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Solubilities and vapour pressures of saturated aqueous solutions of sodium tetraborate, sodium carbonate, and magnesium sulfate and freezing-temperature lowerings of sodium tetraborate and sodium carbonate solutions

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Abstract

Solubilities and vapour pressures of water over saturated solutions of sodium tetraborate, sodium carbonate, and magnesium sulfate and freezing-temperature lowerings of sodium tetraborate and sodium carbonate solutions were determined and compared with the literature data. These results permitted the evaluation of osmotic and activity coefficients and molar enthalpies of vaporization.

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Keywords: Vapour pressures; Saturated solutions; Water activities; Osmotic and activity coefficients; Molar enthalpies of vaporization

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1. Introduction

Thermodynamic properties of aqueous solutions of strong electrolytes were considered in many of our investigations dealing with solubilities [1–3], vapour pressure [4–11], and freezing-temperature depressions of salts [1,12,13]. In this work, three more inorganic salts, sodium tetraborate (borax), sodium carbonate, and magnesium sulfate, which are of a significant geochemical interest, are examined. Considering the importance of aqueous solutions of these salts (for example, the carbonate system is the predominant acid–base buffering system in natural waters), the solubility, vapour pressure, and cryoscopic measurements were performed in order to obtain an improved description of these systems.

Cryoscopic studies in the ($\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$) system were performed by Menzel [14] and Platford [15]. Solubility of sodium tetraborate in water as a function of temperature were determined by Horn and van Wagener [16] (tabulated in the Stephen and Stephen [17] compilation of solubilities), Blasdale and Slansky [18] (reported and discussed also by Linke [19]), Menzel and Schultz [20], Nies and Hulbert [21], and only at $T = 298.15 \text{ K}$ by Platford [22]. Vapour pressures over saturated aqueous solutions of borax were reported only by Dienis [23]. In the case of (sodium carbonate + water) system, the freezing temperatures were determined by Loomis [24] (other old measurements are summarized in International Critical Tables [25]) and especially by Ender [26]. In main tabulations [17,19,25], the solubilities of sodium carbonate are based on the Wells and MacAdam [27] and Sayer and Todd [28] experiments (see also Waldeck et al. [29]). Vapour pressures over saturated aqueous solutions of sodium carbonate were determined by Diesnis [23], O'Brien [30], and others [25]. Solubilities of magnesium sulfate in water, in the $T = 273$ to 373 K temperature interval, are tabulated in International Critical Tables [25] and in Linke [19] (see also Ting and McCabe [31] and for temperatures higher than $T = 341 \text{ K}$, Robson [32]). Vapour pressures of saturated solutions of magnesium sulfate were considered by Diesnis [23] (who also cited old values of vapour pressures, published by Wiedemann [33] in 1874), Winston and Bates [34], Kangro and Groeneveld [35], and others [25,36].

In this work, solubilities of salts in water and vapour pressures over saturated aqueous solutions of sodium tetraborate, sodium carbonate, and magnesium sulfate and freezing-temperature lowerings in solutions of sodium tetraborate and sodium carbonate were determined and discussed. From these measurements, osmotic coefficients, activity coefficients (applying the Gibbs–Duhem equation), and the molar enthalpies of vaporization were derived.

2. Experimental

Sodium tetraborate decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (>0.990 mass fraction), sodium carbonate decahydrate, and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (>0.990 mass fraction) were supplied by Riedel-de Haen and magnesium sulfate monohydrate, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$

(>0.995 mass fraction) by Frutarom Laboratory Chemicals, Haifa. Reagents were used in experiments without further purification.

Cryoscopic measurements [1,12,13,37–41] were performed in a jacketed vessel cooled or heated by running alcohol from a Julabo refrigerating bath. Precisely, weighed amounts of salt and double distilled water were introduced into the vessel. Homogeneity of temperature of the (solution + ice) mixture was ensured by mixing with a mechanical stirrer (85–120 rpm). Temperature as a function of time was measured with a Hart Scientific Model 1502 thermometer equipped with a printer. The sensitivity of this thermometer is ± 0.001 K. The thermometer served to determine the freezing temperature of a double distilled water used in experiments, $T_f(\text{H}_2\text{O})$ and the freezing temperatures of investigated solutions, $T_f(m)$. These temperatures were determined from the temperature versus time curves using the Moulin method [41]. In this method, $T_f(m)$ is derived from an interception of the hyperbola and straight lines which were determined from cooling curves using a computer programme that we prepared. The error in the *freezing-point depression* of solution of molality m , $\theta(m) = T_f(\text{H}_2\text{O}) - T_f(m)$ is estimated to be ± 0.002 K.

The vapour pressures over saturated solutions were determined using the Rortronic Hygroskop DT1 which is equipped with a measuring station WA-14TH. Saturated solutions with an excess of solid phase were placed in the measuring station in disposable polystyrene sample cups. The change of temperature was obtained by an external-mantle of the station which was heated or cooled by running water from an external thermostat. After the thermal equilibrium was attained, the systems needed about 1 h to reach the (vapour + liquid) equilibrium. Thermal stability of the measuring system is estimated to be ± 0.05 K and the sensitivity of the used hygrometer is about ± 0.003 kPa at $T = 298.15$ K. The applied procedure was frequently checked by determining vapour pressures of saturated solutions of sodium chloride [42].

Saturated solutions with an excess of the solid phase were stirred in double-wall tubes thermostated by circulating water. Fluctuations of temperature were less than ± 0.01 K. The solubility measurements were performed with doubly distilled water (in both directions, by increasing and decreasing temperature) as described elsewhere [1–3]. In each system under consideration, the (solid + liquid) equilibrium was ensured by checking in preliminary experiments the time of stirring and gravitational settling at few temperatures in the studied temperature interval. In actual experiments, times which were needed to attain the equilibrium were almost doubled (about 1 h of the stirring and 48 h of the settling).

Weighed samples of saturated solutions of sodium tetraborate and sodium carbonate were titrated with standardized 0.1 M solutions of HCl using bromocresol green as an indicator. Magnesium sulfate was titrated complexometrically with solutions of EDTA (Merck) using Eriochrome black T as an indicator. At each temperature, reported solubilities are the average value of four independent determinations. Relative error in solubility values is less than 1.5% for sodium tetraborate and sodium carbonate and about 1.5 to 2.0% for magnesium sulfate.

3. Results and discussion

Determined freezing-temperature lowerings of sodium tetraborate and sodium carbonate aqueous solutions $\theta(m)$, together with the literature data [14,15,24–26], are presented in table 1 and plotted in figures 1 and 2. As can be observed, different investigations augment each other and there is reasonable agreement between them. These freezing-temperature depressions can be correlated by

$$\theta(m; \text{Na}_2\text{B}_4\text{O}_7)/\text{K} = 0.479m^{*1/2} + 6.248m^* \quad (1)$$

and

$$\theta(m; \text{Na}_2\text{CO}_3)/\text{K} = 0.218m^{*1/2} + 3.715m^*, \quad (2)$$

where $m^* = m/m^\circ$ and $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$. Values of $\theta(m)$ are directly related to the activities of water a_1 [43] by

$$-\ln a_1 = 9.687 \times 10^{-3}(\theta/\text{K}) + 4.8 \times 10^{-6}(\theta/\text{K})^2. \quad (3)$$

TABLE 1

Experimental freezing-temperature depressions θ of sodium tetraborate and sodium carbonate solutions

$m/(\text{mol} \cdot \text{kg}^{-1})$	θ/K	$m/(\text{mol} \cdot \text{kg}^{-1})$	θ/K	$m/(\text{mol} \cdot \text{kg}^{-1})$	θ/K
Na₂B₄O₇					
0.0010 [15]	0.011	0.1010	0.118	0.0500 [15]	0.403
0.0020 [15]	0.022	0.0123	0.148	0.0503 [14]	0.410
0.0031	0.041	0.0124 [14]	0.126	0.0649	0.552
0.0032	0.050	0.0200 [15]	0.193	0.0655 [14]	0.499
0.0050 [15]	0.054	0.0250	0.250	0.0756 [14]	0.555
0.0053	0.067	0.0391	0.378	0.0797	0.628
0.0063	0.076	0.0446 [14]	0.380	0.0901	0.745
0.0100 [15]	0.104	0.0498	0.417	0.1001	0.784
Na₂CO₃					
0.0036 [26]	0.019	0.0501	0.287	0.1879 [26]	0.794
0.0063	0.043	0.0536 [26]	0.246	0.1991	0.827
0.0068 [26]	0.036	0.0700 [25]	0.319	0.2000 [24]	0.834
0.0100 [24]	0.051	0.0708 [26]	0.319	0.2000 [25]	0.834
0.0100 [25]	0.051	0.0723 [26]	0.325	0.2488 [26]	1.035
0.0130	0.076	0.0937 [26]	0.414	0.2494	1.078
0.0131 [26]	0.070	0.0984 [26]	0.433	0.2668 [26]	1.107
0.0165 [26]	0.083	0.0992 [26]	0.437	0.2999	1.299
0.0179 [26]	0.089	0.0996	0.446	0.3251 [26]	1.314
0.0200 [24]	0.099	0.1000 [24]	0.442	0.3492	1.378
0.0200 [25]	0.099	0.1000 [25]	0.440	0.4000 [25]	1.552
0.0250	0.138	0.1115 [26]	0.487	0.4002	1.626
0.0321 [26]	0.153	0.1397 [26]	0.601	0.4467 [26]	1.825
0.0361 [26]	0.171	0.1423 [26]	0.611	0.4500	1.858
0.0400 [25]	0.189	0.1499	0.654	0.4703 [26]	1.911
0.0418 [26]	0.196	0.1740 [26]	0.738	0.5009	2.023
0.0200 [24]	0.232	0.1809 [26]	0.766		

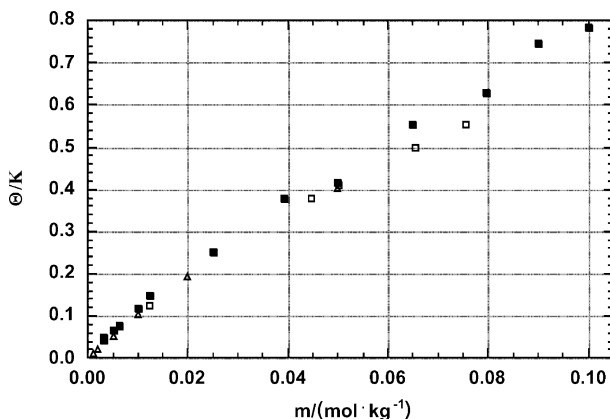


FIGURE 1. Experimental freezing-temperature lowerings of aqueous solutions of sodium tetraborate, plotted against concentration m in $\text{mol} \cdot \text{kg}^{-1}$. □, [14]; △, [15]; ■, this work.

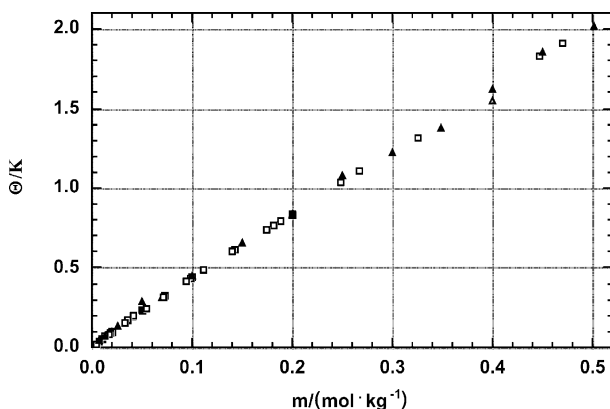


FIGURE 2. Experimental freezing-temperature lowerings of aqueous solutions of sodium tetraborate, plotted against concentration m in $\text{mol} \cdot \text{kg}^{-1}$. ■, [24]; △, [25]; □, [26]; ▲, this work.

The activity of water a_1 leads to the osmotic coefficient $\phi(m)$ of components

$$\phi(m) = -55.508 \ln a_1 / (\nu m), \quad (4)$$

where ν is the *total number of ions or particles formed from an electrolyte entity*. The value of ν can be determined by considering that at infinite dilution [43–45]

$$\lim_{m \rightarrow 0} (\theta / \lambda m) = \nu, \quad (5)$$

where $\lambda = 1.86 \text{ kg} \cdot \text{mol}^{-1} \text{ K}$ is the *cryoscopic constant of water*, and at finite concentrations $\theta / \lambda m$ represents the *apparent number of ions*. As can be seen in figure 3, the expected limit $\nu = 3$, is approached for sodium carbonate. The form of the $\theta / \lambda m$ curve supports this value in spite of a large scattering of our results in the low concentration region. However, the case of sodium tetraborate solutions is more

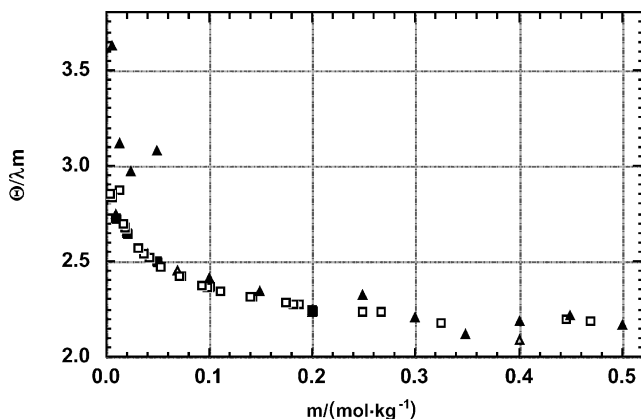


FIGURE 3. The apparent number of particles in solution, $\theta/\lambda m$, plotted against concentration of sodium carbonate m in $\text{mol} \cdot \text{kg}^{-1}$. ■, [24]; △, [25]; □, [26]; ▲, this work.

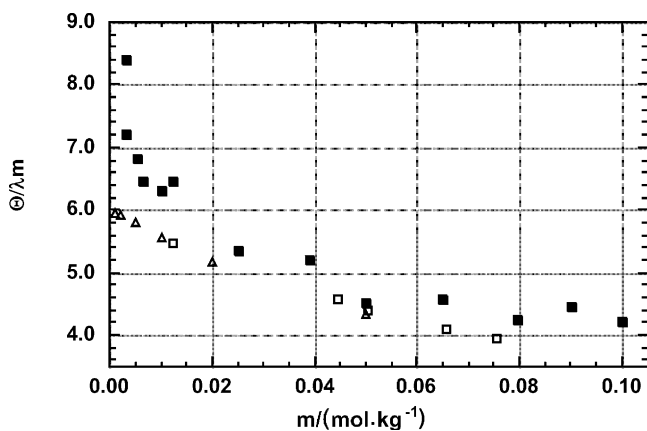
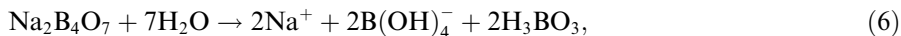


FIGURE 4. The apparent number of particles in solution, $\theta/\lambda m$, plotted against concentration of sodium tetraborate m in $\text{mol} \cdot \text{kg}^{-1}$. □, [14]; △, [15]; ■, this work.

complex (figure 4). Platford [15,22] treated the freezing-temperature depressions and isopiestic measurements at $T = 298.15 \text{ K}$, by introducing $\nu = 6$, which is consistent with the following hydrolysis reaction:



Thus, the solution consists of an electrolyte $\text{NaB}(\text{OH})_4$ and a nonelectrolyte boric acid [46]. Because borax in solution can be formed by mixing aqueous sodium metaborate (NaBO_2) and H_3BO_3 , it is possible to calculate the excess free energy of mixing, however the actual energy change indicates that borax in solution has behaviour more complicated than that represented by Eq. (6) [22]. This conclusion is supported by our freezing-temperature results (figure 4) which are rather consistent

with $\nu = 7$ and not with $\nu = 6$. At low concentrations, our results lead even to $\nu = 8$ – 9 , but the accuracy of measurements in this region is very low to accept these values. In table 2 are presented osmotic coefficients of sodium carbonate and sodium tetraborate (based on Eq. (1) and with $\nu = 6$ and $\nu = 7$), together with those determined from cryoscopic and isopiestic experiments at $T = 298.15$ K by Platford [15,22]. Osmotic coefficients of sodium carbonate at $T = 298.15$ K were reported by Goldberg [46] and Robinson and Macaskill [47]. Water activities of magnesium sulfate solutions at $T = 273.15$ K were considered by Platford [48].

The mean activity coefficients γ_{\pm} can be evaluated using the Gibbs–Duhem equation in the form [49]

$$\ln \gamma_{\pm} = \phi - 1 + 2 \int_0^{m^{1/2}} (\phi - 1)/m^{1/2} d(m^{1/2}), \quad (7)$$

but because the integrand limit, $(\phi - 1)/m^{1/2}$ as $m \rightarrow 0$, was uncertain, the integral was evaluated from the arbitrary limit, $m^* = 0.01 \text{ mol kg}^{-1}$ and with the corresponding $\phi^* = \phi(m^* = 0.01 \text{ mol} \cdot \text{kg}^{-1})$, i.e.,

$$\ln(\gamma_{\pm}/\gamma_{\pm}^*) = \phi - \phi^* + 2 \int_{m^{*1/2}}^{m^{1/2}} (\phi - 1)/m^{1/2} d(m^{1/2}). \quad (8)$$

TABLE 2

Osmotic coefficients ϕ of sodium tetraborate and sodium carbonate at freezing temperatures T_f and sodium tetraborate at $T = 298.15$ K [15]

$m/(\text{mol} \cdot \text{kg}^{-1})$	ϕ		ϕ^a	ϕ^b	ϕ^c
	$\nu = 6$	$\nu = 7$	$\nu = 6$	$\nu = 6$	$\nu = 3$
0.01	0.990	0.848	0.928	0.890	1.056
0.02	0.864	0.740	0.867		0.942
0.03	0.808	0.693			0.891
0.04	0.775	0.664			0.861
0.05	0.752	0.645	0.723	0.760	0.841
0.06	0.736	0.630			0.825
0.07	0.723	0.619			0.814
0.08	0.712	0.610			0.804
0.09	0.703	0.603			0.796
0.10	0.696	0.597		0.671	0.790
0.15					0.767
0.20				0.562	0.753
0.25					0.744
0.30					0.738
0.35					0.732
0.40					0.728
0.45					0.725
0.50					0.722

^a $\text{Na}_2\text{B}_4\text{O}_7$: [15], T_f .

^b $\text{Na}_2\text{B}_4\text{O}_7$: [15], $T = 298.15$ K.

^c NaCO_3 : this work, T_f .

The integrand was expressed as a polynomial of $m^{1/2}$ and the integral (8) was evaluated analytically to give the ratio of activity coefficients. In the case of borax, Platford [15] assumed that $\gamma_{\pm}^* = 0.870$ and the same value is also used here. For sodium carbonate, the activity coefficient $\gamma_{\pm}^* = 0.716$ was calculated from the Debye–Hückel equation in the Güntelberg form [43]

$$\ln \gamma_{\pm} = -1.1324 |z_+ z_-| I^{1/2} / (1 + I^{1/2}), \quad (9)$$

where in our case $|z_+ z_-| = 2$ and $I = 3m^*$. Introducing these values of coefficients, the activity coefficients of sodium tetraborate (for $\nu = 6$ and $\nu = 7$) and those of sodium carbonate are presented in table 3.

Vapour pressures of saturated solutions of sodium tetraborate, sodium carbonate, and magnesium sulfate together with the literature data are presented in table 4 and in figures 5–7. In the case of borax, only few measurements were performed by Diesnis [23] and they agree well with our determinations (figure 5). Vapour pressures over sodium carbonate solutions for $T > 304$ K are systematically higher in our experiments than those from the literature [23,25,30] (figure 6). Vapour pressures of saturated magnesium sulfate solutions were measured many times [23,25,33–36] and there is a reasonable agreement with our results (figure 7). It is worthwhile to note that old measurements of Wiedemann [33] from 1874 are comparable with much further determinations.

TABLE 3

Activity coefficients γ_{\pm} of sodium tetraborate and sodium carbonate at freezing temperatures T_f and sodium tetraborate at $T = 298.15$ K [15]

$m/(\text{mol} \cdot \text{kg}^{-1})$	γ_{\pm}		γ_{\pm}^a	γ_{\pm}^b	γ_{\pm}^c
	$\nu = 6$	$\nu = 7$	$\nu = 6$	$\nu = 6$	$\nu = 3$
0.01	0.870	0.870			0.716
0.02	0.726	0.674			0.637
0.03	0.642	0.573			0.624
0.04	0.586	0.509			0.548
0.05	0.544	0.462	0.547	0.575	0.518
0.06	0.510	0.426			0.495
0.07	0.482	0.392			0.477
0.08	0.460	0.374			0.460
0.09	0.441	0.355			0.446
0.10	0.424	0.339		0.430	0.434
0.15					0.387
0.20				0.345	0.357
0.25					0.334
0.30					0.316
0.35					0.302
0.40					0.290
0.45					0.280
0.50					0.271

^a $\text{Na}_2\text{B}_4\text{O}_7$: [15], T_f .

^b $\text{Na}_2\text{B}_4\text{O}_7$: [15], $T = 298.15$ K.

^c NaCO_3 : this work, T_f .

TABLE 4

Vapour pressures p of saturated aqueous solutions of sodium tetraborate, sodium carbonate and magnesium sulfate at temperatures T

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
Na ₂ B ₄ O ₇ (aq)					
278.15	0.875	295.75 [23]	2.657	309.45	5.851
279.35	0.951	295.85	2.743	310.55	6.200
280.55	1.033	296.75	2.885	311.45	6.503
281.35	1.079	297.75	3.014	312.55	6.913
282.75	1.198	298.35 [23]	3.113	313.15	7.109
283.95	1.299	298.75	3.228	314.05	7.449
285.35	1.425	299.55	3.395	315.25	7.936
286.35	1.510	300.55	3.600	316.25	8.353
287.35	1.587	300.75 [23]	3.567	316.85	8.654
289.25	1.821	302.45	3.948	318.05	9.207
290.15	1.932	304.14 [23]	4.263	318.55	9.349
291.05	2.008	304.25	4.435	319.65	9.879
292.05	2.167	305.15	4.658	320.75	10.48
292.15 [23]	2.140	306.05	4.895	321.75	10.96
292.95	2.280	306.35	4.953	322.75	11.39
293.25 [23]	2.289	306.95 [23]	5.157	323.75	11.98
293.65	2.284	307.85	5.385		
295.05	2.610	309.35	5.825		
Na ₂ CO ₃ (aq)					
280.15	0.905	298.15 [30]	2.912	308.45	5.406
281.15	0.889	298.15 [30]	2.633	308.75 [25]	4.533
282.05	1.029	298.65 [23]	2.893	309.15 [25]	4.640
282.95	1.013	298.75	2.986	309.25	5.494
283.15 [30]	1.216	299.45	2.972	309.75	5.818
283.65	1.150	299.75	3.160	310.05	5.852
284.45	1.140	300.45	3.311	310.55	5.840
285.15	1.279	300.65 [25]	3.200	311.05	6.027
285.75	1.271	300.65	3.320	311.55	6.368
286.85	1.442	300.85 [23]	3.334	312.45	6.499
287.35	1.451	301.25	3.464	312.55	6.720
288.15 [25]	1.640	301.65	3.527	313.15 [25]	5.813
289.35	1.810	301.65	3.708	313.15 [30]	5.766
289.45 [23]	1.735	302.25	3.708	313.35	6.998
289.95	1.753	302.75	3.900	313.45	6.840
290.25	1.938	303.15 [30]	3.693	313.55	6.975
290.75	1.856	303.15 [25]	3.573	314.35	7.159
291.35	2.076	303.25	3.911	314.65	7.425
291.65 [30]	1.959	303.25	3.911	314.75	7.311
291.85 [23]	1.995	303.45 [23]	3.665	315.75	7.883
292.85	2.121	303.65	4.111	315.85	7.737
293.15 [23]	2.148	304.15 [25]	3.720	316.15	7.989
293.15 [25]	2.253	304.15	4.113	316.95	8.184
293.15 [30]	2.151	304.25	4.293	317.25	8.459
293.15	2.151	304.75	4.293	317.55	8.452
293.35	2.181	305.15 [25]	3.840	318.15 [30]	7.613
293.75	2.157	305.15	4.658	318.25	8.907
294.15	2.268	305.25	4.560	318.65	8.914

TABLE 4 (continued)

<i>T</i> /K	<i>p</i> /kPa	<i>T</i> /K	<i>p</i> /kPa	<i>T</i> /K	<i>p</i> /kPa
Na ₂ B ₄ O ₇ (aq)					
294.35	2.261	305.30 [25]	3.867	319.25	9.364
294.95 [25]	2.372	305.95	4.554	319.35	9.321
295.85	2.547	306.15	4.777	319.55	9.334
295.95	2.549	306.25 [25]	3.933	320.45	9.808
296.15 [23]	2.532	306.85	4.784	320.55	9.960
296.45	2.693	307.15 [25]	4.227	321.05	10.04
296.75	2.689	307.15	5.019	322.05	10.57
297.35	2.818	307.25 [23]	4.469	323.15	9.880
297.55	2.813	307.35	5.076	323.55	11.53
297.65 [30]	2.676	307.85	5.036	325.25	12.38
298.15 [25]	2.853 [25]	308.15 [25]	4.427	328.15 [30]	12.72
298.15 [30]	2.633 [30]	308.35	5.240	333.15 [30]	16.20
MgSO ₄ (aq)					
281.15	1.002	295.45 [33]	2.133	307.15	4.838
281.75	1.044	295.55	2.528	307.35 [23]	4.709
282.95	1.136	296.45	2.621	307.95	5.019
283.15 [25]	1.067	296.85 [23]	2.583	309.05	5.351
283.55	1.183	297.35	2.803	309.80 [33]	4.747
284.75 [33]	1.280	297.45 [33]	2.373	309.85	5.553
285.15	1.268	298.15 [36]	2.861	311.05	5.934
285.35	1.343	298.15 [35]	2.781	311.75	6.149
286.95	1.434	298.15 [34]	2.820	312.95	6.536
287.75	1.575	298.35	2.937	313.15 [33]	6.293
288.85	1.625	299.55	3.202	313.35 [33]	6.173
289.65	1.780	299.55 [23]	3.047	313.55	6.794
290.65 [23]	1.787	300.25	3.293	314.85	7.196
290.75	1.836	301.45	3.559	315.45	7.619
291.85	2.029	302.00 [23]	3.505	316.85	7.936
292.65	2.070	302.25	3.652	317.05	7.883
292.85 [23]	2.049	302.95 [33]	3.533	318.55 [33]	8.120
293.15 [34]	2.105	303.15 [33]	3.733	318.75	8.703
293.15 [25]	2.120	303.35	3.959	318.95	8.852
293.15 [23]	2.048	304.25	4.091	323.15 [33]	10.09
293.75	2.286	304.35 [23]	4.011	325.05 [23]	10.92
294.40 [23]	2.245	305.25	4.397		
294.55	2.335	306.15	4.545		

The temperature dependence of the vapour pressure of saturated solutions is given by the Clausius–Clapeyron equation [50]

$$d(\ln p)/d(1/T) = -\Delta_{\text{cr}\rightarrow\text{g}}H_m(T)/R, \quad (10)$$

where $\Delta_{\text{cr}\rightarrow\text{g}}H_m(T)$ is the molar enthalpy change associated with evaporating of water and simultaneously crystallizing the salt. If it is assumed that over the considered range of temperature, $\Delta_{\text{cr}\rightarrow\text{g}}H_m(T)$ depends linearly on temperature, the integral form of Eq. (10) is

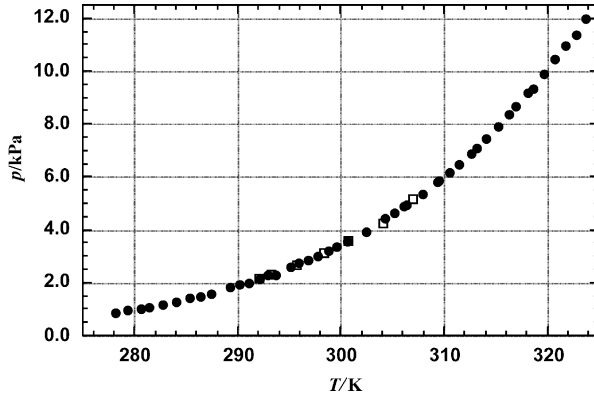


FIGURE 5. Vapour pressures of saturated aqueous solutions of sodium tetraborate p plotted against temperature T . □, [23]; ●, this work.

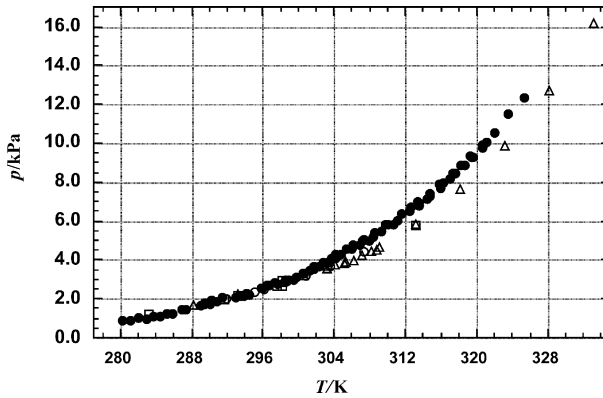


FIGURE 6. Vapour pressures of saturated aqueous solutions of sodium carbonate p plotted against temperature T . ○, [23]; △, [25]; □, [30]; ●, this work.

$$\ln\{p(\text{Na}_2\text{B}_4\text{O}_7, T, m)/\text{kPa}\} = 65.773 - 7298.4(T/\text{K})^{-1} - 7.0483 \ln(T/\text{K}),$$

$$R^2 = 0.9999, \tag{11}$$

$$\ln\{p(\text{Na}_2\text{CO}_3, T, m)/\text{kPa}\} = 157.67 - 11568(T/\text{K})^{-1} - 20.674 \ln(T/\text{K}),$$

$$R^2 = 0.9987, \tag{12}$$

and

$$\ln\{p(\text{MgSO}_4, T, m)/\text{kPa}\} = 101.70 - 8886.9(T/\text{K})^{-1} - 12.430 \ln(T/\text{K}),$$

$$R^2 = 0.9997, \tag{13}$$

The parameters in this and similar equations were evaluated by an unweighted multivariate least-squares method using only our vapour pressures. In table 5 are

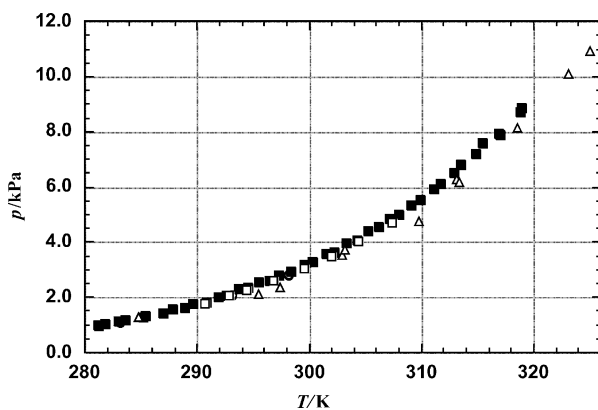


FIGURE 7. Vapour pressures of saturated aqueous solutions of magnesium sulfate p plotted against temperature T . □, [23]; ○, [25,34–36]; △, [33]; ■, this work.

reported at 5 K intervals the values of vapour pressures p , solubilities of $m = m_{\text{sat}}$ (determined in this work), activities of water $a_1 = p/p^*$, osmotic coefficients ϕ , and the molar enthalpies of vaporization $\Delta_{\text{cr} \rightarrow \text{g}} H_m(T)$ (based on Eqs. (11)–(13)). The vapour pressures p^* of pure water at a given T were evaluated from the Saul and Wagner equation [51].

At $T = 298.15$ K, it is possible to compare osmotic coefficients determined here (table 5) with those that were reported in the literature. The Platford [15] result based on isopiestic measurements with sodium tetraborate solutions, $\phi(\text{Na}_2\text{B}_4\text{O}_7, m_{\text{sat}} = 0.1543 \text{ mol} \cdot \text{kg}^{-1}) = 0.611$ is far from our value determined by the hygrometric method, $\phi(\text{Na}_2\text{B}_4\text{O}_7, m_{\text{sat}} = 0.1685 \text{ mol} \cdot \text{kg}^{-1}) = 0.967$. Since the solubilities used in calculations are in both cases similar, the difference in osmotic coefficients results mainly from different water activities. However, the vapour pressure of water over saturated solution of sodium tetraborate as determined by Diesnis [23] using the isoteniscopic method (i.e., by the direct experimental technique) is close to our value (table 4, figure 5). Thus, findings based on two independent methods support the conclusion that the Platford value is rather incorrect.

There is also an unsatisfactory situation in the case of saturated sodium carbonate solutions. Voznesenskaya [36] reported that $\phi(\text{Na}_2\text{CO}_3, m_{\text{sat}} = 2.77 \text{ mol} \cdot \text{kg}^{-1}) = 0.831$ when Robinson and Macaskill [47] gave $\phi(\text{Na}_2\text{CO}_3, m_{\text{sat}} = 3.0 \text{ mol} \cdot \text{kg}^{-1}) = 0.739$ (based mainly on this investigation). Goldberg [46] suggested that $\phi(\text{Na}_2\text{CO}_3, m_{\text{sat}} = 2.767 \text{ mol} \cdot \text{kg}^{-1}) = 0.722$ as compared with the osmotic coefficient presented here, $\phi(\text{Na}_2\text{CO}_3, m_{\text{sat}} = 2.75 \text{ mol} \cdot \text{kg}^{-1}) = 0.521$. It is difficult to judge correctness of these results because inexplicably large differences in vapour pressures ($p = 2.633$ – 2.912 kPa [25,30] at $T = 298.15$ K when our result is $p = 2.933$ kPa) are observed in different investigations (table 4). Differences in vapour pressures of saturated magnesium sulfate solutions are not so significant ($p = 2.781$ – 2.861 kPa [34–36] when our vapour pressure is $p = 2.920$ kPa) but the effect on osmotic coefficients is large: $\phi(\text{MgSO}_4, m_{\text{sat}} = 3.10 \text{ mol} \cdot \text{kg}^{-1}) = 0.916$ [36] as compared with $\phi(\text{MgSO}_4, m_{\text{sat}} = 3.13 \text{ mol} \cdot \text{kg}^{-1}) = 0.725$ (table 5).

TABLE 5

Solubilities m , vapour pressures p , water activities a_1 , osmotic coefficients ϕ , and molar enthalpies of vaporization $\Delta_{\text{cr}\rightarrow\text{g}}H_m(T)$ as a function of temperature T ($R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$m/(\text{mol} \cdot \text{kg}^{-1})$	p/kPa	a_1	ϕ	$\Delta_{\text{cr}\rightarrow\text{g}}H_m(T)/(\text{RK})$
Na₂B₄O₇(aq)					
283.15	0.0741	1.225	0.997	0.319 ^a	5300
288.15	0.0982	1.693	0.993	0.666	5270
293.15	0.1291	2.310	0.988	0.869	5230
298.15	0.1685	3.113	0.983	0.967	5200
303.15	0.2184	4.146	0.977	0.998	5160
308.15	0.2812	5.460	0.970	0.996	5130
313.15	0.3596	7.115	0.964	0.944	5090
318.15	0.4573	9.178	0.957	0.887	5060
323.15	0.5779	11.73	0.950	0.822	5020
Na₂CO₃(aq)					
278.15	0.8529	0.757	0.868	3.08	5820
283.15	1.153	1.092	0.889	1.88	5710
288.15	1.549	1.545	0.906	1.18	5610
293.15	2.07	2.146	0.916	0.766	5510
298.15	2.75	2.933	0.926	0.521	5400
303.15	3.62	3.943	0.929	0.376	5300
308.15	4.46	5.222	0.928	0.291	5200
313.15	4.56	6.818	0.924	0.322	5090
318.15	4.53	8.781	0.916	0.359	4990
323.15	4.47	11.17	0.905	0.415	4890
MgSO₄(aq)					
278.15	2.27	0.812	0.930	0.884	5430
283.15	2.47	1.143	0.931	0.799	5370
288.15	2.69	1.586	0.930	0.750	5310
293.15	2.91	2.167	0.927	0.727	5240
298.15	3.13	2.920	0.921	0.725	5180
303.15	3.36	3.882	0.915	0.738	5120
308.15	3.60	5.097	0.906	0.763	5060
313.15	3.83	6.613	0.896	0.796	4990
318.15	4.07	8.484	0.885	0.836	4930
323.15	4.31	10.77	0.872	0.880	4870

^aOsmotic coefficients calculated with $\nu = 6$.

The composition–temperature relations in the (sodium tetraborate + water) system are rather complex [16–21]. In the investigated temperature interval, sodium tetraborate exists in the solid phase as sodium tetraborate decahydrate, pentahydrate, and tetrahydrate (kernite) with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ transition at $T = 331.65 \text{ K}$ and the metastable $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ transition at $T = 333.95 \text{ K}$ [18–20]. Blasdale and Slansky [18] and Linke [19] pointed out that solubility curve of kernite between $T = 333 \text{ K}$ and $T = 373 \text{ K}$ represents lower concentrations of sodium tetraborate than those of the pentahydrate at corresponding temperatures. The pentahydrate possesses a remarkable degree of stability being thermodynamically metastable with respect to the tetrahydrate in the same temper-

ature interval. Thus, above $T = 331.65$ K, the stable solid phase is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ rather than $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ as had been supposed in older investigations (i.e., solutions above sodium tetraborate pentahydrate are supersaturated with respect to kernite [21]). Determined in this work, solubilities of borax in water are presented in table 6 and they are plotted together with the literature values in figure 8. The sodium tetraborate decahydrate solubility branch is easily and satisfactorily reproduced, but the situation with the tetrahydrate solubility branch is different (figure 8). Our solubilities for $T > 333$ K are systematically higher than those reported in

TABLE 6

Solubilities m of sodium tetraborate, sodium carbonate, and magnesium sulfate in water as a function of temperature T

T/K	$m/(\text{mol} \cdot \text{kg}^{-1})$	T/K	$m/(\text{mol} \cdot \text{kg}^{-1})$	T/K	$m/(\text{mol} \cdot \text{kg}^{-1})$
$\text{Na}_2\text{B}_4\text{O}_7$					
279.15	0.0668	318.15	0.4375	337.15	1.1167
284.15	0.0840	321.65	0.5219	338.15	1.2028
288.65	0.1042	322.15	0.5282	340.15	1.2705
293.65	0.1300	323.35	0.5671	340.65	1.3605
298.15	0.1622	326.15	0.6133	341.15	1.421
301.15	0.2000	326.65	0.6231	342.15	1.461
303.15	0.2018	326.95	0.6243	345.15	1.713
305.15	0.2375	327.15	0.6970	345.65	1.714
307.15	0.2407	328.15	0.6802	348.15	1.736
308.15	0.2554	330.15	0.8935	348.65	1.756
309.65	0.2994	330.65	0.8794	352.65	2.04
312.15	0.3215	331.15	0.8794	355.15	2.19
313.15	0.3280	332.15	0.9752	359.65	2.36
314.65	0.3732	332.35	0.9394	363.65	2.45
317.15	0.4025	334.15	1.0553		
317.65	0.4359	335.15	1.1617		
Na_2CO_3					
279.15	0.8998	316.15	4.60	332.35	4.33
284.15	1.0480	317.15	4.56	333.15	4.27
288.65	1.572	317.65	4.48	334.15	4.48
293.65	2.15	320.65	4.56	336.65	4.42
298.15	2.83	322.15	4.46	337.15	4.34
303.15	3.83	323.15	4.41	338.15	4.25
306.15	4.43	326.95	4.39	340.65	4.26
308.15	4.79	327.15	4.46	341.15	4.38
311.15	4.70	328.15	4.38	342.15	4.34
313.15	4.60	330.15	4.32	343.15	4.30
313.65	4.62	332.15	4.40		
MgSO_4					
278.15	2.29	303.15	3.28	328.15	4.61
283.15	2.45	308.15	3.57	333.15	4.74
288.15	2.63	313.15	3.83	338.15	4.89
293.15	2.82	318.15	4.09	343.15	5.18
298.15	3.04	323.15	4.36		

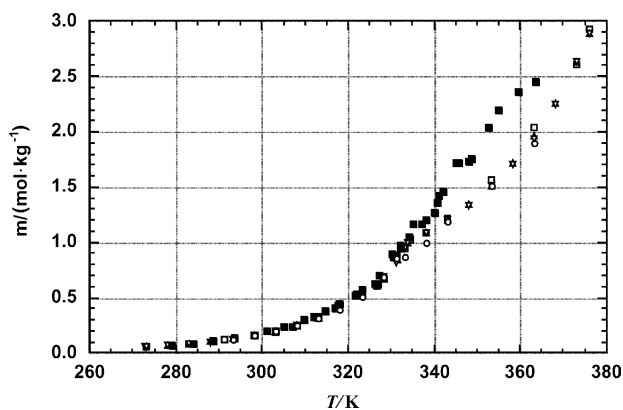


FIGURE 8. Solubility of sodium tetraborate in water m plotted against temperature T . \square , [16]; \triangle , [18]; \circ , [20]; ∇ , [21]; \blacksquare , this work.

the literature (i.e., above the “literature” pentahydrate solubility curve). Considering that the chemical analysis is not the problem (a nice agreement observed for $T < 333$ K) it is not clear why this happens. Formally, the solubilities of borax reported here as a function of temperature T can be correlated by

$$\ln(m/\text{mol} \cdot \text{kg}^{-1}) = -29.150 - 2756.1(T/\text{K})^{-1} + 6.4260 \ln(T/\text{K}),$$

$$R^2 = 0.9915. \quad (14)$$

Solubilities of sodium carbonate in water are presented in table 6 and in figure 9. As can be seen, two distinct branches of solubility for decahydrate and monohydrate are observed [17,19,25,27–29] (transition from decahydrate to heptahydrate occurs near $T = 305$ K and finally to monohydrate near $T = 306$ to 308 K [19,52]). There

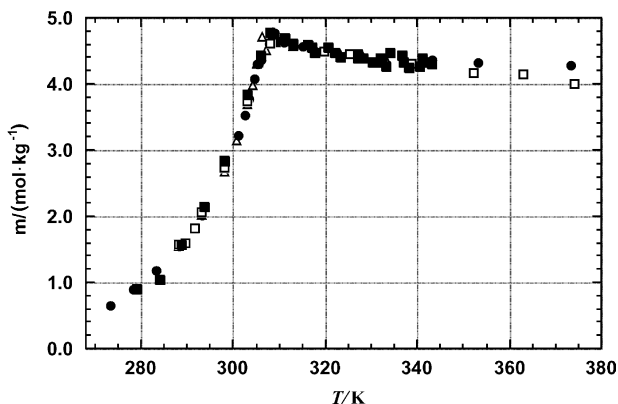


FIGURE 9. Solubility of sodium carbonate in water m plotted against temperature T . \triangle , [25]; \bullet , [27]; \square , [28]; \blacksquare , this work.

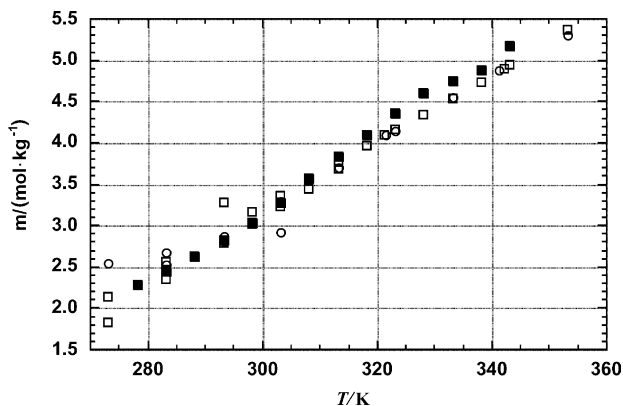


FIGURE 10. Solubility of magnesium sulfate in water m plotted against temperature T . □, [19]; ○, [25]; ■, this work.

is a satisfactory agreement between our results and those coming from other investigations (figure 9). Since solubility of sodium carbonate decahydrate increases and monohydrate decreases as temperature increases, two equations are needed to express the determined solubilities

$$\ln(m/\text{mol} \cdot \text{kg}^{-1}) = -71.006 - 1032.8(T/\text{K})^{-1} + 13.248 \ln(T/\text{K}), \quad T < 309\text{K},$$

$$R^2 = 0.9932, \quad (15)$$

and

$$\ln(m/\text{mol} \cdot \text{kg}^{-1}) = 0.70826 + 255.32(T/\text{K})^{-1}, \quad T > 309, \quad R^2 = 0.9120, \quad (16)$$

In the temperature interval investigated, magnesium sulfate in the solid phase exists in a number crystal forms but the stable hydrates are magnesium sulfate heptahydrate, hexahydrate (transition temperature is near $T = 321$ K) and above $T = 342$ K, monohydrate (kieserite) [19,52,53]. However, as can be observed in figure 10, where are plotted solubilities in the (magnesium sulfate + water) system, the formation of different hydrates has no visible effect on the solubility curve. Our measurements (table 6) can be correlated by the following equation:

$$\ln(m/\text{mol} \cdot \text{kg}^{-1}) = 39.172 - 2795.9(T/\text{K})^{-1} - 5.0309 \ln(T/\text{K}),$$

$$R^2 = 0.9965, \quad (17)$$

All results from various investigations follow the common curve, but the scatter of experimental solubilities is relatively large (figure 10).

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