

TABLE III.

The cubical coefficients of expansion of the following salts are found to be:

	70-50°.	50-25°.	25-0°.
NaCl <sup>1</sup> .....	0.000074	0.000106	0.000125
NaBr.....	.....	0.000119	0.000122
NaI.....	.....	0.000136	0.000135
KCl <sup>1</sup> .....	0.000083	0.000117	0.000084
KBr <sup>1</sup> .....	.....	0.000125	0.000112
KI <sup>1</sup> .....	.....	0.000114	0.000122
RbCl.....	.....	0.000082	0.000111
RbBr.....	.....	0.000101	0.000113
RbI.....	.....	0.000092	0.000112
CsCl.....	0.000109	0.000136	0.000137
CsBr.....	.....	0.000137	0.000141
CsI.....	.....	0.000146	0.000146

We are greatly indebted to the Carnegie Institution for very generous assistance in pursuing this investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

### THE DENSITIES AND CUBICAL COEFFICIENTS OF EXPANSION OF CERTAIN SUBSTANCES: $As_2O_3$ , $PbCl_2$ , $PbBr_2$ , $NdCl_3$ .

By GREGORY PAUL BAXTER AND CHARLES FRANCIS HAWKINS.

Received November 15, 1915.

Investigations now in progress or just completed in this laboratory have required an exact knowledge of the specific gravities of the compounds mentioned in the title, in order that, in weighing these substances, corrections for the buoyant effect of the air might be made with certainty. Since the experimental work was performed with considerable care, and since incidentally the cubical coefficients of expansion of three of these substances were found, the results are presented here by themselves.

The specific gravities were found by displacement of toluene in pycnometers, while the coefficients of expansion were computed from the specific gravities at different temperatures.

Two forms of pycnometer were employed. One was devised by Baxter and Hines<sup>2</sup> for experiments with very hygroscopic substances, and is a modification of a pycnometer described by T. W. Richards for the determination of the specific gravity of solids. A weighing bottle was provided with two glass stoppers, one of which was of ordinary shape and was used

<sup>1</sup> Fizeau, *Compt. rend.*, 64, 314 (1867), found the linear coefficients of expansion of sodium chloride and of potassium chloride, bromide, and iodide to have at 40° the values 0.000040, 0.000038, 0.000042 and 0.000043, whence the cubical coefficients of expansion may be calculated to be 0.000120, 0.000114, 0.000126 and 0.000129.

<sup>2</sup> *Am. Chem. J.*, 31, 220 (1904).

during the weighing of the substance. Into the other were sealed two capillary tubes which served to fill the bottle with liquid. The weighing bottle and the pycnometer stopper were both made of thick glass in order to avoid distortion when the stopper was inserted.

The salt, contained in a platinum boat, was fused in a suitable atmosphere in a quartz tube which was connected by a ground joint with a bottling apparatus, by means of which the boat, after being heated, could be transferred to the weighing bottle without exposure to moist air.<sup>1</sup> The salt was heated until fusion had taken place and the fused salt was limpid and free from bubbles of gas. The boat was then allowed to cool, and after the fusion atmosphere had been displaced by nitrogen, and the nitrogen in turn by dry air, the boat was transferred to the weighing bottle and weighed.

After the weighing of the salt, the ordinary stopper was removed, enough toluene to cover the boat and salt was quickly poured into the bottle, and the pycnometer stopper, which had been weighed with a small quantity of sirupy phosphoric acid to make the joint tight, was inserted. In order to expel the air contained in the crevices of the salt the pycnometer was placed in a vacuum desiccator, which was then exhausted, and the toluene was allowed to boil gently for some time with frequent jarring. By means of the capillary tubes the bottle was completely filled with toluene, and, while the pycnometer was immersed as far as possible in a water thermostat at 25°, the toluene was adjusted to a mark etched upon one of the capillaries. The weight of the system was then determined, after the pycnometer had been wiped with a clean, slightly moist cloth and had been allowed to stand in the balance case for a few moments. Prolonged standing in the balance case produced no difference in weight. After a second adjustment of the toluene the system was again weighed, and sometimes a third setting was made. In every case the weights agreed within a few tenths of a milligram. The weight of the pycnometer containing the empty boat and filled with toluene was determined several times. From the average of these weights, the weight of the salt, and the weight of the system including the salt and filled with toluene, the specific gravity of the salt was calculated.

The pycnometer described above was not adapted to determinations below the temperature of the room, since it had no reservoir for expansion of the liquid. For work both at 0° and at 50° a graduated flask was used as described by Baxter and Wallace.<sup>2</sup> The neck of this flask had been constricted at one point to 2.5 mm., which secured an accuracy in setting of about 0.3 mg. of toluene. Since comparatively large amounts

<sup>1</sup> Richards and Parker, *Proc. Am. Acad.*, **32**, 59 (1897).

<sup>2</sup> See preceding paper, *THIS JOURNAL*, **38**, 259 (1916).

of solid were used with this pycnometer the accuracy of setting was ample for the purpose.

Both pycnometers were "set" in water thermostats, the temperatures of which were controlled within a few hundredths of a degree, by means of toluene regulators at 25° and 50°, and by means of a large amount of washed cracked ice at 0°. The method of heating the water of the thermostat by passing a current through the water between carbon electrodes, as recently proposed by Derby,<sup>1</sup> was found to serve very satisfactorily at 50°. The thermometers were carefully corrected by comparison with a standard thermometer.

One specimen of arsenic trioxide was the commercial article, which was in the form of a fine powder. Another specimen was resublimed in a current of nitrogen by Mr. G. L. Wendt. As both were exposed to the air for some time before use they were probably octahedral.

Lead chloride was precipitated from lead nitrate and after washing was recrystallized from water. Finally it was fused in a current of hydrochloric acid gas. The fused material was irregular in appearance, and as the determinations with the bottle pycnometer gave discordant results, further experiments were made in the flask pycnometer with salt which, after fusion in hydrochloric acid, had been finely ground in an agate mortar. Since the latter experiments gave concordant results, which were somewhat higher than those obtained with the bottle pycnometer, it seemed highly probable that the latter were vitiated by pockets of gas in the fused material.

Lead bromide was precipitated from pure lead nitrate with hydrobromic acid, and was crystallized from concentrated hydrobromic acid solution before fusion in nitrogen containing hydrobromic acid gas. Determinations made with both pycnometers were concordant, although the material used in the flask pycnometer was finely powdered.

Praseodymium chloride was purified by Mr. O. J. Stewart and fused in a current of hydrochloric acid gas. Because of the hygroscopic nature of the anhydrous salt, determinations were made with the bottle pycnometer only, at 25°.

Toluene was dried over metallic sodium and distilled, the first and last portions being discarded. The specific gravities of the two specimens of the same sample of toluene were determined in both pycnometers.

Weights were carefully standardized to tenths of a milligram. Vacuum corrections are applied as follows:

Toluene.....	+0.00125
As <sub>2</sub> O <sub>3</sub> .....	+0.000166
PbCl <sub>2</sub> .....	+0.000059
PbBr <sub>2</sub> .....	+0.000035
NdCl <sub>3</sub> .....	+0.000154

<sup>1</sup> THIS JOURNAL, 35, 1767 (1913).

The assumption is made that an "apparent" gram of water occupies, 1.01313 cc. at 50°, 1.00400 cc. at 25°, 1.00119 cc. at 0°.

Specific Gravity and Coefficient of Expansion of Toluene.

Sample of toluene.	Temp.	Pycnometer.	Apparent wt. of H <sub>2</sub> O content. Grams.	Volume. cc.	Wt. of toluene in vac. Grams.	Spec. grav.	Coefficient of expansion. <sup>1</sup>
I....	50°	Flask	24.3408	24.6605	20.6566	0.83764	(50-25°)
	25°	Flask	24.5442	24.6424	21.2232	0.86125	0.000111 (25-0°)
	0°	Flask	24.5991	24.6283	21.7806	0.88437	0.000106
II....	25°	Bottle	11.2314	11.2763	9.7123	0.86130	.....
	50°	Flask	24.3408	24.6605	20.6561	0.83762	(50-25°)
	25°	Flask	24.5454	24.6436	21.2238	0.86123	0.000111 (25-0°)
	0°	Flask	24.5991	24.6283	21.7797	0.88433	
	25°	Bottle	11.2332	11.2781	9.7130	0.86123	0.000106

Specific Gravity and Cubical Coefficient of Expansion of As<sub>2</sub>O<sub>3</sub>.<sup>2</sup>

Temp.	Pycnometer.	Wt. of As <sub>2</sub> O <sub>3</sub> in vacuum. Grams.	Wt. toluene displaced in vac. Grams.	Sp. gr. toluene.	Sp. gr. As <sub>2</sub> O <sub>3</sub> .	Cubical coeff. expansion of As <sub>2</sub> O <sub>3</sub> .
25°	Flask	17.5146	3.9013	0.86125	3.867	(50-25°)
50°	Flask	27.0732	5.8881	0.83764	3.851	0.00012
25°	Flask	27.0732	6.0350	0.86125	3.863	(25-0°)
0°	Flask	27.0732	6.1802	0.88437	3.874	0.00011

<sup>1</sup> The values given in this column agree almost exactly with those found for Samples II and III in the preceding paper.

<sup>2</sup> Previous determinations:

- 3.695 octahedral } Guibourt, *Berz. Jahresb.*, 7, 128 (1828).
- 3.739 amorphous }
- 3.729 at 17.2°. Herapath, *Phil. Mag.*, 64, 321 (1829).
- 3.703 } Karsten, *Schweig. J.*, 65, 394 (1832).
- 3.720 }
- 3.884 Filhol, *Ann. chim. phys.*, [3] 21, 415 (1847).
- 3.798 Taylor, *Gmelin's Handb.*, 1, 69 (1848).
- 3.698 vitreous, LeRoyet and Dumas, *Ibid.*
- 3.85 native, Claudet, *Jahresb.*, 21, 230 (1868).
- 3.80 regular } Rammelsberg, "Handb. d. Krystallog. u. phys. Chem.,"
- 4.00 rhombic } Abt. I, 1881.
- 3.682 amorphous } Winkler, *J. prakt. Chem.*, 31, 247 (1884).
- 3.643 crystalline }
- 3.70 Leonhard, Clarke's "Const. of Nature," Pt. I, 48 (1888).

Specific Gravity and Cubical Coefficient of Expansion of  $\text{PbCl}_2$ .<sup>1</sup>

Temp.	Pycnometer.	Wt. $\text{PbCl}_2$ in vac. Grams.	Wt. toluene dis- placed in vac. Grams.	Sp. gr. toluene.	Sp. gr. $\text{PbCl}_2$ .	Cub. coeff. expansion of $\text{PbCl}_2$ .
25°	Bottle	5.3723	0.7960	0.86125	5.813	....
25°	Bottle	9.0828	1.3511	0.86125	5.790	....
25°	Bottle	7.3128	1.0922	0.86125	5.766	....
25°	Bottle	5.5365	0.8118	0.86125	5.874	....
25°	Bottle	6.6033	0.9791	0.86125	5.808	....
25°	Bottle	6.5749	0.9757	0.86125	5.804	....
25°	Bottle	6.2361	0.9222	0.86125	5.824	....
50°	Flask	32.0341	4.5697	0.83762	5.872	....
50°	Flask	25.7836	3.6774	0.83762	5.873	....
				Av.,	5.872	(50-25°)
25°	Flask	32.0341	4.6890	0.86123	5.884	0.00009
25°	Flask	25.7836	3.7727	0.86123	5.886	....
				Av.,	5.885	(25-0°)
0°	Flask	32.0341	4.8044	0.88433	5.896	0.00009
0°	Flask	25.7836	3.8642	0.88433	5.901	....
				Av.,	5.899	

Specific Gravity and Cubical Coefficient of Expansion of  $\text{PbBr}_2$ .<sup>2</sup>

Temp.	Pycnometer.	Wt. $\text{PbBr}_2$ in vac. Grams.	Wt. toluene dis- placed in vac. Grams.	Sp. gr. toluene.	Sp. gr. $\text{PbBr}_2$ .	Cub. coeff. expansion of $\text{PbBr}_2$ .
25°	Bottle	7.3694	0.9531	0.86125	6.659	....
25°	Bottle	6.9347	0.8984	0.86125	6.648	....
						(50-25°)
50°	Flask	23.1459	2.9171	0.83762	6.644	0.00009
25°	Flask	23.1459	2.9926	0.86123	6.659	(25-0°)
0°	Flask	23.1459	3.0651	0.88433	6.676	0.00010

Specific Gravity of  $\text{PrCl}_3$ .

Temp.	Pycnometer.	Wt. $\text{PrCl}_3$ in vac. Grams.	Wt. toluene dis- placed in vac. Gram.	Sp. gr. toluene.	Sp. gr. $\text{PrCl}_3$ .
25°	Bottle	3.6689	0.7862	0.8612	4.019
25°	Bottle	4.5130	0.9669	0.8612	4.020
				Av.,	4.020 <sup>3</sup>

<sup>1</sup> Previous determinations:

- 5.29 Munro, Clarke's "Constants of Nature," Pt. I, 24 (1888).  
 5.238 native, Dana, "Mineralogy," 1892.  
 5.802 unfused } Karsten, *Schweig. J.*, 65, 394 (1832).  
 5.682 fused }  
 5.802 cryst., Schabus, *Jahresb.*, 3, 322 (1850).  
 5.78 Schiff, Clarke's "Constants of Nature," *Loc. cit.*  
 5.805 15°, Stolba, *J. prakt. Chem.*, 97, 503 (1866).  
 5.88 Brugelmann, *Ber. d. deutsch chem. Gesell.*, 17, 2359 (1891).

<sup>2</sup> Previous determinations:

- 6.630 Karsten, *Schweig. J.*, 65, 394 (1832).  
 6.611 17.5°, Kremers, *Jahresb.*, 5, 397 (1852).  
 6.572 19.2° precipitated, Keck, Clarke's "Constants of Nature," Pt. I, 32 (1888).

<sup>3</sup> Matignon found the value 4.017 at 18°, *Compt. rend.*, 140, 340 (1905).

## SUMMARY.

Substance.	Temperature.	Specific gravity.	Cub. coeff. of expansion.
As <sub>2</sub> O <sub>3</sub> .....	50°	3.851	(50-25°)
	25°	3.865	0.00012 (25-0°)
	0°	3.874	0.00011
PbCl <sub>2</sub> .....	50°	5.872	(50-25°)
	25°	5.885	0.00009 (25-0°)
	0°	5.899	0.00009
PbBr <sub>2</sub> .....	50°	6.644	(50-25°)
	25°	5.669	0.00009 (25-0°)
	0°	6.676	0.00010
PrCl <sub>3</sub> .....	25°	4.020	

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO.]

### STUDIES IN CONDUCTIVITY. III. FURTHER STUDIES ON THE BEHAVIOR OF THE ALKALI METAL FORMATES IN (ANHYDROUS) FORMIC ACID.

BY H. I. SCHLESINGER AND CLYDE COLEMAN.<sup>1</sup>

Received December 4, 1915.

The work herein reported is a continuation of that of Schlesinger and Martin<sup>2</sup> on the conductivity of formic acid solutions of formates. It was shown by them that the formates of sodium, potassium, ammonium and phenyl ammonium obey *the law of chemical equilibrium* over a fairly large range of concentration *even though these salts are highly ionized*, provided that the degree of ionization is calculated without reference to the viscosity of the solutions. When a viscosity correction was made it was found that the agreement between the law and the experimental data disappeared. It was pointed out, however, that the viscosity data might have been somewhat inaccurate because a small viscometer of the Ostwald type was used. Hence it seemed necessary to repeat the viscosity determinations under more favorable experimental conditions. Furthermore, since the simple inverse proportionality between viscosity and conductivity, as predicted by Stokes' law does not usually fit experimental data on conductivity, information on the possible relation was sought by

<sup>1</sup> The work presented in this article constitutes the basis of a dissertation submitted by Clyde Coleman to the faculty of the University of Chicago in part fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> THIS JOURNAL, 36, 1589 (1914). We shall use the abbreviation S. and M. hereafter in referring to this paper.