

# IUPAC-NIST Solubility Data Series. 92. Metal Carbonates. Part 1. Solubility and Related Thermodynamic Quantities of Cadmium(II) Carbonate in Aqueous Systems

**H. Gamsjäger, Editor<sup>a)</sup>**

*Montanuniversität Leoben, 8700 Leoben, Austria*

**M. C. F. Magalhães, Editor<sup>b)</sup>**

*Department of Chemistry and CICECO, University of Aveiro, 3810 Aveiro, Portugal*

**E. Königsberger, Editor<sup>c)</sup>**

*School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, Western Australia 6150, Australia*

**K. Sawada, Editor<sup>d)</sup>**

*Department of Chemistry, Niigata University, 950-2181 Niigata, Japan*

**B. R. Churagulov, Compiler**

*Department of Chemistry, Moscow State University, Vorobjevy Gory, Moscow RF-119899, Russia*

**P. Schmidt, Compiler**

*Dorfstrasse 30 oII, A-8041 Graz, Austria*

**D. Zeng, Compiler**

*Qinghai Institute of Salt Lakes, Xinning Road, No. 18, Xining 810008, China*

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This paper, devoted to cadmium(II) carbonate, is the first in a series dedicated to the solubility of compounds relevant to mobility of metals in the environment. Here, we present compilations and critical evaluation of the experimental solubility data for cadmium(II) carbonate, otavite, in aqueous ternary and higher-order systems. The solubility of cadmium(II) carbonate depends on temperature, carbon dioxide partial pressure, pH, the presence of complexing ions, and ionic strength of the solution. Papers referring to solubility of cadmium(II) carbonate have been published since 1901; the thorough search of the literature in this field covered the period from 1901 through 2009. The compilation of the available experimental data is introduced with a critical evaluation. The evaluation of the experimental data considers the possible correlation between the data obtained under similar experimental conditions of temperature, carbon dioxide partial pressure, electrolyte, and ionic strength. Those experiments where the solid phase was well identified and the interactions between the electrolyte and the dissolved cadmium(II) ion were considered practically negligible were used to determine the thermodynamic properties of the solid cadmium(II) carbonate. Recommended values for the thermodynamic quantities are  $\lg^* K_{ps0}^\circ = 6.11 \pm 0.10$ ,  $\Delta_f G^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(674.3 \pm 0.6) \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(752.2 \pm 0.8) \text{ kJ mol}^{-1}$ ,  $S^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = (103.9 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1}$ . © 2011 American Institute of Physics. [doi:10.1063/1.3645087]

Key words: cadmium(II) carbonate; solubility; solubility product; Gibbs energy of formation; enthalpy of formation; entropy.

<sup>a)</sup> Author to whom correspondence should be addressed: Electronic mail: [gamsjaeg@mu-leoben.at](mailto:gamsjaeg@mu-leoben.at).

<sup>b)</sup> Electronic mail: [mclara@ua.pt](mailto:mclara@ua.pt).

<sup>c)</sup> Electronic mail: [e.koenigsberger@murdoch.edu.au](mailto:e.koenigsberger@murdoch.edu.au).

<sup>d)</sup> Electronic mail: [sawada@sc.niigata-u.ac.jp](mailto:sawada@sc.niigata-u.ac.jp).

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## 1. Preface

This paper, devoted to cadmium(II) carbonate, is the first in a series dedicated to the solubility of compounds relevant to the mobility of metals in the environment. Here are presented compilations and critical evaluations of the experimental solubility data for cadmium(II) carbonate, otavite, in aqueous ternary and higher-order systems. By thoroughly searching the literature published between 1901 and 2009, 18 papers<sup>1–18</sup> referring to experimental work on solubility of cadmium(II) carbonate have been found. In a previous compilation on some sparingly soluble salts of zinc(II) and cadmium(II) in water and in aqueous electrolyte solutions, carried out by Clever *et al.*<sup>19</sup> in 1992, the solubility of cadmium(II) carbonate was included. These authors also had access to a preprint of Stipp *et al.*'s careful work on cadmium(II) carbonate solubility, which was subsequently published in 1993.<sup>14</sup> Thus, Ref. 19 provided a valuable basis for the present review.

Due to the characteristics of the carbonate system, the most reliable results must be obtained from ternary or higher-order aqueous systems. In fact, the literature search showed that no solubility data for the binary system (solid + water) have ever been measured.

The compilation of the available experimental data is introduced with a critical evaluation. Recommendations for solubility measurements and evaluations involving sparingly soluble ionic compounds have been summarized by Gamsjäger and Königsberger.<sup>20</sup> The critical analysis of the published experimental data focuses on:

- verification of the purity and crystallinity of the solid used before and after the experiment;
- description of the experimental design focusing on reagents used, experimental methods, and temperature;
- in the case of the controlled atmosphere systems, the partial pressure of the carbon dioxide over the aqueous solution; and
- experimental determination of all the relevant chemical parameters (concentrations or molalities of the dissolved ions).

The evaluation of the experimental data considers the possible correlation between the data obtained under similar experimental conditions of temperature, carbon dioxide partial pressure, background electrolyte, and ionic strength. Those experiments<sup>5,12–14,16,17</sup> where the solid phase was well identified and the interactions between the electrolyte and the dissolved cadmium(II) ion were considered practically negligible were used to determine the thermodynamic properties of the solid cadmium(II) carbonate.

To describe the dependence of the solubility of sparingly soluble ionic solids on solution composition, the appropriately generalized solubility constant (definition in Ref. 21) is used. According to the Guidelines of the IUPAC-NIST Solubility Data Series,<sup>22</sup> it provides information on Gibbs energy of formation of ionic solids. To obtain the standard solubility constant valid at ionic strength  $I = 0 \text{ mol kg}^{-1}$  from the

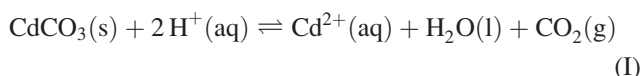
solubility data determined in ionic media containing non-complexing electrolytes of an ionic strength  $I$  in excess of the interacting ionic species, it is recommended to extrapolate the experimental solubility constants using the Brønsted-Guggenheim-Scatchard specific ionic interaction (SIT) model. This model predicts a linear relationship between the left-hand side of Eq. (1) and the molality-based stoichiometric ionic strength  $I$  ( $= \frac{1}{2} \sum_i z_i^2 m_i$ ) of the background 1:1 electrolyte.<sup>22</sup> Note that the left-hand side of Eq. (1) contains the measured  $\lg^* K_{ps0}$ ,<sup>e</sup> the ionic charge  $z$  ( $\Delta z^2 = 2$ ), and the Debye-Hückel term,  $D = \frac{A\sqrt{I}}{1+B\sqrt{I}}$

$$\lg^* K_{ps0} - \Delta z^2 D + \lg a_{\text{H}_2\text{O}} = \lg^* K_{ps0}^\circ - \Delta \varepsilon I, \quad (1)$$

where  $A = 0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  and  $B = 1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ , at 298.15 K, and  $a_{\text{H}_2\text{O}}$  is the activity of water. The reaction interaction coefficient  $\Delta \varepsilon = \varepsilon(\text{Cd}^{2+}, \text{ClO}_4^-) - 2\varepsilon(\text{H}^+, \text{ClO}_4^-)$  (for the case of solutions containing perchlorate as non-complexing ion) and the solubility constant  $\lg^* K_{ps0}^\circ$  at  $I = 0$  can be obtained as slope and intercept, respectively, of a linear least-squares fit to the data.<sup>22</sup>

The solubility constant can be calculated from thermodynamic data obtained by other methods than solubility measurements. The first value published for the solubility product of cadmium(II) carbonate, at 298.15 K, was calculated by Kelley and Anderson<sup>23</sup> from the relations  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  and  $-\Delta_{\text{sln}} G^\circ(T)/RT = \ln K_{s0}^\circ$ , where  $\Delta_{\text{sln}} G^\circ = \Delta_f G^\circ(\text{Cd}^{2+}) + \Delta_f G^\circ(\text{CO}_3^{2-}) - \Delta_f G^\circ(\text{CdCO}_3)$ . The entropy of formation of cadmium(II) carbonate was calculated from the reaction of cadmium(II) carbonate decomposition using the entropy of reaction at 298.15 K, the entropy of cadmium(II) oxide, and the entropy of carbon dioxide. The value of the entropy of cadmium(II) carbonate obtained by Kelley and Anderson<sup>23</sup> ( $105.4 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is similar to that proposed in this paper calculated by a completely different and independent method. However, the considerable uncertainty in the values then published for the enthalpy of formation for cadmium(II) oxide, associated with an unfavorable choice of that enthalpy of formation, originated in a low value for the Gibbs energy of  $\text{CdCO}_3$  formation as well as the low value ( $\lg K_{s0}^\circ = -13.74$ ) proposed by these authors for the solubility product of cadmium(II) carbonate.

In order to avoid the use of the stability constant for the reaction of formation of the cadmium(II) carbonate aqueous species ( $\text{CdCO}_3(\text{aq})$ ), whose value is still provisional,<sup>24</sup> the calculations of the solubility constant  $^*K_{ps0}$  of reaction I:



were carried out with the experimental values obtained at  $\text{pH} < 8$ . Powell *et al.*<sup>24</sup> report that the ion  $\text{Cd}^{2+}$  is the domi-

nant species until  $\text{pH} \leq 8.6$ , but they remark on the large uncertainty of the stability (formation) constants for the  $\text{Cd}^{2+}$ -carbonato complexes which has implications on reliable speciation. For  $\text{pH} > 9.5$ , Powell *et al.*<sup>24</sup> show that more than 95% of the total dissolved cadmium(II) exists in aqueous solution as  $\text{CdCO}_3(\text{aq})$ . On the other hand, only four authors<sup>3,9,12,18</sup> published solubility data for  $\text{pH} > 8$ , and Rai *et al.*<sup>12</sup> showed that for  $\text{pH} > 12$  cadmium(II) hydroxide is a solid phase thermodynamically more stable than cadmium(II) carbonate.

The first experimental value found for the solubility of cadmium(II) carbonate was determined by Immerwahr<sup>1</sup> in 1901 using an electrochemical cell consisting of metallic cadmium as cadmium(II) ion-sensitive electrode and the "normal" calomel electrode as reference electrode. Unfortunately, the experimental set-up was not quite appropriate and the conditions to which the reported solubility refers are ambiguous. Nevertheless, Immerwahr's idea to determine solubility products using electrochemical cells was a seminal one. Later Saegusa<sup>2</sup> determined the solubility of cadmium(II) carbonate measuring also electrochemical potentials, and his result is analyzed in the critical evaluation.

The majority of the experimental data were determined for the temperature of 298.15 K and 101.325 kPa total pressure, however, a few data were determined at other temperatures and pressures. Karnaukhov *et al.*<sup>6</sup> made measurements of solubility only at 291.15 K, Cecal and Ciuchi<sup>11</sup> measured the solubility only at 293.65 K, Lake and Gooding<sup>3</sup> determined the solubility also at 273.15 and 323.15 K, Saegusa<sup>2</sup> determined the solubility also at 308.15 K, Stipp *et al.*<sup>14</sup> measured the solubility also at 278.15 and 323.15 K and concluded that there was no variation of the solubility in that range of temperatures, Gamsjäger *et al.*<sup>15</sup> also concluded that the solubility constant  $\lg^* K_{ps0}^\circ$  could be considered constant until the temperature of 348.15 K. Shlyapnikov and Stern<sup>7,8</sup> made measurements also at the temperature of 473.15 K and pressures of 5.0 and 10.0 MPa, being the only experimental data published for these high pressures and temperature.

All published data used water as the only solvent, with the exception of the work of Cecal and Ciuchi.<sup>11</sup> These authors measured the solubility of cadmium(II) carbonate in mixtures of water-methanol, water-ethanol and water-propan-2-ol. As these are the only data published under these experimental conditions, it is impossible to make a critical evaluation of the results.

A set of experiments<sup>1,4,7-9,11,17</sup> was done in aqueous medium containing chloride in equilibrium with solid cadmium(II) carbonate. In aqueous solutions containing chlorides with  $\text{pH} < 8.5$ , it is necessary to take into account the formation of cadmium(II)-chlorido complexes<sup>24</sup> that increase the solubility of the cadmium(II) carbonate. The extent of the chloride complexation depends not only on the pH but also on the chloride concentrations in solution. Each experiment was done under different physical (temperature and pressure) and chemical (solutions composition) conditions, thus the critical analysis has to be done case by case.

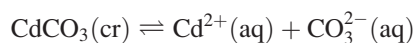
<sup>e</sup> $^*K_{ps0}$  is the representation of the solubility product,  $p$  indicates that a gas is involved in the equilibrium, 0 that the central metal ion has no ligands, and <sup>\*</sup> that a proton is involved in the equilibrium.<sup>22</sup>

## 2. Solubility in the System CdCO<sub>3</sub> + CO<sub>2</sub> + Non-Complexing Electrolytes + H<sub>2</sub>O

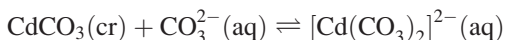
### 2.1. Critical evaluation of the solubility of CdCO<sub>3</sub> in acidic aqueous solutions

Components:	Evaluators:
(1) Cadmium(II) carbonate; CdCO <sub>3</sub> ; [513-78-0]	H. Gamsjäger, Lehrstuhl für Physikalische Chemie,
(2) Carbon dioxide; CO <sub>2</sub> ; [124-38-9]	Montanuniversität Leoben, Leoben, Austria
(3) Sodium perchlorate; NaClO <sub>4</sub> ; [7601-89-0]	E. Königsberger, School of Chemical and Mathematical
(4) Potassium perchlorate, KClO <sub>4</sub> ; [7778-74-7]	Sciences, Murdoch University, Murdoch, Australia
(5) Perchloric acid; HClO <sub>4</sub> ; [7601-90-3]	August 2010
(6) Sodium nitrate; NaNO <sub>3</sub> ; [7631-99-4]	
(7) Nitric acid; HNO <sub>3</sub> ; [7697-37-2]	
(8) Water; H <sub>2</sub> O; [7732-18-5]	

The solubility of cadmium(II) carbonate, CdCO<sub>3</sub>, in aqueous solutions according to reactions such as



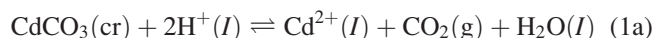
or



is based on its standard Gibbs energy of formation  $\Delta_f G_m^\circ$  (CdCO<sub>3</sub>, cr, 298.15 K). A reliable method for the determination of solubility constants as well as the standard Gibbs energy of formation of sparingly soluble metal carbonates involves solubility and electrode potential measurements. The same ionic medium is employed as solvent when both solubility and redox equilibria are studied. The first metal carbonate investigated by this method was otavite,<sup>5</sup> CdCO<sub>3</sub>.

#### $\lg^* K_{ps0}$ and $\Delta_f G^\circ$ (CdCO<sub>3</sub>, cr, 298.15 K)

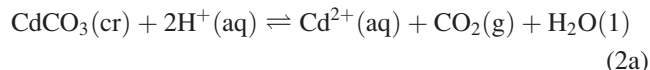
At constant ionic strength  $I$  of an inert electrolyte, for example NaClO<sub>4</sub>, the solubility constant according to Eqs. (1a)–(1c) can be calculated from concentrations (or molalities) directly, as the activity coefficients remain essentially constant,



$$\lg^* K_{ps0} = \lg\{m^\circ m_{\text{Cd}^{2+}} p_{\text{CO}_2} / [p^\circ (m_{\text{H}^+})^2]\} \quad (1b)$$

$$\Delta_{\text{sln}} G^\circ(I) = -RT \ln(10) \lg^* K_{ps0}, \quad (1c)$$

where  $m^\circ = 1 \text{ mol kg}^{-1}$  and  $p^\circ = 1 \text{ bar} = 0.1 \text{ MPa}$ . Thermodynamic standard quantities of ions refer, however, to infinite dilution as indicated by the equations,



$$\lg^* K_{ps0}^\circ = \lg \left[ a_{\text{Cd}^{2+}} a_{\text{H}_2\text{O}} f_{\text{CO}_2} / (a_{\text{H}^+})^2 \right] \quad (2b)$$

$$\Delta_{\text{sln}} G^\circ = -RT \ln(10) \lg^* K_{ps0}^\circ. \quad (2c)$$

In Eq. (2b),  $a_i$  is the activity of  $i$  and  $f_{\text{CO}_2}$  is the fugacity of carbon dioxide. If  $p_{\text{tot}} \leq 1 \text{ bar}$ ,  $f_{\text{CO}_2} \approx p_{\text{CO}_2}$ . As the standard Gibbs energies of formation of CdCO<sub>3</sub>(cr), CO<sub>2</sub>(g), and H<sub>2</sub>O(l) are the same in Eqs. (1a) and (2a), the following relationship between pairs of solubility constants, standard electrode potentials, and equilibrium vapor pressures of aqueous electrolyte medium and pure water ensues.

$$\lg^* K_{ps0}^\circ = \lg^* K_{ps0} + \lg(p_{\text{H}_2\text{O}}^I / p_{\text{H}_2\text{O}}^*) + \frac{2F}{RT \ln(10)} (E_i^{\circ'} - E_0^\circ) \quad (3)$$

In Eq. (3),  $p_{\text{H}_2\text{O}}^I / p_{\text{H}_2\text{O}}^* = a_{\text{H}_2\text{O}}$ , the water activity of the electrolyte medium,  $E_i^{\circ'}$  and  $E_0^\circ$  are the standard potentials of the Cd<sup>2+</sup> | Cd electrode in the electrolyte medium and at infinite dilution, respectively.

The water activity of an electrolyte mixture, containing NaClO<sub>4</sub> of molality  $m = I$  as the supporting electrolyte, is given by the equation,

$$\lg a_{\text{H}_2\text{O}} = -2 I \varphi_m M(\text{H}_2\text{O}) / \ln(10), \quad (4)$$

where  $\varphi_m$  is the osmotic coefficient (on molality basis) of the NaClO<sub>4</sub> solution and  $M(\text{H}_2\text{O})$  the molar mass of water. The osmotic coefficients of sodium perchlorate solutions have been taken from Ref. 25 and the following fitting equation was obtained and used in this critical evaluation

$$\lg a_{\text{H}_2\text{O}} = -\frac{2IM(\text{H}_2\text{O})(1+k_1I)}{(1+k_2I+k_3I^2)\ln(10)}, \quad (5)$$

where  $k_1 = 10.6627 \text{ kg mol}^{-1}$ ,  $k_2 = 12.1156 \text{ kg mol}^{-1}$ , and  $k_3 = -0.3416 \text{ kg}^2 \text{ mol}^{-2}$ .

For the determination of the standard electrode potential Cd<sup>2+</sup> | Cd, it is experimentally advantageous to use saturated cadmium amalgam as a Cd<sup>2+</sup> ion-selective electrode. The electrode potential of saturated cadmium amalgam vs. pure cadmium is independent of ionic strength, see Eqs. (6a) and (6b), and has been determined definitively by Parks and La Mer,<sup>26</sup> whose results were consistent with those of Getman.<sup>27</sup>



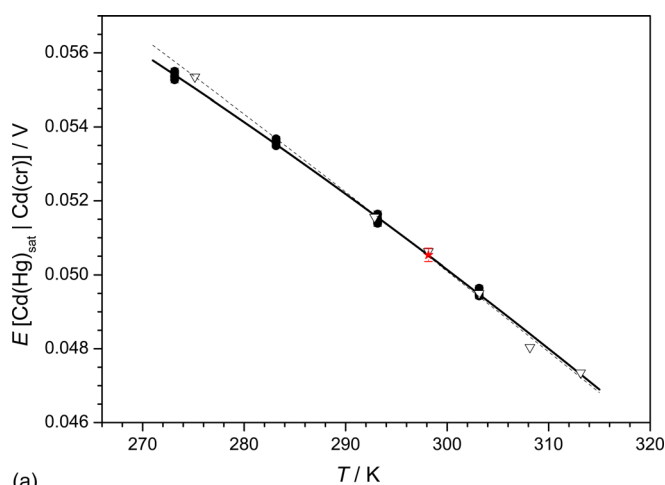
$$\Delta_f G^\circ[\text{Cd}(\text{Hg, satd})] = 2F E^\circ[\text{Cd}|\text{Cd}(\text{Hg, satd})] \quad (6b)$$

The results of Parks and La Mer<sup>26</sup> were also used by Longhi *et al.*<sup>28</sup> for their study on thermodynamic quantities of the

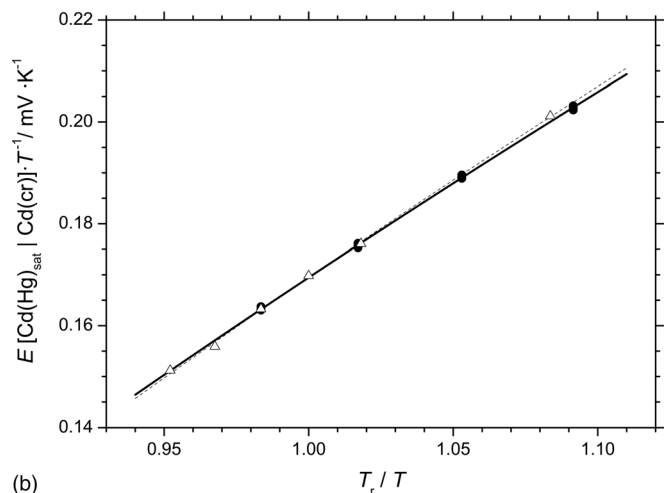
cadmium–amalgam electrode in aqueous media. The standard value of  $E^\circ[\text{Cd}|\text{Cd}(\text{Hg, satd})]$  at  $T = 298.15$  K has been calculated by empirical fitting equations:  $E^\circ[\text{Cd}|\text{Cd}(\text{Hg, satd})]/V = a + b(\theta/^\circ\text{C}) + c(\theta/^\circ\text{C})^2 + d(\theta/^\circ\text{C})^3$  (Ref. 26) and  $E^\circ[\text{Cd}|\text{Cd}(\text{Hg, satd})]/V = A + B(T/\text{K}) + C(T/\text{K})^2$  (Ref. 28), respectively. In this work, Ulich's<sup>29</sup> second approximation ( $\partial\Delta_{r(6a)}C_p/\partial T = 0$ ) was preferred as a semi-empirical fitting equation, see Fig. 1(a). It is noted in passing that Ulich's<sup>29</sup> second approximation is equivalent to a three-term Clarke–Glew equation,<sup>21</sup> see Fig. 1(b). Thus, its advantage is that the fit parameters can be related to thermodynamic quantities.<sup>30</sup>

The weighted mean of the measurements of Parks and La Mer<sup>26</sup> and Getman<sup>27</sup> was selected for this critical evaluation,

$$E^\circ[\text{Cd}|\text{Cd}(\text{Hg, satd}), 298.15 \text{ K}] = (50.53 \pm 0.17) \text{ mV}.$$



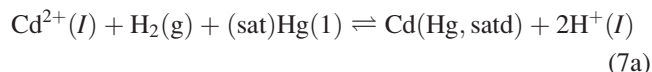
(a)



(b)

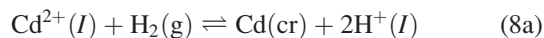
FIG. 1. (Color online) (a) Cell potential  $\text{Cd}(\text{s})|\text{Cd}^{2+}|\text{Cd}(\text{Hg, satd})$ . ●, ▽ exp. data (Refs. 26 and 27), respectively, (red) ★  $E^\circ(298.15 \text{ K})/V = (0.05053 \pm 0.00017)$ , weighted mean of Refs. 26 and 27. Ulich's<sup>29</sup> second approximation:  $E^\circ/V = a + b(T/\text{K}) + c(T/\text{K}) \ln(T/\text{K})$ ; ● solid line:  $a_1 = 1.2132 \times 10^{-2}$ ,  $b_1 = 2.056 \times 10^{-3}$ ,  $c_1 = -3.38 \times 10^{-4}$ ; ▽ dotted line:  $a_2 = 8.2328 \times 10^{-2}$ ,  $b_2 = 5.13 \times 10^{-4}$ ,  $c_2 = -1.09 \times 10^{-4}$ . (b) Cell potential  $\text{Cd}(\text{s})|\text{Cd}^{2+}|\text{Cd}(\text{Hg, satd})$ . ●, ▽ exp. data (Refs. 26 and 27), respectively, Three-term Clarke–Glew equation:  $T_r = 298.15 \text{ K}$ ,  $E^\circ(298.15 \text{ K}) = (50.53 \pm 0.17) \text{ mV}$ ,  $E^\circ/T^{-1}/\text{mV K}^{-1} = A + B(T_r/T) - C \ln(T_r/T)$ ; ● solid line:  $A_1 = 0.1276$ ,  $B_1 = 0.0419$ ,  $C_1 = -0.3370$ ; ▽, dotted line:  $A_2 = 0.0751$ ,  $B_2 = 0.0944$ ,  $C_2 = -0.2938$ .

At constant ionic strength, the standard electrode potential of  $\text{Cd}^{2+}|\text{Cd}(\text{Hg, satd})$ , Eqs. (7a) and (7b), remains constant when the concentration (or molality) product remains constant, because the activity coefficients remain essentially constant, as in Eqs. (1a) and (1b),



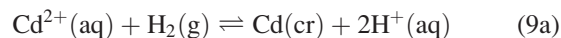
$$E_I^\circ[\text{Cd}^{2+}|\text{Cd}(\text{Hg, satd})] = [RT \ln(10)/2F] \lg[(m_{\text{H}^+})^2 (m_{\text{Cd}^{2+}} m^\circ)^{-1}]. \quad (7b)$$

Combining Eqs. (6a) and (6b) and (7a) and (7b) results in the equations,



$$E_I^\circ(\text{Cd}^{2+}|\text{Cd}) = E_I^\circ[\text{Cd}^{2+}|\text{Cd}(\text{Hg, satd})] - E^\circ[\text{Cd}|\text{Cd}(\text{Hg, satd})]. \quad (8b)$$

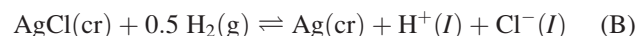
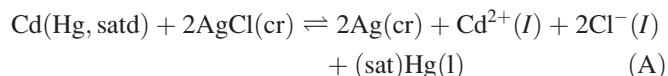
The standard electrode potential  $E^\circ(\text{Cd}^{2+}|\text{Cd})$  refers, however, to infinite dilution as indicated by the equations,



$$E^\circ(\text{Cd}^{2+}|\text{Cd}) = [RT \ln(10)/2F] \lg[(a_{\text{H}^+})^2 (a_{\text{Cd}^{2+}})^{-1}] \quad (9b)$$

$$\Delta_r G_m^\circ(\text{Cd}^{2+}, \text{aq}) = 2F E^\circ(\text{Cd}^{2+}|\text{Cd}) \quad (9c)$$

When the equilibria of reactions (1a) and (7a) are studied in the same ionic medium, the standard solubility constant  $\lg^* K_{ps0}^\circ$  can be calculated by Eq. (3) and the Gibbs energy for metal carbonate formation becomes accessible, without any non-thermodynamic assumptions. Kraft<sup>31</sup> measured the electrode potentials of cells A and B at  $I = 1.0, 2.0,$  and  $3.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) at  $298.15 \text{ K}$ .



Figures 2(a) and 2(b) show that  $E_m^{\circ'}(\text{A}) - [RT \ln(10)/F] 3D$  and  $E_m^{\circ'}(\text{B}) - [RT \ln(10)/F] 2D$  vs. molality ( $\approx I$ ) of the background electrolyte ( $\text{NaClO}_4$ ) fall on straight lines. This is in accordance with the SIT model, which is described comprehensively in Appendix B of the OECD NEA volumes on chemical thermodynamics (e.g., Ref. 32).

For

$$E_0^\circ(\text{Cd}^{2+}|\text{Cd}, 298.15 \text{ K}) = -(402.82 \pm 0.78) \text{ mV},$$

the value listed by and consistent within the NEA auxiliary data bank (see again Ref. 32) has been considered to be most reliable, as it is essentially the value recommended by CODATA.<sup>33</sup> The uncertainty was also estimated by Cox

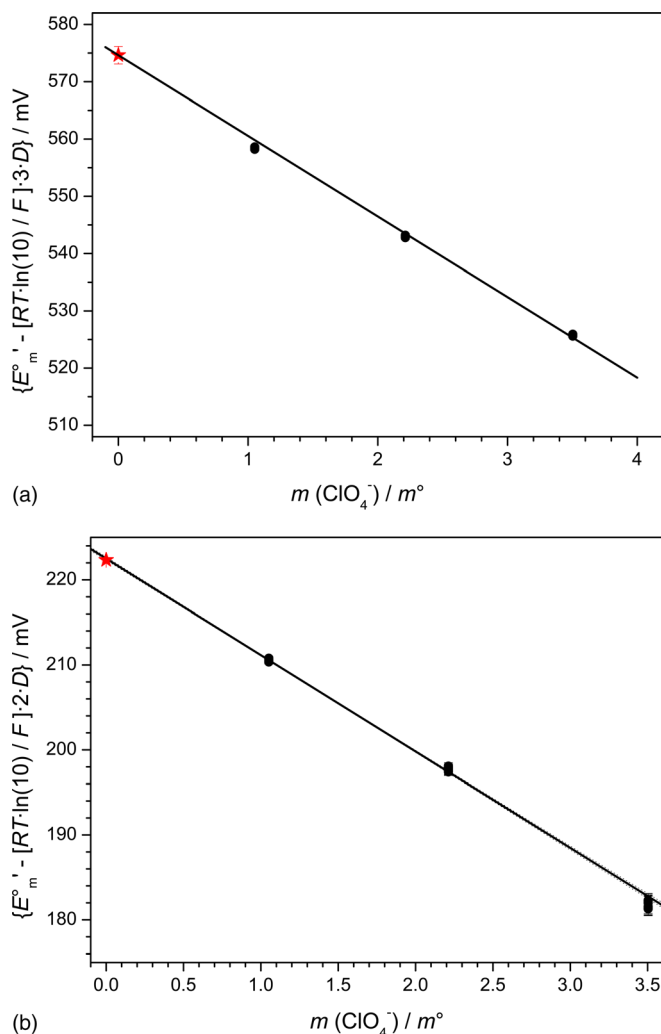
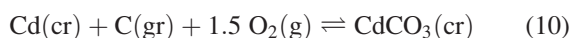


FIG. 2. (Color online) (a) Measurements on cell (A) at  $T = 298.15$  K. Reaction of cell A:  $\text{Cd}(\text{cr}) + 2 \text{AgCl}(\text{s}) \rightleftharpoons 2 \text{Ag}(\text{s}) + \text{Cd}^{2+}(\text{I}) + 2 \text{Cl}^{-}(\text{I})$  (AI)  $\text{Cd}(\text{Hg, satd}) \rightleftharpoons \text{Cd}(\text{cr})$  (AII) ● exp. data (Ref. 31), (red) ★  $E^{\circ} = (574.63 \pm 1.50)$  mV, (AI) from NEA aux. data, e.g., Ref. 32, (AII) from this review, solid line; line fit through  $E^{\circ}$ , slope =  $-(14.755 \pm 0.030)$  mV  $\text{kg mol}^{-1}$  (conf. lim.),  $\Delta\varepsilon = (0.499 \pm 0.001)$   $\text{kg mol}^{-1}$ . (b) Measurements on cell (B) at  $T = 298.15$  K. Reactions of cell B:  $0.5 \text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}(\text{s}) + \text{H}^{+}(\text{I}) + \text{Cl}^{-}(\text{I})$ . ● exp. data (Ref. 31), (red) ★  $E^{\circ} = (222.33 \pm 0.22)$  mV from NEA aux. data, e.g., Ref. 32,  $E^{\circ} = 222.35$  mV (Ref. 33), solid line: linear fit through NEA and CODATA value, slope =  $-(11.246 \pm 0.061)$  mV  $\text{kg mol}^{-1}$  (conf. lim.),  $\Delta\varepsilon = (0.190 \pm 0.001)$   $\text{kg mol}^{-1}$ .

*et al.*<sup>33</sup> This value for  $E^{\circ}(\text{Cd}^{2+} | \text{Cd})$  is being used throughout this review.

The Gibbs energy for cadmium(II) carbonate formation according to Eq. (10) can be calculated with Eq. (11), where  $\Delta_{\text{sln}}G^{\circ}(I)$  values for varying ionic strengths  $I$  have been taken from Refs. 5, 13, and 16.  $\Delta_{\text{r}}G^{\circ}[\text{Cd}^{2+}(\text{I})]$  values were calculated from experimental data of Kraft,<sup>31</sup> assuming that the SIT model is applicable for the whole range of ionic strengths investigated ( $0 \leq I/\text{mol kg}^{-1}(\text{Na})\text{ClO}_4 \leq 5.35$ ).



$$\begin{aligned} \Delta_{\text{r}}G^{\circ}(\text{CdCO}_3, \text{cr}) &= \Delta_{\text{r}}G^{\circ}[\text{Cd}^{2+}(\text{I})] + \Delta_{\text{r}}G^{\circ}(\text{CO}_2, \text{g}) \\ &\quad + \Delta_{\text{r}}G^{\circ}[\text{H}_2\text{O}(\text{l})] - \Delta_{\text{sln}}G_{\text{m}}^{\circ}(\text{I}) \end{aligned} \quad (11)$$

The results for  $\lg^*K_{\text{ps}0}^{\circ}(\text{CdCO}_3, 298.15 \text{ K})$  and  $\Delta_{\text{r}}G^{\circ}(\text{CdCO}_3, \text{cr}, 298.15 \text{ K})$  obtained by Refs. 5, 13, and 16 are listed in Table 1. The following mean values ( $\pm u$ ) were obtained:  $\lg^*K_{\text{ps}0}^{\circ}(\text{CdCO}_3, 298.15 \text{ K}) = (6.14 \pm 0.09)$  and  $\Delta_{\text{r}}G^{\circ}(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(674.19 \pm 0.52)$   $\text{kJ mol}^{-1}$ .

Alternatively,  $\lg^*K_{\text{ps}0}^{\circ}(\text{CdCO}_3)$  and  $\Delta_{\text{sln}}G_{\text{m}}^{\circ}(\text{aq})$  can be found as the intercept of a SIT plot  $\lg^*K_{\text{ps}0}^{\circ} - \Delta z^2 D + \lg a_{\text{H}_2\text{O}}$  vs.  $I$  (Ref. 22), see Fig. 3. This intercept and the values for  $\Delta_{\text{r}}G^{\circ}(\text{Cd}^{2+}, \text{aq})$ ,  $\Delta_{\text{r}}G^{\circ}(\text{CO}_2, \text{g})$ , and  $\Delta_{\text{r}}G^{\circ}(\text{H}_2\text{O}, \text{l})$  from the NEA auxiliary data bank result in:  $\lg^*K_{\text{ps}0}^{\circ}(\text{CdCO}_3, 298.15 \text{ K}) = (6.09 \pm 0.05)$  and  $\Delta_{\text{r}}G^{\circ}(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(674.51 \pm 0.34)$   $\text{kJ mol}^{-1}$ . From the slope of the SIT plot,  $\varepsilon(\text{Cd}^{2+}, \text{ClO}_4^{-}) = (0.35 \pm 0.04)$   $\text{kg mol}^{-1}$  was obtained; this value conforms to the  $\text{ClO}_4^{-}$  interaction coefficients of  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$  (Ref. 34).

Rai *et al.*<sup>12</sup> investigated the solubility product of cadmium(II) carbonate painstakingly at low ionic strengths. Although their solubility product is slightly different, the corresponding data fall at least equally close on the curves calculated by themselves<sup>12</sup> and by Gamsjäger *et al.*,<sup>35</sup> respectively. Moreover, the 1993 solubility product of Stipp *et al.*<sup>14</sup> agrees with the 1965 value of Gamsjäger *et al.*<sup>5</sup> within the experimental uncertainty, although it was determined at extremely low ionic strengths again. In Table 2, the most reliable experimentally determined values of  $\lg^*K_{\text{ps}0}^{\circ}(\text{CdCO}_3)$  and  $\Delta_{\text{r}}G^{\circ}(\text{CdCO}_3, \text{cr})$  are listed together with the estimated uncertainties, using data from Refs. 5, 12–14, and 16. The mean values weighted by uncertainties are

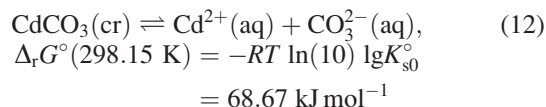
$$\lg^*K_{\text{ps}0}^{\circ}(\text{CdCO}_3) = (6.11 \pm 0.03)$$

and

$$\Delta_{\text{r}}G^{\circ}(\text{CdCO}_3, \text{cr}, 298.15) = -(674.30 \pm 0.16) \text{ kJ mol}^{-1}.$$

The calculated uncertainties of  $\lg^*K_{\text{ps}0}^{\circ}(\text{CdCO}_3)$  and  $\Delta_{\text{r}}G^{\circ}(\text{CdCO}_3, \text{cr})$  appear rather small, but are statistically correct, as the values are assumed to follow a Gaussian distribution. Thus, the evaluators suggest to increase the uncertainties to 0.10 lg units and 0.6  $\text{kJ mol}^{-1}$ , respectively, as these values agree with their experimental expertise.

With the CODATA (Ref. 33) key values for  $\text{Cd}^{2+}$  and  $\text{CO}_3^{2-}$  follows the Gibbs energy of reaction,



and

$$\lg K_{\text{s}0}^{\circ} = -(12.03 \pm 0.13).$$

#### $\Delta_{\text{r}}H^{\circ}(\text{CdCO}_3, \text{cr}, 298.15 \text{ K})$

The solubility of otavite,  $\text{CdCO}_3$ , is almost independent of temperature at an ionic strength of  $1.0 \text{ mol kg}^{-1} \text{ NaClO}_4$ .

TABLE 1. Solubility constant  $\lg^*K_{ps0}^\circ$ , Eq. (3), and Gibbs energy of formation  $\Delta_f G^\circ(\text{CdCO}_3, \text{cr})$ , Eq. (11), at 298.15 K,  $E_I^\circ = -(E_{\text{cellA}}^\circ - E_{\text{cellB}}^\circ) - E^\circ(\text{Cd}|\text{Cd}(\text{Hg})_{\text{sat}})$ ,  $E_0^\circ = -402.82 \text{ mV}$ .

No	$I/\text{mol kg}^{-1}$	$\lg^*K_{ps0}$	$\lg\alpha_{\text{H}_2\text{O}}$	$(E_{\text{cellA}}^\circ - E_{\text{cellB}}^\circ)/\text{mV}$	$\text{Cd}^{2+} \text{Cd} (E_I^\circ - E_0^\circ)/\text{mV}$	$\lg^*K_{ps0}^\circ$	$\text{CdCO}_3(\text{cr}) \Delta_f G^\circ/\text{kJ mol}^{-1}$	Refs.
1	0.1500	6.2747	-0.0022	359.25	-6.95	6.0375	-674.78	16
2	0.1500	6.2777	-0.0022	359.25	-6.95	6.0405	-674.77	16
3	0.1500	6.2487	-0.0022	359.25	-6.95	6.0115	-674.93	16
4	0.1650	6.3697	-0.0024	359.43	-7.13	6.1261	-674.28	16
5	0.1660	6.3717	-0.0024	359.44	-7.15	6.1277	-674.27	16
6	0.1660	6.4717	-0.0024	359.44	-7.15	6.2277	-673.70	16
7	0.1660	6.5907	-0.0024	359.44	-7.15	6.3467	-673.02	16
8	0.1670	6.5297	-0.0024	359.45	-7.16	6.2853	-673.37	16
9	0.5060	6.4237	-0.0072	361.22	-8.93	6.1146	-674.34	16
10	0.5060	6.3537	-0.0072	361.22	-8.93	6.0446	-674.74	16
11	0.5500	6.4197	-0.0078	361.31	-9.02	6.1071	-674.39	16
12	0.5500	6.4837	-0.0078	361.31	-9.02	6.1711	-674.02	16
13	0.9820	6.3057	-0.0140	361.52	-9.22	5.9799	-675.11	16
14	0.9820	6.3767	-0.0140	361.52	-9.22	6.0509	-674.71	16
15	1.0000	6.3617	-0.0143	361.51	-9.22	6.0359	-674.79	16
16	1.0020	6.3487	-0.0143	361.51	-9.22	6.0229	-674.87	16
17	1.0000	6.3717	-0.0143	361.51	-9.22	6.0459	-674.74	16
18	1.0000	6.2577	-0.0143	361.51	-9.22	5.9319	-675.39	16
19	1.0510	6.3957	-0.0150	361.48	-9.19	6.0700	-674.60	16
20	2.1490	6.3337	-0.0316	360.01	-7.72	6.0412	-674.76	16
21	2.1500	6.4187	-0.0316	360.01	-7.72	6.1262	-674.28	16
22	4.3290	6.3397	-0.0679	355.25	-2.95	6.1719	-674.02	16
23	4.3310	6.3667	-0.0679	355.24	-2.95	6.1991	-673.86	16
24	4.3310	6.3087	-0.0679	355.24	-2.95	6.1411	-674.19	16
25	5.3490	6.4057	-0.0867	352.74	-0.45	6.3039	-673.26	16
26	5.3500	6.4017	-0.0867	352.74	-0.45	6.3000	-673.29	16
27	5.3500	6.2827	-0.0867	352.74	-0.45	6.1810	-673.97	16
28	5.3500	6.2427	-0.0867	352.74	-0.45	6.1410	-674.19	16
29	5.3500	6.2917	-0.0867	352.74	-0.45	6.1900	-673.91	16
30	3.0000	6.4047	-0.0452	358.30	-6.01	6.1564	-674.10	13
31	3.0000	6.4107	-0.0452	358.30	-6.01	6.1624	-674.07	13
32	3.0000	6.4497	-0.0452	358.30	-6.01	6.2014	-673.85	13
33	3.0000	6.3957	-0.0452	358.30	-6.01	6.1474	-674.16	13
34	3.0000	6.4287	-0.0452	358.30	-6.01	6.1804	-673.97	13
35	3.0000	6.4107	-0.0452	358.30	-6.01	6.1624	-674.07	13
36	3.0000	6.3957	-0.0452	358.30	-6.01	6.1474	-674.16	13
37	3.5034	6.3983	-0.0536	357.18	-4.89	6.1795	-673.97	5
38	3.5034	6.3483	-0.0536	357.18	-4.89	6.1295	-674.26	5
39	3.5034	6.3983	-0.0536	357.18	-4.89	6.1795	-673.97	5
40	3.5034	6.3883	-0.0536	357.18	-4.89	6.1695	-674.03	5
41	3.5034	6.3183	-0.0536	357.18	-4.89	6.0995	-674.43	5
42	3.5034	6.3683	-0.0536	357.18	-4.89	6.1495	-674.14	5
43	3.5034	6.5283	-0.0536	357.18	-4.89	6.3095	-673.23	5
44	3.5034	6.4783	-0.0536	357.18	-4.89	6.2595	-673.52	5
						<b>(6.141 ± 0.092)</b>	<b>-674.19 ± 0.52</b>	

The SIT analysis of ( $I$ ,  $\lg^*K_{ps0}$ ) data at 25 °C (see Fig. 3) results in

$$\lg^*K_{ps0}(\text{CdCO}_3, 298.15 \text{ K}, I = 1.0 \text{ mol kg}^{-1} \text{ NaClO}_4) = 6.43 \pm 0.10$$

A least-squares analysis of ( $T$ ,  $\lg^*K_{ps0}$ ) data at  $I = 1.0 \text{ mol kg}^{-1} \text{ NaClO}_4$  (see Figs. 4(a), and 4(b)) leads to

$$\lg^*K_{ps0}(\text{CdCO}_3, 298.15\text{--}348.15 \text{ K}, I = 1.0 \text{ mol kg}^{-1} \text{ NaClO}_4) = 6.39 \pm 0.14.$$

The uncertainty ranges of these mean values overlap, and so  $\Delta_{\text{sln}}H^\circ$  vanishes within the experimental uncertainty.

$$\Delta_{\text{sln}}H^\circ = -R \ln(10) \partial(\lg^*K_{ps0}) / \partial(1/T) = (0.0 \pm 5.6) \text{ kJ mol}^{-1}$$

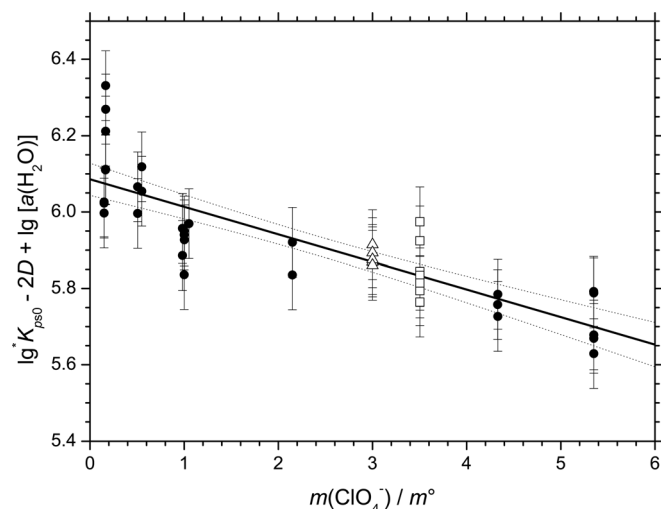


FIG. 3. SIT plot of reaction:  $\text{CdCO}_3(\text{cr}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Cd}^{2+}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ .  $\square$ ,  $\Delta$ ,  $\bullet$  exp. data from Refs. 5, 13, and 16, respectively, solid line: linear fit, all data weighted by common uncertainties, dotted line: 95% confidence limits,  $\lg^*K_{ps0}^\circ = (6.085 \pm 0.047)$ ,  $\Delta\varepsilon = (0.072 \pm 0.016) \text{ kg mol}^{-1}$ ,  $\varepsilon(\text{Cd}^{2+}, \text{ClO}_4^-) = (0.35 \pm 0.04) \text{ kg mol}^{-1}$ .

$$\Delta_f H^\circ(\text{CdCO}_3, \text{cr}) = \Delta_f H^\circ(\text{Cd}^{2+}, \text{aq}) + \Delta_f H^\circ(\text{CO}_2, \text{g}) + \Delta_f H^\circ(\text{H}_2\text{O}, \text{l}) - \Delta_{\text{sln}} G^\circ$$

$$\Delta_f H^\circ(\text{CdCO}_3, \text{cr}) = -(755.3 \pm 5.6) \text{ kJ mol}^{-1}$$

### $S^\circ(\text{CdCO}_3, \text{s}, 298.15 \text{ K})$

The standard entropy of  $\text{CdCO}_3$  can also be calculated from this information.

$$\begin{aligned} \Delta_{\text{sln}} S^\circ &= (\Delta_{\text{sln}} H^\circ - \Delta_{\text{sln}} G^\circ) / 298.15 \\ &= [(0.0 \pm 5.6) + (34.88 \pm 0.57)] \times 1000 / 298.15 \\ &= (117 \pm 19) \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

With CODATA values<sup>33</sup> for  $S^\circ(\text{Cd}^{2+}, \text{aq})$ ,  $S^\circ(\text{CO}_2, \text{g})$ , and  $S^\circ(\text{H}_2\text{O}, \text{l})$ , one obtains

$$\begin{aligned} S^\circ(\text{CdCO}_3, \text{cr}) &= S^\circ(\text{Cd}^{2+}, \text{aq}) + S^\circ(\text{CO}_2, \text{g}) + S^\circ(\text{H}_2\text{O}, \text{l}) \\ &\quad - \Delta_{\text{sln}} S^\circ \\ &= (94 \pm 19) \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Clearly, low-temperature heat capacity measurements result in a more precise value<sup>36</sup>

$$S^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = (103.9 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1},$$

but in cases where these heat capacity data are not known, solubility measurements still provide approximate values of standard entropies for metal carbonates.

### Recommended Set of Thermodynamic Quantities

With the Gibbs energy of  $\text{CdCO}_3(\text{cr})$  dissolution,  $\Delta_{\text{sln}} G^\circ(\text{aq})$  calculated from  $\lg^*K_{ps0}^\circ$  values obtained by solubility measurements of different authors,<sup>5,12-14,16,17</sup> the SIT analysis of this work (see Table 2), the standard entropy of  $\text{CdCO}_3(\text{cr})$  determined by Archer,<sup>36</sup> the pertinent CODATA key values<sup>32,33</sup> for  $\text{Cd}^{2+}(\text{aq})$ ,  $\text{CO}_2(\text{g})$ , and  $\text{H}_2\text{O}(\text{l})$ , the following set of thermodynamic quantities can be recommended:

$$\lg^*K_{ps0}^\circ(298.15 \text{ K}) = (6.11 \pm 0.10)$$

$$\lg K_{s0}^\circ = \lg[a_{\text{Cd}^{2+}} a_{\text{CO}_3^{2-}}] = -(12.03 \pm 0.13)$$

$$\Delta_f G^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(674.3 \pm 0.6) \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(752.2 \pm 0.8) \text{ kJ mol}^{-1}$$

$$S^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = (103.9 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1}.$$

When the relationship

$$\begin{aligned} \Delta_f G^\circ(\text{CdCO}_3, \text{cr}) &= \Delta_f H^\circ(\text{CdCO}_3, \text{cr}) \\ &\quad - T^\circ \Delta_f S^\circ(\text{CdCO}_3, \text{cr}), \end{aligned}$$

where  $T^\circ = 298.15 \text{ K}$ , and the CODATA key values<sup>33</sup> for  $\text{Cd}(\text{cr})$ ,  $\text{C}(\text{cr}, \text{graphite})$ , and  $\text{O}_2(\text{g})$  were used, essentially the same value for  $\Delta_f H^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(752.24 \pm 0.65) \text{ kJ mol}^{-1}$  was obtained.

Very similar results were achieved<sup>16</sup> when the thermodynamic analysis was based on the Pitzer model<sup>37</sup>:  $\lg^*K_{ps0}^\circ(298.15 \text{ K}) = (6.14 \pm 0.10)$ ,  $\Delta_f G^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(674.2 \pm 0.6) \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = -(752.1 \pm 0.6) \text{ kJ mol}^{-1}$ ,  $S^\circ(\text{CdCO}_3, \text{cr}, 298.15 \text{ K}) = (103.9 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1}$ .

TABLE 2. Mean values of  $\lg^*K_{ps0}^\circ$  and  $\Delta_f G^\circ(\text{CdCO}_3)$  at 298.15 K.

No	$\lg^*K_{ps0}^\circ$	$u$	$\text{CdCO}_3(\text{cr}) \Delta_f G^\circ / \text{kJ mol}^{-1}$	$u / \text{kJ mol}^{-1}$	Refs.	Remarks
1	6.140	0.15	-674.34	0.84	5	kcal converted to kJ
2	5.910	0.10	-675.50	0.71	12	CODATA values used for conversion
3	6.165	0.04	-674.05	0.22	13	
4	6.052	0.10	-674.70	0.60	14	CODATA values used for conversion
5	6.123	0.10	-674.30	0.59	16	New experimental data used only
6	6.087	0.20	-674.50	1.37	17	CODATA values used for conversion
7	6.085	0.05	-674.51	0.34	This work	SIT approach, see Fig. 3
	<b>6.11</b>	<b><math>\pm 0.03</math></b>	<b>-674.31</b>	<b><math>\pm 0.16</math></b>	This work	Mean values weighted by uncertainties

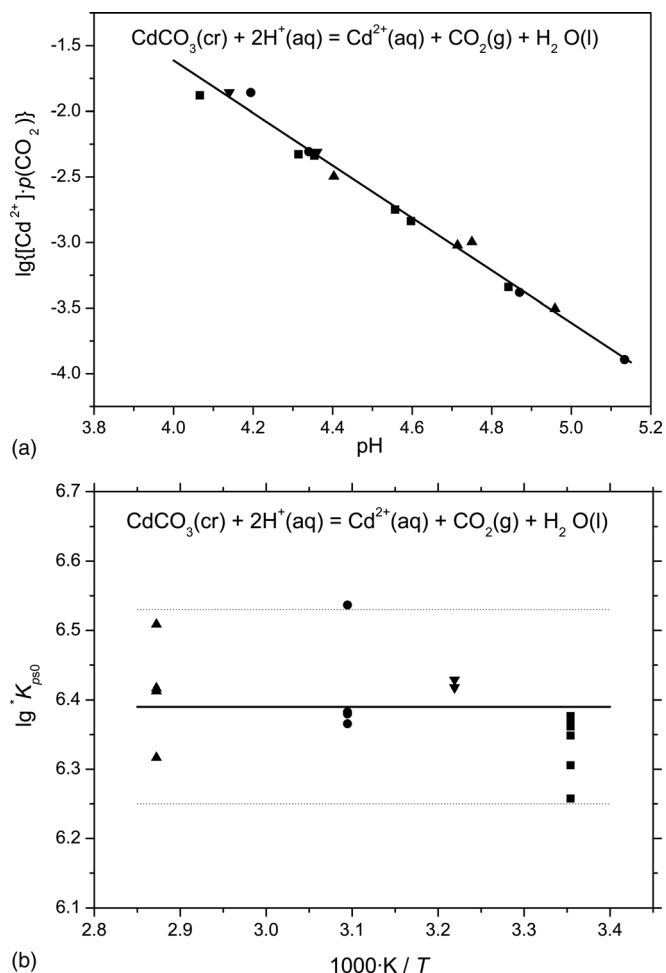
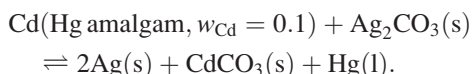


FIG. 4. (a) Temperature dependence of  $\text{CdCO}_3$  solubility. ■ 25 °C; ▼ 37.5 °C; ● 50 °C; ▲ 75 °C, exp. data (Ref. 16),  $I = 1.0 \text{ mol kg}^{-1}$  (Na)ClO<sub>4</sub>, theoretical slope = -2.00; 25–75 °C:  $\lg^* K_{ps0} = (6.39 \pm 0.14)$ , 25 °C:  $\lg^* K_{ps0} = (6.43 \pm 0.10)$ . (b) Temperature dependence of  $\text{CdCO}_3$  solubility. ■ 25 °C; ▼ 37.5 °C; ● 50 °C; ▲ 75 °C, exp. data (Ref. 16),  $I = 1.0 \text{ mol kg}^{-1}$  (Na)ClO<sub>4</sub>,  $\lg^* K_{ps0} = (6.39 \pm 0.14)$ .

The values  $\Delta_f G^\circ(\text{CdCO}_3, \text{cr}) = -673.8 \text{ kJ mol}^{-1}$  and  $\lg K_{s0}^\circ = -11.94$  were obtained from the potential measured by Saegusa<sup>2</sup> for the reversible cell represented by the equation



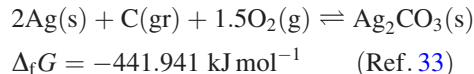
The potential of this cell ( $E$ ) can be related to the Gibbs energy of reaction ( $\Delta_r G$ ),

$$\Delta_r G = -zFE$$

$$\begin{aligned} \Delta_r G &= -2 \times 96485.34151 \times 1.1540 \\ &= -222.69 \times 10^3 \text{ J mol}^{-1}. \end{aligned}$$

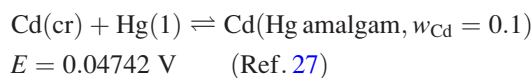
To calculate the Gibbs energy of formation of cadmium(II) carbonate, the CODATA key value<sup>33</sup> for the Gibbs energy of formation of  $\text{Ag}_2\text{CO}_3(\text{cr})$  and the value published by

Getman<sup>27</sup> for the potential of Cd(Hg amalgam,  $w_{\text{Cd}} = 0.1$ ) formation were used.



According to Getman,<sup>27</sup>  $\Delta_r G$  of Cd amalgam depends on Cd content (see Figs. 1(a) and 1(b)).

For the reaction



$$\begin{aligned} \Delta_{\text{mix}} G &= -2 \times 96485.34151 \times 0.04742 \\ &= -9.151 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

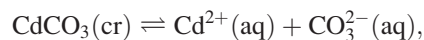
$$\Delta_r G^\circ(\text{CdCO}_3, \text{cr}, 298 \text{ K}) = -673.78 \text{ kJ mol}^{-1}$$

The solubility product was also calculated using the CODATA key values<sup>33</sup> for the Gibbs energy of formation of carbonate and cadmium(II) ions.

$$\Delta_f G^\circ(\text{CO}_3^{2-}, \text{aq}, 298 \text{ K}) = -527.90 \text{ kJ mol}^{-1} \quad (\text{Ref. 33})$$

$$\Delta_f G^\circ(\text{Cd}^{2+}, \text{aq}, 298 \text{ K}) = -77.75 \text{ kJ mol}^{-1} \quad (\text{Ref. 33})$$

For the reaction,



$$K_{s0}^\circ = 1.16 \times 10^{-12} \text{ and } \lg K_{s0}^\circ = -11.94.$$

## 2.2. Experimental Data

### Components:

- (1) Cadmium(II) carbonate;  $\text{CdCO}_3$ ; [513-78-0]
- (2) Potassium carbonate;  $\text{K}_2\text{CO}_3$ ; [584-08-7]
- (3) Potassium hydrogencarbonate;  $\text{KHCO}_3$ ; [298-14-6]
- (4) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

### Original Measurements:

- <sup>2</sup>F. Saegusa, J. Chem. Soc. Japan, Pure Chem. Sect. **70**, 127 (1949).

### Variables:

$T/\text{K} = 298.15$  and  $308.15$

### Prepared by:

K. Sawada and H. Gamsjäger

### Experimental Values

The potential difference of the reversible cell represented by the diagram,  $\text{Cd(Hg amalgam, } w_{\text{Cd}} = 0.1) | \text{CdCO}_3 | 0.1 \text{ mol dm}^{-3} \text{ K}_2\text{CO}_3, 0.1 \text{ mol dm}^{-3} \text{ KHCO}_3 | \text{Ag}_2\text{CO}_3 | \text{Ag}$  was found to be  $E = 1.1540 \text{ V}$  at 25 °C.

The standard Gibbs energy of formation ( $\Delta_f G^\circ$ ), the enthalpy of formation ( $\Delta_f H^\circ$ ) of cadmium(II) carbonate, and its entropy ( $S^\circ$ ) and solubility product ( $K_{s0}^\circ$ ), at 25 °C were calculated by Saegusa<sup>2</sup> using reduction potentials published by Latimer<sup>38</sup> as auxiliary variables.

	$\Delta_f G^\circ/\text{kJ mol}^{-1}$	$\Delta_f H^\circ/\text{kJ mol}^{-1}$	$S^\circ/\text{kJ mol}^{-1}$	$K_{s0}^\circ$
$\text{CdCO}_3$	-669.13	-749.05	96.6	$2.5 \times 10^{-12}$

## Auxiliary Information

## Method/Apparatus/Procedure:

The potential difference of this electrochemical cell was measured at 25 and 35 °C by a Leeds and Northrup type K (Kohlrausch) potentiometer with a mirror galvanometer. There was no difference in the electric potential values between 25 and 35 °C.

## Source and Purity of Materials:

Silver carbonate was precipitated by passing a slow stream of carbon dioxide through a solution of silver ammine complex. Cadmium(II) carbonates were prepared by adding potassium hydrogencarbonate to metal sulfate solution under cooling. The formation of pure cadmium(II) carbonate was confirmed by a potentiometric titration. Cadmium amalgam was prepared by electrolyzing cadmium(II) sulfate solution with purified mercury as a cathode.

## Estimated Error:

Nothing specified, no estimates possible.

## Components:

- (1) Cadmium(II) carbonate; CdCO<sub>3</sub>; [513-78-0]
- (2) Sodium perchlorate; NaClO<sub>4</sub>; [7601-89-0]
- (3) Perchloric acid; HClO<sub>4</sub>; [7601-90-3]
- (4) Carbon dioxide; CO<sub>2</sub>; [124-38-98]
- (5) Water; H<sub>2</sub>O; [7732-18-5]

## Original Measurements:

<sup>5</sup>H. Gamsjäger, H. U. Stuber, and P. Schindler, *Helv. Chim. Acta* **48**, 723 (1965).

## Variables:

$c_{\text{H}^+}$ ,  $p_{\text{CO}_2}$  at  $p_{\text{tot}} \approx 1.01 \times 10^5$  Pa  
 $T = 298.15$  K, and  $I = 3$  mol dm<sup>-3</sup>

## Prepared by:

H. Gamsjäger and P. Schmidt

## Experimental Values

Composition of the saturated solutions in CdCO<sub>3</sub> + CO<sub>2</sub> + H<sub>2</sub>O system, at 25 °C and  $I = 3.0$  mol dm<sup>-3</sup> (NaClO<sub>4</sub>)

CdCO <sub>3</sub> origin	$-\lg c_{\text{H}^+}$	$p_{\text{CO}_2}/\text{atm}$	$10^2 c_{\text{Cd}^{2+}}/\text{mol dm}^{-3}$
Lehrmann and Spear <sup>40</sup>	4.27 <sub>1</sub>	0.169 <sub>5</sub>	4.88 <sub>1</sub>
Lehrmann and Spear <sup>40</sup>	4.25 <sub>4</sub>	0.169 <sub>5</sub>	4.93 <sub>0</sub>
Lehrmann and Spear <sup>40</sup>	4.11 <sub>2</sub>	0.340 <sub>6</sub>	4.96 <sub>5</sub>
Lehrmann and Spear <sup>40</sup>	4.11 <sub>2</sub>	0.341 <sub>2</sub>	4.95 <sub>5</sub>
Lehrmann and Spear <sup>40</sup>	3.86 <sub>6</sub>	0.917 <sub>1</sub>	4.87 <sub>3</sub>
Lehrmann and Spear <sup>40</sup>	3.89 <sub>4</sub>	0.921 <sub>0</sub>	4.78 <sub>4</sub>
puriss. Merck	3.96 <sub>7</sub>	0.921 <sub>0</sub>	4.87 <sub>7</sub>
puriss. Merck	3.94 <sub>7</sub>	0.921 <sub>0</sub>	4.87 <sub>7</sub>

The selected data given in the table refer to an initial concentration of  $c_{\text{H}^+} = 9.833 \times 10^{-2}$  mol dm<sup>-3</sup>.

## Auxiliary Information

## Method/Apparatus/Procedure:

In a solubility cell, described in Schindler *et al.*,<sup>39</sup> crystalline CdCO<sub>3</sub> was equilibrated with HClO<sub>4</sub><sup>-</sup> and NaClO<sub>4</sub><sup>-</sup>-containing solutions. The H<sup>+</sup> ion concentration (determined potentiometrically) became constant after 24–36 h, and then the Cd<sup>2+</sup> concentration was determined by complexometric titration and calculated from the charge and proton balance.

## Source and Purity of Materials:

Chemically pure materials were used. Samples of CdCO<sub>3</sub> were either prepared according to Lehrmann and Spear<sup>40</sup> (11 determinations) or commercially obtained (18 determinations) in reagent-grade quality (CdCO<sub>3</sub> puriss. Merck). Both samples showed only the x-ray diffraction pattern of CdCO<sub>3</sub>, otavite.

## Estimated Error:

The maximum deviation from the mean value of  $\lg(c_{\text{Cd}^{2+}} p_{\text{CO}_2} c_{\text{H}^+}^{-2})$  was stated to be  $\pm 0.15$ .

## Components:

- (1) Cadmium(II) carbonate; CdCO<sub>3</sub>; [5123-78-0]
- (2) Perchloric acid; HClO<sub>4</sub>; [7601-90-3]
- (3) Sodium perchlorate; NaClO<sub>4</sub>; [7601-89-0]
- (4) Carbon dioxide; CO<sub>2</sub>; [124-38-98]
- (5) Water; H<sub>2</sub>O; [7732-18-5]

## Original Measurements:

<sup>13</sup>E. Königsberger, R. Hausner, and H. Gamsjäger, *Geochim. Cosmochim. Acta* **55**, 3505 (1991).

## Variables:

$T = 298.15$  K,  $p_{\text{CO}_2}$ , pH, and  $I = 3.0$  mol kg<sup>-1</sup>

## Prepared by:

M. C. F. Magalhães

## Experimental Values

Composition of the saturated solutions in CdCO<sub>3</sub> + CO<sub>2</sub> + H<sub>2</sub>O system at 25 °C, and  $I = 3.0$  mol dm<sup>-3</sup>.

No.	pH <sub>ini</sub>	pH <sub>eq</sub>	$m_{\text{Cd}^{2+}}/\text{mol kg}^{-1}$	$p_{\text{CO}_2}/\text{atm}$
1	1.970	4.815	0.00528	0.108 <sub>7</sub>
2	1.501	4.585	0.0156	0.108 <sub>7</sub>
3a	0.976	4.345	—	0.107 <sub>6</sub>
3b	0.976	3.850	0.0522	0.927 <sub>3</sub>
4 <sup>a</sup>	—	4.865	0.000545	0.927 <sub>3</sub>
5	1.501	4.119	0.0157	0.927 <sub>3</sub>
6	1.970	4.341	0.00539	0.928 <sub>4</sub>

<sup>a</sup>3.00 mol kg<sup>-1</sup> NaClO<sub>4</sub> was used as initial solution.

## Auxiliary Information

## Method/Apparatus/Procedure:

Cadmium(II) carbonate was reacted with aqueous solutions of initial composition  $m_{\text{H}^+} = H$  mol kg<sup>-1</sup>,  $m_{\text{Na}^+} = (3.00 - H)$  mol kg<sup>-1</sup>,  $m_{\text{ClO}_4^-} = 3.00$  mol kg<sup>-1</sup> at fixed partial pressures of CO<sub>2</sub> (solution S<sub>A</sub>). The suspension contained in a thermostated vessel (25.00 ± 0.01) °C was stirred by a magnetic bar at a rate of 250 rpm. Care was taken to avoid evaporation and condensation within the vessels, and CO<sub>2</sub> and N<sub>2</sub>/CO<sub>2</sub> mixtures were presaturated with water. Molalities of H<sup>+</sup> and Cd<sup>2+</sup> were measured potentiometrically using the following galvanic cells calibrated against standard solutions (S<sub>A</sub> or S<sub>B</sub>) of well-known concentrations.  
Ag, AgCl | 2.90 mol kg<sup>-1</sup> NaClO<sub>4</sub>, 0.10 mol kg<sup>-1</sup> NaCl || 3.00 mol kg<sup>-1</sup> NaClO<sub>4</sub> | X  
X = S<sub>A</sub> or S | glass electrode or S<sub>B</sub> or S | Cd<sup>2+</sup> sensitive electrode.  
S<sub>B</sub> standard solution of Cd<sup>2+</sup>  $m_{\text{Cd}^{2+}} = C$  mol kg<sup>-1</sup>,  
 $m_{\text{Na}^+} = (3.00 - 2C)$  mol kg<sup>-1</sup>,  $m_{\text{ClO}_4^-} = 3.00$  mol kg<sup>-1</sup>.

**Source and Purity of Materials:**

Cadmium(II) carbonate was from Merck puriss. Analytical grade perchloric acid and sodium perchlorate were used. High purity CO<sub>2</sub> and N<sub>2</sub>/CO<sub>2</sub> mixtures were commercially prepared and analyzed.

**Estimated Error:**

$\Delta T = \pm 0.01$  K.

**Components:**

- (1) Cadmium(II) carbonate; CdCO<sub>3</sub>; [513-78-0]
- (2) Sodium perchlorate; NaClO<sub>4</sub>; [7601-89-0]
- (3) Sodium hydroxide; NaOH; [1310-73-2]
- (4) Perchloric acid; HClO<sub>4</sub>; [7601-90-3]
- (5) Carbon dioxide; CO<sub>2</sub>; [124-38-9]
- (6) Water; H<sub>2</sub>O; [7732-18-5]

**Original Measurements:**

<sup>12</sup>D. Rai, A. R. Felmy, and D.A. Moore, *J. Solution Chem.* **20**, 1169 (1991).

**Variables:**

Composition of the solution  
 $T = 298.15$  K, pH, ionic strength,  $p_{\text{CO}_2}$

**Prepared by:**

M. C. F. Magalhães

**Experimental Values**

Concentrations of Cd in aqueous solutions of NaClO<sub>4</sub> 0.01 mol dm<sup>-3</sup> equilibrated with CdCO<sub>3</sub>(s) at  $p_{\text{CO}_2}$  of 0.0003, 0.001, and 0.138 atm, at different pH.

$p_{\text{CO}_2} = 0.0003$ atm		$p_{\text{CO}_2} = 0.001$ atm		$p_{\text{CO}_2} = 0.138$ atm	
pH	[Cd <sup>2+</sup> ] <sub>tot</sub> <sup>a</sup> /mol dm <sup>-3</sup>	pH	[Cd <sup>2+</sup> ] <sub>tot</sub> <sup>a</sup> /mol dm <sup>-3</sup>	pH	[Cd <sup>2+</sup> ] <sub>tot</sub> <sup>a</sup> /mol dm <sup>-3</sup>
5.90	1.66 × 10 <sup>-2</sup>	5.49	3.02 × 10 <sup>-2</sup>	4.50	8.32 × 10 <sup>-3</sup>
5.91	6.76 × 10 <sup>-3</sup>	5.51	3.02 × 10 <sup>-2</sup>	4.52	1.58 × 10 <sup>-2</sup>
5.99	1.05 × 10 <sup>-2</sup>	5.52	1.51 × 10 <sup>-2</sup>	4.95	2.40 × 10 <sup>-3</sup>
5.99	4.68 × 10 <sup>-3</sup>	5.66	8.318 × 10 <sup>-3</sup>	4.98	2.29 × 10 <sup>-3</sup>
6.10	2.69 × 10 <sup>-3</sup>	5.70	1.12 × 10 <sup>-2</sup>	5.35	3.02 × 10 <sup>-4</sup>
6.36	1.07 × 10 <sup>-3</sup>	5.71	1.12 × 10 <sup>-2</sup>	5.73	5.89 × 10 <sup>-5</sup>
6.47	6.46 × 10 <sup>-4</sup>	5.72	7.94 × 10 <sup>-3</sup>	5.73	7.94 × 10 <sup>-5</sup>
6.63	3.72 × 10 <sup>-4</sup>	5.73	8.32 × 10 <sup>-3</sup>	5.75	7.94 × 10 <sup>-5</sup>
6.63	2.69 × 10 <sup>-4</sup>	5.75	4.786 × 10 <sup>-3</sup>	6.09	1.86 × 10 <sup>-5</sup>
6.63	1.86 × 10 <sup>-4</sup>	5.80	5.25 × 10 <sup>-3</sup>	6.47	4.47 × 10 <sup>-6</sup>
6.81	1.07 × 10 <sup>-4</sup>	5.82	4.47 × 10 <sup>-3</sup>	6.55	2.51 × 10 <sup>-6</sup>
7.25	1.32 × 10 <sup>-5</sup>	5.87	2.818 × 10 <sup>-3</sup>	6.57	2.63 × 10 <sup>-6</sup>
7.32	1.32 × 10 <sup>-5</sup>	5.95	4.27 × 10 <sup>-3</sup>	6.65	1.55 × 10 <sup>-6</sup>
7.40	6.61 × 10 <sup>-6</sup>	5.96	3.16 × 10 <sup>-3</sup>	6.88	8.71 × 10 <sup>-7</sup>
7.50	4.47 × 10 <sup>-6</sup>	5.98	2.88 × 10 <sup>-3</sup>	6.95	6.31 × 10 <sup>-7</sup>
7.53	1.51 × 10 <sup>-5</sup>	6.01	1.74 × 10 <sup>-3</sup>	6.96	5.75 × 10 <sup>-7</sup>
7.62	3.98 × 10 <sup>-6</sup>	6.09	1.58 × 10 <sup>-3</sup>	6.97	7.94 × 10 <sup>-7</sup>
7.84	1.86 × 10 <sup>-6</sup>	6.09	1.38 × 10 <sup>-3</sup>	6.97	4.90 × 10 <sup>-7</sup>
8.00	3.72 × 10 <sup>-7</sup>	6.17	7.94 × 10 <sup>-4</sup>	7.00	4.90 × 10 <sup>-7</sup>
8.08	4.17 × 10 <sup>-7</sup>	6.18	6.166 × 10 <sup>-4</sup>	7.16	1.95 × 10 <sup>-7</sup>
8.24	3.31 × 10 <sup>-7</sup>	6.23	5.62 × 10 <sup>-4</sup>	7.16	3.16 × 10 <sup>-7</sup>
8.30	4.90 × 10 <sup>-7</sup>	6.25	4.90 × 10 <sup>-4</sup>	7.14	3.72 × 10 <sup>-7</sup>
8.35	1.38 × 10 <sup>-7</sup>	6.35	2.692 × 10 <sup>-4</sup>	7.25	1.95 × 10 <sup>-7</sup>
8.47	8.91 × 10 <sup>-7</sup>	6.41	2.57 × 10 <sup>-4</sup>	7.30	2.34 × 10 <sup>-7</sup>
8.50	9.55 × 10 <sup>-7</sup>	6.43	1.698 × 10 <sup>-4</sup>	7.32	3.16 × 10 <sup>-7</sup>
8.55	6.76 × 10 <sup>-8</sup>	6.45	1.51 × 10 <sup>-4</sup>	7.35	1.95 × 10 <sup>-7</sup>
8.63	3.55 × 10 <sup>-8</sup>	6.49	1.32 × 10 <sup>-4</sup>	7.62	1.17 × 10 <sup>-7</sup>

$p_{\text{CO}_2} = 0.0003$ atm		$p_{\text{CO}_2} = 0.001$ atm		$p_{\text{CO}_2} = 0.138$ atm	
pH	[Cd <sup>2+</sup> ] <sub>tot</sub> <sup>a</sup> /mol dm <sup>-3</sup>	pH	[Cd <sup>2+</sup> ] <sub>tot</sub> <sup>a</sup> /mol dm <sup>-3</sup>	pH	[Cd <sup>2+</sup> ] <sub>tot</sub> <sup>a</sup> /mol dm <sup>-3</sup>
8.91	1.17 × 10 <sup>-7</sup>	6.53	1.023 × 10 <sup>-4</sup>	7.71	9.55 × 10 <sup>-8</sup>
		6.58	9.55 × 10 <sup>-5</sup>		
		6.63	7.24 × 10 <sup>-5</sup>		
		6.75	3.31 × 10 <sup>-5</sup>		
		6.84	2.188 × 10 <sup>-5</sup>		
		6.86	1.995 × 10 <sup>-5</sup>		
		6.89	1.82 × 10 <sup>-5</sup>		
		7.00	1.175 × 10 <sup>-5</sup>		
		7.08	8.710 × 10 <sup>-6</sup>		
		7.09	8.51 × 10 <sup>-6</sup>		
		7.15	8.13 × 10 <sup>-6</sup>		
		7.15	7.41 × 10 <sup>-6</sup>		
		7.20	5.50 × 10 <sup>-6</sup>		
		7.20	5.50 × 10 <sup>-6</sup>		
		7.20	4.37 × 10 <sup>-6</sup>		
		7.24	3.39 × 10 <sup>-6</sup>		
		7.25	4.898 × 10 <sup>-6</sup>		
		7.29	2.63 × 10 <sup>-6</sup>		
		7.37	1.78 × 10 <sup>-6</sup>		
		7.37	2.19 × 10 <sup>-6</sup>		
		7.45	2.75 × 10 <sup>-6</sup>		
		7.57	1.445 × 10 <sup>-6</sup>		
		7.59	9.55 × 10 <sup>-7</sup>		
		7.59	9.77 × 10 <sup>-7</sup>		
		7.61	1.259 × 10 <sup>-6</sup>		
		7.71	6.92 × 10 <sup>-7</sup>		
		7.74	1.122 × 10 <sup>-6</sup>		
		7.75	4.37 × 10 <sup>-7</sup>		
		7.98	2.57 × 10 <sup>-7</sup>		
		8.01	1.445 × 10 <sup>-7</sup>		

<sup>a</sup>Calculated by the compilers from  $\lg\{[\text{Cd}^{2+}]_{\text{tot}}/\text{mol dm}^{-3}\}$ ; data taken from Fig. 2 of Ref. 12.

**Auxiliary Information****Method/Apparatus/Procedure:**

0.7–0.9 g crystalline CdCO<sub>3</sub> were equilibrated with 30 cm<sup>3</sup> of 0.01 mol dm<sup>-3</sup> NaClO<sub>4</sub> aqueous solution previously equilibrated with N<sub>2</sub>(g) + CO<sub>2</sub>(g) reaction atmosphere gases. The experiments were carried out in controlled atmosphere vessels containing N<sub>2</sub>(g) + CO<sub>2</sub>(g) mixtures that contained approximately 0.0003, 0.001 or 0.138 atm of CO<sub>2</sub>, for periods ranging from 6 to 57 days.

The pH of the samples was adjusted between 6 and 9 (experiments at 0.0003 atm CO<sub>2</sub>), 5 and 8 (experiments at 0.001 atm CO<sub>2</sub>), and 4.5 and 8 (experiments at 0.138 atm CO<sub>2</sub>).

The solutions were analyzed for Cd, by graphite furnace atomic absorption (GFAA) or inductively coupled-plasma mass spectroscopy (ICP-MS).

**Source and Purity of Materials:**

The crystals of CdCO<sub>3</sub>, with otavite structure, were synthesized by the authors according to published procedures,<sup>41</sup> and dried at 65 °C in a 100% CO<sub>2</sub> environment. A cadmium(II) chloride solution was titrated with potassium carbonate solution to pH 8, at 65 °C. The solid was aged in the parent solution and washed until free of chlorides. The solid was identified by x-ray diffraction analysis.

Distilled and deionized water was used.

N<sub>2</sub>(g)–CO<sub>2</sub>(g) mixtures and CO<sub>2</sub>(g) were commercially manufactured.

NaOH was reagent-grade kept in an inert atmosphere, and the acids were double-distilled.

**Estimated Error:**

Nothing specified. The authors state that the CO<sub>2</sub> concentration labeled as 0.0003 atm ranged from 10<sup>-3.49</sup> to 10<sup>-3.52</sup> and those labeled as 0.001 atm ranged from 10<sup>-2.96</sup> to 10<sup>-3.04</sup>.

**Components:**

- (1) Cadmium(II) carbonate; CdCO<sub>3</sub>; [513-78-0]  
 (2) Potassium perchlorate, KClO<sub>4</sub>; [7778-74-7]  
 (3) Potassium hydroxide; KOH; [1310-58-3]  
 (4) Carbon dioxide; CO<sub>2</sub>; [124-38-9]  
 (5) Water; H<sub>2</sub>O; [7732-18-5]

**Original Measurements:**

<sup>14</sup>S.L. Stipp, G.A. Parks, D.K. Nordstrom and J.O. Leckie, *Geochim. Cosmochim. Acta* **57**, 2699 (1993).

**Variables:**

*T/K* = 278.15, 298.15, and 323.15  
*p*<sub>CO<sub>2</sub></sub>, ionic strength and pH

**Prepared by:**

M. C. F. Magalhães

**Experimental Values**

Composition of the saturated solutions in CdCO<sub>3</sub> + CO<sub>2</sub> + H<sub>2</sub>O system at different temperatures and ionic strength.

Date (1989)	<i>θ</i> /°C	100 <i>φ</i> <sub>CO<sub>2</sub></sub>	pH	pK	pClO <sub>4</sub>	pCd	<i>I</i> /mol dm <sup>-3</sup>
Vessel 1							
21-2	5.0	99.9	4.60 <sub>3</sub>	0.0	0.0	3.25	0.0015
22-2	5.0	99.9	4.60 <sub>5</sub>	0.0	0.0	3.20	0.0017
5-3	25.0	99.9	4.55 <sub>6</sub>	0.0	0.0	3.04	0.0021
6-3	25.0	99.9	4.55 <sub>9</sub>	0.0	0.0	3.13	0.0018
7-3	25.0	99.9	4.54 <sub>0</sub>	0.0	0.0	3.12	0.0018
19-3	25.0	99.9	4.56 <sub>8</sub>	0.0	0.0	3.21	0.0016
9-4	25.0	99.9	4.55 <sub>9</sub>	0.0	0.0	3.19	0.0016
1-3	50.0	99.9	4.56 <sub>8</sub>	0.0	0.0	3.08	0.0019
2-3	50.0	99.9	4.56 <sub>8</sub>	0.0	0.0	3.10	0.0018
Vessel 2							
21-1	5.0	99.9	4.70 <sub>1</sub>	2.00	2.00	3.39	0.0114
22-2	5.0	99.9	4.71 <sub>1</sub>	2.00	2.00	3.36	0.0114
5-3	25.0	99.9	4.76 <sub>6</sub>	2.00	2.00	3.42	0.0113
6-3	25.0	99.9	4.82 <sub>6</sub>	2.00	2.00	3.44	0.0113
7-3	25.0	99.9	4.91 <sub>9</sub>	2.00	2.00	3.43	0.0115
19-3	25.0	99.9	4.88 <sub>9</sub>	2.00	2.00	3.41	0.0115
9-4	25.0	99.9	4.91 <sub>3</sub>	2.00	2.00	3.53	0.0113
1-3	50.0	99.9	4.79 <sub>5</sub>	2.00	2.00	3.41	0.0111
2-3	50.0	99.9	4.84 <sub>7</sub>	2.00	2.00	3.49	0.0110
Vessel 3							
19-3	25.0	99.9	6.76 <sub>0</sub>	1.00	0.0	7.25	0.1090
9-4	25.0	99.9	6.69 <sub>0</sub>	1.00	0.0	7.05	0.0995
Vessel 5							
7-3	25.0	1.03	6.28 <sub>7</sub>	2.00	2.00	4.26	0.0103
19-3	25.0	1.03	6.19 <sub>7</sub>	2.00	2.00	4.17	0.0103
9-4	25.0	1.03	6.12 <sub>5</sub>	2.00	2.00	4.16	0.0103

100 *φ*<sub>CO<sub>2</sub></sub> is the volume fraction of CO<sub>2</sub> in the original gas expressed in volume %; pH represents the -lg activity of H<sup>+</sup>; pK, pClO<sub>4</sub>, and pCd represents -lg analytical concentrations of referred species.

**Auxiliary Information****Method/Apparatus/Procedure:**

≤ 1 g dm<sup>-3</sup> of wet synthetic CdCO<sub>3</sub> was dissolved and precipitated in thermostated aqueous solutions, with adjusted ionic strength (*I* < 0.1 mol dm<sup>-3</sup>) by KClO<sub>4</sub> and pH by KOH, and equilibrated with different N<sub>2</sub>/CO<sub>2</sub> gas mixtures. The gas mixtures were bubbling during all the experiments and were prehumidified with water at the temperature of the experiment. pH was measured with a combination electrode, and cadmium dissolved in the filtered solutions (through 0.45 and 0.2 μm filters) was determined by GFAA.

*p*<sub>CO<sub>2</sub></sub> in the experimental solutions was calculated from the volume fraction of CO<sub>2</sub> in the original gas (100 *φ*<sub>CO<sub>2</sub></sub>) by an equation presented by Plummer and Busenberg.<sup>42</sup>

**Source and Purity of Materials:**

- (1) Cadmium(II) carbonate. Prepared by the reaction of recrystallized reagent-grade Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solutions with ultra-pure K<sub>2</sub>CO<sub>3</sub> aqueous solutions in CO<sub>2</sub> atmosphere (at 1 atm). The crystals were kept in a closed vessel immersed in water.
- (2) Potassium perchlorate. Reagent-grade GFS.
- (3) Potassium hydroxide. Reagent-grade Aldrich.
- (4) Carbon dioxide. Experimental grade 99.9%. Commercially made mixture of 1.03 ± 0.02% CO<sub>2</sub> and N<sub>2</sub> (99.9% purity).
- (5) Water. Filtered, deionized through a MilliQ system and then distilled in a glass still with all-glass tubing.

**Estimated Error:**

Temperature: precision ± 0.1 °C.  
 pH: precision ± 0.005.  
 Δ*p*Cd = ± 0.02.

**Components:**

- (1) Cadmium(II) carbonate; CdCO<sub>3</sub>; [513-78-0]  
 (2) Sodium perchlorate; NaClO<sub>4</sub>; [7601-89-0]  
 (3) Perchloric acid; HClO<sub>4</sub>; [7601-90-3]  
 (4) Carbon dioxide; CO<sub>2</sub>; [124-38-98]  
 (5) Water; H<sub>2</sub>O; [7732-18-5]

**Original Measurements:**

<sup>16</sup>H. Gamsjäger, W. Preis, E. Königsberger, M. C. Magalhães, and P. Brandão, *J. Solution Chem.* **28**, 711 (1999).

**Variables:**

*m*<sub>H<sup>+</sup></sub>, *p*<sub>CO<sub>2</sub></sub> at *p*<sub>tot</sub> ≈ 1 atm,  
 298.15 ≤ *T/K* ≤ 348.15 at  
*I* = 1.00 mol kg<sup>-1</sup>, and  
 0.15 ≤ *I* / mol kg<sup>-1</sup> ≤ 5.35 at  
 298.15 K

**Prepared by:**

M.C.F. Magalhães and H. Gamsjäger

**Experimental Values**

Composition of saturated solutions in CdCO<sub>3</sub> + CO<sub>2</sub> + H<sub>2</sub>O system, at 25 °C and various ionic strengths *I*.

<i>I</i> /mol kg <sup>-1</sup>	10 <sup>5</sup> <i>m</i> <sub>H<sup>+</sup>,eq</sub> /mol kg <sup>-1</sup>	10 <sup>3</sup> <i>m</i> <sub>Cd<sup>2+</sup>,tot</sub> /mol kg <sup>-1</sup>	<i>p</i> <sub>CO<sub>2</sub></sub> /atm
0.150	1.32	3.53	0.0917
0.150	3.06	1.91	0.9207
0.150	5.25	5.26	0.916
0.165	1.03	5.07	0.0486
0.166	1.06	5.42	0.0486
0.166	4.27	5.48	0.971
0.166	3.69	5.45	0.974

$I/\text{mol kg}^{-1}$	$10^5 m_{\text{H}^+, \text{eq}}/\text{mol kg}^{-1}$	$10^3 m_{\text{Cd}^{2+}, \text{tot}}/\text{mol kg}^{-1}$	$p_{\text{CO}_2}/\text{atm}$
0.167	4.11	5.82	0.971
0.506	0.96	5.04	0.0478
0.506	4.82	5.26	0.970
0.550	13.4	5.00	0.928
0.550	12.4	5.00	0.926
0.982	4.86	5.13	0.919
0.982	4.43	5.01	0.919
1.000	2.53	16.0	0.0909
1.002	1.44	5.01	0.0912
1.000	2.77	1.94	0.919
1.000	8.59	14.5	0.912
1.051	13.8	5.04	0.933
2.149	14.7	4.95	0.928
2.150	13.3	5.00	0.921
4.329	14.6	4.56	0.989
4.331	14.1	4.64	0.987
4.331	15.2	4.65	0.991
5.349	13.5	4.88	0.934
5.350	13.7	5.01	0.937
5.350	16.1	5.10	0.977
5.350	16.8	5.10	0.974
5.350	16.2	5.22	0.975

Composition of saturated solutions in  $\text{CdCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$  system, at  $I = 1.00 \text{ mol kg}^{-1}$  and various temperatures  $T$ .

$T/\text{K}$	$m(\text{H}^+)_{\text{init}}/\text{mol kg}^{-1}$	$10^5 m(\text{H}^+)_{\text{eq}}/\text{mol kg}^{-1}$	$10^3 m_{\text{Cd}^{2+}, \text{tot}}/\text{mol kg}^{-1}$	$p_{\text{CO}_2}/\text{atm}$
298.15	0.003	2.77	1.94	0.919
298.15	0.010	4.86	5.13	0.919
298.15	0.010	4.43	5.01	0.919
298.15	0.010	1.44	5.01	0.0912
298.15	0.030	2.53	16.0	0.09090
298.15	0.030	8.60	14.5	0.912
310.65	0.010	4.36	5.51	0.890
310.65	0.030	7.24	15.7	0.886
323.15	0.003	7.34	1.54	0.0833
323.15	0.010	1.35	4.99	0.0833
323.15	0.010	4.57	5.93	0.832
323.15	0.030	6.39	16.7	0.831
348.15	0.003	1.78	1.74	0.579
348.15	0.010	3.95	5.47	0.584
348.15	0.010	1.10	5.48	0.0572
348.15	0.030	1.93	16.5	0.0576

#### Auxiliary Information

##### Method/Apparatus/Procedure:

Two series of solubility measurements were carried out in glass-jacketed thermostated solubility cells operating between 5 and 95 °C. Solid  $\text{CdCO}_3$  was equilibrated with  $\text{HClO}_4$  and  $\text{NaClO}_4$ -containing solutions, at fixed partial pressures of carbon dioxide ranging from 0.05 to 1 atm, until the  $\text{H}^+$  ion concentration (determined potentiometrically) became constant, then the  $\text{Cd}^{2+}$  concentration was determined by complexometric titration.

##### Source and Purity of Materials:

Chemically pure materials were used. Samples of  $\text{CdCO}_3$  (otavite) were commercially obtained in reagent-grade quality ( $\text{CdCO}_3$  puriss. Merck), and characterized by x-ray diffraction analysis.

##### Estimated Error:

Temperature:  $\pm 0.03$  °C.

##### Components:

- (1) Cadmium(II) carbonate;  $\text{CdCO}_3$ ; [513-78-0]
- (2) Sodium nitrate;  $\text{NaNO}_3$ ; [7631-99-4]
- (3) Nitric acid;  $\text{HNO}_3$ ; [7697-37-2]
- (4) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

##### Original Measurements:

<sup>17</sup>A. V. Savenko, and V. S. Savenko, *Geochem. Int.* **47**, 835 (2009).

##### Variables:

$T = 298.15 \text{ K}$   
 $p_{\text{CO}_2}$  atmosphere (0.00034 atm)

##### Prepared by:

M. C. F. Magalhães

#### Experimental Values

Composition of the saturated solution in  $\text{CdCO}_3 + \text{H}_2\text{O}$  system, at 25 °C and in 0.05  $\text{mol dm}^{-3}$   $\text{NaNO}_3 + \text{HNO}_3$  aqueous solutions.

$[\text{Cd}^{2+}]_{\text{tot}}/\mu\text{mol dm}^{-3}$	$\lg\{[\text{Cd}^{2+}]_{\text{tot}}/\text{mol dm}^{-3}\}$	pH
0.60	-6.22	8.05
0.57	-6.24	8.04
0.89	-6.05	7.95
1.35	-5.87	7.89
1.47	-5.83	7.86
5.52	-5.26	7.58
7.12	-5.15	7.52
9.43	-5.03	7.46
18.8	-4.73	7.32

#### Auxiliary Information

##### Method/Apparatus/Procedure:

Solid  $\text{CdCO}_3$  was equilibrated with 0.05  $\text{mol dm}^{-3}$   $\text{NaNO}_3 + \text{HNO}_3$  aqueous solutions over five months until constant total cadmium(II) concentration and pH were reached. The temperature was kept in the range 23–24 °C during the first three months and was kept at  $(25 \pm 1)$  °C during the last two months. The weight ratio solid phase: aqueous solution was 1:100, and the samples were periodically stirred with the lid open to equalize the carbon dioxide partial pressure in the solution and in the atmosphere. The filtered solution was analyzed by atomic absorption for cadmium and the pH was measured potentiometrically.

##### Source and Purity of Materials:

Samples of  $\text{CdCO}_3$  were prepared by the mixture of  $\text{NaHCO}_3$  and  $\text{Cd}(\text{NO}_3)_2$  aqueous solutions left to react for one day in an hermetically sealed plastic vessel. After this time, the excess of carbon dioxide was slowly bled and the solid was washed several times with distilled water, filtered and dried at 105 °C.

There is no reference to the source or purity of the chemical reagents used or the identification of the solid obtained.

##### Estimated Error:

Temperature:  $\pm 1$  °C.

$c_{\text{Cd}^{2+}}$ :  $\pm 2\%$ .

pH:  $\pm 0.005$ .

### 3. Solubility in Ternary Systems

#### 3.1. Critical evaluation of the solubility in the system $\text{CdCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

Components:	Evaluators:
(1) Cadmium(II) carbonate; $\text{CdCO}_3$ ; [513-78-0]	M. C. F. Magalhães, CICECO and Department of Chemistry, University of Aveiro, Aveiro, Portugal
(2) Carbon dioxide; $\text{CO}_2$ ; [124-38-9]	H. Gamsjäger, Lehrstuhl für Physikalische Chemie, Montanuniversität Leoben, Leoben, Austria
(3) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	August 2010

Only Karnaukhov *et al.*<sup>6</sup> and Davis *et al.*<sup>10</sup> determined the solubility of cadmium(II) carbonate in pure water in contact either with the laboratory atmosphere<sup>6</sup> or with controlled carbon dioxide partial pressure atmospheres.<sup>10</sup> Karnaukhov *et al.*<sup>6</sup> do not present any experimental data and only recorded the solubility constant with the value  $\lg K_{s0} = -11.29$ . These authors were aware of the difficulty to get reliable values for the solubility product of sparingly soluble compounds and used an unusual analytical method. The lack of detailed information about the method used and the results obtained does not allow further analysis. Davis *et al.*<sup>10</sup> obtained  $\lg K_{s0}^{\circ} = -(11.31 \pm 0.03)$  from their experimental data. This is similar to the value obtained by Karnaukhov *et al.*<sup>6</sup> Both values are higher than the recommended value of  $\lg K_{s0}^{\circ} = -12.03$ .

Rai *et al.*<sup>12</sup> analyzed the work done by Davis *et al.*<sup>10</sup> in order to understand why their values were about one order of magnitude higher than those previously published and even those obtained by themselves. As both experiments were carried out at low ionic strength, Rai *et al.*<sup>12</sup> concluded that the difference arose from the methodology used by Davis *et al.*<sup>10</sup> The latter only centrifuged the solutions without any further filtration. Rai *et al.*<sup>12</sup> repeated this methodology and found that the value obtained for the concentration of cadmium(II) in solution is much higher in unfiltered samples than in the filtered ones. These authors concluded that the inadequate separation of solids from solution is probably the main source of error in the work of Davis *et al.*<sup>10</sup> The terse description of the experimental work of Karnaukhov *et al.*<sup>6</sup> does not allow understanding the source of errors that led to a solubility product higher than the one recommended here.

#### 3.2. Experimental data in the system $\text{CdCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

Components:	Original Measurements:
(1) Cadmium(II) carbonate; $\text{CdCO}_3$ ; [513-78-0]	<sup>6</sup> A. I. Karnaukhov, V. V. Grinevich, and E. M. Skobets, Zh. Anal. Khim. <b>28</b> , 2298 (1973).
(2) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	
Variables:	Prepared by:
$T = 291.15 \text{ K}$ $p_{\text{CO}_2}$ atmosphere (0.00032 bar)	B. R. Churagulov

#### Experimental Values

The solubility product,  $K_{s0}$ , of cadmium(II) carbonate in water was given by the value  $K_{s0} = 5.1 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$ .

#### Auxiliary Information

##### Method/Apparatus/Procedure:

An isothermal method was applied, using a special glass vessel (volume  $50 \text{ cm}^3$ ) with a magnetic mixer, and with a stopper with holes for electrodes, for the glass tube with solid, for connections to the atmosphere and the nitrogen for purging the test solution, and for a thermometer. The solid salt was placed in the glass tube sealed at one end with filter paper. After equilibrium was reached, the glass tube with solid salt was pulled out from the solution (volume of solution was about  $27 \text{ cm}^3$ ). Then  $3 \text{ cm}^3$  of  $1 \text{ mol dm}^{-3} \text{ KNO}_3$  aqueous solution were added and the electrodes were put in the solution.

The solubility of cadmium(II) carbonate was determined by the method of inversion chronopotentiometry with a given resistance in the oxidation circuit on a silver-amalgamated electrode.

The calomel electrode was used as a reference electrode. The concentration of Cd in saturated solutions was determined by the addition method. A continuous  $\text{N}_2$  flow was bubbled through the solution during electrolysis that was carried out at  $-1.2 \text{ V}$ .

##### Source and Purity of Materials:

Cadmium(II) carbonate was prepared by precipitation from  $\text{K}_2\text{CO}_3$  solution, adding  $\text{Cd}(\text{CH}_3\text{COO})_2$  solutions, and washing the solid with bidistilled water.  $\text{K}_2\text{CO}_3$  and  $\text{Cd}(\text{CH}_3\text{COO})_2$  CP-grade reagents were used.

##### Estimated Error:

Temperature: precision  $\pm 0.1 \text{ K}$ .

Solubility: reproducibility  $\pm 5\%$  (compilers).

Components:	Original Measurements:
(1) Cadmium(II) carbonate; $\text{CdCO}_3$ ; [513-78-0]	<sup>10</sup> J. A. Davis, C. C. Fuller, and A. D. Cook, Geochim. Cosmochim. Acta <b>51</b> , 1477 (1987).
(2) Carbon dioxide; $\text{CO}_2$ ; [124-38-9]	
(3) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	
Variables:	Prepared by:
$T = 298.15 \text{ K}$ $p_{\text{CO}_2}$ , ionic strength	K. Sawada

#### Experimental Values

Composition of the saturated solutions in  $\text{CdCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$  system, at  $25^\circ\text{C}$ .

$p_{\text{CO}_2}/\text{atm}$	$\text{pH}_{\text{eq}}$	$10^4 c_{\text{Cd}^{2+},\text{tot}}/\text{mol dm}^{-3}$	$I/\text{mol dm}^{-3}$
0.25	5.40	4.98	0.00149
0.25	5.38	4.77	0.00142
0.0102	6.33	1.66	0.000498
0.0102	6.32	1.68	0.000504
0.001971	6.81	1.68	0.000324

## Auxiliary Information

## Method/Apparatus/Procedure:

The equilibrium pH and dissolved cadmium(II) concentration of a saturated aqueous solution of cadmium(II) carbonate were measured under a fixed partial pressure of carbon dioxide. Solid cadmium(II) carbonate was added to 100 cm<sup>3</sup> of degassed, deionized water and left to equilibrate at 25 °C with atmospheres containing carbon dioxide in nitrogen with carbon dioxide partial pressure of 0.25, 0.0102, and 0.001971 atm. The pH of the suspension was monitored continuously until a constant pH was obtained (<15 h), and an aliquot of solution was withdrawn for total dissolved cadmium analysis by flame atomic absorption.

## Source and Purity of Materials:

Cadmium(II) carbonate was synthesized by precipitation, at 25 °C, from 0.01 mol dm<sup>-3</sup> cadmium(II) chloride aqueous solutions titrated with 1 mol dm<sup>-3</sup> sodium carbonate solution to pH 7.5. The well-crystallized precipitate was identified as cadmium(II) carbonate (otavite) by x-ray diffraction. The crystals appeared nearly cubic in shape in transmission electron micrographs, with an average edge length of 1.2 μm. High purity, commercially prepared and analyzed gas mixtures were used. Double deionized water and reagent-grade salts were used.

## Estimated Error:

Nothing specified.

### 3.3. Critical evaluation of the solubility in the system CdCO<sub>3</sub> + M<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O

## Components:

- (1) Cadmium(II) carbonate; CdCO<sub>3</sub>; [513-78-0]  
 (2) Potassium carbonate; K<sub>2</sub>CO<sub>3</sub>; [584-08-7]  
 (3) Sodium carbonate; Na<sub>2</sub>CO<sub>3</sub>; [497-19-8]  
 (4) Sodium hydrogencarbonate; NaHCO<sub>3</sub>; [144-55-8]  
 (5) Sodium hydroxide; NaOH; [1310-73-2]  
 (6) Water; H<sub>2</sub>O; [7732-18-5]

## Evaluators:

M. C. F. Magalhães, CICECO and Department of Chemistry, University of Aveiro, Aveiro, Portugal  
 H. Gamsjäger, Lehrstuhl für Physikalische Chemie, Montanuniversität Leoben, Leoben, Austria  
 August 2010

Lake and Goodings<sup>3</sup> and Rai *et al.*<sup>12</sup> investigated the solubility of cadmium(II) carbonate in alkaline solutions. Their experiments were carried out in a closed ternary system composed of cadmium(II) carbonate (otavite) in equilibrium with aqueous solutions of sodium or potassium carbonate in the pH range between 9 and 12. The pH of a solution of sodium or potassium carbonate is around 11, and this was the pH of the experiments done by Lake and Goodings.<sup>3</sup> These authors didn't report the pH of the solutions, but they dissolved cadmium(II) nitrate in aqueous solutions of potassium carbonate with concentrations ranging from 0.25 to 5 mol dm<sup>-3</sup>. The solid obtained from this reaction was also not characterized by the authors, but a comparison made by Rai *et al.*<sup>12</sup> between their own results, obtained from analogous systems with lower ionic strength, and the results of Lake and Goodings,<sup>3</sup> show that all of them fit in the same model.

The solutions used by Rai *et al.*<sup>12</sup> with pH between 9 and 11 fall inside the hydrogencarbonate/carbonate buffer range and contain mixtures of both ions in the necessary proportions. The solutions with pH > 11 were made by mixtures of sodium carbonate and sodium hydroxide.

Rai *et al.*<sup>12</sup> measured the solubility of CdCO<sub>3</sub>(s) at pH ≈ 11 as a function of Na<sub>2</sub>CO<sub>3</sub> concentration and found it necessary to invoke CdCO<sub>3</sub>(aq) and [Cd(CO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> complexes to interpret the results. They also had to derive Pitzer parameters (β°) for the interactions of Cd(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> with Na<sup>+</sup> and K<sup>+</sup>, respectively, to achieve agreement with their CdCO<sub>3</sub>(s) solubilities in Na<sub>2</sub>CO<sub>3</sub>(aq) and with those measured by Lake and Goodings<sup>3</sup> in K<sub>2</sub>CO<sub>3</sub> solutions.

The results obtained from the determination of cadmium(II) carbonate solubility under these experimental conditions listed in Table 3 were re-evaluated by an admittedly

TABLE 3. Solubility of CdCO<sub>3</sub>(cr) in aqueous Na<sub>2</sub>CO<sub>3</sub> (No. 1–28) and K<sub>2</sub>CO<sub>3</sub> (No. 29–36) solutions at 25 °C.

No	lg ( <i>m</i> <sub>CO<sub>3</sub><sup>2-</sup>/<i>m</i><sup>o</sup>)</sub>	<i>I</i> /mol kg <sup>-1</sup>	lg ( <i>m</i> <sub>Cd<sup>2+</sup>,tot/<i>m</i><sup>o</sup>)</sub>	lg { <i>m</i> <sub>[Cd(CO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup>/<i>m</i><sup>o</sup>}</sub>	lg <i>K</i> <sub>s1</sub> <sup>o</sup>	lg <i>K</i> <sub>s2</sub>
1	-2.848	0.004	-7.377	-	-7.377	-
2	-2.731	0.006	-7.558	-	-7.558	-
3	-2.748	0.005	-7.762	-	-7.762	-
4	-2.567	0.008	-7.558	-	-7.558	-
5	-2.511	0.009	-7.687	-	-7.687	-
6	-2.307	0.015	-7.358	-7.741	-	-
7	-2.063	0.026	-7.415	-7.894	-	-5.835
8	-2.009	0.029	-7.192	-7.414	-	-5.406
9	-1.786	0.049	-7.007	-7.138	-	-5.353
10	-1.765	0.052	-7.102	-7.273	-	-5.509
11	-1.737	0.055	-6.992	-7.118	-	-5.382
12	-1.629	0.071	-6.902	-7.002	-	-5.373
13	-1.592	0.077	-6.864	-6.954	-	-5.363
14	-1.014	0.290	-6.920	-7.024	-	-6.010
15	-1.033	0.278	-6.645	-6.697	-	-5.664
16	-0.996	0.302	-6.664	-6.718	-	-5.722
17	-0.996	0.302	-6.313	-6.336	-	-5.340
18	-0.726	0.564	-6.478	-6.513	-	-5.788
19	-0.716	0.577	-6.168	-6.185	-	-5.469
20	-0.453	1.057	-6.093	-6.107	-	-5.654
21	-0.453	1.057	-5.912	-5.921	-	-5.468
22	-0.425	1.127	-5.946	-5.956	-	-5.531
23	-0.290	1.537	-5.688	-5.694	-	-5.403
24	-0.300	1.502	-5.469	-5.473	-	-5.172
25	-0.144	2.152	-5.396	-5.399	-	-5.255
26	-0.099	2.389	-5.287	-5.289	-	-5.190
27	-0.026	2.825	-5.120	-5.122	-	-5.095
28	0.002	3.014	-5.063	-5.064	-	-5.066
29	-0.049	2.683	-4.638	-4.638	-	-4.590
30	0.091	3.703	-4.668	-4.668	-	-4.760
31	0.120	3.958	-4.761	-4.761	-	-4.882
32	0.449	8.435	-4.041	-4.041	-	-4.490
33	0.656	13.573	-3.332	-3.332	-	-3.988
34	0.678	14.292	-3.347	-3.347	-	-4.025
35	0.852	21.315	-2.550	-2.550	-	-3.402
36	0.893	23.473	-2.043	-2.043	-	-2.936

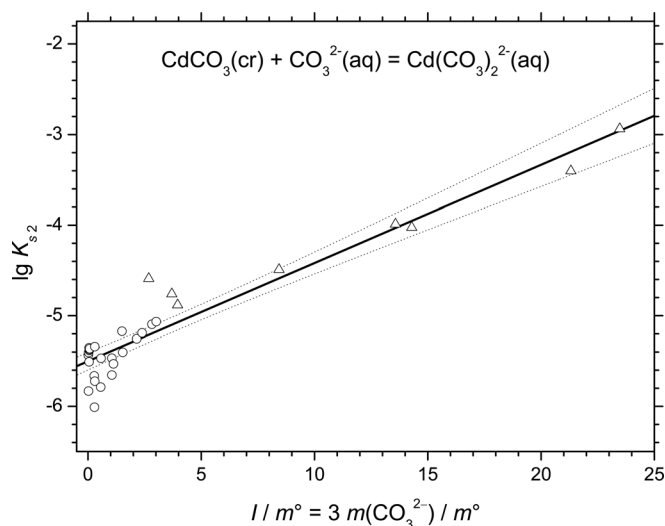
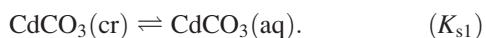
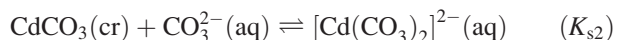


Fig. 5. SIT analysis, linear regression.  $\Delta$  Lake and Goodings;<sup>3</sup>  $\circ$  Rai *et al.*,<sup>12</sup> bold solid line:  $\lg K_{s2}^{\circ} = \lg K_{s2} - \Delta\epsilon I$ , dotted curves: 95% confidence limits,  $\lg K_{s2}^{\circ} = -(5.50 \pm 0.10)$ ,  $\Delta\epsilon = -(0.108 \pm 0.013) \text{ kg mol}^{-1}$ , uncertainties conform to 95% confidence limits.

oversimplified SIT approach which, however, resulted in stability (formation) constants of cadmium(II)-carbonato complexes consistent with those given by Rai *et al.*<sup>12</sup> as well as those provisionally selected by Powell *et al.*<sup>24</sup> At low carbonate molalities (Table 3, No. 1–5), the uncharged species  $\text{CdCO}_3(\text{aq})$  determines the solubility according to



Higher carbonate molalities lead to the formation of the dicarbonato complex  $[\text{Cd}(\text{CO}_3)_2]^{2-}$



As a first approximation, it was assumed that  $\lg K_{s1}$  can be derived from  $\lg[m_{\text{Cd}^{2+},\text{tot}}/m^{\circ}]$  neglecting any ionic strength correction. Reaction ( $K_{s2}$ ) is isocoulombic, so that electrolyte composition should have little influence on the magnitude of  $\lg K_{s2}$  and the Debye-Hückel term vanishes. For the classical SIT approach,  $\lg K_{s2}$  was plotted against the ionic strength  $I \approx 3m_{\text{CO}_3^{2-}}$ , see Fig. 5. At least one third of the data falls outside the 95% confidence range and the data of Lake and Goodings<sup>3</sup> seem to dominate the regression. If non-linear regression was employed for the SIT approach, the same values and uncertainties were obtained for  $\lg K_{s2}^{\circ}$  and  $\Delta\epsilon$ , however, less data seem to fall outside the 95% confidence range and the regression is no longer dominated by the data of Ref. 3, see Fig. 6. For the final comparison of theory and experiment,  $\lg(m_{\text{Cd}^{2+},\text{tot}}/m^{\circ})$  was plotted vs  $\lg(m_{\text{CO}_3^{2-}}/m^{\circ})$ , see Fig. 7. Now only 6 of 36 data pairs fall outside the 95% confidence range. Clearly, regression analysis could have been repeated after having rejected those 6 data pairs as outliers. In view of the fact that the whole data set was taken from Fig. 4 of Rai *et al.*<sup>12</sup> and thus of limited numerical precision, a repetition did not seem justified.

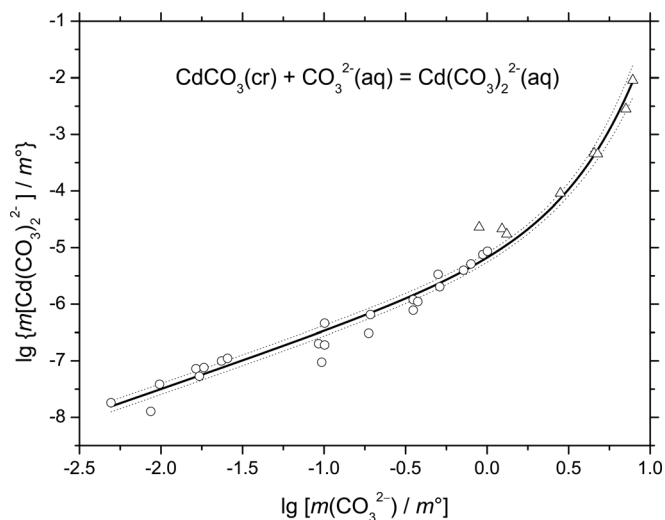


Fig. 6. SIT analysis, non-linear regression.  $\Delta$  Lake and Goodings;<sup>3</sup>  $\circ$  Rai *et al.*,<sup>12</sup> bold solid curve:  $\lg\{m_{[\text{Cd}(\text{CO}_3)_2]^{2-}}/m^{\circ}\} = \lg K_{s2}^{\circ} + \lg[m_{\text{CO}_3^{2-}}/m^{\circ}] - \Delta\epsilon 3[m_{\text{CO}_3^{2-}}/m^{\circ}]$ , dotted curves: 95% confidence limits,  $\lg K_{s2}^{\circ} = -(5.50 \pm 0.05)$ ,  $\Delta\epsilon = -(0.108 \pm 0.007) \text{ kg mol}^{-1}$ , uncertainties conform to  $\sigma$ .

**Tentative set of thermodynamic quantities:** The following values and uncertainties ( $2\sigma$ ) for solubility constants of  $\text{CdCO}_3(\text{cr})$  and interaction parameters of  $[\text{Cd}(\text{CO}_3)_2]^{2-}(\text{aq})$  obtained from the data listed in Table 3 are accepted tentatively,

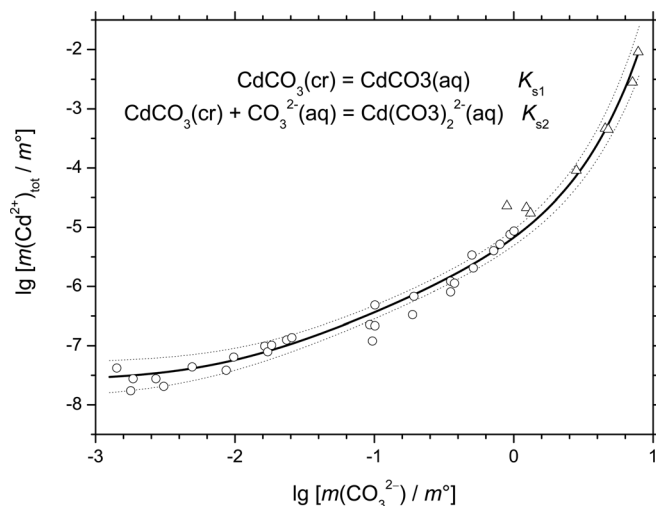
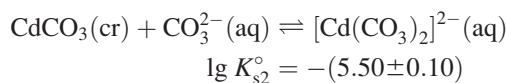
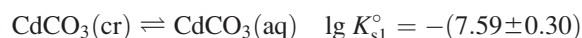


Fig. 7. Solubility of  $\text{CdCO}_3(\text{cr})$  in  $(\text{Na/K})_2\text{CO}_3$  solutions.  $\Delta$  Lake and Goodings,<sup>3</sup>  $\circ$  Rai *et al.*,<sup>12</sup> bold solid curve:  $\lg[m_{\text{Cd}^{2+},\text{tot}}] = \lg\{m_{\text{CdCO}_3} + m_{[\text{Cd}(\text{CO}_3)_2]^{2-}}\}$ , dotted curves: 95% confidence limits,  $\lg K_{s1}^{\circ} = -(7.59 \pm 0.30)$ ,  $\lg K_{s2}^{\circ} = -(5.50 \pm 0.10)$ ,  $\Delta\epsilon = -(0.108 \pm 0.013) \text{ kg mol}^{-1}$ , uncertainties conform to  $2\sigma$ .

$$\varepsilon(\text{Na}^+, [\text{Cd}(\text{CO}_3)_2]^{2-}) = -(0.19 \pm 0.03) \text{ kg mol}^{-1}$$

$$\varepsilon(\text{K}^+, [\text{Cd}(\text{CO}_3)_2]^{2-}) = -(0.09 \pm 0.02) \text{ kg mol}^{-1},$$

where  $\varepsilon(\text{Na}^+, \text{CO}_3^{2-}) = -(0.08 \pm 0.03)$  and  $\varepsilon(\text{K}^+, \text{CO}_3^{2-}) = (0.02 \pm 0.01) \text{ kg mol}^{-1}$  were taken from Table B-5 of Ref. 34.

Combining  $\lg K_{s1}^\circ$  with  $\lg K_{s0}^\circ$  ( $-12.03 \pm 0.13$ ) recommended in this work results in  $\lg K_1^\circ = \lg a_{\text{CdCO}_3} = 4.44 \pm 0.30$ , which agrees with  $\lg K_1^\circ = 4.4 \pm 0.20$  of Ref. 24 and overlaps with  $\lg K_1^\circ = 4.71 \pm 0.1$  of Ref. 12. Combining  $\lg K_{s2}^\circ$  with  $\lg K_{s0}^\circ$  leads to  $\lg \beta_2^\circ = 6.53 \pm 0.20$  which agrees very well with  $\lg \beta_2^\circ = 6.49 \pm 0.10$  of Ref. 12.

Li *et al.*<sup>18</sup> added  $\text{Cd}(\text{NO}_3)_2$  to  $\text{NaHCO}_3$  solutions, adjusted the pH by  $\text{NaOH}$  and  $\text{HNO}_3$ , kept  $[\text{CO}_3^{2-}]_{\text{tot}}$  at  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ , and measured the turbidity by light scattering. From the equilibrium data of pH and  $\lg\{[\text{Cd}^{2+}]_{\text{tot}}\}$ , the solubility product can be roughly estimated; see the compilation sheet for Ref. 18. Due to lack of information, no ionic strength corrections could be applied and thus the data were not reliable enough to be included into the recommended set of solubility data.

Holm *et al.*<sup>15</sup> determined the solubility of cadmium(II) carbonate in solutions of sodium hydrogencarbonate with ionic strengths around  $0.02 \text{ mol dm}^{-3}$  and pH between 6.5 and 8.5. The authors state that the solubility product  $K_{s0}^\circ = (1.64 \pm 0.08) \times 10^{-13}$  was obtained from equilibrium calculations considering corrections for the ionic strength and also the existence of the complexes  $\text{CdCO}_3(\text{aq})$  and  $\text{CdHCO}_3^+(\text{aq})$ . However, in the discussion of the results, the authors recognized that probably this value was underestimated, since the values for the stability constants of those two complex species were uncertain. Considering that the Cd-carbonate complexes are negligible for  $\text{pH} < 8$ , they obtained  $K_{s0}^\circ = (2.51 \pm 0.08) \times 10^{-13}$  ( $\lg K_{s0}^\circ = -12.60$ ), which is still lower than the recommended value. No original data were given in the paper, except those presented in the compilation. Besides the values of pH and total cadmium(II) concentrations, the total concentration of carbonate was determined, but no values were presented in the original work. The lack of experimental values does not allow a further analysis of the results of Holm *et al.*<sup>15</sup>

### 3.4. Experimental data in the system $\text{CdCO}_3 + \text{M}_2\text{CO}_3 + \text{H}_2\text{O}$

Components:	Original Measurements:
(1) Cadmium(II) nitrate–water (1/4); $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ; [10022-68-1]	<sup>3</sup> P. E. Lake and J. M. Goodings, Can. J. Chem. <b>36</b> , 1089 (1958).
(2) Potassium carbonate; $\text{K}_2\text{CO}_3$ ; [584-08-7]	
(3) Water; $\text{H}_2\text{O}$ ; [7732-18-5]	
Variables:	Prepared by:
$T/K = 273.15, 298.15, \text{ and } 323.15$	M. C. F. Magalhães

### Experimental Values

Total concentration of cadmium(II) in solutions of potassium carbonate in equilibrium with cadmium(II) carbonate.<sup>a</sup>

$\theta/^\circ\text{C}$	$c_{\text{Cd}^{2+}, \text{tot}}/\text{mol dm}^{-3}$	$c_{\text{carbonate}, \text{tot}}/\text{mol dm}^{-3}$
0	$1.35 \times 10^{-4}$	3.3
0	$4.7 \times 10^{-4}$	4.55
25	$2.1 \times 10^{-5}$	0.9
25	$2.1 \times 10^{-5}$	1.15
25	$3.4 \times 10^{-4}$	3.45
50	$2.1 \times 10^{-5}$	0.25
50	$2.4 \times 10^{-4}$	1.8
50	$1.4 \times 10^{-3}$	3.1
50	$6.7 \times 10^{-3}$	4.2

<sup>a</sup>Selected from data presented in Fig. 2 of Ref. 3.

### Auxiliary Information

#### Method/Apparatus/Procedure:

Solutions of  $\text{K}_2\text{CO}_3$  ( $0.5 \text{ dm}^3$ ) with concentrations from  $0.25$  to  $5 \text{ mol dm}^{-3}$  were mixed with  $1 \text{ g}$  of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and left in contact, at the temperatures of  $0, 25,$  and  $50^\circ\text{C}$ , for different times, with periodic vigorous shaking, until equilibrium was reached. Samples of the clear liquid were removed from time to time and analyzed polarographically for cadmium, and titrimetrically with standard solutions of  $\text{HCl}$  for carbonate.

#### Source and Purity of Materials:

There is no reference to the purity of the chemical reagents used, and the solids obtained were not identified.

#### Estimated Error:

$c_{\text{cadmium}}: \pm 10\%$ .

$c_{\text{carbonate}}: \pm 5\%$ .

#### Components:

- (1) Cadmium(II) carbonate;  $\text{CdCO}_3$ ;  
[513-78-0]
- (2) Sodium carbonate;  $\text{Na}_2\text{CO}_3$ ;  
[497-19-8]
- (3) Sodium hydroxide;  $\text{NaOH}$ ;  
[1310-73-2]
- (4) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

#### Original Measurements:

<sup>12</sup>D. Rai, A. R. Felmy, and D. A. Moore, J. Solution Chem. **20**, 1169 (1991).

#### Variables:

Composition of the solution  
 $T = 298.15 \text{ K}$ ,  $\text{pH} = 11$ , ionic strength

#### Prepared by:

M. C. F. Magalhães and H. Gamsjäger

### Experimental Values

Concentrations of total cadmium(II) and carbonate in  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$   $0.001 \text{ mol dm}^{-3}$  and  $\text{Na}_2\text{CO}_3$  aqueous solutions, at  $\text{pH} 11$  in closed system.

$\lg(c_{\text{Cd}^{2+}}/c^\circ)^a$	$\lg(c_{\text{carbonate}}/c^\circ)^a$	$\lg(m_{\text{Cd}^{2+}}/m^\circ)^b$	$\lg(m_{\text{carbonate}}/m^\circ)^b$
-7.377	-2.848	-7.377	-2.848
-7.558	-2.731	-7.558	-2.731
-7.762	-2.748	-7.762	-2.748
-7.558	-2.567	-7.558	-2.567

$\lg(c_{\text{Cd}^{2+}}/c^\circ)^a$	$\lg(c_{\text{carbonate}}/c^\circ)^a$	$\lg(m_{\text{Cd}^{2+}}/m^\circ)^b$	$\lg(m_{\text{carbonate}}/m^\circ)^b$
-7.687	-2.511	-7.687	-2.511
-7.358	-2.307	-7.358	-2.307
-7.415	-2.063	-7.415	-2.063
-7.192	-2.009	-7.192	-2.009
-7.007	-1.786	-7.007	-1.786
-7.102	-1.765	-7.102	-1.765
-6.992	-1.737	-6.992	-1.737
-6.902	-1.629	-6.902	-1.629
-6.864	-1.592	-6.864	-1.592
-6.92	-1.015	-6.920	-1.014
-6.645	-1.034	-6.645	-1.033
-6.664	-0.997	-6.664	-0.996
-6.313	-0.997	-6.313	-0.996
-6.479	-0.727	-6.478	-0.726
-6.169	-0.717	-6.168	-0.716
-6.094	-0.455	-6.093	-0.453
-5.913	-0.455	-5.912	-0.453
-5.947	-0.427	-5.946	-0.425
-5.69	-0.293	-5.688	-0.290
-5.471	-0.303	-5.469	-0.300
-5.399	-0.148	-5.396	-0.144
-5.290	-0.103	-5.287	-0.099
-5.124	-0.0309	-5.120	-0.026
-5.067	-0.003	-5.063	0.002

<sup>a</sup>Data taken by compilers from Fig. 4 of Ref. 12.

<sup>b</sup>Converted to molality basis by compilers using Table II-5 of Ref. 34.

### Experimental Values

Concentrations of total cadmium(II) and carbonate in aqueous  $\text{K}_2\text{CO}_3$  solutions, at pH 11 in closed system.

$\lg(c_{\text{Cd}^{2+}}/c^\circ)^{a,b}$	$\lg(c_{\text{carbonate}}/c^\circ)^{a,b}$	$\lg(m_{\text{Cd}^{2+}}/m^\circ)^c$	$\lg(m_{\text{carbonate}}/m^\circ)^c$
-4.648	-0.059	-4.638	-0.049
-4.682	0.077	-4.668	0.091
-4.776	0.105	-4.761	0.120
-4.078	0.412	-4.041	0.449
-3.399	0.589	-3.332	0.656
-3.418	0.607	-3.347	0.678
-2.666	0.736	-2.550	0.852
-2.172	0.764	-2.043	0.893

<sup>a</sup>Data presented in Fig. 4 of Ref. 12.

<sup>b</sup>These data shown graphically in Ref. 12 were originally obtained by Lake and Goodings.<sup>3</sup>

<sup>c</sup>Converted to molality basis by compilers using Table II-5 of Ref. 34.

### Auxiliary Information

#### Method/Apparatus/Procedure:

Around 86 mg of crystalline  $\text{CdCO}_3$  were equilibrated in a closed tube with  $30 \text{ cm}^3$  of  $\text{Na}_2\text{CO}_3$  aqueous solution with concentrations  $>0.01 \text{ mol dm}^{-3}$ , or with  $30 \text{ cm}^3$  of  $\text{Na}_2\text{CO}_3$  aqueous solution with concentrations  $<0.01 \text{ mol dm}^{-3}$  in  $\text{NaOH}$   $0.001 \text{ mol dm}^{-3}$ , for periods from 2 to 31 days. The calculated pH of all the samples was around 11.

The solutions were analyzed for Cd by GFAA or ICP-MS, and for C with a carbon analyzer.

#### Source and Purity of Materials:

The crystals of  $\text{CdCO}_3$ , with otavite structure, were synthesized by the authors according to published procedures<sup>41</sup> and dried at  $65^\circ\text{C}$  in 100%  $\text{CO}_2$  environment. A cadmium(II) chloride solution was titrated with potassium carbonate solution to pH 8 at  $65^\circ\text{C}$ . The solid was aged in the parent solution and washed until free of chlorides. The solid was identified by x-ray diffraction analysis.

Distilled and deionized water was used.

$\text{NaOH}$  was reagent-grade kept in an inert atmosphere, and standard  $\text{Na}_2\text{CO}_3$  solutions were used.

#### Estimated Error:

Nothing specified, no estimates possible.

#### Components:

(1) Cadmium(II) carbonate;  $\text{CdCO}_3$ ;

[513-78-0]

(2) Sodium carbonate;  $\text{Na}_2\text{CO}_3$ ;

[497-19-8]

(3) Sodium hydrogencarbonate;

$\text{NaHCO}_3$ ; [144-55-8]

(4) Sodium hydroxide;  $\text{NaOH}$ ;

[1310-73-2]

(5) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

#### Original Measurements:

<sup>12</sup>D. Rai, A. R. Felmy, and D. A. Moore, J. Solution Chem. **20**, 1169 (1991).

#### Variables:

Composition of the solution

$T = 298.15 \text{ K}$ , pH, ionic strength

#### Prepared by:

M. C. F. Magalhães and H.

Gamsjäger

### Experimental Values

Total concentration of cadmium(II) in solutions with  $0.1 \text{ mol dm}^{-3}$  carbonate, at different pH in closed system.<sup>a</sup>

$-\lg(c_{\text{OH}^-}/c^\circ)$	$\lg(c_{\text{Cd}^{2+}}/c^\circ)$
2.48	-6.44
2.48	-6.78
2.40	-6.50
2.40	-6.57
2.28	-6.44
2.28	-6.81
2.18	-6.39
2.18	-6.76
2.00	-6.44
2.00	-6.66

<sup>a</sup>Data taken from Fig. 5 of Ref. 12.

Total concentration of cadmium(II) in solutions with  $0.01 \text{ mol dm}^{-3}$  carbonate, at different pH in closed system.<sup>a</sup>

$-\lg(c_{\text{OH}^-}/c^\circ)$	$\lg(c_{\text{Cd(II)}}/c^\circ)$
4.79	-7.74
4.47	-7.74
4.13	-7.74
3.85	-7.73
3.51	-7.73
3.19	-7.73
3.01	-7.72
3.00	-7.72

$-\lg(c_{\text{OH}^-}/c^\circ)$	$\lg(c_{\text{Cd(II)}}/c^\circ)$
2.97	-7.71
2.81	-7.71
2.65	-7.71
2.46	-7.71
2.25	-7.49
12.00	-7.47

<sup>a</sup>Data taken from Fig. 6 of Ref. 12.

#### Auxiliary Information

##### Method/Apparatus/Procedure:

Around 86 mg of crystalline  $\text{CdCO}_3$  were equilibrated in a sealed tube with  $30 \text{ cm}^3$  of 0.1 or 0.01  $\text{mol dm}^{-3}$   $\text{Na}_2\text{CO}_3$  or 0.01  $\text{mol dm}^{-3}$   $\text{NaHCO}_3$  aqueous solutions adjusted to different pH values with NaOH solutions. The samples with 0.1  $\text{mol dm}^{-3}$  carbonate were equilibrated for 3 and 117 days and the solutions with 0.01  $\text{mol dm}^{-3}$  carbonate were equilibrated for 3 days. The solutions were analyzed for Cd by GFAA or ICP-MS, and for C with a carbon analyzer.

##### Source and Purity of Materials:

The crystals of  $\text{CdCO}_3$ , with otavite structure, were synthesized by the authors according to published procedures<sup>41</sup> and dried at  $65^\circ\text{C}$  in 100%  $\text{CO}_2$  environment. A cadmium(II) chloride solution was titrated with potassium carbonate solution to pH 8 at  $65^\circ\text{C}$ . The solid was aged in the parent solution and washed until free of chlorides. The solid was identified by x-ray diffraction analysis.

Distilled and deionized water was used.

NaOH was reagent-grade kept in an inert atmosphere, and standard  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  solutions were used.

##### Estimated Error:

Nothing specified, no estimates possible.

##### Components:

(1) Cadmium(II) nitrate–water  
(1/4);  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ;  
[10022-68-1]

(2) Sodium hydrogencarbonate;  
 $\text{NaHCO}_3$ ; [144-55-8]

(3) Nitric acid;  $\text{HNO}_3$ ; [7697-37-2]

(4) Sodium hydroxide; NaOH;  
[1310-73-2]

(5) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

##### Variables:

Composition of salts  
 $T = 298 \text{ K}$

##### Original Measurements:

<sup>18</sup>J. Li, H. X. Tan, and H. B. Xue,  
Environ. Chem. (in Chinese) 8(6), 1  
(1989).

##### Prepared by:

D. Zeng and H. Gamsjäger

#### Experimental Values

Solubility of cadmium(II) nitrate in aqueous sodium hydrogencarbonate solution as a function of pH value at  $25^\circ\text{C}$ .<sup>a</sup>

pH	$-\lg c_{\text{Cd}(\text{NO}_3)_2}$ <sup>b</sup>	$\lg K_{s0} \approx \lg(c_{\text{Cd}^{2+}} c_{\text{CO}_3^{2-}})$ <sup>c</sup>	Equilibrium solid phase
6.6	$3.1 \pm 0.1$	-12.2	Unknown
7.5	$4.0 \pm 0.1$	-12.2	Unknown
7.6	$4.3 \pm 0.1$	-12.4	Unknown
8.0	$5.0 \pm 0.1$	-12.7	Unknown

pH	$-\lg c_{\text{Cd}(\text{NO}_3)_2}$ <sup>b</sup>	$\lg K_{s0} \approx \lg(c_{\text{Cd}^{2+}} c_{\text{CO}_3^{2-}})$ <sup>c</sup>	Equilibrium solid phase
8.4	$5.3 \pm 0.1$	-12.6	Unknown
9.5	$5.3 \pm 0.1$	-11.5	Unknown

<sup>a</sup>In the saturated solution, the total concentration of  $[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$  is kept as  $10^{-3} \text{ mol dm}^{-3}$ ; the data are read by the compiler from the figures in the original literature.

<sup>b</sup>The unit of  $c$  is  $\text{mol dm}^{-3}$ .

<sup>c</sup>Estimated by evaluator.

#### Auxiliary Information

##### Method/Apparatus/Procedure:

$\text{NaHCO}_3$  solutions with different concentrations were prepared by adding  $\text{NaHCO}_3$  stock solution to three-time distilled fresh water. Then, different amounts of  $0.5 \text{ g dm}^{-3}$  stock solution of  $\text{Cd}(\text{NO}_3)_2$  were added to the  $\text{NaHCO}_3$  solution. In this way, solutions with constant total carbonate concentration ( $[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ ) and different concentrations of cadmium(II) ions were formed. With the information  $[\text{CO}_3^{2-}]_{\text{tot}} = 0.001 \text{ mol dm}^{-3}$ , the  $[\text{CO}_3^{2-}]$  concentration can be estimated using the relationship

$$\lg c_{\text{CO}_3^{2-}} \approx \lg[10^{-3}/(10^{-2\text{pH}} 10^{K_1} 10^{K_{12}} + 10^{-\text{pH}} 10^{K_1} + 1)],$$

where  $\lg K_1 = 6.354$  and  $\lg K_{12} = 10.329$ .<sup>33</sup> The turbidity of the solutions was measured by light scattering as a function of pH, the latter being adjusted by addition of NaOH and  $\text{HNO}_3$ . The inflection point of each line was considered as the equilibrium point.

##### Source and Purity of Materials:

Stock solutions of cadmium(II) nitrate were prepared by dissolving spectrum-pure metal Cd in  $\text{HNO}_3$  aqueous solution.  $\text{HNO}_3$  and NaOH used were reagents of guaranteed purity.

##### Estimated Error:

Solubility: nothing specified; precision no better than 10%, as estimated by the compilers.

pH value: nothing specified; precision is estimated to be  $\pm 0.2$  by the compilers.

Temperature: nothing specified.

##### Components:

(1) Cadmium(II) carbonate;  $\text{CdCO}_3$ ;  
[513-78-0]

(2) Cadmium(II) nitrate–water (1/4);  
 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ; [10022-68-1]

(3) Sodium hydrogencarbonate;  
 $\text{NaHCO}_3$ ; [144-55-8]

(4) Nitric acid,  $\text{HNO}_3$ ; [7697-37-2]

(5) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

##### Original Measurements:

<sup>15</sup>P. E. Holm, B. B. H. Andersen,  
and T. H. Christensen, Soil Sci. Soc.  
J. 60, 775 (1996).

##### Prepared by:

M. C. F. Magalhães

#### Experimental Values

pH and total concentration of cadmium(II) in solutions in equilibrium with cadmium(II) carbonate.

No. batches	pH	$c_{\text{Cd}^{2+}, \text{tot}}/\mu\text{g dm}^{-3}$	$c_{\text{Cd}^{2+}, \text{tot}}/\text{mol dm}^{-3}$ <sup>a</sup>
15	6.5–8.5	1–65	$8.9 \times 10^{-9}$ – $5.8 \times 10^{-7}$

<sup>a</sup>Calculated by compiler.

## Auxiliary Information

## Method/Apparatus/Procedure:

Solutions of  $0.022 \text{ mol dm}^{-3} \text{ NaHCO}_3$  and  $8.9 \times 10^{-7} \text{ mol dm}^{-3} \text{ Cd(NO}_3)_2$  ( $500 \text{ cm}^3$ ) were mixed with  $1 \text{ cm}^3$  of a suspension of  $\text{CdCO}_3$  and left to equilibrate at  $25^\circ\text{C}$  in darkness for periods between 1 and 6 weeks. The pH was adjusted to the range 6.5–8.5 by addition of  $\text{HNO}_3$ , pH and specific conductivity were measured directly, by electrodes, prior to sampling. Total Cd was determined after solvent extraction (1% Na diethyldithiocarbamate trihydrate in 4-methyl-pentan-2-one) using graphite furnace atomic absorption spectrometry. Total alkalinity was determined by titration using the Gran method.

## Source and Purity of Materials:

Cadmium(II) carbonate was precipitated from a mixture of cadmium(II) nitrate and sodium carbonate and identified by x-ray diffraction. All reagents were analytical grade (Merck, pro analysis).

## Estimated Error:

The standard error of the mean for the solubility product is  $0.08 \times 10^{-13}$ .

## 4. Solubility in the System $\text{CdCO}_3 + \text{CO}_2 + \text{Chloride-Containing Electrolytes} + \text{H}_2\text{O}$

### 4.1. Critical evaluation of the solubility data

## Components:

- (1) Cadmium(II) carbonate;  $\text{CdCO}_3$ ; [513-78-0]
- (2) Carbon dioxide;  $\text{CO}_2$ ; [124-38-9]
- (3) Cadmium(II) chloride;  $\text{CdCl}_2$ ; [10108-64-2]
- (5) Calcium chloride;  $\text{CaCl}_2$ ; [10043-52-4]
- (4) Sodium chloride;  $\text{NaCl}$ ; [7647-14-5]
- (6) Water;  $\text{H}_2\text{O}$ ; [7732-18-5]

## Evaluators:

M. C. F. Magalhães, CICECO and Department of Chemistry, University of Aveiro, Aveiro, Portugal  
H. Gamsjäger, Lehrstuhl für Physikalische Chemie, Montanuniversität Leoben, Leoben, Austria  
August 2010

In aqueous media containing chloride and cadmium(II) ions, cadmium(II)-chlorido complexes will be formed. These are in fact the dominant species in aqueous media<sup>24</sup> that are slightly acidic and dilute in alkali metal chloride. The Cd(II)-chlorido system is well characterized and stability (formation) constants for this system are recommended by Powell *et al.*<sup>24</sup> Consequently, the solubility of cadmium(II) carbonate is higher in chloride-containing solutions compared to those containing non-complexing electrolytes of the same ionic strength.

The solubility of cadmium(II) carbonate in aqueous media containing chloride ions was determined by Immerwahr,<sup>1</sup> Ben'yash,<sup>4</sup> Shlyapnikov and Stern,<sup>7,8</sup> Miller *et al.*,<sup>9</sup> Cecal and Ciuchi,<sup>11</sup> and Savenko and Savenko.<sup>17</sup> The experiments were all conducted under different conditions of temperature, carbon dioxide partial pressure, and cadmium(II) non-complexing and complexing electrolytes. However, the pH of all must be considered to fall in the slightly acidic and slightly alkaline region even in those cases<sup>1,4,8,11</sup> where this value is not specified. The diversity of experimental condi-

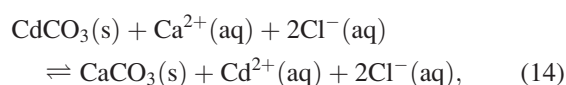
tions does not allow a global analysis, and each experiment will be analyzed in relation to the quality of the published data following the criteria outlined in Sec. 1. For those experiments where it will be possible to make the calculation of the solubility product, the stability (formation) constants recommended by Powell *et al.*<sup>24</sup> will be used.

Immerwahr<sup>1</sup> synthesized cadmium(II) carbonate in the measuring cell by addition of potassium carbonate to the solution containing potassium nitrate and cadmium(II) chloride. The experimental conditions are not well described. Details such as temperature, concentration of the carbonate ion in contact with  $\text{CdCO}_3$ , and criterion of equilibration are lacking. The author was aware that analytical constraints hampered the quantitative interpretation of his results. Clearly his somewhat enigmatic reasoning reflects the developing state of electrochemistry in the beginning of the 20th century, thus Saegusa<sup>2</sup> was the first to successfully determine the solubility constant  $\lg K_{s0}$  of  $\text{CdCO}_3(\text{s})$  by measuring the potentials of appropriate cells.

Ben'yash<sup>4</sup> studied the equilibrium between cadmium(II) carbonate, calcium carbonate and aqueous solutions of calcium chloride. He determined the mass fractions of total chloride and cadmium(II) dissolved in these solutions. In all experiments, the solid phases calcium carbonate and cadmium(II) carbonate were identified. Ben'yash<sup>4</sup> intended to demonstrate that, for high molalities of outer-sphere cations like  $\text{Ca}^{2+}$ , Leden's<sup>43</sup> function for cadmium(II)-chlorido complex formation, see Eq. (13), breaks down and  $m(\text{Cd}_{\text{tot}}^{2+})/m_{\text{Cd}^{2+}} = f(m_{\text{Cl}^-})$  shows a maximum at  $df/dm_{\text{Cl}^-} = 0$ .

$$m(\text{Cd}_{\text{tot}}^{2+})/m_{\text{Cd}^{2+}} = 1 + \beta_1 m_{\text{Cl}^-} + \beta_2 m_{\text{Cl}^-}^2 + \dots + \beta_n m_{\text{Cl}^-}^n \quad (13)$$

From equilibrium,



Ben'yash<sup>4</sup> derived an expression for the molality of  $\text{Cd}^{2+}$  which is not bound to chlorido complexes,  $m_{\text{Cd}^{2+}} = m_{\text{Ca}^{2+}} K_{s0}(\text{CdCO}_3)/K_{s0}(\text{CaCO}_3)$ , by dividing the solubility products of cadmium and calcium carbonate and implied that

$$\begin{aligned} [m(\text{Cd}_{\text{tot}}^{2+})K_{s0}(\text{CaCO}_3)]/[m_{\text{Ca}^{2+}}K_{s0}(\text{CdCO}_3)] \\ = 1 + \beta_1 m_{\text{Cl}^-} + \beta_2 m_{\text{Cl}^-}^2 + \dots + \beta_n m_{\text{Cl}^-}^n. \end{aligned} \quad (13a)$$

This argument, however, leads to Leden's<sup>43</sup> function only when  $\beta_1$  to  $\beta_n$  as well as  $K_{s0}(\text{CdCO}_3)$  and  $K_{s0}(\text{CaCO}_3)$  remain constant over the whole range of  $m_{\text{Cd(II)}}$  and  $m_{\text{Cl}^-}$  investigated, i.e., in an inert electrolyte medium of high and constant ionic strength. As this condition is not fulfilled for  $0.67 \leq m_{\text{Cl}^-}/\text{mol kg}^{-1} \leq 11.60$ , Ben'yash's<sup>4</sup> theoretical conclusions are not considered to be quantitatively valid. His experimental results can be summarized by the empirical function  $m(\text{Cd}_{\text{tot}}^{2+})/m(\text{Ca}_{\text{tot}}^{2+}) = f[m(\text{Cl}_{\text{tot}}^-)]$ , where the

subscript tot indicates total molalities regardless of the respective speciation. This function exhibits a maximum; see Fig. 8. It is certainly of practical interest to ascertain the optimal concentration of calcium chloride for cadmium oxide leaching under the action of carbon dioxide. Although the quotient of solubility products,  $\lg K_{s0}^{\circ}(\text{CdCO}_3) - \lg K_{s0}^{\circ}(\text{CaCO}_3) = -3.58$ , is apparently unfavorable, Cd(II) can be extracted from mixtures of solid oxides or carbonates by  $\text{CaCl}_2$  solutions. This is caused by Cd(II)-chlorido complex formation.

The system investigated by Ben'yash<sup>4</sup> consists of two solid phases and an aqueous solution in a hermetically sealed vessel, at constant temperature. Under these conditions, and as one of the solid phases is calcium carbonate having the structure of calcite (the thermodynamically well characterized stable phase under these experimental conditions), the knowledge of total cadmium(II), chloride and calcium concentrations should suffice to determine the solubility product of cadmium(II) carbonate. The cadmium(II)-chlorido complexes, however, render the evaluation complicated and the result doubtful. Thus, for information on the solubility product of cadmium carbonate, the equilibration according to Eq. (14) would have to be carried out, for example, with  $\text{Ca}(\text{ClO}_4)_2$  in an  $\text{NaClO}_4$  medium of constant ionic strength.

Shlyapnikov and Stern<sup>7,8</sup> determined the solubility of cadmium(II) carbonate in equilibrium with aqueous solutions of sodium chloride at 298.15 K (Ref. 8) and 473.15 K,<sup>7</sup> and 0.1 MPa,<sup>8</sup> and 5.0 MPa.<sup>7,8</sup> At 473.15 K, there is only one value and no evaluation of this result is possible, as there are no other values to compare with it. The value obtained at high temperature was also measured at the pressure of 5.0 MPa, and at this pressure values were determined at 298.15 K as well. These too cannot be evaluated, because they are the only ones published at this pressure and temperature.

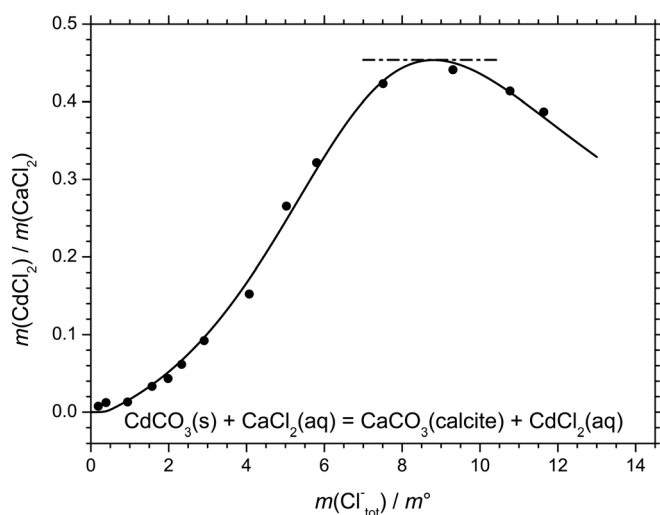


Fig. 8.  $\text{CaCl}_2$  leaching of  $\text{CdCO}_3(\text{cr})$ . ● Ben'yash's<sup>4</sup> experimental data at 298.15 K, recalculated, bold solid curve: rational function,  $m_{\text{CdCl}_2}/m_{\text{CaCl}_2} = [a + b m(\text{Cl}_{\text{tot}}^-)] / \{1 + c m(\text{Cl}_{\text{tot}}^-) + d [m(\text{Cl}_{\text{tot}}^-)]^2\}$ ,  $a = -0.008299$ ,  $b = 0.02200 \text{ kg mol}^{-1}$ ,  $c = -0.18296 \text{ kg mol}^{-1}$ ,  $d = 0.01315 \text{ kg}^2 \text{ mol}^{-2}$ , dash-dot line: leaching curve max.,  $m_{\text{CdCl}_2}/m_{\text{CaCl}_2} = 0.454$ ,  $m(\text{Cl}_{\text{tot}}^-) = 8.799 \text{ mol kg}^{-1}$ .

Miller *et al.*<sup>9</sup> made a set of experiments with soil (mainly quartz with some plagioclase and hornblende) in contact with aqueous solutions, with given pH containing cadmium(II) chloride, in contact with the atmosphere. Experiments were devised to test the hypothesis that precipitation of cadmium(II) carbonate could occur in the described system, and that this reaction competes with soil cationic exchange processes. The authors assumed that the aqueous solutions were in equilibrium with cadmium(II) carbonate formed by the reaction of the dissolved cadmium(II) ions with the carbonate formed by dissolution of atmospheric carbon dioxide in solutions with pH between 7 and 9. No identification of the solid phase was described. The authors mention that the solubility product of cadmium(II) carbonate could be obtained from the measured data, and they give the value  $\lg K_{s0} = -12.14$ , but the final system was not well defined. As the final total concentrations of acetate, calcium and chloride were not measured, it is impossible to calculate the equilibrium composition of the aqueous solution. The value of the solubility product obtained by these authors agrees, however, remarkably well with the value recommended in this work.

Cecal and Ciuchi<sup>11</sup> present a value for the solubility constant of cadmium(II) carbonate at 293.65 K. In this paper, no reference is made to partial pressure of carbon dioxide, concentration of carbonate and pH of the equilibrated solutions. These parameters are crucial for determining the equilibrium concentration of carbonate species. The authors also present a value for the solubility constant calculated considering  $K_s = s^2$  ( $s$  being the value of the determined concentration of cadmium(II) given in the compilation), which is obviously not true for the system under study. The authors considered neither the formation of cadmium(II)-chlorido complexes nor the hydrolysis of the carbonate ions. Considering the time to attain equilibrium recorded by other authors for similar systems, the time allowed by these authors for equilibration between solid and the solution was too short. From the published result, no more considerations can be made.

Savenko and Savenko<sup>17</sup> also determined the solubility of cadmium(II) carbonate in acidified artificial seawater (35‰ salinity) and found that the total concentration of cadmium(II) in solution was approximately 100 times higher than in the solution of  $0.05 \text{ mol dm}^{-3}$  sodium nitrate. The calculations made by these authors show that in seawater only 3.3% of the total dissolved cadmium(II) is in the form of  $\text{Cd}^{2+}$ . This result is in good agreement with the values calculated by Powell *et al.*,<sup>24</sup> which also show that the percentage of all forms of cadmium(II) in saline water are practically constant until pH 8.5. This fact explains the similar slope of the lines that translate the dependence of total concentration of cadmium(II) with pH in seawater and in the solution of  $0.05 \text{ mol dm}^{-3}$  sodium nitrate in the Savenko and Savenko<sup>17</sup> work. No further calculations can be done with the data determined by these authors, as they did not report the complete composition of the synthetic seawater.

## 4.2. Experimental data

Components:	Original Measurements:
(1) Cadmium(II) carbonate; CdCO <sub>3</sub> ; [513-78-0]	<sup>1</sup> C. Immerwahr, Z. Elektrochem. 7, 477 (1901).
(2) Potassium carbonate; K <sub>2</sub> CO <sub>3</sub> ; [584-08-7]	
(3) Cadmium(II) chloride; CdCl <sub>2</sub> ; [10108-64-2]	
(4) Potassium nitrate; KNO <sub>3</sub> ; [7757-79-1]	
(5) Water; H <sub>2</sub> O; [7732-18-5]	
Variables:	Prepared by:
T = 298.15 K p <sub>CO<sub>2</sub></sub> atmosphere (0.00032 bar)	H. Gamsjäger, M.C.F. Magalhães

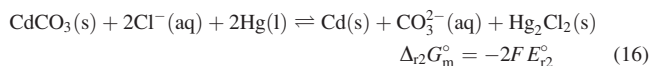
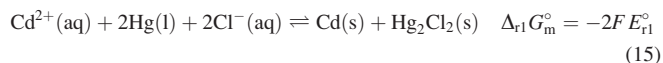
## Experimental Values

Solubility of cadmium(II) carbonate at 25 °C was measured as  $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ .

## Auxiliary Information

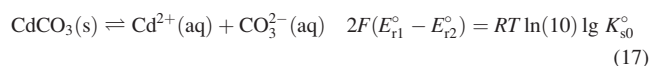
## Method/Apparatus/Procedure:

Immerwahr made a first attempt to study and compare reactions,

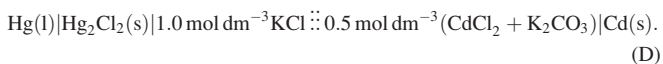
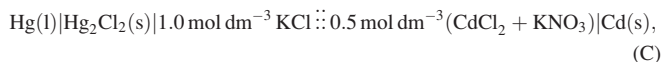


If done correctly, this would lead to the solubility product of cadmium(II) carbonate,

$$\lg K_{s0}^{\circ} = \lg (a_{\text{Cd}^{2+}} a_{\text{CO}_3^{2-}}).$$



For this purpose, the potentials of the following electrochemical cells were measured



As reference electrode the so called "normal" (1.0 mol dm<sup>-3</sup> KCl) calomel electrode was used, see left-hand side of cells (C) and (D). On the right-hand side of cell (D), CdCl<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> solutions were mixed in such proportions that CdCO<sub>3</sub> precipitated and the supernatant solution contained approximately 0.05 mol dm<sup>-3</sup> K<sub>2</sub>CO<sub>3</sub>. The cell potentials were found to be 0.6850 V for cell (C) and 0.782 V for cell (D). The temperature was not reported. The concentration on the right-hand side of cell (D) was given to be [Cd<sup>2+</sup>] = 2.5 × 10<sup>-4</sup> mol dm<sup>-3</sup>. This result can be reproduced by the equation,

$$\lg \{c_{\text{Cd}^{2+}}/c^{\circ}\} = \lg \{0.5\} + \{E(\text{C}) - E(\text{D})\}RT \ln(10)/2F, \quad (18)$$

provided the cell potentials were measured at T = 296 K.

## Source and Purity of Materials:

The cadmium(II) carbonate was prepared in the measuring cell by addition of potassium carbonate to the solution containing cadmium(II) chloride.

## Estimated Error:

Nothing specified.

Components:	Original Measurements:
(1) Cadmium(II) carbonate; CdCO <sub>3</sub> ; [513-78-0]	<sup>4</sup> E. Ya. Ben'yash, Zh. Neorg. Khim. 9, 2726 (1964).
(2) Calcium carbonate; calcite; [13397-26-7]	
(3) Calcium chloride; CaCl <sub>2</sub> ; [10043-52-4]	
(4) Water; H <sub>2</sub> O; [7732-18-5]	
Variables:	Prepared by:
T = 298.15 K Concentration of aqueous CaCl <sub>2</sub> solutions	M. C. F. Magalhães, B. R. Churagulov, H. Gamsjäger

## Experimental Values

The equilibrium concentrations of CdCl<sub>2</sub> in calcium chloride solutions over solid carbonates CaCO<sub>3</sub> and CdCO<sub>3</sub> at 25 °C. Numerical values in parentheses have been calculated by the evaluators using w<sub>Cl<sup>-</sup></sub> and w<sub>Cd<sup>2+</sup></sub> of column 1 and 2.

100w <sub>Cl<sup>-</sup></sub>	100w <sub>Cd<sup>2+</sup></sub>	m <sub>CaCl<sub>2</sub></sub> /mol kg <sup>-1</sup> H <sub>2</sub> O	m <sub>CdCl<sub>2</sub></sub> /mol kg <sup>-1</sup> H <sub>2</sub> O
0.67	0.008	0.091 (0.095)	0.0007 (0.0007)
1.35	0.026	0.192 (0.192)	0.002 (0.002)
3.18	0.065	0.466 (0.466)	0.006 (0.006)
5.12	0.261	0.761 (0.761)	0.025 (0.025)
6.32	0.416	0.950 (0.951)	0.042 (0.041)
7.29	0.671	1.078 (1.099)	0.059 (0.068)
8.82	1.181	1.334 (1.333)	0.122 (0.123)
11.59	2.430	1.766 (1.766)	0.270 (0.269)
13.53	4.500	1.972 (1.986)	0.525 (0.527)
14.98	5.779	2.194 (2.195)	0.706 (0.706)
17.78	8.381	2.628 (2.639)	1.116 (1.116)
20.37	9.884	3.219 (3.228)	1.416 (1.424)
22.31	10.350	3.786 (3.810)	1.594 (1.576)
23.40	10.351	4.194 (4.195)	1.623 (1.624)

## Auxiliary Information

## Method/Apparatus/Procedure:

Aqueous solutions of CaCl<sub>2</sub> with various concentrations were left in contact with solid CdCO<sub>3</sub> and solid CaCO<sub>3</sub> (calcite). An isothermal method using a hermetic glass vessel with a mixer was used. Equilibrium was reached in 8–10 days.

The filtered solutions were analyzed for cadmium and chloride. Cadmium was determined by a polarographic method. Chloride ion was determined by potentiometric titration with AgNO<sub>3</sub> solution. Molality of calcium was calculated from mass fraction of Cd and Cl. For recalculation of column 3 and 4 from the values given in columns 1 and 2, consider a mass of solution m<sub>tot</sub> containing the unit mass of water,

$$m_{\text{tot}}/\text{kg} = b_{\text{CaCl}_2} M_{\text{CaCl}_2} + b_{\text{CdCl}_2} M_{\text{CdCl}_2} + 1.$$

Note that in general *m* symbolizes molality in this text, but for this derivation the symbols *b*, *M*, and *m* designate molality, molar mass, and mass, respectively,

$$w_{\text{Cl}^{-}} = 2(b_{\text{CdCl}_2} + b_{\text{CaCl}_2})M_{\text{Cl}^{-}}/m_{\text{tot}}$$

$$w_{\text{Cd}^{2+}} = b_{\text{CdCl}_2} M_{\text{Cd}^{2+}} / m_{\text{tot}}$$

$$w_{\text{CaCl}_2} = b_{\text{CaCl}_2} M_{\text{CaCl}_2} / m_{\text{tot}}$$

$$w_{\text{CdCl}_2} = w_{\text{Cd}^{2+}} M_{\text{CdCl}_2} / M_{\text{Cd}^{2+}}$$

$$w_{\text{CaCl}_2} = \left( \frac{w_{\text{Cl}^-}}{2M_{\text{Cl}^-}} - \frac{w_{\text{Cd}^{2+}}}{M_{\text{Cd}^{2+}}} \right) M_{\text{CaCl}_2}$$

The molalities  $b_{\text{CaCl}_2}$  and  $b_{\text{CdCl}_2}$  can be obtained by inserting mass fractions  $w_{\text{CaCl}_2}$  and  $w_{\text{CdCl}_2}$  in the appropriate equation of Table 7 of Ref. 44. The composition of the solid phases was determined by chemical analysis, x-ray analysis and thermogravimetric analysis. In all cases, only mixtures of  $\text{CdCO}_3(\text{s})$  and  $\text{CaCO}_3(\text{s})$  were found.

#### Source and Purity of Materials:

The reagents used were CP-grade and PFA-grade.

#### Estimated Error:

Temperature: Precision  $\pm 0.1$  K.

Solubility: Reproducibility  $\pm 0.5\%$  (relative, compilers).

#### Components:

- (1) Cadmium(II) oxide; CdO; [1306-19-0]
- (2) Sodium chloride; NaCl; [7647-14-5]
- (3) Carbon dioxide; CO<sub>2</sub>; [124-38-9]
- (4) Water; H<sub>2</sub>O; [7732-18-5]

#### Original Measurements:

<sup>7</sup>D. S. Shlyapnikov and E. K. Stern, Dokl. Akad. Nauk SSSR **225**, 428 (1975).

#### Variables:

Temperature: 473.15 K  
 $p_{\text{CO}_2} = 5.0$  MPa  
 Concentrations of NaCl  
 (0 and 4.0 mol dm<sup>-3</sup>)

#### Prepared by:

B. R. Churagulov, M. C. F. Magalhães

#### Experimental Values

Solubility of CdO in water (1) and in 4.0 mol dm<sup>-3</sup> NaCl solution (2) at 200 °C and CO<sub>2</sub> pressure of 50 atm.

Solid	Solution pH		$\rho_{\text{Cd}^{2+}} / \text{g dm}^{-3}$	$c_{\text{Cd}^{2+}}^{\text{a}} / \text{mol dm}^{-3}$	$\rho_{\text{NaHCO}_3} / \text{g dm}^{-3}$	$c_{\text{HCO}_3}^{\text{a}} / \text{mol dm}^{-3}$
	(without CO <sub>2</sub> )	Solution pH				
1. CdO	7.01	4.70	2.8500	$2.5353 \times 10^{-2}$	—	—
2. CdO	9.45	5.43	4.5140	$4.0156 \times 10^{-2}$	2.84	$3.38 \times 10^{-2}$

<sup>a</sup>values calculated by the compilers.

#### Auxiliary Information

#### Method/Apparatus/Procedure:

For this isothermal method, a special rotating autoclave was used. The autoclave was equipped with a container for solid carbon dioxide to provide high pressures. With continuous mixing, equilibrium was reached after 24 h. The cadmium(II) concentration was determined by complexometric titration. Analysis for the Cl<sup>-</sup> ions was carried out argentometrically. Analysis for the CO<sub>2</sub> was carried out gas volumetrically. pH values of solutions were determined potentiometrically.

#### Source and Purity of Materials:

Nothing specified for cadmium(II) oxide, sodium chloride, carbon dioxide, and water.

#### Estimated Error:

Temperature: Precision  $\pm 0.5$  K (compilers).

Pressure: Precision  $\pm 1$  atm (compilers).

Solubility: Reproducibility  $\pm 1\%$  (relative, compilers).

#### Components:

- (1) Cadmium(II) oxide; CdO; [1306-19-0]
- (2) Sodium chloride; NaCl; [7647-14-5]
- (3) Carbon dioxide; CO<sub>2</sub>; [124-38-9]
- (4) Water; H<sub>2</sub>O; [7732-18-5]

#### Original Measurements:

<sup>8</sup>D. S. Shlyapnikov and E. K. Stern, Dokl. Akad. Nauk SSSR **249**, 457 (1979).

#### Variables:

Temperature: 298.15 K  
 $p_{\text{CO}_2} = 0.1$  and 5.0 MPa  
 $c_{\text{NaCl}} = 1.0, 2.0,$  and 4.0 mol dm<sup>-3</sup>

#### Prepared by:

B. R. Churagulov

#### Experimental Values

Composition of the saturated solutions and composition of solid phases in system CdO + CO<sub>2</sub> + H<sub>2</sub>O, at 25 °C.

$p_{\text{CO}_2} / \text{atm}$	Initial solution		$\rho_{\text{Cd}^{2+}} / \text{g dm}^{-3}$	$c_{\text{Cd}^{2+}}^{\text{a}} / \text{mol dm}^{-3}$	Composition of solid phases
	$c_{\text{NaCl}} / \text{mol dm}^{-3}$				
1	0		0.23	$2.046 \times 10^{-3}$	CdO + CdCO <sub>3</sub>
1	1		0.48	$4.270 \times 10^{-3}$	CdCO <sub>3</sub>
1	2		1.5	$1.334 \times 10^{-2}$	CdCO <sub>3</sub>
1	4		3.3	$2.936 \times 10^{-2}$	CdCO <sub>3</sub>
50	0		0.4	$3.558 \times 10^{-3}$	CdCO <sub>3</sub>
50	1		2.7	$2.402 \times 10^{-2}$	CdCO <sub>3</sub>
50	2		5.06	$4.501 \times 10^{-2}$	CdCO <sub>3</sub>
50	4		9.6	$8.540 \times 10^{-2}$	CdCO <sub>3</sub>

<sup>a</sup>Concentrations calculated by the compiler.

#### Auxiliary Information

#### Method/Apparatus/Procedure:

Isothermal method using a glass vessel (25 °C and  $p_{\text{CO}_2} = 1$  atm) with continuous flow of CO<sub>2</sub>.

Isothermal method using a special rotating autoclave with a container for solid carbon dioxide to create high pressures. With continuous mixing, equilibrium was reached after 24 h as described in Shlyapnikov and Stern.<sup>45</sup> The cadmium(II) concentration was determined by complexometric titration. Analysis for the Cl<sup>-</sup> ions was carried out argentometrically. Analysis for the CO<sub>2</sub> was carried out gas volumetrically. The composition of the solid phases was determined by x-ray diffraction.

#### Source and Purity of Materials:

Cadmium(II) oxide was prepared by the method described in Koryahin and Angelov.<sup>46</sup>

Sodium chloride, chemical purity and pure for analysis, was additionally recrystallized.

No information was given about the carbon dioxide and the water.

#### Estimated Error:

Temperature: Precision  $\pm 0.5$  K (compiler).

Pressure: Precision  $\pm 1$  atm (compiler).

Solubility: Reproducibility  $\pm 1\%$  (relative, compiler).

<b>Components:</b> (1) Cadmium(II) chloride-water (1/2.5); CdCl <sub>2</sub> ·2.5H <sub>2</sub> O; [7790-78-5] (2) Calcium hydroxide; Ca(OH) <sub>2</sub> ; [1305-62-0] (3) Acetic acid; CH <sub>3</sub> COOH; [64-19-7] (4) Water; H <sub>2</sub> O; [7732-18-5]	<b>Original Measurements:</b> <sup>9</sup> R.L. Miller, D.B. Grove, and K.G. Stollenwerk, U. S. Geological Survey Water Supply Paper <b>2262</b> , 33 (1984).
<b>Variables:</b> <i>T</i> = 298.15 K; pH in the range 5 to 9 <i>p</i> <sub>CO<sub>2</sub></sub> atmosphere (0.00032 bar)	<b>Prepared by:</b> M.C.F. Magalhães

### Experimental Values

Experimental data from carbonate titration of cadmium(II) containing solutions left in contact with atmospheric air, at 25 °C, in a closed vessel.

pH	<i>t</i> /h	<i>c</i> <sub>carbonate,tot</sub> /mol dm <sup>-3</sup>	100 <i>w</i> <sub>Cd<sup>2+</sup>,loss</sub>	10 <sup>6</sup> <i>c</i> <sub>Cd<sup>2+</sup></sub> <sup>a</sup> /mol dm <sup>-3</sup>
9.03	2.0	8 × 10 <sup>-4</sup>	22.0	2.08
8.68	4.5	4 × 10 <sup>-5</sup>	45.1	1.47
8.08	4.5	4 × 10 <sup>-4</sup>	42.5	1.54
7.46	2.5	8 × 10 <sup>-2</sup>	98.9	0.0294

<sup>a</sup>Concentrations calculated by compiler.

### Auxiliary Information

#### Method/Apparatus/Procedure:

Four solutions, containing an aqueous solution of cadmium(II) chloride with initial concentration of cadmium(II) of 300 μg dm<sup>-3</sup>, varying in pH and carbonate concentration, were equilibrated with sand. The sand was predominantly quartz, with some plagioclase and hornblende. Values of pH were adjusted between 5 and 9 with aqueous solutions of either calcium hydroxide or acetic acid. The initial calcium concentration varied with the quantity of calcium hydroxide required to adjust pH.

These solutions were titrated for carbonate species, so a solubility product for CdCO<sub>3</sub> could be obtained.

Calcium and cadmium(II) ion concentrations were analyzed by atomic absorption spectrometry.

#### Source and Purity of Materials:

Sand from the Lubbock, Texas area, acid washed and sieved, was used. The sand had a surface area of 0.5 m<sup>2</sup> g<sup>-1</sup> and consisted of ellipsoidal and spherical particles.

Cadmium(II) chloride: Matheson, Coleman and Bell reagent ACS crystals. Baker-analyzed reagent.

Calcium hydroxide: Baker-analyzed reagent.

#### Estimated Error:

Nothing specified, no estimates possible.

<b>Components:</b> (1) Cadmium(II) carbonate; CdCO <sub>3</sub> ; [513-78-0] (2) Cadmium(II) chloride; <sup>115</sup> CdCl <sub>2</sub> ; [7790-78-5] (3) Water; H <sub>2</sub> O; [7732-18-5]	<b>Original Measurements:</b> <sup>11</sup> A. Cecal and G.-I. Ciuchi, Rev. Roum. Chim. <b>34</b> , 953 (1989).
<b>Variables:</b> <i>T</i> = 293.65 K	<b>Prepared by:</b> M. C. F. Magalhães and H. Gamsjäger

### Experimental Values

Solubility of CdCO<sub>3</sub>(s) in water at 20.5 °C was reported as 1.59 × 10<sup>-5</sup> mol dm<sup>-3</sup>.

### Auxiliary Information

#### Method/Apparatus/Procedure:

A radiochemical method, based on internal isotopic dilution, was used for the determination of solubility in water.

1 g of solid cadmium(II) carbonate was left to equilibrate with an aqueous solution formed by the addition of 10 cm<sup>3</sup> of an aqueous solution of <sup>115</sup>CdCl<sub>2</sub> with concentration 0.15 mg cm<sup>-3</sup> to 90 cm<sup>3</sup> of water.

0.5 cm<sup>3</sup> samples were collected periodically from the solution that was left to rest for 30 min after intermittent stirring.

#### Source and Purity of Materials:

The solid cadmium(II) carbonate was synthesized in the laboratory according to published methods.

The radioactive solution was acquired from IFIN Bucurest and had the specific activity of 3.60 × 10<sup>4</sup> Bq cm<sup>-3</sup>.

#### Estimated Error:

Nothing specified, no estimation possible.

<b>Components:</b> (1) Cadmium(II) carbonate; CdCO <sub>3</sub> ; [513-78-0] (2) Sodium chloride; NaCl; [7647-14-5] (3) Hydrochloric acid; HCl; [7647-01-0] (4) Water; H <sub>2</sub> O; [7732-18-5]	<b>Original Measurements:</b> <sup>17</sup> A. V. Savenko and V. S. Savenko, Geochem. Int. <b>47</b> , 835 (2009).
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#### Variables:

*T* = 298.15 K  
*p*<sub>CO<sub>2</sub></sub> atmosphere (0.00034 atm)

#### Prepared by:

M. C. F. Magalhães

### Experimental Values

Composition of the saturated solution in CdCO<sub>3</sub>-seawater (35‰ salinity) system at 25 °C.

[ΣCd <sup>2+</sup> ]/(μmol dm <sup>-3</sup> )	lg{[ΣCd <sup>2+</sup> ]/mol dm <sup>-3</sup> }	pH
83.6	-4.08	7.90
161	-3.79	7.77
162	-3.79	7.76
181	-3.74	7.74
224	-3.65	7.69
255	-3.59	7.66
259	-3.59	7.66
319	-3.50	7.62
323	-3.49	7.61

## Auxiliary Information

## Method/Apparatus/Procedure:

Solid CdCO<sub>3</sub> was equilibrated with normal seawater (35‰ salinity) over five months until constant total cadmium(II) concentration and pH were reached. The temperature was kept in the range 23–24 °C during the first three months and was kept at (25 ± 1) °C during the last two months. The solid phase:aqueous solution mass ratio was 1:100, and the samples were periodically stirred with the lid open to equalize the carbon dioxide partial pressure in the solution and in the atmosphere. The seawater pH was varied in the range 7.6–7.9 by addition of acidic seawater in which some NaCl (0.2 mol dm<sup>-3</sup>) was substituted by an equivalent amount of HCl. The filtered solution was analyzed by atomic absorption for cadmium and the pH was measured potentiometrically.

## Source and Purity of Materials:

Samples of CdCO<sub>3</sub> were prepared by the mixture of NaHCO<sub>3</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> aqueous solutions left to react for one day in a hermetically sealed plastic vessel. After this time, the excess of carbon dioxide was slowly bled and the solid was washed several times with distilled water, filtered and dried at 105 °C. There is no reference to the source or purity of the chemical reagents used or the identification of the solid obtained.

## Estimated Error:

Temperature: ±1 °C.

$c_{\text{Cd}^{2+}}$ : ±2%.

pH: ±0.005.

## 5. Solubility in Mixed Solvents

## 5.1. Critical evaluation of the solubility data

Components:	Evaluators:
(1) Cadmium(II) carbonate; CdCO <sub>3</sub> ; [513-78-0]	M. C. F. Magalhães, CICECO and Department of Chemistry,
(2) Cadmium(II) chloride; CdCl <sub>2</sub> ; [7790-78-5]	University of Aveiro, Aveiro, Portugal
(3) Water; H <sub>2</sub> O; [7732-18-5]	H. Gamsjäger, Lehrstuhl für
(4) Methanol; CH <sub>3</sub> OH; [67-56-1]	Physikalische Chemie,
(5) Ethanol; CH <sub>3</sub> CH <sub>2</sub> OH; [64-17-5]	Montanuniversität Leoben,
(6) Propan-2-ol; CH <sub>3</sub> CH(OH)CH <sub>3</sub> ; [67-63-0]	Leoben, Austria August 2010

As mentioned in Sec. 1, only Cecal and Ciuchi<sup>11</sup> determined the solubility of cadmium(II) carbonate in solvents other than water. They measured the solubility of cadmium(II) carbonate in mixtures of water–methanol, water–ethanol, and water–propan-2-ol. As was said previously, the paper makes no reference to some experimental conditions that are crucial for determining the equilibrium concentration at saturation of metal carbonates.

The authors also present values of solubility products for each media calculated considering  $K_{s0} = s^2$  (where  $s$  is the value of the total concentration of cadmium(II) determined at saturation), presuming equality of cadmium(II) ion and carbonate concentration,  $[\text{Cd}^{2+}] = [\text{CO}_3^{2-}]$ , which is obviously not true for the system under study. In addition, the period of equilibration was too short, compared to that recorded by other authors for similar systems of equilibration between solid and the solution.

It is not possible to make a deeper evaluation of these results, as they are the only ones recorded in the literature, but taking into account all the above considerations based on the description of the experimental design, the published results seem doubtful.

## 5.2. Experimental data

Components:	Original Measurements:
(1) Cadmium(II) carbonate; CdCO <sub>3</sub> ; [513-78-0]	<sup>11</sup> A. Cecal and G.-I. Ciuchi, Rev. Roum. Chim. <b>34</b> , 953 (1989).
(2) Cadmium(II) chloride; <sup>115</sup> CdCl <sub>2</sub> ; [7790-78-5]	
(3) Water; H <sub>2</sub> O; [7732-18-5]	
(4) Methanol; CH <sub>3</sub> OH; [67-56-1]	
(5) Ethanol; CH <sub>3</sub> CH <sub>2</sub> OH; [64-17-5]	
(6) Isopropanol; propan-2-ol; CH <sub>3</sub> CH(OH)CH <sub>3</sub> ; [67-63-0]	
Variables:	Prepared by:
$T = 293.65 \text{ K}$	M. C. F. Magalhães and H. Gamsjäger
Composition of water–methanol, water–ethanol, and water–propan-2-ol mixtures	

## Experimental Values

Solubility of CdCO<sub>3</sub>(s) in water–methanol mixtures at 20.5 °C.

Composition of the water–methanol media/100φ	Composition of the reaction media <sup>a</sup> /100φ	Solubility/mol dm <sup>-3</sup>
90:10	91:9	1.28 × 10 <sup>-5</sup>
80:20	82:18	1.09 × 10 <sup>-5</sup>
70:30	73:27	9.82 × 10 <sup>-6</sup>
60:40	64:36	9.66 × 10 <sup>-6</sup>
50:50	55:45	9.38 × 10 <sup>-6</sup>
40:60	46:54	9.75 × 10 <sup>-6</sup>
30:70	37:63	9.97 × 10 <sup>-6</sup>
20:80	28:72	1.07 × 10 <sup>-5</sup>
10:90	19:81	1.13 × 10 <sup>-5</sup>

<sup>a</sup>Calculated by the compilers.

Solubility of CdCO<sub>3</sub>(s) in water–ethanol mixtures at 20.5 °C.

Composition of the water–ethanol media/100φ	Composition of the reaction media <sup>a</sup> /100φ	Solubility/mol dm <sup>-3</sup>
90:10	91:9	1.39 × 10 <sup>-5</sup>
80:20	82:18	1.20 × 10 <sup>-5</sup>
70:30	73:27	1.03 × 10 <sup>-5</sup>
60:40	64:36	9.91 × 10 <sup>-6</sup>
50:50	55:45	9.72 × 10 <sup>-6</sup>
40:60	46:54	9.87 × 10 <sup>-6</sup>
30:70	37:63	1.01 × 10 <sup>-5</sup>
20:80	28:72	1.09 × 10 <sup>-5</sup>
10:90	19:81	1.25 × 10 <sup>-5</sup>

<sup>a</sup>Calculated by the compilers.

Solubility of CdCO<sub>3</sub>(s) in water–propan-2-ol mixtures at 20.5 °C.

Composition of the water–isopropanol media/100φ	Composition of the reaction media <sup>a</sup> /100φ	Solubility/mol dm <sup>-3</sup>
90:10	91:9	1.47 × 10 <sup>-5</sup>
80:20	82:18	1.29 × 10 <sup>-5</sup>
70:30	73:27	1.17 × 10 <sup>-5</sup>
60:40	64:36	1.04 × 10 <sup>-5</sup>
50:50	55:45	9.95 × 10 <sup>-6</sup>
40:60	46:54	1.05 × 10 <sup>-5</sup>
30:70	37:63	1.11 × 10 <sup>-5</sup>
20:80	28:72	1.22 × 10 <sup>-5</sup>
10:90	19:81	1.33 × 10 <sup>-5</sup>

<sup>a</sup>Calculated by the compilers.

### Auxiliary Information

#### Method/Apparatus/Procedure:

A radiochemical method, based on internal isotopic dilution, was used for the determination of solubility in water–methanol mixtures.

1 g of solid cadmium(II) carbonate was equilibrated with a solution formed by the addition of 10 cm<sup>3</sup> of an aqueous solution of <sup>115</sup>CdCl<sub>2</sub> with concentration 0.15 mg cm<sup>-3</sup> to 90 cm<sup>3</sup> of a mixture of water–methanol. 0.5 cm<sup>3</sup> samples were collected periodically from the solution that was left to stand for 30 min after intermittent stirring.

#### Source and Purity of Materials:

Solid cadmium(II) carbonate was synthesized in the laboratory according to published methods.

The radioactive solution was acquired from IFIN Bucurest and had the specific activity of 3.60 × 10<sup>4</sup> Bq cm<sup>-3</sup>.

#### Estimated Error:

Nothing specified, no estimation possible.

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