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Thermodynamics of Minerals and Melts

Edited by
R. C. Newton
A. Navrotsky
B. J. Wood



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With 66 Figures



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Series Preface

Today large numbers of geoscientists apply thermodynamic theory to solutions of a variety of problems in earth and planetary sciences. For most problems in chemistry, the application of thermodynamics is direct and rewarding. Geoscientists, however, deal with complex inorganic and organic substances. The complexities in the nature of mineralogical substances arise due to their involved crystal structure and multicomponental character. As a result, thermochemical solutions of many geological-planetological problems should be attempted only with a clear understanding of the crystal-chemical and thermochemical character of each mineral. The subject of physical geochemistry deals with the elucidation and application of physico-chemical principles to geosciences. Thermodynamics of mineral phases and crystalline solutions form an integral part of it. Developments in mineralogic thermodynamics in recent years have been very encouraging, but do not easily reach many geoscientists interested mainly in applications. This series is to provide geoscientists and planetary scientists with current information on the developments in thermodynamics of mineral systems, and also provide the active researcher in this rapidly developing field with a forum through which he can popularize the important conclusions of his work. In the first several volumes, we plan to publish original contributions (with an abundant supply of background material for the uninitiated reader) and thoughtful reviews from a number of researchers on mineralogic thermodynamics, on the application of thermochemistry to planetary phase equilibria (including meteorites), and on kinetics of geochemical reactions.

The success of this venture is assured because of the great interest shown by many scientists who have adorned the list of editors for the series, and by many others who have promised to contribute to the series in coming years. The launching of the series with articles by many eminent physical geochemists was made possible through the efforts of Bob Newton, Alex Navrotsky, and Bernie Wood.

The staff of Springer-Verlag deserves thanks from the geoscientists for accepting the care of the publication of these volumes. I sincerely hope that this series will not only keep geochemists up to date in the field, but will also prove useful in opening up new avenues of research, both in the basic

formulation of thermodynamic theory as applied to planetary research and in direct application to the solution of genetic problems.

November 17, 1980

S. K. Saxena
Brooklyn, New York

Volume Preface

This volume is the outgrowth of a seminar series on thermodynamics of mineral systems held in the spring of 1979 in the Department of the Geophysical Sciences at the University of Chicago. Many of the contributors to this volume participated in the seminar series.

This book is intended to give a cross-section of current activity in many different areas of thermodynamical geochemistry. The contributions were solicited from the standpoints of scope and diversity rather than comprehensive treatment of any particular field. The application of thermodynamics to the earth and planetary sciences is now so great that no single, moderate-sized book can sample every sub-field.

The first article of this volume is a commentary by George Tunell on the basic equation of chemical equilibrium of J. Willard Gibbs, which underlies all of chemical thermodynamics. The succeeding papers are grouped with "minerals" or "melts" and, within each group, generally proceed from general to specialized to applied.

No attempt is made to militate one system of units over another or to achieve uniformity of symbol usage among all of the authors; these things are left to the authors' preferences. The systems of units and the symbols used in this book are all in wide use at the present time. Where many different symbols are used in a paper, a table of notation is given.

The editors hereby acknowledge the invaluable help of the following reviewers: J. V. Chernosky, R. N. Clayton, O. J. Kleppa, Alan Matthews, C. T. Prewitt, and E. F. Westrum.

June 1980

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I. General Principles

1.

The Operational Basis and Mathematical Derivation of the Gibbs Differential Equation, Which Is the Fundamental Equation of Chemical Thermodynamics*

G. Tunell

The basic thermodynamic relations for systems of variable composition were first derived by J. Willard Gibbs in his memoir entitled *On the Equilibrium of Heterogeneous Substances* (1874–1878). From the differential equation expressing the relation between the energy, the entropy, and the masses of the components of a homogeneous system of variable composition Gibbs then derived the conditions of equilibrium in a heterogeneous system, and from these equilibrium conditions he obtained the phase rule.

Donnan (1924) stated that it is now a well-known matter of history how Bakhuis Roozeboom, the first to undertake an extensive experimental exploration of the field of heterogeneous equilibria, had his attention drawn by van der Waals to the theoretical researches of Gibbs, and how Bakhuis Roozeboom found in this work the sure foundation and guide that he required. Donnan stated further that under the influence of Bakhuis Roozeboom and van't Hoff the study of heterogeneous equilibria, treated chiefly from the graphical standpoint, developed rapidly in Holland, and from there, extended to every part of the world. It can fairly be said that van't Hoff, d'Ans, Arrhenius, Lachmann, and Jänecke,¹ by their work on the oceanic salt and potash deposits in Germany, created the science of experimental mineralogy as a special branch of the theory of heterogeneous equilibria. This science has subsequently been applied extensively to the study of igneous and metamorphic rocks at the Geophysical Laboratory of the Carnegie Institution of Washington and other institutions.

It is the purpose of the present writer to show that the Gibbs differential equation, his Eq. (12), which is the fundamental equation of chemical thermodynamics, has a very simple operational basis, and that, from the experimentally determinable relations, this equation can be obtained by a simple mathematical transformation.

In the choice of letters to denote the various thermodynamic quantities, I have generally followed the recommendations of the American Standards

*Part of the material in this article was presented in a lecture in the Department of the Geophysical Sciences of the University of Chicago on June 1, 1979.

¹The original work by van't Hoff and his associates and the subsequent improvements and extensions of the theory of the origin of the German salt and potash deposits have been well summarized by Jänecke (1923).

Table 1. List of symbols used by the present author in this article and the corresponding symbols used by J. Willard Gibbs in his memoir *On the Equilibrium of Heterogeneous Substances*

Quantity	Tunell	Gibbs
Temperature on the Celsius scale	t	
Temperature on the absolute thermodynamic scale	T	t
Pressure	p	p
Volume of a system	V	v
Work done by a system	W	W
Heat received by a system	Q	Q
Heat capacity at constant pressure	c_p	
Latent heat of change of pressure at constant temperature	l_p	
Energy of a system	U	ϵ
Entropy of a system	S	η
Chemical potential of component n in an open system	μ_n	μ_n
Mass of component n in an open system	m_n	m_n

Association set forth in *Letter Symbols for Physics* prepared by the Sectional Committee on Letter Symbols and Abbreviations for Science and Industry.² The correspondence of the symbols used in this article with those used by Gibbs in his memoir entitled *On the Equilibrium of Heterogeneous Substances* is shown in Table 1.

The Gibbs differential equation, his Eq. (12), is as follows (Gibbs, 1874–1878, p. 116; or 1928, Vol. 1, p. 63)

$$dU = T dS - p dV + \mu_1 dm_1 + \mu_2 dm_2 \cdots + \mu_n dm_n.$$

The symbols in this equation have the following significance: U denotes the energy of a phase of variable composition (solution), T its absolute thermodynamic temperature, S its entropy, p its pressure, V its volume, μ_1 the partial derivative of U with respect to m_1 , m_1 the mass of component 1 in the solution, etc. The diagram in Fig. 1 represents a water bath in which there is a system of three chambers. Chamber I contains pure component 1, chamber II contains pure component 2, and chamber III contains a solution consisting of components 1 and 2. Chambers I and III are separated by a semipermeable membrane permeable only to component 1 and chambers II and III are separated by a semipermeable membrane permeable only to component 2. The Gibbs differential equation with two μdm terms then applies to the binary solution in chamber III.

Since the Gibbs differential equation applies to an open system, one would expect that the authors of textbooks on chemical thermodynamics would have

²Published by the American Society of Mechanical Engineers, New York, 1948 (ASA Z 10.6–1948 UDC 003.62:53).

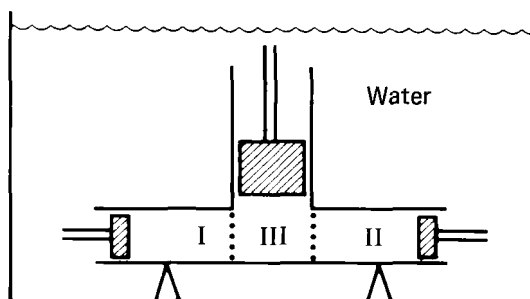


Fig. 1. A thermostat containing a system of three chambers separated by semipermeable membranes. Chambers I and II contain pure components 1 and 2 and chamber III contains a solution made up of components 1 and 2.

done one of two things; one would expect that they would either have explained that it is not necessary to define heat or work in the case of an open system in order to derive this equation or else they would have provided operational definitions of heat and work in the case of open systems if they considered that such definitions were necessary. Actually, however, they have done neither of these things. The authors of all of the textbooks of thermodynamics with which I am acquainted that have discussed Gibbs's Eq. (12) have accepted it without attempting to supply an operational basis for it (Finkelstein, 1969, p. 84; Fleury and Mathieu, 1954, p. 286; Guggenheim, 1950, p. 449; Kirkwood and Oppenheim, 1961, p. 52; Moelwyn-Hughes, 1957, p. 283; Partington, 1950, p. 106; Prigogine, Defay, and Everett, 1954, p. 67; Sommerfeld, Bopp, Meixner, and Kestin, 1956, p. 87; Wall, 1965, p. 189). Thus, for example, Prigogine, Defay, and Everett (1954, p. 66) state that: "For closed systems the first law of thermodynamics establishes the existence of the function of state U . We now *presume* that this function must also exist when *the number of moles varies in an arbitrary manner*" [italics by Prigogine, Defay, and Everett].

Several authors (Guggenheim, 1950, p. 17; Keenan, 1948, p. 449; Moelwyn-Hughes, 1957, pp. 282–283) have correctly indicated that the Gibbs differential equation for an open system is a generalization of the Clausius differential equation for a closed system. Thus I think it may be helpful if we reexamine the operational basis and mathematical proof of the Clausius differential equation as a starting point from which to proceed to the derivation of the Gibbs differential equation.

In classical thermodynamics we begin with temperature t ,³ pressure p , and volume V as measurable quantities. In the case of a one-component system of fixed mass it is then found by experiment that a relation exists between these three quantities

$$\Phi(p, V, t) = 0, \quad (1)$$

³The temperature t is here obtained as a reading on a thermometer (mercury in glass or platinum resistance or nitrogen gas, etc.).

which can in general be solved for any one of the three as a function of the other two. In connection with the operation of steam engines it was found useful to define a quantity, work W done by a body (one-component system of fixed mass), by the equation

$$W = \int_{V_0}^V p dV, \quad (2)$$

where p is given as a function of V by an equation $p = f(V)$ which defines the series of states through which the system passes. The discovery of the heat capacities by Black and Irvine in the late 1700s established the basis for the quantitative study of heat. With the further development of this subject one can say that the heat Q absorbed by a body (one-component system of fixed mass) in passing through a particular series of states can be represented by the line integral

$$Q = \int_{p_0, V_0}^{p, V} \left\{ c_V \left(\frac{\partial t}{\partial p} \right)_V dp + c_p \left(\frac{\partial t}{\partial V} \right)_p dV \right\}, \quad (3)$$

where c_V denotes the heat capacity at constant volume, c_p denotes the heat capacity at constant pressure, where t is given as a function of p and V by the equation of state, and p is given as a function of V by the equation of the path.

By transformation of the integrals in Eqs. (2) and (3) from the (p, V) -plane to the (t, p) -plane we then have

$$W = \int_{t_0, p_0}^{t, p} \left\{ p \left(\frac{\partial V}{\partial t} \right)_p dt + p \left(\frac{\partial V}{\partial p} \right)_t dp \right\}, \quad (4)$$

V being given as a function of t and p by the equation of state, and

$$Q = \int_{t_0, p_0}^{t, p} \{ c_p dt + l_p dp \}, \quad (5)$$

where the path is now defined by the equation $p = \lambda(t)$ and where $l_p = (c_V - c_p)(\partial t / \partial p)_V$.⁴

For a one-component system of fixed mass undergoing a reversible change of state the first law of thermodynamics states that the difference in energy in two states is equal to the heat received minus the work done by the system in passing from the first state to the second state:

$$U(t, p) - U(t_0, p_0) = \int_{t_0, p_0}^{t, p} \left\{ \left(c_p - p \frac{\partial V}{\partial t} \right) dt + \left(l_p - p \frac{\partial V}{\partial p} \right) dp \right\}, \quad (6)$$

⁴The latent heat of change of pressure at constant temperature l_p can thus be evaluated in terms of the heat capacity at constant pressure and the heat capacity at constant volume and the partial derivative $(\partial t / \partial p)_V$ from the equation of state by transformation of the heat integral from the (p, V) -plane to the (t, p) -plane before the introduction of either the first law of thermodynamics or the second law of thermodynamics. However, after the introduction of the first and second laws it can be proved that $l_p = -T(\partial V / \partial T)_p$ (T being the absolute thermodynamic temperature); consequently l_p can then be evaluated from the equation of state without involving c_p or c_V (Bridgman, 1925, p. 10; Tunell, 1960, p. 10, Eq. (16)).

where U denotes the energy of the body, and the second law of thermodynamics states that the difference in entropy in two states is equal to the integral of dQ divided by the absolute thermodynamic temperature of the body, which is a function of t alone:

$$S(t, p) - S(t_0, p_0) = \int_{t_0, p_0}^{t, p} \left\{ \frac{c_p}{T} dt + \frac{l_p}{T} dp \right\}, \quad (7)$$

where T denotes the absolute thermodynamic temperature of the body and S denotes the entropy of the body. From Eq. (6) it then follows according to a theorem on line integrals that are independent of the path (Osgood, 1925, pp. 229–230) that

$$\left(\frac{\partial U}{\partial t} \right)_p = c_p - p \left(\frac{\partial V}{\partial t} \right)_p \quad (8)$$

and

$$\left(\frac{\partial U}{\partial p} \right)_t = l_p - p \left(\frac{\partial V}{\partial p} \right)_t \quad (9)$$

and from Eq. (7) it follows that

$$\left(\frac{\partial S}{\partial t} \right)_p = \frac{c_p}{T} \quad (10)$$

and

$$\left(\frac{\partial S}{\partial p} \right)_t = \frac{l_p}{T}. \quad (11)$$

Equations (1) and (7) can be solved in general for t and p as functions of S and V and since U was originally a function of t and p , we then have U also as a function of S and V , $U = \Psi(S, V)$, and consequently we have

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV. \quad (12)$$

The partial derivatives of U with respect to S and V are obtained by the use of a well-established theorem on the use of Jacobian determinants to express a partial derivative of a function with respect to a new set of independent variables in terms of partial derivatives with respect to an original set of independent variables (Bryan, 1903, p. 113, Eq. (82); Osgood, 1925, p. 150, Exercise 31; Burington and Torrance, 1939, p. 138, Exercise 7; Sherwood and Reed, 1939, p. 174, Eq. (164); Tunell, 1960, pp. 27–32) to be

$$\begin{aligned} \left(\frac{\partial U}{\partial S} \right)_V &= \frac{\partial(U, V)/\partial(t, p)}{\partial(S, V)/\partial(t, p)} = \frac{\begin{vmatrix} \partial U/\partial t & \partial U/\partial p \\ \partial V/\partial t & \partial V/\partial p \end{vmatrix}}{\begin{vmatrix} \partial S/\partial t & \partial S/\partial p \\ \partial V/\partial t & \partial V/\partial p \end{vmatrix}} \\ &= \frac{[c_p - p \partial V/\partial t] \partial V/\partial p - [l_p - p \partial V/\partial p] \partial V/\partial t}{(c_p/T) \partial V/\partial p - (l_p/T) \partial V/\partial t} \\ &= T \end{aligned} \quad (13)$$