

DENSITY DETERMINATION BY A MODIFIED SUSPENSION METHOD; X-RAY MOLECULAR WEIGHT, AND SOUNDNESS OF SODIUM CHLORIDE

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ABSTRACT

A modified suspension method for density determinations up to $d=4.25$ g. cm.⁻³ is described, according to which a pycnometer together with the heavy liquid and the substance (small crystal or fraction of it) is weighed after the pycnometer liquid has been adjusted to the mark at the suspension temperature. Knowing the volume of the pycnometer, the density of the liquid (=to that of the substance) is calculated. The accuracy of the method is at least 3×10^{-4} g. cm.⁻³, and can be still further improved upon. About 3 hrs. are necessary to perform one determination.

The density of purest sublimed sodium chloride, reduced to 20° C. was determined to 2.1638 ± 0.0003 g. cm.⁻³. The x-ray molecular weight was then 58.430 ± 0.010 , lower by 0.024 than the chemical weight. Therefore, NaCl contains vacant sites of at least 3.0×10^{18} per cm.³ at room temperature. One part of these vacancies may be assembled in the form of submicroscopic cracks or cavities in the inside of the crystals.

INTRODUCTION

For the precision determination of atomic and molecular weights by the x-ray-density method^{1,2} reliable density data are necessary. The most precise results are obtained by the flotation or suspension method, which permits determinations of high precision up to $d=4.25$ g. cm.⁻³ By this method Bearden obtained one of the best density values for the diamond.³ Johnston and Hutchison improved the density determinations⁴ and obtained very precise values for lithium fluoride, sodium and potassium chlorides.¹

However, the suspension method, as developed by the authors aforementioned, is difficult to apply, and it requires considerable time to perform one density determination. By some further modifications it was possible to simplify the operations, and to shorten the time required for a determination so that it could be performed in three hours. This method is described below. It was checked by the determination of the densities and the molecular weights of purest sodium chloride and silicon.

¹ Hutchison, C. A., and Johnston, H. L. *J.A.C.S.*, **62**, 3165 (1940); **63**, 1580 (1941); Johnston, H. L., and Hutchison, D. A., *Phys. Rev.*, **62**, 32 (1942); Hutchison, C. A., *J. Chem. Phys.*, **10**, 489 (1942); Hutchison, D. A., *J. Chem. Phys.*, **13**, 383 (1945); Batuecas, T., *Nature*, **165**, 61 (1950).

² Straumanis, M., *Zeit. Physik*, **126**, 49 (1949).

³ Bearden, J. A., *Phys. Rev.*, **54**, 698, 700 (1938).

⁴ Johnston, H. L., and Hutchison, C. A., *J. Chem. Phys.*, **8**, 869 (1940); Hutchison, D. A., *Phys. Rev.*, **66**, 144 (1944).

THE METHOD

The principle of the method is as follows: A piece of a substance, the density of which is to be determined, is immersed in a liquid having approximately the same density as has the substance; the substance, therefore, rises or sinks slowly in the test tube. To obtain the suspension of the substance in the liquid, both are transferred to a pycnometer of a special design, which then is immersed in the water of a thermostat, the temperature of which can be controlled accurately. By raising or lowering the temperature the suspension of the substance in the liquid can be easily achieved. At the suspension temperature the excess liquid is removed (down to the mark) from the pycnometer, and the latter is weighed together with the liquid and substance. Knowing the volume of the pycnometer at the suspension temperature, the density of the liquid, which is equal to the density of the substance at that temperature, can easily be computed. The application of this method is possible only if there is a difference in the cubical expansion coefficients of the liquid

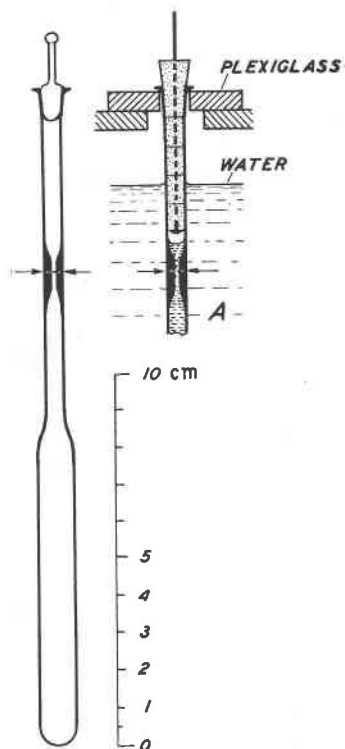


FIG. 1. Pycnometer for density determinations by the suspension method.

and of the substance, which is usually the case. The precision of the determinations increases with that difference. The section through the pycnometer is shown in Fig. 1.

The pycnometer of the dimensions as given in Fig. 1 was made of pyrex glass, heated in a furnace for 18 hrs. at 600° C. in order to remove the internal stresses, and then slowly cooled. The pycnometer after being well cleaned was calibrated at 25, 30, 35 and 40° C., using triple distilled deaerated water. The volume did not change very much with temperature:

Temp. ° C.	25° 0	30° 0	35° 0	40° 0
Volume in cm. ³	4.76847	4.76870	4.76897	4.76930

The volume of the pycnometer for intermediate temperatures was obtained by interpolation. The temperature readings (accuracy $\pm 0.01^\circ$) were made with a thermometer which was compared with another one calibrated by the Bureau of Standards. The weights were also checked and all weighings were reduced to a vacuum. The weighing operations were always performed in the same manner; prior to each weighing the pycnometer stood for 10 minutes in the case of the balance. The funnel tube of the pycnometer was always filled during the experiment with a cork stopper, as shown in Fig. 1A, in order to prevent distillation of components of the heavy liquid to parts of the pycnometer which were at lower temperatures because they were outside of the water of the thermostat. The stopper was removed when, at a certain temperature, the suspension of the substance in the liquid has been attained. Immediately after this the excess water or heavy liquid was sucked by a capillary pipette and by needle-like filter paper strips from the funnel tube of the pycnometer down to the mark. Then the pycnometer, now closed with a glass stopper, was removed from the water bath, dried with chamois, and placed in the balance case where it was left for 10 minutes before being weighed.

The slow change of the water bath temperature and the temperature control was achieved by an adjustable contact thermometer connected through an electronic relay, and with an electric bulb immersed in the bath as a heater. A copper coil for cooling the water of the bath, if necessary, was also provided. The pycnometer was immersed in the water, as shown in Figs. 1A and 2, and the uniformity of the temperature distribution throughout the bath was assured by a stirrer. The adjusting of the level of the liquid, and the cleaning of the funnel tube of the pycnometer was done with the aid of a magnifying glass (Fig. 2). It was assumed that the density of the liquid was equal to that of the sample, if it did not change its position in the middle of the pycnometer during half an hour, as observed through the telescope of the cathetometer.

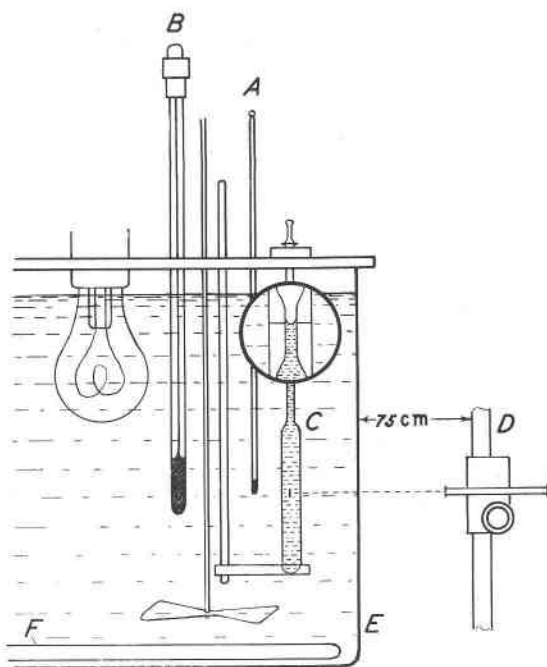


FIG. 2. Pycnometer with heavy liquid and sample in the water bath. *A*—thermometer. *B*—contact thermometer. *C*—pycnometer just before taking it from the bath. *D*—telescope. *E*—glass jar. *F*—cooling coil.

DENSITY OF PUREST SODIUM CHLORIDE AND OF SILICON

For the density determinations purest sodium chloride (Merck) was chosen. The reagent was sublimed in a quartz glass tube in a vacuum at 800°C . The small crystals which grew on the cooler parts of the tube were very clear and cubical in shape. The crystals were removed from the glass, and the best (being quite transparent, without cracks and signs of deformation) were chosen for the determinations. The size of these fragments was approximately 0.5×2 mm., so that they could freely pass the narrow neck of the pycnometer (Fig. 1). Just before the density measurements were made the crystals were heated for 10 minutes at 500° in air.

The heavy liquid used was bromoform.⁵ It has a density of 2.87 g. cm.^{-3} , and ethyl alcohol was added in order to reach the density of sodium chloride. This can be done in a small test tube at room temperature, as previously mentioned. The liquid was saturated with sodium chloride. The sodium chloride crystals transferred together with the liquid to the pycnometer (Fig. 1) showed, of course, different suspension temperatures,

⁵ Krumbein, W. C., *Manual of Sedimentary Petrography*, p. 320 (1938).

because the composition of the liquid each time was not exactly the same. The densities of 9 crystals (out of 10 measured) at the suspension temperature are listed in Table 1. The densities were reduced to 20° C. using the equation:

$$d_{t_1} = d_{t_2}[1 + \alpha(t_2 - t_1)]^3 \quad t_2 > t_1,$$

d_{t_1} is the density at 20° C., d_{t_2} the density at the temperature measured, t_2 and t_1 are the respective temperatures, and α is the expansion coefficient of sodium chloride 40.5×10^{-6} at room temperature, as determined from x-ray measurements.⁶ The table shows that the maximum deviation from the average density value is ± 0.0004 g. cm.⁻³ The standard deviation¹⁵

TABLE 1. DENSITY AND x-RAY MOLECULAR WEIGHT OF PUREST, SUBLIMED SODIUM CHLORIDE

t in ° C.	d_t in g. cm. ⁻³	d_{20} in g. cm. ⁻³	M_x in g. mole ⁻¹
26.12	2.16205	2.16365	58.427
24.82	227	355	23
26.90	186	368	27
24.10	234	342	20
25.24	270	408	38
27.20	213	403	36
24.89	262	390	33
26.50	194	365	26
25.57	273	420	41
	Average	2.1638	58.430
	Max. deviation	± 0.0004	± 0.010

of the present measurements and the mean deviation is between ± 0.0002 and 0.0003 . It is of no importance to mention the probable error as the measurements may still contain a systematic error which is greater than the probable error. The value obtained of $d_{20} = 2.1638$ for sodium chloride is larger than that obtained by Johnston and Hutchison⁷ ($d_{20} = 2.16360 \pm 0.00003$ g. cm.⁻³).

The density of silicon was determined in the same way, using bromoform ethyl alcohol mixtures as a heavy liquid. About 20 determinations with 12 highest purity silicon crystals, containing only 0.03% carbon⁸ were made. The accuracy of determination was approximately the same

⁶ Straumanis, M., and Ievinš, A., *Zeit. anorgan. Chem.*, **238**, 175 (1938); see also Straumanis, M. E., and Aka, E. Z., *J.A.C.S.*, **73**, 5643 (1951).

⁷ Johnston, H. L., and Hutchison, D. A., *Phys. Rev.*, **62**, 32 (1942).

⁸ Lyon, D. W., Olson, C. M., and Lewis, E. D., *J. Electroch. Soc.*, **96**, 359 (1949).

as in the previous case, at least $\pm 3 \times 10^{-4}$ g. cm.⁻³ For silicon an average value $d_{20} = 2.32831$ g. cm.⁻³ was obtained.⁹

THE X-RAY MOLECULAR WEIGHT OF NaCl AND Si.

The densities determined can be checked, computing the x -ray density (d_x) or atomic (A_x) or molecular weight (M_x), if the exact values of the lattice parameters of the substance under investigation are known. A convenient formula for this is as follows, if Siegbahn's wavelengths, expressed in X.U. or in kX are used²:

$$M_x = kN_s v d / n \quad \text{g/mole} \quad (1)$$

where N_s is Siegbahn's Avogadro number (6.0594×10^{23}), v is the volume of the unit cell (in $kX^3 \times 10^{-24}$), d is the density (g. cm.⁻³), and n the number of molecules per unit cell. k is a correction factor which eliminates the errors that were made determining N_s and the wavelengths. The necessity of such a factor for exact molecular weight calculations was previously emphasized by the author in 1944.² The correction factor k is the ratio:

$$\frac{M_1}{M_s} = k = \frac{100.095}{100.075} = 1.00020 \pm 0.00003 \quad (2)$$

where M_1 is the molecular weight of "purest" calcite, being a mixed crystal¹⁰ of a composition similar to the one used by Siegbahn for his x -ray wavelength determinations. M_s is the molecular weight of calcite as accepted by Siegbahn for the calculation of the fundamental value for the lattice spacing of calcite.¹¹ Although the author's paper on atomic and molecular weight determinations, containing the most probable weight for calcite 100.095, was accepted by the Editor of *Zeit. f. Physik* in October 1944, the paper, because of the war did not appear until 1949.²

Birge (at the suggestion of Pabst), also came to the same conclusions concerning the molecular weight of calcite but he had the opportunity to publish his calculations in 1945.¹²

Of course, x -ray molecular weight calculations can also be made using Å units, but in this case the Avogadro number N_0 is necessary. This number can be determined easily from the relation^{13,13a}:

⁹ Straumanis, M. E., and Aka, E. Z., *J. Appl. Phys.*, **23**, 330 (1952).

¹⁰ Ievinš, A., and Straumanis, M., *Z. Physik*, **116**, 194 (1940); see also Andrews, K. W., *Mineral. Mag.*, **29**, 85 (1950). The analyses of the calcite crystals were made by M. Straumanis and A. Dravnieks: *Zeit. analyt. Chem.*, **120**, 168 (1940).

¹¹ Siegbahn, M., "Spektroskopie der Röntgenstrahlen," II Ed. Berlin, J. Springer (1931), p. 43.

¹² Birge, R. T., *Am. Journ. Phys.*, **13**, 67 (1945).

¹³ Straumanis, M. E., *Acta Cryst.*, **2**, 83 (1949).

^{13a} Straumanis, M., *Z. f. Physik*, **126**, 65 (1949).

$$N_0 = \frac{k}{(1.00202)^3} N_s = 6.02403 \times 10^{23} \text{ mole}^{-1} \text{ (chem. scale)} \quad (3)$$

1.00202 being the conversion factor λ_g/λ_c , which is the ratio of wavelengths as determined from grating and from crystal measurements, k is the correction factor, eq. (2), previously established in 1944. Nevertheless N (in the physical scale) as calculated from N_0 (eq. 3) agrees closely with the recent value given by Du Mond and Cohen (in the physical scale)¹⁴:

$$N = (6.02544 \pm 0.00011) \times 10^{23} \text{ and from eq. 3 } (6.02567 \pm 0.00040) \times 10^{23} \text{ mole}^{-1}$$

The conversion factor from chemical to physical atomic weight units is 1.000272 ± 0.000005 . In the first case the error given is the probable error, in the second case it is the standard deviation.¹⁵

Thus the equations for x -ray molecular weight (chemical scale) and density (d_x) calculations are as follows, if the wavelengths are expressed in \AA units:

$$M_x = N_0 v^1 d / n, \quad \text{and} \quad d_x = nM / N_0 v^1 = nM / kvN_s. \quad (4)$$

v^1 is the volume of the unit cell in $\text{\AA}^3 \times 10^{-24}$ (v is in kX^3). Using N instead of N_0 , the molecular weight in the physical scale is obtained.

All of the equations (1) and (4) are exact. Eq. (1) was used for the molecular weight calculations of sodium chloride and of silicon. The lattice parameter of purest sodium chloride for the calculation of v was taken from an earlier work¹⁶: $a_{25} = 5.62872 \pm 0.00003 \text{ kX}$. The parameters for the respective temperatures at which the densities were determined were computed using the expansion coefficient of sodium chloride⁶ at room temperature $\alpha = 40.5 \times 10^{-6}$. The data obtained are shown in Table 1. The output for the mean value of purest sodium chloride is 58.430 which is low by 0.024 or by 0.041% as compared with the chemical molecular weight 58.454. For silicon an average x -ray atomic weight of 28.083 was obtained,⁹ which is higher than the old chemical value of 28.06, but is lower by only 0.007 than the new atomic weight¹⁷ (28.09).

These discrepancies between the chemical and the x -ray molecular weights can be attributed to imperfections in the crystalline substances, or to experimental errors. In estimating these errors a choice can be made as to the two possibilities mentioned. However, some arbitrary factor f has to be introduced into the discussion that follows.

¹⁴ Du Mond, J. W. M., and Cohen, E. R., *Amer. Scient.*, **40**, 447, 458 (1952).

¹⁵ Wilks, S. S., *Statistical Analysis*, Princeton Univ. Press (1951), p. 36.

¹⁶ Straumanis M., and Ievinš, A., *Z. f. Physik*, **109**, 728, 736 (1938).

¹⁷ Wichers, E., *J.A.C.S.*, **74**, 2447 (1952).

SOUNDNESS OF SODIUM CHLORIDE CRYSTALS

The calculus method gives a good possibility for estimating the errors of more complicated measurements. The following equation was used for the calculation of the total error ΔM_x by which the *x*-ray molecular weight determinations (eq. 1) are affected:

$$\frac{\Delta M_x}{M} = \pm \left[\left(\frac{3\partial a}{a} f_1 \right)^2 + \left(\frac{\partial k}{k} f_2 \right)^2 + \left(\frac{\partial d}{d} f_3 \right)^2 \right]^{1/2} \quad (5)$$

n and N_s of equation (1) are constants; ∂a , ∂k , ∂d are the standard deviations of the separate measurements, $\partial a/a \dots$ are the relative errors, and f_1 , f_2 , f_3 are safety factors, each of them equal or larger than 1. The necessity of these factors follows from a consideration that relative errors are accidental or random errors; they reflect the quality of the measurements, but they do not contain the systematic error, which is undoubtedly in any measurement, and which may be even several times as large as the accidental error. It is the task of the investigator to estimate the value of the factor f for each kind of measurement, so that the systematic error becomes included in the deviation (e.g. $3\partial a f_1$).

It was assumed in the case of molecular weight determinations that

$$f_1 = f_2 = f_3 = 2,$$

would take care of the systematic errors. The equation as follows was obtained from eq. (5) for the total error (ΔM_x) of the molecular weight for both, silicon as well as sodium chloride:

$$\Delta M_x = \pm 2.8 \times 10^{-4} M. \quad (6)$$

It was assumed that

$$\frac{\partial a}{a} = 5.3 \times 10^{-6}; \quad \frac{\partial k}{k} = 3 \times 10^{-6}, \quad \text{and} \quad \frac{\partial d}{d} = 13.5 \times 10^{-6}.$$

The deviation ΔM_x may be called "standard absolute deviation."

The calculated error for the atomic weight of silicon according to eq. (6) is $\Delta M_x = \pm 0.008$. The *x*-ray-density weight is only 0.007 lower than the chemical value, and is, therefore, completely within the error limits calculated. Thus we can not come to a conclusion on the soundness of silicon crystals, and at present have to assume that the crystals do not contain any vacancies, or interstitial atoms.¹³ The structure of silicon is sound within the errors of observation, but it is quite evident that eq. (1) can be used for checking the correctness of chemical atomic weights.

While the computed error (eq. 6) for sodium chloride is $\Delta M_x = \pm 0.016$, the difference in *x*-ray and chemical molecular weights is -0.024 . As this difference considerably exceeds the above error of determination, we have to conclude that there are vacant sites in sodium chloride.¹³

The number of vacant sites per cm^3 can be easily computed, as the missing fraction of sodium chloride in the form of holes is about $0.024/58.5 = 4.1 \times 10^{-4}$ mole. Knowing the density, and Avogadro's number, 9.1×10^{18} vacant sites/ cm^3 were found, assuming that each of these sites can be filled by only one ion. The error of the x -ray molecular weight determination is ± 0.016 . If the weight were higher by this quantity, a minimum of 3.0×10^{18} vacancies/ cm^3 at room temperature would be obtained. These concentrations of vacancies of approximately 1:2500 ions or of 1:7300 appear rather high, and it is important to check this result by other independent measurements.

This was possible because a theory of lattice defects has been developed by Schottky¹⁸ and Wagner¹⁹ in order to explain several qualities of crystals, e.g. the electrical conductivity of silver and alkali halides. Wagner and associates showed how to determine the number of vacant sites from conductivity measurements^{19,20}. Seitz²¹ estimated the number of defects in evaporated sodium chloride layers as being 10^{18} per cm^3 , and in metals such as copper in the vicinity of 10^{18} to 10^{19} per cm^3 at the melting point.²² Further determinations were made by Etzel and Maurer,²³ finding the concentration of positive ion vacancies of a pure sodium chloride crystal as being 1.0×10^{17} per cm^3 at temperatures below 550°C . From measurements of dielectric constants Breckenridge computed that there are 2.1×10^{17} vacancies/ cm^3 in sodium chloride at 85°C .²⁴

Thus all these measurements and estimations show that the value of 9.1 or 3.0×10^{18} vacancies cm^{-3} determined for sodium chloride is very reasonable. Thereby the result obtained by the x -ray density method is a completely different, but a direct method.

The still existing difference may be explained by the fact that the conductivity methods detect only those vacancies which take part in the conductivity process. If, because of certain conditions, larger holes are formed, they contribute only partly to the total conductivity of the crystal. But the x -ray-density method detects all the holes, the small vacant sites as well as the submicroscopic cavities, and cracks, if they are inaccessible to the heavy liquid.

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¹⁸ Schottky, W., *Z. phys. Chem.* (B) **29**, 335 (1935); *Z. Elektroch.*, **43**, 33 (1939).

¹⁹ Koch, E., and Wagner, C., *Z. phys. Chem.*, (B) **38**, 295 (1937).

²⁰ Wagner, C., and Hantelmann, P., *J. Chem. Phys.*, **18**, 72 (1950).

²¹ Seitz, F., *Rev. Mod. Phys.*, **18**, 384 (1946); **23**, 328, 335, 336 (1951).

²² Seitz, F., *Phys. Rev.*, **79**, 890 (1950).

²³ Etzel, H. W., and Maurer, R. J., *J. Chem. Phys.* **18**, 1003 (1950).

²⁴ Breckenridge, R. G., *J. Chem. Phys.*, **16**, 959, 966 (1948).