Thermodynamic Aspects of Dissolution Reactions of Metal Oxides, Carbonates and Sulphides in Aqueous Media

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With 1 Figure, 3 Tables

1. Introduction

When thermodynamic principles are applied to geochemical problems, usually closed systems, which can exchange energy but not matter with their environment, are considered. The isothermal, isobaric condition for equilibrium in a closed system is given by $\Delta G = 0$, where ΔG means the derivative of the Gibbs energy of free enthalpy with respect to the extent of reaction. According to equation (1) the standard free enthalpy of a reaction, $\Delta G^{\ominus}$, is merely an alternative way of expressing the equilibrium constant.

$$\Delta G^{\ominus} = - RT \ln K^{\ominus} \tag{1}$$

The importance of equilibrium constants valid at standard conditions $i.e.$ 298.15 K (25 °C), 101.325 kPa (1 atm) is emphasized due to the fact that the standard enthalpy, $\Delta H^{\ominus}$, and volume changes, $\Delta V^{\ominus}$, of many geochemically important reactions vary only slowly with temperature and pressure respectively. Indeed, over limited ranges of temperature and pressure $\Delta H^{\ominus}$ and $\Delta V^{\ominus}$ often remain approximately constant as in equation (2) and (3).

$$\ln \frac{K_T^{\ominus}}{K_{298}^{\ominus}} = \frac{\Delta H^{\ominus}}{R} \left(\frac{1}{298} - \frac{1}{T} \right) \tag{2}$$

$$\ln \frac{K_P^{\ominus}}{K_1^{\ominus}} = - \frac{\Delta V^{\ominus} (P-1)}{RT} \tag{3}$$

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That means once reliable standard equilibrium constants at 25 °C and 1 atm are known, reasonable estimates or at least intelligent guesses of high temperature and pressure equilibrium constants can be made using available thermodynamic data.

Equilibrated chemical systems can be completely described, provided the equilibrium constants of every conceivable independent reaction and the analytical compositions are known. Extensive use of this approach has been made. For example thermodynamic models of ore deposition in hydrothermal systems (HELGESON, 1969, 1970) and the regulation of the chemical composition of natural waters (STUMM & MORGAN, 1970) have been constructed. Obviously, these models are only as good as the underlying assumptions including the respective equilibrium constants. For metal oxides, hydroxides, carbonates and sulphides reliable equilibrium constants in aqueous media were often lacking and therefore experimental methods have been developed for accurate determinations of their solubility constants and free enthalpies of formation, $\Delta_f G^{\ominus}$. These quantities can be used to describe the complicated interactions between solid, aqueous and gaseous phases in the various systems including components such as $M^{2+}-CO_2-H_2S-H_2O$, provided that reactions between individual species and phase transitions to establish stable or metastable equilibria are fast enough to be observed.

2. Experimental Method

2.1. Solubility Measurements

Accurate determinations of solubility constants of metal oxides, hydroxides, carbonates and sulphides in aqueous media depend critically on the following experimental aspects:

(1) Equilibrium between solid and aqueous phases must be established and checked by a sensitive operational criterion. Often applicable is the pH variation method (SCHINDLER, 1963) shown schematically for metal (II) carbonates in Fig. 1. The solid phases are reacted with solutions of varying acid concentration and varying carbon dioxide partial pressure. Equilibrium is indicated when the solubility constants obtained are independent of pH and metal ion concentrations over a wide range of starting conditions. In addition, side reactions are excluded when all experimental data fall on stoichiometric curves given by acid consumption and hydrogen carbonate formation. All ligands of interest in this context such as hydroxide, hydrogencarbonate and hydrogensulphide are connected to the pH via acid-base equilibria. Therefore, the free ligand concentration can be monitored continuously by potentiometric measurements with H^+-sensitive electrodes at constant CO_2- or H_2S-partial pressure.

(2) Only solid starting material is used, which is characterized with respect to its analytical composition and its X-ray structure. After finishing the solubility experiment it is checked by X-ray analysis whether the solid phase undergoes any alteration during the process of equilibration.

(3) The total anionic concentration is kept high by adding inert electrolytes.

Thereby activity coefficient variations are minimized and the solubility constant can be formulated with concentrations instead of activities.

So far three continuously operating solubility cells have been constructed; the first being primarily useful at room temperature (SCHINDLER, REINERT, & GAMS-JÄGER, 1968). For experiments performed at 5 to 95 °C, this cell has been modified to keep evaporation and condensation rates as low as possible (HEINDL & GAMS-JÄGER, 1977; GAMSJÄGER & REITERER, 1979). A semimicro type of solubility cell can be operated with only 5 ml of solvent and 2 to 10 mg of solid. This is effected by the shape of the vessel and the use of solvents partially presaturated with metal ions (REITERER, JOHANNES, & GAMSJÄGER, 1981).

2.2. Synthesis of Pure Neutral Carbonates

Obviously, reliable solubility measurements as described above can only be performed using stoichiometrically and structurally well-defined solid phases. In this context, a method for the synthesis of pure neutral transition metal carbonates was developed. *It seems impossible to precipitate neutral anhydrous manganese(II)-, iron(II)-, cobalt(II)- and nickel(II)-carbonate from aqueous solutions under atmospheric pressure;* even after long ageing periods poorly crystallized substances of variable composition are formed instead.

Many years ago, an autoclave method for the synthesis of pure magnesite was described (JANTSCH & ZEMEK, 1949). An attempt was made to prepare rhodochrosite, $MnCO_3$, siderite, $FeCO_3$, spherocobaltite, $CoCO_3$ and nickel carbonate, $NiCO_3$, using a similar technique. There are two critical aspects of this method. (1) the solutions should never become alkaline during the course of reaction and (2) the carbonate concentration should be raised by applying a high CO_2 pressure. This is achieved by exposing an acidic solution containing the respective metal ions at 140—220 °C to a partial pressure of CO_2 at 40—110 atm, in an autoclave with teflon lining. The solution is slowly neutralized to pH 6 to 7 with ammonia produced by the decomposition of added urea.

Coarse, crystallized products were obtained. Chemical analysis and X-ray-powder pattern showed the products to be pure neutral carbonates.

2.3. Free Enthalpies of Formation

As shown by a simple thermodynamic cycle, solubility constants combined with the respective standard potentials lead to free enthalpies of formation, which are independent of the inert electrolyte added to control the activity coefficients. Sulphides as in Table 1 provide a particularly straight-forward example. Thermodynamic data of the hydrogen sulphide formation are exactly known, hence the standard free enthalpies of sulphide formation can be determined by measuring solubility constants and standard electrode potentials using the same ionic medium.

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Table 1. Thermodynamic cycle for the calculation of $\Delta_f G^{\ominus}$ (MS)

$M^{2+}_{(I)} + H_2S_{(g)} \rightleftharpoons MS_{(s)} + 2\,H^+_{(I)}$	$\Delta G^{\ominus}_1 = RT \ln {}^*K_{pso}$
$M_{(s)} + 2\,H^+_{(I)} \rightleftharpoons M^{2+}_{(I)} + H_{2(g)}$	$\Delta G^{\ominus}_2 = 2\,F\,E^{\ominus}$
$H_{2(g)} + S_{(s)} \rightleftharpoons H_2S_{(g)}$	$\Delta G^{\ominus}_3$
$M_{(s)} + S_{(s)} \rightleftharpoons MS_{(s)}$	$\Delta_f G^{\ominus} = \overset{3}{\underset{i=1}{\Sigma}} \Delta G^{\ominus}_i$

It is easy to set up analogous thermodynamic cycles for oxides, hydroxides and carbonates. Obviously, these are useful only when the standard electrode potential of the corresponding metal ion/metal couple is accurately measureable in the ionic medium used.
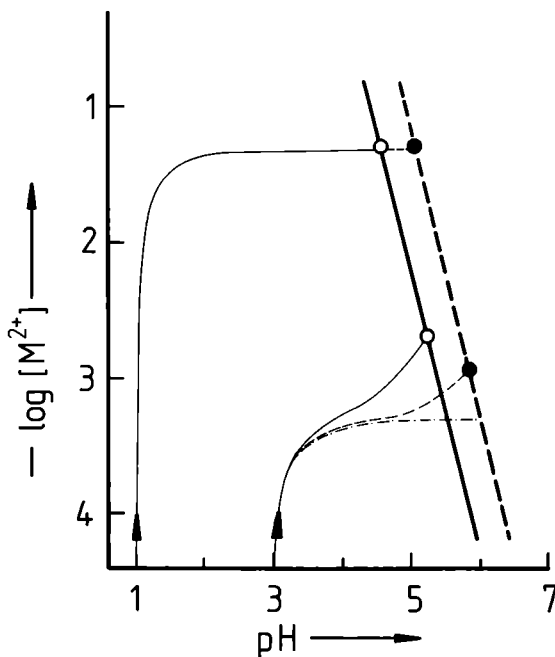

Fig. 1. pH variation method. Dissolution of a metal carbonate, MCO_3, in $HClO_4/NaClO_4$ solutions. Data pairs $\bigcirc$ $\bullet$, pH, $\log[M^{2+}]$ fall on straight lines and stoichiometric curves respectively. Arrows indicate the direction in which equilibrium is attained.

$$- \cdot - \cdot - \cdot - \quad 1/2([H^+]_{initial}-[H^+]_{equilibrium})$$
$$\underline{\hspace{4cm}} \quad p_{CO_2}=0.840\,atm$$
$$- - - - - - \quad p_{CO_2}=0.084\,atm$$

Straight lines and curves are calculated from

$$\log {}^*K_{pso}=\log([M^{2+}]\cdot p_{CO_2}[H^+]^{-2})= \;\;7.60$$
$$\log K_{pl} \;=\log([H^+][HCO_3^-]\cdot p^{-1}_{CO_2})=-7.65$$

3. Results

3.1. Fe^{II}-Sulphides

As an example we studied the solubility constants of synthetic troilite, α-FeS, hexagonal pyrrhotite, $FeS_{1.11}$, monoclinic pyrrhotite, $FeS_{1.14}$ as well as natural monoclinic pyrrhotite from Orawitza in Rumania with the methods just outlined.

As summarized in Table 2, regardless of conspicuously different dissolution rates, almost identical solubility constants were obtained (Table 1). As mentioned earlier, free enthalpies of formation for the various iron(II) sulphide phases can be calculated using a value of the standard electrode potential of the iron(II)/iron couple determined recently in this laboratory (HEINDL, 1979). The agreement of the new value for $\Delta_f G^{\ominus}$ of troilite with that recommended recently by MILLS (1974) is comparatively poor. We believe that our data are more reliable because MILLS' calculations were based on calorimetric experiments and high temperature equilibria, and can be falsified due to the formation of various products FeS_{1+x} as well as the retaining of high temperature modifications.

Table 2. Solubility constants and free enthalpies of FeS-phases

Solid phase	Formula	log*K_{pso}	$\Delta_f G^{\ominus}_{298}$/kcal mol^{-1}
Troilite	α-FeS	3.66 ± 0.05	-22.42 ± 0.11
Pyrrhotite hexagonal	$FeS_{1.11}$	3.67 ± 0.04	-22.39 ± 0.11
Pyrrhotite monoclinic	$FeS_{1.14}$	3.80 ± 0.10	-22.20 ± 0.17
Pyrrhotite monoclinic natural	$FeS_{1.14}$	3.65 ± 0.04	-22.42 ± 0.17
Troilite (MILLS)	α-FeS		-24.09 ± 0.10

$$1/(1-x)Fe_{1-x}S_{(s)} + 2\,H^+_{(I)} \rightleftharpoons Fe^{2+}_{(I)} + H_2S_{(g)} + x/(1-x)S_{(s)}$$

$$\log{}^*K_{pso} = \log \frac{[Fe^{2+}]\,p_{H2S}}{[H^+]^2} \quad (50\,^{\circ}C,\ I = 1.00\,mol\,kg^{-1}\,NaClO_4)$$

3.2. Transition Metal Carbonates

Neutral first row transition metal carbonates have been investigated generally at 50 °C by the method described and the respective standard free enthalpies of formation obtained (REITERER, 1980). Mainly the results for copper(II) and nickel(II) carbonate will be discussed here. No thermodynamically reliable information on $\Delta_f G^{\ominus}_{298}$ of $CuCO_3$ seemed to be available; in particular, it was not at all clear to which solid phase the accepted values refer. According to Table 3 the new value for the standard free enthalpy of formation of copper(II) carbonate is at least 2 kcal mol^{-1} more negative than the one previously accepted.

Table 3. Comparison of $\Delta_f G_{298}^{\ominus}$/kcal mol^{-1} for Ni(II) and Cu(II) carbonate

	NiCO$_3$	CuCO$_3$
This work	−152.7*) −151.7**)	−126.2
KELLEY & ANDERSON	−146.2	−123.4
LATIMER	−147.0	−123.8
BARIN & KNACKE	−144.1	−124.1

*) $E_{Ni^{2+}/Ni}^{\ominus} = -0.250 \, V$
**) $E_{Ni^{2+}/Ni}^{\ominus} = -0.228 \, V$

In aqueous media CuCO$_3$ becomes the stable phase at relatively high partial pressures of carbon dioxide and it is quite understandable that it has not been found in nature. Under the experimental conditions ($0.1 < p_{CO_2} < 1$ atm) of this work malachite is certainly thermodynamically favoured, whereas at atmospheric carbon dioxide partial pressure tenorite is the stable phase. It should be noted, however, that the molar surface area plays an important role in dissolution and precipitation processes. It has been shown, for example, that the solubility order of copper(II) oxide and copper(II) hydroxide, CuO < Cu(OH)$_2$, is reversed below a certain particle size (SCHINDLER, ALTHAUS, HOFER, & MINDER, (1965). A similar effect might explain why well crystallized copper(II) carbonate is transformed into malachite so slowly, and why natural deposits of basic copper(II) carbonates resist conversion into copper(II) oxide.

Nickel(II) carbonate is the most inert of the neutral carbonate phases and therefore solubility experiments were performed at 75−90 °C. The solubility constant extrapolated to 50 °C, however, was completely in line with those of the other first row transition metal carbonates which vary only slightly. The new value for the standard free enthalpy of formation of NiCO$_3$ suffers from the uncertainty of the standard electrode potential. The value is about 8 kcal mol^{-1} more negative than the one previously accepted. At 25 °C nickel(II) carbonate is completely stable with respect to spontaneous decomposition leading to NiO and CO$_2$ as in equation (4)

$$NiCO_{3(s)} \rightleftharpoons NiO_{(s)} + CO_{2(g)} \tag{4}$$
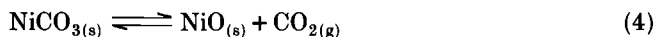
and it is rather astonishing that it has so far never been found in nature.

Presently Gibbsite, γ-Al(OH)$_3$, and Böhmite, γ-AlOOH, are investigated and it seems as if their stability order is reversed with temperature (GAMSJÄGER & MERALLA, 1981) Gibbsite being the stable form below about 55 °C.

Hopefully, the methods described will prove useful in providing reliable basic information for geochemical modelling.

Presently, at least one important generalization concerning remobilization processes can be inferred from solubility studies. *Since the free enthalpies as well as the rates of dissolution and precipitation reactions are usually different it is to be expected that*

the chemical compositions of primary mineral deposits and remobilized zones are likewise different.

References

GAMSJÄGER, H., & REITERER, F. (1979): Investigation of Equilibria Involving Carbon Dioxide, Carbonates and Water. — Environment International, *2*, 419.

GAMSJÄGER, H., & MERALLA, E. (1981): Löslichkeitskonstanten und relative thermodynamische Stabilitäten von Aluminiumhydroxiden. — 7. Internationale Leichtmetalltagung, Leoben-Wien 1981, 214.

HEINDL, R., & GAMSJÄGER, H. (1977): Solubility Constants and Free Enthalpies of Metal Sulphides, Part 6: A New Solubility Cell. — Monatsh., *108*, 1365.

HEINDL, R. (1979): Thermodynamische Untersuchungen am System $Fe^{2+}-H_2S-H_2O$. — Ph. D. Thesis, Montanuniversität Leoben.

HELGESON, H. C. (1969): Thermodynamics of Hydrothermal Systems at elevated Temperatures and Pressures. — Amer. J. Sci., *267*, 729.

HELGESON, H. C. (1970): A Chemical and Thermodynamic Model of Ore deposition in Hydrothermal Systems. — Mineral. Soc. Amer. Spec. Pap., *3*, 155.

JANTSCH, G., & ZEMEK, F. (1949): Über die Darstellung von synthetischem, kristallisiertem Magnesiumkarbonat. — Radex-Rundschau, 110.

MILLS, K. C. (1974): Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides. — Butterworths, London.

REITERER, F. (1980): Löslichkeitskonstanten und Freie Bildungsenthalpien neutraler Übergangsmetallcarbonate. — Ph. D. Thesis, Montanuniversität Leoben.

REITERER, F., JOHANNES, W., & GAMSJÄGER, H. (1981): Semimicro Determination of Solubility Constants: Copper(II) Carbonate and Iron(II) Carbonate. — Mikrochim. Acta, I, 63.

SCHINDLER, P. (1963): Die Bestimmung der Löslichkeitskonstanten von Metalloxiden und -hydroxiden. — Chimia (Switz.), *17*, 313.

SCHINDLER, P., ALTHAUS, H., HOFER, F., & MINDER, W. (1965): Löslichkeitsprodukte von Metalloxiden und -hydroxiden, 10. Mitteilung: Löslichkeitsprodukte von Zinkoxid, Kupferhydroxid und Kupferoxid in Abhängigkeit von Teilchengröße und molarer Oberfläche. Ein Beitrag zur Thermodynamik von Grenzflächen fest-flüssig. — Helv. Chim. Acta, *48*, 1204.

SCHINDLER, P., REINERT, M., & GAMSJÄGER, H. (1968): Zur Thermodynamik der Metallcarbonate. 2. Mitteilung: Löslichkeitskonstanten und Freie Bildungsenthalpien von $Cu_2(OH)_2CO_3$ (Malachit) und $Cu_3(OH)_2(CO_3)_2$ (Azurit) bei 25 °C. — Helv. Chim. Acta, *51*, 1845.

STUMM, W., & MORGAN, J. J. (1970): Aquatic Chemistry. — Wiley Interscience, A Division of John Wiley & Sons, Inc., New York-London-Sydney-Toronto.