

low because the large scale plot of  $\Lambda$  vs.  $\sqrt{c}$  shows detectable curvature over the range used.

When electrolytes behave as potassium perchlorate does, Davies<sup>12</sup> has shown that it is possible to evaluate the limiting conductance by assigning finite equilibrium constants to the salt, and finding the value of  $\Lambda_0$  which yields the most consistent values for the equilibrium constants at various low concentrations. Using potassium chloride as the reference curve for normal univalent electrolytes; the conductance values of Shedlovsky<sup>9</sup> for potassium chloride; and the activity coefficients of Scatchard<sup>10</sup> for potassium perchlorate; the data in Table III were obtained. The limiting conductance that yielded the most consistent values of  $K$  was 140.83.

TABLE III

| $c$   | $\gamma_{\pm}$ | KCl  |  | KClO <sub>4</sub>                              |  | $\Delta$ | $K$ |
|-------|----------------|--|--|--|--|----------|-----|
|       |                | $\Lambda_{\text{obs.}} - \Delta_{\text{L.L.}}$ | $\Lambda_{\text{obs.}} - \Delta_{\text{L.L.}}$ | $\Lambda_{\text{obs.}} - \Delta_{\text{L.L.}}$ | $\Lambda_{\text{obs.}} - \Delta_{\text{L.L.}}$ |          |     |
| 0.001 | 0.965          | 0.10   | -0.03  | 0.13   | 1.03   |          |     |
| .002  | .951           | .20  | -.08   | .28  | .91  |          |     |
| .005  | .923           | .51  | -.12   | .63  | .91  |          |     |
| .010  | .893           | .96  | -.10   | 1.06   | .99  |          |     |
| .020  | .853           | 1.90   | +.08   | 1.82   | 1.02   |          |     |

In Table III,  $\Delta$  is the "conductance deficiency" of potassium perchlorate and  $K = (\gamma_{\pm})^2 c / (1 - \alpha)$  where  $1 - \alpha$  is the degree of association. The limiting conductance of potassium perchlorate so evaluated agrees well with that evaluated by the other two methods; the three values for the limiting conductance being 140.90, 140.88 and 140.83. The last two values should be somewhat

(12) C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927); *J. Chem. Soc.*, 2093 (1938); *ibid.*, 349 (1939).

more accurate than the first which was obtained by extrapolation of  $\Lambda$  vs.  $\sqrt{c}$ . The most probable value of the limiting conductance is  $140.86 \pm 0.06$ .

The best values for the limiting conductances of sodium perchlorate and lithium perchlorate are 117.46 and 105.98 with about the same probable error as for potassium perchlorate.

**Mobility of the Perchlorate Ion.**—Using the limiting conductances obtained in this paper and the known conductances of the cations ( $K^+ = 73.52$ ,  $Na^+ = 50.11$ , and  $Li^+ = 38.69$ ), the limiting conductance of the perchlorate ion would be 67.34, 67.35, and 67.27, respectively. The average of these 67.32 with an estimated error of  $\pm 0.06$  conductance unit is assigned as the limiting conductance of the perchlorate ion. This value is approximately 0.6 of a unit lower than that found by Davies.<sup>1</sup>

### Summary

The electrical conductances of aqueous solutions of sodium, lithium and potassium perchlorates have been determined at 25° over the concentration range of 0.0005–0.1 molar. The limiting equivalent conductances have been evaluated by several methods.

The densities of the solutions of the three salts have been determined over the same concentration range.

The limiting conductance of the perchlorate ion has been calculated using the conductance data of this investigation and the known conductances of the cations.

BLOOMINGTON, INDIANA RECEIVED FEBRUARY 23, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

## The System Ammonium Selenate–Cupric Selenate–Water at 25°

BY G. B. KING AND W. A. BECKMAN

As a part of the more extensive problem of determining solubility relations in ternary systems of selenates, the system  $(NH_4)_2SeO_4$ – $CuSeO_4$ – $H_2O$  has been investigated at 25°. As mentioned in a previous communication,<sup>1</sup> relatively few selenate systems have been studied. From the meager data available on mutual solubility of two selenate salts in water, it appears that these systems follow closely the corresponding sulfate systems, although tendency toward compound formation appears to be less pronounced than in systems of sulfates.

Although the double salt,  $(NH_4)_2Cu(SeO_4)_2 \cdot 6H_2O$  has been prepared by several investigators, no studies of mutual solubilities of the component salts have been reported.

(1) Lawrence and King, *This Journal*, **60**, 1987 (1938).

### Experimental

Procedures followed in solubility determinations were similar to those generally employed in investigations of this nature. Various mixtures of the component salts and water were made up such that considerable solid phase would be present at equilibrium and the mixtures agitated in an electrically controlled thermostat maintained at  $25 \pm 0.05^\circ$  until equilibrium had been attained. The method of making up complexes of known composition was followed in some of the runs. Analyzed portions of the component salts and water were carefully weighed into glass-stoppered tubes of about 60-ml. capacity, followed by rotation at constant temperature.

The preparations of selenic acid and ammonium selenate have been described previously.<sup>2</sup> The copper salt was prepared from reagent quality cupric carbonate and selenic acid. The salt was recrystallized and air dried and stored over partially dehydrated cupric selenate. Analy-

(2) Gilbertson and King, *ibid.*, **58**, 180 (1936); King, *J. Phys. Chem.*, **41**, 797 (1937).

sis for copper showed a purity of  $100 \pm 0.2\%$   $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$ .

Ammonia was determined by distillation into standard acid and titration of the excess acid with sodium hydroxide. Copper was determined iodometrically; to the sample to be analyzed were added a few drops nitric acid, the solution made alkaline with ammonia and warmed to expel the excess, 5 ml. glacial acetic acid added, cooled, excess potassium iodide added and the solution titrated with thiosulfate. Macalpine and Sayce<sup>8</sup> in an investigation of the system  $\text{CuSeO}_4\text{--H}_2\text{SeO}_4\text{--H}_2\text{O}$  reported it necessary to remove selenate by precipitation of the copper with hot sodium hydroxide before titration. In the present work, however, accurate results were obtained without removal of the selenate ion by following the above procedure. Possible interference of selenate ion was checked carefully by determination of known weights of pure copper in the presence of varying amounts of ammonium selenate. End-points were sharp and distinct with no further oxidation of iodide ion within a period of fifteen to thirty minutes. Deviations of determined copper from actual were well within limits of experimental error. It was found, however, that the presence of any selenite completely vitiates the results.

To ensure attainment of equilibrium, samples were withdrawn at intervals and analyzed until concordant results were obtained. In the region of stability of the double salt, it was found that the method of preparing the samples greatly influenced the time required for attainment of equilibrium. Mixing of solutions of the component salts at room temperature resulted in the formation of some finely divided bluish-green solid, sparingly soluble in water. The solid washed with water gave no test for ammonia and was possibly a basic selenate of copper. Several basic cupric selenates have been reported.<sup>4</sup> No attempt was made to identify the solid. Samples prepared in this manner and placed in a thermostat with occasional agitation did not reach equilibrium even after several weeks. However, complexes of known composition made up from the separate solid salts and water, and rotated continuously in a thermostat did reach equilibrium in from one to two weeks. Equilibrium conditions were reached in a few days by preparation of solutions unsaturated with respect to the double salt at temperatures of 60–70°, followed by cooling and spontaneous evaporation of the solution at 25°.

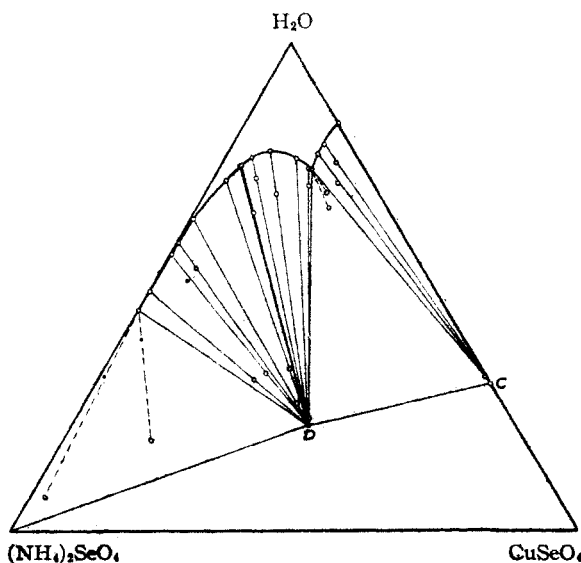


Fig. 1.—25° Isotherm: C represents  $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$ ; D represents  $\text{CuSeO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 \cdot 6\text{H}_2\text{O}$ .

The solid phase separated as pale blue prisms and proved on analysis to be the hexahydrated double salt. Seeding of the solution with crystals of the double salt considerably hastened the attainment of equilibrium.

Samples of solution (4–6 g.) and wet residue (1.5–3 g.) were withdrawn from the solubility tubes, weighed, and made up to 100 ml. Twenty-ml. aliquots were taken for analysis for ammonia and copper content. Compositions of solid phases were determined by the wet residue method of Schreinemakers<sup>5</sup> and by algebraic extrapolation of tie lines<sup>6</sup> through the composition of original complexes and the saturated solutions in equilibrium with these complexes. The double salt was also analyzed directly after washing and air drying. Extrapolation of tie lines gave an average deviation of 0.51%  $(\text{NH}_4)_2\text{SeO}_4$  from the theoretical percentage of  $(\text{NH}_4)_2\text{SeO}_4$  in the double salt hydrate.

## Results

The compositions of saturated solutions, complexes and wet residues are given in Table I and shown graphically in Fig. 1.

The solid phases  $(\text{NH}_4)_2\text{SeO}_4$ ,  $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$  exist at 25° with the congruently soluble double salt hydrate occupying nearly the whole field. As pointed out by Hill, Soth and Ricci,<sup>7</sup> this is a characteristic of most of the picromerite double salts. The solubility of the double salt as determined directly from recrystallized material is 23.26 weight per cent.  $(\text{NH}_4)_2\text{Cu}(\text{SeO}_4)_2$ . The solubility of cupric selenate 16.09 wt. %  $\text{CuSeO}_4$  is in fair agreement

| $(\text{NH}_4)_2\text{SeO}_4$<br>wt. % | $\text{CuSeO}_4$<br>wt. % | $(\text{NH}_4)_2\text{SeO}_4$<br>wt. % | $\text{CuSeO}_4$<br>wt. % | Solid phase    |
|--|---------------------------|--|---------------------------|----------------|
| Satd. soln.                            |                           | Original complex<br>or wet residue     |                           |                |
| 0.0                                    | 16.09                     | ...                                    | ...                       | C <sup>a</sup> |
| 4.89                                   | 15.91                     | 4.56                                   | 19.64                     | C              |
| 6.88                                   | 15.98                     | .37                                    | 67.72                     | C              |
| 9.38                                   | 16.09                     | 9.03                                   | 21.30                     | C + D          |
| 9.46                                   | 16.02                     | 10.40                                  | 23.45                     | C + D          |
| Av. 9.42                               | 16.06                     | ...                                    | ...                       | C + D          |
| 9.82                                   | 15.61                     | 11.51                                  | 17.25                     | D              |
| 10.96                                  | 12.30                     | ...                                    | ...                       | D              |
| 14.67                                  | 7.02                      | 18.02                                  | 12.62                     | D              |
| 18.66                                  | 4.47                      | 35.89                                  | 41.03                     | D              |
| 18.70                                  | 4.47                      | 20.01                                  | 7.33                      | D              |
| 21.40                                  | 3.31                      | 23.97                                  | 10.41                     | D              |
| 21.60                                  | 3.17                      | 35.07                                  | 37.75                     | D              |
| 25.47                                  | 2.20                      | 33.70                                  | 32.79                     | D              |
| 35.25                                  | .49                       | 36.11                                  | 37.36                     | D              |
| 40.29                                  | .23                       | 39.85                                  | 5.74                      | D              |
| 42.71                                  | .13                       | 38.40                                  | 28.75                     | D              |
| 50.20                                  | trace                     | 41.21                                  | 27.59                     | D              |
| 53.81                                  | trace                     | 65.17                                  | 15.72                     | D + A          |
| 53.74                                  | trace                     | ...                                    | ...                       | D + A          |
| 53.96                                  | trace                     | 90.21                                  | 2.72                      | D + A          |
| Av. 53.84                              | trace                     | ...                                    | ...                       | D + A          |
| 54.02                                  | 0.0                       | ...                                    | ...                       | A              |

<sup>a</sup> C =  $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$ ; D =  $(\text{NH}_4)_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; A =  $(\text{NH}_4)_2\text{SeO}_4$ .

(8) Macalpine and Sayce, *J. Chem. Soc.*, 1560 (1932).

(4) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, p. 859.

(5) Schreinemakers, *Z. physik. Chem.*, 11, 75 (1893).

(6) Hill and Ricci, *THIS JOURNAL*, 53, 4305 (1931).

(7) Hill, Soth and Ricci, *ibid.*, 63, 2717 (1940).

with the value of 15.89 reported by Macalpine and Sayce.<sup>3</sup>

### Summary

Solubility relationships in the ternary system

$(\text{NH}_4)_2\text{SeO}_4\text{-CuSeO}_4\text{-H}_2\text{O}$  at 25° have been determined. The double salt hydrate  $(\text{NH}_4)_2\text{SeO}_4\text{CuSeO}_4\cdot 6\text{H}_2\text{O}$  is the stable phase over almost the entire range of concentrations.

PULLMAN, WASH.

RECEIVED FEBRUARY 24, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Silicon Chlorobromides

BY HERBERT H. ANDERSON

Recent studies of the silicon chlorobromides<sup>1,2</sup> have increased our knowledge of these three compounds considerably; however, the information available on melting points and densities is quite scant, while boiling points are fairly well known.

A mixture of the silicon chlorobromides was prepared<sup>1b</sup> by heating equal volumes of  $\text{SiCl}_4$  and  $\text{SiBr}_4$  over a period of seventy hours at 140° in a sealed tube. Repeated fractional distillation of the three chlorobromides provided pure samples boiling at the following uncorrected temperatures:  $\text{SiCl}_3\text{Br}$  at 78.8–79.0°,  $\text{SiCl}_2\text{Br}_2$  at 103.8–104.1°, and  $\text{SiClBr}_3$  at 127.0–127.3°. Portions of each pure compound were used at once in measuring densities, melting points and boiling points.

### Densities, Melting Points and Boiling Points

**Procedures.**—Densities were measured in a calibrated 2-ml. bulb with capillary inlet bearing a reference mark; densities obtained should be accurate to one or two parts per thousand. A suitable value for carbon tetrachloride was obtained. Melting points were obtained as follows: the bulb of a calibrated toluene thermometer was immersed in about 3 ml. of pure chlorobromide in a small tube, which was itself immersed in an alcohol-bath contained in a Dewar flask. The temperature of the alcohol-bath was allowed to change slowly, with agitation of both sample and thermometer; melting points were in good accord with freezing points. Boiling points were measured to 0.2°, followed by immediate observation of the boiling point of carbon tetrachloride or water in identical equipment. *Results* of this investigation are summarized in Table I below; previous values are given when available.

(1) (a) Schumb and Anderson, *THIS JOURNAL*, **59**, 651 (1937); (b) Forbes and Anderson, *ibid.*, **66**, 931 (1944).

(2) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, pp. 962, 978, 980–981.

TABLE I

#### SILICON TETRACHLORIDE TO SILICON TETRABROMIDE

| Com-<br>pound              | B. p., °C.<br>Obs. | Prev.                  | M. p. °C.              | Density <sup>24</sup> | Mol.<br>vol.,<br>ml. |
|----------------------------|--------------------|------------------------|------------------------|-----------------------|----------------------|
| $\text{SiCl}_4$            | ...                | 57.57 <sup>1</sup>     | -70 <sup>2</sup>       | 1.469 <sup>2</sup>    | 115.7                |
| $\text{SiCl}_3\text{Br}$   | 80.3               | 80 <sup>3,4</sup>      | -62 = 1                | 1.826                 | 117.4                |
| $\text{SiCl}_2\text{Br}_2$ | 104.4              | 104 <sup>3,5</sup>     | -45.5 = 1              | 2.172                 | 119.2                |
| $\text{SiClBr}_3$          | 128.0              | 126–128 <sup>3,6</sup> | -20.8 = 1 <sup>b</sup> | 2.497 <sup>2</sup>    | 121.6                |
| $\text{SiBr}_4$            | ...                | 153.4 <sup>4</sup>     | +8 <sup>2</sup>        | 2.812 <sup>2</sup>    | 123.7                |

<sup>1</sup> From value 1.483 at 20°, Mellor, Vol. VI, p. 962.  
<sup>2</sup> Besson<sup>3</sup> gives -39°, on a probably impure compound.  
<sup>3</sup> Reynolds' value, in Mellor, of 2.432 would give a molar volume greater than that of  $\text{SiBr}_4$ .

**Discussion.**—Previously, there was some doubt as to the correct values on  $\text{SiClBr}_3$ . This has been settled. The chief physical properties of the silicon chlorobromides are now known. In examining the liquid ranges in Table I above, we find the value is constant at  $149.0 \pm 0.6^\circ$  in the last three members,  $\text{SiCl}_2\text{Br}_2$ ,  $\text{SiClBr}_3$ , and  $\text{SiBr}_4$ . This regularity has led to a study of liquid ranges of other mixed halides; this is now complete and should be published at a later date. Other work is in progress, including isolation of  $\text{Si}(\text{OCH}_3)_3\text{SCN}$  boiling at about 170.5°.

### Summary

An investigation of the chief physical properties of the silicon chlorobromides has yielded the following new values:  $\text{SiCl}_3\text{Br}$ , m. p. -62°,  $d^{25}$ , 1.826;  $\text{SiCl}_2\text{Br}_2$ , m. p. -45.5°,  $d$  2.172;  $\text{SiClBr}_3$ , m. p. -20.8°,  $d$  2.497. Boiling points of the chlorobromides have been checked also.

CAMBRIDGE, MASSACHUSETTS

RECEIVED DECEMBER 5, 1944

(3) "International Critical Tables."

(4) Schumb and Young, *THIS JOURNAL*, **52**, 1464 (1930).

(5) Besson, *Compt. rend.*, **112**, 531, 788, 1447 (1891).