2. At 0° a single heptahydrate solid solution is formed. At 25° two series of solid solutions, one heptahydrate and the other pentahydrate, are formed.

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A Revision of the Atomic Weight of Potassium

BY GREGORY PAUL BAXTER AND WILLIAM MARSHALL MACNEVIN

In two papers dealing with the analysis of potassium chloride and potassium bromide, Hönigschmid and Goubeau[1] describe experiments which lead to the atomic weight 39.104 for potassium. Although the result agrees with that found by Richards and Archibald[2] it is considerably higher than that obtained later by Richards and Staehler[3] and Richards and Mueller,[4] who analyzed the chloride and bromide, respectively, and obtained the value 39.096. A puzzling situation is thus created, for the difference between the two values, which amounts to nearly 0.01 unit of atomic weight, is far larger than the apparent experimental error of the comparatively simple analytical operations involved and points to a serious uncertainty either in the purity of the potassium salts or silver, or in the analytical operations.

We have made a long series of analyses of potassium chloride, by comparison with silver, using potassium salts of different origin, and have been utterly unable to find any evidence in favor of the higher value. In fact our results confirm very closely those of Richards and Staehler and Richards and Mueller.

The Preparation of Pure Potassium Chloride

Nine different samples of potassium salt were investigated.

Sample A.—The starting point in this case was commercial potassium chlorate of which the original source could not be ascertained. The chlorate was crystallized three times in Pyrex vessels with centrifugal drainage and then was converted to perchlorate and chloride by gentle heating in a platinum dish. After the chloride had been extracted from the mixture with cold water, the perchlorate was twice crystallized in platinum. Next the perchlorate was converted to chloride by heating in a platinum dish and the chloride was twice precipitated with hydrogen chloride. The chloride was then fused in a platinum dish, dissolved in water, the solution filtered through a platinum sponge crucible and evaporated to crystallization. Sample A_2 was obtained by crystallizing the chloride extracted from the perchlorate, three times from hydrochloric acid and once from water.

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(1) Hönigschmid and Goubeau, *Z. anorg. allgem. Chem.*, **163**, 93 (1927); **177**, 102 (1928).

(2) Richards and Archibald, *Proc. Amer. Acad.*, **34**, 373 (1903).

(3) Richards and Staehler, THIS JOURNAL, **29**, 623 (1907).

(4) Richards and Mueller, *ibid.*, **29**, 639 (1907).

Sample B.—Commercial potassium nitrate was recrystallized six times in glass and four times in platinum. From a solution of the product, contained in a quartz flask, the chloride was precipitated by means of hydrogen chloride and centrifugally drained in a porcelain basket. Four precipitations of the chloride with hydrogen chloride at 0° in quartz vessels followed, with centrifugal drainage in platinum baskets. The product was fused in a platinum dish, dissolved and filtered through platinum sponge, twice precipitated as chloride by means of hydrogen chloride, again fused, dissolved and filtered and twice crystallized in platinum.

Sample C.—Commercial potassium chlorate from a second manufacturer was crystallized three times and converted to perchlorate, and the perchlorate was crystallized three times. The chloride prepared from the perchlorate was twice precipitated with hydrogen chloride, fused, and once crystallized from water as described above (Sample C_1). Analysis of this material yielded a value lower than that obtained from all the other samples investigated, which was not altered by two more crystallizations from water (Sample C_2). The potassium nitrate from the analyses was therefore recovered and after conversion to perchlorate was combined with perchlorate mother liquors remaining from the purification. The perchlorate was then crystallized four times in platinum and converted to chloride. The chloride was twice precipitated with hydrogen chloride, fused, dissolved and filtered and fractionally crystallized from water (Sample C_3). All the salt was again recovered and subjected to the same purification as Sample C_3 (Sample C_4).

Sample D.—Two additional specimens of chlorate from the same source as Sample C were purified exactly as in the case of Sample C_1. These are designated D_1 and D_2.

Sample E.—This sample came from a third manufacturer as potassium oxalate and was first crystallized three times as this salt. The purified oxalate was then converted to chloride by passing chlorine into the hot solution. The chloride in turn was three times precipitated with hydrogen chloride, fused, dissolved and filtered, and crystallized from water.

Sample F.—Australian alaunite was ignited to bright redness in a quartz muffle and soluble material extracted with hot water. The alum crystals which separated from the solution after concentration were dissolved and precipitated with perchloric acid. Twelve crystallizations of the perchlorate were followed by conversion to chloride and recrystallization of the chloride.

Sample G.—Commercial potassium carbonate from Stassfurt, Germany, was converted to chlorate and chloride by passing chlorine into the hot solution. The chlorate was successively converted into perchlorate and chloride as previously described. Each salt was subjected to several crystallizations.

Sample H.—The source of this sample was the ashes of hard wood from Brattleboro, Vermont. Mr. D. S. Bliss very kindly extracted the soluble matter for us. The dark brown solution was first saturated with chlorine and evaporated. Since the yield of chlorate was small the salts were converted to nitrate by repeated evaporation with an excess of nitric acid, and the resulting potassium nitrate was five times crystallized. Sodium disappeared during the second crystallization. From the solution of the purified salt, potassium perchlorate was precipitated with perchloric acid and the perchlorate was crystallized three times. Conversion of the perchlorate to chloride and recrystallization of the chloride followed.

The Purification of Silver.—Several samples of pure silver were employed. Sample I was purified by Professor S. Ishimaru[5] and has been used in several investigations besides his own. Sample M was prepared in exactly the same way by Dr. J. P. Marble and Mr. A. D. Bliss[6] and has been used in an investigation on the phosphorus halides by

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(5) Baxter and Ishimaru, THIS JOURNAL, **51**, 1729 (1929).

(6) Baxter and Bliss, *ibid.*, **52**, 4848, 4851 (1930).

Dr. Marble (not yet published). Both these specimens have been found to be normal. Sample H was received from Professor Hönigschmid.

All the operations were carried out in the most careful way with especial precautions to avoid contamination with dust and the products of combustion of illuminating gas. As previously stated the earlier stages in the purification were conducted in Pyrex glass, the later ones in quartz or platinum. Occasional filtrations of the solutions were made through platinum sponge even when there was no evidence of turbidity.

The Preparation of Potassium Chloride for Weighing.—The potassium chloride was invariably fused preparatory to being weighed. In the first three experiments the salt was fused in a weighed platinum crucible over a Bunsen flame with an asbestos plate to deflect the products of combustion. The platinum crucible showed no evidence of being attacked in this process. In all other experiments the salt was contained in a platinum boat which was placed in the quartz ignition tube of a Richards bottling apparatus. It was found advisable to surround the boat with a cylinder of platinum foil, since the quartz was attacked by the vaporized potassium chloride and there was danger of contamination of the boat with silicate.

The boat was initially weighed in a weighing bottle, after it had been filled with dry air by means of the bottling apparatus, by comparison with a similar counterpoise in the usual fashion.

The fusion atmosphere was pure dry nitrogen with the following exceptions. In Analyses 8 and 11 a mixture of nitrogen and hydrogen chloride was used. In these experiments the boat was considerably attacked and the salt contained suspended platinum. Other attempts to use this fusion atmosphere were subject to the same difficulty and the method was finally given up. In Analysis 26 a mixture of hydrogen and hydrogen chloride was passed through the tube during the fusion and the boat remained essentially unchanged in weight. In Analysis 25 the fusion was effected in pure hydrogen. In every case the salt was allowed to solidify in the fusion atmosphere, and then the bottling apparatus was swept out with pure nitrogen if the fusion atmosphere had not consisted of this gas alone, and finally with dry air.

The Method of Analysis.—The salt was dissolved in pure water and diluted until approximately 0.05 normal. A nearly equivalent quantity of silver was weighed by substitution and after solution in nitric acid was diluted to a similar concentration. Precipitation at room temperature was followed by a considerable period of standing with occasional shaking. Finally the end-point was adjusted with 0.01 *N* chloride and silver solutions with the help of a nephelometer. Except in Analyses 5 and 6 the final adjustment of the end-point was never made until several weeks had elapsed, although only slight changes occurred after the first week. In Analyses 5 and 6 only one nephelometric test was made, after about one week. In all the analyses the solution remained at room temperature until the end-point had been determined. In Analyses 16 and 31 the solubility of silver chloride was reduced to one-third its value at room temperature by cooling the analysis with ice, and further nephelometric tests were made with portions which had been withdrawn and brought to room temperature. No shift whatever of the end-point could be detected.

In computing the vacuum corrections the following specific gravities were employed.

Air	0.001293 at 0° and 760 mm.	Potassium chloride	1.988
Weights	8.3	Silver	10.49

Because of the low density of potassium chloride the air density was determined at the time the salt was weighed by weighing a sealed standardized glass globe of 100 cc. exterior volume.[7]

THE ATOMIC WEIGHT OF POTASSIUM: KCl:Ag

Ag = 107.880 Cl = 35.457

Analysis	Sample of KCl	Sample of Ag	KCl in vac., g.	Ag in vac., g.	Ag added, g.	Corr. Ag, g.	Ratio KCl:Ag	At wt. of potassium
1	A_1	I	7.25734	10.50103	+0.00112	10.50215	0.691034	39.092
2	A_1	I	5.92306	8.57091	+ .00030	8.57121	.691041	39.093
3	A_2	I	6.86340	9.93154	.00000	9.93154	.691071	39.096
4	A_1	I	4.47498	6.47557	+ .00010	6.47567	.691045	39.093
5	A_1	I	1.93359	2.79802	.00000	2.79802	.691057	39.094
6	A_2	H	2.37502	3.43697	.00000	3.43697	.691021	39.090
						Average	.691045	39.093
7	B	I	5.52011	7.98801	+ .00005	7.98806	.691045	39.093
8	B	H	5.37543	7.77865	.00000	7.77865	.691049	39.093
9	B	M	5.33013	7.71318	.00000	7.71318	.691042	39.093
						Average	.691045	39.093
10	C_1	I	4.83277	6.99329	+ .00079	6.99408	.690980	39.086
11	C_1	H	5.04591	7.30175	+ .00090	7.30265	.690970	39.085
12	C_1	I	5.54960	8.03045	+ .00060	8.03105	.691018	39.090
13	C_2	I	4.39910	6.35469	+ .00021	6.35490	.690979	39.086
14	C_2	I	4.53273	6.55905	+ .00096	6.56001	.690964	39.084
15	C_3	I	4.45347	6.44419	+ .00038	6.44457	.691042	39.093
16	C_4	I	7.23597	10.47029	.00000	10.47029	.691095	39.098
17	D_1	I	6.17283	8.93220	.00000	8.93220	.691076	39.096
18	D_1	I	7.27021	10.52040	.00000	10.52040	.691058	39.094
19	D_1	I	4.87145	7.04948	− .00002	7.04946	.691039	39.092
20	D_1	I	5.34406	7.73259	+ .00046	7.73305	.691068	39.095
						Average	.691060	39.094
21	D_2	M	6.44377	9.32443	− .00042	9.32401	.691094	39.098
22	D_2	M	5.88056	8.50975	− .00040	8.50935	.691070	39.096
23	D_2	M	5.89358	8.52834	+ .00005	8.52839	.691054	39.094
						Average	.691073	39.096
24	E	I	5.76754	8.34614	+ .00028	8.34642	.691020	39.090
25	E	I	4.68776	6.78384	− .00002	6.78382	.691021	39.090
26	E	I	5.76684	8.34487	.00000	8.34487	.691064	39.095
27	E	H	4.95265	7.16651	.00000	7.16651	.691082	39.097
						Average	.691047	39.093
28	F	M	4.78080	6.91811	− .00004	6.91807	.691060	39.095
29	F	M	5.39065	7.80040	+ .00014	7.80054	.691061	39.095
						Average	.691061	39.095
30	G	I	5.04247	7.29630	− .00002	7.29628	.691101	39.099
31	G	I	4.54922	6.58291	+ .00008	6.58299	.691057	39.094
						Average	.691079	39.097

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(7) Baxter, THIS JOURNAL, **43**, 1317 (1921).

The Atomic Weight of Potassium: KCl:Ag (*Concluded*)

Analysis	Sample of KCl	Sample of Ag	KCl in vac., g.	Ag in vac., g.	Ag added, g.	Corr. Ag, g.	Ratio KCl:Ag	At. wt. of potassium
32	H	M	6.77998	9.81054	+0.00046	9.81100	0.691059	39.094
33	H	M	6.78310	9.81539	− .00014	9.81525	.691078	39.096
						Average	.691069	39.095
			Average of all except Analyses 10–16				.691057	39.094

With the exception of Sample C the results show a satisfactory concordance, in agreement with the value obtained by Richards and Staehler and Richards and Mueller. The low results obtained at first with Sample C cannot be explained in any way known to us. The later results with material at least as pure as that used in the early experiments show no abnormality and this is true also of Samples D_1 and D_2 which presumably had the same source and were purified in the same way. Our results show no evidence of a difference in purity of salt prepared by different methods and from widely different sources. No variation in the isotopic composition of potassium assimilated by plants is evidenced by material from the wood ash which we have examined.

Since our results and those of Richards and his collaborators are lower than those of Hönigschmid, the discrepancy cannot be due to deficiency of halogen in the fused salt, a conclusion supported by Analysis 26, where the fusion atmosphere contained hydrogen chloride. On the other hand, excess of halogen is excluded by the bulk of the analyses where the initially neutral salt was fused in nitrogen.

A low value would be the result of impurity in the silver used as the standard of comparison. However, the three silver samples, one of them prepared by Hönigschmid, seem to be identical.

It is worth while pointing out that with a 5-gram portion of potassium chloride the difference between the silver required in Hönigschmid and Goubeau's experiments and in ours amounts to 1.0 mg., while the sensitiveness of the end-point is only one-tenth as large.

Zintl and Goubeau[8] have confirmed the higher value for potassium by the conversion of potassium nitrate into potassium chloride. Their ratio determined from the weights in air corrected to vacuum, 1.35617, and that determined from the weights of material when actually weighed in vacuum, 1.35611, fall on opposite sides of the value to be expected from the results of Richards, Staehler and Mueller for potassium, 1.35614 (N = 14.008). They attribute the difference in their ratios to adsorption of air by the salts. In an investigation in this Laboratory not yet published, Mr. A. C. Titus has been unable to detect appreciable adsorption of air by potassium chloride or potassium nitrate. On the basis of the air weights corrected to vacuum by Zintl and Goubeau the atomic weight of potassium is 39.088, a value lower rather than higher than that obtained by Richards, Staehler and Mueller.

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[8] Zintl and Goubeau, *Z. anorg. allgem. Chem.*, **163**, 302 (1927).

Our results therefore confirm the conclusion of Richards and Staehler and Richards and Mueller that the atomic weight of potassium is very close to 39.096.

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Kinetics of Dissociation of Typical Hydrocarbon Vapors[1]

BY ROBERT N. PEASE AND JOHN M. MORTON

The reactions of pure hydrocarbons are of special interest from the theoretical standpoint since the breakage and formation of only three types of linkage (the C—C, C—H and H—H bonds) are involved in the whole series. In principle,[2] the activation energies of such reactions can be calculated to a first approximation, but in practice questions arise as to allowances to be made for the nature of substituent groups and of the molecule as a whole. In order to supply data on such points from experiment, rate measurements have been made on representatives of four principal series of hydrocarbons. The substances chosen were *n*-heptane from the paraffin series, ethylbenzene from the substituted benzene series, pentene-2 from the olefin series and cyclohexane from the naphthene series. In addition some comparative data have been obtained on related compounds, namely, benzene, toluene, xylene and ethylcyclohexane.

Method and Apparatus

Rate measurements were made by both flow and static methods, the former being supplemented by analysis. The flow experiments consisted in passing the vapor of the substance through a heated Pyrex reaction tube, and collecting and analyzing the products. The static experiments were run in parallel, the rates of pressure change being simultaneously determined in two reaction tubes, one of which had received an interior coating of potassium chloride.

The flow experiments were carried out as follows. The liquid hydrocarbon dropped from an inclined buret into a vaporizing chamber. The vapor then passed into the reaction tube. The rate of dropping was controlled by adjusting two stopcocks sealed into the line.[3] From the reaction tube, the vapors were led into an ice-cooled trap, and thence through a trap at −79° into a gas buret. The first trap was in reality a buret with water as the confining liquid. This permitted accommodating a quantity of condensed vapors without altering the dead space. The second trap was of small volume (about 3 cc.). The uncondensed gases were analyzed for unsaturated substances soluble in ordinary concentrated sulfuric acid, for ethylene by absorption in bromine water, for hydrogen by oxidation with copper oxide at 250° and for methane and ethane by oxidation with copper oxide at 550°. In some cases butadiene was deter-

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[1] A part of this investigation was financed from funds donated to the American Petroleum Institute by John D. Rockefeller.

[2] Eyring, *Chem. Rev.*, **10**, 103 (1932); Sherman and Eyring, THIS JOURNAL, **54**, 2661 (1932).

[3] The stopcocks were lubricated with a glycerine–glucose preparation.