3. No satisfactory explanation of the influence of the KI on the diffusion of iodine, is offered, though several possible explanations are considered.

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

THE DENSITIES AND CUBICAL COEFFICIENTS OF EXPANSION OF THE HALOGEN SALTS OF SODIUM, POTASSIUM, RUBIDIUM AND CESIUM.

BY GREGORY PAUL BAXTER AND CURTIS CLAYTON WALLACE.

Received November 15, 1915.

For purposes of computation in the preceding paper upon "Changes in Volume upon Solution in Water of the Halogen Salts of Alkalis" it was necessary to know the densities of the solid salts at different temperatures. Since neither these values nor the coefficients of expansion of the salts have been found with accuracy, the problem of determining the densities over the necessary range in temperature, and thus the coefficients of expansion, was undertaken.

The method employed was that of displacement of toluene. In order to reduce the effect of the errors of experiment, a very considerable quantity of salt was used. Furthermore, especial pains were taken, first in drying the salt, and second, in freeing it as far as possible from entangled air when immersed in toluene in the pycnometer.

The pycnometer itself, instead of being of the ordinary stoppered form for solids, was merely a 25 cc. graduated flask, the neck of which was very much constricted at one point to increase accuracy in adjusting the volume of its contents. The diameter of the constriction was about 2.5 mm. which secured an accuracy in setting of about 0.3 mg. of toluene. This form of pycnometer has the advantages, first that the ground surface is not wet with liquid and hence there is no difficulty from evaporation, second that the neck of the flask serves as a reservoir when used at low temperatures.

The volume of the flask at different temperatures was found by weighing it full of water after the liquid had been set at the mark in the thermostats used for finding the densities of the solutions in the preceding paper. The neck of the flask was dried before the meniscus was set. Preparatory to being weighed, the outside of the flask was washed with dilute ammonia solution, wiped with a clean, slightly damp, cotton coth, and was allowed to stand in the balance room for at least one hour. In order to find the densities of the different specimens of toluene, the flask was weighed after being filled with toluene at the temperatures used. No attempt was made to purify the toluene beyond drying it over metallic sodium for some time and distilling without fractionation. In computing the volumes of the flasks the assumption is made that an "apparent" gram of water occupies

1.02378 cc. at 70.19° 1.01315 cc. at 50.04° 1.00400 cc. at 25.00° 1.00119 cc. at 0.00°.

The weights were carefully standardized to tenths of a milligram and the thermometer readings were corrected by comparison with a standard thermometer as described in the preceding paper. The weights of toluene are corrected to the vacuum standard by adding 0.00126 g. for each gram of substance.

TABLE I.

Densities of Toluene Samples.

Temperatures.	70.19°.	50.04°.	25.00°.	0.00°.
Apparent wt. of water	24.3184	24.5605	24.7671	24.8186
Volume of flask I	24.8994	24.8838	24.8662	24.8482
Wt. of toluene I in vac	20.3888	20.8746	21.4661	22.0473
Density of toluene I ref. to water at 4°	0.81885	0.83888	0.86327	0.88728
Wt. of toluene II in vac	....	20.8488	21.4222	21.9848
Density of toluene II ref. to water at 4°	....	0.83784	0.86150	0.88477
Apparent wt. of water	48.407	48.892	49.299	49.406
Volume of flask II	49.563	49.535	49.495	49.465
Wt. of toluene III in vac	40.538	41.478	42.616	43.741
Density of toluene III ref. to water at 4°	0.81790	0.83734	0.87100	0.88428

Coefficients of Expansion of Flasks and Toluol.

Temperature interval.	70.19°–50.04°.	50.04°–25.00°.	25.00°–0.00°.
Flask I	$0.0_{4}31$	$0.0_{4}28$	$0.0_{4}29$
Flask II	$0.0_{4}35$	$0.0_{4}29$	$0.0_{4}28$
Toluene I	0.001198	0.001144	0.001098
Toluene II	....	0.001114	0.001066
Toluene III	0.001167	0.001113	0.001066

It is noticeable not only that the density of Sample I of toluene is markedly higher than those of the other two samples, but also that the coefficient of expansion of this sample is highest, although the change in coefficient of expansion with change in temperature is the same for all three samples.[1] The coefficients of expansion of the flasks are discussed in the preceding paper.

The salts[2] were purified as described in the preceding paper. In the case of potassium chloride, potassium iodide and rubidium iodide the specimens of salt used in the duplicate determinations were prepared at different times. They were thoroughly dried by fusion—the chlorides

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[1] In Landolt-Börnstein, *Tabellen*, 1912, the density of toluene at 0° referred to water at 4° is given as 0.8845 and its cubical coefficient of expansion at 20° as 0.001099. This value for the density corresponds closely to those found for Samples II and III but the above value for the cubical coefficient of expansion is almost identical with that found for Samples I.

[2] Professor H. L. Wells of Yale University very kindly loaned us very pure cesium material. See a preceding paper.

in platinum crucibles in air, the bromides and iodides in a platinum boat contained in a porcelain tube in a current of pure, dry electrolytic hydrogen. Portions of the fused salts after solution in water were found to give essentially neutral solutions.

Since, almost invariably, fused salts contain cavities, owing probably to contraction during cooling, all of the salts were ground in an agate mortar before use and the powdered material was again dried at 250° in an air-bath and preserved in a desiccator until used.

A series of experiments was carried out as follows: The dried salt was transferred to a clean, dry flask which was weighed with its contents. Toluene sufficient to cover the salt was then added and the flask was exhausted until the toluene boiled gently. The boiling was allowed to continue several moments in order to ensure removal of air from the interstices. Next the flask was nearly filled with toluene and brought to constant temperature in the thermostat, at the highest temperature employed. After it had been brought to room temperature, it was cleaned, dried and weighed as described above. The operations were then repeated at lower temperatures successively.

Vacuum corrections were computed from the densities as finally determined and are employed in the tables as follows:

NaCl	+ 0.00042	NaBr	+ 0.00025	NaI	+ 0.00019
KCl	+ 0.00046	KBr	+ 0.00030	KI	+ 0.00024
RbCl	+ 0.00029	RbBr	+ 0.00022	RbI	+ 0.00020
CsCl	+ 0.00016	CsBr	+ 0.00013	CsI	+ 0.00013

TABLE II.

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene ref. to H_2O at 4°.	Density of salt ref. to H_2O at 4°.	Cubical coeff. of expansion of salt.
NaCl[1]........	70.19°	8.6156	3.2782	0.81885	2.1521	
						0.000088
	50.04	...	3.3524	0.83888	2.1559	
						0.000103
	25.00	...	3.4410	0.86327	2.1615	
						0.000126
	0.00	...	3.5255	0.88728	2.1683	
	70.19	14.0885	5.3586	0.81885	2.1528	
						0.000060
	50.04	...	5.4830	0.83888	2.1554	
						0.000109
	25.00	...	5.6271	0.86327	2.1613	
						0.000124
	0.00	...	5.7659	0.88728	2.1680	

[1] Previous determinations of the densities of these salts are as follows:

NaCl:	Clarke, "Constants of Nature," 1873, I...........	...	2.06–2.16
	Retgers, *Z. physik. Chem.*, 3, 289 (1889)..........	17°	2.167
	Krickmeyer, *Ibid.*, 21, 53 (1896).................	20°/4°	2.174

TABLE II (*continued*).

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene ref. to H_2O at 4°.	Density of salt ref. to H_2O at 4°.	Cubical coeff. of expansion of salt.
NaBr[1]........	50.04	21.1619	5.5514	0.83784	3.1939	
						0.000119
	25.00	...	5.6910	0.86150	3.2034	
						0.000122
	0.00	...	5.8270	0.88477	3.2132	
NaI[2].........	50.04	16.5363	3.8217	0.83784	3.6253	
						0.000141
	25.00	...	3.9160	0.86150	3.6380	
						0.000132
	0.00	...	4.0081	0.88477	3.6499	
	50.04	26.7938	6.1686	0.83784	3.6387	
						0.000132
	25.00	...	6.3228	0.86150	3.6507	
						0.000137
	0.00	...	6.4715	0.88477	3.6631	
KCl[3].........	70.19	16.316	6.748	0.81790	1.9776	
						0.000083
	50.04	...	6.897	0.83734	1.9809	
						0.000139
	25.00	...	7.067	0.86100	1.9878	
						0.000084
	0.00	...	7.243	0.88428	1.9920	
	50.04	17.6589	7.4797	0.83888	1.9806	
						0.000116
	25.00	...	7.6752	0.86327	1.9863	
Crystals......	50.04	13.6465	5.7972	0.83888	1.9747	
						0.000096
	25.00	...	5.9515	0.86327	1.9794	
KBr[4].........	50.04	16.6637	5.0955	0.83784	2.7399	
						0.000125
	25.00	...	5.2231	0.86150	2.7485	
						0.000112

[1] NaBr:	Schiff, *Ann.*, **108**, 21 (1858).....................	...	2.952
	Kremers, *Jahresb.*, 10, 67 (1857).................	17.5°	3.079
	Tschermak, *Sitzungsb. d. k. Akad. Wien.*, **45**, 603..	...	3.011
	Favre and Valson, *Compt. rend.*, **77**, 579 (1873)....	17.3°	3.198
[2] NaI:	Schröder, *Ann.*, **192**, 295 (1878)................	...	3.55
	Filhol, *Ann. chim. phys.*, [3] **21**, 415 (1847).......	...	3.45
	Favre and Valson, *Loc. cit*.....................	18.2°	3.654
	Baxter and Brink, THIS JOURNAL, **30**, 46 (1908)...	25°/4°	3.665
[3] KCl:	Clarke, "Constants of Nature," **1888**, Part I......	..	1.836–1.995
	Retgers, *Loc. cit*............................	16°	1.989
	Krickmeyer, *Ibid*............................	20°/4°	1.994
	Buchanan, *Proc. Chem. Soc.*, **21**, 122 (1905).......	23.47°	1.951
	Johnston and Adams, THIS JOURNAL, **34**, 572 (1912) Finely powdered..........................	30°/4°	1.984
[4] KBr:	Karsten, *Schweig. Jour.*, **65**, 394 (1832)...........	..	2.415
	Playfair and Joule, *Mem. Chem. Soc.*, **2**, 401 (1845)	..	2.672

TABLE II (*continued*).

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene ref. to H_2O at 4°.	Density of salt ref. to H_2O at 4°.	Cubical coeff. of expansion of salt.
	0.00	...	5.3491	0.88477	2.7562	
KI............	50.04	17.3647	4.6717	0.83784	3.1142	
						0.000113
	25.00	...	4.7901	0.86150	3.1230	
						0.000120
	0.00	...	4.9046	0.88477	3.1324	
KI[1]...........	50.04	24.3342	6.5557	0.83888	3.1139	
						0.000115
	25.00	...	6.7266	0.86327	3.1229	
						0.000124
	0.00	...	6.8924	0.88728	3.1326	
RbCl[2].........	50.04	10.8005	3.2409	0.83784	2.7922	
						0.000082
	25.00	...	3.3255	0.86150	2.7979	
						0.000111
	0.00	...	3.4061	0.88477	2.8057	
RbBr[3].........	50.04	25.6918	6.4523	0.83888	3.3402	
						0.000101
	25.00	...	6.6232	0.86327	3.3486	
						0.000113
	0.00	...	6.7882	0.88728	3.3581	

	Beamer, Clarke's "Constants of Nature," **1888**, Part I....................................	12.7°	2.712
	Spring, *Ber.*, **16**, 2724 (1893).....................	18°	2.704
	Schröder, "Dichtigkeitsmessungen," Heidelberg, 1873	..	2.690
	Krickmeyer, *Loc. cit*.............................	20°/4°	2.756
	Buchanan, *Ibid*..................................	..	2.679
	Richards and Mueller, *Z. anorg. Chem.*, **53**, 423 (1907)....................................	25°/4°	2.73
[1] KI:	Boullay, *Ann. chim. phys.*, [2] **43**, 266 (1830).....	...	3.078–3.104
	Karsten, *Loc. cit*...............................	...	2.908
	Playfair and Joule, *Ibid*.......................	13°	3.048–3.070
	Filhol, *Ibid*..................................	...	3.056
	Schiff, *Ibid*..................................	...	2.850
	Buignet, *Jahresb.*, **14**, 15 (1861)...............	...	2.970
	Schröder, *Loc. cit*.............................	...	3.077–3.083
	Spring, *Ibid.*, fused...........................	20°	3.012–3.112
	Buchanan, *Loc. cit*.............................	23.4°	3.043
	Baxter and Brink, *Ibid*.........................	25°/4°	3.115
[2] RbCl:	Schröder, *Ibid*................................	22°	2.209
	Buchanan, *Ibid*................................	22.9°	2.706
	Archibald, *J. Chem. Soc.*, **85**, 776 (1904)..........	...	2.753
	Setterberg, *Oefvers Stockh. Förh.*, **39**, 23 (1882)....	...	2.807
[3] RbBr:	Schröder, *Loc. cit*.............................	...	2.780
	Setterberg, *Ibid*...............................	...	3.358
	Archibald, *Ibid*................................	...	3.282
	Buchanan, *Ibid*................................	23°	3.210

TABLE II (*continued*).

Salt.	Temp. ° C.	Wt. salt in vac. Grams.	Wt. toluene displaced in vac. Grams.	Density of toluene ref. to H_2O at 4°.	Density of salt ref. to H_2O at 4°.	Cubical coeff. of expansion of salt.
RbI[1]	50.04	12.8305	3.0397	0.83888	3.5409	
						0.000091
	25.00	...	3.1208	0.86327	3.5490	
						0.000121
	0.00	...	3.1980	0.88728	3.5598	
	50.04	24.2498	5.7348	0.83784	3.5429	
						0.000093
	25.00	...	5.8828	0.86150	3.5512	
						0.000103
	0.00	...	6.0259	0.88477	3.5604	
CsCl[2]	70.19	26.5871	5.5088	0.81885	3.9520	
						0.000109
	50.04	...	5.6311	0.83888	3.9607	
						0.000136
	25.00	...	5.7751	0.86327	3.9742	
						0.000143
	0.00	...	5.9147	0.88728	3.9884	
CsBr[3]	50.04	24.9973	4.7467	0.83888	4.4177	
						0.000137
	25.00	...	4.8680	0.86327	4.4329	
						0.000141
	0.00	...	4.9857	0.66728	4.4486	
CsI[4]	50.04	28.7568	5.3696	0.83888	4.4926	
						0.000146
	25.00	...	5.5056	0.86327	4.5090	
						0.000145
	0.00	...	5.6384	0.88728	4.5253	

As is to be expected from the greater care taken in preparing the salts free from moisture and from cavities, the foregoing density values tend to be higher than the results of earlier determinations, although it is by no means certain that the second difficulty was entirely eliminated. Most of the results need little comment. In the case of sodium iodide, on ac-

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[1] RbI:	Schröder, *Loc. cit.*	...	3.023
	Setterberg, *Ibid.*	...	3.567
	Erdmann, *Arch. Pharm.*, **232**, 25 (1894)	...	3.447
	Buchanan, *Loc. cit.*	24.3°	3.428
	Baxter and Brink, *Ibid.*	25°/4°	3.438
[2] CsCl:	Setterberg, *Ibid.*	...	3.992
	Richards and Archibald, *Proc. Am. Acad.*, **38**, 453 (1903)	20°/4°	3.972
	Buchanan, *Loc. cit.*	23.1°	3.982
[3] CsBr:	Setterberg, *Ibid.*	...	4.463
	Richards and Archibald, *Ibid.*	20°/4°	4.380
	Buchanan, *Ibid.*	21.4°	4.455
[4] CsI:	Setterberg, *Ibid.*	...	4.537
	Beketoff, *Bull. St. Petersb.*, **34**, 197 (1905)	...	4.523
	Buchanan, *Loc. cit.*	22.8°	4.508
	Baxter and Brink, *Ibid.*	25°/4°	4.510

count of the hygroscopicity of the anhydrous salt, the value for the density is less reliable than that found earlier by Baxter and Brink, who investigated salt which could not have come into contact wth moist air. The value for the coefficient of expansion of this salt found in this research is more accurate than the values of the density. Using the value 0.000136 for the coefficient of expansion of sodium iodide and the value 3.665, found by Baxter and Brink for the density at 25°, the density at 50° becomes 3.653 and that at 0° is 3.677. The first two sets of values with potassium chloride were obtained with powdered salt which had previously been fused, the third set with crystals from aqueous solution which had been carefully dried, powdered, and dried as in the experiments with fused salt. Apparently the salt crystallized from aqueous solution has a slightly lower density. Rubidium iodide is here found to have a density considerably higher than the value found by Baxter and Brink. But the latter did not use material of unquestionable purity, and since the material used here was found to be very pure, the later value is to be preferred.

The coefficients of expansion are of the order of magnitude to be expected from the rather meager data previously obtained with anhydrous salts.[1] It can be seen that with any one salt the coefficient of expansion is lower at high temperatures than at low temperatures. In general, chlorides show smallest and iodides largest coefficients, and, while this is by no means always the case, coefficients are usually higher with increasing density and increasing compressibility.

The results of the foregoing research may be summed up in the following brief tables:

TABLE II.

The densities of the following salts are found to be:

	70.19°.	50.04°.	25.00°.	0.00°.
NaCl..................	2.153	2.156	2.161	2.168
NaBr..................	..	3.194	3.203	3.213
NaI..................	..	3.653[2]	3.665[3]	3.677[2]
KCl..................	1.978	1.981	1.987	1.992
KBr..................	..	2.740	2.749	2.756
KI..................	..	3.114	3.123	3.133
RbCl..................	..	2.792	2.798	2.806
RbBr..................	..	3.340	3.349	3.358
RbI..................	..	3.542	3.550	3.560
CsCl..................	3.952	3.961	3.974	3.988
CsBr..................	..	4.418	4.433	4.449
CsI..................	..	4.493	4.509	4.525

[1] K_2SO_4.......... 0.0_3108 20°
Rb_2SO_4......... 0.0_3106 20° Landolt-Börnstein-Roth, *Tabellen*, 1912.
Cs_2SO_4......... 0.0_3105 20°
KNO_3.......... 0.0_3191 20°

[2] Computed from the coefficient of expansion.

[3] Baxter and Brink, *Loc. cit.*

TABLE III.

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

	70–50°.	50–25°.	25–0°.
NaCl[1]	0.000074	0.000106	0.000125
NaBr	....	0.000119	0.000122
NaI	....	0.000136	0.000135
KCl[1]	0.000083	0.000117	0.000084
KBr[1]	....	0.000125	0.000112
KI[1]	....	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.

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[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.

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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[2] 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

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[1] 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.

[2] *Am. Chem. J.*, **31**, 220 (1904).