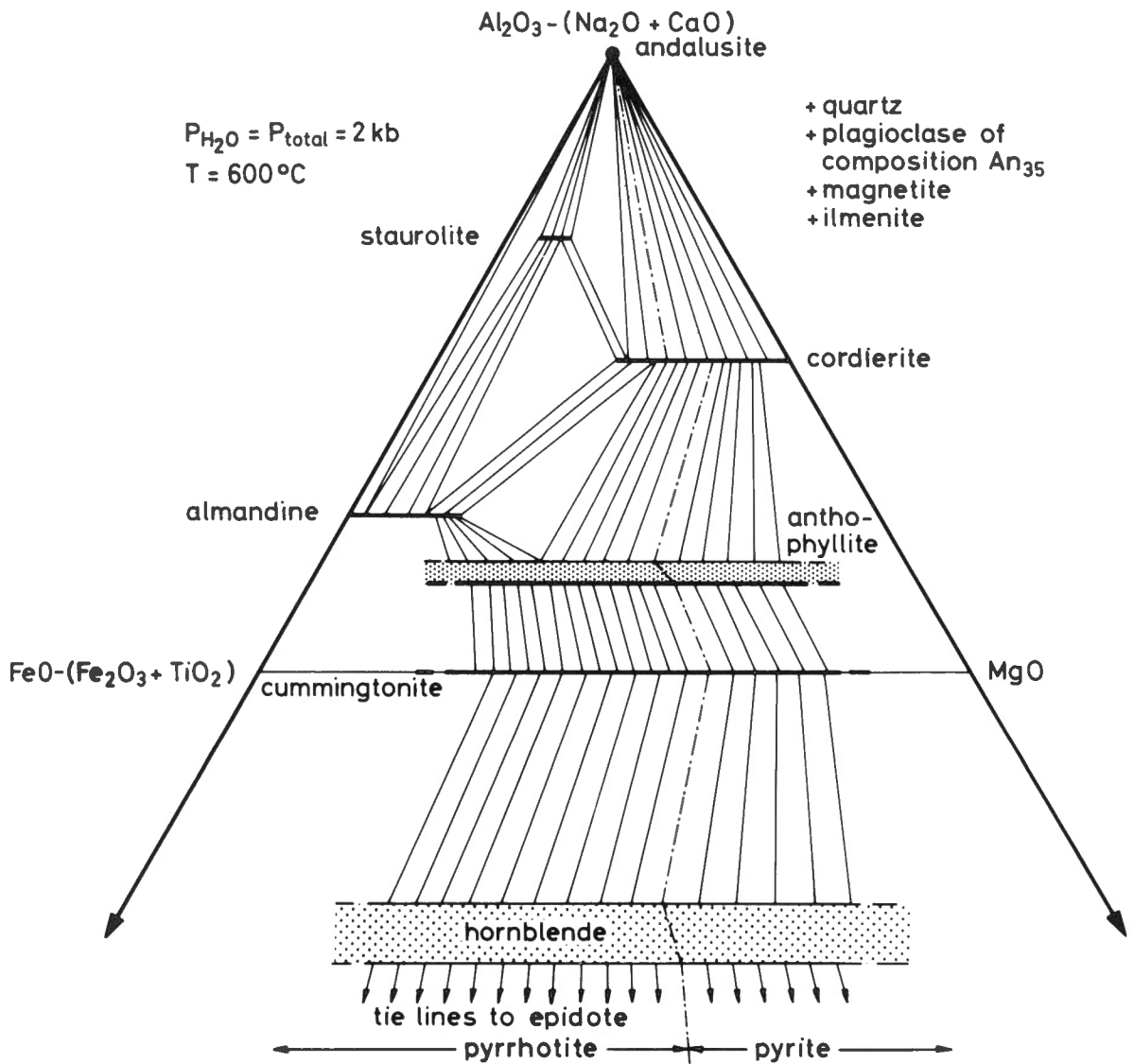
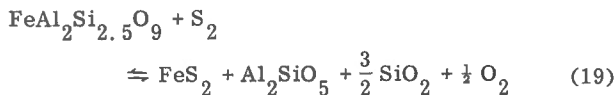


Figure 33. Mineral assemblages from the Coronation mine.

Oxidation reactions may be plotted as a series of contours in the magnetite stability field of a $\log f_{O_2}$ vs. $\log f_{S_2}$ diagram (Froese, 1971). For cordierite this is shown in Fig 31.

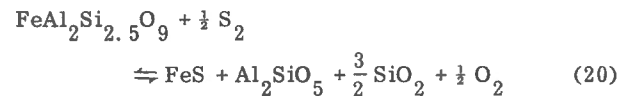
Some contours intersect the pyrite-magnetite boundary and traverse the pyrite field with a slope given by the reaction



$$\log K = \frac{1}{2} \log f_{O_2} - \log f_{S_2}$$

$$\text{or } \log f_{O_2} = 2 \log f_{S_2} + 2 \log K$$

These contours intersect the pyrite - pyrrhotite boundary and pass into the pyrrhotite field. Other contours enter into the pyrrhotite field by intersecting the magnetite-pyrrhotite boundary. Within the pyrrhotite field, the contours represent the reaction



Because a_{FeS} is less than one, the slope will be somewhat steeper than one.

At 600°C and 2 kb, the triple point magnetite-pyrite-pyrrhotite occurs at $\log f_{O_2} = -16.15$. For this oxygen fugacity, the corresponding composition of cordierite ($X_{FeAl_2Si_{2.5}O_9} = 0.36$) may be obtained from reaction (18).

Graphical Representation of Sulphidation Reactions

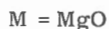
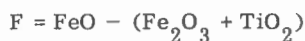
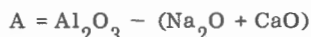
In the graphical representation of mineral assemblages it is convenient to regard systems with fixed amounts of some components (j) and open with respect to other components (k). The partial molar free energy \bar{G}_k of the k components is imposed on the system by the boundary conditions (Thompson, 1970). Consider a system with one k component

$$G_{\text{system}} = \sum \bar{G}_j n_j + \bar{G}_k n_k$$

where n refers to the number of moles.

If \bar{G}_k is constant, G_{system} is a linear function of n_k (Fig. 32). For any given n_k , G_{system} is a minimum at equilibrium; therefore, $\sum \bar{G}_j n_j$ is a minimum. This relationship can be generalized to a system containing several k components.

Therefore, a system with fixed amounts of j components is completely determined by the imposed conditions of P, T and \bar{G}_k of the k components. At constant pressure and temperature, the molar free energy of a gas species in an ideal gaseous solution is determined by specifying its partial pressure. The molar free energy of a solid constituent is determined by its presence as a pure phase or as a component in a phase of specified composition. Thus the presence of quartz, plagioclase of fixed composition, magnetite, and ilmenite determines the molar free energies of SiO_2 , $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, $\text{CaO}\cdot\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3\cdot\text{FeO}$ and $\text{TiO}_2\cdot\text{FeO}$. These may be regarded as k components and the oxides not combined in the k components constitute j components defined as follows



Mineral assemblages from the Coronation mine in Saskatchewan (Froese, 1969a and b; Whitmore, 1969) may be conveniently shown on a triangular diagram using these components (Fig. 33). The tie lines shown are based on the following distribution of iron and magnesium:

cordierite-anthophyllite (Lal and Moorhouse, 1969)
cummingtonite-anthophyllite (Stout, 1971)
cummingtonite-hornblende (Stout, 1971)

On this diagram, the tie line andalusite-cordierite coexisting with pyrite and pyrrhotite (in the presence of quartz and magnetite) may be plotted. The composition of cordierite was calculated in the previous section ($X_{\text{FeAl}_2\text{Si}_2.5\text{O}_9} = 0.36$). Bachinski (1974) measured

the composition of two cordierites from the Coronation mine coexisting with magnetite, pyrite, pyrrhotite and anthophyllite ($X_{\text{FeAl}_2\text{Si}_2.5\text{O}_9} = 0.19$ and 0.22). The

tie line with $X_{\text{FeAl}_2\text{Si}_2.5\text{O}_9} = 0.22$ is shown in Fig. 33.

It is part of a boundary dividing the diagram into a Mg-rich portion coexisting with pyrite and an Fe-rich portion coexisting with pyrrhotite. This boundary has been extended diagrammatically from anthophyllite to hornblende.

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