| COMPONENTS: | EVALUATOR: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Water; $H_2O$; [7732-18-5] | H.D. Lutz,<br>Dept. of Chemistry,<br>University of Siegen,<br>FR Germany.<br><br>May 1983. |

CRITICAL EVALUATION:

Lead sulfite crystallizes from aqueous solutions as the anhydrous salt, $PbSO_3$. The solubility of $PbSO_3$ in water has not been thoroughly investigated. Numerical data have been given by Terres *et al.* (1), Hanus *et al.* (2), Mangan (3), Ermolaev *et al.* (4), and Rodin *et al.* (5) (precipitate identified as $PbSO_3.1/2H_2O$ (5) ? [7446-10-8]), but not under comparable experimental conditions. Thus only Hanus *et al.* (2) and Rodin *et al.* (5) reported on the solubility of lead sulfite in pure water, namely $m(PbSO_3) = 8 \times 10^{-6}$ mol $kg^{-1}$ in hot water (2) and $c(PbSO_3) = 2.5 \times 10^{-6}$ mol $dm^{-3}$ at 293 K and $1.62 \times 10^{-5}$ mol $dm^{-3}$ at 363 K, respectively (5). The data given by Terres *et al.* (1), Mangan (3), and Ermolaev *et al.* (4), which were all obtained in the presence of a third component, may be extrapolated to pure water to be $<< 2.8 \times 10^{-3}$ mol $kg^{-1}$ (molality scale), $< 3.0 \times 10^{-4}$ mol $dm^{-3}$, and $< 1.1 \times 10^{-6}$ mol $dm^{-3}$ (both molarity scale), respectively, at room temperature. The scarce information on the temperature shift of the solubility of $PbSO_3$ is contradictory. A negative temperature coefficient of the solubility is reported by Terres *et al.* (1) and a positive temperature shift by Ermolaev *et al.* (4) and Rodin *et al.* (5). Mangan (3) has found a positive temperature coefficient of solubility below 315 K and a negative one at higher temperatures.

TENTATIVE VALUES

The solubility of $PbSO_3$ in water at room temperature is approximately $1 \times 10^{-6}$ mol $dm^{-3}$ (molarity scale) ($3 \times 10^{-4}$ g/$dm^3$). The temperature coefficient of solubility is probably positive.

The solubility of lead sulfite in water is affected by the presence of a third compound. This is shown by the fragmentary experimental data on the systems $PbSO_3$-$SO_4$-$H_2O$ (1), $PbSO_3$-$NH_4CH_3CO_2$-$H_2O$ (3), and $PbSO_3$-$NaNO_3$-$H_2O$ (4). The solubility of $PbSO_3$ increases to $4 \times 10^{-2}$ mole (10 g)/kg $H_2O$ with increasing $SO_2$ content (1,6) at 298 K, to $1.3 \times 10^{-5}$ mol $dm^{-3}$ (molarity scale) ($3.8 \times 10^{-3}$ g/$dm^3$) with $NaNO_3$ concentration increasing to 400 g/$dm^3$ (4), and to $3.6 \times 10^{-4}$ mol $dm^3$ (0.10 g/$dm^3$) with pH value decreasing to 2.8 (4) and decreases with increasing concentration of ammonium acetate (3,7), all at 293.2 K. It has been further claimed that $PbSO_3$ is insoluble in aqueous alcohol (3) and soluble in solutions of sodium hydroxide (3) and that the solubility of $PbSO_3$ increases in the presence of citrate and tartrate (3).

REFERENCES

1. Terres, E.; Ruhl, G. *Angew. Chem.* 1934, *47*, 332.

2. Hanus, J.; Hovorka, V. *Chem. Listy* 1937, *31*, 489.

3. Mangan, J.L. *N. Z. J. Sci. Technol., Sect. B* 1949, *30*, 323.

4. Ermolaev, M.I.; Kudrina, L. *Tr. Voronezh. Tekhnol. Inst.* 1968, *17*, 201.

5. Rodin, I.V.; Margulis, E.V. *Zh. Neorg. Khim.* 1983, *28*, 532; **Russ. J. Inorg. Chem. (Eng. Transl.)* 1983, *28*, 298.

| COMPONENTS: | EVALUATOR: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Water; $H_2O$; [7732-18-5] | H.D. Lutz,<br>Dept. of Chemistry,<br>University of Siegen,<br>FR Germany.<br><br>May 1983. |

CRITICAL EVALUATION: (continued)

6. Rohrig, A. *J. Prakt. Chem.* 1889, *37*, 217

7. Lewis, J.B. *Ind. Eng. Chem., Anal. Ed.* 1940, *12*, 535.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Water; $H_2O$; [7732-18-5] | Hanus, J.; Hovorka, V.<br>*Chem. Listy* 1937, *31*, 489-500. |
| VARIABLES: | PREPARED BY: |
| One temperature: "hot" | H.D. Lutz |

EXPERIMENTAL VALUES:

The authors report the solubility of $PbSO_3$ in hot water to be

$$2.2 \times 10^{-3} \text{ g/dm}^3 \text{ } H_2O$$

This value is equal to (compiler)

$$m(PbSO_3) = 8.0 \times 10^{-6} \text{ mol kg}^{-1}$$

AUXILIARY INFORMATION

| METHOD APPARATUS/PROCEDURE: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| The loss of weight of lead sulfite was determined by washing with different amounts of hot water. | $PbSO_3$ was precipitated with $Na_2S_2O_5$. |
| | ESTIMATED ERROR:<br>Data given are the results of several experiments with different amounts of hot water. |
| | REFERENCES. |

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Water; $H_2O$; [7732-18-5] | Rodin, I.V.; Margulis, E.V.<br>*Zh. Neorg. Khim.* 1983, *28*, 532-3; *Russ. J. Inorg. Chem. (Eng. Transl.)* 1983, *28*, 298-9. |
| VARIABLES: | PREPARED BY: |
| Three temperatures: 293, 323 and 363 K | B. Engelen |

EXPERIMENTAL VALUES:

The solubility of $PbSO_3.0.5H_2O$ [7446-10-8] in water at various temperatures are reported. The solubility products reported are defined as $K_{so}(PbSO_3.0.5H_2O) = [Pb^{2+}]^2$.

| t/°C | Pb | $PbSO_3$ | | $10^{12}K_{so}$ |
|---|---|---|---|---|
| | $mg/dm^3$ | $mg/dm^{3a}$ | $10^5 c/mol\ dm^{-3}$ | $mol^2\ dm^{-6}$ |
| 20 | 0.52 | 0.72 | 0.25 | 6.25 |
| 50 | 1.41 | 1.95 | 0.68 | 46.2 |
| 90 | 3.35 | 4.64 | 1.62 | 262 |

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:

Saturation method. Equilibrium was established by stirring the saturated solutions in thermostatically controlled glass tubes. Equilibrium was tested for analytically - 2 hr was reported to be sufficient. Lead was determined polarographically.

SOURCE AND PURITY OF MATERIALS:

Lead sulfite was precipitated from $Pb(CH_3COO)_2$ solutions with $Na_2SO_3$.

ESTIMATED ERROR:

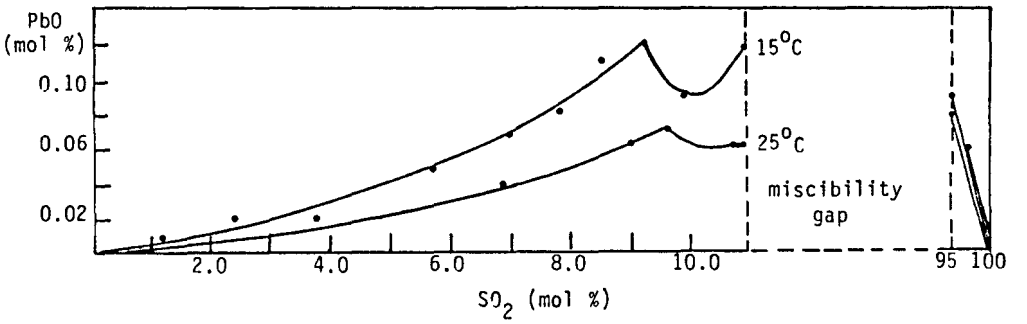
Temperature: ±0.5 K

REFERENCES:

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Sulfur dioxide; $SO_2$; [7446-09-5]<br>3. Water; $H_2O$; [7732-18-5] | 1. Terres, E.; Rühl, G.<br>*Angew. Chem.* 1934, *47*, 322-4.<br>2. Terres, E.; Rühl, G.<br>*Beitrage zur Chemie der schwefligen Saure, Beiheft zu den Zeitschriften des Vereins deutscher Chemiker No 8*, 1934. |
| VARIABLES:<br>Two temperatures: 288 and 298 K<br>Concentration of $SO_2$ | PREPARED BY:<br>H.D. Lutz, B. Engelen |

EXPERIMENTAL VALUES:

The authors report the solubility of lead sulfite in aqueous sulfurous acid solutions at 15 and 25°C. In the first paper, the experimental data are given in a graph. Numerical data are reported in the second paper.

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(continued on next page)

AUXILIARY INFORMATION

| METHOD APPARATUS/PROCEDURE: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| $SO_2$-$H_2O$ mixtures were treated together with solid $PbSO_3$ in closed glass ampoules at the stated temperatures. The solutions obtained were filtered through a fine glass frit and, after oxidation of the sulfite, analysed for sulfate and lead. | $PbSO_3$ was precipitated from a solution of lead acetate with $Na_2SO_3$. |
| | ESTIMATED ERROR: |
| | REFERENCES: |

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Sulfur dioxide; $SO_2$; [7446-09-5]<br>3. Water; $H_2O$; [7732-18-5] | 1. Terres, E.; Ruhl, G.<br>*Angew. Chem.* 1934, 47, 322-4.<br>2. Terres, E.; Ruhl, G.<br>*Beitrage zur Chemie der schwefligen Saure, Beiheft zu den Zeitschriften des Vereins deutscher Chemiker No 8*, 1934. |

EXPERIMENTAL VALUES (continued):

| Composition of saturated solutions | | | |
|---|---|---|---|
| $SO_2$ | PbO | m(PbO)[a] | Solid phase |
| mol % | mol % | $10^{-2}$ mol $kg^{-1}$ | |
| Temperature = 15°C | | | |
| 1.15 | 0.01 | 0.56 | lead sulfite |
| 2.35 | 0.02 | 1.14 | " |
| 5.71 | 0.03 | 1.77 | " |
| 7.82 | 0.08 | 4.82 | " |
| 8.50 | 0.11 | 6.68 | " |
| 9.18 | 0.12 | 7.34 | " |
| 9.80 | 0.09 | 5.54 | $Pb(HSO_3)_2$? |
| 10.92[b] | 0.12 | 7.49 | " |
| Temperature = 25°C | | | |
| 3.71 | 0.02 | 1.15 | lead sulfite |
| 6.85 | 0.04 | 2.38 | " |
| 9.14 | 0.06 | 3.67 | " |
| 9.62 | 0.07 | 4.30 | $Pb(HSO_3)_2$? |
| 10.08[b] | 0.06 | 3.71 | " |

[a] Compilers.

[b] Between 11 and 95 mol % $SO_2$ the mixtures separate into two liquid layers.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Ammonium acetate; $NH_4CH_3CO_2$; [631-61-8]<br>3. Water; $H_2O$; [7732-18-5] | Mangan, J.L.<br>*N.Z.J. Sci. Technol., Sect. B* 1949, *30*, 323-33. |
| VARIABLES:<br>Concentration of $NH_4CH_3CO_2$<br>pH: 4 - 10<br>Temperature: 273 - 329 K | PREPARED BY:<br>H.D. Lutz |

EXPERIMENTAL VALUES:

The author reports the solubility of $PbSO_3$ in aqueous solutions containing various amounts of ammonium acetate at different temperatures and pH values. The author also reports that lead sulfite is insoluble in aqueous alcohol but soluble in sodium hydroxide solutions, and that the solubility of lead sulfite is considerably increased in the presence of citrate and tartrate.

| Solubility of $PbSO_3$[a] | | | Solubility of $PbSO_3$[b] | | |
|---|---|---|---|---|---|
| $NH_4CH_3CO_2$ mol/dm$^3$ soln | $10^3c$ mol dm$^{-3}$ | g/dm$^3$ (compiler) | pH | $10^3c$ mol dm$^{-3}$ | g/dm$^3$ (compiler) |
| 0.5 | 1.80 | 0.517 | 4.8 | 1.04 | 0.299 |
| 1.0 | 1.20 | 0.345 | 5.1 | 0.86 | 0.247 |
| 1.5 | 1.40 | 0.402 | 5.6 | 0.72 | 0.207 |
| 2.0 | 1.40 | 0.402 | 5.9 | 0.56 | 0.161 |
| 3.0 | 1.40 | 0.402 | 6.1 | 0.44 | 0.126 |
| 4.0 | 1.00 | 0.287 | 7.9 | 0.36 | 0.103 |
| 5.0 | 1.60 | 0.460 | 9.0 | 0.74 | 0.213 |

[a] 20°C, pH 6, measured before adding $PbSO_3$.

[b] 20°C, non-saturating solute $NH_4CH_3CO_2$, 1 mol/dm$^3$ soln.

(continued on next page)

AUXILIARY INFORMATION

| METHOD APPARATUS/PROCEDURE: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| $PbSO_3$ was suspended in ammonium acetate solutions of the given concentration and maintained by shaking in a thermostatically controlled flask at the given temperatures for 2 - 3 hr. To prevent oxidation, 5 mass % of sucrose was added to the ammonium acetate solution. The suspended solid was allowed to settle and the saturated solution was filtered rapidly. Sulfite was determined iodometrically. The pH was measured with a glass electrode. | Lead sulfite was precipitated from a solution of lead acetate, washed thoroughly with a 5 mass % sucrose soln, and finally washed with the appropriate ammonium acetate solutions before the solubility was determined. |
| | ESTIMATED ERROR: |
| | REFERENCES. |

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8] | Mangan, J.L. |
| 2. Ammonium acetate; $NH_4CH_3CO_2$; [631-61-8] | *N.Z. J. Sci. Technol., Sect. B* 1949, *30*, 323-33. |
| 3. Water; $H_2O$; [7732-18-5] | |

EXPERIMENTAL VALUES (continued):

| | Solubility of $PbSO_3$[c] | |
|---|---|---|
| t/°C | $10^3$c / mol $dm^{-3}$ | g/$dm^3$ (compiler) |
| 0 | 1.20 | 0.345 |
| 15 | 1.35 | 0.388 |
| 42 | 1.70 | 0.488 |
| 56 | 1.40 | 0.402 |

[c] pH 6, measured before adding $PbSO_3$. Non-saturating solute - $NH_4CH_3CO_2$ 1 mol/$dm^3$ soln.

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Sodium nitrate; $NaNO_3$; [7631-99-4]<br>3. Acetate buffer; $CH_3CO_2H$-$NaCH_3CO_2$ [64-19-7]; [127-09-3]<br>4. Water; $H_2O$; [7732-18-5] | Ermolaev, M.I.; Kudrina, L.T.<br>*Tr. Voronezh. Tekhnol. Inst.* 1968, *17*, 201-3. |
| VARIABLES:<br>Temperature: 293 - 353 K<br>pH value<br>Concentration of $NaNO_3$ | PREPARED BY:<br>H.D. Lutz, B. Engelen |

EXPERIMENTAL VALUES:

The authors report the solubility in solutions of various $NaNO_3$ concentrations for various pH values and temperatures. Experimental data are given in three graphs and as some numerical figures. The solubility increases from 1.1 x $10^{-6}$ to 1.32 x $10^{-5}$ mol/dm$^3$ soln with $NaNO_3$ concentration increasing from 100 g to 400 g/dm$^3$ soln at 20°C (Fig. 1), decreases from 3.64 x $10^{-4}$ to 1.76 x $10^{-5}$ mol/dm$^3$ soln with pH value increasing from 2.8 to 7.0 at 20°C and a $NaNO_3$ concentration of 200 g/dm$^3$ soln (Fig. 2) and increases with increasing temperature; data in Fig. 3 are for pH 4.49 and a $NaNO_3$ concentration of 200 g/dm$^3$ soln.

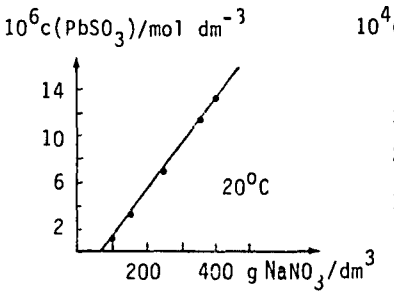


Fig. 1

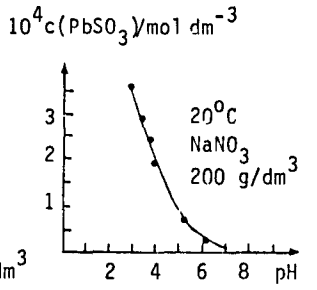


Fig. 2

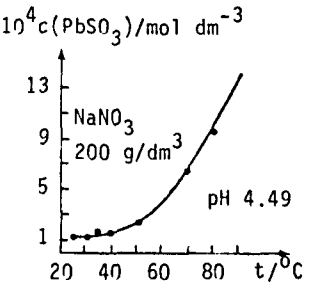


Fig. 3

(continued on next page)

AUXILIARY INFORMATION

| METHOD APPARATUS/PROCEDURE: | SOURCE AND PURITY OF MATERIALS: |
|---|---|
| Saturation method. Equilibrium was established after 8 hr. To avoid oxidation of the sulfite, 0.005% phenylenediamine was added to the solutions. Lead was determined colorimetrically. | Not given. |
| | ESTIMATED ERROR: |
| | REFERENCES: |

| COMPONENTS: | ORIGINAL MEASUREMENTS: |
|---|---|
| 1. Lead sulfite; $PbSO_3$; [7446-10-8]<br>2. Sodium nitrate; $NaNO_3$; [7631-99-4]<br>3. Acetate buffer; $CH_3CO_2H$-$NaCH_3CO_2$ [64-19-7]; [127-09-3]<br>4. Water; $H_2O$; [7732-18-5] | Ermolaev, M.I.; Kudrina, L.T.<br>*Tr. Voronezh. Tekhnol. Inst.* 1968, *17*, 201-3. |

EXPERIMENTAL VALUES (continued):

The following figures are estimated by the compilers from the graphs given by the authors.

Solubility of $PbSO_3$[a]

| t/°C | $10^4 c$ / mol dm$^{-3}$ |
|---|---|
| 25 | 1.3 |
| 30 | 1.3 |
| 35 | 1.5 |
| 40 | 1.6 |
| 50 | 2.3 |
| 60 | 3.7 |
| 70 | 6.3 |
| 80 | 9.0 |

Solubility of $PbSO_3$[b]

| pH | $10^4 c$ / mol dm$^{-3}$ |
|---|---|
| 2.8 | 3.6 |
| 3.3 | 2.9 |
| 3.7 | 2.4 |
| 4.0 | 2.0 |
| 5.0 | 0.87 |
| 5.4 | 0.63 |
| 6.2 | 0.28 |
| 7.0 | 0.18 |

Solubility of $PbSO_3$[c]

| $NaNO_3$ / g/dm$^3$ | $10^6 c$ / mol dm$^{-3}$ |
|---|---|
| 100 | 1.1 |
| 150 | 3.1 |
| 250 | 7.0 |
| 350 | 11.2 |
| 400 | 13.2 |

[a] Non-saturating solute 200 g $NaNO_3$/dm$^3$, pH 4.49.

[b] Non-saturating solute 200 g $NaNO_3$/dm$^3$, temperature 20°C.

[c] 20°C.