

Solubilities of metal carbonates

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Abstract

Solubilities in aqueous media of sparingly-soluble metal carbonates play an important role in chemical processes whether they occur in a laboratory, on an industrial scale, or in the geologic environment. Solubility phenomena (i.e. dissolution and precipitation reactions) of metal carbonates control procedures for preparing, separating and purifying chemicals. Moreover, the interactions of the hydrological cycle with the cycle of carbonate rocks, the naturally occurring dissolution of carbonate minerals in water as well as their precipitation on the ocean floor and in the sediments of rivers and lakes can be described by the principles of solubility, although gigantic quantities of material may be involved.

The experimental methods for the determination of carbonate solubilities are reviewed and the results are discussed within the frame-work of equilibrium thermodynamics. It will be shown that Gibbs functions of pure stoichiometric carbonate phases can be determined by accurately measuring solubilities in aqueous electrolyte systems. In cases where solid-solid phase transformations and recrystallisations are kinetically inhibited, the methods developed were successfully applied to metastable equilibria. Occasionally, solubility data were even employed to estimate activity coefficients of components forming a series of carbonate solid solutions.

Whenever possible the activity coefficients of the reacting species were controlled by use of a constant ionic medium. Solubility constants obtained at various fixed ionic strengths were fitted to the Pitzer equations and extrapolated to infinite dilution. Provided the standard potentials of the respective metal ion/metal electrode are known over a range of ionic strengths the values of solubility constants at infinite dilution can be calculated independently. In any case the optimised *thermodynamic* constants were incorporated in a comprehensive computer model which permits a wide variety of solubility calculations. These are illustrated by a case study of a multicomponent system with industrial relevance.

Introduction

Metal carbonates are simple chemical compounds of industrial and environmental importance. Consequently, one would expect that their thermochemical quantities are sufficiently well known. However, a closer look into compilations of thermodynamic data shows that this optimistic view has to be corrected. Inspection of the thermal decomposition reaction of nickel carbonate, NiCO_3 , reveals, for example, that two grossly discrepant values for the respective standard Gibbs energy difference were listed by Latimer [1]. One of them indicates that NiCO_3 should decompose spontaneously with an equilibrium pressure of about 6 kbar at 25°C. Clearly, it is rather unlikely that a potentially explosive compound forms a mineral, as nickel carbonate does, which is the main constituent of the naturally occurring gaspèite [2]. As shown in Tab. 1 the partial pressure of CO_2 in equilibrium with solid NiCO_3 and NiO changes its order of magnitude from one compilation or paper to the other revealing a disturbing uncertainty in the $\mu^\ominus(\text{NiCO}_3)$ values.

In this paper it will be shown that: 1. Solubility measurements provide a reliable source of information on the Gibbs energy of metal carbonate formation. 2. Based on different sources of experimental data such as standard electrode potentials and/or solubilities a consistent set of

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Table I: Thermal decomposition of NiCO₃ at 25°C

$\mu^\ominus/\text{kJ mol}^{-1}$	NiCO ₃ (s)	⇌	NiO (s)	+	CO ₂ (g)	$\log(p_{\text{CO}_2}/p^\ominus)$	Ref.
KKH	-691.320		-255.847		-457.209	3.81	[1]
standard [†]	-717.421		-255.847		-457.209	-0.76	
	-705.347		-251.931		-457.207	0.66	[4, 5]
KKH	-721.998		-251.070		-457.264	-2.39	[6]
standard [†]	-730.676		-251.028		-457.250	-3.92	[7]
	-737.918		-251.028		-457.250	-5.19	this work

[†]For comparison all Gibbs energies of Tab. I are based on the standard state (KKH) below, used by Barin *et al.* [4, 5], Knacke *et al.* [6, 8] and ChemSage [9]:

$$\begin{aligned} H_{\text{Barin}} &= \Delta_f H_{298}^\ominus + (H^\ominus - H_{298}^\ominus), \\ \mu_{\text{Barin}} &= H_{\text{Barin}} - TS. \end{aligned} \quad (1)$$

Eq. (1) being valid even for the elements in their standard states where conventionally for all temperatures

$$\Delta_f G^\ominus = \Delta_f H^\ominus = 0. \quad (2)$$

Consequently, $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ can be obtained by Eq. (3)

$$\begin{aligned} \Delta_f H^\ominus &= H_{\text{Barin}}^\ominus (\text{for product}) - \sum H_{\text{Barin}}^\ominus (\text{for elements}) \\ \Delta_f G^\ominus &= \mu_{\text{Barin}}^\ominus (\text{for product}) - \sum \mu_{\text{Barin}}^\ominus (\text{for elements}). \end{aligned} \quad (3)$$

thermodynamic parameters can be obtained with the recently developed ChemSage optimiser [3].
3. Provided the relevant thermodynamic parameters are known the phase behaviour of multicomponent carbonate electrolyte systems can be predicted.

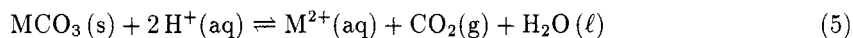
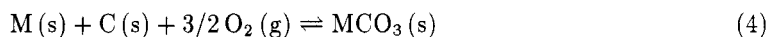
From solubility constants to Gibbs functions and back again:

The original method for the determination of standard Gibbs functions of (divalent) metal carbonates is based on measurements of electrode potentials and solubilities by “pH-variation” [10]. Essentially the same ionic medium is used as solvent in both studies.

The main advantages of this approach are, that: (1) The ionic medium cancels in the course of the calculation, consequently the Gibbs energy of metal carbonate formation, $\Delta_f G^\ominus$ (MCO₃), can be obtained, without any non-thermodynamic assumption; (2) moreover, the constant ionic medium keeps the variation of the activity coefficients at a minimum, thus reliable stoichiometric solubility constants can be measured easily.

Single carbonates

According to Eq. (4) $\Delta_f G^\ominus$ (MCO₃) occurring in Eq. (5) is invariant with respect to the ionic medium, thus a relationship between pairs of solubility constants, standard electrode potentials, and equilibrium vapour pressures of the respective solvents is obtained.



$$\log {}^*K_{p_{\text{CO}_2}}^I = \log \{ [\text{M}^{2+}] p_{\text{CO}_2} [\text{H}^+]^{-2} \} \quad (6)$$

$$\log {}^*K_{ps0}^0 = \log {}^*K_{ps0}^I + \log \left(\frac{p_{\text{H}_2\text{O}}^I}{p_{\text{H}_2\text{O}}^*} \right) + \frac{2F}{RT \ln 10} (E_1^\ominus - E_0^\ominus) \quad (7)$$

Relationship (7) is useful when and only when the ratio of the vapour pressures, $p_{\text{H}_2\text{O}}^I/p_{\text{H}_2\text{O}}^*$, the difference of the standard electrode potentials, $E_1^\ominus - E_0^\ominus$, and the solubility constant at a certain ionic strength, ${}^*K_{ps0}^I$, are easier to measure than the solubility constant at infinite dilution, ${}^*K_{ps0}^0$.

The first metal carbonate studied by this method was otavite, CdCO_3 [11]. Rai *et al.* [12] reinvestigated the solubility product of cadmium carbonate painstakingly at low ionic strengths. Although the solubility product determined by these authors is slightly different, the corresponding experimental data fall according to Fig. 1 at least equally closely on the curves calculated by our and their model, respectively.

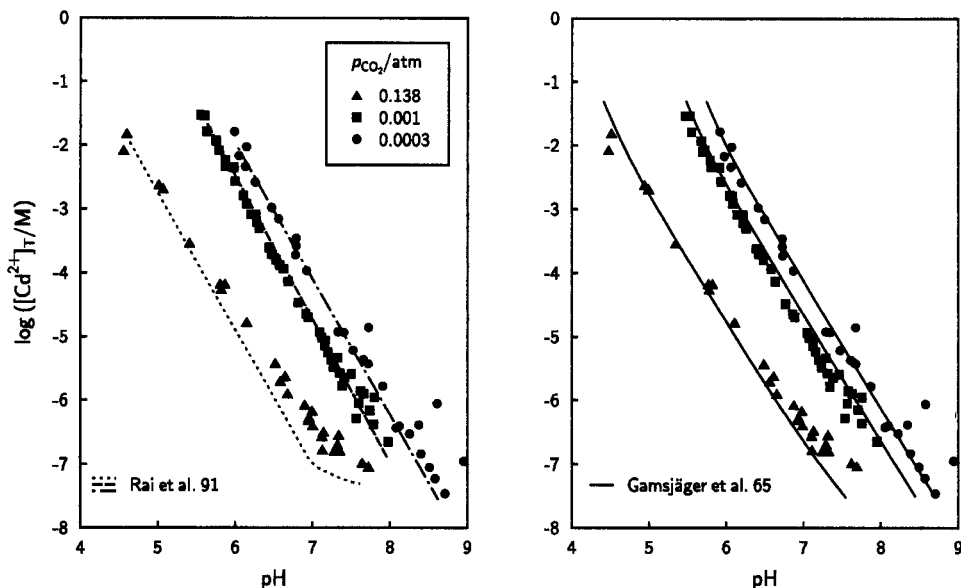


Fig. 1 Solubility of CdCO_3 (otavite) at 25°C

Moreover, the 1993 solubility product of Stipp *et al.* [13] agrees within the experimental uncertainty with our 1965 value, although it was again determined at extremely low ionic strengths. The conclusiveness of our value is corroborated by a study of the cadmium carbonate solubility at variable ionic strengths [14]. With the aid of the new ChemSage optimizing routine [3] solubility data and standard electrode potentials [15] determined at different ionic strengths can be simultaneously used to evaluate the solubility constant at infinite dilution plus the ternary Pitzer parameters $\theta_{\text{Na},\text{Cd}}$ and $\psi_{\text{Na},\text{Cd},\text{ClO}_4}$. The Pitzer optimisation confirms our result from 1965, $\log {}^*K_{ps0}^0 = 6.14 \pm 0.10$ at 25°C.

In a solubility study of manganese carbonate, rhodochrosite, it turned out that even within several weeks hydrothermally synthesised MnCO_3 at 25°C did not equilibrate with the aqueous solutions [16]. Therefore the solubility constant was determined at 50°C and $I = 1 \text{ mol kg}^{-1}$ NaClO_4 [17, 18]. With the constant obtained an improved enthalpy of MnCO_3 formation was calculated using the Davies equation. The improved enthalpy of formation was then employed to extrapolate the solubility constant to 25 and 90°C. A comparison with the results of Wolfram and Krupp [19] in Fig. 2 shows that the latter probably also failed to attain equilibrium at 25°C.

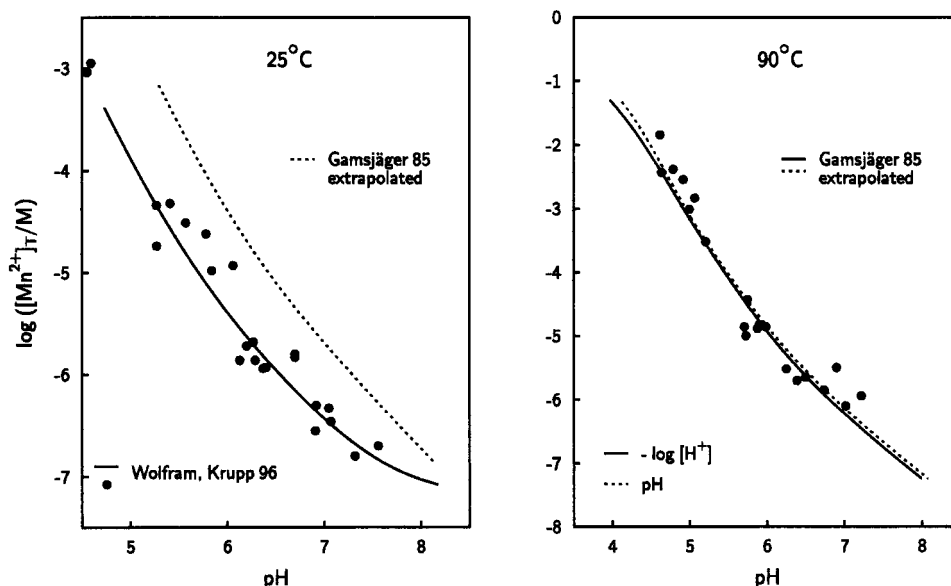


Fig. 2 Solubility of $MnCO_3$ (rhodochrosite)

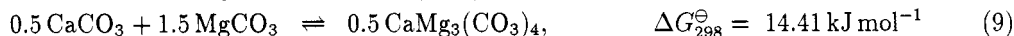
The data at 90°C, however, agree within their experimental uncertainty with our extrapolation, although they were obtained at low and variable ionic strengths.

Our solubility and standard potential data of siderite, $FeCO_3$, determined at 50°C [17, 20] extrapolate to slightly higher $\log K$ -values at 25°C than were obtained experimentally by Bruno *et al.* [21]. Again the much slower equilibration at 25°C may partly be responsible for this discrepancy, which, however, only moderately exceeds an uncertainty of ± 0.2 logarithmic units of the equilibrium constant. On the other hand we found that the NBS data of iron(2+) are not quite satisfactory and could be improved by a study of the temperature dependence of the iron(2+) standard electrode potential.

Obviously the solution chemistry of rhodochrosite, siderite and even otavite is of considerable geochemical interest, as reflected by *Geochim. Cosmochim. Acta* and *J. Sol. Chem.* papers of the nineties [12, 13, 19, 21]. Doubtless the powerful modelling methods developed recently can help to unearth neglected high quality data and link them to these problems.

Double carbonates

This discussion is restricted to the three alkaline earth double carbonates dolomite, huntite and norsethite. Clearly the rock forming dolomite is the most abundant and important of them. Whereas according to Eqs. (8-10) dolomite, $CaMg(CO_3)_2$, is thermodynamically stable with respect to decomposition into the endmembers, huntite, $CaMg_3(CO_3)_4$, and norsethite, $BaMg(CO_3)_2$, are not.



Dolomite is congruently soluble in aqueous media and its phase behaviour may be summarised by a Lippmann diagram [22] which is topologically analogous to an $x - T$ diagram [23], as may be

visualised by inverting Fig. 3. It has to be admitted, however, that only the congruent dissolution and the solubility minimum can experimentally be verified, whereas due to kinetic inhibitions the quasi-eutectic lines and compositions cannot.

At ambient temperature and pressure kinetic inhibitions prevent the precipitation of magnesite or dolomite from solutions supersaturated with respect to these phases, but they permit a complete solubility study of huntite [24]. At 50°C and an ionic strength of 3 mol kg⁻¹ NaClO₄ the quasi-peritectic composition coincides with the metastable solubility minimum. All our attempts failed, to synthesise huntite utilising the thermodynamic information obtained so far.

We met with more success in the case of norsethite. Although norsethite is clearly metastable with respect to decomposition into the endmembers, again congruent dissolution was observed in solubility studies [25]. When seed crystals of witherite are added to a solution already saturated with norsethite, the three phase equilibrium indicated by the quasi-peritectic line of Fig. 3 is comparatively quickly attained. This leads to the apparent paradox that by addition of solid barium carbonate the concentrations of dissolved barium decrease and magnesium increase respectively.

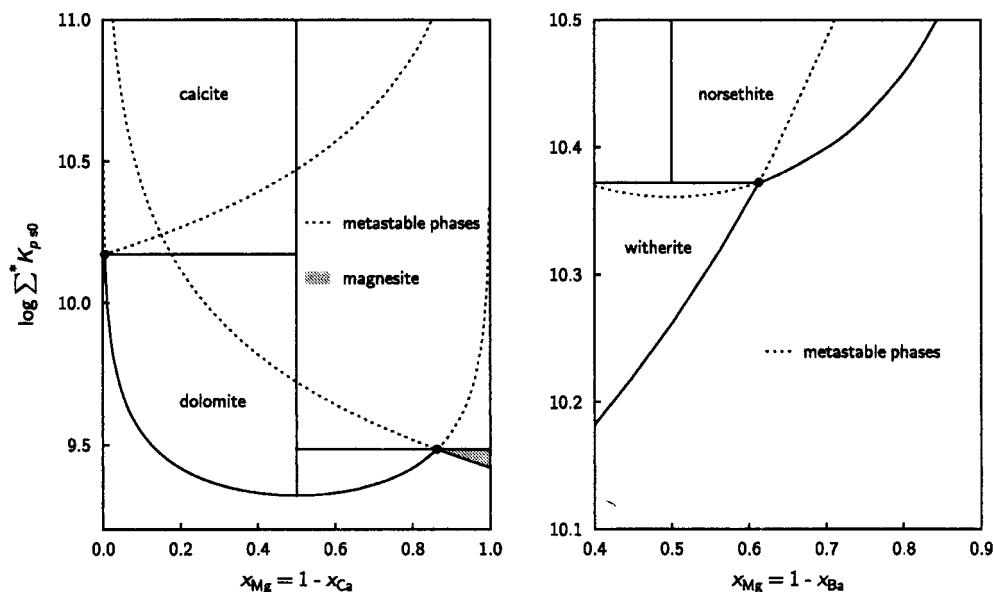


Fig. 3 Phase diagrams in the systems CaCO₃-MgCO₃-H₂O and BaCO₃-MgCO₃-H₂O respectively, at 25°C

The powerful Gibbs energy minimiser, ChemSage [9], can be used to predict conditions for the precipitation of pure norsethite from sodium hydrogencarbonate solutions. As indicated by calculations and borne out by experiments it is much easier to prepare norsethite in a closed system, because the range of Ba²⁺ and Mg²⁺ concentrations useful for the formation of pure norsethite is much larger, than in a system which is opened to the atmosphere. The computer simulation also shows that carbonate solutions [26] are less favourable for the synthesis of norsethite as compared to the closed hydrogencarbonate system, again the suitable range of Ba²⁺ and Mg²⁺ concentrations is much narrower in the former than in the latter. Proper composition of the solutions is indeed very important in order to produce pure norsethite. If one ingredient is out of its portion, the product will be either witherite or hydrated magnesium carbonate or a mixture of one of these with norsethite [26, 27, 28].

The formation of norsethite in trona mines at ambient temperature and atmospheric CO₂ partial pressure can also be explained using the thermodynamic data derived from solubility studies [25].

Experimental methods

Solubility measurements by the pH-variation method require continuously operating cells equipped with hydrogen or metal ion sensitive electrodes separated from the suspended material, an efficient percolation system securing intimate contact between solid and solvent, and a well defined gas phase. The prototype of cells effectively meeting these requirements only operated at 25°C [11, 29]. Consequently, solubility cells working from 5 to 95°C at ambient pressure were developed [30, 31]. For solids which are available only in milligram amounts cells which can be operated with only 5 cm³ of solvent were employed [32].

Nickel carbonate is comparatively inert, so its solubility was studied between 75 and 90°C, with the remarkable result, shown in Fig. 4, that it is nearly independent of temperature at least in this narrow range [17, 20]. Other transition metal carbonates seem to behave similarly [13], however, a generalisation has to wait until enough experimental facts have been collected.

The μ^\ominus value of pure, neutral NiCO₃, gaspéite, calculated on the basis of our solubility data is at least 7 kJ mol⁻¹ more negative than the values proposed previously (see Tab. I). This means that even the solubility predicted by the value closest to ours is 15 to 20 times higher than that determined experimentally, but an error this large is far beyond all realistic expectations.

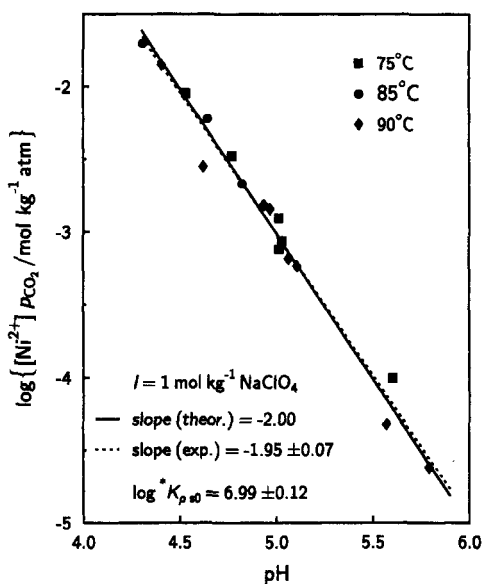


Fig. 4 Solubility of NiCO₃

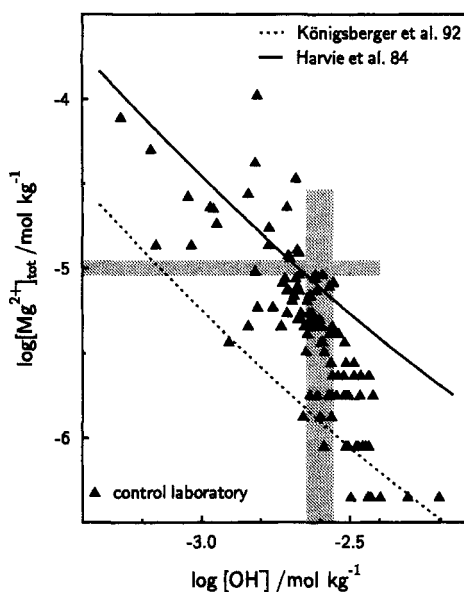


Fig. 5 Solubility of Mg(OH)₂ in brines

The differences between the chemical potentials of calcite and other calcium carbonate phases such as aragonite or vaterite can be measured by galvanic cells without liquid junction equipped with hydrogen or glass electrodes [33].

When these carbonates were equilibrated with CaCl₂ solutions of the same molality and CO₂ atmospheres of the same compositions the measured *e.m.f.*'s of the galvanic cells are directly related to the different hydrogen ion activities and consequently the Gibbs-functions for the calcite → aragonite and the calcite → vaterite transitions were measured accurately.

A similar approach was used to determine the excess Gibbs energies of homogeneous solid mixtures of Co-Mn carbonates [34].

The thermostatted vessel used in these equilibrium studies operated on a similar principle to that of the solubility cells described above [33].

Multicomponent carbonate systems with industrial relevance

The multicomponent multiphase equilibria involved in an Austrian rock-salt brine purification process were modelled with ChemSage [35].

NaCl is extracted from rock-salt deposits by water. This results in the formation of brines, the starting material for common-salt production. These brines are essentially saturated with NaCl but contain also various other salts which on the one hand interfere with the evaporation process (scale formation on heat exchangers and boilers) and are on the other hand undesired impurities in the sodium chloride produced.

The purification process employed operates discontinuously by two steps:

(1) The brine is reacted with calcium hydroxide and sulfate rich mother liquor (from the evaporation process), thereby most of the Mg^{2+} ions are removed as magnesium hydroxide, brucite, and part of the Ca^{2+} ions are precipitated as calcium sulfate, gypsum.

(2) The carbonisation of excess OH^- ions with flue gas containing about 12 vol.% CO_2 results in precipitation of calcium carbonate. The remaining Ca^{2+} ions are finally removed by addition of sodium carbonate.

Thus, the solubilities of CaCO_3 , $\text{Mg}(\text{OH})_2$ and CaSO_4 control the brine purification process.

Because the brucite precipitate can never be quantitatively removed in the first step, a too low OH^- molality in the second step leads to an unacceptable increase in $[\text{Mg}^{2+}]$. As shown in Fig. 5 experimental results obtained by an industrial control laboratory [36] compare reasonably well with brucite solubilities calculated according to literature data [37] (solid line) and our own assessment [38] (dotted line). Adjustment of the OH^- molality to 2 to 3 mmol kg^{-1} (vertical bar) keeps $[\text{Mg}^{2+}]$ safely below $10^{-5} \text{mol kg}^{-1}$ (horizontal bar). Considering the experimental scatter, the Mg^{2+} content of purified brines can be predicted quite well.

Obviously this kind of research is not only of academic but also of industrial importance.

Acknowledgements

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