THE SPECIFIC GRAVITY OF SODIUM CHLORIDE SOLUTIONS.

By H. C. Hahn.

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THE specific gravity and expansion by heat of salt solutions have not received the attention of chemists and physicists to the extent which they deserve. The data for common salt, for example, are only sufficient for technical purposes.

To the best known determinations of the specific gravity of sodium chloride solutions belong those of J. A. Bischof, G. Karsten, and G. T. Gerlach. Since the publication by Bischof in 1810, so many improvements in physical apparatus and more exact determinations of certain necessary factors, have been made, that we need not take his determinations into consideration. Those of G. Karsten, in 1846, show extraordinary diligence. His method is to weigh a glass ball in a salt solution, which stands in a large vessel full of water to be heated gradually. In this method there is danger of the one beam of the balance getting warmer than the other by the ascending current of heated air from the lamp and the hot water. Nevertheless, his method is the best, if modified as explained below. Further, Karsten did not determine the coefficient of expansion of his glass ball, but used the one determined by Munke, which is not admissible in very exact determinations. He does not state that the degrees of the mercurial thermometer were corrected to those of the air thermometer; nor that in calculating the weight of the weights and the glass ball in the vacuum, he took into consideration the amount of water and carbon dioxide in the air. The determinations by Gerlach[1] are the best; but some of the same and some other objections have to be raised against them. He did not determine the coefficient of expansion of his pycnometer, but used the one of Dulong and Petit. Reducing the weights to the vacuum, he assumed the atmosphere to have been saturated with water, which very probably was not the case. He compared the different specific gravities with that of water of 15°, instead of with that of 4°. He did not correct the degrees of the mercurial thermometer, and

[1] Spec. Gewichte der gebräuchlichsten Salzlösungen von verschiedenen Concentrationsgraden, Freiberg, 1859.

instead of calculating a formula for each series of determinations, he calculated the specific gravities of the solutions of certain percentages by interpolation from the two nearest determinations. Some of these defects may yet be corrected. This I have done and give in the following the details with different methods to eliminate errors.

Sodium chloride. Per cent.	Sp. gr. at 15° of mercurial thermometer compared with water of 15°. 1.	Sp. gr. at 15.08° of air thermometer compared with water of 4°. 2.
0	1.000 00	0.999 12
5	1.036 24	1.035 33
10	1.073 35	1.072 40
15	1.111 46	1.110 48
20	1.151 07	1.150 05
25	1.192 28	1.191 23
Saturated at 15°	1.204 33	1.203 27

For the numbers in column 1 different formulas may be calculated, according to the number of figures used. To the values for five, ten, twenty, and twenty-five per cent. corresponds the formula:

$$s = 0.999{,}03 + 0.007{,}203p + 0.000{,}009{,}4p^2 + 0.000{,}000{,}4p^3,$$

when s signifies the specific gravity and p the per cent. of sodium chloride. But the values for naught and fifteen per cent., as calculated by this formula, would be: 0.999,03 and 1.110,54, which are slightly erroneous.

A formula calculated according to the method of least squares, with the use of the 4th power is:

$$s = 0.999{,}12 + 0.007{,}072{,}54p + 0.000{,}024{,}206{,}76p^2,$$

which gives the values of column 3. The sum of least squares is 0.000,000,175.

3.	4.
0.999,12	0.999,12
1.035,09	1.035,12
1.072,26	1.072,30
1.110,65	1.110,69
1.150,25	1.150,27
1.191,06	1.191,04

The differences of the observed and calculated values are larger than of those obtained by the foregoing formula. I calculated therefore another one with the use of the 5th and 6th power:

$$s = 0.999,12 + 0.007,079,96p + 0.000,023,844,27p^2 + 0.000,000,001,002,876p^3,$$

which gives the numbers in column 4, with the sum of least squares = 0.000,000,177,6, which is no improvement on the former formula.

As a specimen of such calculations, I give here the items for the last formula:

$$\begin{aligned}
&s. \\
0.999,12 &= a \\
1.035,33 &= a + 5x + 5^2y + 5^3z \\
1.072,40 &= a + 10x + 10^2y + 10^3z \\
1.110,48 &= a + 15x + 15^2y + 15^3z \\
1.150,05 &= a + 20x + 20^2y + 20^3z \\
1.191,23 &= a + 25x + 25^2y + 25^3z
\end{aligned}$$

p^2.	p^3.	p^4.	p^5.	p^6.
25	125	625	3,125	15,625
100	1,000	10,000	100,000	1,100,000
225	3,375	50,625	759,375	11,390,625
400	8,000	160,000	3,200,000	64,000,000
625	15,625	390,625	9,765,625	244,140,625
1375	28,125	611,975	13,828,125	320,546,875

$p(s-a)$.	$p^2(s-a)$.	$p^3(s-a)$.
0.181,05	0.905,25	4.526,25
0.732,80	7.328,00	73.280,00
1.670,40	25.056,00	375.840,00
3.018,60	60.372,00	1,207.440,00
4.802,75	120.068,70	3,001.718,00
10.405,60	213.729,95	4,622.804,25

According to the method of least squares, we have the following equations:

$$\begin{aligned}
p(s-a) &= p^2x + p^3y + p^4z \\
p^2(s-a) &= p^3x + p^4y + p^5z \\
p^3(s-a) &= p^4x + p^5y + p^6z
\end{aligned}$$

Substituting into these equations the values obtained above, they become:

$$\begin{aligned}
10.405,60 &= 1,375x + 28,125y + 611,975z \\
213.729,95 &= 28,125x + 611,975y + 13,828,125z \\
4,662.804,25 &= 611,975x + 13,828,125y + 320,546,875z
\end{aligned}$$

which further developed give the last formula mentioned above.

Another method is to calculate series of differences of the numbers of the main series. The method is only applicable if the values of p rise or fall in an arithmetical proportion.

The series 2 above gives the following series of differences :

0.999,12				
1.035,33	3621			
1.072,40	3707	86		
1.110,48	3808	105	15	Average.
1.150,05	3957	149	48	25
1.191,23	4118	161	12	

Since each arithmetical series of the nth degree gives n, and only n series of differences, we know at once to which degree the desired formula belongs.

In reconstructing the main series and the series of differences backward, from the first member of the series, *i. e.*, 3621, 86, 25, we get the values given below in column 5.

If s is the first member of the main series, ds that of the first difference series, d_2s that of the second, etc., the nth member of the main series is :

$$S_n = s + (n - 1)\, ds + \frac{(n-1)(n-2)}{1 \times 2}\, d_2s + \frac{(n-1)(n-2)(n-3)}{1 \times 2 \times 3}\, d_3s.$$

The sixth member of the main series is therefore :

$$S_6 = s + 5ds + \frac{5 \times 4}{1 \times 2}\, d_2s + \frac{5 \times 4 \times 3}{1 \times 2 \times 3}\, d_3s.$$

If we substitute in this equation for ds the value 3620, the second member of the main series will be found to be too small by 1 ; the third by 2; the fourth by 3. If for d_2s we substitute 85, the third member will be too small by 1 ; the fourth by 3 ; the fifth by 6, and the sixth by 10. A similar result is obtained if for d_3s we substitute 24. By diminishing ds ($= 3621$) by 1, we get numbers which correspond best with those observed, with the sum of least squares equal to 0.000,000,000,54. They are given in column 6.

5.	6.			
0.999,12	0.999,12			
1.035,33	1.035,32	3620		
1.072,40	1.072,38	3706	86	
1.110,58	1,110,55	3817	111	25
1.150,12	1.150,08	3953	136	25
1.191,27	1.191,22	4114	161	25

To calculate a formula for the values of column 6, we have the following points to consider. The first member of the formula will be: 0.999,12, and the fourth equal to $\frac{0.00025}{1 \times 2 \times 3 \times 5^3}$ $= 0.000,000,333,333$. Any two values of the main series will give the second and third members of the formula, thus:

$$s = 0.999,12 + 0.007,1707 p + 0.000,0122 p^2 + 0.000,000,333,333 p^3.$$

It is generally believed that by the method of least squares formulas corresponding best with the observed values are obtained; but we see that the method of series of differences may give a better result. The above tables and formulas are not convenient in practice, in which generally the specific gravity is known and the per cent. of sodium chloride is sought. It is therefore necessary to construct another formula, corresponding to the reversed condition, for which purpose any four values of column 6 should be sufficient. But it was found impossible to construct out of four, or all six of the numbers, a formula of the third degree which would give exactly the values of column 6.

I calculated therefore from the last formula the per cent. of sodium chloride in a solution whose specific gravity is a little less than 1.00, and likewise the per cent. of sodium chloride in a solution whose specific gravity is a little more than 1.00; and similarly for the solutions of 1.05, 1.10, 1.15, 1.20, 1.25 specific gravities, and found by interpolation the per cent. correspond-ng to the desired specific gravity. For example:

				Specific gravity.
	0.1	sodium	chloride	= 0.999,84
	0.2	"	"	= 1.000,55
Difference	0.1	"	"	= 0.000,71

Therefore 0.077,46 per cent. sodium chloride = 0.000,55 specific gravity.

0.2 — 0.077,46 = 0.122,54 per cent. sodium chloride solution has the specific gravity of 1.00.

In this way the values of column 7 were obtained.

Specific gravity.		7. Per cent. sodium chloride.				
1.00	=	0.122,54				
1.05	=	6.995,95	6.873,41			
1.10	=	13.633,77	6.637,82	0.235,59		
1.15	=	19.990,12	6.356,35	0.281,47	0.045,88	
1.20	=	26.040,00	6.049,88	0.306,46	0.025,00	0.020,88
1.25	=	31.777,53	5.737,73	0.312,35	0.005,88	0.019,12

It is seen at once that with a trifling change a formula of the fourth degree can be calculated, whose second and fourth members are preceded by a minus sign, because the first and third series of differences are diminishing from top to bottom, and whose fifth member is: $\frac{0.02 \times 20^4}{1 \times 2 \times 3 \times 4} = 133,333,333.$

A minimum of changes is obtained if the third series of differences is made the following: 0.045,44, 0.025,44, 0.005,44, and hence we get the following main series:

8.				
0.122,485				
6.996,005	6.873,52			
13.633,715	6.637,71	0.235,81		
19.990,175	6.356,49	0.281,25	0.045,44	
26.039,945	6.049,77	0.306,69	0.025,44	0.02
31.777,585	5.737,64	0.312,13	0.005,44	0.02

from which the following formula is calculated:

$$\text{Per cent.} = 60.209,585 - 626.853,1s + 1067.352,667s^2 - 633.92s^3 + 133,333,333s^4,$$

which, if the specific gravity at 15.08° air thermometer is known exact to the fourth decimal, will give the per cent. of sodium chloride exact to 0.01.

Gerlach determined also the expansion by heat of different solutions of sodium chloride. I tried to find a formula for his values according to the method of least squares, with the help of the fifth power of the temperature; but the calculated values showed differences in the average of 0.000,33 (the largest was 0.000,62).

A main factor in determinations of specific gravity is the knowledge of the specific gravity of the air in the balance case, which depends on the barometric pressure, temperature, and its percentage of water and carbon dioxide. More exact than by calculation is the direct determination, which is made in the same manner as the determination of the specific gravity of the liquid itself. For this purpose I recommend the use of three solid gilded cylinders of pure aluminum of precisely the same weight. Cylinders are to be preferred to globes, and a metal is to be preferred to glass, because cylinders and metal acquire more quickly the temperature of the surrounding medium, and are more conveniently made of equal volume. Each cylinder should weigh at least twenty grams. Since the specific gravity of aluminum is 2.67, a cylinder of two cm. diameter and three cm. length weighs 25.16 grams in air, 9.42 grams in cold water, and 7.95 grams in a liquid of 1.25 specific gravity.

A balance, which indicates one-tenth milligram under a load of 25 grams, will indicate only about five-tenths to one milligram, if the cylinder to be weighed is immersed into a very heavy liquid, so that the weight, respectively loss of weight of a twenty-five gram cylinder in a liquid of 1.25 specific gravity, may be ascertained within the $\frac{0.001}{25} = 0.00004$ part of 1; therefore the specific gravity is correct within at least the fourth decimal.

Before gilding, a hook of platinum wire is fastened to the end of each cylinder. The exact equal weight being established, the cylinders are gilded. If the equality of the weight has been disturbed, it is restored by inverting the lighter cylinder for a short time again in the gold-bath.

After the weighing pans of the balance have been removed, a beaker with freshly distilled water is put under each end of the beam; and by the aid of thin platinum wire an aluminum cylinder is fastened on each of the hangers of the beam, so that the cylinders are immersed in the water. After a time sufficient for the cylinders to acquire the temperature of the water, and after ascertaining that the temperature of the latter is exactly the same in both beakers, it is observed whether the weights of the cylinders in water are equal or not. If there should be any slight difference, the lighter cylinder is transferred to the left side and the difference of the weights made up by a piece of thin platinum wire, to be attached to the hanger of the left-hand beam. The same operation is repeated with the third cylinder, after the removal of the cylinder on the left-hand side.

If this is satisfactorily accomplished, the beakers with water are removed and, when the temperature of the room is nearly 0°, two tumblers are procured, with ground rims and ground covers, the latter each containing in the center a hole of about five-tenths cm. diameter, and near the rim a hole to admit a thermometer, which has a cylindrical vessel, and is graduated on the stem. The one tumbler is filled partly with fused calcium chloride and caustic lime or potash; the other is nearly filled with cold distilled water. The first tumbler is put under the hanger of the left beam, and the other under that of the right-hand beam. After a time, sufficient for the cylinders and the water to acquire the temperature of the surrounding air ($t°$), the weight is read off. It is:

x = the weight of each aluminum cylinder in grams.

y = the volume of each aluminum cylinder in cc.

z = difference of weights, if one is immersed in pure air, the other in pure water.

z_1 = the same, reduced to the vacuum.

a = specific gravity of pure water at $t°$ (air thermometer) and h barometric pressure.

b = specific gravity of dry air at $t°$ (air thermometer), and h barometric pressure.

b_1 = specific gravity of the air at $t°$ (air thermometer) in the balance case.

c = specific gravity of the gilded weights at $t°$ (platinum weights are to be preferred).

Then $$x + ay - z_1 = x + by,$$

or $$\frac{z_1}{a - b} = y \qquad (1)$$

Further $$z_1 = z + z\frac{b_1}{c}$$

or $$z_1 = \frac{z(c + b_1)}{c} \qquad (2)$$

If this value of z_1 is substituted in equation 1, we get: $y = \frac{z(c+b_1)}{c(a-b)}$. The same operation is repeated at about 25°, 50°, and 75°. In the latter two instances the temperatures of the water and air will, of course, differ considerably. From the values ob tained, a table is calculated of the volumes of the aluminum cylinders for each degree of the air thermometer from 0° to 100°.

To ascertain the specific gravity of the air in the balance case at the time, when it is intended to determine the specific gravity of a liquid, the tumbler with pure water and thermometer is put under the left hanger of the balance, the cylinders hooked to the hangers of the beam, the one immersed in the water, the other in the air. After a time, sufficient for the water to have acquired the temperature of the air, the weight is read off. We have then:

$$x + ay - z_1 = x + b_1 y;\ \text{or}\ a - \frac{z(c+b_1)}{cy} = b_1.$$

Substituting for b_1 on the left side repeatedly the value $a - \frac{z(c+b_1)}{cy}$, we get:

$$a - \frac{z}{y} - \frac{za}{cy} + \frac{z^2(c+a)}{c^2y^2} - \frac{z^3(c+a)}{c^3y^3} + \frac{z^4(c+a)}{c^4y^4} - \frac{z^5}{c^5y^5} = b_1;$$

i. e., the specific gravity of the air, if that of the water is assumed to be 1.00. If $t°$ is not 4.1° C., b_1 has to be divided by a and the formula becomes:

$$1 + \frac{\left(\frac{z^2(c+a)}{c^2y^2} + \frac{z^4(c+a)}{c^4y^4}\right) - \left(\frac{z}{y} + \frac{za}{cy} + \frac{z^3(c+a)}{c^3y^3} + \frac{z^5}{c^5y^5}\right)}{a} = b_1$$

The aluminum cylinder on the right hand is thence removed and the tumblers with the liquid to be examined, into which the third cylinder and a thermometer had already been immersed, is put in its place, the cylinder hooked to the hanger, and the weight ascertained.

If the specific gravity of a liquid at a high temperature is to be determined (*i. e.*, the expansion coefficient), a hole directly underneath the hanger of the right-hand beam passes through the upper and lower bottoms of the balance case and also through the table. Through this hole passes a platinum wire connected with the one cylinder hanging in the beaker, containing the liquid, on a water-bath over a Bunsen burner.

When the liquid in the beaker has about the desired temperature, the lamp is extinguished and the weight of the cylinder ascertained.

Now the thermometer is read off again and the weight again ascertained. If the temperature has risen in the meantime the operation is repeated, till the weight is less than at the first reading. The averages of all temperatures and of all weights are taken and used for the computation.

A SHORT STUDY OF METHODS FOR THE ESTIMATION OF SULPHUR IN COAL.[1]

By G. L. Heath.

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As manufacturer's requirements with regard to certain metallurgical processes become more exacting from year to year, the determination of sulphur in the fuel must become more important. The interest taken in this subject is evidenced by the appointment of the committee from the society who have just made their preliminary report. The writer has been led, as a matter of interest, to communicate some experimental work upon the determination of sulphur.

There has been a little controversy, or doubt, as to the relative accuracy of the two "sintering" or "ignition" methods in general use as compared with each other, or with the old method of fusion with sodium carbonate and potassium nitrate. It must be assumed and understood that the following work was done rather to study methods and show precautions necessary, than to obtain close check results. This remark explains a discrepancy in results on one coal of very high sulphur content, since the methods which will now be described as used by the writer, were purposely not modified to suit that special case.

1. THE "FUSION" METHOD.

This is so well given in the text-books with so little variation that full description is unnecessary.[2] Blair's modifications used.

[1] Read at the meeting of the New York Section, June 3, 1898.

[2] Blair's Analysis of Iron, *1888*, p. 245.