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IAPWS Guideline Statement
Solubility of Sodium Sulfate in aqueous mixtures of sodium chloride and sulfuric acid from water to concentrated solutions, from 250 °C to 350 °C

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(This guideline is a Revision of the edition of 1990
and contains 6 numbered pages)

IAPWS GUIDELINE (CONTINUED)
(1990)

This formulation of the solubility compositions of sodium sulfate in solutions of sodium chloride and sulfuric acid from pure water to concentrated solutions has been authorized by the International Association for the Properties of Water and Steam (IAPWS) for issuance as an IAPWS guideline. In the judgement of IAPWS, the formulation represents the best available at the time of issue.

The original Guideline was based on the International Practical Temperature Scale of 1968 (IPTS-68) considered in September, 1989, Prague, Czechoslovakia and was recommended for use in the power industry with the understanding that new measurements or theoretical developments may lead to improved formulations.

This Guideline has now been reviewed by IAPWS following the adoption of the International Temperature Scale of 1990 (ITS-90).

The maximum percentage error in the solubility of sodium sulfate resulting from differences in the temperature scales ITS-90 and IPTS-68 is 0.8% at 350 $^{\circ}$C and zero molatity of both sulfuric acid and sodium chloride. For other parts of the temperature and molatity range the error is less than 0.1% and small compared with the precision of the experimental measurements and the differences between solubilities calculated from the equation presented in the Guideline and experimental values, (see Table 1). Thus, the formulation and solubilities in this Guideline are valid with ITS-90 temperatures.

The Guideline was prepared under the direction of Working Group B, "Chemical Thermodynamics in Power Cycles", under the co-chairmanship of O.I. Martynova (USSR) and Albert Bursik (FRG). The Guideline was reviewed and approved by the National Committees of the members of IAPWS (Canada, Czechoslovakia, FRG, France, Japan, UK, USA, USSR, and associate member Argentina). IAPS Guidelines and Releases can be obtained from the Executive Secretary of IAPWS.

Steam power cycles operate with demineralized water that generally contain in practice unavoidable "parts per billion" of natural impurities. Sulfate, chloride, and sodium are among the major solute impurity ions present. There may be an acidic environment (H^+/OH^- greater than unity). Temperature gradients in steam generators may concentrate impurities by many orders of magnitude through localized boiling. Sodium sulfate decreases in solubility under particular conditions of boiling concentration. Since other impurities concentrate also, knowledge of the solubility behaviour of sodium sulfate ranging from that in (pure) water to concentrated $NaCl$-H_2SO_4 solutions provides information for efficient modelling of steam-cycle conditions. With these models, steam-cycle systems may be designed to prevent or reduce precipitation of sodium sulfate in crevices. Present-day nuclear steam cycles operate in the 250 $^{\circ}$C-350 $^{\circ}$C temperature range. Since published experimental measurements covering wide ranges of solution compositions are limited for temperatures outside this range, it is recommended that use of the Guideline be restricted to this range of power plant application.

The Guideline contains an Equation for calculating the solubility of anhydrous sodium sulfate solid in (i) water and in condensed aqueous solutions of (ii) sodium chloride, of (iii) sulfuric acid, and of (iv) both sodium chloride and sulfuric acid over wide ranges of composition. The application range of temperature is from 250 $^{\circ}$C to 350 $^{\circ}$C, which encompasses the general range of operating temperatures for most subcritical steam genrators.

The Equation for the solubility of sodium sulfate in water and the above electrolyte solutions is given on page 3. The estimated uncertainties in the supporting experimental measurements, the ranges of application of the Equation and its ability in reproducing the measurements, and a reference to the supporting document where the Equation and experimental data were originally reported are given on page 4. A comparison of representative values of solubility calculated by the Equation and observed (interpolated) from the experimental data reported, referenced, and applied in the supporting document is presented in Table 1.

Recommended interpolation equation for the solubility of sodium sulfate in aqueous mixtures of sodium chloride and sulfuric acid

The available data are reproduced by the equation given below, wherein:

S = Molal Solubility of Sodium Sulfate (Na_2SO_4, anhydrous), [mol kg^{-1} (water)];
$\overline{S}$ = S/(mol kg^{-1});
m_1 = Molality of Sulfuric Acid (H_2SO_4), [mol kg^{-1} (water)];
$\overline{m}_1$ = m_1 /(mol kg^{-1});
m_2 = Molality of Sodium Chloride (NaCl, anhydrous), [mol kg^{-1} (water)];
$\overline{m}_2$ = m_2/(mol kg^{-1});
T = Absolute temperature, ITS-90*; and
$\overline{T}$ = T/K.

The recommended equation is:

$$\overline{S} = A_{00} + A_{10} \cdot \overline{m}_1 + A_{20} \cdot \overline{m}_1^{\,2} + A_{30} \cdot \overline{m}_1^{\,3} + A \cdot \overline{m}_2 + A_{02} \cdot \overline{m}_2^{\,2} + A_{03} \cdot \overline{m}_2^{\,3} + A_{11} \cdot \overline{m}_1 \cdot \overline{m}_2,$$

where the A_{ij} are the following functions of temperature:

A_{00} = $-\ 0.8085987\ \overline{T} + 81.461375 + 0.10537803\ \overline{T} \ln \overline{T}$,
A_{10} = $3.4636364\ \overline{T} - 281.63322 - 0.46779874\ \overline{T} \ln \overline{T}$,
A_{20} = $-\ 6.0029634\ \overline{T} + 480.60108 + 0.81382854\ \overline{T} \ln \overline{T}$,
A_{30} = $4.4540258\ \overline{T} - 359.36872 - 0.60306734\ \overline{T} \ln \overline{T}$,
A_{01} = $0.4909061\ \overline{T} - 46.556271 - 0.064612393\ \overline{T} \ln \overline{T}$,
A_{02} = $-\ 0.002781314\ \overline{T} + 1.722695 + 0.0000013319698\ \overline{T} \ln \overline{T}$,
A_{03} = $-\ 0.014074108\ \overline{T} + 0.99020227 + 0.0019397832\ \overline{T} \ln \overline{T}$,
A_{11} = $-\ 0.87146573\ \overline{T} + 71.808756 + 0.11749585\ \overline{T} \ln \overline{T}$.

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* See page 1 for comments on the small effect caused by the change from IPTS-68 to ITS-90.

The Equation reproduces the experimental solubilities in the temperature range 250 °C to 350 °C. The applicable ranges of solution compositions saturated by sodium sulfate are from 0 to 0.75 mol kg^{-1} sulfuric acid, from 0 to 2.25 mol kg^{-1} sodium chloride, and up to 4.5 mol kg^{-1} sodium chloride in the absence of sulfuric acid, which are the ranges of the original experimental study in the supporting document listed below.

The precision of the experimental measurements evaluated were generally within ± 1 to ± 4% as estimated by the original authors of the supporting document. The agreement of solubility values calculated by the Equation with experimental values is estimated by the original authors to be generally within ± 4% to ± 6% at temperatures between 250 °C and 275 °C, within ± 1% to ± 3% between 275 °C and 300 °C, and within ± 2% to ± 6% between 300 °C to 350 °C except for those measurements at 350 °C that are below 0.4 molal. In Table 1 representative calculated and observed (interpolated from experimental data) values are compared.

The supporting document for this Guideline is:

M H Lietzke and W L Marshall, "Sodium Sulfate Solubilities in High Temperature Aqueous Sodium Chloride and Sulfuric Acid Solutions - Predictions of Solubility, Vapor Pressure, and Speciation", Journal of Solution Chemistry, 1986, 15, 903-917. All published works contributing to the Guideline are referenced and discussed in this document.

TABLE 1 Calculated and observed molal solubilities $(\bar{S})$ of sodium sulfate in aqueous mixtures of sodium chloride and sulfuric acid

250 °C

$\bar{m}_1$	$\bar{m}_2$	$\bar{S}_{(Obs.)}$	$\bar{S}_{(Calcd.)}$
0.0	0.0	3.13	3.54
0.0	1.0	2.35	2.46
0.0	1.5	2.05	2.08
0.0	2.0	1.83	1.80
0.0	2.5	1.66	1.59
0.0	3.0	1.49	1.44
0.0	3.5	1.35	1.34
0.0	4.0	1.27	1.26
0.0	4.5	1.20	1.20
0.25	0.083	(3.20)*	3.31
0.50	0.167	(3.23)*	3.38
0.75	0.25	(3.35)*	3.37
0.25	0.25	(2.95)*	3.13
0.50	0.50	(2.95)*	3.11
0.75	0.75	(3.10)*	3.08
0.25	0.75	(2.50)*	2.68
0.50	1.50	(2.50)*	2.60
0.75	2.25	(2.80)*	2.85

275 °C

$\bar{m}_1$	$\bar{m}_2$	$\bar{S}_{(Obs.)}$	$\bar{S}_{(Calcd.)}$
0.0	0.0	2.47	2.51
0.0	1.0	1.85	1.87
0.0	1.5	1.67	1.66
0.0	2.0	1.55	1.52
0.0	2.5	1.44	1.42
0.0	3.0	1.35	1.35
0.0	3.5	1.27	1.29
0.0	4.0	1.23	1.24
0.0	4.5	1.20	1.18
0.25	0.083	2.60	2.58
0.50	0.167	--	2.83
0.75	0.25	--	3.04
0.25	0.25	2.46	2.46
0.50	0.50	2.66	2.65
0.75	0.75	2.82	2.83
0.25	0.75	2.12	2.18
0.50	1.50	--	2.31
0.75	2.25	2.62	2.62

300 °C

$\bar{m}_1$	$\bar{m}_2$	$\bar{S}_{(Obs.)}$	$\bar{S}_{(Calcd.)}$
0.0	0.0	1.67	1.61
0.0	1.0	1.36	1.33
0.0	1.5	1.28	1.26
0.0	2.0	1.25	1.23
0.0	2.5	1.22	1.22
0.0	3.0	1.20	1.22
0.0	3.5	1.18	1.21
0.0	4.0	1.18	1.19
0.0	4.5	1.17	1.15
0.25	0.083	1.95	1.87
0.50	0.167	2.26	2.28
0.75	0.25	2.72	2.66
0.25	0.25	1.86	1.82
0.50	0.50	2.14	2.18
0.75	0.75	2.48	2.54
0.25	0.75	1.68	1.68
0.50	1.50	2.06	2.02
0.75	2.25	2.44	2.42

325 °C

$\bar{m}_1$	$\bar{m}_2$	$\bar{S}_{(Obs.)}$	$\bar{S}_{(Calcd.)}$
0.0	0.0	0.67	0.81
0.0	1.0	0.89	0.84
0.0	1.5	0.90	0.88
0.0	2.0	0.95	0.93
0.0	2.5	0.99	0.99
0.0	3.0	1.03	1.04
0.0	3.5	1.07	1.09
0.0	4.0	1.10	1.11
0.0	4.5	1.13	1.11
0.033	0.0	0.84	0.85
0.066	0.0	0.90	0.89
0.102	0.0	0.97	0.94
0.334	0.0	1.47	1.37
0.675	0.0	2.27	2.12
0.25	0.083	1.10	1.20
0.50	0.167	1.70	1.73
0.75	0.25	2.20	2.25
0.25	0.25	1.15	1.19
0.50	0.50	1.61	1.71
0.75	0.75	2.18	2.23
0.25	0.75	1.18	1.19
0.50	1.50	1.77	1.73
0.75	2.25	2.27	2.26

*Values in parentheses at 250 °C are extrapolated over a 5 to 20 K range.

Table 1 (contd.)

350 °C

$\overline{m}_1$	$\overline{m}_2$	$\overline{S}_{(\mathrm{Obs.})}$	$\overline{S}_{(\mathrm{Calcd.})}$
0.0	0.0	0.16	0.13
0.0	1.0	0.41	0.39
0.0	1.5	0.53	0.51
0.0	2.0	0.63	0.63
0.0	2.5	0.73	0.74
0.0	3.0	0.82	0.83
0.0	3.5	0.91	0.92
0.0	4.0	0.99	1.00
0.0	4.5	1.07	1.06
0.047	0.0	0.27	0.18
0.077	0.0	0.31	0.22
0.122	0.0	0.39	0.29
0.394	0.0	0.93	0.87
0.788	0.0	1.89	1.84
0.25	0.083	--	0.55
0.50	0.167	1.13	1.17
0.75	0.25	1.77	1.80
0.25	0.25	--	0.59
0.50	0.50	1.18	1.24
0.75	0.75	1.88	1.89
0.25	0.75	--	0.71
0.50	1.50	1.52	1.44
0.75	2.25	2.12	2.13