hoped that the colloidal tungstic acid can be prepared in the near future and its stability studied.

Conclusions. The electrical conductivity appeared to be the best property to use in studying the stability or instability of these salts. Knorre followed the transformation of a paratungstate by titration. But this changes the composition of the mixtures and may lead to doubtful results. The refractometer was not applicable because of the great dilution of the solutions. The results so far obtained are chiefly valuable in indicating the *rate* of change of the tungstates in question. Assuming that the transformation products may be new salts or mixtures of several known salts, it is obvious that these solutions will only possess properties characteristic of the salts taken when freshly made up, and certainly not after prolonged boiling. The effect of a transformation has been overlooked especially in solubility determinations. For example, Marignac stated that the solubility of ammonium paratungstate was still slowly increasing even at the end of a year. His final result is obviously too high as are also probably those in the case of the other paratungstates.[1]

The conductivity data so far obtained are insufficient to decide whether the transformation consists in the addition or rearrangement of water, a hydrolytic dissociation, or a decomposition of one salt into a mixture of two others, as suggested by Knorre. The data at hand are submitted for the benefit of others at work upon similar problems; and as rapidly as possible further conductivity data will be collected upon metatungstic acid and its salts. The possibility of these salts being partly hydrogen or acid salts is being considered, and it is hoped that before long the tungstates can be classified as simply as the phosphates.

UNIVERSITY OF PENNSYLVANIA, 1906.

DENSITIES OF LITHIUM, SODIUM, POTASSIUM, RUBIDIUM AND CAESIUM

BY THEODORE WILLIAM RICHARDS AND FRANCIS NEWTON BRINK
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The densities of the alkali metals are of especial interest for several reasons. In the first place, they include the lowest of all the metallic densities; in the next place, the highest members of this series of elements have the largest atomic volumes of all solid substances, each of the metals forming a cusp in the atomic volume curve. Again, these are the most compressible of metals, and have the largest coefficients of expansion; two properties which are closely concerned with volume, and, therefore, with density.

[1] Cf. Taylor, loc. cit.

Many determinations of the densities of these metals have been made in the past by various investigators,[1] but oddly enough there appears to be no published statement of any investigation concerning the density of lithium since it was first investigated by Bunsen fifty years ago. This is the more remarkable because lithium, being the lightest of all metals, would naturally be supposed to have been the object of considerable interest in this respect.

The attention of one of the present writers was called to this matter some years ago on account of a series of investigations upon the significance of atomic volume and atomic compressibility. In the course of the determinations of the compressibility of lithium, it became important to know the precise density of the sample in hand, and accordingly, this was determined with great care by the method of floating. The determination led to a surprising result, indicating a density nearly ten per cent. less than that given by Bunsen. So large an error naturally led to the suspicion that Bunsen's lithium was impure, the admixture of almost any substance in so light a material tending to cause an excessive density.

This inference led to a further suspicion concerning the results for most of the other alkali metals, as these results are by no means consistent with one another, and usually not accompanied with any descriptions of analytical tests, or proofs of the purity of the material used. Obviously the whole matter needed a systematic and careful revision, as indeed is the case with most of the recorded data concerning densities. The investigation was undertaken not merely as a matter of curiosity with regard to these light metals, but rather primarily to afford accurate data for theoretical inference concerning the significance of changing atomic volume.

Method of Determination.—In the following investigation, the method of floating, devised in the first place by Davy in 1808 for determining the specific gravity of sodium, was used in the cases of all the alkali metals with the exception of caesium. He mixed a heavy and light liquid until he obtained a mixture in which pieces of sodium neither rose nor sank, but remained suspended within the body of the liquid. It only remained then to determine the specific gravity of the liquid.

In this method there are two sources of error. First, because the oxides of these metals are more dense than the metals themselves, the presence of any oxide raises the specific gravity. Second, any action of the metals on the solution by which a gas is evolved has the opposite effect, because of adhering bubbles. These tendencies tend to counterbalance one another, but it is by no means safe to allow them to come into play with that expectation.

[1] For details see Landolt-Börnstein, Meyerhoffer, Physiche-Chemische Tabellen, 3d ed., p. 224.

It became, therefore, a matter of importance to find two liquids of suitable densities which could be used for this purpose. In the case of sodium, Davy used oil of sassafras and kerosene. Experimentation, however, with oil of sassafras showed that its use was entirely out of the question, since it gave with sodium a bluish green precipitate and the sodium itself became covered with a layer of the same substance. The oil gradually became dark brown in color and finally opaque.

Several other liquids were tried and found wanting. The liquids finally decided upon for this work were liquid paraffin oil and carbon tetrachloride. The paraffin oil was obtained from rectified Pennsylvania kerosene, rejecting all boiling below 150° or above 250°. These liquids were used in all the determinations made by the floating method. They were distilled over and kept in contact with sodium until all moisture was removed and there was evidence of no further action of the sodium on the liquids. In the case of the carbon tetrachloride, this required some time, but finally a point was reached where the sodium could be kept in the liquid for a sufficient length of time without appreciably losing its bright metallic lustre.

The determinations were carried out at 20° in a carefully regulated thermostat. A small piece of the metal after being pressed, and cut under oil until wholly bright, was placed in a large test-tube containing the paraffin oil, and carbon tetrachloride was added until the metal rose and remained suspended within the body of the liquid. Fresh pieces of metal were added from time to time so as to find the specific gravity of a fresh piece rather than that of one which had been in the liquid for some time. The pieces were examined with especial care for minute bubbles, whose combined effect may be very considerable. The liquid, of course, should be well stirred to insure uniform density throughout. Owing to the volatility of the carbon tetrachloride, the Ostwald pycnometers, used for determining the density of the mixture, were fitted with ground glass caps. All weights were reduced to the vacuum standard.

Because it was impossible to find a liquid in which lithium would not float, weighed pieces of platinum wire were wound around weighed pieces of lithium, and each of these different combinations was investigated as if it had been a piece of heavier metal.

Caesium was investigated in a pycnometer for solids because no heavy liquid seems to exist upon which it will not act. Paraffin oil was used as the liquid to be displaced.

Other details will be discussed under the headings of the respective metals.

Lithium.--The lithium used was the purest preparation of a German firm. Spectroscopic tests revealed no sodium or potassium, and qualitative analysis discovered only iron and aluminum. For quantitative

analysis 0.41 gram was dissolved in alcohol. After oxidation it yielded 0.0028 gram of mixed ferric and aluminic oxides, of which 0.0008 was shown by titration to be ferric oxide, leaving 0.0020 gram of aluminic oxide. In another determination 0.44 gram of lithium yielded 0.0022 gram of aluminic oxide, in satisfactory agreement with the first. Thus the metal possessed the following composition.

Lithium, by difference	99.59 per cent.
Aluminum	0.27 per cent.
Iron	0.14 per cent.
	100.00

The lithium retained its bright metallic lustre during the "floating" there being no apparent action between the liquid and the metal during the time required to make a determination. The metal was kept under paraffin oil, and the weight of each piece was obtained in the following manner. After pressing in a pellet-machine and cutting, the piece was wrapped with a weighed platinum wire. The clinging oil was then removed by dipping the metal into successive portions of naphtha, and the naphtha was allowed to evaporate in a current of hydrogen. From out of the tube containing hydrogen the bit of lithium with its platinum wire was quickly dropped into a weighed vessel containing paraffin oil, the gain in weight being quickly noted.

The specific volume (X) was calculated as follows : Let W equal the weight of the lithium, W^1, the weight of the platinum, 21.5, the density of the platinum, and D the average observed density of the system. Then

$$X = \frac{W + W^1}{DW} - \frac{W^1}{21.5\ W}$$

The three pycnometers held respectively 8.2269, 8.7258, 8.7544 grams of water at 20°, and weighed in air. All weights were reduced to the vacuum standard.

DENSITY OF LITHIUM.

Exp.	Weight of Lithium and Platinum gram.	Weight of Platinum gram.	Weight of Oil in Pycnometer grams.	Volume of Pycnometer Milliliters.	Density of Lithium.
1	0.1436	0.0718	8.591	8.250	0.534
2	"	"	9.106	8.750	0.534
3	"	"	9.139	8.779	0.534
4	0.1301	"	10.225	8.779	0.539
5	"	"	10.188	8.750	0.539
6	0.1407	"	8.854	8.250	0.540
7	"	"	9.420	8.779	0.539
8	"	"	9.367	8.750	0.539
				Average	0.537

Even this low value, 0.537 is probably somewhat too high, because of the slight impurities. Assuming that the metallic iron and aluminum present neither contract nor expand on alloying with lithium, the most probable density of the pure metal may be very simply calculated, as follows :

If x = true density of lithium,

$$\frac{99.59}{x} = \frac{100}{0.537} - \frac{0.27}{2.5} - \frac{0.14}{7.8}. \quad \text{Therefore } x = 0.534.$$

This density, 0.534, is even lower than that found by Richards and Bonnet[1] 0.552. Because all impurities of a metallic nature in so light a metal as lithium would tend to raise the specific gravity rather than to lower it, the new value is undoubtedly more nearly correct than the older one.

Sodium.—The first series of experiments was made with the best quality of sodium to be obtained in commerce. Care was taken to cut the pieces free from superficial oxide. No other impurities besides traces of iron and magnesium were found upon analyzing this sodium qualitatively. Three grams were slowly oxidized by exposure to a moist atmosphere for quantitative analysis, and from this were obtained 0.0016 gram of ferric oxide and 0.0038 gram of magnesium pyrophosphate. Thus the composition of the specimen was

Sodium (by difference)...............................	99.94 per cent.
Iron..	0.03
Magnesium..	0.03
	100.00

These impurities are not enough to affect the density to a significant extent. Probably the metal contained traces of hydrogen as well, but it will be shown that this also is without important effect on the density. This specimen is designated as I in the table below.

Another determination was made with sodium fused in a current of dry hydrogen. After fusion in a wide tube the metal was allowed to run through a narrow tube into a bulb. In this way the oxide was removed and a lump of metal was obtained having a bright, clean surface. This was sample II.

The third series of experiments were made with sodium which had been fused in hydrogen and then distilled in a vacuum, in order to determine if occluded hydrogen has a perceptible effect upon the specific gravity. The operation was carried out in a piece of apparatus similar to that used in the second preparation, except that it had two bulbs instead of one. The apparatus is depicted in Figure 1.

[1] Jahrbuch über die Fortschritte der Chemie, 8, 324. Proc. Am. Acad., 39, 584 (1904).

The first bulb was filled as before and the fine tube sealed off at A. The apparatus was evacuated by means of a mercury pump, and the sodium was distilled over into the second bulb without any difficulty. The pump was operated during the distillation in order to remove the hydrogen as it boiled out of the sodium. To remove the sodium the tube was cut as near as possible to the bulb in order to make a large
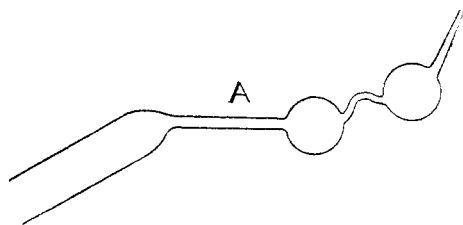

Fig. 1.

opening. The sodium was then melted and run out under oil. The sodium clings strongly to the glass, and if the attempt is made to break the bulb and remove the metal by cutting, more or less hydroxide is formed, and small pieces of glass are likely to find their way into the metal.

These specimens of sodium were floated in the mixed liquid, a number of pieces being used in each trial. The density of the liquid, and there-fore that of the sodium was found as follows :

DENSITY OF SODIUM.

Exp. No.	Samples of Sodium.	Weight of liquid in pycnometer.	Volume of pycnometer.	Density of Sodium.
9	I	8.010	8.250	0.9709
10	I	8.499	8.750	0.9712
11	I	8.501	8.750	0.9715
12	I	8.011	8.250	0.9711
13	I	8.012	8.250	0.9712
14	I	8.502	8.750	0.9716
15	II	8.525	8.779	0.9710
16	III	8.016	8.250	0.9716
17	III	8.526	8.779	0.9711
18	III	8.504	8.750	0.9718
19	III	8.009	8.250	0.9708
20	III	8.526	8.779	0.9710
21	III	8.498	8.750	6.9711

Average density of Sodium = 0.9712

Evidently sodium saturated with hydrogen (Sample (II) is essentially the same in density as distilled sodium free from hydrogen) (III), the difference between the two being no greater than the limit of error of the experimentation. The crude sample (I) is very nearly identical.

Potassium.—In the case of potassium also several preparations of the metals were employed.   At first the purest metal obtainable in commerce was used; for a second series the potassium had been fused in hydrogen in an apparatus of potash glass similar to that used for sodium ; for the third series the metal was fused under paraffin oil and the film of oxide removed from the melted potassium; for the fourth series the potassium had been fused until tranquil in a vacuum; and for the fifth series the potassium was distilled in a vacuum and finally fused under oil.   These specimens are numbered I, II, III, IV and V respectively in the table which follows.   Even the crudest of these specimens was found upon careful analysis to contain no impurity besides 0.03 per cent. of magnesium.

When floating this metal on the mixture of paraffin oil and tetrachloride greater care than before must be used because of the greater tendency of the potassium to act on the liquids.   As in the case of sodium, a mixture of approximately the right density may be obtained with two or three pieces and the final adjustment made with fresh pieces.   The metal was pressed before using.

THE DENSITY OF POTASSIUM

Exp. No.	Sample of Potassium.	Weight of mixed liquid in pycnometer.	Volume of pycnometer.	Density of Potassium.
22	I	7.112	8.250	0.862
23	I	7.568	8.779	0.862
24	I	7.121	8.250	0.863
25	I	7.577	8.779	0.863
26	II	7.549	8.750	0.863
27	III	7.114	8.250	0.862
28	III	7.106	8.250	0.861
29	III	7.111	8.250	0.862
30	III	7.570	8.779	0.862
31	III	7.541	8.750	0.862
32	III	7.118	8.250	0.863
33	III	7.570	8.779	0.862
34	III	7.549	8.750	0.863
35	IV	7.108	8.250	0.861
36	IV	7.562	8.779	0.861
37	IV	7.539	8.750	0.862
38	IV	7.111	8.250	0.862
39	V	7.562	8.779	0.861
40	V	7.540	8.750	0.862
Average density of potassium				0.8621

This result for the density of potassium is between the extreme values given by other experimenters, but inclines rather to the lower than to the upper limit.   The reason for this is undoubtedly because a small admixture of oxide considerably increases the density of the metal, the oxide

occupying less space than the metal from which it was made. In our own experiments, before precautions were taken to eliminate the oxide, densities as high as 0.869 were repeatedly found. The preceding table includes all the determinations in which the metal was properly handled and protected from air.

Rubidium.—The metal used in this work was prepared from a sample of rubidium chloride, which showed in the spectroscope no traces of the other alkali metals. Twenty grams of this chloride were converted into the dichloriodide,[1] which was three times recrystallized by cooling from a twenty per cent. solution of hydrochloric acid, with occasional addition of iodine. The salt was dried at 20°, and slowly raised to 150° where all the iodine and the excess of chlorine were driven off, giving the normal chloride.

The normal chloride was converted into neutral sulphate in a platinum dish, and the sulphate in aqueous solution was converted into the hydroxide by adding an excess of recrystallized barium hydroxide. The excess was added to prevent the formation of rubidium carbonate, the barium carbonate being filtered off after partial evaporation.

The dried and fused hydroxide was, while still warm, removed from the iron crucible, and quickly mixed, and ground up thoroughly with one-half its weight of magnesium powder,[2] and transferred to a small iron pipe of the shape shown in the diagram.
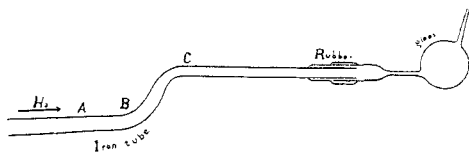

Fig. 2.

This pipe had been heated beforehand with an internal current of hydrogen in order to remove oxide and other impurities. The material was spread in a thin layer from the point *b* towards *a* in order to prevent the clogging of the tube. A strong current of dry hydrogen was then passed through the apparatus until all air was removed. The heating should be started at C and after a time extended to *b*; it was found best not to heat back of *b* before the reaction started. After the reaction had begun, the tube was heated to redness along all the part occupied by the rubidium material, but not too rapidly. The heating continued

[1] Wells, Am. J. Sci. (3) **43**, 17 (1901); also Chem. News, **84**, 2184 (1901).
[2] Cl. Winkler, 1 (1890).

about an hour and a half, and the metal distilled over in drops, into the receiver of glass. This was slipped over the iron tube, the joint being made with a rubber tube over both. At the close of the distillation, the bulb of the receiver was sealed at both ends. The rubidium was kept under viscous paraffin oil, which is less attacked by rubidium than the lighter kinds.

Upon analysis, 0.193 gram of rubidium yielded a trace of ferric oxide and 0.0015 gram of magnesium pyrophosphate, but gave evidence of no other impurities. The iron was estimated colorimetrically as about 0.02 per cent. Hence its composition may be taken as

Rubidium	=	99.82
Magnesium	=	0.16
Iron	=	0.02
		100.00

This amount of magnesium is not enough to affect considerably the specific gravity of the metal.

The difficulties of getting the specific gravity of rubidium are, of course, much greater than in the case of sodium, lithium or potassium, owing to the greater chemical activity of the metal. Pieces became covered with a gray coating of rather loose bulky structure and if kept for some time in the liquid, became specifically lighter, partially because of the coating and partially because of the bubbles on its surface. For this reason a large number of freshly cut pieces must be used in each floating.

DENSITY OF RUBIDIUM.

No. of Exp.	Weight of mixed liquid in pycnometer.	Volume of pycnometer.	Density of Rubidium.
41	12.641	8.250	1.532
42	13.409	8.750	1.532
43	12.645	8.250	1.533
44	13.412	8.750	1.533
45	12.633	8.250	1.531
46	13.401	8.750	1.532
47	12.645	8.250	1.533
48	13.416	8.750	1.533
			1.5324

This value 1.532 is somewhat higher than that found by previous experimenters, 1.52. It is possible that the difference is due to the very great purity of the metal which was used in the present series of experiments, or to the fact that we eliminated accidental cavities by pressing the metal and by using many pieces in each test.

Caesium.—The metal had been prepared in the same manner as the rubidium, namely, by the distillation of the hydroxide with magnesium

powder.   The material from which it was made was of the highest purity having been part of a specimen which had been used in the determination of the atomic weight of caesium.

Because it was impossible to find a heavy mixed liquid upon which caesium would not act, the "floating" method was given up.   The specific gravity was determined by finding the weight of paraffin oil of known specific gravity, which was displaced by a known weight of caesium.   There was some action between the oil and the metal by which a brown coating was formed, but no gas evolved.   Observations extending over a period of about seventy-two hours showed a resulting increase in weight amounting to nearly 0.4 mg. per hour when approximately one gram of material was acted upon.

The caesium was weighed by drawing it up as liquid into a small pipette with a fine capillary outlet, filled with hydrogen.   After weighing, it was forced out through the capillary into the pycnometer by hydrogen pressure.   In this instrument it solidified, and the remaining volume was filled with oil.

The figures need not be given in full, because the results were not very satisfactory, the observed density ranging from 1.85 to 1.90.   The average, 1.873, is not far from the results of Setterberg, 1.878, and Eckardt and Graefe, 1.886 ; but cannot be considered as more accurate than either of those.   Lack of time prevented further work upon the subject.   The results are nevertheless of value as confirming the lower figures for this interesting substance, as against the much higher results of older experimenters.

Alloy of Sodium and Potassium.—Previous to the work on caesium, an alloy of sodium and potassium had been used for practice.   This alloy, being liquid at the room temperature, could be handled in the same way as the caesium.   The work was carried on in exactly the same way in the two cases.   The results are now given because they are of interest in showing that very little change in volume occurs when the two metals were alloyed.

Analysis showed the alloy to have the following composition :

Potassium	39.9 per cent.
Sodium	60.1
	100.0

for 0.7439 gram of the alloy yielded 1.8413 gram of potassium chlorplatinate.

In Experiment 49, 0.2302 gram of alloy displaced 0.2147 gram of high boiling paraffin oil having at 20° the density 0.8565.   The result for the density of the alloy is 0.9181.

In Experiment 50, 0.4505 gram of alloy displaced 0.4192 gram. of oil, yielding as a result 0.9199.

The average of these two results is 0.9190, or about one per cent. less than the average density of the two solid metals composing it.   Thus

$$0.399 \times 0.862 = 0.344$$
$$0.601 \times 0.971 = 0.584$$
$$\overline{0.928}$$

This expansion upon forming the liquid alloy is noticeably less than that which occurs upon melting the metals separately, sodium expanding 2.5 per cent. and potassium 2.4 per cent.[1]   Hence it is to be inferred that the formation of the alloy from the liquefied metals would cause a slight contraction instead of an expansion.

Summary.—The densities and atomic volumes of the five alkali metals at 20° were found as follows, many preparations being used, and great care being exercised in all cases except that of caesium.

	Deusities.	Atomic weights (Ag=107.93).	Atomic volumes (Ag=107.93).
Lithium	0.534	7.0	13.1
Sodium	0.9712	23.008	23.70
Potassium	0.8621	39.114	45.38
Rubidium	1.532	85.48	55.8
Caesium	1.87	133.8	71.0

The density of an alloy of 39.9 per cent. of potassium and 60.1 per cent. of sodium was found to be 0.919.

THE VAPOR PRESSURE OF IODINE.

BY GREGORY PAUL BAXTER, CHARLES HENDEE HICKEY AND WALTER CHAPIN HOLMES.

The vapor pressure of solid iodine was first accurately determined by Ramsay and Young[2], who obtained the following values by coating with iodine the bulb of a thermometer covered with asbestos, and measuring manometrically the tension of this iodine at different temperatures.

Temperature. Degrees.	Pressure. mm.	Temperature. Degrees.	Pressure. mm.
58.1	4.9	91.8	28.95
64.5	6.05	91.9	29.6
66.3	6.25	96.8	37.8
75.2	11.5	102.7	50.65
80.4	15.15	105.7	59.85
86.0	21.25	113.8	87.0

For the vapor pressure below 58° we are dependent partly upon ex-

[1] Vincentini and Omodei (1888).
[2] J. Chem. Soc., 49, 453 (1886).