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2006

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Publication approved by Central Canada Division

Original manuscript submitted: 2006-04-05
Final version approved for publication: 2006-05-19

Correction date:

An outline of reaction equilibrium

E. Froese

Abstract: The consideration of the mole numbers of chemical species as variables characterizing a macroscopic state makes it possible to define the affinity of a chemical reaction in terms of thermodynamic concepts. This approach leads to the basic relationship of reaction equilibrium in a closed system with one chemical reaction:

$$\left(\frac{\partial \boldsymbol{G}}{\partial \xi}\right)_{P,T} = \sum v_i \overline{G}_i$$

where $\boldsymbol{G}$ is the total Gibbs energy, ξ is the extent of reaction, $\overline{G}_i$ is the partial molar Gibbs energy of a species, and v_i is the stoichiometric coefficient. The partial derivative $\left(\frac{\partial \boldsymbol{G}}{\partial \xi}\right)_{P,T}$ is commonly designated as the Gibbs energy change of reaction and given the symbol ΔG. At arbitrary values of ξ, ξ can be regarded as a constraint keeping the system in a metastable equilibrium. Upon release of this constraint, a negative value of ΔG indicates a tendency of the reaction to proceed from reactants to products. Relationships required to evaluate ΔG at a given pressure, temperature, and composition of solid and gaseous species are discussed.

Résumé : Si l'on considère le nombre de moles de chaque espèce chimique comme une variable caractérisant un état macroscopique, on peut alors définir l'affinité d'une réaction chimique en termes de concepts thermodynamiques. Cette approche permet d'établir une relation fondamentale décrivant l'équilibre de réaction dans un système fermé où se déroule une seule réaction chimique :

$$\left(\frac{\partial \boldsymbol{G}}{\partial \xi}\right)_{P,T} = \sum v_i \overline{G}_i$$

où $\boldsymbol{G}$ est l'énergie de Gibbs totale, ξ est le degré d'avancement de la réaction, $\overline{G}_i$ est l'énergie molaire de Gibbs partielle d'une espèce, et v_i est le coefficient stœchiométrique. La dérivée partielle $\left(\frac{\partial \boldsymbol{G}}{\partial \xi}\right)_{P,T}$ est couramment appelée changement d'énergie de Gibbs de la réaction, et désignée par le symbole ΔG. À des valeurs arbitraires de ξ, on peut considérer ξ comme une contrainte qui maintient le système dans un équilibre métastable. Une valeur négative de ΔG lorsque cette contrainte est enlevée indique que la réaction a tendance à procéder des réactifs vers les produits. Les relations nécessaires pour évaluer ΔG à des valeurs données de la pression, de la température et de la composition des espèces solides et gazeuses sont examinées dans cet article.

INTRODUCTION

Thermodynamics is a branch of macroscopic physics, characterized by extending its field of study to include thermal phenomena. It has widespread applications in most fields of science. It provides the principles of chemical equilibrium and, in this form, is essential in the study of reactions among substances of geological interest. Here an outline of the thermodynamics of reaction equilibrium is given, with emphasis on reactions at higher temperatures corresponding to metamorphic conditions. It is assumed that the reader has a standard textbook, e.g. Denbigh (1981), readily available. The present paper is a revision of parts of GSC Papers 75-43 and 80-28 (Froese, 1976, 1981), placing greater emphasis on presenting a chemical reaction as a constrained equilibrium. In assigning a Gibbs energy content of a compound, the concept of apparent free energy of formation (Berman, 1988) is used. The Temkin model for multisite solutions is discussed with an appropriate cautionary note (Wood and Nicholls, 1978). In the thermodynamics of an electrochemical cell, the partial molar Gibbs energy of electrons is explicitly used, following the discussion in Denbigh (1981) of a cell not performing work.

Thermodynamic analysis singles out a portion of matter, known as a system, for study in terms of its macroscopic properties and its interaction with the surroundings. The state of the system is defined by its macroscopic properties or state variables; if these persist with time, the system is in a state of equilibrium. State properties show some interdependence, but at least two variables are independent. Usually two state variables, e.g. pressure and temperature, can be imposed on the system as external conditions by the surroundings. In some cases, this will determine all other properties within the system and the system is in a state of stable equilibrium; however, there are systems which are not uniquely defined by two imposed conditions. Thus $CaCO_3$, at the same pressure and temperature, may exist either as aragonite or as calcite. The definition of such systems requires the specification of an additional internal parameter known as a constraint. A system subject to an internal constraint is in a state of metastable equilibrium. This concept plays a central role in chemical thermodynamics (Schottky et al., 1929) and has been extensively discussed and used by Anderson (2005).

Changing the external conditions and internal constraints may induce a transition of the system to a new state; this is known as a process. Chemical thermodynamics considers only quasistatic processes during which all state variables are defined at each stage of the process. Hence a quasistatic process consists of a continuous succession of equilibrium states (Callen, 1985). If a system is subject to a constraint, and if the constraint is released in small steps, an irreversible process takes place in one direction and the system passes through a series of metastable, constrained equilibrium states. The process

will stop when the constraint is totally released. At this stage, the constraint is no longer a state variable and the system is in a state of stable, unconstrained equilibrium defined entirely by the external conditions. If a process can be induced by a slight disturbance of this equilibrium, it is known as a reversible process and takes the system through a sequence of stable equilibrium states. Thus the transformation of aragonite to calcite in the stability field of calcite represents an irreversible process and the transformation of aragonite to calcite on the aragonite-calcite equilibrium pressure-temperature curve is a reversible process.

Thermodynamics seeks to find a measure of irreversibility as the driving force of a chemical reaction and to define the conditions of stable equilibrium. This requires comparing states at different stages of constraint. The importance of constraint lies in fixing the macroscopic properties of different metastable states at the same external conditions, thus making them accessible to thermodynamic analysis. Without a constraint, only the stable equilibrium state would exist. In thermodynamics, pressure and volume are accepted as given by mechanics and three new state variables are derived: temperature, internal energy, and entropy. In addition to the five fundamental variables, the mole numbers of chemical species must be considered as state variables in chemical thermodynamics and the principles of chemical equilibrium are developed from relationships between these state variables.

TEMPERATURE

The property experienced physiologically as degree of hotness tends to equalize between adjacent systems; they reach the same temperature. This makes it possible to use the properties of one system as a thermometer to measure the temperature of another system. Long familiarity with the perfect gas law suggests the PV product of one mole of a gas for this purpose. This product can be extrapolated to zero pressure, where it becomes independent of the nature of the gas. Thus

$$T = (PV)_{P \to 0} \text{ J} \cdot \text{mol}^{-1} \tag{1}$$

At the triple point of water (liquid water, ice, and steam)

$$T = 2271.2 \text{ J} \cdot \text{mol}^{-1} \tag{2}$$

Introducing a new unit

$$1 \text{ K (kelvin)} = 8.3145 \text{ J} \cdot \text{mol}^{-1} \tag{3}$$

$$T = \frac{2271.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}}{8.3145 \text{ J} \cdot \text{mol}^{-1}} = 273.16 \text{ K} \tag{4}$$

where 8.3145 J·mol^{-1}·K^{-1} is the gas constant R. Assuming a linear temperature scale, there exists a zero temperature.

RESTRICTIONS IN THE TREATMENT OF REACTION EQUILIBRIUM

In order to define the state of a closed system, i.e. one of fixed bulk composition, the mole number of species must be given, in addition to two properties imposed on the system by the surroundings, e.g. pressure and temperature. In a system with only one chemical reaction, the mole number of any species n_i is given by

$$n_i = n_i^o + v_i \xi \tag{5}$$

Where n_i^o is the number of moles initially present, v_i is the stoichiometric coefficient, and ξ is the extent of reaction defined by this relationship (De Donder, 1920; Schottky et al., 1929; Prigogine and Defay, 1954). If the system initially consists of the number of moles of reactants as given by the reaction equation, ξ can vary from 0 to 1. In a closed system, the initial number of moles n_i^o of all species is constant and

$$dn_i = v_i d\xi \tag{6}$$

Thus there is only one independent composition state variable ξ. In the treatment of reaction equilibrium, the extent of reaction ξ will be considered as the only possible constraint.

Chemical thermodynamics deals only with systems of uniform pressure and temperature equal to those of the surroundings. Also, the composition of each phase in the system is assumed to be uniform. With these restrictions, irreversibility can be introduced only by a variation of ξ.

THE FIRST AND SECOND LAWS

The laws of thermodynamics will be illustrated by means of an example showing different paths connecting states 1 and 2 in a closed system consisting of one mole of $CaCO_3$ (Fig. 1). The paths include the reaction

$$\text{aragonite} = \text{calcite} \tag{7}$$

with ξ going from 0 to 1.

According to the first law, if the heat q and work w in going from state 1 to state 2 could be measured, one would find, independent of path, their sum to be constant, thus defining the change in a new state variable, the internal energy U:

$$U\,(P_2, T_2, \xi=1) - U\,(P_1, T_1, \xi=0) = \int_1^2 dq + \int_1^2 dw \tag{8}$$

The values of q and w are positive, if energy is added to the system.

In differential form and assuming only PV work

$$dU = dq - PdV \tag{9}$$

where dU is the differential of a function of state of three variables P, T, ξ. In a quasistatic process, the state variables are defined at each stage and, consequently, they are functions of one independent variable that determines the sequence of states along the path connecting the two states. Since heat and work depend on the path, dq and dw are differentials of a function of a single variable (Tunell, 1932).

Aragonite and calcite coexist in stable equilibrium along a curve in the P-T field along which slight perturbations will induce a reversible process. The curve becomes a surface in the P-T-ξ diagram, and a line along this surface represents a sequence of stable equilibrium states. According to the second law, $\frac{q}{T}$ along any path which includes a line along this surface in P-T-ξ space defines the difference in a state variable, the entropy S:

$$S\,(P_2, T_2, \xi=1) - S\,(P_1, T_1, \xi=0) = \int_1^2 \frac{dq_{rev}}{T} \tag{10}$$

or, in differential form

$$dS = \frac{dq_{rev}}{T} \tag{11}$$

However, for a path which includes the transformation of aragonite to calcite in the P-T stability field of calcite, representing an irreversible process or a sequence of metastable equilibrium states
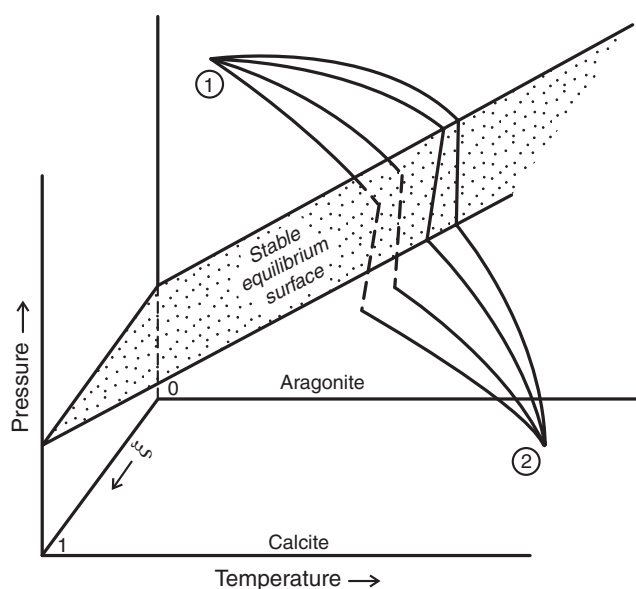
$$\frac{dq}{T} < dS \tag{12}$$

Figure 1. Irreversible and reversible paths of taking one mole of $CaCO_3$ from state 1 to state 2.

or

$$dq = TdS - dq' \qquad (13)$$

where q' is a positive number; it is the heat leaving the system as a consequence of irreversible changes in the system and thus is a measure of irreversibility. For historical reasons, q' has been burdened with the mystifying name of uncompensated heat. Its explicit evaluation plays a central role in De Donder's formulation of chemical thermodynamics (*see* Prigogine and Defay, 1954). The combination of equations 9 and 13 relates q' to the five fundamental variables:

$$dU + PdV - TdS = -dq' \qquad (14)$$

REACTION EQUILIBRIUM

The evaluation of dq' is greatly facilitated by keeping two variables constant. Of particular interest is the restriction of constant pressure and temperature:

$$d(U + PV - TS)_{P,T} = -dq' \qquad (15)$$

Defining the expression in brackets as G, the total Gibbs energy of the system

$$dG_{P,T} = -dq' \qquad (16)$$

In the absence of gradients in pressure, temperature, and composition, the only irreversible process here considered giving rise to variation in q' is entirely due to the change in mole numbers of the species. In order to evaluate q' in terms of mole numbers, an additional postulate is introduced (Denbigh, 1981, p. 77). It is assumed that the mole numbers of species can be treated as state variables and, therefore, G is a function of the mole numbers and dG can be expressed by

$$dG_{P,T} = \sum \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j} dn_i \qquad (17)$$

The partial derivative is the partial molar Gibbs energy $\overline{G}_i$, which, for a pure species, is the same as the molar Gibbs energy G_i. Its definition seems to require that the mole numbers are independent variables, as they are in an open system; however, this definition is also commonly used in closed systems where they can not vary independently (e.g. Prigogine and Defay, 1954; Denbigh, 1981). In such case, one can write

$$dG_{P,T} = \sum \overline{G}_i dn_i = -dq' \qquad (18)$$

If there is only one reaction, $dn_i = v_i d\xi$ and, making this substitution and dividing by $d\xi$, one obtains

$$\left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \sum v_i \overline{G}_i = -\frac{dq'}{d\xi} \qquad (19)$$

where $\frac{dq'}{d\xi}$ is the affinity of a reaction as defined by De Donder (*see* Prigogine and Defay, 1954). The partial derivative $\left(\frac{\partial G}{\partial \xi} \right)_{P,T}$ has unfortunately acquired the designation Gibbs energy change of reaction and the symbol ΔG, a practice criticized by several authors (Bent, 1973; Spencer, 1974; Craig, 1987; MacDonald, 1990); however, in spite of the recommendation to uproot this "weed in the field of thermodynamics" (Bent, 1973), it continues to thrive. In contrast to normal usage, ΔG in this case refers to a rate of change and is measured in J•mol^{-1}. The Gibbs energy change of reaction, ΔG, is zero for a reversible reaction (stable equilibrium) and negative for an irreversible reaction (constrained or metastable equilibrium) proceeding to the right side of the reaction equation. It is instructive to plot $G_{P,T}$ versus ξ (Fig. 2). If $\left(\frac{\partial G}{\partial \xi} \right)_{P,T}$ for a given ξ is negative, the reaction will proceed if the constraint ξ is released. Two cases can be recognized. A reaction involving pure species terminates at $\xi = 1$ without $\left(\frac{\partial G}{\partial \xi} \right)_{P,T}$ reaching zero, or, if reactant and product species form solutions, zero is reached at some intermediate value of ξ (MacDonald, 1990; Anderson, 2005).

Equation 19 provides, in striking simplicity, the fundamental thermodynamic relationship governing reaction equilibrium. Its immense practical importance stems from the fact that ΔG can be obtained from the partial molar Gibbs energies of the species. This, in turn, makes it unnecessary for the closed system, represented by either one side of the reaction
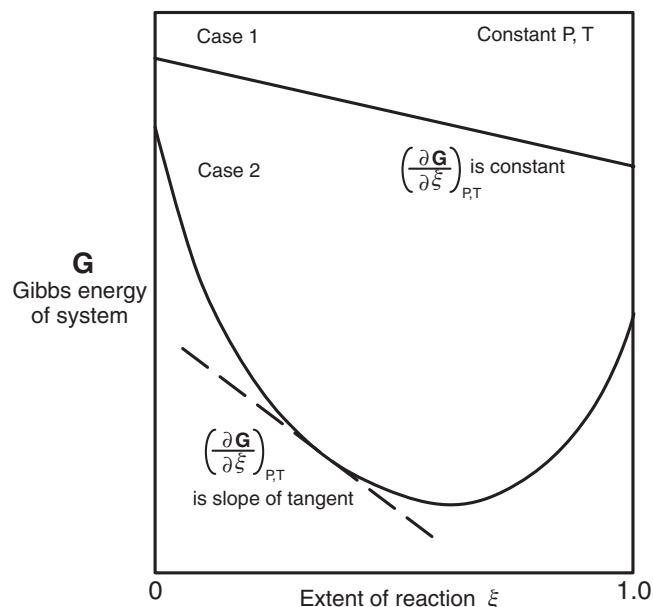

Figure 2. The variation of the Gibbs energy of a system **G** with the extent of reaction ξ.

equation, to exist physically. It can be assembled in a virtual form from the properties of the species. In the extreme case, a participating species may exist in a solution, and the other species in the solution may not be involved in the reaction and thus not belong to the closed system represented by the reaction equation. Clearly, no physical system boundary can pass through the solution. Practial application of this equation, however, has to contend with the considerable problem of finding measurable quantities for the partial molar Gibbs energies of the individual species. An energy datum must be established from which to measure $\bar{G}$; then various energy increments are calculated according to the variation of the molar Gibbs energy G with temperature and pressure, and the variation of the partial molar Gibbs energy $\bar{G}$ with composition. For this purpose, a standard state, designated by the superscript ^{o}, is established for each species, as follows:

Solids: pure species, in a specified crystallographic modification, at $P = 1$ bar and at any temperature.

Gases: the hypothetical perfect gas at $P = 1$ bar (designated as P^o) and at any temperature.

THE VARIATION OF G WITH TEMPERATURE

The following discussion involves only molar properties. Use will be made of the definition $G = H - TS$, where H (enthalpy) is equal to $U + PV$, and the variation of H and S with temperature will be considered separately. The enthalpy H can be regarded as a function of P and T and

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{20}$$

At $P = 1$ bar, H is the standard enthalpy H^o and the last term is zero. $\left(\dfrac{\partial H^o}{\partial T}\right)_P$ is the standard heat capacity C_P^o. Thus

$$dH^o = C_P^o dT \tag{21}$$

and

$$H_T^o = H_{298}^o + \int_{298}^T C_P^o dT \tag{22}$$

The enthalpy of a compound AB is given by

$$H_{298,AB}^o = H_{298,A}^o + H_{298,B}^o + \Delta H_{f,298,AB}^o \tag{23}$$

where the last term is the enthalpy of formation from the elements, which can be measured. The enthalpies of the elements are not known. Any number can be assigned to them, since they cancel out in a reaction equation. Usually a convention of zero enthalpy in a specified state at 298.15 K is chosen. Thus $H_{298}^o = \Delta H_{f,298}^o$. If the compound changes to a

different modification, the enthalpy of transition ΔH_{tr}^o must be added to H^o and, beyond the transition temperature, a different C_P^o must be used in the integration. Thus

$$H_T^o = H_{298}^o + \int_{298}^{T_{tr}} C_P^o dT + \Delta H_{tr}^o + \int_{T_{tr}}^T C_P^o dT \tag{24}$$

The molar entropy of a compound at $P = 1$ bar is given by

$$S_{0K,AB}^o = S_{0K,A}^o + S_{0K,B}^o + \Delta S_{f,0K,AB}^o \tag{25}$$

In this case, the temperature of formation is taken at 0 K in order to make use of the third law of thermodynamics. The observation that the entropy change of a reaction tends to decrease with decreasing temperature led to the generalization that, for a reaction involving ordered compounds, ΔS^o would approach zero as the temperature approaches 0 K. The entropies of the elements at 0 K are not known, but since they cancel out in a reaction equation, the common convention is to assign to them, in an ordered state, a value of zero. Thus $S_{0K}^o = \Delta S_{f,0K}^o = 0$.

Since

$$H = U + PV \tag{26}$$

$$dH = dU + PdV + VdP \tag{27}$$

Also

$$dU = TdS - PdV \tag{28}$$

Thus

$$dH = TdS + VdP \tag{29}$$

At a constant pressure of $P = 1$ bar

$$dH^o = TdS^o \tag{30}$$

$$dS^o = \frac{C_P^o dT}{T} = C_P^o d\ln T \tag{31}$$

$$S_T^o = \int_0^T C_P^o d\ln T \tag{32}$$

For a polymorphic transition, the entropy of transition has to be added and, beyond the transition temperature, a new heat capacity function must be used in the integration. Thus

$$S_T^o = \int_0^{T_{tr}} C_P^o d\ln T + \frac{\Delta H_{tr}^o}{T_{tr}} + \int_{T_{tr}}^T C_P^o d\ln T \tag{33}$$

The standard molar Gibbs energy is obtained from the relationship

$$G_T^o = H_T^o - TS_T^o \tag{34}$$

In subsequent formulas, the subscript T will be dropped but a specified temperature, at a pressure of 1 bar, is indicated by the superscript ^{o}. The numerical value of G^o incorporates the convention that H_{298}^o and S_{0K}^o of the elements in a specified state have been assigned values of zero. G^o as used here is designated as the apparent free energy of formation (ΔG_a) at a specified temperature and 1 bar in Berman (1988).

THE VARIATION OF G WITH PRESSURE

Since

$$G = U + PV - TS \tag{35}$$

$$dG = dU + PdV + VdP - TdS - SdT \tag{36}$$

Also

$$dU = TdS - PdV \tag{37}$$

Thus

$$dG = VdP - SdT \tag{38}$$

At constant temperature

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{39}$$

and

$$G^* - G^o = \int_1^P V\,dP \tag{40}$$

where G* is the molar Gibbs energy at pressure P. For solids, the apparent free energy of formation (ΔG_a) at a specified temperature and pressure in Berman (1988) is given by $G^* = G^o + \int_1^P V\,dP$. This is the relationship used to calculate the variation of G with P for solids and could also be used for gases; however, at this stage, some asymmetry creeps into the development in an attempt to retain the services of the perfect gas law even in an imperfect world. For a perfect gas

$$G^{*\,perf} - G^o = \int_{P^o}^P \frac{RT}{P}\,dP = \int_{P^o}^P RT\,d\ln P$$
$$= RT\ln\frac{P}{P^o} \tag{41}$$

where $G^{*\,perf}$ is the molar Gibbs energy of the perfect gas at pressure P, and P^o is equal to 1 bar. This relationship is represented by a straight line on a plot of G versus $\ln P$ (Fig. 3). The real gas deviates from this behaviour, but the molar Gibbs energy of the real gas approaches that of the perfect gas as $P \to 0$. Fortunately, the difference in volume ($V^{real} - V^{perf}$) approaches a fixed value as $P \to 0$. For this reason, a fugacity coefficient φ can be defined and evaluated by the relationship

$$RT\ln\varphi = G^* - G^{*\,perf} = \int_0^P (V^{real} - V^{perf})\,dP \tag{42}$$

where G^* is the Gibbs energy of the real gas at pressure P. Two energy increments can be added as follows (Fig. 3)

$$G^{*\,perf} - G^o = RT\ln\frac{P}{P^o} \tag{43}$$

$$G^* - G^{*\,perf} = RT\ln\varphi \tag{44}$$

$$G^* - G^o = RT\ln\frac{P\varphi}{P^o} \tag{45}$$

Defining the fugacity $f = P\varphi$

$$G^* - G^o = RT\ln\frac{f}{P^o} \tag{46}$$

For gases, the apparent free energy of formation (ΔG_a), at a specified temperature and pressure, in Berman (1988) is given by $G^* = G^o + RT\ln\frac{f}{P^o}$. The molar Gibbs energy G^*, at a specified temperature and pressure, is given by
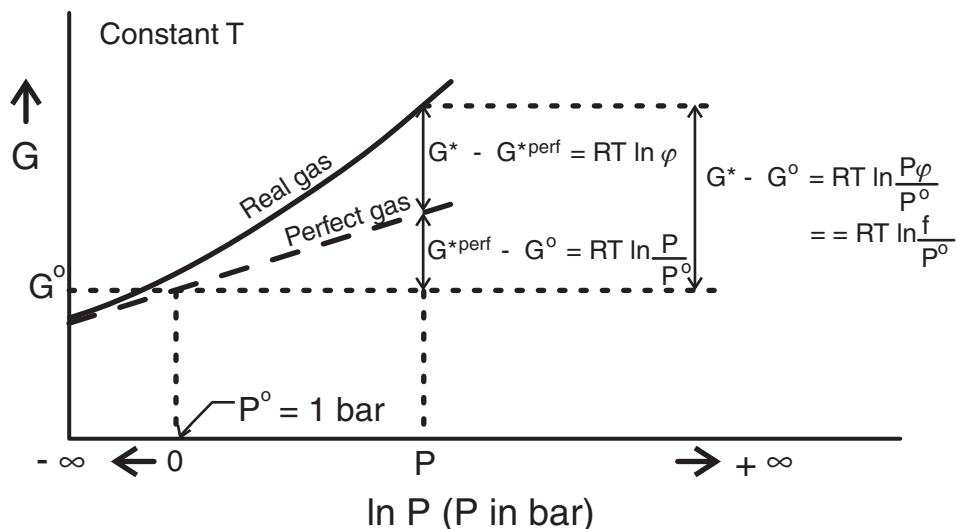
Solids:

$$G^* = G^o + \int_1^P V\,dP \tag{47}$$

Figure 3. Definition of fugacity.

Gases:

$$G^* = G^o + RT\ln\frac{P}{P^o} + RT\ln\varphi \qquad (48)$$

$$G^* = G^o + RT\ln\frac{f}{P^o} \qquad (49)$$

(P^o is commonly omitted).

THE VARIATION OF $\overline{G}$ WITH COMPOSITION

This is the most troublesome part of chemical thermodynamics because there is no thermodynamic relationship for this variation. Resort is taken to the model of an ideal solution, which can be derived from statistical mechanics and is defined by

$$\left(\frac{\partial\overline{G}}{\partial\ln X}\right)_{P,T} = RT \qquad (50)$$

where $\overline{G} = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$ is the partial molar Gibbs energy of a

species, best visualized as the Gibbs energy of one mole as it exists in a solution, and X is the mole fraction. If the composition scale is chosen so that the mole fraction approaching zero cannot be negative, and for a particular choice of mixing units (e.g. Fe and Mg, not Fe_2 and Mg_2, in olivine), a solution approaches ideal behaviour as $X \rightarrow 1$ (Raoult's Law) and as $X \rightarrow 0$ (Henry's Law). Thus, for a solution following Raoult's Law

$$\overline{G}^{ideal} - G^* = RT\ln X \qquad (51)$$

A deviation from Raoult's Law can be used to define and evaluate an activity coefficient γ by

$$\overline{G} - \overline{G}^{ideal} = RT\ln\gamma \qquad (52)$$

and defining the activity a as $X\gamma$ the following relationship (Fig. 4) is obtained

$$\overline{G} - G^* = RT\ln X + RT\ln\gamma = RT\ln a \qquad (53)$$

The partial molar Gibbs energy $\overline{G}$, at a given temperature, pressure, and mole fraction is given by

Solids:

$$\overline{G} = G^o + \int_1^P VdP + RT\ln X + RT\ln\gamma \qquad (54)$$

$$\overline{G} = G^o + \int_1^P VdP + RT\ln a \qquad (55)$$

Gases:

$$\overline{G} = G^o + RT\ln\frac{P}{P^o} + RT\ln\varphi + RT\ln X + RT\ln\gamma \qquad (56)$$

$$\overline{G} = G^o + RT\ln\frac{f}{P^o} + RT\ln a \qquad (57)$$

So far the effects of pressure and composition have been clearly separated, but in order to conform to accepted confusion, one can define the fugacity in a gaseous solution by $f = P\varphi X\gamma$. Thus

$$RT\ln\frac{f}{P^o} = RT\ln\frac{P}{P^o} + RT\ln\varphi \\ + RT\ln X + RT\ln\gamma \qquad (58)$$

and equation 56 becomes

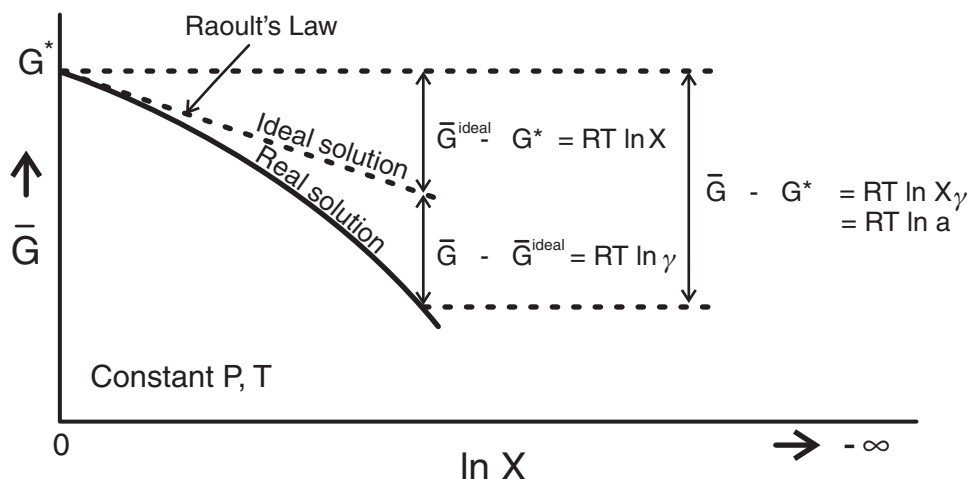$$\overline{G} = G^o + RT\ln\frac{f}{P^o} \qquad (59)$$

Figure 4. Definition of activity based on Raoult's Law.

In Berman (1988), for a gaseous species in a solution, the apparent free energy of formation (ΔG_a), at a given temperature, pressure, mole fraction, and activity coefficient is given by $\overline{G} = G^o + RT1n\dfrac{f}{P^o}$.

In an ideal solution, $\ln\gamma$ is zero and setting $P_{partial} = PX$

$$RT1n\frac{f}{P^o} = RT1n\frac{P_{partial}\varphi}{P^o} \qquad (60)$$

This relationship is known as the Lewis and Randall rule. In all these equations, P^o is commonly omitted because it is equal to 1 bar. A further complication can be achieved by combining $\varphi\gamma$ into one deviation term and calling it the fugacity coefficient in a nonideal solution.

THE EQUILIBRIUM CONSTANT

The various expressions for the for the partial molar Gibbs energy can now be substituted in the equation $\Delta G = \sum v_i \overline{G}_i$ to give

$$\Delta G = \Delta G^o + \int_1^P \Delta V_s \, dP + RT1nQ \qquad (61)$$

where ΔV_s is the volume change of solids involved in the reaction and Q is the continuous product of activity and fugacity terms with each a and f raised to the power of its stoichiometric coefficient. For pure species, the partial molar Gibbs energy is identical to the molar Gibbs energy and it has been used in the summation leading to equation 61. Since for solids $G^* = G^o + \int_1^P VdP$, if a reaction involves solids only, the following relationship is valid

$$\Delta G = \Delta G^* + RT1nQ \qquad (62)$$

For stable equilibrium, ΔG is zero and

$$\Delta G^o = -RT1nK - \int_1^P \Delta V_s \, dP \qquad (63)$$

where Q, for the stable equilibrium condition, has been replaced by K, the equilibrium constant. This marks the arrival of the "most useful equation in chemical thermodynamics" (Anderson, 2005). Since for each species $G^o = H^o - TS^o$, for a reaction

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (64)$$

AN EXAMPLE CALCULATION

Goldschmidt (1912), on the basis of limited thermodynamic data and various approximations, calculated the pressure-temperature conditions of a reaction of geological significance:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2 \qquad (65)$$
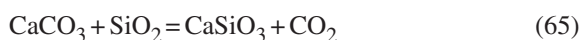
This will be repeated here using a program (GEOTAB) and a database (JUN92.GSC) provided by R.G. Berman. The database is a somewhat modified version of the one published in Berman (1988). As an example, at 2 kbar and 723°C, the thermodynamic properties listed in Table 1 are obtained. Therefore

$$\Delta G = \Delta G^o + \int_1^P \Delta V_s \, dP$$
$$+ RT1nf_{CO_2} = +21 \text{ J•mol}^{-1} \qquad (66)$$

At 2 kbar and 724°C, $\Delta G = -58$ J•mol^{-1} Thus the equilibrium temperature at 2 kbar is bracketed between 723°C and 724°C. In Figure 5, the two calculations are compared.

The program GEOTAB also gives $\overline{G}_{CO_2}$ for a specified mole fraction in an ideal mixture (as ΔG_a) or in a nonideal mixture of CO_2 and H_2O (as ΔG_a) and $RT1nf_{CO_2}$ can be obtained from the relationship $\overline{G}_{CO_2} = G^o_{CO_2} + RT1nf_{CO_2}$. Thermodynamic data at 656°C and 2 kbar indicate that this is the equilibrium temperature for a mole fraction of $X_{CO_2} = 0.5$ in an ideal solution (Table 2). Similarly, the equilibrium temperature for the same mole fraction in a nonideal solution of CO_2 - H_2O is 661°C at 2 kbar (Table 3).

PROBLEMS IN MULTISITE (RECIPROCAL) SOLUTIONS

There has been much temptation, frequently not resisted, to apply the ideal solution model to each distinctive lattice site in a crystal. This approach can be traced back to Temkin (1945) working on fused salt solutions. The ideal solution model assumes inert mixing, without interaction of constituents. If applied to one lattice site, this model accounts for the difference between the partial molar Gibbs energy in solution $\overline{G}$ and the molar Gibbs energy of the pure species G^*; however, for mixing on two lattice sites, this is the case only if a rather stringent requirement is met, i.e. that $\Delta G = 0$ for an internal exchange reaction among species. Wood and Nicholls (1978) have drawn attention to this limitation. Using $(Fe,Mg)(Al,Cr)_2O_4$ spinels as an example, the exchange reaction is

$$MgAl_2O_4 + FeCr_2O_4 = FeAl_2O_4 + MgCr_2O_4 \qquad (67)$$

The Temkin model gives the following expressions for $\overline{G}$

$$\overline{G}_{FeAl_2O_4} = G^*_{FeAl_2O_4} + RT1n(X_{Fe}Y_{Al}^2) \qquad (68)$$

$$\overline{G}_{MgCr_2O_4} = G^*_{MgCr_2O_4} + RT1n(X_{Mg}Y_{Cr}^2) \qquad (69)$$

$$\overline{G}_{MgAl_2O_4} = G^*_{MgAl_2O_4} + RT1n(X_{Mg}Y_{Al}^2) \qquad (70)$$

$$\overline{G}_{FeCr_2O_4} = G^*_{FeCr_2O_4} + RT1n(X_{Fe}Y_{Cr}^2) \qquad (71)$$

Table 1. Thermodynamic data at 2 kbar and 723°C, $X_{CO_2} = 1.0$.

	$G°(\Delta G_a$ at 1 bar)	$G*(\Delta G_a$ at 2 kbar)	$G*(\Delta G_a$ at 2 kbar, $X_{CO_2}=1.0)$	$\int_1^P VdP$	$RT\ln f_{CO_2}$ $(f=P\varphi)$
$CaCO_3$	- 1 348 551	- 1 341 058	–	7 493	–
SiO_2	- 980 994	- 976 263	–	4 731	–
$CaSiO_3$	- 1 765 097	- 1 756 988	–	8 109	–
CO_2	- 628 297	–	- 560 312	–	67 985
$\Delta G°$	- 63 849	–	–	–	–
$\int_1^P \Delta V_s dP$	–	–	–	- 4 115	–

Table 2. Thermodynamic data at 2 kbar and 656°C, $X_{CO_2} = 0.5$ in an ideal solution.

	$G°(\Delta G_a$ at 1 bar)	$G*(\Delta G_a$ at 2 kbar)	$\overline{G}(\Delta G_a$ at 2 kbar, $X_{CO_2}=0.5, \gamma=1)$	$\int_1^P VdP$	$RT\ln f_{CO_2}$ $(f=P\varphi X)$
$CaCO_3$	-1 334 147	- 1 326 673	–	7 474	–
SiO_2	- 973 383	- 968 652	–	4 731	–
$CaSiO_3$	- 1 751 137	-1 743 043	–	8 094	–
CO_2	- 615 750	–	- 552 275	–	63 475
$\Delta G°$	- 59 357	–	–	–	–
$\int_1^P \Delta V_s dP$	–	–	–	- 4 111	–

Table 3. Thermodynamic data at 2 kbar and 661°C, $X_{CO_2} = 0.5$ in a nonideal solution of $CO_2 - H_2O$.

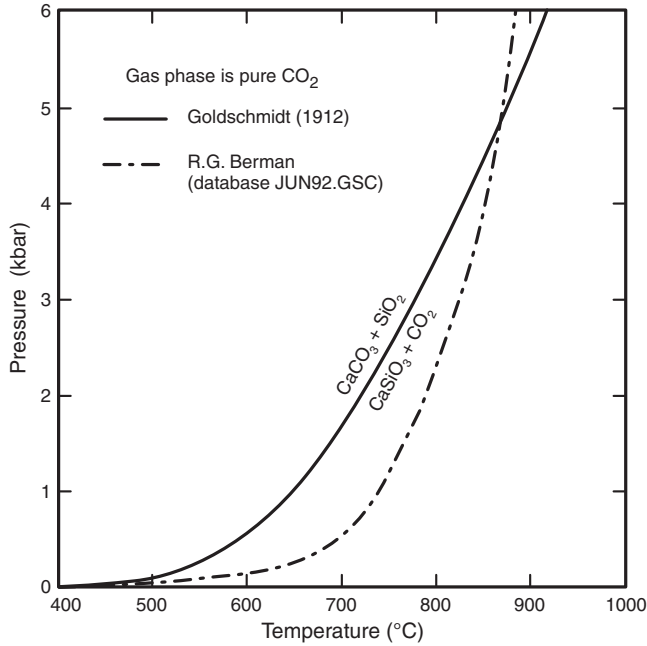|	$G°(\Delta G_a$ at 1 bar)	$G*(\Delta G_a$ at 2 kbar)	$\overline{G}(\Delta G_a$ at 2 kbar, $X_{CO_2}=0.5, \gamma \neq1)$	$\int_1^P VdP$	$RT\ln f_{CO_2}$ $(f=P\varphi X\gamma)$
$CaCO_3$	-1 335 202	- 1 327 726	–	7 476	–
SiO_2	- 973 940	- 969 208	–	4 732	–
$CaSiO_3$	- 1 752 158	-1 744 064	–	8 094	–
CO_2	- 617 106	–	- 552 843	–	64 263
$\Delta G°$	- 60 122	–	–	–	–
$\int_1^P \Delta V_s dP$	–	–	–	- 4 114	–

Figure 5. The formation of wollastonite at metamorphic conditions.

where X is the atomic fraction on the tetrahedral site and Y is the atomic fraction on the octahedral site. The power of two arises from the fact that there are two atoms on the octahedral site. From the relationship $\Delta G = \sum v_i \overline{G}_i$ it follows that

$$\Delta G = \Delta G^* + RT\ln\frac{(X_{Fe}Y_{Al}^2)(X_{Mg}Y_{Cr}^2)}{(X_{Mg}Y_{Al}^2)(X_{Fe}Y_{Cr}^2)} \tag{72}$$

If, as above, the last term contains atomic fractions only, i.e. there are no activity coefficients, it is equal to unity and ΔG can be zero only if ΔG^* is zero. This is generally not the case and for the spinel exchange reaction it is about 10 kJ•mol^{-1} (Wood and Nicholls, 1978). In order to make $\Delta G = 0$, a deviation term equal to $-\Delta G^*$ must be introduced when applying the ideal solution model to more than one lattice site. Thus

$$\Delta G = \Delta G^* + RT\ln\frac{(X_{Fe}Y_{Al}^2)(X_{Mg}Y_{Cr}^2)}{(X_{Mg}Y_{Al}^2)(X_{Fe}Y_{Cr}^2)} - \Delta G^* \tag{73}$$

The value of $-\Delta G^*$ can be partitioned among the partial molar Gibbs energy values of the species (Wood and Nicholls, 1978), as follows

$$\overline{G}_{FeAl_2O_4} = G^*_{FeAl_2O_4} + RT\ln(X_{Fe}Y_{Al}^2) - X_{Mg}Y_{Cr}\Delta G^* \tag{74}$$

$$\overline{G}_{MgCr_2O_4} = G^*_{MgCr_2O_4} + RT\ln(X_{Mg}Y_{Cr}^2) - X_{Fe}Y_{Al}\Delta G^* \tag{75}$$

$$\overline{G}_{MgAl_2O_4} = G^*_{MgAl_2O_4} + RT\ln(X_{Mg}Y_{Al}^2) + X_{Fe}Y_{Cr}\Delta G^* \tag{76}$$
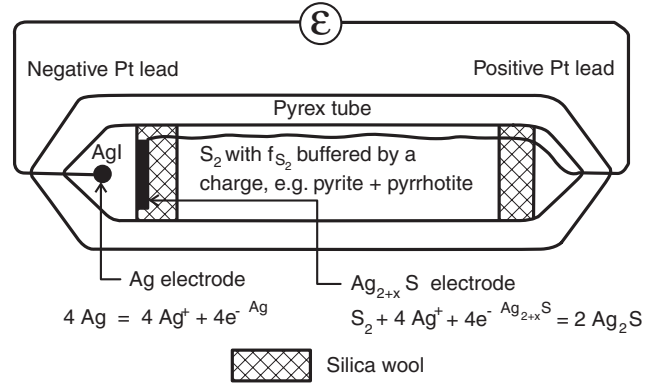
Figure 6. The electrochemical cell Ag|AgI|Ag$_{2+x}$S, S$_2$ (Schneeberg, 1973).

$$\overline{G}_{FeCr_2O_4} = G^*_{FeCr_2O_4} + RT\ln(X_{Fe}Y_{Cr}^2) + X_{Mg}Y_{Al}\Delta G^* \tag{77}$$

It is seen that only for low values of ΔG^* does the Temkin model give a reasonable approximation to the energy difference $\overline{G} - G^*$, but in looking desperately for an approximation, it may be necessary to accept this additional limitation, as has been done, unwittingly, prior to the publication of Wood and Nicholls (1978).

THE ELECTRON AS A SPECIES

The development of solid electrolytes made it possible to extend electrochemical investigations to higher temperatures (Sato, 1971). For this reason, the behaviour of the electron as a species will be examined by considering an electrochemical cell (Fig. 6) which has been used to measure the sulphur fugacity (Schneeberg, 1973). The Ag and Ag$_{2+x}$S electrodes are in contact with the same electrolyte AgI. Two reactions are taking place, each in stable equilibrium:

Ag electrode

$$4Ag = 4Ag^+ + 4e^{-Ag} \tag{78}$$

$$4\overline{G}_{Ag} = 4\overline{G}_{Ag+} + 4\overline{G}_{e-}^{Ag} \tag{79}$$

Ag$_{2+x}$S electrode

$$S_2 + 4Ag^+ + 4e^{-Ag_{2+x}S} = 2Ag_2S \tag{80}$$

$$\overline{G}_{S_2} + 4\overline{G}_{Ag^+} + 4\overline{G}_{e-}^{Ag_{2+x}S} = 2\overline{G}_{Ag_2S} \tag{81}$$

These reactions are related by two significant features:

1) $\overline{G}_{Ag^+}$ is the same for both because the electrolyte is a conductor for Ag$^+$ ions.

2) $\overline{G}_{e^-}$ is different for the two reactions because the electrolyte is an insulator for electrons and, importantly, the difference can be measured by an electromotive force in a wire of the same metal connecting the electrodes.

Adding the two reactions, one obtains

$$4Ag + S_2 = 2Ag_2S - 4(e^{-Ag_{2+x}S} - e^{-Ag}) \tag{82}$$

$$4\overline{G}_{Ag} + \overline{G}_{S_2} = 2\overline{G}_{Ag_2S} - 4(\overline{G}_{e^-}^{Ag_{2+x}S} - \overline{G}_{e^-}^{Ag}) \tag{83}$$
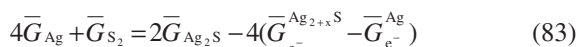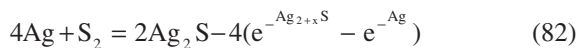
For the cell reaction without the electrons

$$\Delta G = 2\overline{G}_{Ag_2S} - 4\overline{G}_{Ag} - \overline{G}_{S_2} \tag{84}$$

and

$$\Delta G = 4(\overline{G}_{e^-}^{Ag_{2+x}S} - \overline{G}_{e^-}^{Ag}) \tag{85}$$

The cell reaction is irreversible and represents a constrained or metastable equilibrium. The system has a value of **G** higher than the minimum which is maintained by blocking the flow of electrons. If the cell is short-circuited, the reaction will go to completion (treating $Ag_{2+x}S$ as approximately stoichiometric) and the system will achieve a minimum **G**. For a common range of sulphur fugacity, e.g. f_{S_2} buffered by the coexistence of pyrite and pyrrhotite, reaction 82 will proceed to the right.

For a charged species, the partial molar Gibbs energy includes an additional term given by $z\mathcal{F}\phi$, where z is the charge number of the species, $\mathcal{F}$ is the Faraday constant (96 485 J•V^{-1}•mol^{-1}) and ϕ is the electrical potential of the phase in which the species occurs (Guggenheim, 1967). If two wires of the same metal are attached to the two electrodes, $\overline{G}_{e^-}$, in each case, is the same in the electrode and the wire. The difference in $\overline{G}_{e^-}$ between the two wires, and thus between the two electrodes, is related to the difference in the electrical potential ϕ of the two wires as follows (Denbigh, 1981):

$$(\overline{G}_{e^-}^{Ag_{2+x}} - \overline{G}_{e^-}^{Ag} = -\mathcal{F}(\phi^{Ag_{2+x}S} - \phi^{Ag}) \tag{86}$$

where the minus sign is due to the negative charge of the electron. The difference in electrical potential between leads of the same metal attached to the electrodes can be measured by an electromotive force $\mathcal{E}$ and, taking $\mathcal{E} = (\phi^{Ag_{2+x}S} - \phi^{Ag})$, according to the convention used in Denbigh (1981),

$$\Delta G = -4\mathcal{F}\mathcal{E} \tag{87}$$

Thus, at 1 bar,

$$(2G_{Ag_2S}^o + 2RT\ln a_{Ag_2S} - 4G_{Ag}^o - G_{S_2}^o) \\ -RT\ln f_{S_2} = -4\mathcal{F}\mathcal{E} \tag{88}$$

By measuring $\mathcal{E}$ for a known f_{S_2}, the expression in brackets can be obtained and, if the activity of Ag_2S is nearly independent of f_{S_2}, an unknown f_{S_2} can be determined by measuring $\mathcal{E}$.

ACKNOWLEDGMENTS

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