Solubility of gypsum in MSO4 solutions (M = Mg, Mn, Co, Ni, Cu, Zn) at 298.15 K and 313.15 K

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Solid–liquid phase equilibria in the systems K_2SO_4–MSO_4–H_2O (M = Co, Ni, Cu) from ambient to enhanced temperatures

Georgia Wollmann, Wolfgang Voigt[*]

Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, 09599 Freiberg, Sachsen, Germany

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ABSTRACT

Reviewing the literature solubility isotherms in the ternary systems K_2SO_4–MSO_4–H_2O (M = Co, Ni, Cu, Zn) revealed a lack at ambient temperatures. The solid–liquid phase equilibria have been determined in the systems K_2SO_4–MSO_4–H_2O (M = Co, Ni, Cu) at T = 313 K. With increasing bivalent metal sulfate concentration, the solubility of potassium sulfate rises until the two-salt point is reached. Reciprocally, the solubility of the bivalent metal sulfate hydrates ($CoSO_4 \cdot 7H_2O$, α-$NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$) increases with rising potassium sulfate concentration. In all three systems the double salts of Tutton's type $K_2SO_4 \cdot MSO_4 \cdot 6H_2O$ (M = Co, Ni, Cu) are formed.

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1. Introduction

Polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, a triple salt relatively common in rock salt formations is considered being a natural bivalent heavy metal sink. This assumption is supported by the possibility to substitute magnesium by different bivalent metal ions, such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} [1]. Phase equilibrium studies to verify this assumption require investigations of the respective quaternary systems, which are complex and very time-consuming due to the extreme slow formation kinetics of polyhalite at 298 K. Therefore, our strategy is to perform the investigations at slightly enhanced temperature of 313 K and to combine the experimental results with a thermodynamic model like Pitzer's equations. Parametrization of thermodynamic models describing solid–liquid equilibria in these systems requires a large body of reliable data from binary and ternary systems.

Reviewing the literature for solubility data disclosed limited data of the ternary systems K_2SO_4–MSO_4–H_2O and $CaSO_4$–MSO_4–H_2O (M = Co, Ni, Cu) at ambient temperatures. The solubility of gypsum ($CaSO_4 \cdot 2H_2O$) in MSO_4 solutions (M = Mg, Mn, Co, Ni, Cu, Zn) were determined by us recently at 298 and 313 K [2].

The three title systems are examined sufficiently at 298 K [3–8]. At higher temperatures, investigations of the systems K_2SO_4–MSO_4–H_2O (M = Co, Ni) are performed mainly by Benrath et

al. [9,10], though he did not provide information about the experimental procedure. Further data on these systems determined at ambient temperatures regard mostly two-salt points [11–17]. Studies of the system K_2SO_4–$CuSO_4$–H_2O were accomplished by Caven and Mitchell [7] for temperatures above 298 K. However, they give only three data points per temperature.

In order to improve the data situation at ambient temperatures we performed solid–liquid equilibrium study of the systems K_2SO_4–MSO_4–H_2O (M = Co, Ni, Cu) at 313 K.

2. Experimental

2.1. Equilibration and phase separation

All salts employed in the study (K_2SO_4 p.a. Reachim; $CoSO_4 \cdot 7H_2O$ p.a. ABCR, $NiSO_4 \cdot 6H_2O$ p.a. Merck; $CuSO_4 \cdot 5H_2O$ p.a. Fluka) were analyzed by powder X-ray diffraction and the water content determined by thermal analyses.

For the determination of the solid–liquid equilibria, different amounts of potassium sulfate, bivalent metal sulfate and deionized water (Seralpur Pro 90 CN) were weighed into waterproof and tightly sealed glass bottles (50 mL) assuring a liquid level of at least three-quarters of the bottle. In the case of the copper containing system, around 0.5 g of 65% HNO_3 (p.a. Fluka) was weighed additionally into the bottles to prevent the formation of basic double salts. The samples were then placed in a water bath thermostat (type ED, Julabo Labortechnik GmbH with a stirring drive of 15, H + P Labortechnik AG) at 313 K, so that they were covered by water. If the salts were solubilized completely after 24 h, potassium sul-

* Corresponding author. Tel.: +49 3731 394338; fax: +49 3731 394058.
  E-mail address: Wolfgang.Voigt@chemie.tu-freiberg.de (W. Voigt).

Table 1
Molal solubility m in the system K_2SO_4–$CoSO_4$–H_2O $T = 313$ K, δs is the uncertainty of the cation analysis.

m (mol kg^{-1})									
K_2SO_4	$10^3\ \delta s$	$CoSO_4$	$10^3\ \delta s$	Solid phase[a]	K_2SO_4	$10^3\ \delta s$	$CoSO_4$	$10^3\ \delta s$	Solid phase[a]
0	–	2.990	32	CoS7	0.5623	7.5	1.023	7.3	DS
0.0991	1.3	3.020	30	CoS7	0.6680	8.9	0.7670	6.2	DS
0.1984	2.6	3.061	28	CoS7	0.7240	11	0.6294	4.7	DS
0.2976	4.1	3.105	31	CoS7	0.7706	8.5	0.5264	3.6	DS
0.3016	4.1	3.101	30	CoS7 + DS	0.8150	12	0.4470	3.4	DS
0.3484	4.8	2.732	29	DS	0.8607	9.5	0.4263	2.9	DS
0.3861	5.1	2.224	24	DS	0.9131	9.9	0.4000	3.1	KS + DS
0.4159	5.5	2.016	22	DS	0.8911	9.1	0.1433	1.2	KS
0.4980	6.1	1.496	15	DS	0.8621	8.4	0	–	KS
0.5193	6.0	1.283	8.3	DS					

[a] CoS7-$CoSO_4$·$7H_2O$, DS-K_2SO_4·$CoSO_4$·$6H_2O$, KS-K_2SO_4.

fate and bivalent metal sulfate were added. This was repeated until a solid occurred that did not dissolve within 24 h. While equilibrating, the samples were stirred with a Teflon-covered magnetic stirrer for varying duration. Equilibration times lasted up to 56 days but not less than 40 days after a solid appeared. The temperature uncertainty was ±0.1 K.

After equilibration the stirring was stopped, the solid phase settled down for at least 12 h and the solution became clear. The samples were placed on a platform positioned inside the thermostat in such a way, that the bottles could be opened and kept at the equilibration temperature. A frit of glass fiber membrane with 0.6 μm pore size (MN 85/70, Macherey & Nagel) was lowered into the solution and then a certain mass of clear solution was taken out for chemical analysis. Finally, the solid of each sample was separated by suction filtration, washed with 4–5 mL of ethanol and then air-dried. Identification of the solid was performed by powder X-ray diffraction.

2.2. Analytics

The concentration of potassium and nickel were determined gravimetrically as potassium tetraphenylborate and bis-[dimethylglyoximato]-nickel(II), respectively. Cobalt and copper were analyzed titrimetrically with EDTA, using Murexid as indicator. The average of double (gravimetry) and triple (titration) determinations gave the result. The errors of the gravimetrical analyzed ions, potassium and nickel, were calculated from pre-investigations of the methods with known concentrations, and resulted in a deviation of 1–1.5%. The error of the ions M^{2+} (M = Co, Cu) is based on the titration error caused by the drop size (0.03 mL) of the titration solution. The resulting errors are within 0.5–1.0% of the total amount of metal ion in the experimental solution.

The powder X-ray diffraction analysis was conducted on a D5000 (Siemens) using Cu Kα radiation in the 10–50° range 2θ

and a collection time of 1 s/0.02° step. The recorded patterns were matched against the PDF2-file of the International Centre for Diffraction Data and our own database. Thermal analyses were performed with a DTA/TG 22 (Seiko) using 10–20 mg of sample in a crucible of platinum at a heating rate of 5 K/min up to 773 K under nitrogen flow.

3. Results and discussion

The solubility data obtained are listed in Tables 1–3 and plotted in Figs. 1 and 2. The curves in the following figures are estimated solubility lines drawn by eye.

In all three systems, K_2SO_4·MSO_4·$6H_2O$, known as Tutton's salt, is the only double salt formed. The concentration range of the crystallization branch of Tutton's salt varies with the bivalent metal ion. While K_2SO_4·$NiSO_4$·$6H_2O$ forms from 0.04 molal of $NiSO_4$ to saturated nickel sulfate saturated solutions, the crystallization of K_2SO_4·$CoSO_4$·$6H_2O$ requires concentrations above 0.4 molal of $CoSO_4$.

3.1. The system K_2SO_4–$CoSO_4$–H_2O

The system K^+, Co^{2+}/$SO_4{}^{2-}$//H_2O is the one of the title systems best described in the literature. Caven and Johnston [3] and Filippov and Yakovleva [4] performed isothermal investigations at 298 K. At high concentrations of cobalt sulfate, the data sets differ slightly from each other. Some years later, Filippov and Rumyantsev [5] discussed his own experimental results of 1979 [4] again giving data points calculated with Pitzer's equation; these resemble the data of Caven and Johnston [3] more than those in his original experiments of 1979 [4].

Benrath [9] described the polytherm of the system in 1932, using his own determined two-salt points [9] and the isothermal data of Caven and Johnston [3]. During investigations of the

Table 2
Molal solubility m in the system K_2SO_4–$NiSO_4$–H_2O $T = 313$ K, δs is the uncertainty of the cation analysis.

m (mol kg^{-1})									
K_2SO_4	$10^3\ \delta s$	$NiSO_4$	$10^3\ \delta s$	Solid phase[a]	K_2SO_4	$10^3\ \delta s$	$NiSO_4$	$10^3\ \delta s$	Solid phase[a]
0	–	3.092	48	NiS6	0.3721	4.1	0.1688	1.8	DS
0.0352	0.53	3.112	47	NiS6	0.4268	4.7	0.1168	1.3	DS
0.0995	1.51	3.183	48	NiS6 + DS	0.5249	5.8	0.08338	0.92	DS
0.1068	1.6	3.174	48	DS	0.6002	6.7	0.07026	0.79	DS
0.1234	1.8	2.545	36	DS	0.7539	8.6	0.05010	0.57	DS
0.1461	2.0	2.058	27	DS	0.7901	9.1	0.04812	0.55	DS
0.1650	2.1	1.512	19	DS	0.8437	9.8	0.04492	0.52	KS + DS
0.1883	2.3	1.015	12	DS	0.8515	10	0.04630	0.53	KS + DS
0.2302	2.6	0.5870	6.7	DS	0.8341	9.6	0.02689	0.39	KS
0.2398	2.7	0.4465	5.0	DS	0.8619	9.8	0.02890	0.33	KS
0.2867	3.1	0.2724	3.0	DS	0.8621	8.4	0	–	KS

[a] NiS6-α-$NiSO_4$·$6H_2O$, DS-K_2SO_4·$NiSO_4$·$6H_2O$, KS-K_2SO_4.

Table 3
Molal solubility m in the system $K_2SO_4–CuSO_4–H_2O$ $T = 313$ K, δs is the uncertainty of the cation analysis.

m (mol kg^{-1})									
K_2SO_4	$10^3\ \delta s$	$CuSO_4$	$10^3\ \delta s$	Solid phase[a]	K_2SO_4	$10^3\ \delta s$	$CuSO_4$	$10^3\ \delta s$	Solid phase[a]
0	–	1.828	4.6	CuS5	0.5390	3.6	0.6647	1.1	DS
0.0933	0.39	1.851	4.8	CuS5	0.6188	4.4	0.4654	2.0	DS
0.1961	1.4	1.913	4.5	CuS5	0.7463	5.3	0.3097	1.1	DS
0.2059	1.6	1.845	4.3	CuS5	0.8077	6.0	0.2726	1.2	DS
0.2991	2.0	1.982	3.1	CuS5	0.8378	5.9	0.2492	1.3	DS
0.3303	2.8	1.971	3.1	CuS5 + DS	0.886	10	0.1968	1.9	KS + DS
0.3403	2.4	1.988	3.3	CuS5 + DS	0.889	10	0.1937	1.9	KS + DS
0.3538	2.3	1.832	1.2	DS	0.877	10	0.1878	1.4	KS
0.3739	2.6	1.610	1.2	DS	0.8745	9.8	0.09298	0.93	KS
0.4162	2.3	1.270	1.6	DS	0.8628	9.4	0.07411	1.7	KS
0.4611	3.1	1.016	1.6	DS	0.8621	8.4	0	–	KS

[a] CuS5-$CuSO_4 \cdot 5H_2O$, DS-$K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, KS-$K_2SO_4$.
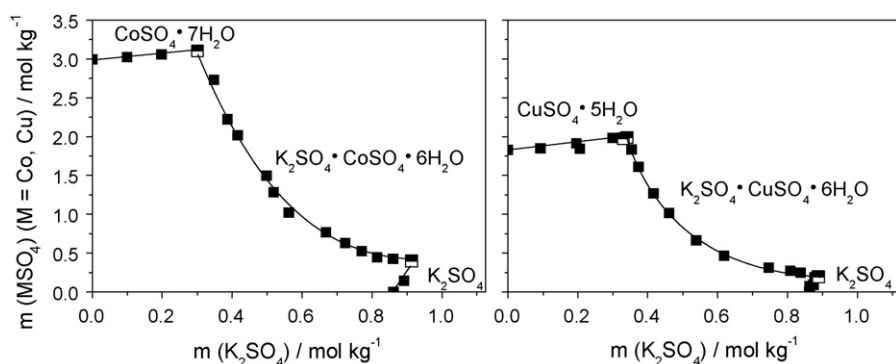
Fig. 1. Solubility diagrams of the systems $K_2SO_4–MSO_4–H_2O$ (M = Co, Cu) at 313 K; half-filled symbol, two-salt point.

reciprocal system $KCl–CoSO_4–H_2O$ seven years later [10], Benrath noticed that his earlier polytherm of 1932 [9] was incorrect, especially at higher temperatures, but without referring to a specific temperature. Thus, Benrath and Ritter [10] examined the system again, determining isothermal solubilities in the temperature range from 273 to 372 K. Unfortunately, they [10] did not give any experimental details, even though they had pointed out the importance of the equilibration times, which should extend for 3 days for solubility determinations at higher temperatures. However, the data of Benrath [9] are contradictory. At 323 K, two two-salt points of $CoSO_4 \cdot 6H_2O–K_2SO_4 \cdot CoSO_4 \cdot 6H_2O$ are given with considerably different molalities of potassium sulfate (Fig. 3). Furthermore, the more concentrated potassium sulfate two-salt
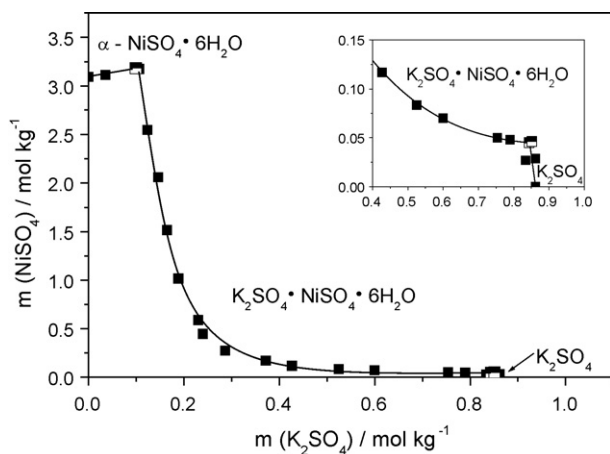
Fig. 2. Solubility diagram of the system $K_2SO_4–NiSO_4–H_2O$ at 313 K; half-filled symbol, two-salt point.
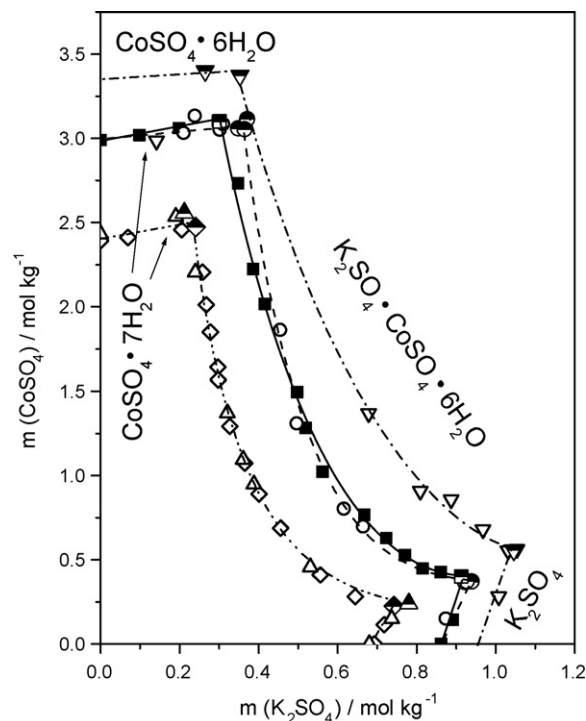
Fig. 3. Solubility diagram of the system $K_2SO_4–CoSO_4–H_2O$. (■) This study at 313 K, (○) [10] at 311 K, (◇) [4] at 298 K, (△) [3] at 298 K, (▽) [10] at 323 K; half-filled symbol.
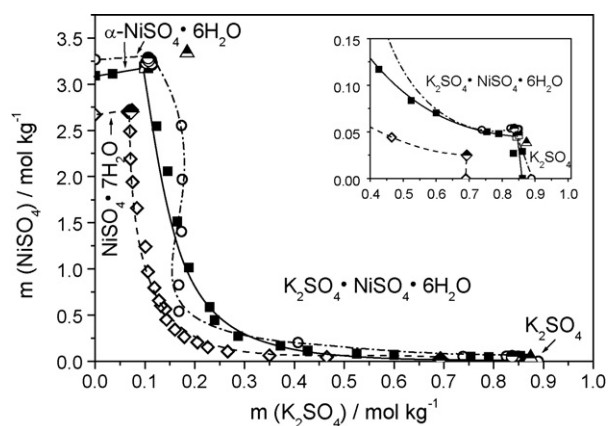
Fig. 4. Solubility diagram of the system K_2SO_4–$NiSO_4$–H_2O. (■) This study at 313 K; (△) [9] at 313 K; (◇) [5] at 298 K (two-salt points calculated with Pitzer's equation); (○) [17] at 318 K; half-filled symbol, two-salt point.

point for $CoSO_4 \cdot 6H_2O$–$K_2SO_4 \cdot CoSO_4 \cdot 6H_2O$ and the two-salt point of $CoSO_4 \cdot 7H_2O$–$K_2SO_4 \cdot CoSO_4 \cdot 6H_2O$ are both at around 0.3 molal of K_2SO_4 differing only by the concentration of cobalt sulfate.

A comparison of the data of this study with the values of Benrath and Ritter [10] determined at 311 K shows noticeable differences for highly concentrated cobalt sulfate solutions (Fig. 3). The crystallization branch of $K_2SO_4 \cdot CoSO_4 \cdot 6H_2O$ found here fits the pattern of the isotherms at 298 K and at 323 K, and thus the Benrath data at 313 K must be partly in error.

3.2. The system K_2SO_4–$NiSO_4$–H_2O

In the system K^+, $Ni^{2+}/SO_4^{2-}//H_2O$, isothermal solubility data are published for 293, 298 and 318 K [5,6,17]. Caven and Johnston [6] and Filippov and Rumyantsev [5] provided the data at 298 K. However the data points of Caven and Johnston [6] at 298 K were excluded by Benrath [9], who performed polythermal investigations in the system.

As can be seen in Fig. 4, the two-salt point of α-$NiSO_4 \cdot 6H_2O$–$K_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ of Benrath [9] given for 313 K is at a noticeably higher molality of potassium sulfate than the data point found in this study. Regrettably, Benrath [9] did not give any details on experimental procedure. However, the data of Druzhinin and Usmanova [17] determined at 318 K scatter considerably and show a very strange form for the $K_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ branch. The two-salt point of α-$NiSO_4 \cdot 6H_2O$–$K_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ was measured four times at 311 K with only slight differences in concentrations. Furthermore, the values are provided for a temperature only 5 K above the one of this study. For that reason, they should be of similar concentration. Therefore, the two-salt point of Druzhinin and Usmanova [17] seems more precise than that published by Benrath [9].

The course of the crystallization branch of K_2SO_4 fits the inclination of the isotherm at 298 and 318 K. Here, contrary to the systems with $CoSO_4$ and $CuSO_4$, the solubility of potassium sulfate decreases with increasing concentration of nickel sulfate at elevated temperatures.

3.3. The system K_2SO_4–$CuSO_4$–H_2O

Only limited data of the solubility are published for the system K^+, $Cu^{2+}/SO_4^{2-}//H_2O$. Caven and Mitchell [7] determined isothermal data at 298, 324 and 334 K, and compared them with values reported by Meerburg at 308 and 313 K. The original paper of Meerburg could not be obtained. Therefore, Meerburg's data points were
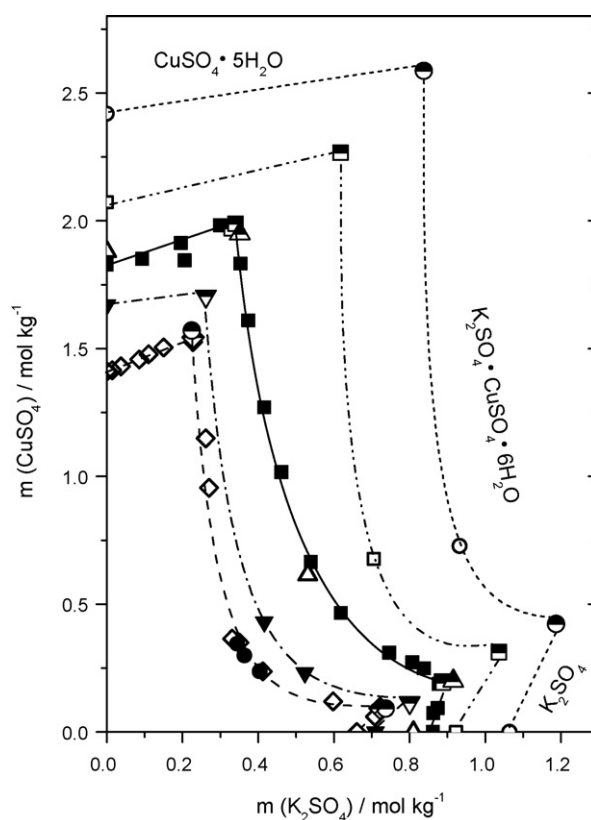

Fig. 5. Solubility diagram of the system K_2SO_4–$CuSO_4$–H_2O. (■) This study at 313; (△) Meerburg from [7] at 313 K; (◇) [7] at 298; (●) [8] at 298; (▼) Meerburg from [7] at 303 K; (□) [7] at 324; (○) [7] at 334; half-filled symbol, two-salt point.

estimated from the diagram drawn by Caven and Mitchell [7]. A comparison of the data of this study showed good agreement with the values of Meerburg at 313 K (Fig. 5).

From 298 to 313 K, the course of the $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$ branch decreases with increasing temperature. Therefore, the findings of Caven and Mitchell [7] seem odd at 324 and 334 K. From the experimental details provided, no reason for the difference can be deduced.

4. Conclusion

The solid–liquid phase equilibria in the systems K_2SO_4–MSO_4–H_2O (M = Co, Ni, Cu) were determined by isothermal saturation method at 313 K.

In the three systems potassium sulfate, the corresponding bivalent metal sulfate hydrate ($CoSO_4 \cdot 7H_2O$, α-$NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$) and the double salt $K_2SO_4 \cdot MSO_4 \cdot 6H_2O$ are formed. The Tutton's salt shows in all systems a wide stability field. In the system K_2SO_4–$NiSO_4$–H_2O the crystallization field of the double salt dominates and decreases the existence field of K_2SO_4.

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