

Solid-liquid phase equilibrium in the LiBr-CaBr₂-H₂O system at 35 °C and 50 °CC. Christov^{1*}, T. Tsenov¹, N. Ivanova², S. Donchev¹¹Department of Chemistry, Faculty of Natural Sciences, Shumen University "Konstantin Preslavski",
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The investigation of the phase diagrams of lithium bromide mixed systems is of practical importance with a view to explain the distribution of bromide ions in natural evaporated deposits during crystallization of salts as a result of sea water evaporation, during treatment of natural deposits, production of bromide mineral resources, and especially in improvement of the technology for extraction of lithium from brine deposits. In this study, the solubility of bromide minerals in the mixed system LiBr-CaBr₂-H₂O was investigated at 35 °C and 50 °C by physico-chemical analysis. The compositions of the thoroughly suction-dried solid phases were specified by the Schreinemakers graphic method. At T=35°C the equilibrium crystallization of LiBr·2H₂O (cr), LiBr·H₂O (cr), CaBr₂·4H₂O (cr) and CaBr₂·2H₂O (cr) was established. At T = 50°C precipitation of LiBr·H₂O (cr), CaBr₂·4H₂O (cr) and CaBr₂·2H₂O (cr) was established. The solubility of lithium bromide solids sharply decreases in a ternary system with added calcium bromide solids at both temperatures. It was concluded that the phase transition temperature (PPT) LiBr·CaBr₂·5H₂O (cr) → LiBr·H₂O (cr) + CaBr₂·4H₂O (cr) lies in the temperature range from 25°C to 35°C.

Keywords: phase equilibrium; bromide minerals solubility; mixed system LiBr-CaBr₂-H₂O

INTRODUCTION

The behavior of bromide as a trace element in vaporizing seawater and the diagenetic reactions of evaporates are of prime importance for geochemical studies on marine chemical sediments [1-4]. The experimental and thermodynamic modeling investigation of the phase diagrams of lithium bromide mixed systems is of practical importance with a view to explain the distribution of bromide ions in natural evaporated deposits during crystallization of salts as a result of sea water evaporation, during treatment of natural deposits, production of bromide mineral resources, and especially in improvement of the technology for extraction of lithium from brine deposits [5-9].

In recent years, there has been a noticeable increase in lithium production due to the growing interest in this valuable resource, which aligns with the escalating demand for electric vehicles and cordless consumer electronics. Lithium is used for the production of lithium-ion batteries, in ceramics and glass, lubricants, polymer production, and air conditioning. The production of lithium batteries is expected to increase in the coming years due to the decarbonization of key markets [9-11]. With the rapidly developing new energy industry in the world the global demand for lithium resources continually

grows. The demand for lithium carbonate is expected to increase from 265 kt in 2015 to 498 kt in 2025. The most efficient and cost-effective way to produce lithium is from brines. The extraction from brine, however, carries great environmental risks due to the large consumption of water and the pollution of underground sources of drinking water [12, 13]. Experimental and theoretical studies on solid-liquid phase equilibrium in mixed lithium systems in combination with major ocean cations (Na⁺, K⁺, Mg⁺, Ca⁺), halide (Cl⁻, Br⁻, I⁻), and sulfate (SO₄²⁻) mixed systems at temperatures ranging from 0°C to 50°C are of high importance in improvement of the technology for extraction of lithium from brine deposits [5-8, 9-11].

The need to determine the required conditions for extracting lithium from natural brines and salt deposits of the marine type constitutes the motivation behind the study of aqueous solutions of lithium and magnesium, and calcium halides over a wide temperature range. The solubility data for lithium-magnesium chloride/bromide (1-1 + 2-1) mixtures of the type LiX-MgX₂-H₂O (X=Cl, Br) are available in a temperature range from 0° to 75°C. According to these data a lithium carnallite double salt (LiCl·MgCl₂·7H₂O (cr)) precipitates from saturated chloride solutions [3, 5, 14].

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According to the data, the lithium and magnesium bromide ternary system is of simple eutonic type at temperatures ranging from 25 °C to 75 °C [5, 7, 14]. The experimental solubility data for LiCl-MgCl₂-H₂O, and LiBr-MgBr₂-H₂O systems are also validated by development of the Pitzer approach thermodynamic solid liquid equilibrium model at standard temperature [5], and at T = 75 °C [7] for the lithium-magnesium bromide system. The experimental data for LiX-CaX₂-H₂O (X=Cl, Br) systems are scarce. Solubility data for the chloride system are available from 0 °C to 50 °C. According to these data a double salt with stoichiometry 1-1-5 (LiCl.CaCl₂.5H₂O (cr)) precipitates in the ternary system at 0°, 10°, and 25 °C [6, 11]. There is no field of equilibrium crystallization of the double salt LiCl.CaCl₂.5H₂O (cr) at 40° and 50 °C (see Fig. 6 in ref. [11]). The solubility data for the LiBr-CaBr₂-H₂O system are available only at standard temperature. In a previous study [6] we corrected the available solubility data [14] for this bromide system. Precipitation of the double salt LiBr.CaBr₂.5H₂O (cr) has been established at 25 °C. The experimental solubility data at standard temperature for the LiBr-CaBr₂-H₂O system are also validated by development of a thermodynamic solid liquid equilibrium model [6]. Precipitation of the double salt LiBr.CaBr₂.5H₂O(cr) was also fully confirmed by the solubility study of Cui *et al.* [9] at 25 °C. In this study we determined the solubilities in the LiBr-CaBr₂-H₂O system at 35 °C and 50 °C. The reported new solubility data are of high importance for development of an accurate T-variable (from 0 °C to 50 °C) solid-liquid equilibrium thermodynamic model for lithium bromide rich brines, and therefore in improvement of the technology for extraction of lithium resources from brine deposits.

EXPERIMENTAL

In this study, the bromide minerals' solubility in the mixed system LiBr-CaBr₂-H₂O was investigated at T = (35 and 50) °C. The solubility of bromide minerals in the ternary system was studied by the method of isothermal decrease of the supersaturation [1, 4-7, 15, 16]. Different weight ratios of solid LiBr, and CaBr₂ were used for each experiment. Crystal salts in excess of the solubilities at T=(35 and 50) °C

were mixed with water. The solution was heated until the solid phases were completely dissolved and then transferred to a double-walled glass thermostat and cooled rapidly to the desired temperature of 35 °C and 50 °C. The quick cooling of the solution, followed by agitation with a magnetic stirrer, ensured a fast decrease of the supersaturation. Equilibrium was attained by continuous stirring for 24 h.

The solid lithium bromide and calcium bromide samples were from Fluka with mass fraction purity of 0.999. The solids were used without further purification. Samples of the liquid and wet solid phases were withdrawn for analysis. Their separation has been achieved by a Cooch filter (G-3). Weighed amounts of the liquid and the wet solid phase were diluted to a definite volume and analyzed for determining solution composition. The compositions of the saturated solutions and the corresponding wet solid phase were established using the methods described in our previous studies [1-3, 6, 16]. Calcium ion was determined by complexometric titration with Eriochrome black T as indicator [6, 17]. Merck ammonium buffer solution (ammonium chloride/ammonia) was used for maintaining the high pH (pH = 10-11) of solutions in the complexometric titration process [6]. The amount of bromide was found by titration with silver nitrate solution (the Mohr method) [17, 6]. The concentration of lithium ion [Li⁺] was calculated by the balance reaction: [Li⁺] = [Br⁻]_{total} - 2x[Ca²⁺] [6, 16]. The compositions of the thoroughly suction-dried solid phases were specified by the Schreinemakers' graphic method [18], see also refs. [1, 2, 6, 16].

RESULTS AND DISCUSSION

The results from the solubility measurements in the LiBr-CaBr₂-H₂O system are presented in Table 1 and Figure 1, and Table 2 and Figure 2 at T = 35 °C, and T=50 °C, respectively. The experimental error is within the range of ± (0.1 to 0.3) per cent. Each experimental result represents the arithmetical mean of three parallel determinations.

Table 1. Experimental mass fraction w and molality solubility of lithium and calcium bromide solid phases in the (m_1 LiBr + m_2 CaBr₂) (aq) system at T = 35°C

Liquid phase, 10 ² w		Liquid phase, molality (m/mol·kg ⁻¹)		Wet solid phase, 10 ² w		Solid phase
LiBr	CaBr ₂	LiBr	CaBr ₂	LiBr	CaBr ₂	
62.5	0.0	19.2	0.0	66.3	0.0	LiBr·2H ₂ O (cr)
57.9	5.80	18.3	0.80	69.8	1.31	LiBr·2H ₂ O (cr)
50.7	13.8	16.5	1.94	65.7	3.20	LiBr·2H ₂ O (cr)
47.3	18.3	15.8	2.66	66.9	3.19	LiBr·2H ₂ O (cr)
42.3	23.4	14.2	3.41	65.6	4.30	LiBr·2H ₂ O (cr)
40.7	27.1	14.6	4.21	76.7	5.03	LiBr·H ₂ O (cr)
37.2	30.0	13.1	4.58	72.1	7.10	LiBr·H ₂ O (cr)
32.9	34.5	11.6	5.29	59.1	16.0	LiBr·H ₂ O (cr)
31.9	38.2	12.3	6.39	72.7	7.58	LiBr·H ₂ O (cr)
28.8	41.7	11.2	7.07	64.9	10.3	LiBr·H ₂ O (cr)
27.9	43.3	11.2	7.52	72.4	10.4	LiBr·H ₂ O (cr)
26.6	44.7	10.7	7.79	60.4	16.9	LiBr·H ₂ O (cr)
25.0	46.4	10.1	8.12	42.5	36.1	E ^a
24.5	46.9	9.86	8.20	41.1	38.6	E ^a
24.8	47.2	10.2	8.43	17.8	62.9	E ^a
24.1	47.7	9.84	8.46	36.8	42.9	E ^a
23.2	48.5	9.4	8.56	3.53	76.9	CaBr ₂ ·2H ₂ O(cr)
21.5	50.7	8.91	9.12	7.80	71.2	CaBr ₂ ·2H ₂ O(cr)
18.1	52.8	7.16	9.08	8.1	69.0	CaBr ₂ ·2H ₂ O(cr)
14.9	54.2	5.55	8.78	10.5	59.6	CaBr ₂ ·4H ₂ O(cr)
12.1	56.8	4.48	9.14	3.85	67.4	CaBr ₂ ·4H ₂ O(cr)
9.70	58.4	3.50	9.16	2.85	68.1	CaBr ₂ ·4H ₂ O(cr)
6.97	60.6	2.47	9.35	0.93	71.5	CaBr ₂ ·4H ₂ O(cr)
4.90	62.0	1.70	9.37	0.81	70.9	CaBr ₂ ·4H ₂ O(cr)
2.80	63.8	0.97	9.56	0.98	70.2	CaBr ₂ ·4H ₂ O(cr)
0.0	66.1	0.0	9.76	0.0	71.2	CaBr ₂ ·4H ₂ O(cr)

^aE = LiBr·H₂O (cr)+ CaBr₂·2H₂O (cr)

Table 2. Experimental mass fraction w and molality solubility of lithium and calcium bromide solid phases in the (m_1 LiBr + m_2 CaBr₂) (aq) system at T = 50°C

Liquid phase, 10 ² w		Liquid phase, molality (m/mol·kg ⁻¹)		Wet solid phase, 10 ² w		Solid phase
LiBr	CaBr ₂	LiBr	CaBr ₂	LiBr	CaBr ₂	
65.9	0.0	22.2	0.0	74.6	0.0	LiBr·H ₂ O (cr)
60.5	5.59	20.5	0.83	73.1	2.90	LiBr·H ₂ O (cr)
57.3	9.60	19.9	1.45	74.0	3.80	LiBr·H ₂ O (cr)
53.4	13.5	18.6	2.04	69.6	7.10	LiBr·H ₂ O (cr)
43.7	25.8	16.5	4.23	67.1	10.3	LiBr·H ₂ O (cr)
38.6	31.5	14.8	5.25	55.9	19.8	LiBr·H ₂ O (cr)
33.9	37.2	13.5	6.44	53.5	22.2	LiBr·H ₂ O (cr)
28.9	42.8	11.7	7.56	41.8	32.4	LiBr·H ₂ O (cr)
27.5	45.1	11.6	8.26	38.1	53.4	E ^a
27.0	46.1	11.6	8.57	26.9	59.8	E ^a
26.8	46.0	11.4	8.46	19.2	68.4	E ^a
25.5	47.9	11.0	8.99	7.50	74.3	CaBr ₂ ·2H ₂ O(cr)
22.2	50.5	9.36	9.25	5.20	75.8	CaBr ₂ ·2H ₂ O(cr)
16.9	55.4	7.0	9.98	3.10	78.1	CaBr ₂ ·2H ₂ O(cr)
12.4	59.5	5.07	10.6	2.40	80.9	CaBr ₂ ·2H ₂ O(cr)
6.00	64.9	2.37	11.2	3.10	71.8	CaBr ₂ ·4H ₂ O(cr)
2.68	67.2	1.02	11.1	0.90	73.1	CaBr ₂ ·4H ₂ O(cr)
0.0	70.2	0.0	11.8	0.0	72.6	CaBr ₂ ·4H ₂ O(cr)

^aE = LiBr·H₂O (cr)+ CaBr₂·2H₂O (cr)

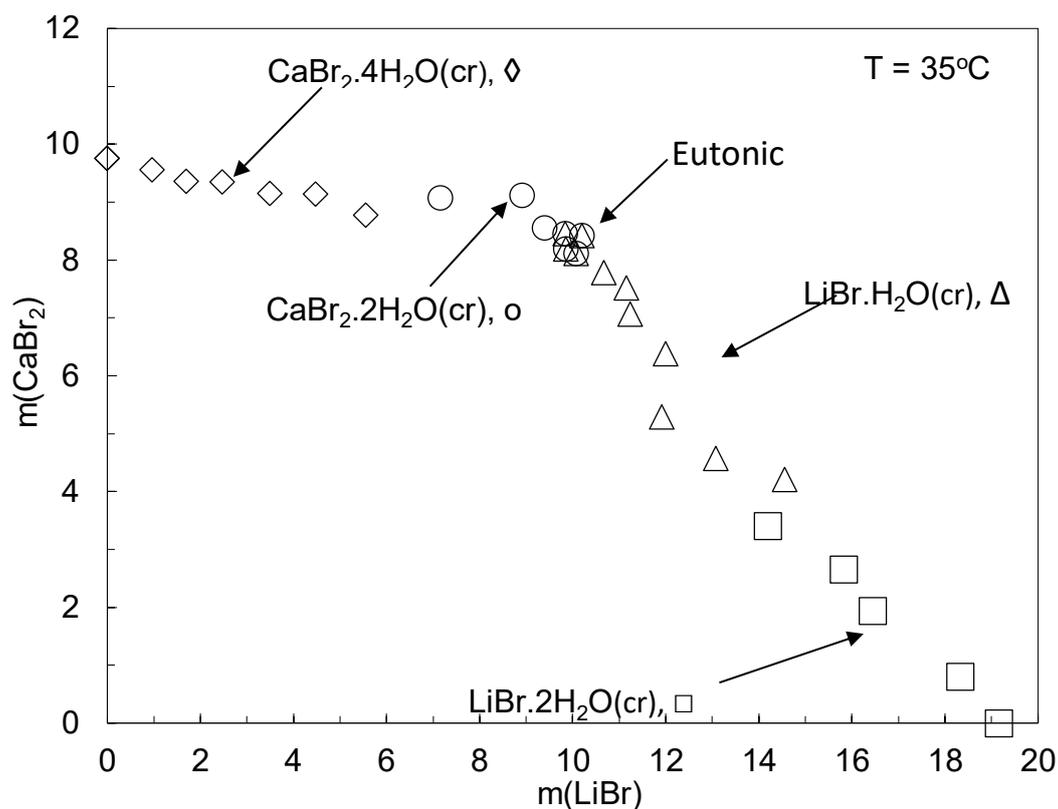


Fig. 1. Experimental molality solubility (mol.kg⁻¹) of LiBr.2H₂O (cr) (open squares), LiBr.H₂O (cr) (open triangles), CaBr₂.4H₂O (cr) (open diamonds), and CaBr₂.2H₂O (cr) (open circles) in the system LiBr-CaBr₂-H₂O at T=35°C

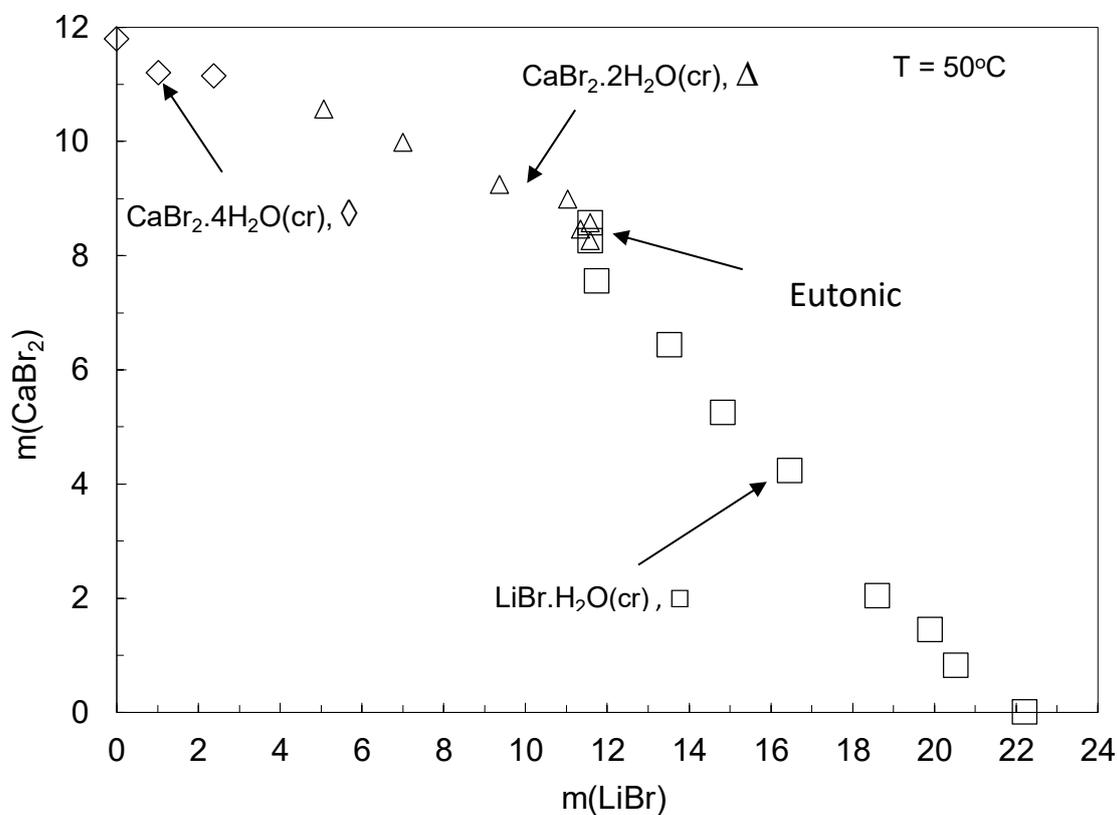


Fig. 2. Experimental molality solubility (mol.kg⁻¹) of LiBr.H₂O (cr) (open squares), CaBr₂.4H₂O (cr) (open diamonds) and CaBr₂.2H₂O (cr) (open triangles) in the system LiBr-CaBr₂-H₂O at T=50°C

The data presented on Tables 1 and 2, and Figs. 1 and 2 show that the solubilities of lithium bromide and calcium bromide solids in binary systems sharply increase with temperature. According to data LiBr·2H₂O (cr) and LiBr·H₂O (cr) precipitate in binary system LiBr-H₂O at 35 °C, and 50°C, respectively. The determined here solubility of LiBr·H₂O (cr) in binary system at 50°C is very close to those reported in a previous experimental study [5]. According to data presented on Tables 1 and 2, and Figs. 1 and 2 CaBr₂·4H₂O (cr) crystallized in the binary system CaBr₂-H₂O at both temperatures. Precipitation of tetrahydrate is in agreement with the temperature variable model and recommendations given in the literature. According to the 0-100 °C solid-liquid equilibrium model of Christov [4] the (CaBr₂·6H₂O (cr) ↔ CaBr₂·4H₂O (cr)) phase transition in water is predicted to occur at a temperature of 32.1°C, which is only by 2.1 C lower than the transition temperature accepted in the compilation of Kirgintsev *et al.* [19] (34.2°C). The determined here solubility of CaBr₂·4H₂O (cr) in pure water at 50°C is very close to those reported in previous experimental studies [4, 16]. The determined here composition of precipitating calcium bromide solids (CaBr₂·4H₂O at T=50°C), and concentration of saturated binary CaBr₂-H₂O solutions at both temperatures (T=35°C and T=50°C) are in excellent agreement with solubility measurements and thermodynamic phase equilibrium models at standard temperature [6], and in a wide range of temperatures from 0° to 100°C (see Fig. 2 in Christov [4]).

In the mixed system LiBr-CaBr₂-H₂O the equilibrium crystallization of LiBr·2H₂O (cr), LiBr·H₂O (cr), CaBr₂·4H₂O (cr) and CaBr₂·2H₂O (cr) has been established at 35°C. At T = 50°C precipitation of LiBr·H₂O (cr), CaBr₂·4H₂O (cr) and CaBr₂·2H₂O (cr) has been determined. The solubilities of lithium bromide solids sharply decrease in ternary system with adding calcium bromide solids at both temperatures. According to data presented in Christov *et al.* [6] and in this study, the phase transition temperature (PPT) LiBr·CaBr₂·5H₂O (cr) → LiBr·H₂O (cr) + CaBr₂·4H₂O (cr) lies within the temperature range from 25°C to 35°C. From the experimental data obtained in this study and modeling study presented in Lassin and André [11] it can be concluded that in both lithium-calcium halide systems LiCl-CaCl₂-H₂O and LiBr-CaBr₂-H₂O double salts with stoichiometry 1-1-5 precipitate only at low temperature below or equal to standard. According to the reference data [11] at T ≥ 40°C only simple

salts precipitate from a saturated mixed lithium-calcium chloride system. According to the data presented in this study at T ≥ 35°C only simple salts precipitate from saturated mixed lithium-calcium bromide system.

There are several invariant point data given in Tables 1 and 2. Development of solid-liquid equilibria model for the mixed system LiBr-CaBr₂-H₂O is the best approach to determine which of these data points is the actual invariant point and to plot the solubility isotherms at 35°C and 50°C. Development of a solid-liquid equilibria model for mixed systems at constant temperature requires as a first step construction a not-concentration restricted models for corresponding binary subsystems. For the mixed system under study LiBr-CaBr₂-H₂O the experimental activity data for both binary subsystems (LiBr-H₂O and CaBr₂-H₂O) are available only at 25°C. These data are used to construct models for binaries and using our own solubility data to develop model for mixed system LiBr-CaBr₂-H₂O at 25°C (ref. 10). In this study we reported solubility data for LiBr-CaBr₂-H₂O at 35°C and 50°C. The reported data can be used to evaluate mixing Pitzer parameters and to develop a model for a mixed system only in case of availability of activity data for binary subsystems at 35°C and 50°C. The widely used temperature variable model for CaBr₂-H₂O described in a previous study of Christov [4] can be used in a model development for the mixed system LiBr-CaBr₂-H₂O. New low- and high-molality activity data for binary LiBr-H₂O at 35°C and 50°C are needed to develop a solid-liquid equilibrium model for the mixed system under study. The data presented here are a very good base to develop an accurate T-variable solid-liquid equilibrium thermodynamic model for lithium bromide-rich brines in the temperature range with importance for improvement of technology for extraction of lithium resources (from 0°C to 50°C).

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REFERENCES

1. C. Balarew, C. Christov, *Compt. rend. Acad. Bulg. Sci.*, **45**, 49 (1992). ISSN 2367-5535

- C. Balarew, C. Christov, S. Petrenko, V. Valyashko, *J. Solution Chem.*, **22**, 173 (1993). <https://doi.org/10.1007/BF00650683>
- C. Christov, C. Balarew, *J. Solution Chem.*, **24**, 1171 (1995). <https://doi.org/10.1007/BF00972963>
- C. Christov, *Calphad*, **35**, 42 (2011). doi:10.1016/j.calphad.2010.11.001
- C. Christov, C. Balarew, V. Valyashko, S. Petrenko, *J. Solution Chem.*, **23**, 595 (1994). DOI:10.1007/BF00972747
- C. Christov, S. Velikova, K. Ivanova, *J. Chem. Thermodyn.*, **32**, 1505 (2000). doi:10.1006/jcht.2000.0688
- C. Christov, *J. Chem. Thermodyn.*, **27**, 1267 (1995). <https://doi.org/10.1006/jcht.1995.0133>
- C. Christov, *J. Chem. Thermodyn.*, **37**, 1036 (2005). <https://doi.org/10.1016/j.jct.2005.01.008>
- R. Cui, C. Peng, G. Nie, S. Sang, H. Ren, W. Li, *Front. Chem.*, **11**, 1093435 (2023). 10.3389/fchem.2023.109343
- A. Lassin, C. Christov, L. André, M. Azaroual, *Amer. J. Sci.*, **315**, 204 (2015). DOI: [10.2475/03.2015.02](https://doi.org/10.2475/03.2015.02)
- A. Lassin, L. André, *J. Chem. Thermodyn.*, **176**, 1 (106927). (2023). doi.org/10.1016/j.jct.2022.106927
- N. Greenfield, Lithium Mining Is Leaving Chile's Indigenous Communities High and Dry (Literally) (2022). <https://www.nrdc.org/stories/lithium-mining-leaving-chiles-indigenous-communities-high-and-dry-literally>.
- V. Marcinov, J. Klimko, Z. Takáčová, J. Pirošková, A. Miškufová, M. Sommerfeld, C. Dertmann, B. Friedrich, D. Oráč, *Metals*, **13**, 1213 (2023). <https://doi.org/10.3390/met13071213>.
- A. Zdanovskii, E. Soloveva, E. Liahovskaia, N. Shestakov, P. Shleimovich, L. Abutkova, L. Cheremnih, T. Kulikova, *Experimentalnie dannie po rastvorimosti*, vols. I-1, I-2, II-1 and II-2, Khimizdat, St. Petersburg, 2003.
- C. Christov, *J. Chem. Thermodyn.*, **32**, 285 (2000) <https://doi.org/10.1006/jcht.1999.0564>
- S. Donchev, I. Ismailov, I. Parushev, C. Christov, *Res. J. Pharm. Biol. Chem. Sci. (RJPBCS)* **10** (5), 83 (2019) <https://doi.org/10.33887/rjpbcs/2019.10.5.12>
- G. Schwarzenbach, H. Flashka, *Komplexometrische Titration (in Russian)*, Izd. Khimiya, Moscow, 1970.
- F. Schreinemakers, *Z. Physik. Chem.*, **11**, 75 (1893) (see also refs. 1, 2, 15, and 16).
- A. Kirgintsev, L. Trushnikova, V. Lavrentieva, *Solubility of inorganic compounds in water*, Izd. Khimiya, St. Petersburg, 1972.