

Density of Potassium Chloride

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The density of potassium chloride has been determined by the method of "crystal suspension" in a liquid mixture of bromoform, *n*-hexanol, and *n*-pentanol. The density of the liquid mixture at the average suspension temperature of fifty-three different crystals was taken as the density of the potassium chloride. The value determined was:

$$\rho_{28.098^\circ\text{C}} = 1.98651 \pm 0.00002 \text{ g/ml}$$

which when corrected to 25°C gave:

$$\begin{aligned} \rho_{25^\circ\text{C}} &= 1.98721 \pm 0.00002 \text{ g/ml} \\ &= 1.98715 \pm 0.00002 \text{ g/cm}^3. \end{aligned}$$

It was found that six precipitations of potassium chloride from aqueous solutions with hydrogen chloride were necessary to effect purification to constant density ($\pm 4 \times 10^{-6}$ g/ml). Exposure of crystals to the atmosphere was found

to produce some manner of surface contamination which resulted in a change of density by as much as 7×10^{-4} g/ml within two hours. Storage of crystals over phosphorus pentoxide under vacuum eliminated this effect. An annealing of crystals for four hours at 50° below the melting point with gradual cooling over a period of four hours was found necessary to obtain agreement of suspension temperatures among different crystals. By combination of density and x-ray data, atomic weights have been calculated. The values of the atomic weights of fluorine and calcium were found to be 18.9967 ± 0.0010 and 40.0851 ± 0.0011 , respectively. In the crystals of calcite, lithium fluoride, and potassium chloride which were used to obtain the data underlying these calculations, there is no evidence for a secondary structure as proposed by Zwicky.

I. INTRODUCTION

A PRECISION method for the determination of the densities of solid crystalline substances has been developed by C. A. Hutchison and H. L. Johnston.¹

The method consists of suspending² crystals of the substance whose density is to be determined in a liquid of the proper density. The above workers applied this method to the determination of the density of very pure lithium fluoride. Later, H. L. Johnston and the writer³ were able, with certain refinements of the method, to obtain a value for the density of very pure sodium chloride with reduced probable error over that of the lithium fluoride determination. The present paper deals with the application of the "suspension method" to the determination of the absolute density of very pure potassium chloride.

The purposes of the present determination are: (1) to obtain density data which, in conjunction

with x-ray data, can be used in the calculation of various physical constants, e.g., atomic weights,^{3,4} and Avogadro's number;⁵ (2) to obtain density data which can be used in detecting changes in isotopic abundance ratios of the elements potassium and chlorine due to a given isotopic separation process.^{1(b),6}

The most accurate values for the density of potassium chloride, reported to the present time in the literature, appear to be those of Kohler⁷ and of Tu.⁸

Kohler determined the density to be $1.9901 \pm 0.00015 \text{ g/cm}^3$ at 15°C while Tu obtained the value $1.98930 \pm 0.00014 \text{ g/cm}^3$ at 18°C. When correction is made for the coefficient of thermal expansion of potassium chloride,⁹ Kohler's value reduces to

$$\rho_{25^\circ} = 1.9879 \pm 0.00015 \text{ g/cm}^3$$

and Tu's value reduces to

$$\rho_{25^\circ} = 1.98773 \pm 0.00014 \text{ g/cm}^3.$$

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¹ (a) C. A. Hutchison and H. L. Johnston, *J. Am. Chem. Soc.* **62**, 3165 (1940); (b) H. L. Johnston and C. A. Hutchison, *J. Chem. Phys.* **8**, 869 (1940).

² In previous papers the words "float" and "flotation" are used. These words do not clearly express what is done. Since the temperature is found at which a crystal would be suspended by a given suspension medium, the writer has used the words "suspend" and "suspension" in place of the above words.

³ H. L. Johnston and D. A. Hutchison, *Phys. Rev.* **62**, 32 (1942).

⁴ (a) C. A. Hutchison and H. L. Johnston, *J. Am. Chem. Soc.* **63**, 1580 (1941); (b) C. A. Hutchison, *J. Chem. Phys.* **10**, 489 (1942).

⁵ R. T. Birge, *Phys. Rev.* **61**, 206A (1942).

⁶ H. L. Johnston and D. A. Hutchison, *J. Chem. Phys.* **10**, 469 (1942).

⁷ J. Kohler, *Zeits. f. Physik* **78**, 375 (1932).

⁸ Y. Tu, *Phys. Rev.* **40**, 662 (1932).

⁹ $\alpha(\text{cubical}) = 113 \times 10^{-6}$, Klemm, Tilk, and Mullenheim, *Zeits. f. anorg. allgem. Chemie* **176**, 1 (1928).

Kohler's value exceeds the result of the present determination by 0.038 percent while Tu's value is greater by 0.029 percent. Neither of these workers attempted purification of his potassium chloride, but used the best commercial product available. Their larger values may be due in part to the presence of impurities and to a greater extent to the effect of prolonged exposure to the atmosphere, which, as found in the present work, generally increases the density value (see Table II).

The result of this investigation on very pure potassium chloride when corrected to 25°C gives

$$\begin{aligned}\rho_{25^\circ} &= 1.98721 \pm 0.00002 \text{ g/ml} \\ &= 1.98715 \pm 0.00002 \text{ g/cm}^3\end{aligned}$$

with reduced probable error when compared with other determinations.

II. EXPERIMENTAL DESCRIPTION

A. Preparation of Chemically Pure Potassium Chloride

Chemically pure potassium chloride was prepared by a method similar to that used by H. L. Johnston and the writer³ in their work on the density of sodium chloride. In essence this is the method employed by Richards and Wells¹⁰ in their determinations of the atomic weights of sodium and chlorine.

Pure hydrochloric acid was prepared by distillation of C. P. Baker's Analyzed reagent hydrochloric acid to which had been added a small quantity of C.P. potassium permanganate. The distillation was carried out in a still composed of a flask and condenser made from pure fused quartz. The middle third of the distillate was saved from each distillate of two successive distillations. The pure hydrochloric acid was stored for future use in clean Pyrex bottles, the inner surface of which had been exposed to concentrated C.P. hydrochloric acid for about four months prior to storing.

Pure sulphuric acid was prepared in a similar manner by double distillation of C. P. Baker's Analyzed reagent sulphuric acid. This acid was also stored in Pyrex which had been exposed to

C.P. sulphuric acid for about four months prior to storing.

Pure sodium chloride which was used in the generation of pure hydrogen chloride was fractionally precipitated three times from saturated aqueous solutions of sodium chloride by the addition of hydrogen chloride. The beginning material was Baker's Analyzed C.P. sodium chloride. The hydrogen chloride used in these precipitations was generated by the reaction of pure sulphuric acid (see above) with an aqueous solution of Baker's Analyzed C.P. sodium chloride and pure hydrochloric acid (see above).

Pure water which was used in all reagent preparations was obtained by double distillation from an alkaline permanganate water solution in a pure fused quartz still. Water used in the determination of the volume of the glass bob (see below) was triply distilled and had a specific conductivity of about 10^{-7} ohm⁻¹.

Pure hydrogen chloride which was used in the purification of potassium chloride was generated by the reaction of pure sulphuric acid (see above) with an aqueous solution of pure sodium chloride (see above) and pure hydrochloric acid (see above). The generated gas was passed through two tubes containing ground glass covered with pure sulphuric acid (see above) and finally through a tube containing Baker's Analyzed C.P. phosphorus pentoxide which had been sublimed into this tube.

Purification of the potassium chloride used in the density determination was effected by successively precipitating potassium chloride from a saturated aqueous solution by the addition of pure hydrogen chloride (see above). After each precipitation the potassium chloride was centrifuged to remove the mother liquor. The beginning material was Baker's Analyzed C.P. potassium chloride. Precise density determinations showed that after four precipitations the densities of the potassium chloride from different samples did not agree within the experimental limits of the density determination (see Table III). However, constant density values were obtained from different potassium chloride samples after six precipitations. As a precautionary measure eight precipitations were performed.

After the eight successive precipitations, the hydrochloric acid was expelled from the purified

¹⁰ T. W. Richards and R. C. Wells, "A revision of the atomic weights of sodium and chlorine," Carnegie Institute of Washington, Publication No. 28 (1905).

salt by fusion in a platinum crucible. The salt on cooling was dissolved in pure, triple-distilled water (see above) and given three crystallizations.

B. Preparation and Calibration of the Suspension Liquid

For the crystal suspensions a liquid had to be found which had the proper density, the proper change of density with temperature, and which would not decompose or react with the potassium chloride crystals. A suitable liquid mixture, similar to that used by H. L. Johnston and C. A. Hutchison^{1(a)} in their determination of the density of lithium fluoride, was found to have the following composition: bromoform, 40.00 ml; *n*-hexanol, 881 drops; *n*-pentanol, 832 drops (52 drops equal 1 ml). The suspension liquid was prepared as follows: Baker's bromoform (boiling point range, 150°–151°C) U.S.P. IX, was washed with water, dried with calcium chloride, and distilled under vacuum. The middle third of the distillate was collected in a receiver containing a small amount of *n*-hexanol and *n*-pentanol (25 drops of each) which acted as a negative catalyst preventing decomposition. The composition of the bromoform was adjusted to that of the above suspension liquid with Eastman practical grade alcohols. The isothermal density of this suspension liquid was found to remain constant within the experimental limits of error ($\pm 5 \times 10^{-6}$ g/ml) of the density determination for a period of about seven days. Suspension temperatures after the seven-day period were corrected by means of the standard crystals suspended within the seven-day period.

The density of the suspension liquid at different temperatures was determined by means of hydrostatic weighings. A Pyrex glass bob about 9.4 ml in volume which contained mercury for additional weight was weighed in air, in water, and in the suspension liquid at different temperatures. As in the sodium chloride work,³ to eliminate surface tension effects¹¹ at the point of entrance of the 0.01" platinum suspension wire into the liquid, an auxiliary mercury-weighted Pyrex bob about 1.1 ml in volume was attached to the lower end of the suspension wire. The large bob was detachable from the auxiliary bob. The

¹¹ Osborne, McKelvey, and Bearce, *Bull. U. S. Bur. Stand.*, Reprint No. 197 (1912).

weighing procedure has been described previously.³ Two series of weighings were made in the suspension liquid, those of the wire suspension with the auxiliary bob immersed and those of the wire suspension with the auxiliary bob and large bob immersed.

TABLE I. Density of the bromoform mixture as a function of temperature. The bob volume at 25.000°C was taken as 9.41336 ml and corrected to the temperature of each weighing by means of the cubical coefficient of thermal expansion of Pyrex.

Temperature (Centigrade)	Density (g/ml) (at <i>T</i>)	Density (g/ml) (at 28.098°C)
29.320	1.98422	1.98652
29.068	1.98468	1.98651
28.819	1.98515	1.98651
28.547	1.98567	1.98652
28.304	1.98611	1.98650
28.048	1.98661	1.98652
27.806	1.98706	1.98651
27.543	1.98756	1.98651
27.310	1.98799	1.98651
27.060	1.98846	1.98651
26.802	1.98894	1.98650
26.556	1.98940	1.98650
26.301	1.98989	1.98651
26.072	1.99032	1.98651
25.794	1.99084	1.98650
25.553	1.99128	1.98649
25.289	1.99178	1.98649
25.027	1.99229	1.98651

The precise volume of the bob was determined by weighings in triple-distilled water (see above) which had been heated to about 80°C before use to expel dissolved gases. Twenty sets of weighings were made in water at temperatures ranging from 26.174°C to 27.769°C. These twenty independent volume determinations when corrected to 25.000°C by use of the cubical coefficient of thermal expansion of Pyrex glass¹² yielded an average bob volume of 9.41336 ± 0.00002 ml. The densities of the water at the various temperatures were obtained from the *International Critical Tables*.¹³ The average deviation from the mean of the twenty determinations was ± 0.00001 ml, and the extreme deviation was -0.00009 ml. All weighings were corrected for the buoyant effect of air.

The temperatures at which the weighings were made were determined with a Beckmann ther-

¹² R. M. Buffington and W. M. Latimer, *J. Am. Chem. Soc.* **48**, 2305 (1926). The cubical expansion coefficient was taken as three times the linear coefficient given as 3.6×10^{-6} at 300°K.

¹³ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1928), Vol. III, p. 25.

meter graduated in 0.01° intervals. The scale of this thermometer was shown to be quite uniform by the U. S. Bureau of Standards calibration of the scale. A standard mercury in glass thermometer with a temperature range of 18° to 28°C and with graduations in 0.01° intervals, the scale of which had been calibrated by the U. S. Bureau of Standards, was compared with the Beckmann thermometer at nine different temperatures at 0.5° intervals over a temperature range of 1° to 5° Beckmann. The comparison at the extremes of the temperature range gave

$$1.000^\circ \text{ Beckmann} = 29.320^\circ \text{C}$$

and

$$5.000^\circ \text{ Beckmann} = 25.289^\circ \text{C}.$$

The densities of the bromoform suspension liquid are given in column two of Table I at temperatures covering the range 25.027°C to 29.320°C.

TABLE II. Suspension temperatures of crystals grown from Baker's Analyzed C. P. potassium chloride.*

Crystal designation	Suspension temperatures in ° Beckmann			See footnotes ^a		
	Newly prepared	After 4 days	After 7 days			
A2-1	1.998	2.010	2.007			
A2-2	1.991	1.999	2.005			
A2-3	2.009	2.004	2.007			
A2-4	1.986	2.013	2.018			
V2-1	1.999	1.992	1.990			
V2-2	1.995	1.987	1.984			
V2-3	1.887	1.896	1.899			
V2-4	2.006	1.994	1.997			
V4-1	1.984	1.986	1.984	1.985	1.998	1.972
V4-2	1.995	1.995	1.996	1.998	2.017	1.991
V4-3	1.988	1.990	1.989	1.987	2.024	1.999
V4-4	1.976	1.977	1.975	1.975	1.974	1.975

* Explanation: All crystal segments whose suspension temperatures are given in this table were taken from the same melt. The crystal designation A2 denotes crystals which were annealed for two hours at 50° below their melting point and stored exposed to the atmosphere. The designation V2 denotes a two-hour annealing period and storage over phosphorus pentoxide under vacuum. The designation V4 denotes a four-hour annealing period with gradual cooling to room temperature over a period of four hours together with storage over phosphorus pentoxide under vacuum. The Beckmann thermometer graduations are such that increases in numerical values are decreases in temperature.

^a After the seventh day, crystals V4-1, V4-2, and V4-3 were exposed to the atmosphere for twenty minutes and then resuspended. The suspension temperatures are given in the first column. The second column gives the suspension temperatures after exposure to the atmosphere for two hours. Crystal V4-4 was not exposed. The third column gives the suspension temperatures after a four-hour annealing at 50° below the melting point.

C. Preparation of Suspension Crystals

The suspension crystals were grown from a melt of purified potassium chloride (see Section A) by the method developed by Kyropolous¹⁴

¹⁴ S. Kyropolous, *Zeits. f. anorg. allgem. Chemie* **154**, 308 (1926).

which has been described previously.¹ Similar to the procedure of the density determination for sodium chloride,³ a four-hour annealing period of about 50° below the melting point was found necessary as shown in Table II. After annealing, the crystals were cooled gradually over a period of four hours. Phosphorus pentoxide was introduced at about 150°C into the furnace around the platinum crucibles containing the crystals. At 60° to 70°C the crystals were removed from the furnace and, with platinum-tipped forceps, were placed in small glass bottles which previously had been heated to about 65°C. The bottles were stored immediately in a desiccator over phosphorus pentoxide under vacuum.

The above procedure was found necessary as evidenced from the observations recorded in Table II. The time required to transfer a crystal from its desiccator to the suspension liquid is short enough that the crystal is not contaminated. The length of time that a crystal may stay in the suspension liquid without change of the suspension temperature is about one week, and then any change is largely due to decomposition of the suspension liquid.

It will be seen from the data of Table II that generally crystals which were exposed to the atmosphere for about two hours or more were suspended at lower temperatures indicating an apparently greater density. This may to a certain degree account for the discrepancy between the value of the density in the present determination and those of Tu⁸ and Kohler.⁷ The remainder of the discrepancy may be due to the lesser purity of the potassium chloride used by the other workers and to the lesser precision inherent in their methods. (See Tables II and III.)

D. Data for the Absolute Density

Fifty-eight crystal segments were suspended to determine the suspension temperature of the purified potassium chloride. The suspension temperatures are summarized in Table IV.

The average suspension temperature of the fifty-three unstarred crystals in Table IV was 1.989° Beckmann with an average deviation of ± 0.000 and an extreme deviation of +0.003 which is equivalent to -5.6×10^{-6} g/ml in the density of potassium chloride. This extreme

TABLE III. Suspension temperatures of crystals taken at various stages of the purification as outlined in Section A.*

Crystal designation	Suspension temperatures in ° Beckmann
4-1	1.982
4-2	1.999
4-3	1.978
4-4	1.984
6-1	1.987
6-2	1.989
6-3	1.988
6-4	1.987
8-1	1.989
8-2	1.989
8-3	1.987
8-4	1.988

* Explanation: The crystals designated at 4- were grown from potassium chloride that had been precipitated four times with hydrogen chloride from aqueous solutions, followed by fusion in platinum, three crystallizations from triple-distilled water, and a four-hour annealing period at about 50° below their melting point. Those crystals designated as 6- differed in treatment from the 4- in that they were given six precipitations with hydrogen chloride from water. Those designated as 8- were given eight hydrogen chloride precipitations.

TABLE IV. Suspension temperatures of fifty-eight crystals which were prepared and preserved as described above.

Number of crystals suspended at temperatures specified	Suspension temperatures (° Beckmann)
1	1.999*
1	1.998*
1	1.995*
1	1.992
2	1.991
4	1.990
37	1.989
7	1.988
2	1.987
1	1.984*
1	1.980*

* The starred temperatures were not considered in determining the average suspension temperature since they may be excluded on the basis of defects or on the basis that they lie outside a 0.003° range from the mean of the fifty-eight crystals suspended.

deviation is within the experimental limits of the determination.

When the experimental densities of the bromoform mixture (see column 2 of Table I) are plotted against temperature, a straight line is obtained. The slope of this line is $-1.883 \pm 0.004 \times 10^{-3}$ g/ml/degree. Comparison of the Beckmann thermometer with the standard thermometer, calibrated by the U. S. Bureau of Standards, yielded 1.989° Beckmann equal to 28.098°C. By employing the value of the thermal coefficient of density change, the entries in column 2 of Table I have been corrected to the

average suspension temperature, 28.098°C. The corrected values are given in column 3 of Table I. The average of these values, 1.98651 g/ml, is taken as the best value for the density of the suspension liquid at 28.098°C. The value for the absolute density of potassium chloride can be stated as

$$\rho_{28.098^\circ\text{C}} = 1.98651 \pm 0.00002 \text{ g/ml.}$$

When this value is corrected to 25°C by use of the cubical coefficient of thermal expansion of potassium chloride,⁹ the value obtained is

$$\begin{aligned} \rho_{25^\circ\text{C}} &= 1.98721 \pm 0.00002 \text{ g/ml} \\ &= 1.98715 \pm 0.00002 \text{ g/cm}^3. \end{aligned}$$

III. MOLECULAR WEIGHT COMPARISONS. THE ATOMIC WEIGHTS OF FLUORINE AND CALCIUM

It has been shown that combination of crystal densities and x-ray data can be used in the comparison of molecular weights.^{3,4} With the assumption of certain atomic weights, other atomic weights may be calculated. Combination of the density of potassium chloride obtained in this determination and the density of lithium fluoride obtained by C. A. Hutchison and H. L. Johnston^{1(a)} with the x-ray data of Tu¹⁵ and that of Straumanis, Ievins, and Karlsons¹⁶ makes possible the calculation of the atomic weight of fluorine. The resulting atomic weight is found to be 18.9967 ± 0.0010 . Combination of the data on potassium chloride with the density of calcite obtained by Bearden¹⁷ and the x-ray data on calcite of Tu⁸ and Bearden¹⁷ gives 40.0851 ± 0.0011 as the atomic weight of calcium. A detailed account of the calculations of these and other atomic weights will appear elsewhere.¹⁸

The results of these atomic weight calculations do not support the hypothesis of Zwicky,¹⁹ who proposed a secondary structure for perfect crystals which requires periodic variations in the grating spaces in a direction normal to the crystal planes.

¹⁵ Y. Tu, Phys. Rev. **40**, 662 (1932).

¹⁶ Straumanis, Ievins, and Karlsons, Zeits. f. physik. Chemie **B42**, 143 (1939).

¹⁷ J. A. Bearden, Phys. Rev. **38**, 2089 (1931).

¹⁸ D. A. Hutchison, to be published elsewhere.

¹⁹ F. Zwicky, Proc. Nat. Acad. Sci. **15**, 816 (1929); **16**, 211 (1930).