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Thermodynamics of “Scale” Mineral Solubilities. 2. $SrSO_4$(s) in Aqueous NaCl

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$SrSO_4$ solubilities in water and aqueous NaCl are reviewed. The coefficients required to calculate $\Delta C_p{}^\circ$, ΔH°, ΔG°, ΔS°, and K_{sp} for the solubility equilibrium as a function of temperature are given. These thermodynamic quantities are calculated and compared with the available literature values. Activity coefficients are calculated with a modified Pitzer formalism. A computer program is used to predict $SrSO_4$(s) solubilities in NaCl solutions up to 125 °C.

Introduction

In our first paper on “scale” minerals, we reviewed and correlated $BaSO_4$(s) solubilities in aqueous NaCl up to 4.0 *m* and at temperatures up to 300 °C (*1*). In this article we discuss $SrSO_4$(s) solubilities.

$SrSO_4$ “scale” formation has become a growing concern in oil production systems. The appearance of Sr in oil field “scales” has been primarily in the presence of $BaSO_4$ “scale” (*2*), but almost pure $SrSO_4$ “scales” have been observed in several production fields around the world. This “scale” formation is primarily a result of subsurface commingling of waters, which results in a water supersaturated with $SrSO_4$ (*3*). Gates and Caraway (*4*) analyzed California oil-well “scales” and found in a $BaSO_4$-type “scale” a significant amount of strontium along with iron, calcium, magnesium, and some carbonates.

Literature

Gallo (*5*) studied the solubility in water at different temperatures and observed a maximum at 40 °C. Muller (*6*) measured the solubility in water, NaCl solutions, and KCl solutions at 25 °C. Lieser (*7*) measured the solubility in water and Na_2SO_4 solutions at 25 °C.

The earliest systematic solubility measurements above 100 °C were made by Booth and Bidwell (*8*). There is a great deal of scatter in their data, and an anomalous solubility maximum just below the critical temperature of water was reported. The solubility of $SrSO_4$ and the effect of various anions on the solubility were reported by Lambert and Hume-Rothery (*9*) and Campbell and Cook (*10*). Enusun and Turkevich (*11*) reported the solubility in water at 25 °C. Dryssen, Ivanova, and Aren (*12*) studied the effectiveness of a Barnstead column for measuring the solubility of calcium, strontium, and lead sulfates at different sulfate concentrations, but only at a constant ionic strength of 0.2 *m* at 25 °C. Lucchesi and Whitney (*13*) determined the solubility in aqueous NaCl, Na_2SO_4, HCl, and H_2SO_4 by a radiotracer method at 0 and 25 °C. Brower and Renault (*14*) measured the enthalpy of mixing for (Ba,Sr)SO_4 solid solutions by calorimetry as approximately zero at 25 and 61 °C. Solubility was measured at various concentrations of Na^+, K^+, $NH_4{}^+$, Ca^{2+} and Mg^{2+} chlorides, NH_4NO_3, and in Na^+, Ca^{2+}, and Mg^{2+} sulfates. They observed that $SrSO_4$ leaches selectively from the solid solution at 25 °C.

Davies and Collins (*15*) reported the solubility at 25 °C in aqueous NaCl, KCl, $CaCl_2$, $MgCl_2$, KBr, $NaHCO_3$, and $Na_2B_4O_7$ and in three synthetic brines. They found that plots of $SrSO_4$ solubility as a function of ionic strength reached a maximum near $I = 1.0$ *m*. Strubel (*16*) studied the solubility of celestite obtained from different countries and synthetic $SrSO_4$ in water and 0.1, 0.5, 1.0, and 2.0 *m* NaCl concentrations from 20 to 100 °C and in 2 *m* NaCl at 200-600 °C. A sharp increase in solubility was observed at >400 °C. North (*17*) and MacDonald and North (*18*) reported the solubility in 0.65 M NaCl at 2, 22, and 35 °C and in seawater at 2 °C and pressures up to 1000 atm. The observed solubility in distilled water did not appear to be greatly influenced by temperature, but they noticed that there was considerable deviation from theoretical solubility and proposed a $SrSO_4 \cdot 3H_2O$ solid phase present at 2 and 22 °C for pressures greater than 500 atm. This does not have support from the alkaline earth sulfate literature. Jacques, Gollerg, and Whiteside (*19*) reported the solubility in NaCl, $CaCl_2$, and brine mixtures at 25, 40, 71.1, and 100 °C. A solubility maximum near an ionic strength of 2.5 *m* was observed. Fletcher, French, and Collins (*20*) determined the concentration product at 50, 75, 122, and 156 °F in 0.1-5.25 *m* NaCl solutions. The concentration solubility product was expressed as a function of ionic strength at each temperature. Solubility was predicted in NaCl and $CaCl_2$ solutions by using these equations. Culberson, Latham, and Bates (*21*) measured the solubility in synthetic seawater and in 0.7 *m* NaCl and found that the solubility predicted by using the Pitzer equations (*22*) was 18% lower than the experimental results for $SrSO_4$ and 25% lower for gypsum. Rogers (*23*) has applied the Pitzer formalism (*22*) in computing the solubilities of gypsum, $SrSO_4$, and $BaSO_4$ in saline waters at 25 °C. Recently, Vetter and co-workers (*31*) measured the solubilities in NaCl (0-25 wt %), $CaCl_2$ (0-4 wt %), $MgCl_2$ (0-4 wt %), and their mixtures at 25, 75, 95, and 125 °C. Their data at 25 °C up to 2.56 *m* NaCl are up to 5% higher than Jacques et al.'s (*19*) data, but the values are up to 26% lower at higher NaCl concentrations. At all other temperatures, their data is up to 33% lower than other (*16*, *19*) data. Schulien (*25*) reported the solubility data on $BaSO_4$ and $SrSO_4$ at 80, 100, and 120 °C up to a pressure of 6000 psi in 0.1-2.0 *m* NaCl solutions. Reardon and Armstrong (*26*) studied the solubility in water, seawater, and up to 5 *m* NaCl solutions. Their study in NaCl solutions was restricted to lower temperatures, from 10 to 40 °C. Most recently, Butt and co-workers (*27*) studied the solubility of $SrSO_4$ in NaCl, formation and injection brines, and synthetic brines up to 3.2 *m* ionic strength at 25, 50, and 75 °C. Their data is in good agreement with others at 25 °C but is 10% lower at 50 and 75 °C. In summary, lack of reliable $SrSO_4$ solubility data in aqueous NaCl solutions above 100 °C forced us to limit this study to temperatures below that.

Calculational Approach

The solubility equilibrium for $SrSO_4$(s) is

$$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4{}^{2-}(aq)$$

The thermodynamic solubility product is given by

$$K_{sp} = a_{Sr^{2+}(aq)} a_{SO_4{}^{2-}(aq)} \quad (1)$$

and for pure $SrSO_4$ dissolving

$$K_{sp} = s^2 \gamma_\pm{}^2 \quad (2)$$

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Table I. Coefficients To Calculate Thermodynamic Quantities for the Species and Equilibrium Using the Equations

$$C_p = A + BT + C/T^2$$

$$\Delta H^\circ = AT + BT^2/2 - C/T + I_h$$

$$\Delta S^\circ = A \ln T + BT - C/2T^2 + I_s$$

$$-\Delta G^\circ = AT \ln T + BT^2/2 + C/2T - I_h - I_g T$$

species	A	B	$10^{-6}C$	I_h	I_g	I_s
SO_4^{2-} (aq)	818.323	−1.845 81	−49.7126	−1 237 946	5762.58	−4371.65
Sr^{2+}(aq)	−85.584	0.0	6.9521	−496 569	−656.85	494.13
$SrSO_4$(s)	91.199	0.055 65	0.0	−1 482 767	1003.49	−419.19
equilib	641.541	−1.901 46	−42.7605	−251 748	4102.24	−3458.33

Table II. Thermodynamic Quantities at Different Temperatures for the Species

T/°C	ΔH°/kJ mol^{-1}	ΔG°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	C_p°/J K^{-1} mol^{-1}
		SO_4^{2-}(aq)		
0.0	−901.28	−758.02	48.1	−352.2
25.0	−909.27	−744.54	20.1	−291.2
50.0	−916.04	−730.45	−1.7	−254.2
75.0	−922.12	−715.86	−19.9	−234.4
100.0	−927.87	−700.84	−35.8	−227.5
125.0	−933.57	−685.44	−50.6	−230.2
150.0	−939.44	−669.68	−64.9	−240.4
175.0	−945.64	−653.57	−79.1	−256.4
200.0	−952.30	−637.10	−93.6	−277.1
225.0	−959.53	−620.26	−108.5	−301.5
250.0	−967.40	−603.04	−123.9	−329.0
275.0	−975.99	−585.43	−139.9	−358.9
300.0	−985.36	−567.41	−156.6	−390.9
		Sr^{2+}(aq)		
0.0	−545.40	−557.57	−32.6	7.6
25.0	−545.40	−558.68	−32.6	−7.4
50.0	−545.74	−559.78	−33.7	−19.0
75.0	−546.33	−560.85	−35.4	−28.2
100.0	−547.14	−561.87	−37.7	−35.7
125.0	−548.11	−562.82	−40.2	−41.7
150.0	−549.21	−563.71	−42.9	−46.8
175.0	−550.44	−564.53	−45.7	−51.0
200.0	−551.76	−565.28	−48.5	−54.5
225.0	−553.16	−565.96	−51.4	−57.6
250.0	−554.63	−566.57	−54.3	−60.2
275.0	−556.16	−567.10	−57.2	−62.4
300.0	−557.75	−567.57	−60.0	−64.4
		$SrSO_4$(s)		
0.0	−1455.78	−1350.49	107.6	106.4
25.0	−1453.10	−1340.97	117.0	107.8
50.0	−1450.39	−1331.68	125.8	109.2
75.0	−1447.64	−1322.60	133.9	110.6
100.0	−1444.86	−1313.72	141.7	112.0
125.0	−1442.05	−1305.03	149.0	113.4
150.0	−1439.19	−1296.51	155.9	114.7
175.0	−1436.31	−1288.16	162.5	116.1
200.0	−1433.39	−1279.98	168.9	117.5
225.0	−1430.43	−1271.95	175.0	118.9
250.0	−1427.44	−1264.07	180.8	120.3
275.0	−1424.42	−1256.33	186.5	121.7
300.0	−1421.36	−1248.74	191.9	123.1

where s is the solubility in moles per kilogram of H_2O and $\gamma_\pm$ is the mean activity coefficient. s is an experimental value, and $\gamma_\pm$ is a calculated value depending on the model chosen for it in computing the K_{sp} values. Therefore, the literature K_{sp} values are not independent of the assumptions made about $\gamma_\pm$. We have chosen to use the most consistent literature s data as our basic working tool. We then develop expressions for ΔH°, ΔG°, ΔS°, and K_{sp} from fundamental thermodynamic data. Using the critically evaluated s data, expressions for activity coefficients are derived within the context of the Pitzer formalism (*22*). Finally, K_{sp} and $\gamma_\pm$ expressions are "fine-tuned" to reproduce the best experimental data as closely as possible.

Details of the calculational approach and the equations for C_p°, ΔH°, ΔG°, and ΔS° and $\ln K_{sp}$ for $SrSO_4$ system are the same as those used for $BaSO_4$ (*1*). Here we give only the $\ln K_{sp}$ equation as

$$\ln K_{sp} = A \ln T/R + BT/2R + C/2RT^2 - I_h/RT - I_g/R \tag{3}$$

The coefficients for different species and for the equilibrium are given in Table I. The C_p°, ΔH°, ΔG°, and ΔS° values at different temperatures for Sr^{2+}, SO_4^{2-}, and $SrSO_4$(s) are given in Table II. These thermodynamic quantities and K_{sp} for the equilibrium are reported in Table III along with the Khodakovskiy (*28*) data for comparison. They computed the coefficients for C_p°, ΔH°, ΔG°, and ΔS° and $\log K_{sp}$ from the available solubility constants. According to them, ΔC_p° was expressed with a single coefficient, c', as $-2c'T$. This is not sufficient to accurately represent the thermodynamic quantities and causes the large differences between their values and ours, as shown in Table III. The $\log K_{sp}$ values are plotted as a function of temperature in Figure 1. The Khodakovskiy values are higher from the lowest temperature, and the difference increases continuously with temperature. The K_{sp} values reported at 0 °C by North and at 25 °C by Culberson (*21*) and Rogers (*23*) are also shown for comparison. Our predicted values pass through a maximum around 30 °C whereas the Khodakovskiy values decrease continuously from 0 to 300 °C.

The treatment for the calculation of the mean activity coefficient of $SrSO_4$ is the same as that for $BaSO_4$, which we described in our earlier paper (*1*). Hence, only the final equation is given here:

$$\ln \gamma_\pm = 4f^\gamma + m_M(2B_{MS} + 2EC_{MS}) + m_N(B_{MC} + B_{NS} + E(C_{MC} + C_{NS})) + m_M^2(4B'_{MS} + 2C_{MS}) + m_M m_N(4B'_{MC} + 4B'_{NS} + 2C_{MC} + 2C_{NS}) + m_N^2(4B'_{NC} + 2C_{NC}) + m_N({}^E\theta_{MN} + {}^E\theta_{SC}) + 4m_M m_N(\theta'_{MN} + \theta'_{SC}) + m_N({}^S\theta_{MN} + {}^S\theta_{SC}) + m_M m_N(\psi_{MNS} + \psi_{MSC}) + m_N^2/2(\psi_{MNC} + \psi_{NSC}) \tag{4}$$

where the subscripts M, N, S, and C refer to Sr^{2+}, Na^+, SO_4^{2-}, and Cl^- ions, respectively, and all other terms have their usual significance. The Pitzer coefficients $\beta^{(0)}$, $\beta^{(1)}$, and $\beta^{(2)}$ for $SrSO_4$ at temperatures other than 25 °C can be calculated by using the equation

$$\beta^{(i)} = a + b(T - T_r) + c(T^2 - T_r^2) \tag{5}$$

by setting $a = \beta^{(i)}$ value of $CaSO_4$ at 25 °C and where b and c are the parameters reported for $MgSO_4$ by Holmes and Mesmer (*29*). The coefficient sources for the parameters are given in Table IV. The coefficients for $SrSO_4$ and $SrCl_2$ are given in Table V. γ_{cal} is given by the equation

$$\ln \gamma_{cal} = \ln \gamma_\pm^* + m_M((B_1 + B_2 I^{1/2} + B_3 I) + (B_4 + B_5 I^{1/2} + B_6 I)T + (B_7 + B_8 I^{1/2} + B_9 I)T^2 + (B_{10} + B_{11} I^{1/2} + B_{12} I)T^3) \tag{6}$$

Table III. Thermodynamic Quantities and the Solubility Product at Different Temperatures

	$\Delta C_p°$/J K^{-1} mol^{-1}		$\Delta H°$/kJ mol^{-1}		$\Delta G°$/kJ mol^{-1}		$\Delta S°$/J K^{-1} mol^{-1}		$-\log K_{sp}$		
T/°C	this work	ref *28*	this work	ref *28*	this work	ref *28*	this work	ref *28*	this work	ref *28*	Strubel
0	−451.0		9.10		34.90		−92.1		6.675	6.384	6.759
25	−406.4	−147.3	−1.57	−2.44	37.75	36.52	−129.5	−130.7	6.613	6.394	6.633
50	−382.4	−159.6	−11.39	−6.27	41.45	39.94	−161.1	−143.0	6.700	6.452	6.667
75	−373.2	−172.0	−20.81	−10.42	45.89	43.67	−189.2	−155.4	6.886	6.548	6.815
100	−375.1	−184.3	−30.14	−14.87	51.01	47.71	−215.1	−167.7	7.141	6.674	7.047
123	−385.3	−196.6	−39.63	−19.63	56.76	52.05	−239.7	−180.0	7.446	6.825	7.339
150	−401.9	−209.0	−49.46	−24.70	63.11	56.71	−263.7	−192.4	7.791	6.997	7.677
175	−423.5	−221.3	−59.77	−30.08	70.06	61.68	−287.3	−204.8	8.166	7.185	8.048
200	−449.1	−233.7	−70.67	−35.77	77.60	66.95	−311.0	−217.1	8.566	7.387	8.443
225	−478.0	−246.1	−82.25	−41.77	85.73	72.53	−334.8	−229.5	8.989	7.602	8.856
250	−509.4	−258.4	−94.59	−48.07	94.46	78.42	−359.0	−241.8	9.431	7.826	9.280
275	−543.1	−270.7	−107.74	−54.69	103.80	84.62	−383.5	−254.1	9.891	8.060	9.713
300	−578.4	−283.1	−121.76	−61.61	113.76	91.13	−408.5	−266.5	10.368	8.302	10.150

Table IV. Sources for Pitzer Coefficients

system	at 25 °C	ref	at other temp	ref
Sr–SO_4	$CaSO_4$ model	*23*	$MgSO_4$ model	*29*
Sr–Cl	$SrCl_2$ actual	*23*	$CaCl_2$ model	*30*
Na–SO_4	Na_2SO_4 actual	*31*	Na_2SO_4 actual	*31*
Na–Cl	NaCl actual	*32*	NaCl actual	*32*

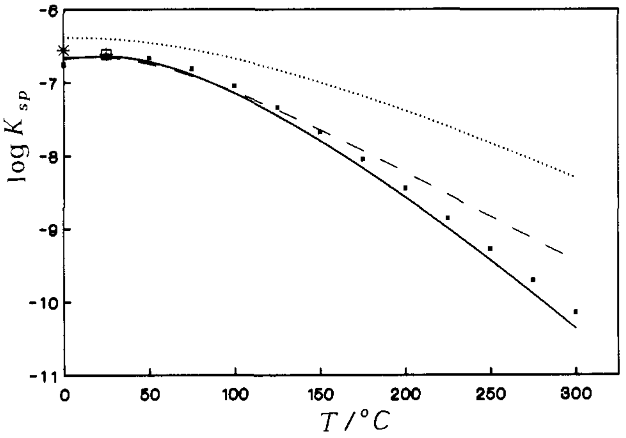

Figure 1. log K_{sp} vs T/°C: — this work; ···, Khodakovskiy et al.; ■, Strubel; – –, Reardon and Armstrong; +, Rogers; •, North; □, Culberson et al.

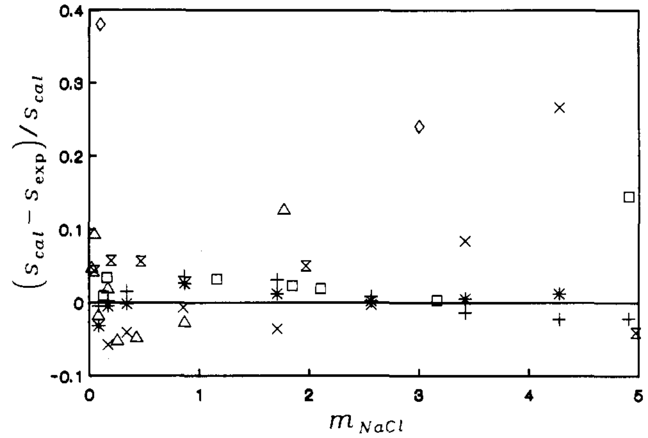

Figure 2. Relative deviation, $[(s_{cal} - s_{exp})/s_{cal}]$, vs molality of NaCl at 25 °C: +, Pitzer formalism; •, Jacques et al.; □, Butt et al.; ×, Vetter et al.; ◇, Lucchesi and Whitney; △, Davies and Collins; ⧖, Reardon and Armstrong.

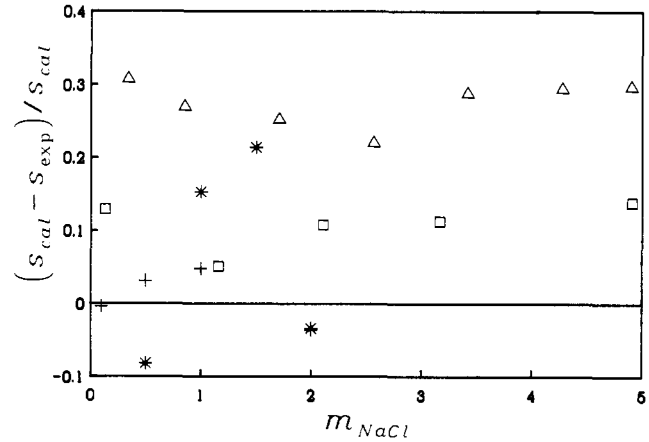

Figure 3. Relative deviation, $[(s_{cal} - s_{exp})/s_{cal}]$, vs molality of NaCl at 75 °C: □, Butt et al.; △, Vetter et al.; •, Schulien at 80 °C; +, Strubel at 70 °C.

where $\gamma_\pm{}^*$ is calculated from eq 4 without the $^S\theta$ and ψ parameters, which we believe are dependent on ionic strength. The coefficients are given in Table VI, which may not have any real physical significance except that they reproduce the literature values. Until we get the actual Pitzer parameters for $SrSO_4$ and $SrCl_2$ as a function of temperature and $^S\theta$ and ψ probably as a function of ionic strength also, eq 6 is just an alternative. The sequence of analysis and the flow chart of the program are same as that for $BaSO_4$ (*1*).

Solubility Check

The plots of $SrSO_4$ solubility against concentration of NaCl at 25 °C are shown in Figure 2. Our predicted values are in excellent agreement with the data of Jacques (*3*). Even at higher concentrations of NaCl, the maximum percentage difference is only 3.2. Rogers' values (*23*), predicted by using Pitzer's equation and K_{sp} = 2.43 × 10^{-7}, are also in good

Table V. Coefficients for $SrSO_4$ and $SrCl_2$ in the Equation for β's or C^ϕ as a Function of Temperature

$$\beta^{(i)} \text{ or } C^\phi = a + b(T - T_r) + (T^2 - T_r^2) + d(1/T - 1/T_r) + e \ln (T/T_r)$$

salt	function	a	b	c	d	e
$SrSO_4$	$\beta^{(0)}$	0.20000	0.002916	-3.872×10^{-6}	0	0
	$\beta^{(1)}$	3.1973	0.00124	1.809×10^{-5}	0	0
	$\beta^{(2)}$	−54.24	0.8283	−0.001782	0	0
$SrCl_2$	$\beta^{(0)}$	0.2918	−0.1390	6.826×10^{-5}	5108.0	46.48
	$\beta^{(1)})$	1.5603	−0.01647	2.346×10^{-5}	498.24	0.0
	C^ϕ	−0.00446	0.2462	-1.184×10^{-4}	−9676.3	−84.83

Table VI. Coefficients in Eq 6

$B_1 = 5.85120 \times 10^4$
$B_2 = -5.04085 \times 10^4$
$B_3 = 1.05712 \times 10^4$
$B_4 = -5.43328 \times 10^2$
$B_5 = 4.72342 \times 10^2$
$B_6 = -1.00413 \times 10^2$
$B_7 = 1.67755$
$B_8 = -1.47354$
$B_9 = 0.318368$
$B_{10} = -1.72155 \times 10^{-3}$
$B_{11} = 1.52942 \times 10^{-3}$
$B_{12} = -3.35874 \times 10^{-4}$

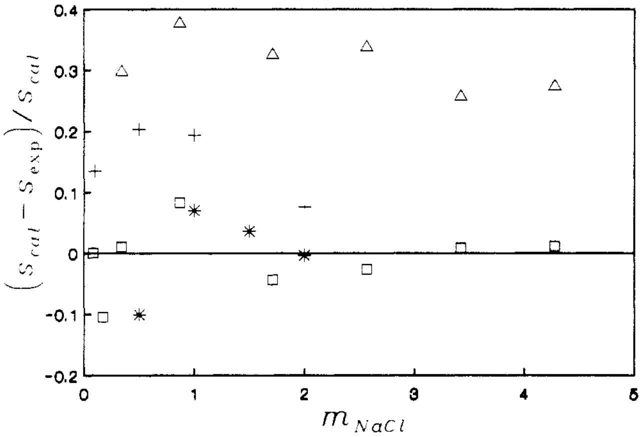

Figure 4. Relative deviation, $[(s_{cal} - s_{exp})/s_{cal}]$, vs molality of NaCl at 100 °C: □, Jacques et al.; △, Vetter et al. at 95 °C; *, Schulien; +, Strubel.

agreement with Jacques' data with a maximum percent difference of 3.6. Our values are in good agreement with the Davies and Collins (*15*) data up to 1.0 *m* NaCl, with a difference of 5.2%, but with a difference of 12.7% at 1.77 *m* NaCl. Rogers' values at low concentrations of NaCl have a 10.2% difference with the experimental values. Our values are 5.5% higher than Culberson's (*21*) data at 0.7 *m* NaCl; 38.0 and 24.0% lower at 0.1 and 3.0 *m* NaCl, respectively, from Lucchesi and Whitney's (*13*) values; and 14–32%, higher than Brower and Renault's (*14*) values over the NaCl concentration of 0.025–1.0 *m*. Vetter's (*24*) values deviate up to 27% at higher NaCl concentrations. Our predicted values are in excellent agreement with the Reardon and Armstrong (*26*) data, within ±5.7%.

The predicted values at other temperatures up to 100 °C are also in good agreement with Jacques' (*19*) data, Strubel's (*16*) data, and the Reardon and Armstrong (*26*) data, but are 22–70% higher from 75 to 125 °C than the Vetter (*24*) data. Our predicted values are 13% lower to 21% higher with the Schulien (*25*) data at 80–120 °C and 10–14% higher at 50 and 75 °C with the Butt (*27*) data. The average difference from the Jacques (*19*) data is 2.8% in 0.08–2.28 *m* NaCl over the temperature range 25–100 °C (32 points); for Strubel's data from 20 to 100 °C up to 2 *m* NaCl (36 points) the average difference is 5.4%; for Reardon and Armstrong data from 10 to 40 °C up to 5 *m* NaCl (25 points) the average difference is 4.2%.

Jacques's solubility data against temperature at a given NaCl concentration up to 0.87 *m* reaches a maximum around 30 °C; above this concentration of NaCl up to 2.56 *m*, solubility decreases continuously whereas at higher NaCl concentrations, a solubility minimum around 70 °C was observed. As we cannot get reliable extrapolated data at higher temperatures and do not have good experimental data, we restrict our prediction up to 100 °C at this time.

This program is effective up to 100 °C and from 0.05 to 5.0 *m* NaCl. Due to the lack of good data at higher temperatures, we could not get consistent values for the coefficients (B_1, B_2, etc.) to predict the solubility above 100 °C. The pure Pitzer formalism can be used to predict the $SrSO_4$ solubilities in NaCl solutions at 25 °C only, as θ and ψ values are not available at higher temperatures.

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