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 \( d = 4.25 \text{ g. cm}^{-3} \) 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 \( 3 \times 10^{-4} \text{ g. cm}^{-3} \), 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\( ^\circ \) C. was determined to 2.1638 \( \pm \) 0.0003 g. cm\(^{-3} \). The x-ray molecular weight was then 58.430 \( \pm \) 0.010, lower by 0.024 than the chemical weight. Therefore, NaCl contains vacant sites of at least \( 3.0 \times 10^{14} \) 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 \( d = 4.25 \text{ g. cm}^{-3} \). By this method Bearden obtained one of the best density values for the diamond.\(^3\) Johnston and Hutchison improved the density determination\(^4\) and obtained very precise values for lithium fluoride, sodium and potassium chlorides.\(^4\)

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.


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


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.
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
daerated water. The volume did not change very much with tempera-
ture:

<table>
<thead>
<tr>
<th>Temp. °C.</th>
<th>25°.0</th>
<th>30°.0</th>
<th>35°.0</th>
<th>40°.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume in cm.³</td>
<td>4.76847</td>
<td>4.76870</td>
<td>4.76897</td>
<td>4.76930</td>
</tr>
</tbody>
</table>

The volume of the pycnometer for intermediate temperatures was ob-
tained by interpolation. The temperature readings (accuracy ± 0.01°)
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. Immedi-
ately 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 neces-
sary, was also provided. The pycnometer was immersed in the water,
as shown in Figs. 1A and 2, and the uniformity of the temperature dis-
tribution 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 pyc-
nometer was done with the aid of a magnifying glass (Fig. 2). It was as-
sumed 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.
Density Determination by a Modified Suspension Method

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°C in air.

The heavy liquid used was bromoform. 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,

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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:

$$d_t = d_o [1 + \alpha(t_2 - t_1)]$$

$\alpha$ is the expansion coefficient of sodium chloride $40.5 \times 10^{-6}$ at room temperature, as determined from x-ray measurements. The table shows that the maximum deviation from the average density value is $\pm 0.0004$ g. cm.$^{-3}$. The standard deviation of the present measurements and the mean deviation is between $\pm 0.0002$ 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 Hutchison\(^7\)( $d_{20} = 2.16360 \pm 0.00003$ 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% carbon\(^8\) were made. The accuracy of determination was approximately the same.

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as in the previous case, at least \( \pm 3 \times 10^{-4} \) g. cm.\(^{-3}\) For silicon an average value \( d_s = 2.32831 \) 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 used\(^2\):

\[
M_x = kN_avd/n \quad \text{g/mole} \quad (1)
\]

where \( N_a \) is Siegbahn’s Avogadro number \( (6.0594 \times 10^{23}) \), \( v \) is the volume of the unit cell \( (\text{in kX}^3 \times 10^{-24}) \), \( d \) is the density \( (\text{g. cm.}^{-3}) \), and \( n \) the number of molecules per unit cell. \( k \) is a correction factor which eliminates the errors that were made determining \( N_a \) and the wavelengths. The necessity of such a factor for exact molecular weight calculations was previously emphasized by the author in 1944.\(^3\) 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 crystal\(^10\) 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 Zei.t. 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\(^13,13a\):


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

1.00202 being the conversion factor \( \lambda_0/\lambda_c \), 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)\(^{14}\):

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

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 Å units:

\[ M_x = N_0v^1d/n, \quad \text{and} \quad d_x = nM/N_0v^1 = nM/kvN. \quad (4) \]

\( v^1 \) is the volume of the unit cell in Å\(^3\) \times 10\(^{-24} \) (\( v \) is in kX\(^2 \)). 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 work\(^{16}\): \( a_{56} = 5.62872 \pm 0.00003 \) kX. The parameters for the respective temperatures at which the densities were determined were computed using the expansion coefficient of sodium chloride\(^6\) 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 weight\(^{17}\) (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.

\(^{17}\) 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 \( \Delta M \) by which the x-ray molecular weight determinations (eq. 1) are affected:

\[
\frac{\Delta M}{M} = \pm \left[ \left( \frac{3 \sigma_a}{a} f_1 \right)^2 + \left( \frac{\sigma_k}{k} f_2 \right)^2 + \left( \frac{\sigma_d}{d} f_3 \right)^2 \right]^{1/2}
\]

\( n \) and \( N_e \) of equation (1) are constants; \( \sigma_a, \sigma_k, \sigma_d \) are the standard deviations of the separate measurements, \( \sigma_a/a \ldots \) 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. \( 3 \sigma_a f_1 \)).

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 (\( \Delta M \)) of the molecular weight for both, silicon as well as sodium chloride:

\[
\Delta M = \pm 2.8 \times 10^{-5} M.
\]

It was assumed that

\[
\frac{\sigma_a}{a} = 5.3 \times 10^{-6}; \quad \frac{\sigma_k}{k} = 3 \times 10^{-6}, \quad \text{and} \quad \frac{\sigma_d}{d} = 13.5 \times 10^{-6}.
\]

The deviation \( \Delta M \) may be called "standard absolute deviation."

The calculated error for the atomic weight of silicon according to eq. (6) is \( \Delta M = \pm 0.008 \). 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 \( \Delta M = \pm 0.016 \), 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 × 10⁻⁴ mole. Knowing the density, and Avogadro’s number, 9.1 × 10¹⁸ 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 × 10¹⁸ 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 measurements¹⁹,²⁰. Seitz²¹ estimated the number of defects in evaporated sodium chloride layers as being 10¹⁵ per cm.³, and in metals such as copper in the vicinity of 10¹⁵ to 10¹⁶ 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 × 10¹⁷ per cm.³ at temperatures below 550° C. From measurements of dielectric constants Breckenridge computed that there are 2.1 × 10¹⁷ 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 × 10¹⁸ 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).
²¹ Seitz, F., Rev. Mod. Phys., 18, 384 (1946); 23, 328, 335, 336 (1951).