IUPAC-NIST Solubility Data Series. 95. Alkaline Earth Carbonates in Aqueous Systems. Part 1. Introduction, Be and Mg

Alex De Visscher, *Editor, Evaluator*[a)]
Department of Chemical and Petroleum Engineering, and Centre for Environmental Engineering Research and Education (CEERE), Schulich School of Engineering, University of Calgary, Calgary, AB, T2N 1N4 Canada

Jan Vanderdeelen, *Evaluator*[b)]
Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, Ghent University, B-9000 Ghent, Belgium

Erich Königsberger, *Compiler*[c)]
School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA, 6150, Australia

Bulat R. Churagulov, *Compiler*
Department of Chemistry, Moscow State University, Moscow, Russia

Masami Ichikuni, *Compiler* and **Makoto Tsurumi,** *Compiler*
Department of Environmental Chemistry, Tokyo Institute of Technology, Nagatsuda, Yokohama, Japan

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The alkaline earth carbonates are an important class of minerals. This volume compiles and critically evaluates solubility data of the alkaline earth carbonates in water and in simple aqueous electrolyte solutions. Part 1, the present paper, outlines the procedure adopted in this volume in detail, and presents the beryllium and magnesium carbonates. For the minerals magnesite ($MgCO_3$), nesquehonite ($MgCO_3{\cdot}3H_2O$), and lansfordite ($MgCO_3{\cdot}5H_2O$), a critical evaluation is presented based on curve fits to empirical and/or thermodynamic models. Useful side products of the compilation and evaluation of the data outlined in the introduction are new relationships for the Henry constant of CO_2 with Sechenov parameters, and for various equilibria in the aqueous phase including the dissociation constants of $CO_2(aq)$ and the stability constant of the ion pair $MCO_3^0(aq)$ ($M =$ alkaline earth metal). Thermodynamic data of the alkaline earth carbonates consistent with two thermodynamic model variants are proposed. The model variant that describes the $Mg^{2+}-HCO_3^-$ ion interaction with Pitzer parameters was more consistent with the solubility data and with other thermodynamic data than the model variant that described the interaction with a stability constant.
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Key words: aqueous solution; beryllium carbonate; magnesium carbonate; solubility; thermodynamics.

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a)Electronic mail: adevissc@ucalgary.ca.
b)Electronic mail: jan.vanderdeelen@ugent.be.
c)Electronic mail: e.koenigsberger@murdoch.edu.au.

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1. Preface

1.1. Scope of the volume

Solubilities of alkaline earth metal carbonates in water and aqueous solutions are of interest in many areas such as biology, geology, hydrology, medicine, and environmental sciences. Of particular significance is the interaction between alkaline earth metal carbonates and carbon dioxide during CO_2 storage in underground aquifers.

This volume contains compilations and evaluations of the solubilities of the alkaline earth carbonates in water and simple electrolyte solutions. Solid phases containing mixed carbonates or mixed carbonates and hydroxides, solubilities in mixed or non-aqueous solvents, solubilities in supercritical water, and solubilities in sea water are excluded. The volume is organized as follows:

Part 1 (this paper): Introduction, Be, Mg
Part 2: Ca
Part 3: Sr, Ba, Ra

Literature through 2009 was searched. For each of beryllium carbonate and radium carbonate, only one reference is available, and the solubilities given are doubtful. For magnesium carbonate about 25 references are available. Data are available for three mineralogical types: the anhydrous salt $MgCO_3$ (magnesite), the trihydrate $MgCO_3 \cdot 3H_2O$ (nesquehonite), and the pentahydrate $MgCO_3 \cdot 5H_2O$ (lansfordite). For calcium carbonate, about a hundred references were found covering three well-defined crystallographical forms of anhydrous salt (calcite, aragonite, and vaterite) and two hydrates, the monohydrate (monohydrocalcite) and the hexahydrate (ikaite). There are fewer than 20 references each for strontium carbonate (strontianite) and barium carbonate (witherite).

1.2. Unit conversions for compilations

The general equations for unit conversions are given in the Introduction to the Solubility Data Series.[1,2] For many conversions, like from mol l^{-1} to mol kg^{-1}, a density of the liquid solution is needed.

The conversion from amount concentration to molality in an aqueous system containing a dissolved salt and dissolved CO_2 is given by

$$\frac{m_{\mathrm{salt}}}{\mathrm{mol\,kg^{-1}}} = \frac{1000\dfrac{c_{\mathrm{salt}}}{\mathrm{mol\,l^{-1}}}}{\dfrac{\rho_{\mathrm{solution}}}{\mathrm{kg\,m^{-3}}} - \dfrac{M_{\mathrm{salt}}}{\mathrm{kg\,kmol^{-1}}}\dfrac{c_{\mathrm{salt}}}{\mathrm{mol\,l^{-1}}} - \dfrac{M_{\mathrm{CO_2}}}{\mathrm{kg\,kmol^{-1}}}\dfrac{c_{\mathrm{CO_2}}}{\mathrm{mol\,l^{-1}}}}, \quad (1)$$

with m_{salt} the molality of the salt, c_{salt} its amount concentration, ρ_{solution} the solution density, M_{salt} the molar mass of the salt, $M_{\mathrm{CO_2}}$ the molar mass of CO_2, and $c_{\mathrm{CO_2}}$ its concentration. If multiple salts are dissolved, each salt will result in a term in the denominator of Eq. (1).

In systems open to CO_2(g), the dominant dissolved species in equilibrium with an alkaline earth carbonate is the alkaline earth metal ion, and bicarbonate, unlike systems in the absence of added CO_2, where the dominant species are the metal and the carbonate ions. Hence, in open systems the value of M_{salt} applicable in Eq. (1) is 62 g mol^{-1} larger than the value of the metal carbonate. Improper use of Eq. (1) leads to errors in excess of 5% at a concentration of 1 mol l^{-1}, which occurs in the case of nesquehonite and lansfordite at high CO_2 partial pressures.

The dissolved CO_2 concentration in open systems is on the order of 0.035 mol l^{-1} per bar of CO_2 partial pressure at 25 °C, and is strongly temperature dependent. Hence, not accounting for dissolved CO_2 can also generate errors in excess of 5%, when the partial pressure is 40 bar. Even salting out needs to be accounted for in some extreme cases, especially when working with nesquehonite or lansfordite. Not accounting for this effect would overestimate the dissolved CO_2 concentration, and the molality. If none of these precautions are taken, the error made can be in excess of 10%. Hence, the nature of the dissolved salt, the dissolution of CO_2 and its salting out were appropriately accounted for.

When mass concentrations analyzed as MCO_3 (M = alkaline earth metal) are to be converted to molalities in systems open to CO_2(g), the appropriate equation is

$$\frac{m_{\mathrm{M(HCO_3)_2}}}{\mathrm{mol\,kg^{-1}}} = \frac{1000\,\dfrac{\rho_{\mathrm{MCO_3}}}{\mathrm{g\,l^{-1}}}\Big/\dfrac{M_{\mathrm{MCO_3}}}{\mathrm{g\,mol^{-1}}}}{\dfrac{\rho_{\mathrm{solution}}}{\mathrm{g\,l^{-1}}} - \dfrac{M_{\mathrm{M(HCO_3)_2}}}{\mathrm{g\,mol^{-1}}}\dfrac{\rho_{\mathrm{MCO_3}}}{\mathrm{g\,l^{-1}}}\Big/\dfrac{M_{\mathrm{MCO_3}}}{\mathrm{g\,mol^{-1}}} - \dfrac{M_{\mathrm{CO_2}}}{\mathrm{g\,mol^{-1}}}\dfrac{c_{\mathrm{CO_2}}}{\mathrm{mol\,l^{-1}}}}. \tag{2}$$

Solubility of CO_2 and salting out are discussed in later sections.

1.2.1. Density of pure water

A standard equation of state for fluid water was developed by Wagner and Pruß[3] that accurately predicts all water properties in a wide range of temperatures and pressures. The disadvantage of this approach is that the equation for density is an implicit one, making density calculations inconvenient for compilation purposes. Therefore, an approximate explicit equation was developed. The starting point of the approach is the explicit equation suggested by Wagner and Pruß[3] for the density of liquid water at the saturated vapor pressure, ρ_{sat}, as a function of temperature, which is valid from the triple point to the critical point of water,

$$\rho_{\mathrm{sat}} = \rho_{\mathrm{c}}\left(1 + b_1\theta^{1/3} + b_2\theta^{2/3} + b_3\theta^{5/3} + b_4\theta^{16/3} + b_5\theta^{43/3} + b_6\theta^{110/3}\right), \tag{3}$$

where

$\rho_c = 322$ kg m^{-3} (critical density)
$\theta = 1 - T/T_c$
$T_c = 647.096$ K (critical temperature)
$b_1 = 1.99274064$
$b_2 = 1.09965342$
$b_3 = -0.510839303$
$b_4 = -1.75493479$
$b_5 = -45.5170352$
$b_6 = -6.74694450 \times 10^5$

The water density was then corrected for pressure using an equation based on Tait's law, but with temperature-dependent coefficients A and B,

$$\rho = \frac{\rho_{\mathrm{sat}}}{1 - \dfrac{A\rho_{\mathrm{sat}}/(\mathrm{kg\,m^{-3}})}{B}\ln(1 + B(p/\mathrm{kPa} - p_{\mathrm{v}}/\mathrm{kPa}))}. \tag{4}$$

The saturated vapor pressure p_v in Eq. (4) was also taken from Wagner and Pruß,[3]

$$p_{\mathrm{v}} = p_{\mathrm{c}}\exp\left(\frac{T_{\mathrm{c}}}{T}(a_1\theta + a_2\theta^{1.5} + a_3\theta^3 + a_4\theta^{3.5} + a_5\theta^4 + a_6\theta^{7.5})\right), \tag{5}$$

with

$p_c = 22064$ kPa (critical pressure)
$T_c = 647.096$ K (critical temperature)
$a_1 = -7.85951783$
$a_2 = 1.84408259$
$a_3 = -11.7866497$
$a_4 = 22.6807411$
$a_5 = -15.9618719$
$a_6 = 1.80122502$

Equation (4) with 4th-order polynomials in θ for A and B were fitted to predictions of the Wagner and Pruß[3] equation of state in the temperature range 273.15–473.15 K and the pressure range from p_v to 20 000 kPa. The coefficients A and B in Eq. (4) resulting from this fit are

$$A = \alpha_0 + \alpha_1\theta + \alpha_2\theta^2 + \alpha_3\theta^3 + \alpha_4\theta^4, \tag{6}$$

with

$\alpha_0 = 7.4242997 \times 10^{-9}$
$\alpha_1 = -5.3019784 \times 10^{-8}$
$\alpha_2 = 1.6188583 \times 10^{-7}$
$\alpha_3 = -2.3371482 \times 10^{-7}$
$\alpha_4 = 1.3239697 \times 10^{-7}$

$$B = \beta_0 + \beta_1\theta + \beta_2\theta^2 + \beta_3\theta^3 + \beta_4\theta^4 \tag{7}$$

$\beta_0 = 6.1180105 \times 10^{-5}$
$\beta_1 = -4.4068335 \times 10^{-4}$
$\beta_2 = 1.3633547 \times 10^{-3}$
$\beta_3 = -2.0035442 \times 10^{-3}$
$\beta_4 = 1.1496256 \times 10^{-3}$

The consistency of Eq. (4) with the Wagner and Pruß[3] equation of state is 0.004% (0.04 kg m^{-3}) or better in the entire range tested.

1.2.2. Density of electrolyte solutions

Densities of electrolyte solutions were calculated with the method of Krumgalz *et al.*,[4] based on the Pitzer model. When data was unavailable in Ref. 4, data of Krumgalz *et al.*[5] valid at 25 °C were used, with pure water density data at the temperature of interest. In their model, Krumgalz *et al.*[4] used the somewhat obsolete pure water density calculations of Kell[6] because those data or very similar values were used in most experimental determinations of electrolyte solution densities. In this work, the newly derived equations were used because the Kell[6] equation is limited to 1 atm pressure.

At 273.15–373.15 K and 101.325 kPa, the deviation between the Wagner and Pruß[3] equation of state and the Kell[6] equation is up to about 0.015 kg m^{-3} (standard deviation 0.0061 kg m^{-3}). The deviation between the Wagner and Pruß[3] equation of state and the new equation is up to about 0.0062 kg m^{-3} (standard deviation 0.0046 kg m^{-3}). The difference between the Kell[6] model and the new equation is up to about 0.017 kg m^{-3} (standard deviation 0.0090 kg m^{-3}). Hence, the choice to use the new equation for water density with the Krumgalz*et al.*[4] model for electrolyte solution density introduces a negligible inconsistency. Kell[7] presented a comprehensive equation for water density, including pressure effects for up to 10 atm. Because of the limited pressure range, this equation was not investigated in any detail.

To test the error introduced by applying the Krumgalz model to high pressures, predictions with the model for NaCl solutions were compared with values tabulated by Rogers and Pitzer.[8] At atmospheric pressure, the model predicted densities up to 0.16 kg m^{-3} lower than the values are tabulated by Rogers and Pitzer.[8] At 20 000 kPa, the model predictions were up to 2.5 kg m^{-3} above the tabulated values (NaCl(aq) has a negative apparent compressibility). Hence, unit conversions for concentrated electrolyte solutions at high pressures should be made with great care. However, in dilute solutions ($m < 0.1$ mol kg^{-1}) the error is acceptable (<0.11 kg m^{-3}).

Even when solubilities of alkaline earth carbonates in pure water are converted from mol l^{-1} to mol kg^{-1}, it is useful to account for changes in solution density. For instance, the solubility of the anhydrous $CaCO_3$ polymorphs is around 0.01 mol kg^{-1} at 25 °C and $p(CO_2) = 1$ atm. The dominant ions in solution are Ca^{2+} and $HCO_3{}^-$. The density of a 0.01 mol kg^{-1} $Ca(HCO_3)_2$ solution is about 998.33 kg m^{-3}, whereas the density of pure water is about 997.04 kg m^{-3}. Not accounting for this effect would introduce an error of about 0.13%.

1.2.3. Influence of dissolved gases on water density

Kell[7] investigated the influence of dissolved N_2, O_2, Ar, and CO_2 on the density of water. The combined effect of N_2, O_2, and Ar was found to be about 0.0003% and can be ignored. The effect of CO_2 on the solution density depends on the temperature and the CO_2 partial pressure. Its estimation requires a value of the apparent molar volume of CO_2(aq). As CO_2 is a fairly ideal solute in the pressure range of interest, it is assumed that apparent molar volume equals partial molar volume. Kell[7] reviewed the literature available at the time, and tentatively put forward a value of 38 cm^3 mol^{-1}, with literature values ranging from 28 to 38 cm^3 mol^{-1}. This range was confirmed by Hnědkovský *et al.*,[9] who reported apparent molar volumes for a wide temperature range. However, they found a pronounced temperature dependence. Their values compare well with other studies in the literature and are largely consistent with the Wagner and Pruß[3] equation of state.[10] When their data at 25–200 °C are fitted to a parabolic equation in T/K, the following is obtained:

$$V_\phi/(\mathrm{cm^3\,mol^{-1}}) = 58.309 - 0.19758(T/\mathrm{K}) + 0.00038030(T/\mathrm{K})^2. \tag{8}$$

When this equation is applied at 0 °C and 25 °C, values of 32.7 and 33.2 cm^3 mol^{-1} are obtained, respectively. These values compare well with values of the partial molar volume suggested by Weiss[11] (32.3 ± 0.5 cm^3 mol^{-1}), Barbero *et al.*[12] (32.8 ± 1.2 cm^3 mol^{-1}), and Spycher *et al.*[13] (32.6 ± 1.3 cm^3 mol^{-1}). Based on these values, densities were calculated at 0 °C (CO_2 solubility at partial pressure 1 bar about 0.075 mol kg^{-1}) and at 25 °C (CO_2 solubility at partial pressure 1 bar about 0.033 mol kg^{-1}). At 0 °C, the density effect is negligible (<0.1 kg m^{-3}) for partial pressures below 0.12 bar, but is as high as 0.85 kg m^{-3} at a partial pressure of 1 atm. At $p(CO_2) = 12.5$ bar, the error introduced by ignoring the density effect is as large as 1%. At 25 °C, the density effect is negligible (<0.1 kg m^{-3}) for partial pressures below 0.28 bar, and is 0.36 kg m^{-3} at a partial pressure of 1 bar.

The calculation of the solubility of CO_2 is discussed in Sec. 1.3.3.

1.2.4. Ambient CO_2 mole fraction and altitude correction of total pressure

In many studies total pressure is not reported, or simply reported as atmospheric pressure. Neither is CO_2 mole fraction in the gas phase mentioned in some older studies, or merely indicated as "ambient." However, barometric pressure depends on altitude, and the ambient CO_2 mole fraction has increased considerably in the last 150 years. Hence, approximations were required to deal with such cases.

Barometric pressure p can be estimated with reasonable accuracy using a single, constant temperature, using the following equation:

$$p = p_0 \exp\left(-\frac{Mgh}{RT}\right), \tag{9}$$

in which p_0 is the barometric pressure at sea level (assumed to be 101 325 Pa), M is the molar mass of air (0.029 kg mol^{-1}), g is the acceleration due to gravity (9.80665 m s^{-2}), h is the altitude of the measurement (m), and R is the ideal gas constant (8.314472 J mol^{-1} K^{-1}). Using a temperature of 15 °C (288.15 K) leads to the approximate equation,

$$p/\text{kPa} = 101.325 \exp(-0.00012\, h/\text{m}). \tag{10}$$

Unless ambient temperatures are extreme, the potential error of Eq. (10) is less than the natural variation of the ambient barometric pressures up to altitudes of well above 1000 m.

Ambient CO_2 concentrations have been measured at Mauna Loa, Hawaii, since 1958,[14] and from Antarctic ice cores by Etheridge *et al.*[15] Recently the validity of the ice core measurements was confirmed by Siegenthaler *et al.*[16] Ice core data of Etheridge *et al.*[15] were systematically below the Mauna Loa data by about 0.5–1 ppm (parts per million by mole fraction). The standard deviation between the ice core data and the Mauna Loa data was typically about 1–1.5 ppm. The data from both sources were pooled and empirical equations were fitted to the concentration to obtain relationships with year. The results were as follows:

$$\begin{aligned}
1800-1939\text{:}\ & y(CO_2)/\text{ppm} \\
&= 274.70 + 5.803 \\
&\quad \times \exp(0.0131073\ (t/\text{year} - 1800)) \\
1940-1952\text{:}\ & y(CO_2)/\text{ppm} = 310.6 \\
1953-2004\text{:}\ & y(CO_2)/\text{ppm} \\
&= 277.03 + 1.2806 \\
&\quad \times \exp(0.0214357\ (t/\text{year} - 1800)).
\end{aligned} \tag{11}$$

The number of data points for the three periods is 30, 3, and 68. The standard deviation between the model and the data is 1.1 ppm, 0.75 ppm, and 1.2 ppm, respectively. When necessary, the above equations were used to estimate ambient CO_2 concentrations.

Johnston and Walker[17] pointed out that ambient air has variable CO_2 concentration, which leads to a serious loss of accuracy when used in the determination of the solubility constant of an alkaline earth carbonate. They recommend the use of synthetic air-CO_2 mixtures. Hence, experiments with ambient air should be treated with caution even when plausible estimates as given above are used.

1.3. Evaluations

The compiled data were evaluated in various ways including the following:

- Data obtained with faulty or suspicious methodology were rejected. An example is boiling the suspension after adding the metal carbonate to eliminate CO_2. This method has the potential to eliminate CO_2 evolved from the dissolution of the metal carbonate, or, conversely, trap CO_2 dissolved prior to adding the metal carbonate due to the alkaline nature of the minerals. Either way, the system is undefined because the total carbonate concentration is unknown.
- Empirical equations were fitted to the data, and outliers were detected and eliminated.
- A simple thermodynamic model was developed for the $MCO_3 + H_2O$ and $MCO_3 + H_2O + CO_2$ data (M = Mg, Ca, Sr, Ba). The model was used to derive a solubility constant of the alkaline earth carbonate for each measurement. The solubility constants are then plotted versus temperature. Outliers and data with spurious trends were eliminated. Some data points rejected by the empirical model turned out to be fairly accurate when considered with the thermodynamic model. In such cases, the data points were reverted to accepted status. The $MCO_3 + H_2O$ data were more difficult to evaluate than the $MCO_3 + H_2O + CO_2$ data. Hence, the $MCO_3 + H_2O + CO_2$ data were evaluated first, and thermodynamic solubility constant correlations were fitted. These were introduced in the $MCO_3 + H_2O$ model, and the data were evaluated by comparison with the model results.
- For some cases, the consistency between the data sets was checked against independent thermodynamic data. For the specific case of calcite, aragonite, and vaterite, all data were treated as a single data set, using thermodynamic data to convert all solubility constants to calcite.

The empirical equations and the thermodynamic model are discussed below. We stress that the model is used as a tool for evaluating data, not as an end of its own. Hence, we do not recommend any model. Thermodynamic data presented are data either predicted by this particular model, or most consistent with the model, and should not be construed as "reference" thermodynamic data.

1.3.1. Empirical equations for solubility

For an empirical equation to be a useful tool in the detection of outliers in solubility data, it is necessary that the equation has a realistic temperature and pressure dependence in a wide range of conditions, with a limited number of adjustable parameters. To that effect, an equation that mimics some thermodynamic aspects of alkaline earth carbonate solubility was selected. De Visscher and Vanderdeelen[18] argued that the solubility (s) of an alkaline earth carbonate is approximately proportional to the cubic root of the CO_2 fugacity:

$$s/(\text{mol kg}^{-1}) = \sqrt[3]{\frac{4K_s K_c K_1 a_w}{K_2 \gamma_{M^{2+}} \gamma^2_{HCO_3^-}} \frac{f(CO_2)}{\text{bar}}}, \tag{12}$$

where K_s is the solubility constant of MCO_3, K_c is the solubility constant of CO_2, K_1 and K_2 are the first and second acid dissociation constant of CO_2/carbonic acid, $f(CO_2)$ is the fugacity of CO_2, and the γ values are activity coefficients. Hence, the logarithm of the solubility can be written as

$$\lg\left(\frac{s}{\mathrm{mol\,kg^{-1}}}\right)=\frac{1}{3}\lg\left(\frac{4K_sK_cK_1a_w}{K_2\gamma_{M^{2+}}\gamma^2_{HCO_3^-}}\right)+\frac{1}{3}\lg\left(\frac{f(CO_2)}{\mathrm{bar}}\right). \tag{13}$$

By assuming an equation of the form $a+b/T+c\lg T$ for the first logarithm on the right-hand side of Eq. (13), an equation of the following form is obtained:

$$\lg\left(\frac{s}{\mathrm{mol\,kg^{-1}}}\right)=a+b\lg\left(\frac{f(CO_2)}{\mathrm{bar}}\right)+\frac{c}{T/\mathrm{K}}+d\lg\left(\frac{T}{\mathrm{K}}\right). \tag{14}$$

Note that the fitting parameters (a, b, …) in the equations in this section are not meant to have the same meaning in each equation. When ideal gas behavior is assumed, the fugacity can be considered equal to the partial pressure. However, when such an equation is adopted, all the non-idealities of the system are absorbed in parameter b (which should approximate $1/3$). Preliminary tests with nesquehonite ($MgCO_3{\cdot}3H_2O$) solubility data in the $MgCO_3+H_2O+CO_2$ system showed that this led to an unrealistically large value of b (0.38), making the equation unreliable for use in an extended pressure range. Making b temperature dependent did not solve the problem because it led to an unrealistically large temperature dependence of b with the $MgCO_3+H_2O+CO_2$ dataset. Instead, a more realistic assumption relating fugacity to partial pressure was used. When a second-order virial equation of state of the form,

$$pV_m=RT(1+ap) \tag{15}$$

is used, then the relationship between fugacity and partial pressure is

$$\lg\left(\frac{f(CO_2)}{\mathrm{bar}}\right)=\lg\left(\frac{p(CO_2)}{\mathrm{bar}}\right)+\frac{a}{\ln(10)}\frac{p(CO_2)}{\mathrm{bar}}. \tag{16}$$

If it is assumed that a is linearly dependent on temperature, then the following equation is obtained:

$$\lg\left(\frac{f(CO_2)}{\mathrm{bar}}\right)=\lg\left(\frac{p(CO_2)}{\mathrm{bar}}\right)+bp(CO_2)/\mathrm{bar}+c(T/\mathrm{K})(p(CO_2)/\mathrm{bar}). \tag{17}$$

Substitution in Eq. (14) leads to an equation of the form,

$$\lg\left(\frac{s}{\mathrm{mol\,kg^{-1}}}\right)=a+b\lg\left(\frac{p(CO_2)}{\mathrm{bar}}\right)+c\frac{p(CO_2)}{\mathrm{bar}}+d\frac{T}{\mathrm{K}}\frac{p(CO_2)}{\mathrm{bar}}+\frac{e}{T/\mathrm{K}}+f\lg\left(\frac{T}{\mathrm{K}}\right). \tag{18}$$

Equation (18) showed a more realistic value of b (0.347) in the preliminary analysis with nesquehonite, and was retained for the evaluation.

1.3.2. Thermodynamic model for solubility

The following reactions are considered in the model:

$$MCO_3\cdot xH_2O(cr)\rightleftharpoons M^{2+}(aq)+CO_3^{2-}(aq)+xH_2O(l)\qquad K_s=(M^{2+})(CO_3^{2-})a_w^x(m^\circ)^{-2}, \tag{19}$$

$$CO_2(g)\rightleftharpoons CO_2(aq)\qquad K_c=(CO_2(aq))f^{-1}(CO_2(g))(f^\circ)(m^\circ)^{-1}, \tag{20}$$

$$CO_2(aq)+H_2O(l)\rightleftharpoons H^+(aq)+HCO_3^-(aq)\qquad K_1=(H^+)(HCO_3^-)(CO_2(aq))^{-1}a_w^{-1}(m^\circ)^{-1}, \tag{21}$$

$$HCO_3^-(aq)\rightleftharpoons H^+(aq)+CO_3^{2-}(aq)\qquad K_2=(H^+)(CO_3^{2-})(HCO_3^-)^{-1}(m^\circ)^{-1}, \tag{22}$$

$$H_2O(l)\rightleftharpoons H^+(aq)+OH^-(aq)\qquad K_w=(H^+)(OH^-)a_w^{-1}(m^\circ)^{-2}, \tag{23}$$

$$M^{2+}(aq)+OH^-(aq)\rightleftharpoons MOH^+(aq)\qquad K_{MOH^+}=(MOH^+)(M^{2+})^{-1}(OH^-)^{-1}(m^\circ), \tag{24}$$

$$M^{2+}(aq)+CO_3^{2-}(aq)\rightleftharpoons MCO_3^0(aq)\qquad K_{MCO_3^0}=(MCO_3^0)(M^{2+})^{-1}(CO_3^{2-})^{-1}(m^\circ), \tag{25}$$

$$M^{2+}(aq)+HCO_3^-(aq)\rightleftharpoons MHCO_3^+(aq)\qquad K_{MCO_3^+}=(MHCO_3^+)(M^{2+})^{-1}(HCO_3^-)^{-1}(m^\circ). \tag{26}$$

In Eqs. (19)–(26), round brackets denote activities, f denotes fugacity, a_w refers to water activity, m° is the standard activity (1 mol kg^{-1}), and f° is the standard fugacity (1 atm was used as data were compiled in atm). The last equation was treated as an optional equation in the evaluation, as the existence of this ion pair has been subject to continuing debate for almost 50 years. The CO_2 dissolution reaction (Eq. (20)) was only considered in the so-called open system (see Sec. 1.3.2.1).

1.3.2.1. Model equations for open system. By open system, we mean the $MCO_3 + H_2O + CO_2$ system containing a solid MCO_3 phase, a gas phase containing a known partial pressure of CO_2, and an aqueous phase in equilibrium with the two other phases.

The condition of charge neutrality in the aqueous phase leads to the following equation:

$$2[M^{2+}] + [MOH^+] + [MHCO_3^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \tag{27}$$

This equation is written in terms of activities:

$$\frac{2(M^{2+})}{\gamma_{M^{2+}}} + \frac{(MOH^+)}{\gamma_{MOH^+}} + \frac{(MHCO_3^+)}{\gamma_{MHCO_3^+}} + \frac{(H^+)}{\gamma_{H^+}} = \frac{(HCO_3^-)}{\gamma_{HCO_3^-}} + \frac{2(CO_3^{2-})}{\gamma_{CO_3^{2-}}} + \frac{(OH^-)}{\gamma_{OH^-}}. \tag{28}$$

To calculate solubility, each term in this equation will be calculated in terms of the free metal ion activity (M^{2+}). First a relationship between free metal ion activity and hydrogen ion activity is derived from Eqs. (19)–(22),

$$(H^+) = \sqrt{\frac{K_cK_1K_2}{K_s}\frac{f^{1/2}(CO_2)}{(f^\circ)^{1/2}}}\, a_w^{(1+x)/2}(M^{2+})^{1/2}(m^\circ)^{1/2}. \tag{29}$$

The following relations can be derived from the reaction equilibria:

$$(HCO_3^-) = K_cK_1\frac{f(CO_2)a_w}{(f^\circ)(H^+)}(m^\circ)^2, \tag{30}$$

$$(CO_3^{2-}) = K_cK_1K_2\frac{f(CO_2)a_w}{(f^\circ)(H^+)^2}(m^\circ)^3, \tag{31}$$

$$(OH^-) = \frac{K_w a_w}{(H^+)}(m^\circ)^2, \tag{32}$$

$$(MOH^+) = K_{MOH^+}K_w\frac{a_w(M^{2+})}{(H^+)}(m^\circ), \tag{33}$$

$$(MCO_3^0) = K_{MCO_3^0}K_cK_1K_2\frac{f(CO_2)a_w(M^{2+})}{(f^\circ)(H^+)^2}(m^\circ)^2, \tag{34}$$

$$(MHCO_3^+) = K_{MHCO_3^+}K_cK_1\frac{f(CO_2)a_w(M^{2+})}{(f^\circ)(H^+)}(m^\circ). \tag{35}$$

By substitution of Eq. (29), the following equations can be derived:

$$(HCO_3^-) = \sqrt{\frac{K_sK_cK_1}{K_2}\frac{f^{1/2}(CO_2)a_w^{(1-x)/2}}{(f^\circ)(M^{2+})^{1/2}}}(m^\circ)^{3/2}, \tag{36}$$

$$(CO_3^{2-}) = K_s\frac{(m^\circ)^2}{a_w^x(M^{2+})}, \tag{37}$$

$$(OH^-) = K_w\sqrt{\frac{K_s}{K_cK_1K_2}\frac{(f^\circ)a_w^{(1-x)/2}}{f^{1/2}(CO_2)(M^{2+})^{1/2}}}(m^\circ)^{3/2}, \tag{38}$$

$$(MOH^+) = K_{MOH^+}K_w\sqrt{\frac{K_s}{K_cK_1K_2}}\frac{(M^{2+})^{1/2}a_w^{(1-x)/2}}{f^{1/2}(CO_2)}(f^\circ)^{1/2}(m^\circ)^{1/2}, \tag{39}$$

$$(MCO_3^0) = \frac{K_{MCO_3^0}K_s}{a_w^x}(m^\circ), \tag{40}$$

$$(MHCO_3^+) = K_{MHCO_3^+}\sqrt{\frac{K_sK_cK_1}{K_2}\frac{f^{1/2}(CO_2)}{(f^\circ)}}\, a_w^{(1-x)/2}(M^{2+})^{1/2}(m^\circ)^{1/2}. \tag{41}$$

Substitution into Eq. (28) leads to the following:

$$\begin{aligned}
&\frac{2(M^{2+})}{\gamma_{M^{2+}}} + \frac{K_{MOH^+}K_w}{\gamma_{MOH^+}}\sqrt{\frac{K_s}{K_cK_1K_2}}\frac{a_w^{(1-x)/2}(M^{2+})^{1/2}}{f^{1/2}(CO_2)}(f^\circ)^{1/2} \\
&\times (m^\circ)^{1/2} + \frac{K_{MHCO_3^+}}{\gamma_{MHCO_3^+}}\sqrt{\frac{K_sK_cK_1}{K_2}f^{1/2}(CO_2)a_w^{(1-x)/2}} \\
&\times (M^{2+})^{1/2}(m^\circ)^{1/2} + \frac{1}{\gamma_{H^+}}\sqrt{\frac{K_cK_1K_2}{K_s}\frac{f^{1/2}(CO_2)}{(f^\circ)^{1/2}}} \\
&\times a_w^{(1+x)/2}(M^{2+})^{1/2}(m^\circ)^{1/2} \\
&= \frac{1}{\gamma_{HCO_3^-}}\sqrt{\frac{K_sK_cK_1}{K_2}\frac{f^{1/2}(CO_2)a_w^{(1-x)/2}}{(f^\circ)^{1/2}(M^{2+})^{1/2}}}(m^\circ)^{3/2} \\
&+ \frac{2K_s}{\gamma_{CO_3^{2-}}}\frac{(m^\circ)^2}{a_w^x(M^{2+})} \\
&+ \frac{K_w}{\gamma_{OH^-}}\sqrt{\frac{K_s}{K_cK_1K_2}\frac{(f^\circ)a_w^{(1-x)/2}}{f^{1/2}(CO_2)(M^{2+})^{1/2}}}(m^\circ)^{3/2}.
\end{aligned} \tag{42}$$

This is a fourth-order polynomial in $(M^{2+})^{1/2}$. After rearrangement, one obtains

$$\begin{aligned}
&\frac{(\mathrm{M}^{2+})^2}{(m^\circ)^2}\frac{2}{\gamma_{\mathrm{M}^{2+}}}+\frac{(\mathrm{M}^{2+})^{3/2}}{(m^\circ)^{3/2}}\left(\begin{array}{l}\frac{K_{\mathrm{MOH}}K_{\mathrm{w}}}{\gamma_{\mathrm{MOH}^+}}\sqrt{\frac{K_{\mathrm{s}}}{K_{\mathrm{c}}K_1K_2}}\frac{(f^\circ)^{1/2}a_{\mathrm{w}}^{(1-x)/2}}{f^{1/2}(\mathrm{CO}_2)}+\frac{K_{\mathrm{MHCO}_3^+}}{\gamma_{\mathrm{MHCO}_3^+}}\sqrt{\frac{K_{\mathrm{s}}K_{\mathrm{c}}K_1}{K_2}}\frac{f^{1/2}(\mathrm{CO}_2)}{(f^\circ)^{1/2}}a_{\mathrm{w}}^{(1-x)/2}\\
+\frac{1}{\gamma_{\mathrm{H}^+}}\sqrt{\frac{K_{\mathrm{c}}K_1K_2}{K_{\mathrm{s}}}}\frac{f^{1/2}(\mathrm{CO}_2)}{(f^\circ)^{1/2}}a_{\mathrm{w}}^{(1+x)/2}\end{array}\right)\\
&-\frac{(\mathrm{M}^{2+})^{1/2}}{(m^\circ)^{1/2}}\left(\frac{1}{\gamma_{\mathrm{HCO}_3^-}}\sqrt{\frac{K_{\mathrm{s}}K_{\mathrm{c}}K_1}{K_2}}\frac{f^{1/2}(\mathrm{CO}_2)}{(f^\circ)^{1/2}}a_{\mathrm{w}}^{(1-x)/2}+\frac{K_{\mathrm{w}}}{\gamma_{\mathrm{OH}^-}}\sqrt{\frac{K_{\mathrm{s}}}{K_{\mathrm{c}}K_1K_2}}\frac{(f^\circ)^{1/2}a_{\mathrm{w}}^{(1-x)/2}}{f^{1/2}(\mathrm{CO}_2)}\right)\\
&-\frac{2K_{\mathrm{s}}}{\gamma_{\mathrm{CO}_3^{2-}}}\frac{1}{a_{\mathrm{w}}^x}=0
\end{aligned} \quad (43)$$

This equation has one positive real root, $(\mathrm{M}^{2+})^{1/2}(m^\circ)^{-1/2}$, which can be obtained by iteration. The solubility of the metal carbonate, s, can be calculated as

$$s=[\mathrm{M}^{2+}]+[\mathrm{MOH}^+]+[\mathrm{MHCO}_3^+]+[\mathrm{MCO}_3^0]. \quad (44)$$

Substitution of the appropriate equations leads to

$$\begin{aligned}
s=&\frac{(\mathrm{M}^{2+})}{\gamma_{\mathrm{M}^{2+}}}+\frac{K_{\mathrm{MOH}}K_{\mathrm{w}}}{\gamma_{\mathrm{MOH}^+}}\sqrt{\frac{K_{\mathrm{s}}}{K_{\mathrm{c}}K_1K_2}}\frac{a_{\mathrm{w}}^{(1-x)/2}(\mathrm{M}^{2+})^{1/2}}{f^{1/2}(\mathrm{CO}_2)}\\
&\times(f^\circ)^{1/2}(m^\circ)^{1/2}\\
&+\frac{K_{\mathrm{MHCO}_3^+}}{\gamma_{\mathrm{MHCO}_3^+}}\sqrt{\frac{K_{\mathrm{s}}K_{\mathrm{c}}K_1}{K_2}}\frac{f^{1/2}(\mathrm{CO}_2)}{(f^\circ)^{1/2}}a_{\mathrm{w}}^{(1-x)/2}(\mathrm{M}^{2+})^{1/2}(m^\circ)^{1/2}\\
&+\frac{K_{\mathrm{MCO}_3^0}K_{\mathrm{s}}}{a_{\mathrm{w}}^x}(m^\circ).
\end{aligned} \quad (45)$$

Equations (43) and (45) calculate the solubility of an alkaline earth carbonate for a given set of equilibrium constants (and hence the temperature), including K_s, and the fugacity of CO_2. In practice, our intention was to derive a value of K_s for each solubility measurement. For that purpose, the value of s was determined for different values of K_s, and K_s was determined from s by iteration. Within each iteration, the activity coefficients and the water activity need to be known. They were calculated with the Pitzer formalism, but for that the concentration of all the species need to be known. Hence, an iteration within the iteration was needed where Eq. (43) was solved with provisional values of the activity coefficients, and the resulting concentrations were entered in the Pitzer equations to obtain activity coefficients for the next iteration, until convergence was reached.

1.3.2.2. Model equations for closed system. By closed system, we mean the $MCO_3 + H_2O$ system containing a solid MCO_3 phase and an aqueous phase. Experimentally this system is much more challenging than the open system because contamination of CO_2 from the surroundings can influence the solubility markedly. Some studies attempted to minimize this effect by stripping the solution with a CO_2-free gas after addition of MCO_3. However, this leads to a system that cannot be described as $MCO_3 + H_2O$. Such systems were evaluated with great caution, or rejected. Because the dissolution rate of the $MCO_3 + H_2O$ system is extremely low, equilibration can take weeks or months. Also, due to the low solubility of most $MCO_3 + H_2O$ systems, recrystallization is extremely slow, which increases the risk of crystal size effects. For these reasons, the evaluation of the open system was conducted first, and closed system measurements were evaluated by comparison with model predictions using K_s values obtained in the open system evaluation.

Again the charge balance was used as a starting point (Eq. (28)). This time a second balance is needed, as the amount of alkaline earth metal in the solution must equal the amount of total carbonate,

$$\begin{aligned}
&[\mathrm{M}^{2+}]+[\mathrm{MOH}^+]+[\mathrm{MHCO}_3^+]+[\mathrm{MCO}_3^0]\\
&\quad=[\mathrm{CO}_2(\mathrm{aq})]+[\mathrm{HCO}_3^-]+[\mathrm{CO}_3^{2-}]\\
&\qquad+[\mathrm{MHCO}_3^+]+[\mathrm{MCO}_3^0].
\end{aligned} \quad (46)$$

Two species contain both a metal atom and a carbonate species, and can be left out of the balance. The equation is written in terms of activities,

$$\frac{(\mathrm{M}^{2+})}{\gamma_{\mathrm{M}^{2+}}}+\frac{(\mathrm{MOH}^+)}{\gamma_{\mathrm{MOH}^+}}=\frac{(\mathrm{CO}_2(\mathrm{aq}))}{\gamma_{\mathrm{CO}_2}}+\frac{(\mathrm{HCO}_3^-)}{\gamma_{\mathrm{HCO}_3^-}}+\frac{(\mathrm{CO}_3^{2-})}{\gamma_{\mathrm{CO}_3^{2-}}}. \quad (47)$$

All the activities in Eqs. (28) and (47) are written in terms of the M^{2+} activity and the H^+ activity, in order to obtain two equations with two unknowns,

$$(\mathrm{HCO}_3^-)=\frac{K_{\mathrm{s}}}{K_2}\frac{(\mathrm{H}^+)}{a_{\mathrm{w}}^x(\mathrm{M}^{2+})}(m^\circ), \quad (48)$$

$$(\mathrm{CO}_3^{2-})=K_{\mathrm{s}}\frac{1}{a_{\mathrm{w}}^x(\mathrm{M}^{2+})}(m^\circ)^2, \quad (49)$$

$$(\mathrm{OH}^-)=\frac{K_{\mathrm{w}}a_{\mathrm{w}}}{(\mathrm{H}^+)}(m^\circ)^2, \quad (50)$$

$$(\mathrm{MOH}^+)=K_{\mathrm{MOH}^+}K_{\mathrm{w}}\frac{a_{\mathrm{w}}(\mathrm{M}^{2+})}{(\mathrm{H}^+)}(m^\circ), \quad (51)$$

$$(\mathrm{CO}_2(\mathrm{aq}))=\frac{K_{\mathrm{s}}}{K_1K_2}\frac{(\mathrm{H}^+)^2}{a_{\mathrm{w}}^{1+x}(\mathrm{M}^{2+})}, \quad (52)$$

$$\left(\mathrm{MCO_3^0}\right) = K_{\mathrm{MCO_3^0}} K_\mathrm{s} \frac{1}{a_\mathrm{w}^x} (m^\circ), \tag{53}$$

$$\left(\mathrm{MHCO_3^+}\right) = \frac{K_{\mathrm{MHCO_3^+}} K_\mathrm{s}}{K_2} \frac{(\mathrm{H^+})}{a_\mathrm{w}^x}. \tag{54}$$

Substitution of the above equations into Eq. (47), and solving for the metal ion activity, leads to

$$\left(\mathrm{M^{2+}}\right) = \sqrt{\frac{\dfrac{K_\mathrm{s}(\mathrm{H^+})^2}{K_1 K_2 \gamma_{\mathrm{CO_2}} a_\mathrm{w}^{1+x}} + \dfrac{K_\mathrm{s}(\mathrm{H^+})(m^\circ)}{K_2 \gamma_{\mathrm{HCO_3^-}} a_\mathrm{w}^x} + \dfrac{K_\mathrm{s}(m^\circ)^2}{\gamma_{\mathrm{CO_3^{2-}}} a_\mathrm{w}^x}}{\dfrac{1}{\gamma_{\mathrm{M^{2+}}}} + \dfrac{K_{\mathrm{MOH^+}} K_\mathrm{w} a_\mathrm{w}}{\gamma_{\mathrm{MOH^+}}(\mathrm{H^+})}(m^\circ)}}. \tag{55}$$

Substitution of the same equations in the charge balance Eq. (28) leads to

$$\begin{aligned}
&\frac{2\left(\mathrm{M^{2+}}\right)}{\gamma_{\mathrm{M^{2+}}}} + \frac{K_{\mathrm{MOH^+}} K_\mathrm{w} a_\mathrm{w}\left(\mathrm{M^{2+}}\right)}{\gamma_{\mathrm{MOH^+}}(\mathrm{H^+})}(m^\circ) \\
&\quad + \frac{K_{\mathrm{MHCO_3^+}} K_\mathrm{s}(\mathrm{H^+})}{\gamma_{\mathrm{MHCO_3^+}} K_2 a_\mathrm{w}^x} + \frac{(\mathrm{H^+})}{\gamma_{\mathrm{H^+}}} \\
&\quad = \frac{K_\mathrm{s}(\mathrm{H^+})}{K_2 \gamma_{\mathrm{HCO_3^-}} a_\mathrm{w}^x \left(\mathrm{M^{2+}}\right)}(m^\circ) + \frac{2K_\mathrm{s}}{\gamma_{\mathrm{CO_3^{2-}}} a_\mathrm{w}^x \left(\mathrm{M^{2+}}\right)}(m^\circ)^2 \\
&\quad\quad + \frac{K_\mathrm{w} a_\mathrm{w}}{\gamma_{\mathrm{OH^-}}(\mathrm{H^+})}(m^\circ)^2.
\end{aligned} \tag{56}$$

By substituting Eq. (55) into Eq. (56), an equation in $(\mathrm{H^+})$ is obtained, which can be solved iteratively. Once $(\mathrm{H^+})$ is known, $(\mathrm{M^{2+}})$ can be calculated, as well as the concentration of all the species. Again, an additional iteration is required to calculate the activity coefficients and the water activity. The solubility predicted with the model is compared with measured values for evaluation.

1.3.2.3. The Pitzer ion interaction formalism. According to the Pitzer framework,[19–22] the activity coefficient of a cation M and an anion X can be described as follows:

$$\begin{aligned}
\ln \gamma_X = z_X^2 F &+ \sum_c m_c (2B_{cX} + ZC_{cX}) \\
&+ \sum_a m_a \left(2\phi_{Xa} + \sum_c m_c \psi_{cXa}\right) \\
&+ \sum\nolimits_{c>c'} \sum m_c m_{c'} \psi_{cc'X} \\
&+ |z_X| \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{nX},
\end{aligned} \tag{57}$$

$$\begin{aligned}
\ln \gamma_M = z_M^2 F &+ \sum_a m_a (2B_{Ma} + ZC_{Ma}) \\
&+ \sum_c m_c \left(2\phi_{Mc} + \sum_a m_a \psi_{Mca}\right) \\
&+ \sum\nolimits_{a>a'} \sum m_a m_{a'} \psi_{Maa'} \\
&+ z_M \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{nM},
\end{aligned} \tag{58}$$

with

$$\begin{aligned}
F = -A_\phi \left(\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln\left(1 + b\sqrt{I}\right)\right) &+ \sum_c \sum_a m_c m_a B'_{ca} \\
+ \sum\nolimits_{c>c'} \sum m_c m_{c'} \phi'_{cc'} &+ \sum\nolimits_{a>a'} \sum m_a m_{a'} \phi'_{aa'}.
\end{aligned} \tag{59}$$

In the above equations, the subscripts a and c refer to anions and cations, respectively; z_i is the charge number of ion i, and Z $(= \sum_a m_a z_a + \sum_c m_c z_c)$ is a measure of the charge molality. B_{ij} and C_{ij} are single-electrolyte parameters, ϕ_{ij} is a binary ion interaction parameter for ions with a charge of the same sign, ψ_{ijk} is a ternary ion interaction parameter, and λ_{ni} is an ion-neutral species interaction parameter.

B_{ij} and B'_{ij} are functions of ionic strength and depend on two input parameters, $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$. Parameters C_{ij} are written in terms of input parameters C_{ij}^{ϕ}. The parameters ϕ_{ij} are written in terms of input parameters θ_{ij}. Details, as well as comprehensive tables of ion interaction parameters, are given by Pitzer.[23] An abridged version of the model description is given in Pitzer.[24] The Pitzer parameters used in this volume are given below (Secs. 1.3.3.6 and 1.3.3.7).

In the equations, A_ϕ is the Debye-Hückel parameter, and b is a constant, taken to be 1.2. Methods to calculate A_ϕ are given by Bradley and Pitzer,[25] and by Archer and Wang.[26] The latter scheme was used here. The difference between the two schemes is negligible for the conditions considered in this review.

1.3.2.4. Some thoughts on the calcium bicarbonate ion pair. The existence of the calcium bicarbonate ($\mathrm{CaHCO_3^+}$) ion pair (and other alkaline earth bicarbonate ion pairs) has been subject to controversy for several decades. As discussed below (Sec. 1.3.3.6), most studies conducted at low ionic strength point at the existence of these ion pairs (e.g., Plummer and Busenberg[27]), whereas studies conducted at higher ionic strength do not point at any ion pairing (e.g., Pitzer *et al.*,[28] He and Morse[29]). De Visscher and Vanderdeelen[30] showed that some calcium carbonate solubility data are consistent with the existence of the calcium bicarbonate ion pair, whereas other solubility data are inconsistent with such an ion pair. Their assumption is that crystal defects (e.g., surface charge) could explain why some solubility data are seemingly inconsistent with the existence of the calcium bicarbonate ion pair.

What may resolve the inconsistency in the data is to assume that the ion pair exists, but is so weak that it disintegrates at elevated ionic strength. This could be described mathematically by means of specific ion interaction coefficients between $\mathrm{CaHCO_3^+}$ and the dominant counter ion (e.g., $\mathrm{Cl^-}$). Harvie *et al.*[31] followed this approach for $\mathrm{MgOH^+}$. Given the speculative nature of this approach, it was not adopted here, but the $\mathrm{MHCO_3^+}$ ion pair was included in the above thermodynamic models as an optional species in this volume with a stability constant, as opposed to using Pitzer parameters for the $\mathrm{M^{2+}{-}HCO_3^-}$ interaction. The model variant with a $\mathrm{MHCO_3^+}$ ion pair (no $\mathrm{M(HCO_3)_2}$ Pitzer parameters) will be denoted

Model 1 in the evaluations; the model variant without $MHCO_3^+$ ion pair (with $M(HCO_3)_2$ Pitzer parameters) will be denoted Model 2.

1.3.3. Thermodynamic data

For the thermodynamic model, an attempt was made to use equations generating accurate thermodynamic data in as wide a range of conditions as possible. However, some of the equations may lose accuracy rapidly beyond 100 °C or 2 atm CO_2 partial pressure. Given the current interest in CO_2 storage in underground aquifers in the presence of alkaline earth carbonate minerals, studies to extend the validity of thermodynamic data to more extreme conditions are much needed.

1.3.3.1. Solubility of CO_2. Critical reviews of the solubility of CO_2 have been made by Crovetto[32] and by Carroll *et al.*[33] Compilations are available from Scharlin *et al.*[34] De Visscher and Vanderdeelen[18] found that the evaluation of Crovetto[32] at 0–80 °C is more consistent with the thermodynamic data of CODATA[35] than the evaluation of Carroll *et al.*[33] Thermodynamic properties derived from different models are given in Table 1. A more recent review of CO_2 solubility data is by Fernández-Prini *et al.*[36] However, their correlation has poor consistency with CODATA.[35]

From the above studies, the equation of Crovetto[32] is the most appealing one because of its higher consistency with CODATA, and because it is based on a large data set. However, the equation is valid for temperatures up to 80 °C only, which is not adequate for the current evaluation. Crovetto[32] also developed an equation valid from 100 °C to the critical point of water. This equation corresponds well with the equation of Fernández-Prini *et al.*[36] to within a few percent (except at the critical point), whereas the other correlations typically deviate 10% or more in the high-temperature range.

The equations of Crovetto[32] do not account for the fact that a small fraction of the dissolved CO_2 will dissociate to bicarbonate according to the reaction,

$$CO_2(aq) + H_2O(l) \quad \rightleftharpoons \quad H^+(aq) + HCO_3^-(aq). \tag{60}$$

Hence, the Henry constants derived by Crovetto[32] are overestimates. At a CO_2 partial pressure of 1 bar, the speciation introduces an error ranging from about 0.2% at 0 °C to about 0.6% at 75 °C. Since most experimental data used in the review of Crovetto[32] were at pressures around atmospheric, the low-temperature equation of Crovetto[32] was corrected to account for this effect. The speciation of dissolved CO_2 was calculated at 5 °C intervals in the range 0–80 °C. The ratio of CO_2(aq) to total dissolved CO_2 (including HCO_3^-(aq)) is the correction factor that needs to be multiplied by Crovetto's Henry constant to obtain the real Henry constant. The correction factor f_C depends on temperature as follows:

$$f_C = 6.9621 \times 10^{-9}(T/\mathrm{K})^3 - 6.0423 \times 10^{-6}(T/\mathrm{K})^2 + 1.67501 \times 10^{-3}T/\mathrm{K} + 0.84953, \tag{61}$$

in which T is the temperature in K. This equation is valid in the temperature range 0–80 °C. The correction was only applied to the low-temperature equation of Crovetto,[32] because the high-temperature equation was obtained at much higher $p(CO_2)$, which favors CO_2(aq).

To obtain an equation that is highly accurate in a wide temperature interval, an equation of the same form as Fernández-Prini *et al.*[36] was adopted, and fitted to values of the Henry constant predicted by the corrected low-temperature equation of Crovetto[32] at 0–80 °C in steps of 5 °C, and to values of the high-temperature equation of Crovetto[32] at 100–360 °C in steps of 20 °C. Larger steps were taken in the high temperature range to reflect the fact that the high-temperature correlation is less accurate than the low-temperature correlation. In its original form, the equation of Fernández-Prini *et al.*[36] could be fitted to the values with an accuracy of 0.026 ln units, which was deemed inadequate for the current purpose. The addition of a constant term to the equation improved the fit to an accuracy of 0.0064 ln units, well within the accuracy of either equation of Carroll.[33] The constant term was statistically highly significant. The equation is

$$\ln\left(\frac{k_H}{p_{1v}}\right) = \frac{A}{T_r} + \frac{B\tau^{0.355}}{T_r} + CT_r^{-0.41}\exp(\tau) + D, \tag{62}$$

in which k_H is the Henry constant defined as $f(CO_2(g))/x(CO_2(aq))$ (bar) with $f(CO_2(g))$ the fugacity of $CO_2(g)$, $x(CO_2(aq))$ the mole fraction of CO_2(aq), p_{1v} is the saturated vapor pressure of water (bar), T_r is the reduced temperature, T/T_c with T_c the critical temperature of water, $\tau = 1 - T_r$, and A, B, C, and D are empirical constants.

The fit obtained with this procedure led to a predicted enthalpy of dissolution for CO_2 at 25 °C of −19.98 kJ mol^{-1}, which is too high to be consistent with CODATA[35] (see Table 1). The CODATA value is based on accurate calorimetric measurements of Berg and Vanderzee.[37,38] The cause of the discrepancy is the fact that both equations derived by Crovetto[32] appear to overestimate k_H around 100 °C, leading to an overestimated temperature dependence of k_H at 25 °C. This is probably due to the limited number of data points in this range available to Crovetto.[32] Adding a term in τ did not improve the fit. To eliminate the bias created by this, the data used in the analysis was restricted to 0–70 °C for the

TABLE 1. Thermodynamic properties of the dissolution of CO_2 at 25 °C derived from different semi-empirical equations

Source	$\Delta_r H°$/kJ mol^{-1}	$\Delta_r S°$/J mol^{-1} K^{-1}
CODATA[35]	−19.748 ± 0.167[a]	−94.425 ± 0.61
Harned and Davis[50]	−19.68	−94.05
Plummer and Busenberg[27]	−19.98	−95.24
Carroll *et al.*[33]	−19.43	−93.21
Crovetto[32]	−19.79	−94.56
Fernández-Prini *et al.*[36]	−19.06	−92.17
New equation	−19.881	−94.869

[a]Confidence interval based on Berg and Vanderzee.[37,38]

low-temperature equation, and 160–360 °C for the high-temperature equation. This brought the prediction of the value of $\Delta_r H^\circ$ of dissolution of $CO_2(g)$ within the confidence interval of the experimental value of Berg and Vanderzee.[37,38] The values of A, B, C, and D are $A = -9.14122$, $B = 2.81920$, $C = 11.28516$, and $D = -0.80660$.

For use in thermodynamic calculations involving electrolytes, it is appropriate to convert k_H to mol kg^{-1} bar^{-1}, which yields the numeric value of the solubility constant for infinite dilution K_c,

$$CO_2(g) \rightleftharpoons CO_2(aq), \tag{63}$$

which means $K_c = 55.508/(k_H \text{ bar}^{-1})$. These values, corrected for pressure using the partial molar volume of Eq. (8) and converted to a reference pressure of 1 atm, were used in the evaluations.

Table 2 compares the new equation with the correlations of Crovetto.[32] The agreement is good when the correlations are compared in their temperature range of application, but the agreement is less at 80–150 °C. The data compiled in Scharlin *et al.*[34] do not allow for an unequivocal determination of non-idealities in dissolved CO_2. For that reason, no such non-idealities were assumed.

1.3.3.2. Salting out of CO_2. Salting out of CO_2 can have a significant effect on concentration to molality conversions in concentrated salt solutions, at $p(CO_2) > 10$ bar. Hence, the effect was incorporated in the unit conversions and in the thermodynamic models.

There are two formalisms to express salting out, which are mathematically equivalent. The first approach is the Pitzer approach discussed in Sec. 1.3.2.3. The second approach is the Sechenov (sometimes spelled Setschenow) equation, here applied to CO_2,

$$\lg \frac{c_{CO_2}}{\text{mol l}^{-1}} = \lg \frac{c^0_{CO_2}}{\text{mol l}^{-1}} - k_{scc} c_s, \tag{64}$$

with c_{CO_2} the CO_2 solubility (mol l^{-1}) in the presence of salt s, $c^0_{CO_2}$ the solubility in the absence of salt in otherwise identical conditions, c_s the salt concentration (mol l^{-1}), and k_{scc} (l mol^{-1}) the Sechenov coefficient.

The salt concentration can be indicated by the concentration-based ionic strength $I(c_s)$ as well. In that case the Sechenov coefficient is denoted $k_{sI(c)c}$. When the Sechenov equation is written in terms of molality, the coefficient is denoted k_{smm}. As with the Pitzer formalism, the Sechenov coefficients resulting from a salt $M_m X_x$ can be split into an anion and a cation contribution,[39]

$$k_{M_m X_x cc} = m\, k_{Mcc} + x\, k_{Xcc}. \tag{65}$$

Selected values of $k_{sI(c)c}$ for the most relevant salts were taken from Scharlin *et al.*[34] based on the recommended values, and the evaluator's assessment of the reliability of the data. The reader is referred to Ref. 34 for the sources of all the data, but the most reliable data were generally the ones of Sechenov,[40] Markham and Kobe,[41] Onda *et al.*,[42] and Yasunishi and Yoshida.[43] The data were used to estimate values of k_{Mcc} and k_{Xcc}, as well as their temperature dependence, in a single regression. It was assumed that the Sechenov coefficients of ions of the same charge have the same temperature dependence. K_{Hcc}, the Sechenov coefficient of H^+, is taken equal to 0 by convention. The measured values of $k_{sI(c)c}$ and their temperature dependence are given in Table 3, together with their

TABLE 2. Henry constant of CO_2 predicted in this study and by Crovetto[32]

t/°C	k_H (bar) this study	K_c (mol kg^{-1} bar^{-1}) this study	k_H (bar), low t Crovetto[32]	k_H (bar), high t Crovetto[32]
0	722.5	0.07683	724.8	
20	1427.0	0.03890	1428.7	
40	2357.4	0.02355	2345.9	
60	3391.1	0.01637	3371.5	
80	4378.7	0.01268	4391.6	
100	5194.3	0.01069		5312.7
120	5763.2	0.009632		5840.3
140	6064.7	0.009153		6097.2
160	6118.5	0.009072		6115.6
180	5968.1	0.009301		5944.1
200	5665.0	0.009798		5633.9
220	5258.5	0.01056		5230.7
240	4790.2	0.01159		4771.4
260	4291.7	0.01293		4283.7
280	3784.8	0.01467		3786.0
300	3281.6	0.01692		3288.5
320	2784.8	0.01993		2792.8
340	2283.1	0.02431		2287.4
360	1724.1	0.03220		1721.2

TABLE 3. Sechenov coefficients for CO_2 in various electrolyte solutions,[34] together with fitted values

Salt	T/K	$k_{sI(c)c}$ (measured)	$k_{sI(c)c}$ (fitted)
HF	298.07	−0.0096	−0.0103
	293.02	−0.0130	−0.0070
	303.02	−0.0081	−0.0135
HNO_3	298.15	−0.0119	−0.0129
	288.15	−0.0075	−0.0065
NH_4Cl	298.15	0.0242	0.0265
	288.15	0.0317	0.0330
$(NH_4)_2SO_4$	298.15	0.0518	0.0534
	288.15	0.0531	0.0583
	308.15	0.0487	0.0485
NH_4NO_3	298.15	0.0187	0.0106
$MgCl_2$	298.15	0.0581	0.0578
	288.15	0.0637	0.0629
	308.15	0.0547	0.0526
$MgSO_4$	298.15	0.0671	0.0701
	273.15	0.0788	0.0808
	313.15	0.0625	0.0636
$Mg(NO_3)_2$	298.15	0.0465	0.0471
	273.35	0.0599	0.0599
	313.15	0.0415	0.0394

TABLE 3. Sechenov coefficients for CO_2 in various electrolyte solutions,[34] together with fitted values—Continued

Salt	T/K	$k_{sI(c)c}$ (measured)	$k_{sI(c)c}$ (fitted)
$CaCl_2$	298.15	0.0626	0.0612
	308.15	0.0548	0.0560
$Ca(NO_3)_2$	298.15	0.0504	0.0506
$SrCl_2$	295	0.0667	0.0667
	281	0.0750	0.0739
	289.4	0.0720	0.0696
	303	0.0590	0.0626
$BaCl_2$	298.15	0.0715	0.0715
LiCl	298.15	0.0749	0.0832
Li_2SO_4	298.15	0.1036	0.0912
NaCl	298.15	0.0995	0.0945
	288.15	0.1010	0.1010
	308.15	0.0931	0.0880
NaBr	298.15	0.0842	0.0887
	288.15	0.0981	0.0952
	293.15	0.0874	0.0920
NaI	293.15	0.0726	0.0772
Na_2SO_4	298.15	0.0983	0.0987
	288.15	0.1072	0.1036
	308.15	0.0894	0.0938
$NaNO_3$	298.15	0.0777	0.0786
	288.2	0.0874	0.0850
	308.15	0.0723	0.0721
KCl	298.15	0.0664	0.0667
KBr	298.15	0.0672	0.0609
KI	298.15	0.0541	0.0495
KNO_3	298.15	0.0429	0.0508
	273.15	0.0682	0.0670
	313.15	0.0372	0.0411
RbCl	298.15	0.0580	0.0580
CsCl	298.15	0.0440	0.0440

fitted values from the regression. The estimated single-ion Sechenov coefficients are given in Table 4, as well as their temperature dependence. Table 4 also contains $\lambda_{CO_2,i}$ values for the Pitzer formalism (in concentration units), together with values put forward by Harvie *et al.*,[31] Pitzer,[23] and He and Morse[29] (in molality units). Despite the difference between concentration and molality, the agreement is fairly good. The estimates also correlate fairly well with the Sechenov values for benzene estimated by De Visscher.[39] The estimates were used in the compilations for unit conversion, and in the evaluations for modeling (assuming $k_{scc} = k_{smm}$ as an approximation). As can be seen from the tables, there are no data for bicarbonates and carbonates. However, ions with charge −1 tend to have a low Sechenov coefficient, and carbonates do not occur at high concentrations in the systems studied. Hence, it is assumed that the Sechenov coefficient (and corresponding Pitzer parameters) are equal to 0 at 298.15 K for both ions. For the sake of consistency, the temperature dependence was assumed to be the same as the temperature dependence of similar (2-1 or 2-2) electrolytes. The only alkaline earth carbonates with sufficiently high solubility to create significant salting out of CO_2 are nesquehonite and lansfordite.

TABLE 4. Single-ion Sechenov coefficients and Pitzer λ parameters for CO_2 in electrolytes, with temperature dependence

Ion (i)	k_{icc} (298.15 K)	λ_{i,CO_2} (298.15 K) (this study)	λ_{i,CO_2}[a] (298.15 K) (Refs. 23, 29, and 31)
H^+	0[b]	0[b]	0[b]
Li^+	0.0802	0.0923	—
Na^+	0.0915	0.1054	0.100
K^+	0.0637	0.0734	0.051
Rb^+	0.0550	0.0633	—
Cs^+	0.0410	0.0472	—
Mg^{2+}	0.1673	0.1926	0.183; 0.19460
Ca^{2+}	0.1776	0.2045	0.183; 0.19775
Sr^{2+}	0.1892	0.2178	—
Ba^{2+}	0.2085	0.2401	—
NH_4^+	0.0236	0.0271	—
F^-	−0.0103	−0.0119	—
Cl^-	0.0030	0.0034	0.005[c]
Br^-	−0.0028	−0.0032	—
I^-	−0.0143	−0.0164	—
NO_3^-	−0.0129	0.0149	—
SO_4^{2-}	0.1131	0.1302	—
HSO_4^-	—	—	−0.003

Charge	$\frac{dk_{icc}}{dT}$/K^{-1}	$\frac{d\lambda_{i,CO_2}}{dT}$/K^{-1}
+	0[b]	0[b]
−	−0.000649	−0.000747
2+	−0.000247	−0.000284
2−	−0.001474	−0.001697

[a]In molality units.
[b]By convention.
[c]Harvie *et al.*[31] report −0.005.

1.3.3.3. Fugacity of the gas phase. The evaluation of Crovetto[32] of CO_2 solubility, on which the correlation used here is based, explicitly accounts for non-idealities of the gas phase. Hence, for consistency, the model used here should incorporate such effects as well. Crovetto[32] used second virial coefficients to calculate gas fugacities at low temperatures (<80 °C) and low pressures (<2 atm), and cubic equations of state at higher temperatures and pressures. In the current evaluation, the objective is to achieve high accuracy (<0.1% error in fugacity) in as high a temperature range as possible, but at least in the 0–100 °C temperature and 0–2 bar pressure range. We followed Crovetto[32] in adopting the virial equation, but we included third virial coefficients as well. Virial equations are usually written in terms of molar volume or density, but following Spycher and Reed[44] we used pressures instead. The relevant equations are given below. For a pure gas, the compressibility factor is calculated as

$$Z = 1 + B'p + C'p^2, \quad (66)$$

in which B' and C' are the second and third virial coefficients of the pure compound, and p is the total pressure (bar). B' and C' are functions of temperature, calculated as described below. For a binary mixture of gases i and j, the compressibility factor is calculated as

$$Z = 1 + B'_{\mathrm{mix}} p + C'_{\mathrm{mix}} p^2, \tag{67}$$

in which

$$B'_{\mathrm{mix}} = y_i^2 B'_{ii} + 2 y_i y_j B'_{ij} + y_j^2 B'_{jj}, \tag{68}$$

$$C'_{\mathrm{mix}} = y_i^3 C'_{iii} + 3 y_i^2 y_j C'_{iij} + 3 y_i y_j^2 C'_{ijj} + y_j^3 C'_{jjj}. \tag{69}$$

In these equations, B'_{ii} and B'_{jj} are second virial coefficients of pure i and pure j, respectively. B'_{ij} is a second virial interaction parameter. C'_{iii} and C'_{jjj} are third virial coefficients of pure i and pure j, respectively. C'_{iij} and C'_{ijj} are two different third virial interaction parameters. y_i and y_j are mole fractions of components i and j, respectively.

The basis of our fugacity model is the work of Spycher and Reed,[44] who proposed equations to predict all the second and third virial coefficients of the H_2O-CO_2 system at temperatures up to 350 °C. A more complicated system spanning a much wider range of conditions has been proposed by Duan *et al.*,[45,46] but their level of detail is not required for the current application.

The equations of Spycher and Reed were critically evaluated using independent data. Pure H_2O virial coefficients were tested with predictions of the Wagner and Pruß[3] equation of state. Pure CO_2 virial coefficients were tested with predictions of the Span and Wagner[47] equation of state. Mixture data were evaluated with data of Patel and Eubank,[48] an accurate data set that was not used to derive the Spycher and Reed equations.

Pure H_2O vapor compressibility factor predictions (92 in total) were made from the Wagner and Pruß[3] equation of state from low pressure to saturated vapor pressure, in the temperature range 0–225 °C. The data were predicted well with the Spycher and Reed fugacity model, with a standard deviation of 0.00080 in Z. However, systematic deviations were observed, and a re-evaluation of the parameters yielded a markedly improved fit, with a standard deviation of 0.00022 in Z. The resulting equations are

$$B'_{\mathrm{H_2O,H_2O}}/\mathrm{bar}^{-1} = b_2/(T/\mathrm{K})^2 + b_1/(T/\mathrm{K}) + b_0, \tag{70}$$

in which T is the temperature (K), and $b_2 = -12740.03$, $b_1 = 43.67297$, $b_0 = -0.0403470$.

$$C'_{\mathrm{H_2O,H_2O,H_2O}}/\mathrm{bar}^{-2} = c_2/(T/\mathrm{K})^2 + c_1/(T/\mathrm{K}) + c_0, \tag{71}$$

in which $c_2 = -72.2734$, $c_1 = 0.0196293$, and $c_0 = 0.000209532$.

Pure CO_2 vapor compressibility factor predictions (148 in total) were made from the Span and Wagner[47] equation of state, from low pressure to saturated vapor pressure, from 0 °C to the critical temperature, and up to 100 bar above the critical temperature, up to 225 °C. If the critical region was avoided, the Spycher and Reed fugacity model performed moderately well, but inadequately for the current purposes, with a standard deviation of 0.0084 in Z, 10 times less accurate than the original model for H_2O. Again, systematic deviations were observed, especially at 0–100 °C. A re-evaluation of the parameters improved the fit to a standard deviation of 0.0033 in Z, still inadequate for the current purpose. The systematic deviations remained, with most of the lack of fit attributable to incorrect temperature dependence of B' and C'. Hence, the equations for B' and C' were expanded to

$$B'_{\mathrm{CO_2,CO_2}}/\mathrm{bar}^{-1} = b_3/(T/\mathrm{K})^3 + b_2/(T/\mathrm{K})^2 + b_1/(T/\mathrm{K}) + b_0, \tag{72}$$

$$C'_{\mathrm{CO_2,CO_2,CO_2}}/\mathrm{bar}^{-2} = c_3/(T/\mathrm{K})^3 + c_2/(T/\mathrm{K})^2 + c_1/(T/\mathrm{K}) + c_0. \tag{73}$$

This reduced the standard deviation considerably, but now systematic deviations occurred near the critical region, due to the inadequacy of the cubic virial equation. The points with the highest deviation between the Span and Wagner[47] equation and the virial equation were progressively eliminated until the fit between the models for the remaining data were of the same accuracy as the pure H_2O equations and the mixture equations (see below). After eliminating 7 points, a standard deviation of 0.00022 in Z was obtained, and none of the residuals exceeded 0.001. The resulting coefficients were

$b_3 = -414041$
$b_2 = 2249.61$
$b_1 = -6.01878$
$b_0 = 0.0056274$
$c_3 = -8869.62$
$c_2 = 48.8470$
$c_1 = -0.0859163$
$c_0 = 0.000048233$

The equation is valid for pressures up to 21 bar at 0 °C, up to 28 bar at 25 °C, up to 48 bar at 50 °C, up to 100 bar at 75 °C, up to 75 bar at 100 °C, and up to 100 bar at 125–225 °C. It was noted that inclusion of points near the critical region caused systematic deviations in the entire pressure range. This, in combination with the larger temperature range of the original equations, is probably what caused the systematic deviations of the original model. At pressures above the validity range, the equation of state of Span and Wagner[47] was used for calculations, assuming that the influence of water vapor at such high CO_2 partial pressures is negligible.

A moderate agreement between the Patel and Eubank[48] data and the original model of Spycher and Reed[44] was observed (standard deviation 0.0069 in Z), which improved slightly after optimizing the pure-substance virial coefficients (standard deviation 0.0066 in Z). Re-estimation of the coefficients in the equations improved the fit to a standard deviation of 0.0012. Analysis of the residuals revealed that there was an outlier in the data reported by Patel and Eubank.[48] As the residual of this point was almost exactly -0.02 in Z, it is assumed that there was a typing error in the original paper. At $T = 473.15$ K, $p = 21.8205$ bar, $y(CO_2) = 0.90$, the reported value of $Z = 0.99710$ should be corrected to $Z = 0.97710$. This improved the fit to a standard deviation of 0.00020. Remarkably, this standard deviation is less than half of the measurement uncertainty estimated by Patel and Eubank[48] for their own data (0.05%). At 2% water, where the influence of water is very limited, the standard deviation is about 0.00024, indicating that the data of Patel and Eubank are highly consistent with the Span and Wagner[47] equation of state. It is concluded that the data set is reliable enough for use in a critical evaluation. The virial coefficients of interaction between H_2O and CO_2 can be calculated as follows:

$$B'_{H_2O,CO_2}/\mathrm{bar}^{-1} = -2\,641.62/(T/\mathrm{K})^2 + 9.292\,05/(T/\mathrm{K}) - 0.009\,180\,0, \quad (74)$$

$$C'_{H_2O,H_2O,CO_2}/\mathrm{bar}^{-2} = -80.800\,5/(T/\mathrm{K})^2 + 0.294\,921\,3/(T/\mathrm{K}) - 0.000\,264\,526, \quad (75)$$

$$C'_{H_2O,CO_2,CO_2}/\mathrm{bar}^{-2} = -1.198\,6/(T/\mathrm{K})^2 + 0.002\,555\,9/(T/\mathrm{K}) + 0.000\,000\,207. \quad (76)$$

From the virial coefficients, the fugacity coefficients ϕ can be calculated. For a pure gas, the fugacity coefficient is given by

$$\ln\phi = B'p + \frac{C'p^2}{2}. \quad (77)$$

For component i in a binary gas mixture of components i and j, the fugacity coefficient ϕ_i is given by

$$\ln\phi_i = \left(2\left(y_1B'_{1i} + y_2B'_{2i}\right) - B'_{\mathrm{mix}}\right)p + \left(3\left(y_1^2C'_{i11} + 2y_1y_2C'_{i12} + y_2^2C'_{i22}\right) - 2C'_{\mathrm{mix}}\right)\frac{p^2}{2}. \quad (78)$$

For this equation, the total pressure was converted from atmosphere to bar.

1.3.3.4. Dissociation constants of carbonic acid. Accurate estimates of K_1 and K_2 of CO_2(aq) are crucial for an accurate determination of the solubility constant based on solubility measurements. Langmuir[49] pointed out that $CaCO_3$ solubility measurements based on $p(CO_2)$ and $m(Ca^{2+})$ were inconsistent with solubility measurements based on $p(CO_2)$ and pH when the value of $-\lg K_1$ accepted at the time (6.362 at 25 °C) was used, but that the inconsistency disappeared when an older value of Harned and Davis[50] was used (6.351). The value of 6.362 has been proven incorrect in the meantime.

The most widely used correlations for the dissociation constants of carbonic acid are the ones of Plummer and Busenberg.[27] Their equation yields a value of $-\lg K_1 = 6.351$, consistent with Harned and Davis.[50] De Visscher and Vanderdeelen[18] pointed out that this value is slightly different from the value obtained with CODATA,[35] and suggested a way to establish consistency with CODATA.[35] The values of the enthalpy of reaction and the entropy of reaction at 25 °C are given in Table 5.

TABLE 5. Enthalpy and entropy of the first dissociation of CO_2 at 298.15 K estimated from different sources

Source	$\Delta_rH°$/kJ mol^{-1}	$\Delta_rS°$/J mol^{-1} K^{-1}
CODATA[35]	9.155 ± 0.063[a]	−90.91 ± 1.13
Plummer and Busenberg[27]	9.109	−91.052
Li and Duan[54]	9.063	−91.366
Harned and Davis[50] (new smoothing)	9.407	−90.044
Harned and Davis[50] reanalyzed	9.155[b]	−90.819
New equation	9.155[b]	−90.813

[a]Confidence interval based on Berg and Vanderzee.[37,38]
[b]Forced.

It is interesting to note that Plummer and Busenberg[27] did not trust the values of the Henry constant of Harned and Davis,[50] but did consider the values of the first dissociation constant of CO_2(aq) (K_1) of the same authors to be highly accurate. The determination of K_1 with the methodology of Harned and Davis[50] requires values of the Henry constant, so an incorrect value of the Henry constant would propagate into an incorrect value of K_1. Plummer and Busenberg[27] did not make any attempt to correct for this effect. Their equation for K_1 as a function of temperature yields values that correspond well with those of Harned and Davis[50] (standard deviation 0.00099 lg units). Hence it is worthwhile to consider the accuracy of the Harned and Davis[50] Henry constants.

When the Henry constants of Harned and Davis[50] are compared with predictions of the new equation derived in this study, deviations up to about 1.9% are obtained. The main causes of the difference are experimental error, incorrect smoothing (when the smoothing technique of Harned and Davis[50] is repeated, the values obtained differ by up to 0.0036 lg units from the smoothed values reported by the authors), assumption of ideal gas, and neglecting dissociation of CO_2(aq). The values of K_1 of Harned and Davis[50] were recalculated using the procedure given below.

The original raw data were obtained with a Harned cell (i.e., a platinum electrode in the presence of hydrogen gas and a silver chloride-silver electrode without liquid junction) using a CO_2-H_2 mixture as the gas phase.[50] Care had been taken to have barometric pressure and an equilibrium water vapor pressure in the cell. Measurements were done at 0–50 °C, various CO_2-H_2 mixing ratios, and an equimolal mixture of NaCl and $NaHCO_3$ in aqueous solution with molalities m_1 of each salt ranging from 0.002 m to 0.1 m. The electromotive force of the cell is given by

$$E = E° + \frac{RT}{F}\ln\frac{f(H_2)^{1/2}}{a(H^+)a(Cl^-)}, \quad (79)$$

with E° the standard potential of the electrochemical cell (V), R the ideal gas constant (8.314472 J mol^{-1} K^{-1}),[51] F the Faraday constant (96 485.3383 C mol^{-1}),[51] $f(H_2)$ the fugacity of H_2(g) (bar), and $a(H^+)$ and $a(Cl^-)$ the activities of H^+ and Cl^-, respectively. The values of E° were taken from Harned and Ehlers,[52] and converted to 1 bar standard pressure.

The equilibrium constant K_1 is defined as

$$K_1 = \frac{a(\mathrm{H}^+)a(\mathrm{HCO}_3^-)}{a(\mathrm{CO_2(aq)})a_\mathrm{w}}. \quad (80)$$

In the present analysis, CO_2(aq) and H_2O are assumed to be an ideal solute and an ideal solvent, respectively. Hence, $a(CO_2(aq)) = m(CO_2(aq))$ and $a_w = x(H_2O)$. An auxiliary variable, K'_1, is defined as

$$K'_1 = K_1 \frac{\gamma(\mathrm{Cl}^-)}{\gamma(\mathrm{HCO}_3^-)}. \quad (81)$$

In K'_1 the electrostatic effects of the activity coefficients are cancelled, leaving only specific ion interaction effects. Hence, at the low concentration limit, K'_1 can be expected to depend linearly on electrolyte concentration m_1. Together with the definition of the solubility constant of CO_2,

$$K_\mathrm{c} = \frac{m(\mathrm{CO_2(aq)})}{f(\mathrm{CO_2(g)})}\frac{(f^\circ)}{(m^\circ)} = \frac{m(\mathrm{CO_2(aq)})}{\phi(\mathrm{CO_2(g)})\,p(\mathrm{CO_2(g)})}\frac{(f^\circ)}{(m^\circ)}, \quad (82)$$

the above equations can be combined and solved for $-\lg(K'_1)$,

$$-\lg K'_1 = \frac{F}{RT\,\ln 10}(E - E^\circ) - \frac{1}{2}\lg\frac{p(\mathrm{H_2})}{(f^\circ)} + \lg\left(a_\mathrm{w} K_\mathrm{c}\,\frac{\phi(\mathrm{CO_2})\,p(\mathrm{CO_2})}{(f^\circ)}\right). \quad (83)$$

In the calculation, it was assumed that H_2 did not have an effect on the fugacities of H_2O and CO_2 in the gas phase. For each experimental point of Harned and Davis,[50] the corresponding value of $-\lg(K'_1)$ was calculated. To account for non-idealities of the gas phase, the values of $(p(CO_2) + p(H_2O))$ and $y(H_2O)$ were determined iteratively to obtain the desired values of $f(H_2O)$ and p. Fugacity coefficients were determined using the model described above. The 252 data points were fitted to an equation of the following form:

$$-\lg K'_1 = A + \frac{B}{T/\mathrm{K}} + C\,\lg(T/\mathrm{K}) + DT/\mathrm{K} + E\,m_1/(m^\circ) + F\frac{m_1/(m^\circ)}{T/\mathrm{K}}. \quad (84)$$

Note that italic K stands for equilibrium constant, whereas roman K stands for kelvin (needed to balance units). Preliminary analysis, as well as simple smoothing of the original K_1 data, indicated that there is a slight inconsistency with the CODATA[35] enthalpy of reaction at 25 °C. The latter is based on accurate calorimetric measurements of Berg and Vanderzee.[37,38] For that reason, Eq. (84) was made consistent with the measured enthalpy of reaction of $H_1 = 9155$ J mol^{-1} at $T_1 = 298.15$ K using the approach described below. The procedure is derived here for the more general temperature relationship of Eq. (85).

$$\lg K = A + \frac{B}{T/\mathrm{K}} + C\lg(T/\mathrm{K}) + D\,T/\mathrm{K} + \frac{E}{T^2/\mathrm{K}^2}. \quad (85)$$

The enthalpy of reaction is given by the following general equation:

$$\Delta_\mathrm{r}H^\circ = RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \ln 10\cdot RT^2\frac{\mathrm{d}\lg K}{\mathrm{d}T}. \quad (86)$$

Equation (85) is substituted into Eq. (86) and applied to $\Delta_r H^\circ = H_1$ for $T = T_1$,

$$H_1 = \ln 10\cdot RT_1^2\left(-\frac{B}{T_1^2/\mathrm{K}} + \frac{C}{\ln 10\cdot T_1} + D - \frac{2E}{T_1^3/\mathrm{K}^2}\right). \quad (87)$$

Equation (87) is solved for D,

$$D = \frac{H_1}{RT_1^2/\mathrm{K}\ln 10} + \frac{B}{T_1^2/\mathrm{K}} - \frac{C}{T_1\ln 10} + \frac{2E}{T_1^3/\mathrm{K}^2}. \quad (88)$$

Substitution of D in Eq. (85) leads to

$$\lg K - \frac{H_1 T}{RT_1^2\ln 10} = A + \left(\frac{1}{T/\mathrm{K}} + \frac{T}{T_1^2/\mathrm{K}}\right)B + \left(\lg(T/\mathrm{K}) - \frac{T}{T_1\ln 10}\right)C + \left(\frac{1}{T^2/\mathrm{K}^2} + \frac{2T}{T_1^3/\mathrm{K}^2}\right)E. \quad (89)$$

Coefficients A, B, C, and E can be obtained by linear regression of $\lg K - H_1T/RT_1^2 \ln 10$ using $1/T + T/T_1^2$, $\lg T - T/T_1 \ln 10$, and $1/T^2 + 2T/{T_1}^3$ as independent variables. With an equation of the form of Eq. (84), the coefficient E in Eq. (89) becomes zero.

The model fit revealed that the data set contained a large number of outliers. These outliers tended to cluster, indicating that their nature was not random. Hence, all experimental data with a deviation of at least 3 standard deviations between the experimental value of $-\lg(K'_1)$ and the fitted value were eliminated, and the regression was repeated. Each successive regression revealed new outliers. During the analysis it was observed that all six experimental values of $-\lg(K'_1)$ at $m_1 = 0.10385$ mol kg^{-1} were above the fitted values, indicating that this is also a cluster of outliers. Since the next value of m_1 was 0.03687 mol kg^{-1}, there was no reliable way of testing the accuracy of these data. For this reason, all data at $m_1 = 0.03687$ mol kg^{-1} were discarded. Eventually 231 data points were retained for the final regression. This regression led to the following coefficients for Eq. (84):

$A = -499.857\,532$
$B = 16\,097.228$
$C = 195.980\,815\,8$
$D = -0.109\,766\,58$
$E = -0.987\,44$
$F = 190.28$

The sum of squares of the residuals was 0.006338, leading to a standard deviation of 0.00530 lg units between the experimental values and the fitted values of $-\lg(K'_1)$. A value of ±0.0159 was used as a threshold deviation for defining outliers. The residuals of the remaining data were checked for correlation with $p(CO_2)$. The correlation coefficient obtained was 0.05. Hence it was concluded that the non-ideality of the gas phase was accounted for adequately, and non-ideality of CO_2(aq) was negligible. Equation (89) was used to generate K_1 values ($m_1 = 0$) at 5 °C intervals from 0–50 °C. The results are shown in Table 6 together with the original values of Harned and Davis.[50]

As indicated above, the equation of Plummer and Busenberg[27] for K_1 corresponds well with the original values of Harned and Davis.[50] At higher temperatures, the values correspond well with the data of Read[53] (standard deviation 0.011 lg units). A more recent correlation was developed by Li and Duan.[54] This correlation does not follow the values of Harned and Davis as well (standard deviation 0.0092 lg units, almost 10 times higher than the Plummer and Busenberg[27] equation). This is probably because Li and Duan[54] included data in the derivation that was considered inaccurate by Plummer and Busenberg.[27] The major advantage of the Li and Duan[54] equation is that it includes the effect of pressure. Other studies that became available since the study of Plummer and Busenberg[27] are Patterson *et al.*[55] and Park *et al.*[56] Neither of these seems to agree with the well-established earlier studies to within experimental error, and were not considered here.

The temperature-dependent portion of the equation of Li and Duan[54] has the same form as the equation used by Plummer and Busenberg.[27] Such an equation was fitted to the data of Read[53] at water vapor pressure and the reanalyzed data of Harned and Davis,[50] and combined with the pressure-dependent portion of the equation of Duan and Li[57] (the coefficients of Li and Duan[54] contain errors). Because of the difference in accuracy of the measurements, the data of Harned and Davis[50] obtained in an electrochemical cell were given a ten times higher weight than the data of Read[53] obtained with conductivity measurements. When the heat of reaction at 298.15 K was not forced to be 9155 J mol^{-1} (the value of Berg and Vanderzee[37,38]), a significantly different value was obtained. Hence, the value was forced to be 9155 J mol^{-1} using the approach expressed in Eq. (89). The result is

$$\lg K_1 = A + \frac{B}{T/\mathrm{K}} + C\lg\frac{T}{\mathrm{K}} + D\frac{T}{\mathrm{K}} + \frac{E}{(T/\mathrm{K})^2} + \left(\frac{F}{T/\mathrm{K}} + \frac{G}{(T/\mathrm{K})^2} + \frac{H\lg\frac{T}{\mathrm{K}}}{T/\mathrm{K}}\right)\left(\frac{p}{\mathrm{bar}} - \frac{p_\mathrm{v}}{\mathrm{bar}}\right) + \left(\frac{I}{T/\mathrm{K}} + \frac{J}{(T/\mathrm{K})^2} + \frac{K\lg\frac{T}{\mathrm{K}}}{T/\mathrm{K}}\right)\left(\frac{p}{\mathrm{bar}} - \frac{p_\mathrm{v}}{\mathrm{bar}}\right)^2, \quad (90)$$

with

$A = -441.490\,479$
$B = 26\,901.052\,7$
$C = 157.201\,690\,7$
$D = -0.072\,199\,67$
$E = -2\,003\,878.4$
$F = -19.578\,015\,21$
$G = 925.620\,014\,9$
$H = 6.714\,256\,299$
$I = 0.003\,645\,431\,058$
$J = -0.174\,388\,404\,4$
$K = -0.001\,240\,187\,350$

In Eq. (90), p_v is the maximum of 1 bar and the saturated vapor pressure of water. Predictions of Eq. (90) at 0–50 °C are given in Table 6. The standard deviation between this equation and the reanalyzed data of Harned and Davis[50] is about 0.001 lg units. The standard deviation between the equation and the data of Read[53] is about 0.012 lg units. Thermodynamic properties of the first dissociation of CO_2/carbonic acid were calculated from Eq. (90) and compared with other sources. The result is shown in Table 5. The reanalysis yielded an entropy very close to the CODATA[35] value.

The new equation (Eq. (90)) was used in the calculation of K_1 in the evaluation.

Few determinations of K_2 of CO_2/carbonic acid are available in the literature. The most accurate determination is by Harned and Scholes.[58] These data do not suffer from the issues associated with determinations of K_1, because the CO_2 concentration in the gas phase is negligible. Plummer and Busenberg[27] relied heavily on these data for the determination of their semi-empirical equation for K_2. Thermodynamic data derived from this equation are not consistent with CODATA[35] to within experimental error (see Table 7). The enthalpy of reaction derived from the Duan and Li[57] equation was closer to the CODATA[35] value, but this equation

TABLE 6. Values of $-\lg(K_1)$ from the Harned and Davis[50] experiments obtained with different data analysis techniques

t/°C	Original data analysis	$-\lg(K_1)$ Reanalyzed	Combined with Read[53] data	Plummer and Busenberg[27]
0	6.5787	6.57944	6.57860	6.57782
5	6.5170	6.51517	6.51463	6.51555
10	6.4640	6.46080	6.46044	6.46258
15	6.4187	6.41535	6.41507	6.41802
20	6.3809	6.37792	6.37764	6.38108
25	6.3519	6.34768	6.34738	6.35106
30	6.3268	6.32388	6.32363	6.32733
35	6.3094	6.30582	6.30576	6.30933
40	6.2978	6.29286	6.29489	6.29655
45	6.2902	6.28442	6.28558	6.28855
50	6.2851	6.27996	6.28237	6.28493

TABLE 7. Enthalpy and entropy of the second dissociation of CO_2 at 298.15 K estimated from different sources

Source	$\Delta_rH°$/kJ mol^{-1}	$\Delta_rS°$/J mol^{-1} K^{-1}
CODATA[35]	14.698 ± 0.105[a]	-148.4 ± 1.5
Plummer and Busenberg[27]	14.901	−147.766
Plummer and Busenberg[27] recalculated	14.698[b]	−148.433
Duan and Li[57]	14.681	−148.754

[a]Confidence interval based on Berg and Vanderzee.[37,38]
[b]Forced.

was not considered, for the same reason as with K_1. Therefore, predictions of Eq. (85) with the original Plummer and Busenberg[27] coefficients were generated at 5 °C intervals for temperatures from 0 to 220 °C. New coefficients were then calculated by linear regression using the approach of Eq. (89) and the heat of reaction calculated from CODATA.[35] lg K_2 data at 0–50 °C were given a 10 times higher weight than the rest of the data, because this is the temperature range of the electrochemical data of Harned and Scholes,[58] which is considered more accurate than other data sets. Again, pressure dependence as calculated by Duan and Li[57] was included in the equation. The following result was obtained:

$$\lg K_2 = A + \frac{B}{T/\mathrm{K}} + C \lg\frac{T}{\mathrm{K}} + D\frac{T}{\mathrm{K}} + \frac{E}{(T/\mathrm{K})^2} + \left(\frac{F}{T/\mathrm{K}} + \frac{G}{(T/\mathrm{K})^2} + \frac{H \lg\frac{T}{\mathrm{K}}}{T/\mathrm{K}}\right)\left(\frac{p}{\mathrm{bar}} - \frac{p_\mathrm{v}}{\mathrm{bar}}\right) + \left(\frac{I}{T/\mathrm{K}} + \frac{J}{(T/\mathrm{K})^2} + \frac{K \lg\frac{T}{\mathrm{K}}}{T/\mathrm{K}}\right)\left(\frac{p}{\mathrm{bar}} - \frac{p_\mathrm{v}}{\mathrm{bar}}\right)^2, \quad (91)$$

with

$A = -332.530\,6$
$B = 17\,540.07$
$C = 120.133\,93$
$D = -0.065\,459\,69$
$E = -1\,277\,752.3$
$F = -12.817\,976\,24$
$G = 603.241\,703\,5$
$H = 4.419\,625\,804$
$I = 0.001\,398\,425\,42$
$J = -0.071\,418\,479\,43$
$K = -0.000\,473\,667\,239\,5$

The entropy of reaction derived from this equation is consistent with CODATA[35] to within experimental error (see Table 7).

1.3.3.5. Ionization constant of water. The most comprehensive evaluation of the ionization constant of water is by Marshall and Franck.[59] They developed an equation calculating lg K_w as a function of temperature and water density. Naturally, the equation is very sensitive to the value of the water density, so very accurate values need to be used. Marshall and Franck derived their equation using the 1967 steam tables,[60] which are somewhat different from the more recent Wagner and Pruß[3] equation of state. The effect of the difference on the predictions of the Marshall and Franck equation is less than 0.001 lg units at low temperature, and 0.001–0.003 at 200–300 °C. Given the fact that the exact value of K_w is not critical for thermodynamic calculations related to alkaline earth carbonate solubilities, this accuracy is sufficient. In the evaluation, pure water densities for K_w were calculated with the Wagner and Pruß[3] equation of state. In the course of this study, a new standard for lg K_w values was published by Bandura and Lvov.[61] For applications in aqueous solution thermodynamics, the difference between the old and new formulations is small (a few percent or less).

The $\Delta_rH°$ of ionization predicted by the equation of Marshall and Franck[59] was 55.557 kJ mol^{-1}, slightly different from their own reported value (55.65 kJ mol^{-1}), and significantly different from the CODATA[35] recommended value (55.815 ± 0.08 kJ mol^{-1}). The formulation of Bandura and Lvov[61] (Model II in their paper) leads to a $\Delta_rH°$ value of 56.378 kJ mol^{-1}, even less consistent with the CODATA value. The new formulation was not used for that reason. Note that the uncertainty of 0.08 kJ mol^{-1} is a conservative estimate, based on the uncertainty of the individual compounds. In critical evaluations where accurate values of K_w are more important, a re-evaluation of Model II of Bandura and Lvov[61] would be useful.

1.3.3.6. Metal-carbonate ion pairing. Both bicarbonate and carbonate can form ion pairs with alkaline earth metal ions in aqueous solution. The metal carbonate ion pair is only significant at extremely low solubility, i.e., at low CO_2 partial pressure, and at high pH. The metal-bicarbonate ion pair has a significant effect on solubility calculation at all conditions and slightly influences the CO_2 partial pressure dependence of the solubility. Unfortunately, the properties of $MHCO_3^+$ are more subject to debate than the properties of the MCO_3^0 ion pair.

The relevant stability constants of the ion pairs are defined as follows:

$$K_{\mathrm{MHCO_3^+}} = \frac{(\mathrm{MHCO_3^+})}{(\mathrm{M^{2+}})(\mathrm{HCO_3^-})}, \quad (92)$$

$$K_{\mathrm{MCO_3^0}} = \frac{(\mathrm{MCO_3^0})}{(\mathrm{M^{2+}})(\mathrm{CO_3^{2-}})}. \quad (93)$$

The first measurements of $MgHCO_3^+$ and $CaHCO_3^+$ were made by Greenwald[62] using a titration technique and solubility measurements in $KHCO_3$ at approximately 22 °C. With the titration technique, Greenwald found a value of $K_{\mathrm{MHCO_3^+}}$ of 5.9 ± 0.3 for Mg and 6.3 ± 0.4 for Ca. Based on solubility measurements, a value of 6.6 ± 1.0 was obtained for Ca. Jacobson and Langmuir[63] were very critical of these results. They were obtained at supersaturation with respect to the alkaline earth carbonate, so there was a risk of precipitation, which would have led to an overestimate of the stability constant. Also, recalculated values were quite different from the original ones.

An overview of experimental values of $K_{MHCO_3^+}$ is given in Table 8. Data of Neuman *et al.*,[64] Hostetler,[65] Langmuir,[66] Nakayama,[67] Jacobson and Langmuir,[63] Martynova *et al.*,[68] Pytkowicz and Hawley,[69] Siebert and Hostetler,[70] Plummer and Busenberg,[27] Le Guyader *et al.*,[71] Busenberg *et al.*,[72] and Busenberg and Plummer[73] are listed. The tabulated values are not very consistent, as was also observed by Burton.[74] In Burton's[74] review, it was suggested that the determination of stability constants depends on assumptions about the existence of other ion pairs, e.g., in the calculation of the ionic strength.

It has been observed that the association of metal bicarbonates has a pronounced Δc_p, as does the first dissociation of carbonic acid. However, the following reaction has a negligible Δc_p:

$$M^{2+}(aq) + H_2O(l) + CO_2(aq) \rightleftharpoons MHCO_3^+(aq) + H^+(aq). \tag{94}$$

Hence, the equilibrium constant K of this reaction can be described as $A + B/T$ with great accuracy over an extended temperature range.[75]

Hence, it is much easier to determine the temperature dependence of the equilibrium constant of reaction (94). Based on this idea, and the data of Table 8, an equation of the form $A + B/T$ was fitted to the data, transformed to Eq. (94) by adding Eq. (21) to Eq. (26) (i.e., adding Eq. (90) to the $\lg K_{MHCO_3^+}$ data), and the resulting equation was transformed back to an equation for $\lg K_{MHCO_3^+}$ by subtraction of Eq. (90). The result is an equation of the form of Eq. (85). For $\lg K_{MgHCO_3^+}$ and $\lg K_{CaHCO_3^+}$, the data of Pytkowicz and Hawley[69] were discarded as they reported stoichiometric instead of thermodynamic constants and the results deviated by almost an order of magnitude from other data; for $\lg K_{CaHCO_3^+}$, the datum of Neuman *et al.*[64] was discarded because the temperature of the experiment was not reported,

TABLE 8. Stability constants of alkaline earth bicarbonate ion pairs

Source	M	$t/°C$	$\lg K$	Method
Greenwald[62]	Mg	22	0.771 ± 0.022	Titration[a]
	Ca	22	0.799 ± 0.027	Titration[a]
			0.820 ± 0.061	Solubility of $CaCO_3$[a]
Neuman *et al.*[64]	Ca	n.i.[b]	0.387 ± 0.095	Cation exchange; $I = 1$ mol l^{-1}
Hostetler[65]	Mg	25	0.95 ± 0.1	pH of $CO_2/MgCl_2$ solutions
Langmuir[66]	Mg	25	1.37	pH and solubility of nesquehonite
Nakayama[67]	Ca	25	1.249 ± 0.019	Ca-selective electrode[c]
			1.268 ± 0.027	pH of $CaCl_2/CO_2$ solutions[c]
Nakayama and Rasnick[80]	Ba	25	1.519 ± 0.024	pH of $BaCl_2/CO_2$ solutions
	Sr	25	1.244 ± 0.039	pH of $SrCl_2/CO_2$ solutions
Jacobson and Langmuir[63]	Ca	15	0.88	Conductometry
		25	0.99	
		35	1.16	
		45	1.29	
Martynova *et al.*[68]	Ca	22	1.27	Ion-selective electrodes[d]
		60	1.64	
		70	1.77	
		80	1.82	
		90	1.94	
		98	2.01	
Pytkowicz and Hawley[69]	Mg	25	0.21	Titration[e]
	Ca	25	0.29	Titration[e]
Siebert and Hostetler[70]	Mg	10	1.051 ± 0.018	Potentiometric titration
		25	1.066 ± 0.012	
		40	1.108 ± 0.006	
		55	1.160 ± 0.011	
		70	1.230 ± 0.017	
		90	1.337 ± 0.007	
Plummer and Busenberg[27]	Ca	25	1.29 ± 0.04	pH of bicarbonate solutions[f]
		4.4	0.91 ± 0.06	Solubility of aragonite at varying $p(CO_2)$
		15.1	0.97 ± 0.06	
		25	1.14 ± 0.07	
		35	1.17 ± 0.07	
		45	1.21 ± 0.10	
		65	1.21 ± 0.08	
		80	1.27 ± 0.08	
		90	1.35 ± 0.10	
Le Guyader *et al.*[71]	Ca	25	1.14	Solubility of calcite at varying $p(CO_2)$

TABLE 8. Stability constants of alkaline earth bicarbonate ion pairs—Continued

Source	M	$t/°C$	lg K	Method
Busenberg *et al.*[72]	Sr	5	0.933 ± 0.058	pH of bicarbonate solutions
		5.3	0.846 ± 0.216	
		25	1.142 ± 0.068	
		25	1.220 ± 0.080	
		45	1.455 ± 0.027	
		46	1.505 ± 0.093	
		60	1.699 ± 0.068	
		80	2.020 ± 0.030	
Busenberg and Plummer[73]	Ba	5	0.764 ± 0.074	pH of bicarbonate solutions
		25	0.935 ± 0.063	pH of bicarbonate solutions
		25	1.049 ± 0.022	Conductometry
		25	0.950 ± 0.050	Witherite solubility at varying $p(CO_2)$
		45	1.225 ± 0.021	pH of bicarbonate solutions
		60	1.467 ± 0.057	
		79.3	1.753 ± 0.061	
		80	1.752 ± 0.084	

[a]Methods were criticized by Jacobson and Langmuir.[63]
[b]Not indicated.
[c]Accuracy probably overrated.[63]
[d]Unclear method, especially on data analysis and interpretation.
[e]Value reported is the stoichiometric stability constant.
[f]Average of two different electrode solutions.

and because of deviation from the other data. Due to fewer data points and the lack of consistency between studies, the Ba data should be considered with more caution than the other data. The following coefficients were obtained:

$$\text{for all } \lg K_{\mathrm{MHCO_3^+}} \quad C = -157.201\,690\,7, \quad D = 0.072\,199\,67, \quad E = 2\,003\,878.4$$

$$\text{for } \lg K_{\mathrm{MgHCO_3^+}} \quad A = 437.909\,531, \quad B = -27\,415.302\,3$$

$$\text{for } \lg K_{\mathrm{CaHCO_3^+}} \quad A = 439.872\,327, \quad B = -27\,988.839\,0$$

$$\text{for } \lg K_{\mathrm{SrHCO_3^+}} \quad A = 442.037\,210, \quad B = -28\,608.225\,9$$

$$\text{for } \lg K_{\mathrm{BaHCO_3^+}} \quad A = 440.836\,635, \quad B = -28\,283.573\,9$$

The activity coefficient of MCO_3^0 has also led to confusion in the literature. Reardon and Langmuir[76] investigated the activity coefficient of $MgCO_3^0$ and found that it followed the following relationship with the ionic strength at 25 °C:

$$\lg \gamma\left(\mathrm{MgCO_3^0}\right) = -0.63I. \tag{95}$$

This is a much stronger ionic strength dependence than normally encountered with neutral species. Millero and Thurmond[77] found

$$\lg \gamma\left(\mathrm{MgCO_3^0}\right) = +0.056I. \tag{96}$$

Königsberger *et al.*[78] also found an increase of the activity coefficient of $MgCO_3^0$ in the presence of $NaClO_4$ ($\lambda(\mathrm{MgCO_3^0}, \mathrm{ClO_4^-}) = 0.081$). In a later paper, a slight decreasing effect was found ($\lambda(\mathrm{MgCO_3^0}, \mathrm{ClO_4^-}) = -0.07$),[79] which was the result of a slightly different choice for the stability constant of $MgCO_3^0$. A non-zero value of $\lambda(\mathrm{MgCO_3^0}, \mathrm{ClO_4^-})$ could indicate that what Reardon and Langmuir[75] observed was a specific ion interaction.

Greenwald[62] estimated $K_{\mathrm{MgCO_3^0}}$ to be 230 and $K_{\mathrm{CaCO_3^0}}$ to be 1000, based on titration experiments at approximately 22 °C. Reardon and Langmuir[76] found a value of 690 for Mg at 25 °C in their determinations of the activity coefficient of the ion pair. An overview of these and other literature values is given in Table 9. Values of Nakayama,[67] Nakayama and Rasnick,[80] Lafon,[81] Beneš and Selecká,[82] Martynova *et al.*,[68] Pytkowicz and Hawley,[69] Reardon and Langmuir,[83] Siebert and Hostetler,[84] Plummer and Busenberg,[27] Le Guyader *et al.*,[71] and Busenberg and Plummer[73] are listed.

Plummer and Busenberg[27] used a value of −0.5 as a coefficient of I in Eq. (95) in their calculations. Harvie *et al.*[31] assumed an activity coefficient of unity for $MgCO_3^0$. He and Morse[29] followed this example for the sake of consistency because they used some of the parameters of Harvie *et al.*[31] Königsberger *et al.*[79] did not introduce an ionic strength dependence other than a Pitzer parameter for the $\mathrm{MgCO_3^0}-\mathrm{ClO_4^-}$ ion-neutral interaction. Given the inconsistency of the data, it seems appropriate to follow the example of He and Morse.[29] In the absence of strong electrolytes, the effect of $\gamma(\mathrm{MgCO_3^0})$ on solubility calculations is negligible.

TABLE 9. Stability constants of alkaline earth carbonate ion pairs

Source	M	$t/°C$	lg K	Method
Greenwald[62]	Mg	22	2.37	Titration[a]
	Ca	22	3.0	Titration[a]
Nakayama[67]	Ca	25	1.984 ± 0.027	Ca-selective electrodes[b]
Lafon[81]	Ca	25	3.1 ± 0.3	Literature solubility data calcite
Beneš and Selecká[82]	Ba	25	3.78	Dialysis
Martynova *et al.*[68]	Ca	22	4.39	Ion-specific electrodes[c]
		60	5.34	
		70	5.55	
		80	5.74	
		90	5.82	
		98	6.00	
Pytkowicz and Hawley[69]	Mg	25	2.05	Titration[d]
	Ca	25	2.21	Titration[d]
Reardon and Langmuir[83]	Mg	10	2.79 ± 0.10	Potentiometric titration
		25	2.88 ± 0.05	
		41	3.03 ± 0.07	
		51.5	3.17 ± 0.08	
	Ca	9.5	3.04 ± 0.04	
		25	3.15 ± 0.08	
		41	3.35 ± 0.11	
Reardon and Langmuir[83]	Mg	25	2.84	pH of solutions[e]
Siebert and Hostetler[84]	Mg	10	2.89 ± 0.019	Potentiometric titration[f]
		25	2.984 ± 0.028	
		40	3.07 ± 0.021	
		55	3.18 ± 0.026	
		70	3.28 ± 0.042	
		90	3.41 ± 0.067	
Plummer and Busenberg[27]	Ca	5.5	3.13 ± 0.02	pH of $CaCl_2/K_2CO_3$ solutions
		25	3.20 ± 0.07	
		40	3.42 ± 0.11	
		60	3.63 ± 0.16	
		80	3.92 ± 0.18	
Le Guyader *et al.*[71]	Ca	25	4.44	Solubility of calcite
Millero and Thurmond[77]	Mg	25	3.00	Potentiometric titration
Busenberg *et al.*[73]	Sr	4.7	2.571 ± 0.052	pH of $SrCl_2/K_2CO_3$ solutions
		25	2.764 ± 0.067	
		40	2.974 ± 0.071	
		60	3.284 ± 0.061	
		80	3.506 ± 0.142	
Busenberg and Plummer[73]	Ba	5	2.556 ± 0.021	pH of $BaCl_2/K_2CO_3$ solutions
		25	2.697 ± 0.048	
		40	2.786 ± 0.041	
		60	3.012 ± 0.042	
		80	3.227 ± 0.044	
Felmy *et al.*[90]	Sr	22	2.81	Solubility of $SrCO_3$ in Na_2CO_3 solutions[g]
	Ca	22	3.15	Solubility of $CaCO_3$ in Na_2CO_3 solutions[g]

[a]Methods were criticized by Jacobson and Langmuir.[63]
[b]Accuracy probably overrated.[63]
[c]Unclear method, especially on data analysis and interpretation.
[d]Value reported is the stoichiometric stability constant.
[e]Consistent with lg$\gamma(MgCO_3^0) = -0.63I$.
[f]No ionic strength dependence was assumed (average I was around 0.1 mol kg^{-1}). Hence, lg K could be overestimated by as much as 0.06.
[g]Pitzer model used.

Sverjensky *et al.*[85] developed a correlation that allowed a tentative calculation of the stability constants of the alkaline earth metal carbonate ion pairs up to about 350 °C and the saturated vapor pressure of water. It is worthwhile to note that the values are on the order of 10^7 at 300 °C, so significant ion pairing should be expected at high temperatures.

Based on the data of Table 9 and the predictions of Sverjensky *et al.*,[85] coefficients of Eq. (85) were determined for the stability constants of the MCO_3^0 ion pairs. The data of Greenwald[62] were not used due to deviations from other data for Mg, and due to the critique of Jacobson and Langmuir;[63] data of Pytkowicz and Hawley[69] were not used because of the difference with the other data, and because the values are stoichiometric, not thermodynamic; data of Nakayama[67] were discarded due to large deviation from other data, and the critique of Jacobson and Langmuir;[63] data of Martynova *et al.*[68] were discarded due to lack of clarity of the methods used, and due to inconsistency with other data; data of Le Guyader *et al.*[71] and Beneš and Selecká[82] were discarded due to large deviation from other data. The coefficients of Eq. (85) for the metal carbonate ion pairs obtained are

$$\text{for } \lg K_{\mathrm{MgCO_3^0}}: \quad A = 2\,403.544\,158, \quad B = -133\,162.968\,6, \quad C = -869.007\,205\,4, \quad D = 0.363\,806\,38, \quad E = 7\,808\,760.2$$

$$\text{for } \lg K_{\mathrm{CaCO_3^0}}: \quad A = 3\,423.002\,821, \quad B = -198\,599.919\,8, \quad C = -1\,226.637\,029\,0, \quad D = 0.483\,834\,83, \quad E = 12\,202\,744.3$$

$$\text{for } \lg K_{\mathrm{SrCO_3^0}}: \quad A = 2\,135.555\,983, \quad B = -120\,124.315\,7, \quad C = -769.940\,147\,5, \quad D = 0.319\,815\,38, \quad E = 7\,108\,522.7$$

$$\text{for } \lg K_{\mathrm{BaCO_3^0}}: \quad A = 3\,191.711\,219, \quad B = -184\,628.673\,2, \quad C = -1\,145.182\,852\,2, \quad D = 0.456\,233\,23, \quad E = 11\,364\,494.3$$

Pitzer's virial formalism for describing ion activity coefficients forms an alternative to using ion pair equilibrium constants in some cases. Pitzer *et al.*[28] recommend using ion pair equilibrium constants when they are on the order of 1000 or greater. For smaller values of the stability constant, they recommend relying on the Pitzer formalism. Harvie *et al.*[31] suggested a limit of 500 for 2-2 type ion pairs, and 20 for 2-1 type ion pairs. When the stability constant exceeds these values, the ion activity coefficient at low electrolyte concentration is not well represented by the Pitzer formalism. Harvie *et al.*[31] concluded this from a comparison between the Pitzer model and the extended Debye-Hückel model with ion pairing. This analysis did not consider any specific interaction between the ion pair and the indifferent electrolyte.

The relevant Pitzer parameters for this study are the ones for $M(HCO_3)_2$. Reported values are summarized in Table 10. The parameters of Pitzer *et al.*[28] are based on electrochemical measurements in a Harned cell, in aqueous $M(HCO_3)_2$–MCl_2 mixtures (M = Mg and Ca). Their values were confirmed by He and Morse,[29] who used potentiometric titrations of the carbonic acid system in $CaCl_2$ and $MgCl_2$ solutions for their determinations, at 0–90 °C. The values of Harvie *et al.*[31] were obtained from solubility data of calcite, and reported "within a range of possible values consistent with the data". Loos *et al.*[86] based their values on solubilities as well. The values deviate widely from the other reported values, and should not be used for any other purpose than to describe a limited calcite solubility data set. For $Mg(OH)_2$, the values of the Pitzer parameters reported by Harvie *et al.*[31] are much closer to values reported by others, probably because K'_1 and K'_2 data in seawater were included in the estimate. It is concluded that estimating Pitzer parameters from alkaline earth carbonate solubility data alone is not recommended.

Temperature relationships for the Pitzer parameters of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ were derived from data of Pitzer *et al.*[28] and He and Morse[29] (for 0–90 °C). To avoid excessive curvature (second-order term) that would lead to extreme values upon extrapolation, the curvature was based on other ion pairs in an extended temperature range.[24] The results are

TABLE 10. Pitzer parameters for $M(HCO_3)_2$

Source	M	t/°C	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Millero and Thurmond[77]	Mg	25	0.0193	0.584	—
Harvie *et al.*[31]		25	0.329	0.6072	—
Pitzer *et al.*[28]		25	0.033	0.85	—
He and Morse[29]		0	0.129	0.476	—
		25	0.03	0.80	—
		50	−0.085	1.816	—
		75	−0.16	2.250	—
		90	−0.24	2.569	—
Harvie *et al.*[31]	Ca	25	0.4	2.977	—
Pitzer *et al.*[28]		25	0.28	0.3	—
He and Morse[29]		0	0.481	0.428	—
		25	0.20	0.30	—
		50	−0.007	0.242	—
		75	−0.21	0.206	—
		90	−0.467	0.162	—
Loos *et al.*[86]		25	−0.104	1.68	—
De Visscher and Vanderdeelen[18]		25	1.45	−3.86	−1.01

$$\beta^{(0)}_{\mathrm{Mg(HCO_3)_2}} = -1.9113 + \frac{769.53}{T} - \frac{57330}{T^2}, \quad (97)$$

$$\beta^{(1)}_{\mathrm{Mg(HCO_3)_2}} = 14.3043 - \frac{5590.60}{T} + \frac{483720}{T^2}, \quad (98)$$

$$\beta^{(0)}_{\mathrm{Ca(HCO_3)_2}} = -3.7313 + \frac{1371.42}{T} - \frac{57330}{T^2}, \quad (99)$$

$$\beta^{(1)}_{\mathrm{Ca(HCO_3)_2}} = 4.3005 - \frac{2819.46}{T} + \frac{483720}{T^2}. \quad (100)$$

The ionic strength dependence of the stability constant of $CaHCO_3^+$ can be captured by the Pitzer formalism as well, with, for example, Pitzer parameters for the $CaHCO_3^+ - Cl^-$ interaction (compare the approach of Harvie *et al.*[31] for $MgOH^+$), as discussed above (see Sec. 1.3.2.4). A similar approach, but with a λ (ion-neutral) interaction parameter, was used by Königsberger *et al.*[78,79] for the interaction between $MgCO_3^0$ and ClO_4^-.

The interpretation of solubility data in terms of ion pairing with bicarbonate and carbonate has been in debate since Langmuir's 1968 paper.[49] He noted that, while measurable stability of the ion pairs has been observed, the pH dependence of calcite solubility found by Grèzes and Basset[87] is inconsistent with the existence of the $CaCO_3^0$ ion pair.

De Visscher and Vanderdeelen[30] used a Pitzer model to examine the consistency between $CaCO_3$ solubility data and the existence of carbonate and bicarbonate ion pairs. They did not find any inconsistency between the examined solubility data and the existence of the $CaCO_3^0$ ion pair. With respect to $CaHCO_3^+$, the solubility data could be divided into two subsets: one consistent with the existence of the ion pair and one inconsistent with its existence. The study of Grèzes and Basset[87] belonged to the latter. So what Langmuir[49] interpreted as inconsistent with the existence of the calcium carbonate ion pair can also be interpreted as inconsistent with the existence of the calcium bicarbonate ion pair. Lafon[81] pointed out that the data of Grèzes and Basset[87] closely agree with predictions assuming a $CaCO_3^0$ ion pair, whereas the absence of the ion pair would require an unrealistically high solubility constant of $CaCO_3$. Although the sources are not always entirely clear on this point, it seemed to us that the studies that had taken the most efforts to eliminate error due to small crystal size, crystal defects or surface charge were in the group that are consistent with the existence of the bicarbonate ion pair. Hence, we concluded that the inconsistency is an experimental artifact of a number of solubility studies, at least at low ionic strength.

In the current study, two options were evaluated. The first option (Model 1) was to use a stability constant for the $MHCO_3^+$ ion pair (Eq. (85) with the coefficients given above), and to set the Pitzer parameters for $M(HCO_3)_2$ equal to zero. No Pitzer parameters for $MHCO_3^+$ interactions with other ions were assumed, and neither was an ionic strength dependence of $K_{MHCO_3^+}$, which may render Model 1 unrealistic at high ionic strength. The second option (Model 2) was to set the ion pair stability constant equal to zero, and to use the respective Pitzer parameters (Eqs. (97)–(100)). For Sr and Ba, the same values as for Ca were used.

1.3.3.7. *Other ion pairs.*

Davies and Hoyle[88] found that the stability constant of the $CaOH^+$ ion pair is 20. This means that hydrolysis of calcium is negligible at pH values normally encountered in alkaline earth carbonate solubility measurements. Nancollas[89] reports lg K_{MOH^+} values of 2.58, 1.40, 0.83, and 0.64 for Mg, Ca, Sr, and Ba, respectively. Harvie *et al.*[31] pointed out that the Pitzer model adequately accounts for this ion pair. However, they did include a stability constant for $MgOH^+$ in their model (154; lg $K_{MgOH^+} = 2.19$). Felmy *et al.*[90] explicitly included a $CaOH^+$ ion pair in their Pitzer model ($K_{CaOH^+} = 14.8$; lg $K_{CaOH^+} = 1.17$), but they did not include a $SrOH^+$ ion pair. Additional measurements on the MOH^+ ion pair were reported by Stock and Davies,[91] Bell and Prue,[92] Bell and George,[93] Gimblett and Monk,[94] Bates *et al.*,[95] Martynova *et al.*,[68] McGee and Hostetler,[96] Seewald and Seyfried,[97] and a compilation of Baes and Mesmer.[98] These are summarized in Table 11. It is clear from the data of Seewald and Seyfried[97] that the $CaOH^+$ ion pair becomes more important as the temperature increases, which will have to be addressed in future modeling efforts at higher temperatures.

Harvie *et al.*[31] found that no stability constant is needed for the $CaOH^+$ interaction, but it is remarkable that they needed to include a $\beta^{(2)}$ parameter in their model, which is normally restricted to 2-2 electrolytes. The parameter $\beta^{(2)}$ in these models is, in fact, meant to emulate the ion pair stability constant. For $MgOH^+$ they used a lg K of 2.188, which is within the experimental error of the experimental value of McGee and Hostetler.[96] Königsberger *et al.*[79] largely followed the approach of Harvie *et al.*,[31] but assumed ion pairing between Ca^{2+} and OH^- (stability constant about 12 at 25 °C; lg $K = 1.078$) along with the $Ca(OH)_2$ Pitzer parameters of Harvie *et al.*,[31] who assumed no such ion pairing in their model. Unlike Harvie *et al.*,[31] Königsberger *et al.*[79] needed this inclusion of a stability constant to correctly predict portlandite ($Ca(OH)_2$) solubility. They used a value consistent with Harvie *et al.*[31] for the magnesium ion pair (lg $K = 2.215$). Pitzer parameters for this class of interactions are given in Table 12. We followed Königsberger *et al.*[79] in including both a stability constant and Pitzer parameters in the model, except for $MgOH^+$, which has a sufficiently high equilibrium constant to replace Pitzer parameters; we assumed $\beta^{(2)} = 0$ for all 1-2 ion pairs. For $Sr(OH)_2$, we assumed Pitzer parameters that are the average of the parameters for Ca and Ba. The stability constants used were

$$\lg K_{\mathrm{MgOH^+}} = -0.9904 + \frac{279.22}{T} + 0.0076236T, \quad (101)$$

$$\lg K_{\mathrm{CaOH^+}} = -4.2598 + \frac{480.19}{T} + 0.0131108T, \quad (102)$$

$$\lg K_{\mathrm{SrOH^+}} = -1.1979 + \frac{176.49}{T} + 0.0048189T, \quad (103)$$

TABLE 11. Stability constants of alkaline earth hydroxide ion pairs

Source	M	$t/°C$	lg K	Method
Stock and Davies[91]	Mg	25	2.59[a]	Conductometric titration
Bell and Prue[92]	Ca	25	1.29	Rate of OH^- catalyzed reaction
	Ba	25	0.64	Rate of OH^- catalyzed reaction
Bell and George[93]	Ca	0	1.37	Solubility $CaIO_3$ in KOH(aq)[b]
		25	1.40	
		40	1.48	
Gimblett and Monk[94]	Ca	15	1.337±0.018	Potentiometry
		25	1.367±0.020	
		35	1.398±0.021	
	Sr	5	0.780±0.025	
		15	0.804±0.014	
		25	0.824±0.014	
		35	0.860±0.015	
		45	0.893±0.017	
	Ba	5	0.620±0.035	
		15	0.602±0.017	
		25	0.638±0.018	
		35	0.688±0.021	
		45	0.721±0.022	
Bates *et al.*[95]	Ca	0	1.02	Potentiometry[c]
		10	1.12	
		25	1.14	
		40	1.375	
Martynova *et al.*[68]	Ca	22	1.3	Ion-selective electrodes
		60	2.80	
		70	3.06	
		80	3.50	
		90	3.56	
		98	3.88	
McGee and Hostetler[96]	Mg	10	2.182±0.08	Potentiometric titration
		25	2.206±0.05	
		40	2.291±0.03	
		55	2.372±0.03	
		70	2.445±0.04	
		90	2.544±0.09	
Baes and Mesmer[98]	Mg	25	3.56	Compilation
	Ca	25	1.15	Compilation
	Sr	25	0.71	Compilation
	Ba	25	0.53	Compilation
Seewald and Seyfried[97]	Ca	100	2.06	Solubility of $Ca(OH)_2$[d]
		200	2.85	
		300	3.99	
		350	4.79	
Felmy *et al.*[90]	Ca	22	1.17	Solubility of $Ca(OH)_2$[e]
	Sr	22	—	Solubility of $Sr(OH)_2$[f]

[a]Recalculated as 2.19 by Harvie *et al.*[31]
[b]Value reported is the stoichiometric stability constant.
[c]Data analysis required the assumption that $\gamma(Cl^-) = \gamma(OH^-)$.
[d]At 500 bar.
[e]With Pitzer parameters.
[f]No ion pairing required when Pitzer parameters were used.

$$\lg K_{BaOH^+} = -1.4394 + \frac{181.80}{T} + 0.0049638T. \qquad (104)$$

These equations are based on the data in Table 11, except the data of Baes and Mesmer,[98] which are not original data and deviate from other values, the data of Bell and George,[93] which are stoichiometric stability constants, and Martynova *et al.*,[68] which showed poor correspondence with other data and proved unreliable for other ion pairs as well. For the data point of Stock and Davies,[91] the recalculated value of Harvie *et al.*[31] was used.

From solubility data of nesquehonite ($MgCO_3{\cdot}3H_2O$) in concentrated Na_2CO_3 solutions, Königsberger *et al.*[78]

TABLE 12. Single-electrolyte Pitzer parameters for $M(OH)_2$

Source	Electrolyte	$t/°C$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
Harvie *et al.*[31]	$Ca(OH)_2$	25	−0.1747	−0.2303	−5.72[a]	
Pitzer[23]	$Ba(OH)_2$	25	0.172	1.2		

[a]Not used in the current study

TABLE 13. Two-electrolyte ion interactions

Source	Parameter	Value	$t/°C$
Harvie *et al.*[31]	θ(Mg, H)	0.10	25
Harvie *et al.*[31]	θ(Ca, H)	0.092	25
Pitzer[23]	θ(Mg, Ca)	0.007	25
Pitzer[23]	θ(Sr, H)	0.0642	25
Pitzer[23]	θ(Ba, H)	0.0708	25
Harvie *et al.*[31]	$\theta(OH, CO_3)$	0.10	25
Harvie *et al.*[31]	$\theta(HCO_3, CO_3)$	−0.04	25

concluded the existence of a $Mg(CO_3)_2^{2-}$ ion pair. Felmy *et al.*[90] concluded the existence of $Ca(CO_3)_2^{2-}$ and $Sr(CO_3)_2^{2-}$ ion pairs in similar experiments in concentrated Na_2CO_3 solutions. However, they indicated that there is an alternative explanation (activity coefficient decrease) of their data that does not require assuming these ion pairs. However, Königsberger *et al.*[78] could not explain the linear increase in solubility with increasing Na_2CO_3 concentration by a decrease of the activity coefficient. Given the pronounced activity coefficient decrease of $MgCO_3^0$ with increasing ionic strength found by Reardon and Langmuir,[76] the existence of $Ca(CO_3)_2^{2-}$ and $Sr(CO_3)_2^{2-}$ ion pairs, while the most plausible explanation, is not proven. The stability constant can be defined as the equilibrium constant of the reaction:

$$M^{2+}(aq) + 2CO_3^{2-} \rightleftharpoons M(CO_3)_2^{2-}(aq).$$

For Sr, Felmy *et al.*[90] found a value of lg K of 3.31; for Ca they found a value of 3.88.

Königsberger *et al.*[79] included a $Mg(CO_3)_2^{2-}$ species in their thermodynamic model, based on their study,[78] where Na_2CO_3 was found to increase the solubility of nesquehonite and eitelite. The stability constant was determined, and a value of lg $K = 3.91$ was found. They analyzed data on the stability of $MgCO_3^0$ in the presence of $NaClO_4$ and found that the electrolyte increased $\gamma(MgCO_3^0)$. In their 1999 study,[79] they found a decrease. Pitzer parameters depend on each other, as well as on thermodynamic equilibrium constants selected in the evaluation. The seeming inconsistency is due to a difference in the value of $K_{MCO_3^0}$ used in the two studies. Riesen *et al.*[99] and Königsberger *et al.*[78] also included a $Mg(HCO_3)_2^0$ ion pair, with stoichiometric stability constant lg K' of 0.6.

In the current study, no species of the form $M(CO_3)_2^{2-}(aq)$ or $M(HCO_3)_2^0(aq)$ were assumed.

Alkali metals and alkaline earth metals form ion pairs with chloride to some extent.[74,100] However, the stability constants are small (<10), and this effect can be accounted for adequately using the Pitzer approach. In the case of the alkali chlorides, the stability constants are less than 1, so the existence of the ion pairs is questionable.[101] It is not possible to clearly distinguish such ion pairing from other forms of ion interactions.

Table 13 summarizes some relevant Pitzer parameters for this study.

1.3.4. Independent thermodynamic data

Bäckström[102] investigated the heat of transition of aragonite into calcite by calorimetric measurements of the heats of solution of calcite and aragonite in aqueous acid solutions. The result was 126 ± 84 J mol^{-1}. If the measured value is correct, thermodynamic data of the solubility of calcite and aragonite should be consistent with this data to within experimental error. Königsberger *et al.*[103] investigated the Gibbs free energy of the aragonite-calcite transition by a potentiometric technique involving a calcite-saturated solution and an aragonite-saturated solution. They found that the Gibbs free energy of transition is −830 J mol^{-1}, and the enthalpy of transition is 540 J mol^{-1}, significantly higher than the calorimetric data of Bäckström.[102] In a later study they adjusted their values to -840 ± 20 J mol^{-1} and 440 ± 50 J mol^{-1}, respectively. Rock and Gordon,[104] using a similar technique, found a Gibbs free energy of transition of −1381 J mol^{-1}, which is inconsistent with the other studies. This value is discarded for that reason. Hacker *et al.*[105] determined the calcite-aragonite transition pressure at temperatures of 200–800 °C. Crawford and Fyfe[106] obtained a value at 100 °C. These results can be converted to a Gibbs free energy of transition by means of the thermodynamic relationship,

$$dG = v dp - S dT. \tag{105}$$

Additional information is obtained from c_p data of calcite and aragonite reported by Barin *et al.*,[107] which leads to the following Δc_p relationship for the aragonite-calcite transition:

$$\Delta_{a\to c} c_p/(J\,mol^{-1}\,K^{-1}) = 18.0257 - 0.0185620T - \frac{1\,006\,352}{T^2}. \tag{106}$$

Equation (106) is valid between 298 and 700 K. This equation predicts much higher enthalpies of transition at elevated temperature than measured by Wolf *et al.*[108] However, Wolf *et al.*'s enthalpy of transition is inconsistent with the temperature dependence of the transition pressure measured by Hacker *et al.*[105] For that reason, Eq. (106) is kept. Equation (106) allows calculation of the thermodynamics of transition from aragonite to calcite over the entire temperature range using only the enthalpy and Gibbs free energy of transition at 298.15 K. These two variables were used as adjustable variables to obtain the best fit with the Gibbs free energy data of Königsberger *et al.*,[103] of Hacker *et al.*,[105] and of Crawford and Fyfe.[106] The best fit was obtained with a Gibbs free energy of transition of −832.1 J mol^{-1} and an enthalpy of transition of 290.1 J mol^{-1}. The analysis indicates that the Königsberger *et al.*[103] data overestimate the temperature dependence of the Gibbs free energy, whereas the calorimetric data of Bäckström[102] underestimate it. Based on this information, the coefficients to Eq. (85) for $\lg K_{a\to c}$ are derived. The result is as follows:

$A = -6.116\,08$
$B = 398.779$
$C = 2.167\,991$
$D = -0.000\,484\,780$
$E = -26\,282.67$.

These results lead to an entropy of transition of 3.76 J mol^{-1} K^{-1}, almost identical to the value measured calorimetrically by Stavely and Linford[109] (3.72 J mol^{-1} K^{-1}).

Similar reasoning was applied to the measurements of Wolf *et al.*[110] on the vaterite-calcite transition. Based on their c_p data of vaterite and calcite, and enthalpies of transition at 313 K and at 630–770 K, the following equation for the heat capacity of transition is estimated:

$$\Delta_{v\to c}c_p/(\mathrm{J\,mol^{-1}\,K^{-1}}) = -32.0965 + 0.05132595T - \frac{1\,506\,324}{T^2}. \tag{107}$$

Assuming a Gibbs free energy of transition at 298.15 K of -3100 J mol^{-1}, the coefficients to Eq. (85) for $\lg K_{v\to c}$ are derived as follows:

$A = 10.819\,28$
$B = -466.995$
$C = -3.860\,312$
$D = 0.001\,340\,469$
$E = 39\,340.34$.

Based on the thermodynamics of transition, solubility data on aragonite and vaterite can be evaluated by comparing the equivalent calcite solubility, and *vice versa*.

When the heat of dissolution of an alkaline earth carbonate can be calculated from reliable thermodynamic data (e.g., magnesite, calcite), the temperature dependence of the solubility constant can be calculated. This can improve the accuracy of the evaluation when data are scarce (e.g., magnesite).

1.3.5. Solubility in salt solutions: a SIT approach

The specific ion theory (SIT) is a modified form of a formalism proposed by Guggenheim[111] and others to describe activity coefficients in concentrated electrolytes. In its modern form, the general equation for the activity coefficient of an ion in a complex electrolyte mixture is

$$\lg\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+1.5\sqrt{I}} + \sum_j \varepsilon(i,j)m_j, \tag{108}$$

where A is the Debye-Hückel constant (0.5115 at 25 °C)[112] and $\varepsilon(i,j)$ is the specific ion interaction parameter. The summation is over all the ions, but $\varepsilon(i,j) = 0$ whenever i and j are ions of the same sign. $\varepsilon(i,j)$ is determined from $\gamma_\pm$ data of the single electrolyte i_mj_n (assuming ions i^{n+} and j^{m-}):

$$\lg\gamma_\pm = -\frac{mnA\sqrt{I}}{1+1.5\sqrt{I}} + \frac{2mn}{m+n}\varepsilon(i,j)m_{i_mj_n}. \tag{109}$$

Hence, no mixed-electrolyte data is needed to predict activity coefficients in mixtures, making this method less accurate, but less prone to error propagation than the Pitzer model.

The water activity is calculated from the osmotic coefficient ϕ:

$$a_w = \exp\left(-\phi M_{H_2O}\sum_i m_i\right), \tag{110}$$

where M_{H_2O} is the molar mass of water (0.01801528 kg mol^{-1}), m_i is the molality of ion i, and the summation is over all ions. The osmotic coefficient is calculated as

$$\varphi = 1 - \frac{2\ln(10)A}{(1.5)^3\sum_i m_i} \times\left(1+1.5\sqrt{I} - \frac{1}{1+1.5\sqrt{I}} - 2\ln\left(1+1.5\sqrt{I}\right)\right) + \frac{\ln(10)}{2\sum_i m_i}\sum_i\sum_j \varepsilon(i,j)m_im_j, \tag{111}$$

where the summations are over all ions. Again, $\varepsilon(i,j) = 0$ whenever i and j are ions of the same sign. Values of $\varepsilon(i,j)$ are taken from Preis and Gamsjäger,[113] or derived from $\gamma_\pm$ data.[112]

In open systems ($MgCO_3 + H_2O + CO_2$), the approximate Eq. (12) is a convenient way to predict solubilities in the presence of electrolytes, where $\gamma_{M^{2+}}$ and $\gamma_{HCO_3^-}$ are calculated from Eq. (108). Values of $\varepsilon(M^{2+}, HCO_3^-)$ are not available, but as the molalities of M^{2+} and HCO_3^- tend to be small compared with the added salt, this should not affect the result markedly.

1.4. Remaining issues

The most significant open issue in our understanding of the solubility of the alkaline earth carbonates is our limited knowledge of the properties of the alkaline earth carbonate and bicarbonate ion pairs. Here are some suggestions to resolve those issues.

Pitzer *et al.*[28] investigated the Mg-HCO_3 and Ca-HCO_3 interactions in a Harned cell at 25 °C. This is probably the most reliable route to a better understanding of this interaction. Experiments should be conducted at lower chloride concentrations than investigated by Pitzer *et al.*, to include the ionic strength range usually observed in solubility experiments. On the other hand, data at high Mg^{2+} and HCO_3^- concentrations are needed to cover the range of concentrations found in nesquehonite and lansfordite solubility measurements. Experiments should also be conducted at temperatures other than 25 °C, and for Ba and Sr as well. In particular, high-temperature (100–300 °C) data should be determined, as $K_{\mathrm{MHCO}_3^+}$ is expected to be orders of magnitude larger in this temperature range compared to room temperature, and therefore easier to detect. As indicated by Harvie *et al.*,[31] high-temperature determinations would be useful for the Mg-OH interaction as well, and possibly even for other M-OH interactions.

Some researchers measured both pH and dissolved alkaline earth metal concentration in their solubility measurement. Langmuir[66] demonstrated how the pH can be used to quantify ion pairing in these experiments. The disadvantage of this is that pH is a single-ion quantity that is not unequivocally defined at the high ionic strengths that occur when dissolving hydrated magnesium carbonates. A thermodynamically more rigorous option would be to determine solubility in a Harned cell in the presence of small quantities of chloride, and with a CO_2-H_2 gas phase. However, in view of the slow dissolution rates usually observed in solubility experiments, care must be taken not to leach electrode solution from the reference electrode.

2. Solubility of Beryllium Carbonate

2.1. Critical evaluation of the solubility of beryllium carbonate in aqueous systems

Components:	Evaluator:
(1) Beryllium carbonate; $BeCO_3$; [13106-47-3] (2) Carbon dioxide; CO_2; [124-39-8] (3) Water; H_2O; [7732-18-5]	Jan Vanderdeelen, Department of Applied Analytical and Physical Chemistry, Ghent University, Ghent, Belgium

It might be surprising that only one very old reference[114] is found for the solubility of beryllium carbonate in water. At that time, little care was given to control of experimental conditions such as temperature and partial pressure of CO_2. In addition, little information is given on the purity or crystallinity of the carbonate. From Gmelin,[115] it is questionable whether $BeCO_3$(cr) is a stable solid in the absence of CO_2(g) or at ordinary CO_2 partial pressure, although it may be stable at higher pressures.

If $BeCO_3$(cr) actually exists, it should have a higher solubility than $MgCO_3$(cr) and be subject to hydrolysis in contact with water to form hydroxo complexes or mixed hydroxy carbonates.

2.2. Data for the solubility of beryllium carbonate in aqueous systems

Components:	Original Measurements:
(1) Beryllium carbonate; $BeCO_3$; [13106-47-3] (2) Carbon dioxide; CO_2; [124-39-8] (3) Water; H_2O; [7732-18-5]	[114] G. Klatzo, Die Constitution der Beryllerde, Dissertation, Dorpat (1868); J. Prakt. Chem. **106**, 207 (1869); Z. Chem. **5**, 129 (1869).
Variables:	**Prepared by:**
T/K: ambient $p(CO_2)$/bar: unknown	J. Vanderdeelen

Experimental Values

25 ml of water contained 0.0897 g $BeCO_3 \cdot 4H_2O$.
Solubility (compiler): 0.0254 mol l^{-1}.

Auxiliary Information

Method/Apparatus/Procedure:
35 ml of the solution were evaporated, calcined and weighed as BeO.

Source and Purity of Materials:
$BeCO_3$: powdered beryl (Limoges) was calcined in the presence of K_2CO_3 until a liquid mixture was obtained. After cooling, H_2SO_4 was added, and the mixture was heated and filtered. The filtrate was concentrated by evaporation. After several precipitations, concentrated $(NH_4)_2SO_4$ solution was added and the mixture was shaken vigorously for 10 h. This procedure was repeated several times. Basic beryllium carbonate was precipitated by boiling, collected on a filter and washed with hot water. The solid was suspended in water, flushed with CO_2(g) for 36 h and filtered in a CO_2 atmosphere. The filtrate was diluted with H_2SO_4. After 3 weeks, crystals of $BeCO_3 \cdot 4H_2O$ were formed as verified by analysis.

Estimated Error:
No estimates possible.

3. Solubility of Magnesium Carbonate

3.1. Critical evaluation of the solubility of magnesium carbonate in aqueous systems

Components:	Evaluators:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Sodium chloride; NaCl; [7647-14-5] (3) Sodium carbonate; Na_2CO_3; [497-19-8] (4) Sodium sulfate; Na_2SO_4; [7757-82-6] (5) Potassium hydrogen carbonate; $KHCO_3$; [298-14-6] (6) Sodium nitrate; $NaNO_3$; [7631-99-4] (7) Magnesium chloride; $MgCl_2$; [7786-30-3] (8) Sodium hydroxide; NaOH; [1310-73-2]	Alex De Visscher, Department of Chemical and Petroleum Engineering, and Centre for Environmental Engineering Research and Education (CEERE), Schulich School of Engineering, University of Calgary, Calgary, Alberta, Canada
(9) Sodium hydrogen carbonate; $NaHCO_3$; [144-55-8] (10) Sodium perchlorate; $NaClO_4$; [7601-89-0] (11) Perchloric acid; $HClO_4$; [7601-90-3] (12) Potassium chloride; KCl; [7447-40-7] (13) Ammonium chloride; NH_4Cl; [12125-02-9] (14) Lithium chloride; LiCl; [7447-41-8] (15) Water; H_2O; [7732-18-5] (16) Carbon dioxide; CO_2; [124-37-9]	Jan Vanderdeelen, Department of Applied Analytical and Physical Chemistry, Ghent University, Ghent, Belgium

Magnesium carbonate, $MgCO_3$, [546-93-0] occurs in three crystalline varieties: anhydrous, commonly known as magnesite, $MgCO_3$ [13717-00-5], trihydrate, $MgCO_3 \cdot 3H_2O$ [5145-46-0], referenced as nesquehonite [14457-83-1], as well as pentahydrate, $MgCO_3 \cdot 5H_2O$, [61042-72-6] called lansfordite [5145-47-1]. Although hydrates with a gradual increase from 1 to 5 water molecules have been cited by Gmelin,[115] it is questionable whether they are not to be considered as mixtures of the physically identified anhydrous, tri- and pentahydrate. Synthesis and chemical characterization of the anhydrous and both hydrated magnesium carbonates are given by Menzel.[116] The anhydrous form occurs widely as an alteration product of rocks rich in magnesium, as beds in metamorphic rocks, in sedimentary deposits and as a gangue mineral in hydrothermal ore veins. In Europe it is found in excellent crystalline form at Obersdorf in Austria and at Snarum, Norway. The trihydrate form, nesquehonite, occurs as a recent product formed under normal atmospheric conditions of temperature and pressure. It is mainly found at Nesquehoning near Lansford, Pennsylvania, USA. The pentahydrate seems often to be found in association with the trihydrate. The references for aqueous solubility data of magnesite and nesquehonite, as shown in the compilation sheets, also mention the synthesis of both. A very straightforward synthesis and crystal structure investigation of lansfordite is given by Liu *et al*.[117]

3.1.1. Overview of solubility data

A synoptic review on the specifications of the crystallographic variety of the magnesium carbonate used, the number of data shown in the 32 primary literature sources[66,78,79,110–146] at the specific temperature or range and the system involved to which the magnesium carbonate solubility data refer is shown in Table 14. From these references three separate groups, based on the mineralogical variety, were identified:

1. Magnesite, $MgCO_3$, [13717-00-5];[118,122–125,128,129,134–137,140–144]
2. Nesquehonite [14457-83-1] or $MgCO_3 \cdot 3H_2O$ [5145-46-0];[66,78,79,119–122,126,129–134,137,139,142,145,146]
3. Lansfordite [5145-47-1] or $MgCO_3 \cdot 5H_2O$ [61042-72-6].[127,133,138,139]

The four data of Lubavin,[122] of which two refer to magnesite and two to nesquehonite, as well as the four by Halla and van Tassel,[141] were discarded because the partial pressure of CO_2 used in the experiments is referenced as "unknown" by the authors. Moreover, in the latter reference there is a pronounced difference between the results obtained using a natural and a synthetic magnesite, making them unreliable for further consideration. The data of Auerbach[126] were rejected because the system was a closed system with a gas phase of unknown volume. Hence, the system is not properly defined. Cesaro[127] found nesquehonite crystals in the system after an experiment with lansfordite. The experiment was conducted at unknown "ambient" temperature. For these reasons, the data were rejected. The data of Leick[135] cannot be kept for further consideration because the solubility was determined in boiling water, which means that the total carbonate of the dissolved magnesite is not conserved, and there is no equilibrium with a known CO_2 partial pressure. This makes the system neither closed nor open to $CO_2(g)$ for the purpose of this evaluation. Furthermore, Königsberger *et al*.[79] showed that the magnesite-brucite

TABLE 14. Overview of magnesium carbonate solubility data in aqueous systems

Ref.	Temperature range/°C	Solid phase	Number of data	System used	Considered for evaluation
118	5	$MgCO_3$	6	$MgCO_3 + H_2O + CO_2$	Yes
119	10–40	$MgCO_3 \cdot 3H_2O$	7	$MgCO_3 \cdot 3H_2O + H_2O + CO_2$	Yes
	19	$MgCO_3 \cdot 3H_2O$	1	$MgCO_3 \cdot 3H_2O + H_2O$	Yes
120	13.4–100	$MgCO_3 \cdot 3H_2O$[a]	17	$MgCO_3 \cdot 3H_2O + H_2O + CO_2$	Yes
121	12	$MgCO_3 \cdot 3H_2O$[a]	1	$MgCO_3 \cdot 3H_2O + H_2O$	Yes
	3.5–50	$MgCO_3 \cdot 3H_2O$[a]	6	$MgCO_3 \cdot 3H_2O + H_2O + CO_2$	Yes
	12	$MgCO_3 \cdot 3H_2O$[a]	8	$MgCO_3 \cdot 3H_2O + H_2O + CO_2$	Yes
122	26	$MgCO_3 \cdot 3H_2O$	1	$MgCO_3 \cdot 3H_2O + H_2O + CO_2$	No
	26	$MgCO_3$	1	$MgCO_3 + H_2O + CO_2$	No
	26	$MgCO_3 \cdot 3H_2O$	1	$MgCO_3 \cdot 3H_2O + H_2O + CO_2 + NaCl$	No
	26	$MgCO_3$	1	$MgCO_3 + H_2O + CO_2 + NaCl$	No
123	12–16	$MgCO_3$	1	$MgCO_3 + H_2O$	Yes
124	≈22[b]	$MgCO_3$	1	$MgCO_3 + H_2O + CO_2$	Yes
125	23	$MgCO_3$	1	$MgCO_3 + H_2O$	Yes
	23	$MgCO_3$	7	$MgCO_3 + H_2O + NaCl$	Yes
	24	$MgCO_3$	1	$MgCO_3 + H_2O$	Yes
	24	$MgCO_3$	8	$MgCO_3 + Na_2SO_4 + H_2O$	Yes
	25	$MgCO_3$	1	$MgCO_3 + H_2O$	Yes
	25	$MgCO_3$	7	$MgCO_3 + H_2O + Na_2CO_3$	Yes
	35.5	$MgCO_3$	9	$MgCO_3 + H_2O + Na_2SO_4$	Yes
	37.5	$MgCO_3$	6	$MgCO_3 + H_2O + CO_2 + NaCl$	Yes

TABLE 14. Overview of magnesium carbonate solubility data in aqueous systems—Continued

Ref.	Temperature range/°C	Solid phase	Number of data	System used	Considered for evaluation
126	15, 25, 35	$MgCO_3{\cdot}3H_2O$	3	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	No
	15, 25, 35	$MgCO_3{\cdot}3H_2O$[c]	27	$MgCO_3{\cdot}3H_2O + H_2O + CO_2 + KHCO_3$	No
127	Ambient	$MgCO_3{\cdot}5H_2O$	1	$MgCO_3{\cdot}5H_2O + H_2O + CO_2$	No
128	≈0	$MgCO_3$	12	$MgCO_3 + H_2O$	Yes
	≈0	$MgCO_3$	6	$MgCO_3 + H_2O + NaCl$	Yes
	≈0	$MgCO_3$	6	$MgCO_3 + H_2O + NaNO_3$	Yes
	≈0	$MgCO_3$	6	$MgCO_3 + H_2O + Na_2SO_4$	Yes
	≈0	$MgCO_3$	3	$MgCO_3 + H_2O + Na_2CO_3$	Yes
	≈0	$MgCO_3$	3	$MgCO_3 + H_2O + MgCl_2$	Yes
129	20	$MgCO_3$[d]	1	$MgCO_3 + H_2O + CO_2$	Yes
	20	$MgCO_3$[d]	1	$MgCO_3 + H_2O + CO_2 + NaCl$	Yes
	20	$MgCO_3{\cdot}3H_2O$	2	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
130	25	$MgCO_3{\cdot}3H_2O$	12	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
131	25	$MgCO_3{\cdot}3H_2O$	6	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
132	18	$MgCO_3{\cdot}3H_2O$	8	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
	0–60	$MgCO_3{\cdot}3H_2O$	8	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
133	5–60	$MgCO_3{\cdot}3H_2O$	12	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
	−1.8 to 20	$MgCO_3{\cdot}5H_2O$	6	$MgCO_3{\cdot}5H_2O + H_2O + CO_2$	Yes
134	18	$MgCO_3$	4	$MgCO_3 + H_2O$	Yes
	18	$MgCO_3$	2	$MgCO_3 + H_2O + CO_2$	Yes
	18	$MgCO_3{\cdot}3H_2O$	2	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
135	100	$MgCO_3$	4	$MgCO_3 + H_2O$	No
	100	$MgCO_3$	5	$MgCO_3 + H_2O + NaCl$	No
	100	$MgCO_3$	5	$MgCO_3 + H_2O + Na_2SO_4$	No
	100	$MgCO_3$	4	$MgCO_3 + H_2O + Na_2CO_3$	No
	100	$MgCO_3$	4	$MgCO_3 + H_2O + NaOH$	No
136	25, 38.8	$MgCO_3$	2	$MgCO_3 + H_2O + CO_2$	Yes
137	25	$MgCO_3$	1	$MgCO_3 + H_2O + CO_2$	Yes
	25	$MgCO_3{\cdot}3H_2O$	1	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
138	0	$MgCO_3{\cdot}5H_2O$	4	$MgCO_3{\cdot}5H_2O + H_2O + CO_2$	Yes
139	0–53.5	$MgCO_3{\cdot}3H_2O$	9	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
	0–15	$MgCO_3{\cdot}5H_2O$	3	$MgCO_3{\cdot}5H_2O + H_2O + CO_2$	Yes
140	25–200	$MgCO_3$	7	$MgCO_3 + H_2O$	Yes
141	21	$MgCO_3$	4	$MgCO_3 + H_2O + CO_2$	No
66	25	$MgCO_3{\cdot}3H_2O$	1[e]	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	No
142	25, 50	$MgCO_3$	21	$MgCO_3 + H_2O + CO_2 + NaClO_4 + HClO_4$	No
	25, 50	$MgCO_3{\cdot}3H_2O$	6	$MgCO_3 + H_2O + CO_2 + NaClO_4 + HClO_4$	No
143	25	$MgCO_3$	15	$MgCO_3 + H_2O + CO_2 + NaClO_4 + HClO_4$	No
144	≈90	$MgCO_3$	3	$MgCO_3 + H_2O + CO_2$	Yes
78	25	$MgCO_3{\cdot}3H_2O$	3	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
	25	$MgCO_3{\cdot}3H_2O$	13	$MgCO_3{\cdot}3H_2O + H_2O + CO_2 + Na_2CO_3$	Yes
79	25–50	$MgCO_3{\cdot}3H_2O$	10	$MgCO_3{\cdot}3H_2O + H_2O + CO_2$	Yes
145	25–40	$MgCO_3{\cdot}3H_2O$	3	$MgCO_3{\cdot}3H_2O + H_2O$	Yes
	15–35	$MgCO_3{\cdot}3H_2O$	36	$MgCO_3{\cdot}3H_2O + H_2O + NaCl$	Yes
	15–35	$MgCO_3{\cdot}3H_2O$	33	$MgCO_3{\cdot}3H_2O + H_2O + NH_4Cl$	Yes
	15–35	$MgCO_3{\cdot}3H_2O$	36	$MgCO_3{\cdot}3H_2O + H_2O + MgCl_2$	Yes
	25	$MgCO_3{\cdot}3H_2O$	12	$MgCO_3{\cdot}3H_2O + H_2O + KCl$	Yes
146	25–35	$MgCO_3{\cdot}3H_2O$	24	$MgCO_3{\cdot}3H_2O + H_2O + NaCl + MgCl_2$	No
	25–35	$MgCO_3{\cdot}3H_2O$	24	$MgCO_3{\cdot}3H_2O + H_2O + MgCl_2 + NH_4Cl$	No
	25–35	$MgCO_3{\cdot}3H_2O$	24	$MgCO_3{\cdot}3H_2O + H_2O + LiCl$	Yes
	25–35	$MgCO_3{\cdot}3H_2O$	24	$MgCO_3{\cdot}3H_2O + H_2O + MgCl_2 + LiCl$	No

[a]Although the mineralogical variety used is not clearly specified by the authors, after examination of the solubility data it is assumed that the solid refers to magnesium carbonate trihydrate (evaluators).
[b]Authors state that the temperature refers to an "approximate" value.
[c]Some data of this reference refer to supersaturated concentrations of $KHCO_3$(aq) which may generate a second solid phase or a mixed solid phase made up by magnesium carbonate and potassium carbonate or hydrogen carbonate.
[d]Authors state that an amorphous natural magnesium carbonate was used.
[e]The single result is given in terms of pH-$p(CO_2)$ data, amounting to 7.11 at $p(CO_2) = 0.97$ atm.

($Mg(OH)_2$) phase transition occurs thermodynamically at CO_2 partial pressures on the order of 10^{-7} atm at room temperature and at increasing partial pressures with increasing temperature. Other studies with similar difficulties will be discussed in the evaluation. The data of Riesen[142] and Horn[143] refer to systems with two added electrolytes ($HClO_4$ and $NaClO_4$) and were not analyzed here. However, analysis by the compiler reveals issues with both studies. Most data of Dong *et al*.[146] refer to systems with two added electrolytes as well, and were not considered. Garrels *et al*.[147] state that, notwithstanding the use of very pure natural magnesite, no conclusive pH at equilibrium of the aqueous magnesium carbonate suspension was recorded, so this reference was neither compiled nor evaluated. Because in the study of Roques[148] analytical data were only displayed graphically and did not allow a proper quantification, we decided to reject the data for both the compilation and the evaluation.

3.1.2. Analytical methods used for dissolved magnesium determination

The solubility of magnesium carbonate in water was measured by various methods summarized here:

(a) in some references,[118,120,124,134] no clear analytical method was mentioned by the authors;
(b) sampling of a defined volume of the supernatant at equilibrium, followed by evaporation to dryness and weighing of the residue as $MgCO_3$ or as MgO after calcination;[119,127,132]
(c) titration of the alkalinity of the solution at equilibrium using a standardized HCl or H_2SO_4 solution,[121,123,126,128,130,136,137,141] or by titration with a standard $NaHSO_4$ solution;[129]
(d) after equilibration of the suspension, the excess of solid was determined by weighing and compared to the initial mass added;[122]
(e) soluble magnesium was precipitated as $MgNH_4PO_4$ or as $Mg_2P_2O_7$ and weighed,[125,128,131,133,135,137] using the first precipitate; in one case[131] it was redissolved in an acid and titrated with an alkaline solution;
(f) complexometric titration with EDTA;[78,79,137–140,142–145]
(g) pH measurement of the solution at equilibrium;[66]
(h) atomic absorption spectrometry;[144]
(i) total carbon determination as TOC.[145,146]

3.1.3. Magnesite

3.1.3.1. $MgCO_3 + H_2O + CO_2$. Nine references[118,122,124,129,134,136,137,141,144] reported primary data of the $MgCO_3 + H_2O + CO_2$ system. Two[122,141] of these have been rejected *a priori* in Sec. 3.1.1. The remaining seven[118,124,129,134,136,137,144] will be evaluated here. In total, there are only 16 data points, covering the temperature range 5–91 °C and the $p(CO_2)$ range 0.00029–6 atm. Hence, a critical evaluation can only be tentative at best.

Of the 16 data points, the point of Cameron and Briggs[124] should be considered with caution because the temperature was given as "approximate." The data point of Wells[129] should be considered with caution because the magnesite was described by the author as "amorphous." From the context, it seems that the material was not amorphous in a strict sense, but the crystals were too small to be visible to the naked eye. One other data point, by Bär,[134] requires caution because it refers to "precipitated $MgCO_3$" with a solubility almost ten times higher than a magnesite sample. One data point of Christ and Hostetler[144] did not show equilibrium, and is discarded *a priori*, leaving 15 data points. The data are shown in Table 15.

For a quick test of the reliability of the data, the value of $s/p^{1/3}(CO_2)$ (in mol kg^{-1} bar$^{-1/3}$) was plotted versus temperature. The result is shown in Fig. 1. A group of 10 data points (of which one is invisible due to overlap) shows $s/p^{1/3}(CO_2)$ values below 0.02 mol kg^{-1} bar$^{-1/3}$ and decreases with temperature, as expected. The other six data points are at much higher values and show no particular trend. These are considered outliers for the following reasons. Four of these are from Wagner,[118] a data set with irregular and unrealistically strong pressure dependence. These points can be discarded for that reason. One of the other points is the measurement of Bär[134] with precipitated $MgCO_3$, and is discarded as well. The remaining point is by Cameron and Briggs[124] and is very close to the outlier of Bär.[134] It is discarded for that reason. None of the discarded data points have sufficiently high solubility to be due to nesquehonite or lansfordite. The two data points of Wagner[118] at $s/p^{1/3}(CO_2) < 0.02$ mol kg^{-1} bar$^{-1/3}$ were discarded as well.

With only 7 data points remaining, the empirical equation for open systems (see Sec. 1.3.1), which has 6 adjustable parameters, cannot be reliably fitted. Hence, an evaluation with this equation was not attempted.

A thermodynamic model (see Sec. 1.3.2.1) was fitted to each data point using the solubility constant as the only fitting parameter. Two variants were used. Model 1 assumes the existence of a $MgHCO_3^+$ ion pair (no $Mg(HCO_3)_2$ Pitzer parameters); Model 2 assumes no such ion pair, but includes $Mg(HCO_3)_2$ Pitzer parameters. The result is shown as calculated solubility constant as a function of temperature in Fig. 2 (Model 1) and Fig. 3 (Model 2). An equation of the form of Eq. (85) is fitted to the solubility constant data. The coefficients D and E were kept equal to zero because of the small number of data points.

An unconstrained regression led to a predicted lg K_s of -7.9140 for Model 1 and a predicted lg K_s of -7.8243 for Model 2 at 25 °C. The predicted temperature derivative of lg K_s was -0.0020 K^{-1} for Model 1 and $+0.0051$ K^{-1} for Model 2. Based on thermodynamic data of Cox *et al*.[35] and Chase,[149] a Gibbs free energy of dissolution of 44.844 kJ mol^{-1} and an enthalpy of dissolution of -30.54 kJ mol^{-1} is calculated. These lead to a lg K_s of -7.86 and a temperature derivative of lg K_s of -0.0180 K^{-1}. The uncertainty of lg K_s based on the thermodynamic data is at least 0.2, whereas the uncertainty of its temperature derivative is only a few percent. It follows that the unconstrained regression leads to an accurate estimate of lg K_s, but not of its temperature derivative. For this reason, the regression was constrained to be

TABLE 15. Data collected for the evaluation of the solubility of magnesite in the system $MgCO_3 + H_2O + CO_2$

Ref.	$t/°C$	$p(CO_2)/atm$	Primary solubility data (authors)	Molality Mg(aq) $m/mol\ kg^{-1}$ (evaluators)	Considered by evaluators
			Mass ratio ($MgCO_3/H_2O$)		
118	5	1	1/761	0.0156	No
	5	2	1/744	0.0160	No
	5	3	1/134	0.0890	No
	5	4	1/110.7	0.1079	No
	5	5	1/110	0.1085	No
	5	6	1/76	0.1576	No
			Mass conc. $Mg^{2+}/g\ l^{-1}$		
124	22[c]	0.00029	0.182	0.00749	No
129	20	0.00029	0.018	0.00074	Yes
			Mass conc. $MgCO_3\ g\ l^{-1}$		
134	18	0.00031	0.08	0.00095	Yes
	18	0.00031	0.7	0.00830	No
			Amount conc. $MgCO_3/mmol\ l^{-1}$		
136	25	0.955	16.5	0.01657	Yes
	38.8	0.932	12.87	0.01298	Yes
			Molality $MgCO_3/mmol\ kg^{-1}$ solution		
137	25	0.987	16.5	0.01649	Yes
			Molality $MgCO_3/mmol\ kg^{-1}$		
144	90.3	0.312	1.98	0.00198	Yes
	91	0.0274	0.95	0.00095	Yes
	90.5	0.308	1.74	0.00174	No

[a]Approximate value.

consistent with an enthalpy of dissolution of -30.54 kJ mol^{-1} using an approach similar to the one outlined in Sec. 1.3.3.4. Based on Eqs. (85) and (87), assuming $D = 0$ and $E = 0$, the following equations are derived for the data analysis:

$$\lg K_s - \frac{H_1 \lg(T/K)}{RT_1} = A + B\left(\frac{1}{(T/K)} + \frac{\ln 10 \cdot \lg(T/K)}{(T_1/K)}\right), \tag{112}$$

$$C = \frac{H_1}{RT_1} + \frac{B \ln 10}{(T_1/K)}, \tag{113}$$

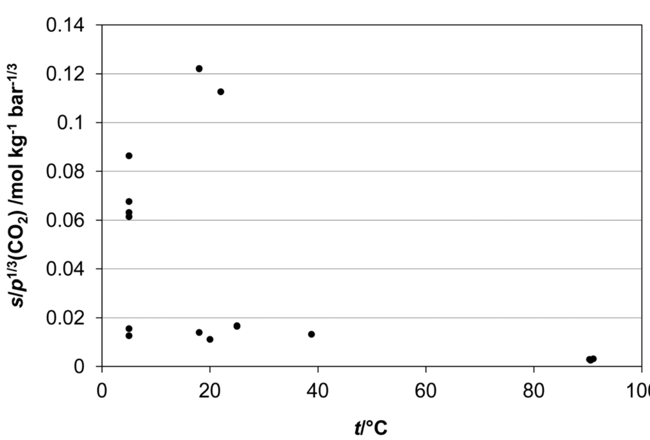

FIG. 1. Solubility of magnesite in $MgCO_3 + H_2O + CO_2$ systems divided by the cubic root of the equilibrium CO_2 partial pressure.

where A, B, and C are coefficients of Eq. (85); $H_1 = -30540$ J mol^{-1}, and $T_1 = 298.15$ K.

All seven data points corresponded well with the fitted equation after constrained regression, and were accepted in the evaluation. The result is as follows:

For Model 1: $A = 37.3217$; $B = -607.21$; $C = -17.39522$

For Model 2: $A = 50.4529$; $B = -1238.00$; $C = -21.88062$.

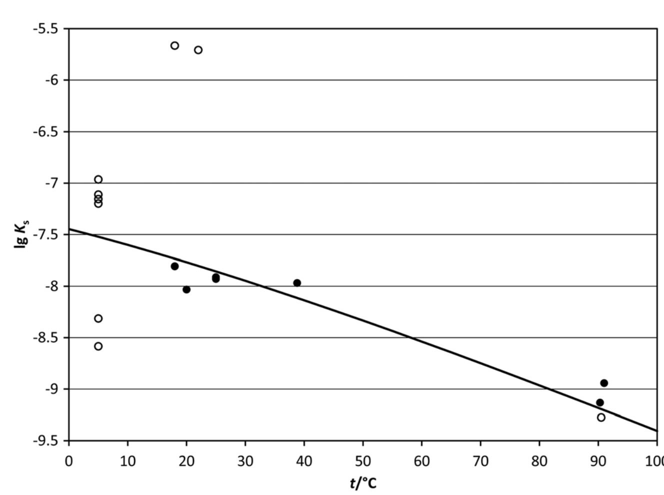

FIG. 2. Solubility constants of magnesite derived from solubility data in the system $MgCO_3 + H_2O + CO_2$ (solid symbols: accepted data; open symbols: rejected data) with Model 1 (with $MgHCO_3^+$ ion pair); predictions of Eq. (114) (line).

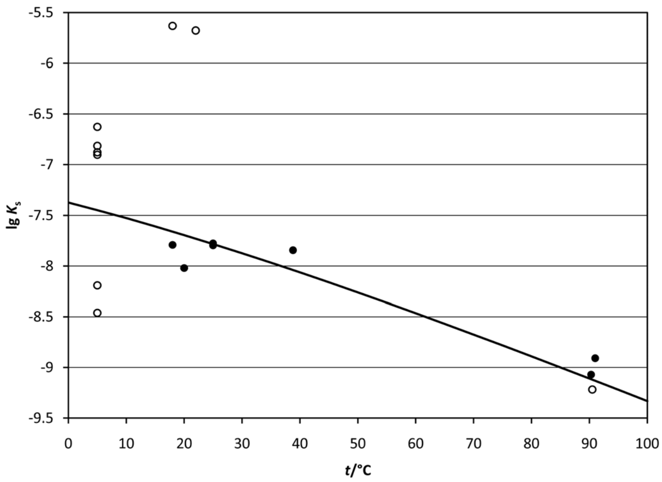

FIG. 3. Solubility constants of magnesite derived from solubility data in the system $MgCO_3 + H_2O + CO_2$ (solid symbols: accepted data; open symbols: rejected data) with Model 2 (without ion pair); predictions of Eq. (115) (line).

Bénézeth *et al.*[150] conducted electrochemical measurements of the solubility constant of magnesite. In the temperature range 0–70 °C, their K_s values are within 25% of the values of Model 1 reported here, and within 10% of Model 2. However, at higher temperature, our models seriously overestimate the solubility. It follows that the Δc_p° of solution is much more strongly negative than the above coefficients suggest.

Considering the good agreement between our calculated values of K_s and the measured values of Bénézeth *et al.*,[150] it seems reasonable to adopt the Δc_p° value found by Bénézeth *et al.*,[150] -387.97 J mol^{-1} K^{-1}, and force the lg K_s expression to be consistent with this value. Because $\Delta c_p^\circ = C/R$ in Eq. (85) when $D = E = 0$, this means setting C equal to -46.66201. From Eq. (113) it follows that B equals -4446.81, and A is the only remaining variable. A is simply the weighted average of lg $K_s - B/(T/\mathrm{K})$ $- C$ lg(T/K). A value of 122.5203 is obtained for Model 1 and a value of 122.5940 for Model 2. Hence, the following expressions are obtained:

For Model 1:

$$\lg K_s = 122.5203 - 4446.81/(T/\mathrm{K}) - 46.66201 \lg(T/\mathrm{K}) \tag{114}$$

For Model 2:

$$\lg K_s = 122.5940 - 4446.81/(T/\mathrm{K}) - 46.66201 \lg(T/\mathrm{K}) \tag{115}$$

The temperature dependence of K_s obtained with the equations and derived from the individual data points is shown in Fig. 2 for Model 1 and in Fig. 3 for Model 2.

At 25 °C, Eqs. (114) and (115) predict lg K_s of -7.8565 for Model 1 and lg K_s of -7.7828 for Model 2. Both values are consistent with thermodynamic data. The following thermodynamic data of dissolution at 25 °C are obtained from Eqs. (114) and (115): 44.84 kJ mol^{-1} (Model 1) and 44.42 kJ mol^{-1} (Model 2) for $\Delta_{sol}G^\circ$, and -252.84 J mol^{-1} K^{-1} (Model 1) and -251.43 J mol^{-1} K^{-1} (Model 2) for $\Delta_{sol}S^\circ$. As indicated above, a value of -30.54 kJ mol^{-1} was set for $\Delta_{sol}H^\circ$.

Equations (114) and (115) were used to make predictions of the solubility with Model 1 and Model 2. The result is shown in Table 16 for all data points. The difference between the model predictions is a subjective measure of the uncertainty of the actual solubility. The deviation between the models is highest at low temperature and at low CO_2 partial pressure, and lower at medium and high temperatures. However, due to the limited number of data points, these

TABLE 16. Evaluation of magnesite solubility in the system $MgCO_3 + H_2O + CO_2$. Model 1 = with $MgHCO_3^+$; Model 2 = no $MgHCO_3^+$

Ref.	t/°C	$p(CO_2)$/atm	Measured solubility/mol kg^{-1}	Fitted solubility (Model 1)/mol kg^{-1}	Deviation from Model 1 (%)	Fitted solubility (Model 2)/mol kg^{-1}	Deviation from Model 2 (%)	Accepted
118	5	1	0.0156	0.03518	−55.66	0.03138	−50.29	No
	5	2	0.0160	0.04848	−67.20	0.04193	−62.08	No
	5	3	0.0890	0.05863	50.94	0.04975	77.91	No
	5	4	0.1079	0.06714	59.51	0.05617	90.66	No
	5	5	0.1085	0.07459	44.52	0.06172	74.67	No
	5	6	0.1576	0.08094	92.73	0.06664	134.11	No
124	22[a]	0.00029	0.00749	0.00088	752.57	0.00092	709.75	No
129	20	0.00029	0.00074	0.00093	−20.14	0.00098	−24.11	Yes
134	18	0.00031	0.00095	0.00101	−5.99	0.00106	−10.58	Yes
	18	0.00031	0.00830	0.00101	721.34	0.00106	681.22	No
136	25	0.955	0.01657	0.01748	−5.63	0.01646	−0.27	Yes
	38.8	0.932	0.01298	0.01129	15.19	0.01088	19.48	Yes
137	25	0.987	0.01649	0.01773	−6.96	0.01667	−1.03	Yes
144	90.3	0.312	0.00198	0.00189	4.99	0.00191	3.76	Yes
	91	0.0274	0.00095	0.00076	24.56	0.00079	30.03	Yes
	90.5	0.308	0.00174	0.00187	−6.85	0.00189	−7.96	No

[a]Approximate value.

TABLE 17. Data collected for the evaluation of the solubility of $MgCO_3$ in the system $MgCO_3 + H_2O + CO_2 + NaCl$

Ref.	$t/°C$	$p(CO_2)$/ atm	Molality NaCl m_2/mol kg^{-1}	Solubility $MgCO_3$ m_1/mol kg^{-1}	Accepted
125	37.5	1[a]	0.120	0.2100	No
	37.5	1[a]	1.012	0.2161	No
	37.5	1[a]	2.182	0.2030	No
	37.5	1[a]	3.016	0.1837	No
	37.5	1[a]	4.205	0.1553	No
	37.5	1[a]	5.829	0.0816	No
129	20	0.00029	0.469	0.0012	Yes

[a]Equilibrated at room temperature.

remain tentative estimates of the actual solubility. The fit provided a slightly smaller sum of squares of the residuals for Model 1 (0.171 lg units squared) than for Model 2 (0.188 lg units squared). There is no significant quality difference between the fits.

3.1.3.2. $MgCO_3 + H_2O + CO_2 + NaCl$. The number of solubility data of this quaternary system is limited to seven: six from Cameron and Seidel[125] at 37.5 °C and a CO_2 partial pressure of 1 atm, and one from Wells[129] at 20 °C and atmospheric CO_2 partial pressure. The data are shown in Table 17. After an approximately constant magnesite solubility, a steady decrease with increasing concentration of NaCl(aq) was found in the data of Cameron and Seidel.[125] The solubility does not extrapolate to a realistic solubility at zero NaCl (see Sec. 3.1.3.1). Hence, this data set is not accepted for further analysis. The data point of Wells[129] was accepted because the solubility reported in this reference in the absence of NaCl (0.00074 mol kg^{-1}) was accepted, and because extrapolation to the solubility in the presence of 0.469 mol kg^{-1} NaCl using SIT (0.00138 mol kg^{-1}) corresponds well with the measured value (0.0012 mol kg^{-1}). The SIT procedure is outlined in Sec. 1.3.5. For the SIT extrapolation, an ion interaction parameter for $MgCl_2$ was obtained by fitting the SIT model to activity-coefficient data of Robinson and Stokes.[112] The value obtained was 0.184. The value for $NaHCO_3$, 0, was taken from Preis and Gamsjäger.[113] The

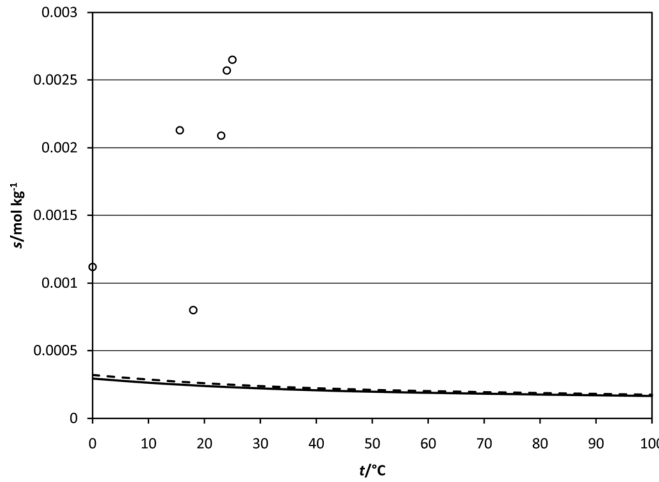

FIG. 4. Solubility of magnesite in the system $MgCO_3 + H_2O$ measured (open symbols: rejected data) and predicted with Model 1 (solid line) and Model 2 (dashed line).

value for $Mg(HCO_3)_2$, which influences the calculation to a much lesser extent, was assumed to be equal to zero.

3.1.3.3. $MgCO_3 + H_2O$. For this system, six references[123,125,128,134,135,140] are found in the primary literature. One of them[134] was rejected *a priori* in Sec. 3.1.1. Data of Morey[140] were also rejected due to transformations to calcium hydroxide found by the author. The analytical data of the four remaining references[123,125,128,134] are shown in Table 18. Comparing the data, it is clear that there is no consistency in the data. This is probably because, for all the references that present a detailed methodology,[123,125,128] the solution was stripped after adding $MgCO_3$, indicating that these are not pure $MgCO_3 + H_2O$ systems. As indicated in Sec. 3.1.1, there is a risk of brucite formation under these conditions.[79]

Thermodynamic models for this system (see Sec. 1.3.2.2) with solubility constants of Eqs. (114) and (115) were used to make predictions of the solubility consistent with the data for systems open to CO_2 (Sec. 3.1.3.1). Again, Model 1 assumes $MgHCO_3^+$ ion pairing; Model 2 assumes no such ion pairing; the interaction is calculated with Pitzer parameters instead. The result is shown in Fig. 4 and in Table 19.

TABLE 18. Data collected for the evaluation of the solubility of magnesite in the system $MgCO_3 + H_2O$

Ref.	$t/°C$	Primary solubility data (authors)	Molality Mg(aq) m/mol kg^{-1} (evaluators)	Considered by evaluators
		Mass conc. Mg/mg per 100 ml		
123	15.6	51.8	0.00213	Yes
		Mass conc. $MgCO_3$/g l^{-1}		
125	23	0.176	0.00209	Yes
	24	0.216	0.00257	Yes
	25	0.223	0.00265	Yes
		Mass conc. $MgCO_3$/mg l^{-1}		
128	0	94.3	0.00112	Yes
		Mass conc. $MgCO_3$/g l^{-1}		
134	18	0.067	0.00080	Yes

TABLE 19. Comparison of magnesite solubility in the system $MgCO_3 + H_2O$ with model predictions

Ref.	$t/°C$	Measured solubility/mol kg^{-1}	Solubility Model 1/mol kg^{-1}	Deviation from Model 1 (%)	Solubility Model 2/mol kg^{-1}	Deviation from Model 2 (%)	Accepted
123	15.6	0.00213	0.000248	758.85	0.000269	691.01	No
125	23	0.00209	0.000232	800.20	0.000251	731.85	No
	24	0.00257	0.000230	1016.12	0.000249	931.83	No
	25	0.00265	0.000228	1060.22	0.000247	973.08	No
128	0	0.00112	0.000292	283.06	0.000320	250.39	No
134	18	0.00080	0.000243	229.86	0.000263	204.13	No

All experimental points are far above the model predictions, indicating that none of these systems were entirely free of external CO_2. Apparently, brucite formation was not an issue in these experiments. In fact, Cameron and Seidel[125] indicated specifically that they opened the stopper of the flask periodically after boiling to expel CO_2. This may have introduced external CO_2 back into the system. Stripping CO_2 out of a solution is less effective after adding magnesite because of its alkaline nature, trapping the CO_2 as bicarbonate. Hence, none of the experimental data are acceptable.

The data of Morey[140] are below the predicted values in Fig. 4, confirming that the results were influenced by a less soluble phase.

3.1.3.4. $MgCO_3 + H_2O +$ salt. Five references[125,128,135,142,143] contain analytical data for these systems. The analytical data of Leick[135] were omitted because the author states that a possible conversion from magnesium carbonate towards hydroxide might have occurred during boiling, which probably results from the metastability of the former in the absence of an external CO_2 supply. Based on similar reflections, the analytical data of two of the remaining references[125,128] are treated with suspicion.

Two references[125,128] contain analytical data for the system $MgCO_3 + H_2O + NaCl$. The concentrations of NaCl added vary considerably in the two data sets. The data are shown in Table 20. Both sources have rejected data on the $MgCO_3 + H_2O$ system, and neither has solubility data that extrapolates to a realistic solubility at zero NaCl concentration. For these reasons, none of the data are accepted.

Two references[125,128] contain analytical data for the system $MgCO_3 + H_2O + Na_2SO_4$. The data are shown in Table 21. The data are rejected for the same reasons as discussed for the previous system.

Two references[125,128] contain analytical data for the system $MgCO_3 + H_2O + Na_2CO_3$. The data are shown in Table 22. In spite of the common ion, the data of Cameron and Seidel[125] show a pronounced increase of the solubility with increasing Na_2CO_3 concentrations, which may be due to $Mg(CO_3)_2^{2-}$ ion pair formation.[78] The data of Gothe[128] show a more expected trend, but still extrapolate to too high a concentration at zero Na_2CO_3 concentration. The data are rejected for the same reasons as discussed for the previous systems.

One reference[128] contains analytical data for the system $MgCO_3 + H_2O + NaNO_3$. The data are shown in Table 23.

TABLE 20. Data collected for the evaluation of the solubility of $MgCO_3$ in the system $MgCO_3 + H_2O + NaCl$

Ref.	$t/°C$	Molality NaCl m_2/mol kg^{-1}	Solubility $MgCO_3$ m_1/mol kg^{-1}	Accepted
125	23	0.485	0.00502	No
	23	1.038	0.00637	No
	23	1.888	0.00720	No
	23	2.664	0.00682	No
	23	4.341	0.00599	No
	23	5.207	0.00520	No
	23	6.536	0.00401	No
128	0[a]	0.0100	0.00152	No
	0[a]	0.0200	0.00159	No
	0[a]	0.0502	0.00143	No

[a]Approximate, according to the authors.

TABLE 21. Data collected for the evaluation of the solubility of $MgCO_3$ in the system $MgCO_3 + H_2O + Na_2SO_4$

Ref.	$t/°C$	Molality Na_2SO_4 m_2/mol kg^{-1}	Solubility $MgCO_3$ m_1/mol kg^{-1}	Accepted
125	24	0.178	0.00698	No
	24	0.389	0.00990	No
	24	0.684	0.01229	No
	24	1.165	0.01501	No
	24	1.401	0.01575	No
	24	1.887	0.01670	No
	24	2.077	0.01681	No
	24	2.296	0.01760	No
	35.5	0.002	0.00156	No
	35.5	0.297	0.00691	No
	35.5	0.585	0.00907	No
	35.5	0.840	0.01097	No
	35.5	1.077	0.01175	No
	35.5	1.364	0.01288	No
	35.5	1.652	0.01352	No
	35.5	1.836	0.01376	No
	35.5	2.250	0.01432	No
128	0[a]	0.0025	0.00172	No
	0[a]	0.0050	0.00192	No
	0[a]	0.0125	0.00179	No

[a]Approximate, according to the authors.

TABLE 22. Data collected for the evaluation of the solubility of $MgCO_3$ in the system $MgCO_3 + H_2O + Na_2CO_3$

Ref.	$t/°C$	Molality Na_2CO_3 $m_2/mol\ kg^{-1}$	Solubility $MgCO_3$ $m_1/mol\ kg^{-1}$	Accepted
125	25	0.219	0.00343	No
	25	0.481	0.00607	No
	25	0.819	0.01069	No
	25	1.213	0.01574	No
	25	1.540	0.01969	No
	25	1.747	0.02381	No
	25	2.066	0.02822	No
128	0[a]	0.0050	0.00117	No
	0[a]	0.0100	0.000634	No
	0[a]	0.0250	0.000186	No

[a]Approximate, according to the authors.

The data are rejected for the same reasons as discussed for the previous systems.

One reference[128] contains analytical data for the system $MgCO_3 + H_2O + MgCl_2$. The data are shown in Table 24. The data are rejected for the same reasons as discussed for the previous systems.

3.1.4. Nesquehonite

3.1.4.1. $MgCO_3{\cdot}3H_2O + H_2O + CO_2$. In the compiled literature, 16 references[66,78,79,119–122,126,129–134,137,139] report the aqueous solubility of magnesium carbonate trihydrate, $MgCO_3{\cdot}3H_2O$, in the presence of an external and constant CO_2 supply. Of these, two references[122,126] were rejected *a priori* (see Sec. 3.1.1), and one reference[66] only reported a pH value, leaving 13 references for consideration, with 112 data points. The data are shown in Table 25.

From the seven data points published by Beckurts,[119] only the six obtained at a well-defined CO_2 partial pressure were considered, thus rejecting *a priori* the one referring to an unknown partial pressure. Although not clearly specified by Engel and Ville,[120] we assume after examination that the solubility data refer to magnesium carbonate trihydrate and not to anhydrous magnesium carbonate. All data are retained except the point at 100 °C, which was conducted in boiling water. The data of Engel[121] were retained, except the point at zero CO_2 partial pressure. The data of Haehnel[132] show a marked break in the solubility increase with increasing $p(CO_2)$ at 16–18 atm. This increase was attributed to the precipitation of $Mg(HCO_3)_2$. Indeed, upon decompression, physical change of the precipitate was observed. By working at subzero temperatures, the solid $Mg(HCO_3)_2$ could be isolated. Hence, the data points at $p(CO_2) > 16$ atm need to be discarded. This includes the experiments at constant pressure and varying temperature. Hence, of the 112 data points, 98 are retained.

TABLE 23. Data collected for the evaluation of the solubility of $MgCO_3$ in the system $MgCO_3 + H_2O + NaNO_3$

Ref.	$t/°C$	Molality $NaNO_3$ $m_2/mol\ kg^{-1}$	Solubility $MgCO_3$ $m_1/mol\ kg^{-1}$	Accepted
128	0[a]	0.0100	0.00146	No
	0[a]	0.0200	0.00165	No
	0[a]	0.0501	0.00163	No

[a]Approximate, according to the authors.

TABLE 24. Data collected for the evaluation of the solubility of $MgCO_3$ in the system $MgCO_3 + H_2O + MgCl_2$

Ref.	$t/°C$	Molality $MgCl_2$ $m_2/mol\ kg^{-1}$	Solubility $MgCO_3$ $m_1/mol\ kg^{-1}$	Accepted
128	0[a]	0.0025	0.000557	No
	0[a]	0.0050	0.000468	No
	0[a]	0.0125	0.000419	No

[a]Approximate, according to the authors.

For a quick test of the reliability of the data, the value of $s/p^{1/3}(CO_2)$ (in mol kg^{-1} bar$^{-1/3}$) was plotted versus temperature. The result is shown in Fig. 5. The scatter of the data is considerable. Data sets that deviate substantially from other studies are Beckurts,[119] who found low solubilities, Engel,[120] who found high solubilities with a curvature markedly different than other data sets, Kline,[130] who found divergent CO_2 partial pressure dependence of nesquehonite solubility, Haehnel,[132] who found high solubilities with too strong CO_2 partial pressure dependence, and Bär,[134] whose data essentially agreed with Haehnel's. Königsberger[78] found low solubilities compared to the trend of the empirical model. Without these data sets, the 54 remaining data points fit the empirical regression Eq. (18) well, with a standard deviation of 0.013 in lg scale. The coefficients of Eq. (18) are as follows:

$a = 9.712\,7$
$b = 0.347\,56$
$c = 0.111\,80$
$d = -0.000\,379\,32$
$e = 390.12$
$f = -4.717\,0.$

Coefficient b corresponds well with the expected value (1/3). The predicted solubilities of Eq. (18) are shown in Table 25.

The thermodynamic model variants were fitted to the experimental data to derive solubility constants. Data that were rejected above also corresponded poorly with the other data when solubility constants were compared. Additionally, the data of Mitchell[131] were rejected due to poor correspondence with other data (0.25–0.5 lg units difference in K_s). Now the data of Haehnel[132] below 18 atm are within the range of other data, although there is still a pronounced CO_2 partial pressure dependence of the calculated solubility constant. Likewise, the data of Königsberger[78] correspond well with the other data. The data of these sources are included in the thermodynamic model fits. This leads to 57 accepted data points, the solubilities included in the thermodynamic model fits.

TABLE 25. Data collected for the evaluation of the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2$, and fit with empirical model

Ref.	$t/°C$	$p(CO_2)/atm$	Original data (authors)	Molality Mg(aq)/mol kg^{-1} (evaluators)	Considered	Used in model fit	Molality Mg^{2+}/mol kg^{-1} (fitted)	Deviation (%)
			Mass ratio ($MgCO_3{\cdot}3H_2O/H_2O$)					
119	20	Unknown	1/72.4	0.0999	No	—	—	
	20	2	1/30.5	0.2374	Yes	No	0.3267	−27.33
	20	3	1/26	0.2786	Yes	No	0.3766	−26.03
	20	4	1/21.1	0.3435	Yes	No	0.4168	−17.59
	10	5	1/17.09	0.4243	Yes	No	0.6188	−31.43
	15	5	1/18.60	0.3898	Yes	No	0.5275	−26.10
	40	5	1/44.64	0.1621	Yes	No	0.2487	−34.81
			Mass conc. $MgCO_3$ ρ/g l^{-1}					
120	19.5	0.978	25.79	0.3097	Yes	No	0.2579	20.08
	19.5	2.08	33.11	0.3992	Yes	No	0.3359	18.83
	19.7	3.18	37.3	0.4509	Yes	No	0.3878	16.26
	19.0	4.68	43.5	0.5278	Yes	No	0.4544	16.16
	19.2	5.58	46.2	0.5617	Yes	No	0.481	16.79
	19.2	6.18	48.51	0.5906	Yes	No	0.499	18.36
	19.5	7.48	51.2	0.6248	Yes	No	0.5294	18.03
	18.7	8.98	56.59	0.6928	Yes	No	0.5815	19.14
	13.4	0.973	28.45	0.3414	Yes	No	0.3051	11.88
	19.5	0.982	25.79	0.3097	Yes	No	0.2582	19.93
	29.3	0.962	21.945	0.2638	Yes	No	0.1971	33.83
	46.0	0.906	15.7	0.1893	Yes	No	0.1266	49.57
	62.0	0.789	10.35	0.1254	Yes	No	0.083	51.02
	70.0	0.699	8.1	0.0984	Yes	No	0.0668	47.36
	82.0	0.499	4.9	0.0599	Yes	No	0.0464	29.09
	90.0	0.314	2.4	0.0295	Yes	No	0.0339	−12.93
	100	0	0.0	0.0000	No	—		
			Mass conc. $MgCO_3$ ρ/g l^{-1}					
121	12	0[a]	0.970	0.0115	No	—		
	12	0.486	20.5	0.2451	Yes	Yes	0.2484	−1.33
	12	0.986	26.5	0.3177	Yes	Yes	0.319	−0.41
	12	1.486	31.0	0.3725	Yes	Yes	0.3694	0.83
	12	1.986	34.2	0.4117	Yes	Yes	0.4104	0.33
	12	2.486	36.4	0.4388	Yes	Yes	0.4456	−1.52
	12	2.986	39.0	0.4708	Yes	Yes	0.4769	−1.27
	12	3.486	42.8	0.5180	Yes	Yes	0.5054	2.50
	12	5.986	50.6	0.6155	Yes	Yes	0.6229	−1.19
	3.5	0.992	35.6	0.4272	Yes	Yes	0.4093	4.38
	18	0.980	22.1	0.2649	Yes	Yes	0.269	−1.52
	22	0.974	20.0	0.2398	Yes	Yes	0.2405	−0.31
	30	0.958	15.8	0.1895	Yes	Yes	0.1932	−1.93
	40	0.927	11.8	0.1418	Yes	Yes	0.1479	−4.15
	50	0.878	9.5	0.1145	Yes	Yes	0.1137	0.67
			Mass conc. Mg^{2+} ρ/g l^{-1}					
129	20	0.00029	0.39	0.0158	Yes	Yes	0.0151	4.70
	20	0.00029	0.34	0.0142	Yes	Yes	0.0151	−5.91
130	25	0.9684		0.2135	Yes	No	0.2214	−3.57
	25	0.1116		0.06266	Yes	No	0.1048	−40.18
	25	0.0432		0.04601	Yes	No	0.0753	−38.93
	25	0.0150		0.03127	Yes	No	0.0522	−40.05
	25	0.0069		0.02507	Yes	No	0.0398	−37.05
	25	0.00334		0.02210	Yes	No	0.0309	−28.59
	25	0.00160		0.01859	Yes	No	0.024	−22.43
	25	0.00093		0.01624	Yes	No	0.0198	−18.17
	25	0.000887		0.01593	Yes	No	0.0195	−18.40
	25	0.000845		0.01566	Yes	No	0.0192	−18.42
	25	0.000680		0.01512	Yes	No	0.0178	−15.05
	25	0.000510		0.01437	Yes	No	0.0161	−10.78

TABLE 25. Data collected for the evaluation of the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2$, and fit with empirical model—Continued

Ref.	$t/°C$	$p(CO_2)/atm$	Original data (authors)	Molality Mg(aq)/mol kg^{-1} (evaluators)	Considered	Used in model fit	Molality Mg^{2+}/mol kg^{-1} (fitted)	Deviation (%)
			Amount conc. Mg^{2+} c/mol l^{-1}					
131	25	6	0.376	0.3839	Yes	Yes	0.411	−6.60
	25	9	0.450	0.4617	Yes	Yes	0.469	−1.55
	25	11	0.485	0.4990	Yes	Yes	0.4998	−0.16
	25	13	0.505	0.5207	Yes	Yes	0.5265	−1.10
	25	16	0.530	0.5482	Yes	Yes	0.5607	−2.24
	25	21	0.613	0.6378	Yes	Yes	0.6071	5.06
			Mass% $MgCO_3$ 100 w					
132	18	2	3.50	0.4433	Yes	No	0.3458	28.20
	18	2.5	3.74	0.4762	Yes	No	0.3743	27.23
	18	4	4.28	0.5516	Yes	No	0.4428	24.58
	18	10	5.90	0.7898	Yes	No	0.6205	27.28
	18	16	7.05	0.9708	Yes	No	0.7446	30.37
	18	18	7.49	1.0421	No	—	—	—
	18	35	7.49	1.0578	No	—	—	—
	18	56	7.49	1.0720	No	—	—	—
	0.0	34	8.58	1.2584	No	—	—	—
	5.0	34	8.32	1.2068	No	—	—	—
	10.0	34	7.93	1.1360	No	—	—	—
	18.0	34	7.49	1.0570	No	—	—	—
	30.0	34	6.88	0.9527	No	—	—	—
	40.0	34	6.44	0.8805	No	—	—	—
	50.0	34	6.18	0.8381	No	—	—	—
	60.0	34	5.56	0.7435	No	—	—	—
			Mass% MgO 100 w					
132	5	1	1.530	0.4029	Yes	Yes	0.3927	2.61
	10	1	1.314	0.3431	Yes	Yes	0.3395	1.06
	15	1	1.143	0.2964	Yes	Yes	0.2945	0.63
	20	1	0.9858	0.2541	Yes	Yes	0.2564	−0.89
	25	1	0.8654	0.2220	Yes	Yes	0.2239	−0.84
	30	1	0.7634	0.1950	Yes	Yes	0.1961	−0.55
	35	1	0.6780	0.1727	Yes	Yes	0.1722	0.27
	40	1	0.6017	0.1528	Yes	Yes	0.1517	0.72
	45	1	0.5323	0.1348	Yes	Yes	0.134	0.61
	50	1	0.4718	0.1192	Yes	Yes	0.1186	0.48
	55	1	0.4083	0.1029	Yes	Yes	0.1053	−2.28
	60	1	0.3648	0.0918	Yes	Yes	0.0937	−2.02
			Mass conc. $MgCO_3$ ρ/g l^{-1}					
134	18	1	27.8	0.3340	Yes	No	0.2709	23.29
	18	2	35.1	0.4233	Yes	No	0.3458	22.41
137	25	1		0.2146	Yes	Yes	0.2239	−4.14
139	0	1		0.4234	Yes	Yes	0.4558	−7.11
	5	1		0.4041	Yes	Yes	0.3927	2.92
	8	1		0.3787	Yes	Yes	0.3597	5.29
	20	1		0.2535	Yes	Yes	0.2564	−1.12
	25	1		0.2269	Yes	Yes	0.2239	1.35
	40	1		0.1528	Yes	Yes	0.1517	0.72
	45	1		0.1325	Yes	Yes	0.134	−1.11
	50	1		0.1151	Yes	Yes	0.1186	−2.98
	53.5	1		0.1062	Yes	Yes	0.1091	−2.67
			Molality $MgCO_3$ m/mmol kg^{-1}					
78	25	0.0088	31	0.031	Yes	No	0.0433	−28.47
	25	0.047	58	0.058	Yes	No	0.0776	−25.23
	25	0.108	76	0.076	Yes	No	0.1036	−26.62

TABLE 25. Data collected for the evaluation of the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2$, and fit with empirical model—Continued

Ref.	t/°C	$p(CO_2)$/atm	Original data (authors)	Molality Mg(aq)/mol kg^{-1} (evaluators)	Considered	Used in model fit	Molality Mg^{2+}/mol kg^{-1} (fitted)	Deviation (%)
			Molality $MgCO_3$ m/mol kg^{-1}					
79	25	0.968	0.2199	0.2199	Yes	Yes	0.2214	−0.67
	28	0.962	0.2074	0.2074	Yes	Yes	0.204	1.69
	31	0.955	0.1922	0.1922	Yes	Yes	0.1881	2.21
	33	0.950	0.1810	0.1810	Yes	Yes	0.1782	1.56
	35	0.944	0.1692	0.1692	Yes	Yes	0.1689	0.16
	38	0.934	0.1595	0.1595	Yes	Yes	0.156	2.27
	41	0.922	0.1509	0.1509	Yes	Yes	0.144	4.77
	44	0.909	0.1382	0.1382	Yes	Yes	0.1331	3.84
	47	0.894	0.1265	0.1265	Yes	Yes	0.123	2.85
	50	0.877	0.1196	0.1196	Yes	Yes	0.1137	5.19

[a]Ambiguous.

An equation of the form of Eq. (85) is fitted to the solubility constant data. Using coefficients D and E did not improve the fit between the equation and the data. Hence, they were set equal to 0. The unweighted regression led to a predicted standard Gibbs free energy of dissolution of 32.13 kJ mol^{-1} (Model 1) or 30.06 kJ mol^{-1} (Model 2). Based on the entropy of nesquehonite of 195.627 J mol^{-1} K^{-1} at 25 °C measured calorimetrically by Robie and Hemingway,[151] and the standard entropies reported by Cox *et al.*,[35] a standard entropy of solution of -172.777 J mol^{-1} K^{-1} is obtained. Combining with the standard Gibbs free energies above, a standard enthalpy of solution of -19.39 kJ mol^{-1} (Model 1) or -21.45 kJ mol^{-1} (Model 2) is obtained, which leads to a temperature derivative of lg K_s of -0.0114 (Model 1) or -0.0126 (Model 2). The slopes actually observed were -0.0062 (Model 1) or -0.0088 (Model 2), which are somewhat too low. It was observed that the slope of lg K_s was diminished by the high-pressure data of Engel,[121] which may be due to an inaccurate description of the Mg–HCO_3 ion interactions in the models. For that reason, the experiments of Engel[121] at CO_2 partial pressures above 1 atm were weighted inversely proportional to the pressure in atmospheres. The experiment of Yanat'eva and Rassonskaya[139] at 0 °C unrealistically led to a lg K_s value below the value at 5 °C. For this reason, the data point at 0 °C was given a weight of 0.5. All other accepted data points were given a weight of 1. The new slopes of lg K_s resulting from the weighted regressions are -0.0074 and -0.0098 for Model 1 and Model 2, respectively. The fit is improved but still substantially below the expected values. For that reason, the regressions were forced to be consistent with a given entropy of solution at 25 °C. The approach is similar to the one outlined in Sec. 1.3.3.4. Assuming coefficients E and F in Eq. (85) to be zero, the regression equation is

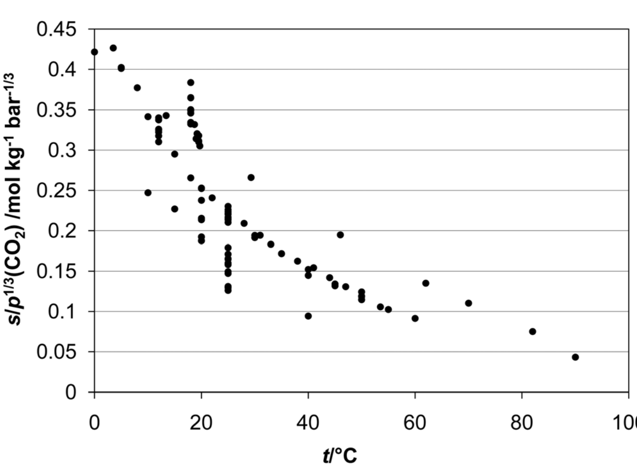

FIG. 5. Solubility of nesquehonite in $MgCO_3{\cdot}3H_2O + H_2O + CO_2$ systems divided by the cubic root of the equilibrium CO_2 partial pressure.

$$\lg K_s - \frac{S_1 \lg T}{R(1+\ln(T_1/\mathrm{K}))} = A\left(1 - \frac{\ln 10}{1+\ln(T_1/\mathrm{K})}\lg T\right) + \frac{B}{(T/\mathrm{K})}, \quad (116)$$

where $T_1 = 298.15$ K, and S_1 is the entropy of solution at T_1. Coefficient C in Eq. (85) is then calculated as

$$C = \frac{S_1 - RA\ln 10}{R(1+\ln T_1)}. \quad (117)$$

A constrained regression with $S_1 = -172.777$ J mol^{-1} K^{-1} led to a marked deterioration of the fit. Considering that the uncertainty of the standard entropy of Mg^{2+}(aq) is 4 J mol^{-1} K^{-1}, and the uncertainty of the standard entropy of CO_3^{2-}(aq) is 1 J mol^{-1} K^{-1}, S_1 was increased to -167.777 J mol^{-1} K^{-1}. The results of the constrained weighted regressions were as follows:

For Model 1 (with $MgHCO_3^+$ ion pair):

$$\lg K_s = 77.6714 - 2913.02/(T/\mathrm{K}) - 29.71573\lg(T/\mathrm{K}). \quad (118)$$

For Model 2 (without $MgHCO_3^+$ ion pair):

$$\lg K_s = -18.2455 + 1464.72/(T/\mathrm{K}) + 3.25981 \lg(T/\mathrm{K}). \quad (119)$$

At 25 °C, these equations predict lg K_s of −5.6286 for Model 1 and lg K_s of −5.2667 for Model 2. Figure 6 shows the solubility constants obtained with Model 1, together with Eq. (118); Fig. 7 shows the solubility constants obtained with Model 2, together with Eq. (119).

Thermodynamic data at 25 °C obtained with the two equations above are 32.13 J mol^{-1} (Model 1) and 30.06 J mol^{-1} (Model 2) for the standard Gibbs free energy of dissolution, and −17.89 J mol^{-1} (Model 1) and −19.96 J mol^{-1} (Model 2) for the standard enthalpy of dissolution. As indicated above, the standard entropy of dissolution was taken to be −167.777 J mol^{-1} K^{-1}.

Based on Eqs. (118) and (119), predicted solubilities were calculated for all data points. The results are shown in Table 26. At pressures near atmospheric, the models agree well, with decreasing agreement towards higher temperatures. At pressure extremes, much less agreement between the models was obtained. The experimental solubilities tend to agree better with Model 2 (no $MgHCO_3^+$) (sum of squares of the residuals 0.112 lg units squared) than with Model 1 (sum of squares of the residuals 0.617 lg units squared). As the same observation was made with lansfordite, it is concluded that $MgHCO_3^+$ is not stable at the high ionic strengths associated with these experiments. Model 1 is not recommended as a description of aquatic systems in equilibrium with either of these minerals. A model variant with Pitzer parameters for the interaction between $MgHCO_3^+$ and other ions, or with an ionic strength dependence of $K_{MgHCO_3^+}$, may not have these weaknesses. However, the development of such models is beyond the scope of this study. Here as well as in the lansfordite case (below), it appears that the CO_2 partial pressure dependence of the measured solubility is systematically less strong than the dependence predicted by the models. We tested if this could be explained by the $Mg(CO_3)_2^{2-}$ ion pair, using the stability constant of Königsberger,[78] but this species takes up less than 1% of the dissolved magnesium. Hence, it is concluded that $Mg(CO_3)_2^{2-}$ does not affect solubility in the absence of added carbonates, and this species was not taken into further consideration. Alternatively, the Pitzer parameters of $Mg(HCO_3)_2$ may not be accurate at the high concentrations encountered here. It follows that some data rejected in this evaluation may actually be valid.

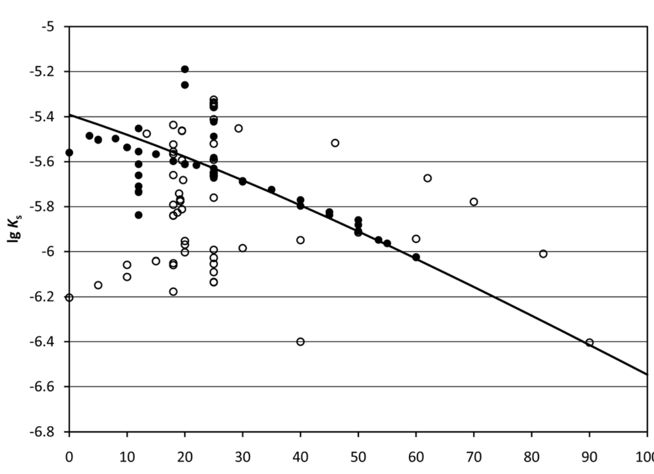

FIG. 6. Solubility constants of nesquehonite derived from solubility data in the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2$ (solid symbols: accepted data; open symbols: rejected data) with Model 1 (with $MgHCO_3^+$ ion pair); predictions of Eq. (118) (line).

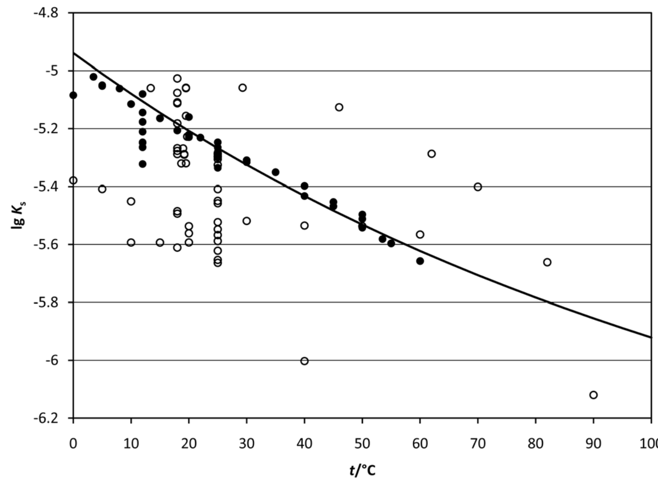

FIG. 7. Solubility constants of nesquehonite derived from solubility data in the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2$ (solid symbols: accepted data; open symbols: rejected data) with Model 2 (without $MgHCO_3^+$ ion pair); predictions of Eq. (119) (line).

3.1.4.2. $MgCO_3{\cdot}3H_2O + H_2O + CO_2 +$ salt. There are three references[78,122,126] reporting data on the solubility of nesquehonite in the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2$ + salt. Two references[122,126] have been rejected *a priori*, Ref. 122 because the CO_2 partial pressure was marked as "unknown," and Ref. 126 because the system was a closed system with a gas phase of unknown volume, leading to an undefined system. The only remaining study[78] reported 13 data on the solubility of nesquehonite in the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2 + Na_2CO_3$. The data are summarized in Table 27.

The data show increasing nesquehonite solubility at high Na_2CO_3 concentrations, which was attributed to the formation of a $Mg(CO_3)_2^{2-}$ ion pair. Based on the accuracy of the solubility data in the $MgCO_3{\cdot}3H_2O + H_2O + CO_2$ system obtained in the same study, it is likely that the data in Table 27 are accurate, but as there is no way of testing this accuracy with independent information, it would be premature to accept these data.

3.1.4.3. $MgCO_3{\cdot}3H_2O + H_2O$. Only three data sets[119,121,145] are available for the solubility of nesquehonite in the system $MgCO_3{\cdot}3H_2O + H_2O$, two of which date back to the 19th century. They are summarized in Table 28. Model

TABLE 26. Evaluation of nesquehonite solubility in the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2$. Model 1 = with $MgHCO_3^+$; Model 2 = no $MgHCO_3^+$

Ref.	t/°C	$p(CO_2)$/atm	Measured solubility/mol kg^{-1}	Fitted solubility (Model 1)/mol kg^{-1}	Deviation from Model 1 (%)	Fitted solubility (Model 2)/mol kg^{-1}	Deviation from Model 2 (%)	Accepted
119	20	2	0.2374	0.3938	−39.72	0.3631	−34.62	No
119	20	3	0.2786	0.5013	−44.43	0.4461	−37.55	No
119	20	4	0.3435	0.5963	−42.39	0.5175	−33.66	No
119	10	5	0.4243	0.9810	−56.75	0.7698	−44.88	No
119	15	5	0.3898	0.8142	−52.12	0.6716	−41.96	No
119	40	5	0.1621	0.3651	−55.60	0.3247	−50.08	No
120	19.5	0.978	0.3097	0.2657	16.56	0.2590	19.56	No
120	19.5	2.08	0.3992	0.4096	−2.54	0.3762	6.12	No
120	19.7	3.18	0.4509	0.5244	−14.02	0.4639	−2.81	No
120	19	4.68	0.5278	0.6790	−22.27	0.5785	−8.76	No
120	19.2	5.58	0.5617	0.7514	−25.25	0.6301	−10.86	No
120	19.2	6.18	0.5906	0.8004	−26.21	0.6645	−11.12	No
120	19.5	7.48	0.6248	0.8939	−30.10	0.7291	−14.31	No
120	18.7	8.98	0.6928	1.0315	−32.84	0.8188	−15.39	No
120	13.4	0.973	0.3414	0.3234	5.55	0.3149	8.41	No
120	19.5	0.982	0.3097	0.2663	16.29	0.2595	19.33	No
120	29.3	0.962	0.2638	0.1952	35.13	0.1916	37.69	No
120	46	0.906	0.1893	0.1205	57.10	0.1219	55.35	No
120	62	0.789	0.1254	0.0771	62.65	0.0831	50.92	No
120	70	0.699	0.0984	0.0615	60.12	0.0691	42.35	No
120	82	0.499	0.0599	0.0413	45.01	0.0510	17.43	No
120	90	0.314	0.0295	0.0288	2.26	0.0390	−24.27	No
121	12	0.486	0.2451	0.2297	6.72	0.2370	3.44	Yes
121	12	0.986	0.3177	0.3418	−7.04	0.3319	−4.28	Yes
121	12	1.486	0.3725	0.4335	−14.08	0.4047	−7.95	Yes
121	12	1.986	0.4117	0.5157	−20.16	0.4660	−11.65	Yes
121	12	2.486	0.4388	0.5903	−25.66	0.5200	−15.61	Yes
121	12	2.986	0.4708	0.6599	−28.65	0.5686	−17.19	Yes
121	12	3.486	0.518	0.7257	−28.62	0.6130	−15.50	Yes
121	12	5.986	0.6155	1.0199	−39.65	0.7952	−22.60	Yes
121	3.5	0.992	0.4272	0.4645	−8.04	0.4411	−3.16	Yes
121	18	0.98	0.2649	0.2791	−5.08	0.2719	−2.58	Yes
121	22	0.974	0.2398	0.2451	−2.15	0.2392	0.27	Yes
121	30	0.958	0.1895	0.1909	−0.72	0.1875	1.08	Yes
121	40	0.927	0.1418	0.1423	−0.37	0.1419	−0.04	Yes
121	50	0.878	0.1145	0.1074	6.61	0.1101	4.03	Yes
129	20	0.00029	0.0158	0.0090	75.47	0.0147	7.66	Yes
129	20	0.00029	0.0142	0.0090	57.70	0.0147	−3.24	Yes
130	25	0.9684	0.2135	0.2229	−4.20	0.2178	−1.97	No
130	25	0.1116	0.06266	0.0730	−14.11	0.0832	−24.65	No
130	25	0.0432	0.04601	0.0471	−2.29	0.0570	−19.27	No
130	25	0.015	0.03127	0.0299	4.56	0.0386	−19.00	No
130	25	0.0069	0.02507	0.0220	14.03	0.0297	−15.69	No
130	25	0.00334	0.0221	0.0167	31.97	0.0238	−7.06	No
130	25	0.0016	0.01859	0.0131	41.82	0.0194	−4.37	No
130	25	0.00093	0.01624	0.0111	46.03	0.0169	−3.84	No
130	25	0.00087	0.01593	0.0109	46.02	0.0166	−4.22	No
130	25	0.000845	0.01566	0.0108	44.74	0.0165	−5.21	No
130	25	0.00068	0.01512	0.0102	48.49	0.0157	−3.97	No
130	25	0.00051	0.01437	0.0094	52.35	0.0148	−3.08	No
131	25	6	0.3839	0.6458	−40.55	0.5540	−30.70	No
131	25	9	0.4617	0.8300	−44.37	0.6926	−33.33	No
131	25	11	0.499	0.9399	−46.91	0.7745	−35.57	No
131	25	13	0.5207	1.0427	−50.06	0.8503	−38.76	No
131	25	16	0.5482	1.1859	−53.77	0.9565	−42.69	No
131	25	21	0.6378	1.4050	−54.60	1.1115	−42.62	No
132	18	2	0.4433	0.4207	5.37	0.3867	14.64	Yes

TABLE 26. Evaluation of nesquehonite solubility in the system $MgCO_3·3H_2O + H_2O + CO_2$. Model 1 = with $MgHCO_3^+$; Model 2 = no $MgHCO_3^+$—Continued

Ref.	$t/°C$	$p(CO_2)/atm$	Measured solubility/mol kg^{-1}	Fitted solubility (Model 1)/mol kg^{-1}	Deviation from Model 1 (%)	Fitted solubility (Model 2)/mol kg^{-1}	Deviation from Model 2 (%)	Accepted
132	18	2.5	0.4762	0.4809	−0.97	0.4326	10.08	Yes
132	18	4	0.5516	0.6384	−13.60	0.5496	0.36	Yes
132	18	10	0.7898	1.1324	−30.25	0.8804	−10.29	Yes
132	18	16	0.9708	1.5303	−36.56	1.1115	−12.66	Yes
132	18	18	1.0421					
132	18	35	1.0578					
132	18	56	1.072					
132	0	34	1.2584					
132	5	34	1.2068					
132	10	34	1.136					
132	18	34	1.057					
132	30	34	0.9527					
132	40	34	0.8805					
132	50	34	0.8381					
132	60	34	0.7435					
133	5	1	0.4029	0.4415	−8.75	0.4217	−4.46	Yes
133	10	1	0.3431	0.3692	−7.06	0.3571	−3.91	Yes
133	15	1	0.2964	0.3114	−4.82	0.3028	−2.12	Yes
133	20	1	0.2541	0.2648	−4.04	0.2577	−1.41	Yes
133	25	1	0.222	0.2269	−2.14	0.2212	0.38	Yes
133	30	1	0.195	0.1957	−0.35	0.1913	1.93	Yes
133	35	1	0.1727	0.1697	1.80	0.1669	3.48	Yes
133	40	1	0.1528	0.1482	3.12	0.1469	4.05	Yes
133	45	1	0.1348	0.1302	3.57	0.1303	3.44	Yes
133	50	1	0.1192	0.1149	3.72	0.1166	2.26	Yes
133	55	1	0.1029	0.1020	0.91	0.1051	−2.07	Yes
133	60	1	0.0918	0.0909	0.97	0.0953	−3.68	Yes
134	18	1	0.334	0.2823	18.32	0.2746	21.65	No
134	18	2	0.4233	0.4207	0.62	0.3867	9.47	No
137	25	1	0.2146	0.2269	−5.40	0.2212	−2.97	Yes
139	0	1	0.4234	0.5332	−20.59	0.4966	−14.74	Yes
139	5	1	0.4041	0.4415	−8.47	0.4217	−4.18	Yes
139	8	1	0.3787	0.3961	−4.40	0.3816	−0.77	Yes
139	20	1	0.2535	0.2648	−4.27	0.2577	−1.64	Yes
139	25	1	0.2269	0.2269	0.02	0.2212	2.60	Yes
139	40	1	0.1528	0.1482	3.12	0.1469	4.05	Yes
139	45	1	0.1325	0.1302	1.80	0.1303	1.68	Yes
139	50	1	0.1151	0.1149	0.15	0.1166	−1.26	Yes
139	53.5	1	0.1062	0.1056	0.53	0.1083	−1.95	Yes
78	25	0.0088	0.0310	0.0241	28.42	0.0322	−3.70	Yes
78	25	0.047	0.0580	0.0489	18.59	0.0589	−1.50	Yes
78	25	0.108	0.0760	0.0720	5.53	0.0820	−7.37	Yes
79	25	0.968	0.2199	0.2228	−1.30	0.2177	0.99	Yes
79	28	0.962	0.2074	0.2031	2.13	0.1988	4.31	Yes
79	31	0.955	0.1922	0.1852	3.80	0.1820	5.58	Yes
79	33	0.950	0.1810	0.1745	3.74	0.1719	5.29	Yes
79	35	0.944	0.1692	0.1645	2.88	0.1625	4.13	Yes
79	38	0.934	0.1595	0.1507	5.83	0.1496	6.59	Yes
79	41	0.922	0.1509	0.1382	9.16	0.1381	9.27	Yes
79	44	0.909	0.1382	0.1270	8.85	0.1278	8.17	Yes
79	47	0.894	0.1265	0.1167	8.39	0.1184	6.80	Yes
79	50	0.877	0.1196	0.1073	11.42	0.1100	8.72	Yes

TABLE 27. Data collected for the evaluation of the solubility of $MgCO_3$ in the system $MgCO_3{\cdot}3H_2O + H_2O + CO_2 + Na_2CO_3$ (all data from Ref. 78 at 25 °C)

$p(CO_2)$/atm	Molality Na_2CO_3 m_2/mol kg^{-1}	Solubility $MgCO_3$ m_1/mol kg^{-1}
0.0088	0.1	0.012
	0.5	0.017
	0.6	0.021
	0.75	0.026
	0.8	0.029
	0.9	0.034
	1.0	0.039
	1.15	0.046
	1.45	0.051
0.047	0.35	0.014
	0.7	0.022
0.108	0.3	0.021
	0.6	0.021

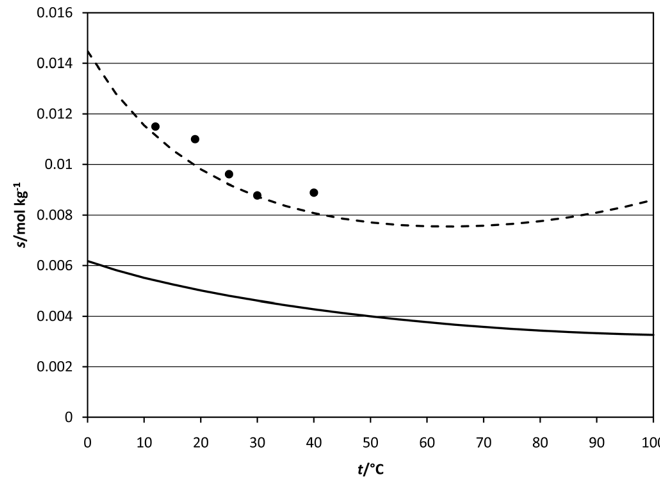

FIG. 8. Solubility of nesquehonite in the system $MgCO_3{\cdot}3H_2O + H_2O$ measured (solid symbols: accepted data) and predicted with Model 1 (solid line) and Model 2 (dashed line).

predictions for all data points were made with Model 1 (with $MgHCO_3^+$ ion pair) and with Model 2 (without $MgHCO_3^+$ ion pair). Measured and predicted solubility data as a function of temperature are shown in Fig. 8 and Table 29. The deviations with predictions of Model 1 are around 100%, but the deviations with Model 2 are only about 0–10%, all underestimations. Considering that there are indications that this model underestimates the solubility at low equilibrium CO_2 partial pressures, this is a good agreement between the model and the data, and all data points are accepted. Further research into the $Mg^{2+}-HCO_3^-$ ion interaction is needed to elucidate this point.

TABLE 28. Data collected for the evaluation of the solubility of nesquehonite in the system $MgCO_3{\cdot}3H_2O + H_2O$

Ref.	t/°C	Primary solubility data (authors)	Molality Mg(aq) m/mol kg^{-1} (evaluators)	Considered by evaluators
		Mass ratio ($MgCO_3{\cdot}3H_2O/H_2O$)		
119	19	1/658	0.0110	Yes
		Mass conc. $MgCO_3$/g l^{-1}		
121	12	0.970	0.0115	Yes
		Molality $MgCO_3$/mmol kg^{-1}		
145	25	0.009612	0.009612	Yes
	30	0.008782	0.008782	Yes
	40	0.008893	0.008893	Yes

3.1.4.4. $MgCO_3{\cdot}3H_2O + H_2O$ + salt. Only two references[145,146] provide data for these systems, both from the same research group. As the $MgCO_3{\cdot}3H_2O + H_2O$ data of this group were accepted, there is reason to believe that the $MgCO_3{\cdot}3H_2O + H_2O$ + salt data are reliable. A SIT approach that can reliably evaluate the data requires more sophistication than was necessary in the $MgCO_3 + H_2O + CO_2$ system, and was not attempted. However, detailed thermodynamic modeling may be of assistance here, and provide new information on the relevant ion interactions.

3.1.5. Lansfordite

3.1.5.1. $MgCO_3{\cdot}5H_2O + H_2O + CO_2$. Only four references[127,133,138,139] dealing with aqueous dissolution of magnesium carbonate pentahydrate in the presence of a fixed partial pressure of CO_2 were found in the literature. The data point of Cesaro[127] was discarded *a priori* (see Sec. 3.1.1),

TABLE 29. Comparison of nesquehonite solubility in the system $MgCO_3{\cdot}3H_2O + H_2O$ with model predictions

Ref.	t/°C	Measured solubility/mol kg^{-1}	Solubility Model 1/mol kg^{-1}	Deviation from Model 1 (%)	Solubility Model 2/mol kg^{-1}	Deviation from Model 2 (%)	Accepted
119	19	0.0110	0.00507	116.99	0.00996	10.43	Yes
121	12	0.0115	0.00540	112.79	0.01113	3.29	Yes
145	25	0.009612	0.00481	99.74	0.00922	4.21	Yes
145	30	0.008782	0.00462	90.11	0.00875	0.37	Yes
145	40	0.008893	0.00428	107.74	0.00808	10.01	Yes

TABLE 30. Data collected for the evaluation of the solubility of lansfordite in the system $MgCO_3{\cdot}5H_2O + H_2O + CO_2$

Ref.	$t/°C$	$p(CO_2)$/atm	Primary solubility data (authors)	Molality Mg^{2+} exp./mol kg^{-1} (evaluators)	Considered for evaluation
			Mass% MgO 100 w		
133	−1.8	0.987	1.526	0.4020	Yes
	0	0.987	1.496	0.3936	Yes
	5	0.987	1.423	0.3732	Yes
	10	0.987	1.363	0.3565	Yes
	15	0.987	1.312	0.3424	Yes
	20	0.987	1.256	0.3270	Yes
			Mass% Mg 100 w		
138	0	1.93	1.16	0.5158	Yes
	0	2.90	1.34	0.6042	Yes
	0	3.87	1.47	0.6699	Yes
	0	9.68	2.02	0.9654	Yes
			Molality $Mg(HCO_3)_2$ m'/mmol kg^{-1}solution		
139	0	1	339.2	0.3580	Yes
	10	1	318.6	0.3349	Yes
	15	1	310.8	0.3262	Yes

leaving only 13 data points from three references. The data are shown in Table 30.

For a quick test of the reliability of the data, the value of $s/p^{1/3}(CO_2)$ (in mol kg^{-1} bar$^{-1/3}$) was plotted versus temperature. The result is shown in Fig. 9. The figure shows that the data have a high degree of consistency. Due to the small number of data points, it was not possible to apply the empirical model of Eq. (18), but given the degree of consistency of the data, none of the data points is rejected for further evaluation.

The thermodynamic model variants were fitted to the experimental data to derive solubility constants. An equation of the form of Eq. (85) is fitted to the solubility constant data. The small number of data points and the narrow temperature interval precluded the use of more than two terms of the equation. Hence, coefficients C, D, and E were set equal to 0. The results were as follows:

For Model 1 (with $MgHCO_3^+$ ion pair):

$$\lg K_s = -0.9359 - 1309.52/(T/\mathrm{K}) \tag{120}$$

For Model 2 (without $MgHCO_3^+$ ion pair):

$$\lg K_s = -2.6026 - 710.97/(T/\mathrm{K}). \tag{121}$$

At 25 °C, these equations predict lg K_s of −5.3281 for Model 1 and lg K_s of −4.9872 for Model 2. Figure 10 shows the solubility constants obtained with Model 1, together with Eq. (120); Figure 11 shows the solubility constants obtained with Model 2, together with Eq. (121).

Based on Eqs. (120) and (121), predicted solubilities were calculated for all data points. The results are shown in Table 31. All data points agree well with the regression fits. The experimental solubilities tend to agree better with Model 2 (no $MgHCO_3^+$) (sum of squares of the residuals 0.015 lg

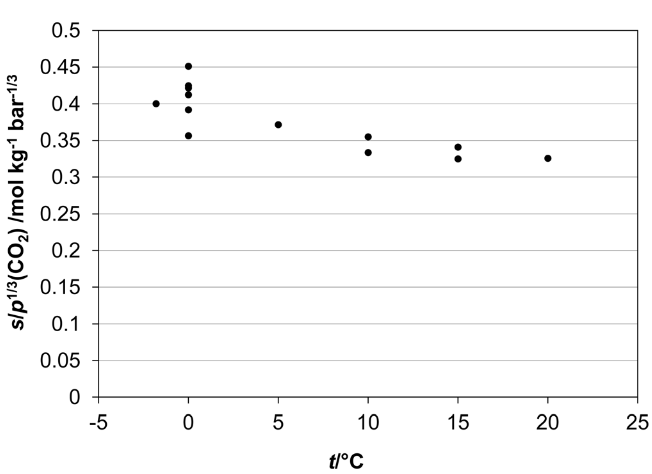

FIG. 9. Solubility of lansfordite in $MgCO_3{\cdot}5H_2O + H_2O + CO_2$ systems divided by the cubic root of the equilibrium CO_2 partial pressure.

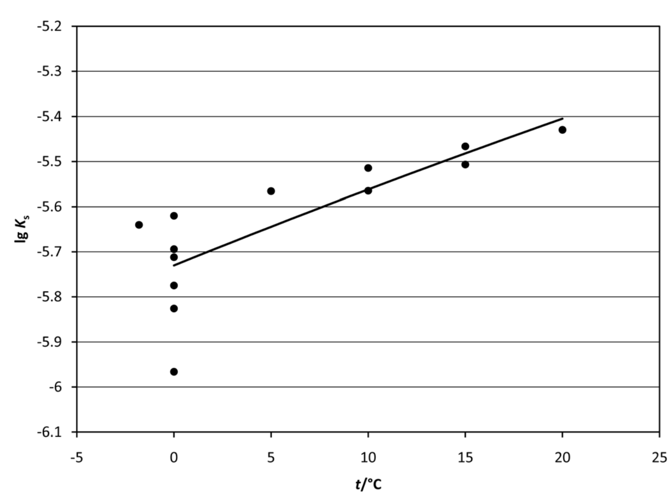

FIG. 10. Solubility constants of lansfordite derived from solubility data in the system $MgCO_3{\cdot}5H_2O + H_2O + CO_2$ (accepted data) with Model 1 (with $MgHCO_3^+$ ion pair); predictions of Eq. (120) (line).

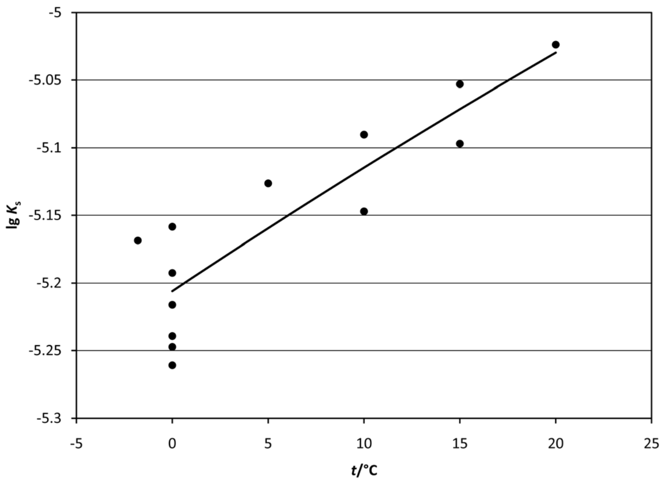

FIG. 11. Solubility constants of lansfordite derived from solubility data in the system $MgCO_3{\cdot}5H_2O + H_2O + CO_2$ (accepted data) with Model 2 (without $MgHCO_3^+$ ion pair); predictions of Eq. (121) (line).

units squared) than with Model 1 (sum of squares of the residuals 0.105 lg units squared). It is concluded that $MgHCO_3^+$ is not stable at the high ionic strengths associated with these experiments. Model 1 is not recommended as a description of aqueous systems in equilibrium with nesquehonite or lansfordite without further modifications. Further improvements of the relevant Pitzer parameters may improve estimates of solubility of nesquehonite and lansfordite, especially at high CO_2 partial pressures.

At water activities approaching 1, the transition temperature between nesquehonite and lansfordite predicted from Eqs. (119) and (121) (Model 2) is 9.93 °C. Ponizovskii *et al.*[138] found a slightly higher transition temperature: 12 °C.

3.1.6. Conclusion

Based on the thermodynamic model fits to the accepted solubility data, it is possible to put forward thermodynamic properties of magnesite, nesquehonite, and lansfordite consistent with the data and the models used. While data will be put forward for both model variants, Model 2 is clearly superior to Model 1 in describing the data. This does not mean that the existence of $MgHCO_3^+$ ion pairs is refuted for magnesium. It is possible that ion interactions between $MgHCO_3^+$ and other ions render Model 1 inaccurate. However, it is beyond the scope of this volume to explore this possibility. Based on systematic trends in the deviations between the models and the accepted solubility data, it is concluded that even Model 2 does not describe the $Mg^{2+}-HCO_3^-$ interaction adequately. Future research should address the description of this interaction, and the accepted solubility data from this volume can offer a valuable testing ground for such an improved description. Given this unresolved issue, the proposed thermodynamic data should not be construed as "recommended."

For magnesite at 25 °C, we follow Chase[149] in proposing $\Delta_f H° = -1111.69$ kJ mol^{-1}, slightly above the values of Königsberger *et al.*[79] Consistent with this, we propose $S° = 65.84$ J mol^{-1} K^{-1} for Model 1, and $S° = 64.43$ J mol^{-1} K^{-1} for Model 2. These values are very close to the value proposed by Chase,[149] 65.84 J mol^{-1} K^{-1}. Considering the findings for nesquehonite (below), an estimate below the measured value should be expected. From the $S°$ values, entropies of formation can be calculated, leading to the following Gibbs free energies of formation: $\Delta_f G° = -1028.12$ kJ mol^{-1} for Model 1 and $\Delta_f G° = -1027.70$ kJ mol^{-1} for Model 2. The better agreement of the calculated K_s data of Model 2 with the measured data of Bénézeth *et al.*[150] favors Model 2.

For nesquehonite at 25 °C, an entropy value of $S° = 190.627$ J mol^{-1} K^{-1} is put forward, five units lower than the value of Robie and Hemingway.[151] The reason to change the entropy of nesquehonite, and not Mg^{2+}(aq) or CO_3^{2-}(aq), is to maintain consistency with CODATA.[35] We propose $\Delta_f H° = -1981.83$ for Model 1, and $\Delta_f H° = -1979.76$ for Model 2. The latter is closer to the value put forward by Königsberger *et al.*[79] From these data,

TABLE 31. Evaluation of lansfordite solubility in the system $MgCO_3{\cdot}5H_2O + H_2O + CO_2$. Model 1 = with $MgHCO_3^+$; Model 2 = no $MgHCO_3^+$

Ref.	t/°C	$p(CO_2)$/atm	Measured solubility/mol kg^{-1}	Fitted solubility (Model 1)/mol kg^{-1}	Deviation from Model 1	Fitted solubility (Model 2)/mol kg^{-1}	Deviation from Model 2	Accepted
133	−1.8	0.987	0.4020	0.3395	18.40	0.3779	6.38	Yes
	0	0.987	0.3936	0.3375	16.62	0.3724	5.68	Yes
	5	0.987	0.3732	0.3338	11.79	0.3582	4.20	Yes
	10	0.987	0.3565	0.3328	7.11	0.3457	3.14	Yes
	15	0.987	0.3424	0.3343	2.43	0.3342	2.44	Yes
	20	0.987	0.3270	0.3381	−3.28	0.3244	0.81	Yes
138	0	1.93	0.5158	0.5009	2.97	0.5076	1.61	Yes
	0	2.90	0.6042	0.6433	−6.08	0.6103	−1.00	Yes
	0	3.87	0.6699	0.7704	−13.05	0.6936	−3.41	Yes
	0	9.68	0.9654	1.4065	−31.36	1.0189	−5.25	Yes
139	0	1	0.3580	0.3401	5.28	0.3747	−4.46	Yes
	10	1	0.3349	0.3354	−0.14	0.3479	−3.72	Yes
	15	1	0.3262	0.3368	−3.16	0.3364	−3.03	Yes

the following Gibbs free energies of formation follow: $\Delta_f G^\circ = -1726.83$ kJ mol^{-1} for Model 1, and $\Delta_f G^\circ = -1724.76$ kJ mol^{-1} for Model 2. The lower $p(CO_2)$ dependence of K_s calculated with Model 2 favors this model.

For lansfordite at 25 °C, no thermodynamic data from the literature are put forward. Consequently, and as the result of the much smaller data set, the thermodynamic data proposed here are substantially less accurate than the values put forward for magnesite and nesquehonite. The enthalpies put forward are $\Delta_f H^\circ = -2596.45$ kJ mol^{-1} for Model 1, and $\Delta_f H^\circ = -2584.99$ kJ mol^{-1} for Model 2. The proposed entropy values are $S^\circ = 180.67$ J mol^{-1} K^{-1} for Model 1, and $S^\circ = 212.58$ J mol^{-1} K^{-1} for Model 2. The Gibbs free energies that follow are $\Delta_f G^\circ = -2199.39$ kJ mol^{-1} for Model 1, and $\Delta_f G^\circ = -2197.44$ kJ mol^{-1} for Model 2. The entropy data put forward here are at variance with the data of Königsberger *et al.*[79] However, our values have a fairly large uncertainty, as no independent thermodynamic data was used. The lower $p(CO_2)$ dependence of K_s, as well as the higher entropy predicted with Model 2, favors this model. Model 1 predicts that lansfordite has a lower entropy than nesquehonite, which is unlikely to be realistic.

3.2. Data for the solubility of magnesium carbonate in aqueous systems

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[118]R. Wagner, J. Prakt. Chem. **102**, 233 (1867).
Variables:	**Prepared by:**
T/K = 278 $p(CO_2)$/bar = 1–6	J. Vanderdeelen Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ at $t = 5$ °C

$p(CO_2)$/atm	Mass ratio ($MgCO_3/H_2O$)	Mass fraction $MgCO_3$ 100w (compiler)	Molality $MgCO_3$/mol kg^{-1} (compiler)[a]
1	1/761	0.1312	0.0156
2	1/744	0.1342	0.0160
3	1/134	0.7407	0.0890
4	1/110.7	0.8952	0.1079
5	1/110	0.9009	0.1085
6	1/76	1.2987	0.1576

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

The author states that at $p(CO_2) = 3$ to 6 atm an important increase of the solubility occurs, while between 4 and 5 atm the increase is very limited.

Auxiliary Information

Method/Apparatus/Procedure:
No information given.

Source and Purity of Materials:
$MgCO_3$: synthetic, no indication about crystallinity.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[119]H. Beckurts, Arch. Pharm. **218**, 429 (1881).
Variables:	**Prepared by:**
T/K = 292–313 $p(CO_2)$/bar = 0–5	J. Vanderdeelen

Experimental Values

Solubility of $MgCO_3 \cdot 3H_2O$

t/°C	$p(CO_2)$ /atm	Mass ratio ($MgCO_3 \cdot 3H_2O/H_2O$)	Mass fraction $MgCO_3 \cdot 3H_2O$ 100w_H (compiler)	Molality $MgCO_3$ m/mol kg^{-1} (comp.)[a]
19	None	1/658	0.1517	0.0110
20	Unknown	1/72.4	1.3624	0.0999
20	2	1/30.5	3.1746	0.2374
20	3	1/26.0	3.7037	0.2786
20	4	1/21.1	4.5249	0.3435
10	5	1/17.09	5.5279	0.4243
15	5	1/18.60	5.1020	0.3898
40	5	1/44.64	2.1910	0.1621

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

Auxiliary Information

Method/Apparatus/Procedure:
The solid was boiled in water, then cooled in the presence or absence of CO_2(g). The suspension was shaken and a sample was filtered and evaporated, then weighed as MgO. Equilibrium was obtained after 36 h.

Source and Purity of Materials:
$MgCO_3$: dolomite (Diez, Lanthal; 54.50 mass% $CaCO_3$, 44.67 mass% $MgCO_3$) was slightly calcinated, then shaken with water. The suspension was flushed with CO_2 at 5–6 atm until most $MgCO_3$ dissolved without dissolving $CaCO_3$. After filtration, the filtrate containing $Mg(HCO_3)_2$ was boiled to precipitate $MgCO_3$. After a few recrystallizations, fine needles were obtained. Analysis gave $MgCO_3 \cdot 3H_2O$.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[120]M. Engel and J. Ville, C. R. Hebd. Seances Acad. Sci., Ser C **93**, 340 (1881).
Variables:	**Prepared by:**
$T/K = 286–373$ $p(CO_2)/bar = 1–9$	J. Vanderdeelen Alex De Visscher

Experimental Values

Solubility of $MgCO_3$

$t/°C$	p/atm	$p(CO_2)/atm$	Mass conc. $MgCO_3$ $\rho/g\ l^{-1}$	Solution density[a] /kg m^{-3}	Molality $MgCO_3$[b] /mol kg^{-1}
19.5	1.0	0.978	25.79	1034.0	0.3097
19.5	2.1	2.08	33.11	1044.3	0.3992
19.7	3.2	3.18	37.3	1050.3	0.4509
19.0	4.7	4.68	43.5	1059.5	0.5278
19.2	5.6	5.58	46.2	1063.4	0.5617
19.2	6.2	6.18	48.51	1066.7	0.5906
19.5	7.5	7.48	51.2	1070.6	0.6248
18.7	9.0	8.98	56.59	1078.7	0.6928
	p/mm Hg	$p(CO_2)$ /mm Hg			
13.4	751	739	28.45	1039.4	0.3414
19.5	763	746	25.79	1034.0	0.3097
29.3	762	731	21.945	1025.8	0.2638
46.0	764	688	15.7	1011.7	0.1893
62.0	764	600	10.35	997.7	0.1254
70.0	765	531	8.1	990.5	0.0984
82.0	765	380	4.9	978.9	0.0599
90.0	765	239	2.4	969.7	0.0295
100.0	765	-	0.0[c]	-	-

[a]According to compiler.
[b]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).
[c]After prolonged boiling.

It is not clear to which mineralogical variety the material used refers. A more thorough examination is required before this extended data set is useful for evaluation (compiler).

Auxiliary Information

Method/Apparatus/Procedure:
No information given.

Source and Purity of Materials:
$Mg(HCO_3)_2$, no other information given.[121]

Estimated Error:
No estimates possible; however, the method systematically overestimates.[121]

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[121]M. Engel, Ann. Chim. Phys. **13**, 344 (1888).
Variables:	**Prepared by:**
$T/K = 276–323$ $p(CO_2)/bar = 0–6, 1$	J. Vanderdeelen Alex De Visscher

Experimental Values

Solubility of $MgCO_3 \cdot 3H_2O$

$t/°C$	p/atm	$p(CO_2)$ /atm	Mass conc. $MgCO_3$[a] $\rho/g\ l^{-1}$	Amount conc. $MgCO_3$[b] /mol l^{-1}	Molality $MgCO_3$[c] /mol kg^{-1}	Solution density[d] /kg m^{-3}
12	0[e]	0[e]	0.970	0.0115	0.0115	1000.9
12	0.5	0.486	20.5	0.2431	0.2451	1028.6
12	1	0.986	26.5	0.3143	0.3177	1037.1
12	1.5	1.486	31.0	0.3677	0.3725	1043.6
12	2	1.986	34.2	0.4056	0.4117	1048.3
12	2.5	2.486	36.4	0.4317	0.4388	1051.6
12	3	2.986	39.0	0.4626	0.4708	1055.4
12	4	3.486	42.8	0.5076	0.5180	1061.1
12	6	5.986	50.6	0.6001	0.6155	1072.6
3.5	1.0[f]	0.992	35.6	0.4222	0.4272	1052.5
18	1.0[f]	0.980	22.1	0.2621	0.2649	1029.4
22	1.0[f]	0.974	20.0	0.2372	0.2398	1025.4
30	1.0[f]	0.958	15.8	0.1874	0.1895	1017.4
40	1.0[f]	0.927	11.8	0.1400	0.1418	1008.6
50	1.0[f]	0.878	9.5	0.1127	0.1145	1001.6

[a]The author claims that analytical results are expressed per liter of water. The method of determination reveals that they are expressed per liter of solution (compiler).
[b]Calculated by compiler.
[c]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).
[d]Estimated by compiler.
[e]CO_2-free water.
[f]The author mentions that these results were obtained at "atmospheric" pressure; elsewhere the author states that water was "loaded with carbonic acid at atmospheric pressure" (translation by compilers).

Solubility of alkaline earth metal carbonate changes proportionally to the cube root of the CO_2 partial pressure (author).

Auxiliary Information

Method/Apparatus/Procedure:
Experiments were conducted in a closed vessel [M. Engel, Ann. Chim. Phys. **7**, 260 (1886)]. The mixture was agitated for 1 h, after which equilibrium was established. Solubility was measured using alkalinity titration with sulfuric acid.

Source and Purity of Materials:
$MgCO_3 \cdot 3H_2O$: trihydrate, no other information given.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Sodium chloride; NaCl; [7647-14-5] (3) Carbon dioxide; CO_2; [124-37-9] (4) Water; H_2O; [7732-18-5]	[122]N. N. Lubavin, Zh. Russ. Fiz-Khim. Obsh. **24**, 389 (1892).
Variables:	**Prepared by:**
T/K = 299 $p(CO_2)$/bar = unknown NaCl = 0, 2.5 mass%	B. R. Churagulov Alex De Visscher

Experimental Values

Solubility of $MgCO_3{\cdot}3H_2O$ at $t = 26$ °C

Mass fraction NaCl 100 w_2	Molality NaCl m_2/mol kg^{-1}	Mass fraction MgO 100w_1	Molality MgO m_1 /mol kg^{-1}	Solid phase
0	0	0.0812	0.0202	$MgCO_3{\cdot}3H_2O$
		0.0027	0.00067	Natural magnesite
2.525	0.4313[a]	0.125	0.0317	$MgCO_3{\cdot}3H_2O$
	0.4320[a]	0.0048	0.00122	Natural magnesite

[a]It was assumed that mass fraction referred to composition before adding $MgCO_3{\cdot}3H_2O$.

No indication of absence or equilibration with atmospheric CO_2; nothing is known about crystallinity.

Auxiliary Information

Method/Apparatus/Procedure:
Suspensions were shaken for 4 days at 26 °C, then filtered. Excess solid was determined gravimetrically and CO_2 by mass loss in a Bunsen gas apparatus. H_2O was found by difference after heating and after correcting for CO_2 loss.

Source and Purity of Materials:
$MgCO_3{\cdot}3H_2O$: trihydrate, obtained by precipitation of $MgSO_4$ with Na_2CO_3. Crystals were washed free of sulfate. Solid was trihydrate by analysis; composition (mass%, determined and theoretical) MgO, 29.78 (28.98); CO_2, 31.56 (31.88); H_2O, 39.01 (39.13); Na absent. Natural magnesite: composition (mass%) MgO, 44.28; CO_2, 46.32; CaO 1.39; Fe_2O_3, 0.43; insol. 5.84; H_2O 2.38.

Estimated Error:
T: precision 0.5 K.
Dissolution data: relative precision 10%.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[123]F. P. Treadwell and M. Reuter, Z. Anorg. Chem. **17**, 170 (1898).
Variables:	**Prepared by:**
T/K = 288	J. Vanderdeelen Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ at $t \approx 15$ °C

t/°C	$p(CO_2)$ /atm	ΣMg/mg per 100 ml	Solubility of $MgCO_3$ /mmol per 100 ml
12.1		201.6	8.295
14.8		201.6	8.295
12.9		201.6	8.295
13.7		201.6	8.295
15.6	0.0135	149.2	6.139
15.3	0.0107	122.4	5.036
14.2	0.0062	86.5	3.559
15.0	0.0060	78.8	3.242
15.1	0.0033	65.5	2.695
15.1	0.0021	59.4	2.444
15.6	0.0014	56.6	2.329
14.6	0.0003	54.5	2.242
14.6	0	53.6	2.205
13.8	0	52.9	2.177
15.4	0	52.0	2.139
16.0	0	51.1	2.102
15.6	0	51.8	2.131

Speciation into $MgCO_3$ and $Mg(HCO_3)_2$ in solution is also calculated by the authors, i.e., mass conc. = 0.6410 g l^{-1} as $MgCO_3$ and 1.9540 g l^{-1} as $Mg(HCO_3)_2$ (authors) or as sum of mass concentration Mg = 0.509 g l^{-1} or amount concentration = 0.0210 mol l^{-1} (compiler) for the last data point.

Auxiliary Information

Method/Apparatus/Procedure:
Starting from the solution obtained below, CO_2 is progressively expelled and the Mg concentration in solution is measured. The sum of bicarbonate and two times the carbonate concentrations are determined by acid titration.

Source and Purity of Materials:
$MgCO_3$: Commercial MgO was the starting material, transformed into carbonate in CO_2-enriched water and transferred to bicarbonate. After several weeks, suspension is filtered and CO_2 is expelled from the solution.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[124]F. K. Cameron and L. J. Briggs, J. Phys. Chem. **5**, 537 (1901).
Variables:	**Prepared by:**
T/K = approx. 295 $p(CO_2)$/bar = atmospheric conditions: 2.9×10^{-4} (compiler)	J. Vanderdeelen Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ at $t \approx 22$ °C and CO_2 mole fraction 3.0×10^{-4} leading to $p(CO_2) = 2.9 \times 10^{-4}$ atm after altitude correction and accounting for water vapor pressure (assumed by compiler; authors state that experiments were carried out at atmospheric conditions)

Equilibration time/d	Mass conc. Mg^{2+}/g l^{-1}	Molality Mg^{2+}/mol kg^{-1} (compiler)
29	0.1530	0.00630
46	0.1837	0.00756
101	0.1808	0.00744
	av.[a] 0.182	av.[a] 0.00749

[a]Average for time = 46 and 101 d.

Auxiliary Information

Method/Apparatus/Procedure:
$MgCO_3$ was suspended in distilled water and air, and washed by passing through dilute H_2SO_4 continuously for different lengths of time.

Source and Purity of Materials:
$MgCO_3$: synthetic with no further specifications.

Estimated Error:
No estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Sodium chloride; NaCl; [7647-14-5]
(3) Sodium sulfate; Na_2SO_4; [7757-82-6]
(4) Sodium carbonate; Na_2CO_3; [497-19-8]
(5) Carbon dioxide; CO_2; [124-37-9]
(6) Water; H_2O; [7732-18-5]

Original Measurements:
[125]F. K. Cameron and A. Seidel, J. Phys. Chem. **7**, 578 (1903).

Variables:
T/K = 296–310
No CO_2 or $p(CO_2)$/bar = 1
Salts: Na_2CO_3, Na_2SO_4 and NaCl at variable concentration

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ (1) in aqueous NaCl (2) solutions, in the absence of CO_2:

Run 1: $t = 23$ °C

Mass conc. NaCl ρ_2/g l^{-1}	Molality NaCl m_2/mol kg^{-1} (compiler)	Mass conc. $MgCO_3$ ρ_1/g l^{-1}	Molality $MgCO_3$ m_1/mmol kg^{-1} (compiler)	Solution density[a]/kg m^{-3}
0.0	0.000	0.176	2.09	996.92
28.0	0.485	0.418	5.02	1016.82
59.5	1.038	0.527	6.37	1041.09
106.3	1.888	0.585	7.20	1070.50
147.4	2.664	0.544	6.82	1094.53
231.1	4.341	0.460	5.99	1142.48
272.9	5.207	0.393	5.20	1170.14
331.4	6.536	0.293	4.01	1199.28

[a]Determined experimentally by the authors. Sample checks prove the density to be accurate to within about 0.2%, hence the authors' densities were used in the unit conversions.

Possibly traces of CO_2(g) may have entered the system and may have been absorbed by the solutions (authors).

Solubility of $MgCO_3$ (1) in aqueous Na_2SO_4 (3) solutions, in the absence of CO_2:

Run 2: $t = 24$ °C

Mass conc. Na_2SO_4 ρ_3/g l^{-1}	Molality Na_2SO_4 m_3/mol kg^{-1} (compiler)	Mass conc. $MgCO_3$ ρ_1/g l^{-1}	Molality $MgCO_3$ m_1/mmol kg^{-1} (compiler)	Solution density[a]/kg m^{-3}
0.00	0.000	0.216	2.57	997.52
25.12	0.178	0.586	6.98	1021.24
54.76	0.389	0.828	9.90	1047.60
95.68	0.684	1.020	12.29	1080.95
160.80	1.165	1.230	15.01	1133.85
191.90	1.401	1.280	15.75	1157.34
254.60	1.887	1.338	16.70	1206.03
278.50	2.077	1.338	16.81	1223.91
305.10	2.296	1.388	17.60	1241.99

[a]Determined experimentally by the authors.

Run 3: $t = 35.5$ °C

Mass conc. Na_2SO_4 ρ_3/g l^{-1}	Molality Na_2SO_4 c_3/mol kg^{-1} (compiler)	Mass conc. $MgCO_3$ ρ_1/g l^{-1}	Molality $MgCO_3$ m_1/mmol kg^{-1} (compiler)	Solution density[a]/kg m^{-3}
0.32	0.002	0.131	1.56	995.15
41.84	0.297	0.577	6.91	1032.89
81.84	0.585	0.753	9.07	1067.23
116.56	0.840	0.904	10.97	1094.77
148.56	1.077	0.962	11.75	1120.38
186.70	1.364	1.047	12.88	1151.70
224.00	1.652	1.088	13.52	1179.82
247.20	1.836	1.100	13.76	1196.32
299.20	2.250	1.130	14.32	1236.52

[a]Determined experimentally by the authors.

Solubility of $MgCO_3$ (1) in aqueous Na_2CO_3 (4) solutions, in the absence of CO_2:

Run 4: $t = 25$ °C

Mass conc. Na_2CO_3 ρ_4/g l^{-1}	Molality Na_2CO_3 m_4/mol kg^{-1} (compiler)	Mass conc. $MgCO_3$ ρ_1/g l^{-1}	Molality $MgCO_3$ m_1/mmol kg^{-1} (compiler)	Solution density[a] /kg m^{-3}
0.00	0.0000	0.223	2.65	996.84
23.12	0.219	0.288	3.43	1019.89
50.75	0.481	0.510	6.07	1047.72
86.42	0.819	0.879	10.69	1082.47
127.30	1.213	1.314	15.74	1118.91
160.80	1.540	1.636	19.69	1147.66
181.90	1.747	1.972	23.81	1166.05
213.20	2.066	2.317	28.22	1189.38

[a]Determined experimentally by the authors.

Solutions were not boiled after the addition of magnesium carbonate.

Solubility of $MgCO_3$ (1) in aqueous NaCl (2) solutions:

Run 5: $t = 37.5$ °C, $p(CO_2) = 1$ atm ("in equilibrium with an atmosphere of carbon dioxide")

Mass conc. NaCl ρ_2/g l^{-1}	Molality NaCl m_2/mol kg^{-1} (compiler)	Mass conc. $Mg(HCO_3)_2$ ρ_1/g l^{-1}	Molality $MgCO_3$ m_1/mmol kg^{-1} (compiler)[a]	Solution density /kg m^{-3} (compiler)
7.0	0.120	30.64	210.0	1034.8
56.5	1.012	30.18	216.1	1040.8
119.7	2.182	27.88	203.0	1085.7
163.7	3.016	24.96	183.7	1117.0
224.8	4.205	20.78	155.3	1159.8
306.6	5.829	10.75	81.6	1217.1

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

According to the authors, reaction flasks were equilibrated with CO_2(g) at room temperature and afterwards the temperature was raised to 37.5 °C.

Auxiliary Information

Method/Apparatus/Procedure:
2 g of $MgCO_3$ was added to 100 ml solution containing a given salt at different concentrations, and then boiled to expel dissolved CO_2. During cooling, the stoppers of suspensions were removed from time to time and then shaken for about 3 d in closed bottles. With NaCl, CO_2(g) was present at 1 atm. Mg was determined gravimetrically as pyrophosphate, carbonate by acid titration, NaCl by argentimetry, sulfate as $BaSO_4$. In presence of Na_2CO_3, Mg was precipitated as $MgNH_4PO_4$ in large excess of NH_3 or NH_4Cl.

Source and Purity of Materials:
$MgCO_3$: pure powdered with no further specifications (authors).

Estimated Error:
No estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Potassium hydrogen carbonate; $KHCO_3$; [298-14-6]
(3) Carbon dioxide; CO_2; [124-37-9]
(4) Water; H_2O; [7732-18-5]

Original Measurements:
[126]F. Auerbach, Z. Elektrochem. **10**, 161 (1904).

Variables:
T/K = 288, 298, and 308
$p(CO_2)$/bar = unknown
Salt: $KHCO_3$ at variable concentrations

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ (1) in aqueous $KHCO_3$ (2) solutions

t/°C	Amount concentration $c_2(K^+)$/mol l^{-1}	Solubility $c_1(Mg^{2+})$/mol l^{-1}	Solid phase
15	0	0.0095	$MgCO_3 \cdot 3H_2O$
	0.0992	0.0131	$MgCO_3 \cdot 3H_2O$
	0.1943	0.0167	$MgCO_3 \cdot 3H_2O$
	0.3992	0.0211	$MgCO_3 \cdot 3H_2O$ (not stable)[a]
	0.2861	0.0192	$MgCO_3 \cdot 3H_2O$ + $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.5243	0.0097	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.6792	0.0074	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.981	0.0028	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
25	0	0.0087	$MgCO_3 \cdot 3H_2O$
	0.0985	0.0115	$MgCO_3 \cdot 3H_2O$
	0.2210	0.0149	$MgCO_3 \cdot 3H_2O$
	0.3188	0.0175	$MgCO_3 \cdot 3H_2O$
	0.3434	0.0181	$MgCO_3 \cdot 3H_2O$
	0.4216	0.0205	$MgCO_3 \cdot 3H_2O$ (not stable)[a]
	0.4985	0.0217	$MgCO_3 \cdot 3H_2O$ (not stable)[a]
	0.3906	0.0196	$MgCO_3 \cdot 3H_2O$ + $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.5893	0.0128	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.6406	0.0117	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.788	0.0089	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	1.125	0.0061	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
35	0	0.0071	$MgCO_3 \cdot 3H_2O$
	0.1092	0.0098	$MgCO_3 \cdot 3H_2O$
	0.2001	0.0132(?)[a]	$MgCO_3 \cdot 3H_2O$
	0.2811	0.0142	$MgCO_3 \cdot 3H_2O$
	0.3704	0.0163	$MgCO_3 \cdot 3H_2O$
	0.4847	0.0177	$MgCO_3 \cdot 3H_2O$
	0.5807	0.0198	$MgCO_3 \cdot 3H_2O$ (not stable)[a]
	0.5088	0.0184	$MgCO_3 \cdot 3H_2O$ + $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.6231	0.0153	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$
	0.9535	0.0119	$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$

[a]Value questioned by the authors.

The system was a closed system with a gas phase of unknown volume. Hence, total carbonate was not conserved in the liquid phase, and the equilibrium CO_2 partial pressure is unknown.

Auxiliary Information

Method/Apparatus/Procedure:
Small amounts of solid were shaken in a thermostat with freshly prepared $KHCO_3$. Equilibrium was attained after 1–4 days. Solutions were quickly filtered, analyzed for total alkalinity by titration versus methyl orange; Mg as $Mg(OH)_2$ after expelling CO_2(g) by boiling and addition of a known amount of NaOH.

Source and Purity of Materials:
$MgCO_3$: prepared according to Knorre [G. V. Knorre, Z. Anorg. Chem. **34**, 260 (1903)] to give fine needle crystals. $M_r = 0.1386$; theor. 0.13841 for $MgCO_3 \cdot 3H_2O$.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[127]G. Cesaro, Bull. Cl. Sci. Acad. R. Belg. **1910**, 234 (1910).
Variables:	**Prepared by:**
T/K= ambient $p(CO_2)$/bar = atmospheric conditions = 3.0×10^{-4} (evaluators)	J. Vanderdeelen Alex De Visscher

Experimental Values

Solubility: mass ratio $MgCO_3 \cdot 5H_2O/H_2O = 1/267$

w_H, mass% of the hydrated form, $MgCO_3 \cdot 5H_2O = 0.373$ (compiler)
w_A, mass% of the anhydrous form, $MgCO_3 = 0.1803$ (compiler) (see below)
Molality Mg^{2+}, $m(Mg^{2+}) = 0.0214$ mol kg^{-1} (compiler).

Nesquehonite crystals were detected by microscope in the residue of the solubility experiment, leading to the conclusion (author) that during the determination of the amount solubilized, which was obtained by evaporation of the solution, both lansfordite and nesquehonite crystals were observed in the residue.
Mass% of hydrated form ($MgCO_3 \cdot 5H_2O$) was converted to mass% of anhydrous form ($MgCO_3$) using: $w_A = M_A w_H / M_H$, where w_A is mass% of the anhydrous form, M_A and M_H the molar masses of the anhydrous and the hydrated form, w_H the mass% of the hydrated form.

Auxiliary Information

Method/Apparatus/Procedure:
Crystals were ground and suspended for two weeks in water at room temperature. Mg content was determined by weighing after evaporation of part of supernatant.

Source and Purity of Materials:
$MgCO_3 \cdot 5H_2O$: calcined dolomite was suspended in water and flushed with CO_2(g) at 5–6 atm until Ca was dissolved. After filtration, the filtrate was let to stand to release CO_2 to the gas phase. Clear, 3–5 mm crystals formed from supersaturated solution. Relative density (1.75) and analysis confirmed the pentahydrate. Chemical analysis revealed the following composition: MgO: 22.80%; CO_2: 25.43%; H_2O: 51.77%.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Sodium carbonate; Na_2CO_3; [497-19-8] (3) Sodium nitrate; $NaNO_3$; [7631-99-5] (4) Sodium sulfate; Na_2SO_4; [7757-82-6] (5) Sodium chloride; NaCl; [7647-14-5] (6) Magnesium chloride; $MgCl_2$; [7786-30-3] (7) Water; H_2O; [7732-18-5]	[128]F. Gothe, Chem. Z. **39**, 305 (1915).
Variables:	**Prepared by:**
T/K= approx. 273 Salts: variable at various mass concentration	J. Vanderdeelen Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ (1) in water and aqueous electrolyte (2) solutions at approximately 0 °C

Salt	Mass conc. ρ_2/g l^{-1}	Molality m_2/mol kg^{-1} (compiler)	Mass conc. $MgCO_3$ ρ_1/mg l^{-1} (titrimetry)	Mass conc. $MgCO_3$ ρ_1/mg l^{-1} (gravimetry)	Mass conc. $MgCO_3$ ρ_1/mg l^{-1} (mean, author)	Molality $MgCO_3$ c_1/mmol kg^{-1} (mean, compiler)	Solution density /kg m^{-3} (compiler)[a]
None			95.8	96.5			
			92.4	94.0			
			90.7	91.0	94.3, $s = 3.3$	1.12, $s = 0.04$	1000.0
			99.1	101.6			
			94.1	92.5			
			92.4	91.9			
$NaNO_3$	0.85	0.0100	122.6	123.1	122.9	1.46	1000.4
	1.7	0.0200	136.1	141.5	138.8	1.65	1001.7
	4.25	0.0501	134.4	140.0	137.2	1.63	1002.7
Na_2CO_3	0.53	0.0050		98.6		1.17	1000.5
	1.06	0.0100		53.5		0.634	1001.1
	2.65	0.0250		15.7		0.186	1002.9

Salt	Mass conc. ρ_2/g l^{-1}	Molality m_2/mol kg^{-1} (compiler)	Mass conc. $MgCO_3$ ρ_1/mg l^{-1} (titrimetry)	Mass conc. $MgCO_3$ ρ_1/mg l^{-1} (gravimetry)	Mass conc. $MgCO_3$ ρ_1/mg l^{-1} (mean, author)	Molality $MgCO_3$ c_1/mmol kg^{-1} (mean, compiler)	Solution density /kg m^{-3} (compiler)[a]
$Na_2SO_4 \cdot 10H_2O$	0.805	0.0025	146.2	143.9	145.1	1.72	1000.2
	1.61	0.0050	159.6	164.5	162.1	1.92	1000.5
	4.03	0.0125	151.2	150.3	150.8	1.79	1001.6
NaCl	0.585	0.0100	126.0	130.6	128.3	1.52	1000.3
	1.17	0.0200	132.7	136.1	134.4	1.59	1000.7
	2.93	0.0502	117.6	124.5	121.0	1.43	1002.1
$MgCl_2 \cdot 6H_2O$	0.51	0.0025	47.0			0.557	1000.0
	1.02	0.0050	39.5			0.468	1000.2
	2.55	0.0125	35.3			0.419	1000.9

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1) for pure water, and values for the pure salt solutions in the case of experiments in salt solutions.

Auxiliary Information

Method/Apparatus/Procedure:
Distilled water or salt solution, 1 l, was added to 0.5 g $MgCO_3$. After evaporation to 200 ml, the flasks were stoppered, cooled in ice overnight and filtered. Carbonate was determined by titration with H_2SO_4 (methyl orange indicator) or by gravimetry as $Mg_2P_2O_7$.

Source and Purity of Materials:
$MgCO_3$: Merck, "very pure."
Salts: Kahlbaum, "pure."

Estimated Error:
See deviation in table.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Sodium chloride; NaCl; [7647-14-5]
(3) Carbon dioxide; CO_2; [124-37-9]
(4) Water; H_2O; [7732-18-5]

Original Measurements:
[129]R. C. Wells, J. Am. Chem. Soc. **37**, 1704 (1915).

Variables:
T/K = 293
$p(CO_2)$/bar = atmospheric conditions (3.0×10^{-4}, compilers)
Salt: none and NaCl

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Solubility of magnesium carbonate at 20 °C and $p(CO_2) = 2.9 \times 10^{-4}$ atm (accounting for altitude correction and water vapor pressure)

Solid phase	Equil. time	Mass conc. ρ_1/g l^{-1} Mg^{2+}	Mass conc. ρ_1/g l^{-1} HCO_3^-	Mass conc. ρ_1/g l^{-1} CO_3^{2-}	Amount conc. c_1/mol l^{-1} (compiler) Mg^{2+}	Solution density /kg m^{-3} (compiler)[a]
Magnesite	37	0.017	0.055			
	61	0.018	0.065			
	Avg.	0.018	0.060		0.00074	999.9
	35[b]	0.028[a]	0.086[a]		0.0012[b]	1020.7
Nesquehonite[c]	47	0.39	0.84	0.29		
	65	0.38	0.83	0.28		
	Avg.	0.39	0.84	0.29	0.0158	1001.9
Nesquehonite[d]	19	0.34	0.61	0.31		
	22	0.35	0.60	0.30		
	29	0.34	0.59	0.32		
	Avg.	0.34	0.60	0.31	0.0142	1001.7

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).
[b]In the presence of 27.2 g NaCl l^{-1} or 0.469 mol kg^{-1}.
[c]When CO_2 was expelled from a supersaturated solution of $Mg(HCO_3)_2$ in water, crystals of $MgCO_3 \cdot 3H_2O$ (as confirmed by chemical analysis) appeared after 3 d. Data on approach to equilibrium are not given here.
[d]From undersaturation.

Auxiliary Information

Method/Apparatus/Procedure:
Air was filtered through cotton and distilled water before bubbling through suspensions of the solid in containers in a thermostat. Samples were taken from 1 h to 30–60 d. Carbonate and bicarbonate were determined by titration with $NaHSO_4$, first with phenolphthalein indicator, then with methyl orange.

Source and Purity of Materials:
$MgCO_3$: Amorphous magnesite, Placer County, Colorado; composition (mass%): MgO: 46.82; CO_2: 51.75; SiO_2: 0.09; Fe_2O_3: 0.11; Al_2O_3: 0.09; CaO: 0.05; H_2O: 0.67; sum: 99.58.
Salts: Kahlbaum "pure."
$MgCO_3 \cdot 3H_2O$: by flushing out CO_2 with air from a supersaturated solution of $Mg(HCO_3)_2$.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[130]W. D. Kline, "Equilibrium in the System Magnesium Carbonate, Carbon Dioxide and Water," Ph.D. dissertation (Yale University, 1923); J. Am. Chem. Soc. **51**, 2093 (1929).
Variables: T/K = 298 $p(CO_2)$/bar = 0.000510–0.9684	**Prepared by:** J. Vanderdeelen

Experimental Values

Solubility data of $MgCO_3 \cdot 3H_2O$ at 25 °C

$p(CO_2)$/atm	Molality total base m/mol kg^{-1}	Molality HCO_3^- m/mol kg^{-1}	Molality CO_3^{2-} m/mol kg^{-1}	Molality Mg^{2+}[a] m/mol kg^{-1}
0.9684	0.4269	0.4269		0.2135
0.1116	0.12536	0.12366	0.00085	0.06266
0.0432	0.09202	0.08998	0.00102	0.04601
0.0150	0.06254	0.06022	0.00116	0.03127
0.0069	0.05014	0.04468	0.00273	0.02507
0.00334	0.04430	0.03548	0.00436	0.02210
0.00160	0.03718	0.02698	0.00510	0.01859
0.00093	0.03248	0.02119	0.00565	0.01624
0.000887	0.03186	0.02046	0.00570	0.01593
0.000845	0.03132	0.01990	0.00571	0.01566
0.000680	0.03024	0.01872	0.00576	0.01512
0.000510	0.02873	0.01710	0.00582	0.01437

[a]$m(MgCO_3)$ calculated from charge balance: $m(MgCO_3) = m(Mg^{2+}) = m(HCO_3^-)/2 + m(CO_3^{2-})$.

Data included in the 1929 paper. From the original data, it was observed that with increasing partial pressure the molality of carbonate reaches a maximum when the pressure is about 0.00038 atm and then gradually decreases. Correspondingly, it was observed that the appearance of the crystals of $MgCO_3 \cdot 3H_2O$ remained unchanged throughout the course of the experiment at all pressures greater than 0.00038 atm, but at lower pressures the solid appeared to become very fined-grained, indicating therefore a change from carbonate to hydroxide. The duration of the experiment was insufficient to ensure complete conversion of the solid phase from carbonate to hydroxide (author). Data in the presence of a $Mg(OH)_2$ solid phase are not reported here.

Auxiliary Information

Method/Apparatus/Procedure:
Fine powder and water were placed in flasks in a thermostat at 25 °C. An air-CO_2(g) mixture was bubbled through the suspension. Equilibrium was reached in 3 days. The effluent gas was analyzed for CO_2 by the $Ba(OH)_2$ method. Total base was found by titration with acid (methyl orange). Bicarbonate was found by adding to $Ba(OH)_2$ solution and titrating excess base with acid (phenolphthalein). Carbonate was found by difference.

Source and Purity of Materials:
$MgCO_3 \cdot 3H_2O$: (1) Kahlbaum trihydrate, contaminated with $Mg(OH)_2$; (2) precipitated by addition of a weak solution of $KHCO_3$ to a concentrated solution of $MgCl_2$ at 20–22 °C. The initial slimy precipitate became granular after 10 min., was washed until free of chloride or potassium, then dried at ca. 25 °C. Next, pure CO_2(g) was bubbled through a suspension of the product for 5 days and the undissolved solid was filtered off. After a few hours, hexagonal crystals formed, which were separated and washed with CO_2-saturated water and dried at room temperature. A second crop formed after 1 d. Analysis (mass% for crops 1 and 2, with theoretical values for $MgCO_3 \cdot 3H_2O$ between brackets); MgO 20.08: 30.2 (28.15); CO_2(g): 31.71, 32.1 (31.81); H_2O (by difference): 39.21, 37.7 (39.04). Similar analyses were found for the Kahlbaum product.

Estimated Error:
No estimates possible.

Components:	**Original Measurements:**
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Carbon dioxide; CO_2; [124-37-9] (3) Water; H_2O; [7732-18-5]	[131]A. E. Mitchell, J. Chem. Soc., Trans. **123**, 1887 (1923).
Variables: T/K = 298 $p(CO_2)$/bar = 6–21	**Prepared by:** J. Vanderdeelen M. Tsurumi M. Ichikuni Alex De Visscher

Experimental Values

Solubility of $MgCO_3 \cdot 3H_2O$ at 25 °C

$p(CO_2)$/atm	Amount conc. Mg^{2+}/mol l^{-1}	Amount conc. CO_2/mol l^{-1}	Molality Mg^{2+} m/mol kg^{-1} (compiler)[a]	Solution density /kg m^{-3} (compiler)
6	0.376	0.896	0.3839	1042.0
9	0.450	1.147	0.4617	1051.3
11	0.485	1.250	0.4990	1055.8
13	0.505	1.350	0.5207	1058.6
16	0.530	1.395	0.5482	1062.3
21	0.613	1.738	0.6378	1072.8

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

Auxiliary Information

Method/Apparatus/Procedure:
Solid was added to a silver vessel about 2/3 filled with water. The particles were small enough to remain in suspension by a flow of CO_2(g). After equilibrium had been reached (no equilibration time provided), the suspension was filtered through cotton wool. CO_2(g) was measured by a Bourdon gauge and CO_2 in solution was measured by the method of Johnston [J. J. Johnston, J. Am. Chem. Soc. **37**, 947 (1916)]. Mg was precipitated as magnesium ammonium phosphate from the boiling solution. After standing 4 h, the precipitate was washed in ammonia and air dried at 60 °C, dissolved in excess dilute sulfuric acid and titrated with KOH (methyl orange end point).

Source and Purity of Materials:
$MgCO_3 \cdot 3H_2O$: 1. Method of Knorre [G. Knorre, Z. Anorg. Chem. **34**, 260 (1903)]. 2. Modification of method of Gjaldbaek [J. K. Gjaldbaek, Kgl. Landbohojskole Aarskrift **1921**, 245 (1921)]. In both, air is blown through a solution of equal volumes of 1 M $MgSO_4$ and 2 M $NaHCO_3$ for 48 h at 18 °C. Both methods gave a crystalline product which was freed from sulfate by washing with water.

Estimated Error:
T: precision ±0.1 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
[132]O. Haehnel, J. Prakt. Chem. **108**, 61 (1924).

Variables:
T/K = 273–333
$p(CO_2)$/bar = 2–56

Prepared by:
J. Vanderdeelen
H. Tsurumi
M. Ichikuni
Alex De Visscher

Experimental Values

Solubility of $MgCO_3 \cdot 3H_2O$

t = 18 °C			$p(CO_2)$ = 34 atm		
$p(CO_2)$/atm	Mass fraction $MgCO_3$ 100w	Molality[a] /mol kg^{-1}	t/°C	Mass fraction $MgCO_3$ 100w	Molality[a] /mol kg^{-1}
2.0	3.5	0.4433	0.0	8.58	1.2584
2.5	3.74	0.4762	5.0	8.32	1.2068
4.0	4.28	0.5516	10.0	7.93	1.1360
10.0	5.90	0.7898	18.0	7.49	1.0570
16.0	7.05	0.9708	30.0	6.88	0.9527
18.0	7.49	1.0421	40.0	6.44	0.8805
35.0	7.49	1.0578	50.0	6.18	0.8381
56.0	7.49	1.0720	60.0	5.56	0.7435

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

Constant solubility at $p(CO_2) > 18$ atm indicates precipitation of $Mg(HCO_3)_2$ (compiler). There were indications that this phase was indeed formed, but converted back to $MgCO_3 \cdot 3H_2O$ upon decompression.

Auxiliary Information

Method/Apparatus/Procedure:
Saturated solutions were prepared in a Pt vessel provided with an electrically driven Pt stirrer and contained in an autoclave. The mixture was stirred vigorously for 1 h, then left to settle for 1/2 h, after which the supernatant was withdrawn through a Pt tube. Equilibrium was always approached from supersaturation by decreasing the CO_2 partial pressure. Mg was determined as MgO after calcining a sample.

Source and Purity of Materials:
$MgCO_3 \cdot 3H_2O$: synthetic material without other details.

Estimated Error:
No estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
[133]G. Takahashi, Eisei Shikenjo Hokoku (Bull. Nat. Hyg. Sci.) **29**, 165 (1927).

Variables:
T/K = 271–333
$p(CO_2)$/bar = approx. 1

Prepared by:
J. Vanderdeelen
M. Tsurumi
M. Ichikuni

Experimental Values

Solubility of $MgCO_3$:
Solid phase: $MgCO_3 \cdot 3H_2O$ and $p(CO_2)$= 1 bar

t/°C	Solution density ρ/kg m^{-3} (exp.)	Mass fraction MgO 100w	Mass fraction CO_2 100w	Solution density ρ/kg m^{-3} (calc.)[a]	Molality $Mg(HCO_3)_2$ /mol kg^{-1} (compiler)
5	1040.7	1.530	3.232	1049.1	0.4029
10	1036.0	1.314	2.736	1040.6	0.3431
15	1032.0	1.143	2.270	1033.9	0.2964
20	1028.7	0.9858	2.109	1027.6	0.2541
25	1025.0	0.8654	1.839	1022.6	0.2220
30	1021.0	0.7634	1.572	1018.0	0.1950
35	1017.0	0.6780	1.381	1013.9	0.1727
40	1013.5	0.6017	1.206	1009.9	0.1528
45	1009.7	0.5323	1.044	1006.0	0.1348
50	1005.0	0.4718	0.922	1002.2	0.1192
55	1000.8	0.4083	0.833	998.2	0.1029
60	998.0	0.3648	0.764	994.6	0.0918

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

Solid phase: $MgCO_3 \cdot 5H_2O$

t/°C	Solution density ρ/kg m^{-3} (exp.)	Mass fraction MgO 100w	Mass fraction CO_2 100w	Solution density ρ/kg m^{-3} (calc.)[a]	Molality $Mg(HCO_3)_2$ /mol kg^{-1} (compiler)
−1.8	1041.1	1.526	3.410	1051.0	0.4020
0	1040.7	1.496	3.219	1049.5	0.3936
5	1039.5	1.423	2.942	1045.6	0.3732

t/°C	Solution density ρ/kg m^{-3} (exp.)	Mass fraction MgO 100w	Mass fraction CO_2 100w	Solution density ρ/kg m^{-3} (calc.)[a]	Molality $Mg(HCO_3)_2$ /mol kg^{-1} (compiler)
10	1038.3	1.363	2.962	1042.2	0.3565
15	1037.3	1.312	2.744	1039.1	0.3424
20	1036.3	1.256	2.606	1035.8	0.3270

[a]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

Auxiliary Information

Method/Apparatus/Procedure:
The solids were placed on a Dewar vessel provided with a mechanical stirrer and a CO_2(g) inlet. After equilibrium had been established, part of the supernatant was withdrawn, filtered and analyzed. Mg was determined gravimetrically as pyrophosphate, dissolved CO_2 as loss of mass after release of gas on adding a mineral acid to the solution.

Source and Purity of Materials:
$MgCO_3{\cdot}3H_2O$: prepared by mixing $MgSO_4$ and Na_2CO_3 solutions in proportion 9:1. The precipitate was washed with CO_2-saturated water. $MgCO_3{\cdot}5H_2O$: prepared as for $MgCO_3{\cdot}3H_2O$, but t/°C = 0 to 5. Dried precipitate contained (mass% with theoretical values in parentheses): CO_2: 24.69 (25.24); MgO: 23.19 (23.11); H_2O (by difference): 52.12 (51.65).

Estimated Error:
No estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
[134]O. Bär, Zentralbl. Mineral. Geol. Paleontol. **1**, 46 (1932).

Variables:
T/K = 291
$p(CO_2)$/bar = 0–2

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ at t = 18 °C

Mass conc. $MgCO_3$ ρ/g l^{-1}	Solution density[a] /kg m^{-3}	Molality $MgCO_3$[b] m/mol kg^{-1}	$p(CO_2)$ /atm	Solid phase
0.067[c]	998.7	8.0×10^{-4}	CO_2 free	Magnesite
0.08	998.7	9.5×10^{-4}	Air saturated[d]	Magnesite
0.7	999.6	8.3×10^{-3}	Air saturated[d]	Precipitated $MgCO_3$
27.8	1037.2	0.3340	1	$MgCO_3{\cdot}3H_2O$
35.1	1047.5	0.4233	2	$MgCO_3{\cdot}3H_2O$

[a]Compiler.
[b]Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).
[c]Average of four values: 0.065, 0.061, 0.069, and 0.072.
[d]Ambient air with $p(CO_2) = 3.1 \times 10^{-4}$ atm (compiler).

Auxiliary Information

Method/Apparatus/Procedure:
No information given.

Source and Purity of Materials:
$MgCO_3$: natural and precipitated solid.
$MgCO_3{\cdot}3H_2O$: no information given.

Estimated Error:
CO_2-free air: see table, footnote c.
Other measurements: no estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Sodium chloride; NaCl; [7647-14-5]
(3) Sodium sulfate; Na_2SO_4; [7757-82-6]
(4) Sodium carbonate; Na_2CO_3; [497-19-8]
(5) Sodium hydroxide; NaOH; [1310-73-2]
(6) Water; H_2O; [7732-18-5]

Original Measurements:
[135]J. Leick, Z. Anal. Chem. **87**, 415 (1932).

Variables:
T/K = 373
salts = variable at various mass concentrations

Prepared by:
J. Vanderdeelen

Experimental Values

Solubility of $MgCO_3$ in aqueous salt (2) solutions at 100 °C

Salt	Mass conc. salt ρ_2/g l^{-1}	Equilibration time /d	Alkalinity against PP[a] /meq l^{-1}[c]	MO[b] /meq l^{-1}[c]	MgO /meq l^{-1}[c]
None		2.5	0.50	1.50	1.50
		5.0	0.50	1.50	1.45
		24	0.20	0.40	0.40
		48	0.15	0.20	0.15
NaCl	5	2.5	0.75	2.30	2.35
	12.5	2.5	1.00	3.30	3.28
	25.0	2.5	1.10	3.70	3.73
	50.0	2.5	1.20	3.90	3.90
	12.5	16	0.25	0.30	0.35
Na_2SO_4	5	2.5	0.85	2.70	2.65
	12.5	2.5	1.40	4.20	4.10
	25.0	2.5	1.90	5.30	5.35
	50.0	2.5	2.50	6.50	6.35
	12.5	16	0.30	0.50	0.45
Na_2CO_3	5[d]	2.5	1.75	5.55	0.45
	12.5[d]	2.5	4.40	13.0	0.27
	50.0[d]	2.5	19.25	50.30	0.28
	12.5[d]	16	7.50	12.60	0.15

Salt	Mass conc. salt ρ_2/g l^{-1}	Equilibration time /d	Alkalinity against PP[a] /meq l^{-1c}	Alkalinity against MO[b] /meq l^{-1c}	MgO /meq l^{-1c}
NaOH	9.0[e]	2.5	2.90	9.50	0.45
	18.0[e]	2.5	9.10	18.50	0.40
	36.0[e]	2.5	25.60	36.25	0.30
	18.0[e]	16	12.25	18.10	0.15

[a]PP: phenolphthalein.
[b]MO: methyl orange.
[c]1 meq MgO = 20 mg MgO l^{-1} or 42 mg $MgCO_3$ l^{-1}.
[d]In meq l^{-1}, 1 meq l^{-1} = 0.5 mmol l^{-1}.
[e]In mmol l^{-1}.

A conversion of magnesium carbonate into hydroxide probably occurred during boiling which results from the instability of magnesium bicarbonate (authors); composition clearly depends upon equilibration time, confirming the instability of this compound (compiler).

Auxiliary Information

Method/Apparatus/Procedure:
To 0.5 g solid material, 400 ml distilled water, freed of CO_2, was added and boiled. After quick filtration, alkalinity in the filtrate was titrated with HCl versus phenolphthalein and methyl orange. Mg was precipitated as phosphate.

Source and Purity of Materials:
$MgCO_3$: synthetic, starting from magnesium bicarbonate, without further details.

Estimated Error:
No estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
[136]F. Halla, Z. Phys. Chem., Abt. A **175**, 63 (1936).

Variables:
T/K= 298 and 312
$p(CO_2)$/bar = approx. 1

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Solubility of $MgCO_3$; solid phase was $MgCO_3$ as magnesite

t/°C	$p(CO_2)$ /mm Hg	$p(CO_2)$ /atm	Amount conc. $MgCO_3$ c/mmol l^{-1}	Solution density[a] ρ/kg m^{-3}	Molality $MgCO_3$ m/mol kg^{-1}
25	726	0.955	16.5	999.3	0.01657
38.8	709	0.933	12.87	994.4	0.01298

[a]Calculated by compiler.

Auxiliary Information

Method/Apparatus/Procedure:
The solid was kept in suspension by a stream of CO_2(g) passing through the thermostated reaction bulb. After equilibrium was reached, 200 ml samples were titrated with H_2SO_4.

Source and Purity of Materials:
$MgCO_3$: natural gel-magnesite from Kraubath, Obersteiermark, Ca-free.

Estimated Error:
T: precision ±0.1 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
[137]L. G. Berg and L. A. Borisova, Zh. Neorg. Khim. **5**, 1283 (1960); Russ. J. Inorg. Chem. (in English) **5**, 618 (1960).

Variables:
T/K = 298
$p(CO_2)$/bar = about 1

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Solubility of $MgCO_3$ at t = 25 °C and $p(CO_2)$ = about 1 atm (given as Mg^{2+} by authors): 16.50 mmol kg^{-1} for magnesite as solid phase; 210 mmol kg^{-1} for nesquehonite as solid phase.

The authors state that the solubility at saturation is expressed in mmol per kg solution (m'_1). To convert to mmol per kg solvent (m_1), the following equation was used iteratively: $m_1 = m'_1/(1 - m'_1 M - m'_2 M_2)$ with M = molar mass of $Mg(HCO_3)_2$ in kg mol^{-1}, and index 2 refers to CO_2. Expressed in mmol per kg solvent, the solubility is 16.49 mmol kg^{-1} for magnesite, and 214.6 mmol kg^{-1} for nesquehonite.

Auxiliary Information

Method/Apparatus/Procedure:
Vessels with inlets for introduction of CO_2(g) were placed on a thermostat at 25 °C. The contents were agitated for 3–8 months until equilibrium was established. Mg was determined gravimetrically as pyrophosphate and with trilon titration against chromogen black ET-00; total alkalinity by acid titration with 0.1 M HCl (methyl orange indicator).

Source and Purity of Materials:
$MgCO_3$: prepared by calcining hydromagnesite at 300–350 °C and $p(CO_2)$ = 70–80 atm and commercial $NaHCO_3$.

Estimated Error:
T: precision ±0.5 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Sodium hydrogen carbonate; $NaHCO_3$; [144-55-8]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Magnesium chloride; $MgCl_2$; [7786-30-3]
(5) Carbon dioxide; CO_2; [124-38-9]
(6) Water; H_2O; [7732-18-5]

Original Measurements:
[138] A. M. Ponizovskii, N. M. Vladimirova, and F. A Gordon-Yanovskii, Zh. Neorg. Khim. **5**, 2587 (1960); Russ. J. Inorg. Chem. (in English) **5**, 1250 (1960).

Variables:
T/K = 273
$p(CO_2)$/bar = 2–10
Salt: various at variable concentrations

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Run 1. Solubility of lansfordite at $t = 0$ °C

$p(CO_2)$/ kg cm^{-2}	$p(CO_2)$[a]/atm	Mass fraction Mg 100w	Molality Mg^{2+}[b] m/mol kg^{-1}	Solid phase
2.0	1.93	1.16	0.5158	$MgCO_3{\cdot}5H_2O$
3.0	2.90	1.34	0.6042	$MgCO_3{\cdot}5H_2O$
4.0	3.87	1.47	0.6699	$MgCO_3{\cdot}5H_2O$
10	9.68	2.02	0.9654	$MgCO_3{\cdot}5H_2O$

[a] Authors data using 1 kg cm^{-2} = 0.968 atm.
[b] Assuming $Mg(HCO_3)_2$ as dominant species (see Sec. 1).

Run 2. Solubility of lansfordite at $t = 0$ °C and $p(CO_2) = 4$ kg cm^{-2} or 3.87 atm

Composition of the liquid phase								
Na^+		Mg^{2+}		Cl^-		HCO_3^-		
Mass% 100w_2	Molality[a] m_2/mol kg^{-1}	Mass% 100w_1	Molality[a] m_1/mol kg^{-1}	Mass% 100w_2	Molality[a] m_2/mol kg^{-1}	Mass% 100w_1	Molality[a] m_1/mol kg^{-1}	Solid phase
7.04	3.29	1.97	0.859	16.08	5.40	0.89	0.147	$NaCl + NaHCO_3 + MgCO_3{\cdot}5H_2O$
1.22	0.537	1.02	0.424			8.35	1.493	$NaHCO_3 + MgCO_3{\cdot}5H_2O$
1.36	0.599	1.07	0.445	0.60	0.170	7.94	1.414	$NaHCO_3 + MgCO_3{\cdot}5H_2O$
1.60	0.707	1.07	0.445	1.93	0.555	6.30	1.102	$NaHCO_3 + MgCO_3{\cdot}5H_2O$
6.96	3.252	1.94	0.814	15.88	5.325	0.87	0.144	$NaCl + NaHCO_3 + MgCO_3{\cdot}5H_2O$
		8.69	3.914	25.21	9.508	0.23	0.038	$MgCO_3{\cdot}5H_2O + MgCl_2{\cdot}6H_2O$
0.05	0.022	8.60	3.872	25.00	9.403	0.27	0.044	$NaCl + MgCO_3{\cdot}5H_2O + MgCl_2{\cdot}6H_2O$
0.14	0.061	8.60	3.872	25.41	9.609	0.18	0.029	$NaCl + MgCO_3{\cdot}5H_2O + MgCl_2{\cdot}6H_2O$

[a] Approximation.

Run 3. Solubility of lansfordite at $t = 0$ °C and $p(CO_2) = 10$ kg cm^{-2} = 9.68 atm

Composition of the liquid phase								
Na^+		Mg^{2+}		Cl^-		HCO_3^-		
Mass% 100w_2	Molality[a] m_2/mol kg^{-1}	Mass% 100w_1	Molality[a] m_1/mol kg^{-1}	Mass% 100w_2	Molality[a] m_2/mol kg^{-1}	Mass% 100w_1	Molality[a] m_1/mol kg^{-1}	Solid phase
0.93	0.408	1.96	0.823			12.32	2.303	$NaHCO_3 + MgCO_3{\cdot}5H_2O$
1.20	0.528	1.87	0.784	2.44	0.705	8.31	1.486	$NaHCO_3 + MgCO_3{\cdot}5H_2O$
2.88	1.289	2.00	0.840	8.85	2.739	2.50	0.420	$NaHCO_3 + MgCO_3{\cdot}5H_2O$
4.96	2.269	2.98	1.264	15.61	5.218	1.26	0.209	$NaCl + NaHCO_3 + MgCO_3{\cdot}5H_2O$

[a] Approximation.

The stable phase was nesquehonite above 12–15 °C and lansfordite below 12 °C. Molalities calculated by compiler. Only the data with a single solid phase were evaluated.

Auxiliary Information

Method/Apparatus/Procedure:
A plastic-lined steel autoclave was used, sealed at the bottom with a porous glass plate and provided with a needle valve to withdraw liquid samples. The lid held a thermometer pocket and two tubes, one for charging the reagents and flushing with CO_2(g), the other attached to a CO_2(g) cylinder through a return valve. Pressure was measured with a gauge. The autoclave was contained in a cooler and its contents were stirred.
Salts were pure grade.
Mg was determined by EDTA titration (chromogen black indicator), Cl^- by Mohr titration, HCO_3^- by acid titration with HCl. Equilibrium was attained in 2–3 days.

Source and Purity of Materials:
$MgCO_3 \cdot 5H_2O$: prepared from a solution of $NaHCO_3$ saturated with CO_2, to which a concentrated solution of $MgSO_4$ was added dropwise in an amount equivalent to the $NaHCO_3$. Nesquehonite started to crystallize in 24 h, continuing for 7–10 days. Crystals were filtered, washed in CO_2-saturated water, then ether. Crystal identity was checked by optical crystallography. The trihydrate transformed into pentahydrate in water below 12 °C.

Estimated Error:
T: precision ±0.2 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
[139]O. K. Yanat'eva and I. S. Rassonskaya, Zh. Neorg. Khim. **6**, 1424 (1961); Russ. J. Inorg. Chem. (in English) **6**, 730 (1961).

Variables:
T/K = 273–363
$p(CO_2)$/bar = approx. 1

Prepared by:
J. Vanderdeelen
M. Tsurumi
M. Ichikuni
Alex De Visscher

Experimental Values

Solubility of magnesium carbonate trihydrate and pentahydrate at $p(CO_2) \approx 1$ atm (elsewhere the authors describe the conditions as "under CO_2 at ~1 atm", which is an ambiguous statement).

t/°C	Specific $Mg(HCO_3)_2$ content m'/mmol kg^{-1} solution[a]	Density solution experimental ρ/g ml^{-1}	Molality $Mg(HCO_3)_2$ m/mmol kg^{-1} solvent[a]	Density solution calculated[b] ρ/kg m^{-3}	Solid phase
0	397.6	1.0470	423.4	1053.1	$MgCO_3 \cdot 3H_2O$
5	380.7	1.0456	404.1	1049.3	$MgCO_3 \cdot 3H_2O$
8	358.1	1.0419	378.7	1045.4	$MgCO_3 \cdot 3H_2O$
0	339.2	1.0404	358.0	1045.1	$MgCO_3 \cdot 5H_2O$
10	318.6	1.0381	334.9	1039.7	$MgCO_3 \cdot 5H_2O$
15	310.8	1.0372	326.2	1037.2	$MgCO_3 \cdot 5H_2O$
20	244.1	1.0285	253.5	1027.6	$MgCO_3 \cdot 3H_2O$
25	219.3	1.0249	226.9	1023.1	$MgCO_3 \cdot 3H_2O$
40	149.3	1.0156	152.8	1009.8	$MgCO_3 \cdot 3H_2O$
45	129.9	1.0132	132.5	1005.7	$MgCO_3 \cdot 3H_2O$
50	113.1	1.0128	115.1	1001.7	$MgCO_3 \cdot 3H_2O$
53.5	104.5	1.0116	106.2	999.2	$MgCO_3 \cdot 3H_2O$
55	100.3	1.0097	101.9	998.0	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$
60	78.4	1.0082	79.4	993.1	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$
70	45.5	1.0056	45.8	983.8	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$
90	17.5	1.0020	17.6	968.0	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$
14[c]	312.0				$MgCO_3 \cdot 3H_2O + MgCO_3 \cdot 5H_2O$
54.3[c]	102.0				$MgCO_3 \cdot 3H_2O + 4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$

[a]To convert specific Mg contents (m'_1) expressed as mol/kg solution to molalities (m_1) as mol/kg solvent with M the molar mass in kg mol^{-1}, the following equation was used: $m_1 = m'_1/(1 - m'_1 M - m'_2 M_2)$ where index 2 refers to CO_2 (compiler). It was assumed that $p(CO_2) = 1$ atm.
[b]According to compiler.
[c]Data were obtained graphically (authors).

Auxiliary Information

Method/Apparatus/Procedure:
Suspensions were stirred continuously in a thermostat for several days; equilibrium was reached in 7–8 h. The liquid was sampled periodically; total alkalinity was titrated with HCl (methyl orange indicator). Mg was determined as by Yanat'eva [O. K. Yanat'eva, Izv. Sekt. Fiz.-Khim. Anal. Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR **20**, 252 (1950)].

Source and Purity of Materials:
$MgCO_3 \cdot 3H_2O$: by mixing solutions of $MgSO_4$ and $NaHCO_3$. Salt was washed, then air-dried. Concentrated solutions of $Mg(HCO_3)_2$ at variable temperatures show branches according to crystallization of the tri- and the pentahydrate.

Estimated Error:
No estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Orignal Measurements:
[140]G. W. Morey, Am. Mineral. **47**, 1456 (1962).

Variables:
$T/K = 298–473$

Prepared by:
J. Vanderdeelen

Experimental Values

Solubility of $MgCO_3$

$t/°C$	Mass fraction $MgCO_3$ $10^6 w$	Molality $MgCO_3/mmol\ kg^{-1}$(compiler)
25	4.2	0.050
60	8.2	0.097
100	11.8	0.140
130	12.8	0.152
160	12.5	0.148
180	11.2	0.133
200	8.0	0.095

XRD showed that $MgCO_3$ was converted completely to $Mg(OH)_2$ above 150 °C, and that some crystals of sepiolite ($2MgO \cdot 3SiO_2 \cdot 2H_2O$) and dolomite were found at the outlet of the reactor. These extraneous phases were attributed to impurities in the magnesite. By titration with NaOH, free CO_2 in the exit water was: none below 150 °C, 0.5, 1, 3, and 7 ppm at 154, 165, 167, and 184 °C, respectively.

Auxiliary Information

Method/Apparatus/Procedure:
The apparatus is described by Morey [G. W. Morey and R. O. Fournier, Am. Mineral. **46**, 688 (1961)]. A stainless steel reaction tube, volume 10 ml, was closed at each end by a stainless steel filter. The tube was placed in a furnace and pure water, free of CO_2, was pumped through at 200 atm (above the vapor pressure of water), so that the water would remain liquid. Mg was determined by EDTA titration.

Source and Purity of Materials:
$MgCO_3$: magnesite from Brazil, crushed, sieved to 24–48 mesh.

Estimated Error:
No estimates possible.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Orignal Measurements:
[141]F. Halla and R. van Tassel, Radex-Rundschau, 42 (1964).

Variables:
$T/K = 294$ (average)
$p(CO_2)/bar$ = unknown

Prepared by:
J. Vanderdeelen
Alex De Visscher

Experimental Values

Solubility of magnesite (1) at $t/°C$ between 19 and 23, average 21 (authors), in the presence of a CO_2 gas phase

Solid phase	Dissolution time /d	Solubility $c_1/mmol\ l^{-1}$
Unknown	800	4.7
Natural magnesite	Unknown	16.0
Synthetic magnesite	141	2.3
Synthetic magnesite	191[a]	2.5
Synthetic magnesite	336	2.5[b]

[a]2.2 mmol l^{-1} $Mg(HCO_3)_2$ solution was used as the initial liquid phase to reduce the dissolution time.
[b]Authors indicate that the dissolved Mg concentration did not increase in the 145 days after the previous experiment.

Auxiliary Information

Method/Apparatus/Procedure:
CO_2 gas was washed in a 20% solution of $KHCO_3$ and then bubbled for 800 days through the magnesite suspension in run 1 and for 141 days in run 2. Presumably concentrations were found by acid titration.

Source and Purity of Materials:
$MgCO_3$: (1) Natural from Kraubach, Steiermark, Austria. Microscopic analysis showed non-crystalline material. Analysis (mass%): MgO: 46.0; CaO: 1.1, Fe_2O_3: 0.3.
(2) Synthetic. By heating 0.2 M $Mg(HCO_3)_2$ overnight in a closed vessel at 150 °C. Analysis (mass%): MgO, 47.2, 52.3 from loss on heating. XRD indicated very pure magnesite.

Estimated Error:
T: ±2 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Orignal Measurements:
[66]D. Langmuir, J. Geol. **73**, 730 (1965).

Variables:
T/K = 298
$p(CO_2)$/bar = 0.97

Prepared by:
J. Vanderdeelen

Experimental Values

For a nesquehonite suspension, the pH at equilibrium is 7.11 at 25 °C and $p(CO_2) = 0.97$ atm.

Auxiliary Information

Method/Apparatus/Procedure:
A few g of solid were placed in a 30 ml reaction vessel in 15 ml distilled water at controlled CO_2 partial pressure. After several days the pH was recorded.

Source and Purity of Materials:
$MgCO_3 \cdot 3H_2O$: synthetic nesquehonite was used: reagent-grade basic magnesium carbonate was dissolved in CO_2-saturated water at room temperature and filtered. The filtrate was degassed at 35 °C. A snowy product was obtained, "X-ray pure" and well crystallized.

Estimated Error:
T: ±0.1 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Carbon dioxide; CO_2; [124-37-9]
(5) Water; H_2O; [7732-18-5]

Orignal Measurements:
[142]W.F. Riesen, "Thermodynamische Untersuchungen am Quaternären System Ca^{2+}–Mg^{2+} – CO_2 – H_2O". Inauguraldissertation (Ph.D. dissertation) (University of Berne, Switzerland, 1969).

Variables:
T/K = 298.15 and 323.15
$p(CO_2)$/bar = 0.488–0.912
pH = 5.2–5.8 ($HClO_4$)
Salt: $NaClO_4$ (background electrolyte)

Prepared by:
E. Königsberger

Experimental Values

Solubility of magnesium carbonate at 25 °C and constant ionic strength $I = 3.0$ mol kg^{-1} (Na)ClO_4

Solid phase	$p(CO_2)$ /atm	$-\lg$(Molality H^+/mol kg^{-1})	Molality ΣMg^{2+} /mol kg^{-1}	$\lg {}^*K_{sp0}$ [a]
Magnesite (natural)	0.912	5.776	0.00889	9.46
	0.912	5.663	0.01349	9.42
	0.912	5.498	0.02748	9.39
	0.912	5.378	0.05284	9.44
	0.912	5.221	0.1030	9.41
			avg.	9.42 ± 0.03[b]
Magnesite (synthetic)	0.912	6.042	0.01047	10.06
	0.912	5.997	0.01219	10.04
	0.912	5.910	0.01849	10.05
	0.912	5.791	0.03020	10.02
	0.912	5.748	0.04046	10.06
	0.912	5.658	0.05395	10.01
			avg.	10.04 ± 0.02[b]
Nesquehonite	0.912	7.122	0.1268	13.31
	0.912	7.061	0.1683	13.31
	0.912	6.986	0.2051	13.24
	0.488	7.194	0.1371	13.21
			avg.	13.27 ± 0.05[b]

[a]${}^*K_{sp0} = [\Sigma Mg^{2+}]\, p(CO_2)/[H^+]^2$.
[b]Compiler.

Solubility of magnesium carbonate at 50 °C and constant ionic strength $I = 3.0$ mol kg^{-1} (Na)ClO_4

Solid phase	$p(CO_2)$ /atm	$-\lg$(Molality H^+/mol kg^{-1})	Molality ΣMg^{2+} /mol kg^{-1}	$\lg {}^*K_{sp0}$ [a]
Magnesite (natural)	0.834	5.586	0.00450	8.75
	0.834	5.474	0.00800	8.77
	0.834	5.224	0.02612	8.79
	0.834	5.083	0.05047	8.79
	0.834	4.978	0.07551	8.75
	0.834	4.910	0.1005	8.74
			avg.	8.77 ± 0.02[b]
Magnesite (synthetic)	0.834	5.767	0.01047	9.33
	0.834	5.764	0.01219	9.36
	0.834	5.663	0.01849	9.36
	0.834	5.631	0.03020	9.35
			avg.	9.35 ± 0.01[b]
Nesquehonite	0.834	7.072	0.0848	12.99
	0.834	6.862	0.1570	12.84
			avg.	12.92 ± 0.08[b]

[a]${}^*K_{sp0} = [\Sigma Mg^{2+}]\, p(CO_2)/[H^+]^2$.
[b] Compiler.

Auxiliary Information

Method/Apparatus/Procedure:
The percolation type solubility cell of Schindler *et al.* [P. Schindler, M. Reinert, and H. Gamsjäger, Helv. Chim. Acta **51**, 1845 (1968)] was used. Measurements were performed using the "pH variation method." Solid phases were equilibrated with $HClO_4$/$NaClO_4$ solutions of varying initial $HClO_4$ molality at constant ionic strength $I = 3.0$ mol kg^{-1} (Na)ClO_4. All equilibrium constants were calculated in terms of molalities. During each dissolution run, p[H] = $-\lg$(Molality H^+/mol kg^{-1}) was measured; constant p[H] indicated solubility equilibrium (equilibration times for magnesite were up to 6 weeks at 25 °C). Before and after each run, electrodes were calibrated in terms of molalities, using $HClO_4$/$NaClO_4$ solutions of constant I. Reference electrodes were connected via 'Wilhelm' salt bridges

($I = 3.0$ mol kg^{-1} $NaClO_4$), and liquid junction potentials were taken into account. Total Mg^{2+} molalities of the equilibrated solutions were determined by complexometric titration with EDTA. When $\lg\{[\Sigma Mg^{2+}]\, p(CO_2)\}$ was plotted vs. p[H], data fell on straight lines with slopes of -2, indicating that equilibrium was attained.

A striking result of this study was that natural and synthetic magnesite samples led to internally consistent but different solubility constants. The author also determined formation constants of magnesium (hydrogen-)carbonato complexes at $I = 3.0$ mol kg^{-1} (Na)ClO_4 using a coulometric method (see also Riesen *et al.*[99]). These complexes were found to increase the solubility of nesquehonite but not that of magnesite. Riesen[142] reported solubility constants of nesquehonite that were corrected for complex formation: $\lg {}^*K_{sp0} = 13.08 \pm 0.03$ for 25 °C and 12.77 ± 0.03 for 50 °C.

Königsberger *et al.*[78] derived a Pitzer model that allowed the calculation of solubility constants for these minerals at zero ionic strength. Appropriate combinations of (trace) activity coefficients of reacting species and water activities for the ionic medium resulted in corrections to $\lg {}^*K_{sp0}$ of -0.18 for magnesite and -0.31 for nesquehonite at 25 °C. Together with the solubility and dissociation constants of carbon dioxide, this results in $\lg K_{s0} = -8.92$ and -8.30 for natural and synthetic magnesite respectively (compiler). Both values are considerably lower than the values shown in Figs. 2 and 3.

For nesquehonite, the results for zero ionic strength and 25 °C are $\lg K_{s0} = -5.39$ (corrected for ion pairing) and $\lg K_{s0} = -5.20$ (without correction for ion pairing). It should be noted that the latter value may have a higher uncertainty because the activity coefficients of the ion pairs were not taken into account during the extrapolation to zero ionic strength. Nevertheless, there is a good agreement of these two values with the calculated curves shown in Figs. 6 and 7, respectively.

For 50 °C, similar calculations employing the temperature-dependent Pitzer model of Königsberger *et al.*[79] give the following results for zero ionic strength: $\lg K_{s0} = -9.67$ and -9.09 for natural and synthetic magnesite, respectively; $\lg K_{s0} = -5.82$ for nesquehonite corrected for ion pairing and $\lg K_{s0} = -5.67$ for nesquehonite without correction for ion pairing (compiler). Again, for magnesite both values are considerably lower than the curves shown in Figs. 2 and 3, while at least the first value for nesquehonite is in reasonable agreement with the calculated curve shown in Fig. 6. Although the Pitzer model is likely to have a larger uncertainty at 50 °C than at 25 °C, the temperature dependence of the solubility constants for magnesite is unusually large.

Source and Purity of Materials:

$MgCO_3$: (i) well crystallized natural sample from Trieben, Austria; (ii) sample synthesized according to Marc and Šimec [R. Marc and A. Šimec, Z. Anorg. Chem. **82**, 17 (1913)].

$MgCO_3{\cdot}3H_2O$: by slow degassing of CO_2 from a solution of $Mg(HCO_3)_2$.

Estimated Error:

T: ±0.1 K.

Components:

(1) Magnesium carbonate; $MgCO_3$; [546-93-0]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Perchloric acid; $HClO_4$; [7601-90-3]

(4) Carbon dioxide; CO_2; [124-37-9]

(5) Water; H_2O; [7732-18-5]

Orignal Measurements:

[143]G. Horn, Radex-Rundschau, 469 (1969).

Variables:

T/K = 298.15

$p(CO_2)$/bar = approx. 1

pH = 5.3–5.9 ($HClO_4$)

Salt: $NaClO_4$ (background electrolyte)

Prepared by:

E. Königsberger

Experimental Values

Solubility of magnesite at 25 °C and constant ionic strength $I = 3.0$ mol l^{-1} (Na)ClO_4

Initial Molarity H^+/mol l^{-1}	$p(CO_2)$ /atm	$-\lg$(Molarity H^+/mol l^{-1})	Molarity ΣMg^{2+}/mol l^{-1}	$\lg {}^*K_{sp0}$[a]
0.20000	0.9186	5.319	0.10180	9.61
0.19940	0.9120	5.297	0.10130	9.56
0.19940	0.9145	5.306	0.10060	9.58
0.08000	0.9165	5.494	0.04488	9.60
0.08000	0.9005	5.535	0.04417	9.67
0.08000	0.9145	5.483	0.04479	9.58
0.02285	0.9191	5.754	0.01518	9.65
0.02285	0.9125	5.746	0.01524	9.64
0.02285	0.9165	5.750	0.01549	9.65
0.01206	0.9108	5.822	0.01009	9.61
0.01206	0.9243	5.866	0.01082	9.73
0.01206	0.9243	5.845	0.01044	9.67
0.00382	0.9191	5.920	0.00675	9.63
0.00382	0.9125	5.937	0.00693	9.67
0.00382	0.9191	5.930	0.00682	9.66
			avg.	9.63 ± 0.05[b]

[a] ${}^*K_{sp0} = [\Sigma Mg^{2+}]\, p(CO_2)/[H^+]^2$.

[b] Compiler.

Auxiliary Information

Method/Apparatus/Procedure:

The percolation type solubility cell of Schindler *et al.* [P. Schindler, M. Reinert, and H. Gamsjäger, Helv. Chim. Acta **51**, 1845 (1968)] was used. Measurements were performed at 25 °C using the "pH variation method." Solid magnesite was equilibrated with $HClO_4/NaClO_4$ solutions of varying initial $HClO_4$ molarity at constant ionic strength $I = 3.0$ mol l^{-1} (Na)ClO_4. All equilibrium constants were calculated in terms of molarities. During each dissolution run, p[H] = $-\lg$(Molarity H^+/mol l^{-1}) was measured; p[H] values that were constant for 3 days indicated solubility equilibrium (equilibration times for magnesite were up to 5 weeks). Before and after each run, electrodes were calibrated in terms of molarities, using $HClO_4/NaClO_4$ solutions of constant I. Reference electrodes were connected via "Wilhelm" salt bridges ($I = 3.0$ mol l^{-1} $NaClO_4$). Total Mg^{2+} molarities of the equilibrated solutions were determined by complexometric titration with EDTA. When $-\tfrac{1}{2}\lg\{[\Sigma Mg^{2+}]\, p(CO_2)\}$ was plotted vs. p[H], data fell on straight lines with slopes of ca. 1, indicating that equilibrium was attained.

The author determined the formation constant of a magnesium hydrogencarbonato complex at $I = 3.0$ mol l^{-1} (Na)ClO_4 from the differences between measured $[\Sigma Mg^{2+}]$ and free $[Mg^{2+}]$ calculated from charge balance. The solubility constant corrected for complex formation was $\lg {}^*K_{sp0} = 9.58 \pm 0.06$,[143] which is not significantly different from the value $\lg {}^*K_{sp0} = 9.63 \pm 0.05$ calculated from the analytical data given above. It should be noted that equilibrium constants for homogeneous reactions calculated from heterogeneous equilibria are often of rather low accuracy.

Königsberger *et al.*[78] derived a Pitzer model that allowed the calculation of solubility constants for magnesite at zero ionic strength. Appropriate combinations of (trace) activity coefficients of reacting species and water activities for an ionic medium of $I = 3.5$ mol kg^{-1} (Na)ClO_4 (corresponding to $I = 3.0$ mol l^{-1} (Na)ClO_4) resulted in corrections to $\lg {}^*K_{sp0}$ of -0.13 for magnesite at 25 °C. Together with the solubility and dissociation constants of carbon dioxide and a correction for the change of concentration units (-0.06), this results in $\lg K_{s0} = -8.59$ at zero ionic strength and 25 °C (compiler). This value is considerably lower than the values shown in Figs. 2 and 3.

Source and Purity of Materials:
$MgCO_3$: sample synthesized according to Jantsch and Zemek [R. Jantsch and F. Zemek, Radex-Rundschau, 110 (1965)]. Chemical analysis in weight % (calculated values between brackets): MgO: 47.86 (47.82); CO_2: 52.16 (52.18). It is mentioned that X-ray analysis (Debye-Scherrer method) before and after equilibration with aqueous media only showed lines attributable to magnesite. Microscopic investigation revealed rather large rhombohedra typical for magnesite.

Estimated Error:
T: ±0.2 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Orignal Measurements:
[144]C. L. Christ and P. B. Hostetler, Am. J. Sci. **268**, 439 (1970).

Variables:
T/K = approx. 363
$p(CO_2)$/bar = 0.0274, 0.308, 0.312

Prepared by:
J. Vanderdeelen

Experimental Values

Approach to saturation for solid phase as $MgCO_3$

Run 1			Run 2			Run 3		
t/°C = 90.3, $p(CO_2)$ = 0.312 atm			t/°C = 91, $p(CO_2)$ = 0.0274 atm			t/°C = 90.5, $p(CO_2)$ = 0.308 atm		
Equil. time/h	pH	Molality Mg^{2+}/mol kg^{-1} × 10^5	Equil. time/h	pH	Molality Mg^{2+}/mol kg^{-1} × 10^5	Equil. time/h	pH	Molality Mg^{2+}/mol kg^{-1} × 10^5
0.5	5.55	66[a]	4.9	7.09	90[a]	0.5	4.88	7[a]
1.8	6.04	115[a]	46	7.00	90[a]	3.5	5.15	16[a]
2.8	6.12	136[a]	94	7.06	95[a]	7.7	5.35	22[a]
6.6	6.30	165[a]	196	7.11	99[a]	24	5.56	38[a]
23	6.26	193[a]	410	7.17	90	48	5.74	51[a]
48	6.29	202[a]	652	7.13	97	102	5.97	73[a]
96	6.30	210	935	7.11	91	168	6.06	86[a]
198	6.38	210	1180	7.25	88	265	6.21	108[a]
413	6.47	197	1391	7.21	107	488	6.29	129[a]
655	6.45	202	1682	7.18	86	751	6.29	131
938	6.44	193	1996	7.13	91	990	6.29	132
1182	6.42	202	2546	7.10	89	1351	6.39	141
1394	6.42	202	3265	7.11	106	1854	6.39	144
1685	6.41	172	3526	7.11	104	2573	6.32	154
1998	6.46	191				3367	6.31	160
2549	6.31	187				3911	6.30	174
3268	6.38	200						
3531	6.40	210						
Mean	6.40	198	Mean	7.15	95			
s.d.	0.05	7	s.d.	0.05	7			

[a]Plots of pH and $m(Mg^{2+})$ against time by the compiler showed that these values in the table could reasonably be deleted to find average values for columns 2, 3, 5, and 6. However, for columns 8 and 9, $m(Mg^{2+})$ rose rapidly to a shoulder value, then continued to increase with time, so that no clear averages could be calculated.

Auxiliary Information

Method/Apparatus/Procedure:
Magnesite was suspended in distilled and deionized water in a thermostated polypropylene vessel and stirred with a PTFE-coated magnetic stirrer. Pure CO_2(g) or a CO_2(g)-N_2 mixture containing 9.7 mol% CO_2, pre-saturated with water at the run temperature, was bubbled through the suspension. Determination of $p(CO_2)$ by Matheson gauge, pH by combination electrode. Samples were filtered through a 0.45 μm Millipore filter and analyzed for Mg by AA. XRD of magnesite before and after experiments did not differ significantly. Trace amounts of Fe (0 to 10^{-6} mol kg^{-1}), K^+ (ca. 10^{-4} mol kg^{-1}), Cl^- (ca. 10^{-4} mol kg^{-1}), and Ca^{2+} (ca. 1–14×10^{-5} mol kg^{-1}) were found in the filtrates.

Source and Purity of Materials:
$MgCO_3$: 1. Magnesite, Red Mountain, CA; dense, fine-grained (runs 1 and 2); 2. Magnesite, Snarum, Norway, aggregates of coarse cleavage fragments (run 3). Ground samples screened to 200–325 mesh/inch. XRD: no indication of other phases.

Estimated Error:
T: ±0.2–0.3 K.
Precision on $m(Mg^{2+})$: ±3 %.
pH: ±0.04.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Sodium carbonate; Na_2CO_3; [497-19-8]
(4) Water; H_2O; [7732-18-5]

Orignal Measurements:
[78]E. Königsberger, P. Schmidt, and H. Gamsjäger, J. Solution Chem. **21**, 1195 (1992).

Variables:
$T/K = 298.15$
$p(CO_2)/atm = 0.0088, 0.047, 0.108$
$m(Na_2CO_3)/mol\ kg^{-1} = 0–1.45$

Prepared by:
Alex De Visscher

Experimental Values

Solubility of $MgCO_3 \cdot 3H_2O$ (1) in aqueous Na_2CO_3 (3) solutions at 298.15 K

$p(CO_2)/atm$	$m_3/mol\ kg^{-1}$	Solubility, $m_1/mmol\ kg^{-1}$
0.0088	0	31
	0.1	12
	0.5	17
	0.6	21
	0.75	26
	0.8	29
	0.9	34
	1.0	39
	1.15	46
	1.45	51
0.047	0	58
	0.35	14
	0.7	22
0.108	0	76
	0.3	21
	0.6	21

Values of m_3 and m_1 were read from a figure in the original paper (compiler).

Auxiliary Information

Method/Apparatus/Procedure:
The percolation type solubility cell of Gamsjäger and Reiterer [H. Gamsjäger and F. Reiterer, Environ. Int. **2**, 419 (1979)] thermostated at 25 °C was used. Partial pressure of H_2O in the gas entering the vessel was kept nearly identical to the partial pressure of the gas leaving the vessel, by presaturation. During each dissolution run, pH was measured. Constant pH indicated equilibrium. Total Mg^{2+} molalities were determined by complexometric titration with EDTA.

Source and Purity of Materials:
Nesquehonite was prepared by aging a $Mg(HCO_3)_2$ solution at room temperature with slow degassing of CO_2. BET area was less than 0.5 $m^2\ g^{-1}$. Chemical analysis in weight % (calculated values between brackets): MgO: 29.17 (29.14); CO_2: 31.77 (31.80). It is mentioned that optical and scanning electron microscopy as well as X-ray analysis before and after equilibration with aqueous media showed no solid phases other than nesquehonite. CO_2 and N_2: "high purity."

Estimated Error:
T: ±0.05 K.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Carbon dioxide; CO_2; [124-37-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
[79]E. Königsberger, L. C. Königsberger, and H. Gamsjäger, Geochim. Cosmochim. Acta **63**, 3105 (1999).

Variables:
$T/K = 298.15–323.15$
$p(CO_2)/bar = $ approx. 1

Prepared by:
E. Königsberger

Experimental Values

Solubility of $MgCO_3$. Solid phase is $MgCO_3 \cdot 3H_2O$ and $p(CO_2) + p(H_2O) = 1$ atm. The results are shown in Fig. 3(a) of Königsberger *et al.*;[79] the numerical values given below were provided by the authors.

$t/°C$	$p(CO_2)/atm$	Molality $\Sigma Mg^{2+}/mol\ kg^{-1}$
25.00	0.968	0.2199
28.00	0.962	0.2074
31.00	0.955	0.1922
33.00	0.950	0.1810
35.00	0.944	0.1692
38.00	0.934	0.1595
41.00	0.922	0.1509
44.00	0.909	0.1382
47.00	0.894	0.1265
50.00	0.877	0.1196

Auxiliary Information

Method/Apparatus/Procedure:
The thermostated percolation type solubility cell of Gamsjäger and Reiterer [H. Gamsjäger and F. Reiterer, Environ. Int. **2**, 419 (1979)] was used. Partial pressure of H_2O in the gas entering the solubility vessel was kept nearly identical to the partial pressure of the gas leaving the vessel. This was achieved by presaturation of pure $CO_2(g)$ and using condensers, which were cooled to ca. 2 °C, on both the presaturation and solubility vessel. Equilibration times were 1 to 3 days, depending on the temperature. Total Mg^{2+} molalities were determined by complexometric titration with EDTA.

Source and Purity of Materials:
Nesquehonite was prepared according to the method described by Königsberger *et al.*[78]

Estimated Error:
T: ±0.05 K.

Components:	Original Measurements:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0] (2) Sodium chloride; NaCl; [7647-14-5] (3) Ammonium chloride; NH_4Cl; [12125-02-9] (4) Magnesium chloride; $MgCl_2$; [7786-30-3] (5) Potassium chloride; KCl; [7447-40-7] (6) Water; H_2O; [7732-18-5]	[145]M. Dong, W. Cheng, Z. Li, and G. P. Demopoulos, J. Chem. Eng. Data **53**, 2586 (2008).
Variables:	**Prepared by:**
T/K = 288.15–313.15 salts: various, at 0–4 mol l^{-1}	Alex De Visscher

Experimental Values

Solubility of $MgCO_3{\cdot}3H_2O$ (1) in water

t/°C	Molality $MgCO_3$/mmol kg^{-1}
25	0.009612
30	0.008782
40	0.008893

Data at higher temperatures were reported as well. However, solid samples from these experiments showed transformation to an amorphous form.

Solubility of $MgCO_3{\cdot}3H_2O$ (1) in aqueous NaCl (2) solutions

t/°C	c_2/mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_2/mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
15	0.1	1.0037	0.1002	13.43
	0.3	1.0101	0.3022	18.48
	0.5	1.0165	0.5064	21.72
	0.7	1.0270	0.7099	23.63
	0.9	1.0361	0.9151	25.55
	1.0	1.0364	1.0225	26.58
	1.5	1.0562	1.5487	28.68
	2.0	1.0758	2.0857	29.99
	2.5	1.0932	2.6397	30.53
	3.0	1.1113	3.2052	29.25
	3.5	1.1306	3.7795	28.53
	4.0	1.1455	4.3873	25.60
25	0.1	1.0012	0.1005	12.72
	0.3	1.0090	0.3026	16.41
	0.5	1.0165	0.5064	19.73
	0.7	1.0241	0.7120	21.42
	0.9	1.0320	0.9189	23.14
	1.0	1.0364	1.0225	22.82
	1.5	1.0563	1.5486	26.04
	2.0	1.0758	2.0857	26.50
	2.5	1.0932	2.6397	27.26
	3.0	1.1113	3.2052	27.32
	3.5	1.1306	3.7795	26.23
	4.0	1.1455	4.3873	25.21
35	0.1	1.0012	0.1005	11.91
	0.3	1.0052	0.3037	15.78
	0.5	1.0148	0.5073	18.02
	0.7	1.0202	0.7148	20.15
	0.9	1.0289	0.9218	21.66
	1.0	1.0333	1.0258	22.05
	1.5	1.0526	1.5545	24.09
	2.0	1.0720	2.0940	25.28
	2.5	1.0897	2.6494	25.89
	3.0	1.1078	3.2173	26.03
	3.5	1.1253	3.8012	25.17
	4.0	1.1432	4.3984	23.92

Solubility of $MgCO_3{\cdot}3H_2O$ (1) in aqueous NH_4Cl (3) solutions

t/°C	c_3/mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_3/mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
15	0.1	1.0011	0.1004	31.97
	0.3	1.0046	0.3035	55.13
	0.5	1.0105	0.5083	67.90
	0.7	1.0144	0.7165	83.09
	0.9	1.0184	0.9276	89.83
	1.0	1.0179	1.0369	92.62
	1.5	1.0273	1.5838	108.9
	2.0	1.0355	2.1540	122.4
	2.5	1.0446	2.7446	138.8
	3.0	1.0495	3.3745	149.2
	3.5	1.0563	4.0272	154.4
25	0.1	1.0013	0.1004	33.30
	0.3	1.0028	0.3040	55.89
	0.5	1.0092	0.5089	70.81
	0.7	1.0120	0.7183	82.84
	0.9	1.0160	0.9299	93.82
	1.0	1.0190	1.0357	98.36
	1.5	1.0259	1.5862	118.21
	2.0	1.0347	2.1558	132.90
	2.5	1.0400	2.7586	146.76
	3.0	1.0479	3.3806	155.98
	3.5	1.0517	4.0487	163.97
35	0.1	1.0003	0.1005	35.62
	0.3	1.0010	0.3046	59.16
	0.5	1.0057	0.5107	71.72
	0.7	1.0084	0.7209	89.31
	0.9	1.0129	0.9329	99.11
	1.0	1.0154	1.0396	102.01
	1.5	1.0227	1.5916	124.71
	2.0	1.0305	2.1656	141.22
	2.5	1.0396	2.7598	154.39
	3.0	1.0459	3.3882	168.54
	3.5	1.0523	4.0459	175.60

Solubility of $MgCO_3 \cdot 3H_2O$ (1) in aqueous $MgCl_2$ (4) solutions

t/°C	c_4 /mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_4 /mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
15	0.1	1.0057	0.1004	9.477
	0.3	1.0206	0.3024	11.68
	0.5	1.0375	0.5051	14.07
	0.7	1.0510	0.7111	15.30
	0.9	1.0661	0.9180	17.66
	1.0	1.0725	1.0232	18.71
	1.5	1.1065	1.5565	23.53
	2.0	1.1415	2.1029	27.71
	2.5	1.1767	2.6633	36.49
	3.0	1.2106	3.2434	41.85
	3.5	1.2438	3.8438	47.66
	4.0	1.2752	4.4725	61.03
25	0.1	1.0035	0.1006	15.59
	0.3	1.0184	0.3031	16.51
	0.5	1.0323	0.5078	18.24
	0.7	1.0471	0.7140	19.85
	0.9	1.0643	0.9197	21.43
	1.0	1.0703	1.0255	22.58
	1.5	1.1065	1.5565	27.13
	2.0	1.1417	2.1024	32.51
	2.5	1.1730	2.6739	38.48
	3.0	1.2052	3.2624	48.36
	3.5	1.2397	3.8612	53.69
	4.0	1.2714	4.4916	58.35
35	0.1	1.0021	0.1007	20.62
	0.3	1.0160	0.3038	21.24
	0.5	1.0321	0.5079	22.06
	0.7	1.0474	0.7137	22.98
	0.9	1.0614	0.9224	22.77
	1.0	1.0680	1.0280	25.88
	1.5	1.1018	1.5642	27.85
	2.0	1.1334	2.1209	30.02
	2.5	1.1716	2.6779	33.58
	3.0	1.2024	3.2724	35.65
	3.5	1.2354	3.8796	38.59
	4.0	1.2609	4.5452	41.18

Solubility of $MgCO_3 \cdot 3H_2O$ (1) in aqueous KCl (5) solutions at 25 °C

c_5/mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_5/mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
0.1	1.0016	0.1006	12.78
0.2	1.0066	0.2017	15.03
0.3	1.0114	0.3033	17.05
0.35	1.0123	0.3549	17.60
0.4	1.0149	0.4061	18.93
0.5	1.0206	0.5085	19.50
0.55	1.0214	0.5610	19.64
0.6	1.02552	0.6118	20.32
0.7	1.0290	0.7166	21.01
0.8	1.0336	0.8214	21.75
0.9	1.0394	0.9256	22.14
1.0	1.0434	1.0322	22.78

Auxiliary Information

Method/Apparatus/Procedure:
200 ml salt solution was introduced in Erlenmeyer flasks equipped with a magnetic stirrer and sealed with a glass stopper. After temperature equilibration in a thermostated water bath, the flask is open briefly to add 3 g of nesquehonite. Standard equilibration time was 6 h. Supernatant was filtered with 0.22 μm syringe filters. Solubility was measured either as Mg by complexometric titration with EDTA, or as C with the TOC method. The remaining solid phase was tested for transformations with X-ray diffraction.

Source and Purity of Materials:
Nesquehonite: synthesized from a 0.5 mol l^{-1} $MgCl_2$ solution and a 0.5 mol l^{-1} Na_2CO_3 solution, mixed at 40 °C. Precipitate was tested with X-ray diffraction. Needle-shaped crystals were obtained. By analyzing a known dissolved amount by complexometric titration, the purity was estimated at 99.4%.

Estimated Error:
T: precision 0.1 K.
Complexometric titration: error $< 0.5\%$.

Components:
(1) Magnesium carbonate; $MgCO_3$; [546-93-0]
(2) Sodium chloride; NaCl; [7647-14-5]
(3) Magnesium chloride; $MgCl_2$; [7786-30-3]
(4) Ammonium chloride; NH_4Cl; [12125-02-9]
(5) Lithium chloride; LiCl; [7447-41-8]
(6) Water; H_2O; [7732-18-5]

Original Measurements:
[146]M. Dong, Z. Li, J. Mi, and G. P. Demopoulos, J. Chem. Eng. Data **54**, 3002 (2009).

Variables:
T/K = 298, 308
salts: LiCl; various, in binary mixtures, at 0-4 mol l^{-1}

Prepared by:
Alex De Visscher

Experimental Values

Solubility of $MgCO_3 \cdot 3H_2O$ (1) in aqueous NaCl (2) + $MgCl_2$ (3) solutions

t/°C	c_2 /mol l^{-1}	c_3 /mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_2 /mol kg^{-1} (compiler)	m_3 /mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
25	0.2	0.05	1.0068	0.2019	0.0505	7.047
	0.2	0.1	1.0116	0.2019	0.1010	7.497
	0.2	0.15	1.0148	0.2023	0.1517	8.054
	0.2	0.2	1.0180	0.2026	0.2026	8.734
	0.2	0.25	1.0224	0.2027	0.2533	9.845
	0.2	0.3	1.0264	0.2028	0.3042	10.73
	0.2	0.35	1.0300	0.2030	0.3553	11.20
	0.2	0.4	1.0332	0.2034	0.4067	12.05
	0.2	0.45	1.0376	0.2034	0.4578	12.51
	0.2	0.5	1.0420	0.2035	0.5088	13.06
	0.2	0.55	1.0452	0.2038	0.5606	13.63
	0.2	0.6	1.0484	0.2042	0.6125	14.29

t/°C	c_2 /mol l^{-1}	c_3 /mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_2 /mol kg^{-1} (compiler)	m_3 /mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
35	0.2	0.05	1.0045	0.2024	0.0506	10.43
	0.2	0.1	1.0087	0.2025	0.1013	10.38
	0.2	0.15	1.0113	0.2030	0.1522	11.09
	0.2	0.2	1.0152	0.2032	0.2032	11.01
	0.2	0.25	1.0191	0.2033	0.2542	11.72
	0.2	0.3	1.0239	0.2033	0.3050	12.24
	0.2	0.35	1.0270	0.2037	0.3564	12.64
	0.2	0.4	1.0306	0.2039	0.4078	13.27
	0.2	0.45	1.0347	0.2040	0.4591	14.10
	0.2	0.5	1.0400	0.2039	0.5098	14.45
	0.2	0.55	1.0421	0.2045	0.5623	14.88
	0.2	0.6	1.0458	0.2047	0.6141	15.50

Solubility of $MgCO_3 \cdot 3H_2O$ (1) in aqueous $MgCl_2$ (3) + NH_4Cl (4) solutions

t/°C	c_3 /mol l^{-1}	c_4 /mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_3 /mol kg^{-1} (compiler)	m_4 /mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
25	0.2	0.1	1.0128	0.2023	0.1012	22.06
	0.2	0.2	1.0160	0.2028	0.2028	29.35
	0.2	0.3	1.0160	0.2039	0.3058	34.99
	0.2	0.4	1.0196	0.2043	0.4085	40.37
	0.2	0.5	1.0212	0.2050	0.5126	44.82
	0.2	0.6	1.0236	0.2057	0.6170	48.04
	0.2	0.7	1.0244	0.2066	0.7232	53.10
	0.2	0.8	1.0260	0.2074	0.8297	55.42
	0.2	0.9	1.0280	0.2082	0.9367	57.69
	0.2	1.0	1.0292	0.2091	1.0453	59.70
	0.2	1.3	1.0336	0.2116	1.3756	62.92
	0.2	1.5	1.0372	0.2132	1.5993	64.50
35	0.2	0.1	1.0100	0.2029	0.1015	24.99
	0.2	0.2	1.0132	0.2034	0.2034	32.35
	0.2	0.3	1.0140	0.2043	0.3065	39.19
	0.2	0.4	1.0152	0.2052	0.4104	45.44
	0.2	0.5	1.0184	0.2056	0.5141	49.55
	0.2	0.6	1.0212	0.2062	0.6185	53.99
	0.2	0.7	1.0208	0.2074	0.7259	59.16
	0.2	0.8	1.0240	0.2079	0.8315	63.16
	0.2	0.9	1.0252	0.2088	0.9394	65.79
	0.2	1.0	1.0272	0.2095	1.0475	67.35
	0.2	1.3	1.0304	0.2124	1.3803	70.02
	0.2	1.5	1.0344	0.2139	1.6041	71.44

Solubility of $MgCO_3 \cdot 3H_2O$ (1) in aqueous LiCl (5) solutions

t/°C	c_5/mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_5/mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
25	0.1	0.9988	0.1005	14.66
	0.2	1.0000	0.2017	17.32
	0.3	1.0040	0.3026	19.36
	0.4	1.0064	0.4043	21.25
	0.5	1.0108	0.5053	22.77
	0.6	1.0112	0.6087	24.48
	0.7	1.0136	0.7114	25.43
	0.8	1.0144	0.8159	27.35
	0.9	1.0204	0.9163	28.18
	1.0	1.0204	1.0225	29.18
	1.3	1.0268	1.3379	32.00
	1.5	1.0320	1.5489	33.76
35	0.1	0.9948	0.1010	16.02
	0.2	0.9976	0.2022	20.43
	0.3	1.0004	0.3037	21.49
	0.4	1.0036	0.4054	25.92
	0.5	1.0052	0.5081	26.75
	0.6	1.0072	0.6111	31.35
	0.7	1.0104	0.7138	32.32
	0.8	1.0128	0.8173	36.06
	0.9	1.0152	0.9211	37.43
	1.0	1.0172	1.0258	39.44
	1.3	1.024	1.3417	40.59
	1.5	1.0304	1.5515	43.27

Solubility of $MgCO_3 \cdot 3H_2O$ (1) in aqueous $MgCl_2$ (3) + LiCl (5) solutions

t/°C	c_3 /mol l^{-1}	c_5 /mol l^{-1}	Solution density ρ/kg l^{-1} (authors)	m_3/mol kg^{-1} (compiler)	m_5/mol kg^{-1} (compiler)	Solubility $MgCO_3$ m_1/mmol kg^{-1}
25	0.5	0.1	1.0356	0.5083	0.1017	12.88
	0.5	0.2	1.0372	0.5096	0.2038	12.99
	0.5	0.3	1.0392	0.5108	0.3065	13.11
	0.5	0.4	1.0424	0.5113	0.4091	13.17
	0.5	0.5	1.0440	0.5127	0.5127	13.26
	0.5	0.6	1.0472	0.5133	0.6159	13.37
	0.5	0.7	1.0492	0.5144	0.7202	13.51
	0.5	0.8	1.0516	0.5154	0.8247	13.48
	0.5	0.9	1.0528	0.5170	0.9307	13.70
	0.5	1.0	1.0552	0.5180	1.0361	13.96
	0.5	1.3	1.0620	0.5212	1.3552	14.20
	0.5	1.5	1.0676	0.5228	1.5684	14.41
35	0.5	0.1	1.0324	0.5099	0.1020	13.71
	0.5	0.2	1.0344	0.5111	0.2044	14.01
	0.5	0.3	1.0368	0.5120	0.3072	14.18
	0.5	0.4	1.0392	0.5130	0.4104	14.42
	0.5	0.5	1.0420	0.5138	0.5138	14.57
	0.5	0.6	1.0440	0.5150	0.6179	14.89
	0.5	0.7	1.0464	0.5159	0.7223	15.14
	0.5	0.8	1.0484	0.5171	0.8274	15.21
	0.5	0.9	1.0500	0.5185	0.9334	15.47
	0.5	1.0	1.0520	0.5198	1.0395	15.63
	0.5	1.3	1.0580	0.5234	1.3609	15.90
	0.5	1.5	1.0648	0.5243	1.5730	16.10

Auxiliary Information

Method/Apparatus/Procedure:
200 ml salt solution was introduced in Erlenmeyer flasks equipped with a magnetic stirrer and sealed with a glass stopper. After temperature equilibration in a thermostated water bath, the flask is open briefly to add 3 g of nesquehonite. Standard equilibration time was 6 hours. Supernatant was filtered with 0.22 μm syringe filters. Solubility was measured either as Mg by complexometric titration with EDTA, or as C with the TOC method. The remaining solid phase was tested for transformations with X-ray diffraction.

Source and Purity of Materials:
Nesquehonite: synthesized from a 0.5 mol l^{-1} $MgCl_2$ solution and a 0.5 mol l^{-1} Na_2CO_3 solution, mixed at 40 °C. Precipitate was tested with X-ray diffraction. Needle-shaped crystals were obtained. By analyzing a known dissolved amount by complexometric titration, the purity was estimated at 99.4 %.[145]

Estimated Error:
T: precision 0.1 K.
Complexometric titration: error < 0.5 %.[145]

Acknowledgments

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