[Contribution from the Department of Chemistry, Dalhousie University]

ATTEMPTS TO SEPARATE THE ISOTOPES OF MERCURY BY CHEMICAL MEANS[1]

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Isotopes of various elements have been partially separated[2] by certain physical methods depending on the inertia of molecules. The question arises whether or not a similar shift in the isotopic ratio may be effected by some chemical process in which differences of mass and consequently of inertia play a determinative role. There is a highly specialized type of reaction which seems to satisfy this requirement. If a single molecule, containing two isotopic atoms of the same element linked together, is capable of ejecting one of these atoms by thermal vibration, then it is plausible to assume that one isotopic variety might be more easily eliminated than the other, since the work on infra-red radiation indicates that the vibrations of two isotopic atoms within the molecule cannot be identical.[3] Although the effect of mass would be extremely small, it is conceivable that it might exert a deciding influence in cases where all other factors are balanced.

An example of this type of reaction is that of a Grignard reagent on lead chloride,[4] thus, $2PbCl_2 + 4RMgX = Pb + R_4Pb + 2MgCl_2 + 2MgX_2$. It has been shown[5] that R_2Pb is one of the intermediates in this reaction and that this compound is partially polymerized. This latter compound, we assume, can break down with the production of metallic lead and the tetravalent organo-lead derivative; $R_2PbPbR_2 = Pb + R_4Pb$.

The use of this reaction to achieve a partial separation of isotopes has yielded conflicting results.[6] This last of these investigations is the most

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[1] A preliminary report has been published in *Trans. Nova Scotian Inst. Sci.*, **17**, Pt. 1, 28 (1927).

[2] For example, see (a) Aston, *Brit. Assocn. Advancement Sci. Repts.*, Birmingham, **1913**, p. 403; (b) "Isotopes," 2nd ed., Arnold, London, **1924**. (c) Brönsted and Hevesy, *Nature*, **106**, 144 (1920); (d) **107**, 619 (1921); (e) *Z. physik. Chem.*, **99**, 189 (1921). (f) Harkins and Hayes, This Journal, **43**, 1803 (1921). (g) Mulliken and Harkins, *ibid.*, **44**, 37 (1922). (h) Egerton and Lee, *Proc. Roy. Soc.* (*London*), **103A**, 499 (1923).

[3] For example, see Loomis, *Nature*, **106**, 179 (1920). Kratzer, *Z. Physik*, **3**, 460 (1920). Mulliken, *Phys. Rev.*, **25**, 119, 259 (1925); **26**, 1 (1925). Grebe and Konen, *Physik. Z.*, **22**, 546 (1921).

[4] Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904).

[5] (a) Möller and Pfeiffer, *Ber.*, **49**, 2441 (1916). (b) Krause and Reissaus, *ibid.*, **55**, 888 (1922).

[6] Positive results: (a) Hofmann and Wölfl, *Ber.*, **40**, 2425 (1907). (b) Ebert, *Ion*, **2**, 277 (1910). (c) Dillon, Clarke and Hinchy, *Sci. Proc. Roy. Soc.* (*Dublin*), **17**, 53 (1922). Negative results: (a) Staehling, *Compt. rend.*, **157**, 1430 (1913). (b) Brennen, *ibid.*, **180**, 282 (1925). (c) Richards, King and Hall, This Journal, **48**, 1530 (1926).

accurate. A sample of lead chloride was fractionated several times, using the Grignard reagent phenylmagnesium bromide. Determinations of the ratio $PbCl_2:2Ag$ gave for the atomic weights of lead from the extreme metallic fraction and from the extreme tetraphenyl lead fraction the values 207.217 and 207.219, respectively. These results are within the limits of experimental accuracy. They finally dispose of the claims of previous investigators that a considerable separation of lead isotopes may be effected with the aid of the Pfeiffer-Truskier reaction. They do not settle definitely whether a difference of mass is without effect in determining the course of the reaction.

A more accurate determination of small differences in the atomic weight of lead would be extremely difficult. Therefore, the author transferred his efforts to attempts to separate the isotopes of mercury by similar chemical reactions. Mercury is a peculiarly suitable material for the determination of minute changes in the isotopic ratio. It is easily purified, and its density can be obtained to within one part in a million. Its isotopic complexity has been established,[7] the mass numbers of its isotopes being 198, 199, 200, 201, 202 and 204. Moreover, many of its compounds containing two mercury atoms are unstable, breaking down to form metallic mercury and a mercuric derivative, reactions similar to that of tetra-alkyl dilead previously discussed.

The basic equation for this type of reaction, $Hg_2X_2 = Hg + HgX_2$, has been made the subject of a previous paper.[8] It is probable that mercurous compounds in solution have the dimolecular form and that the ion is not monovalent, as given in many textbooks. Indeed it is hard to conceive of the ion Hg^+ existing to any extent in solution. According to our present views of atomic constitution, the electron structure for mercury is 2.8.18.32.18.2. It is easy to see that an atom with such a structure would lose two electrons readily, but to lose only one electron should leave a very unstable and extremely reactive substance, since there is no incomplete inner electron shell to which the lone electron may pass.

The dimolecular formula of mercurous compounds has in the past been universally represented as X—Hg—Hg—X. This is not the only conceivable structure. In the formation of mercurous chloride, for instance, the primary reaction is probably $Hg + Cl_2 = HgCl_2$. It is possible that the second atom of mercury loses its valence electrons to the mercuric chloride molecule and then shares an additional pair of electrons from the outer shell of its kernel to give a compound containing a mercury ion surrounded by an additional octet as in $\mathrm{Hg}\ {:}\underset{\mathrm{Cl}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Hg}}}}{:}\mathrm{Cl}$, which

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[7] Aston, *Nature*, **116**, 208 (1926).

[8] King, *Trans. Nova Scotian Inst. Sci.*, **16**, Pt. 3, 115 (1924).

can be represented by the non-electronic formula $Hg{=}HgCl_2$. This type of structure may be applied to other mercurous compounds. Mercurous nitrate, $Hg_2(NO_3)_2 . 2H_2O$, might be represented as mercuro diaquo mercuric nitrate, $[Hg{=}Hg(H_2O)_2](NO_3)_2$, where the mercuric ion, as above, has a covalence of four. If the structure X—Hg—Hg—X is correct, then the course of the decomposition, X—Hg—Hg—X = Hg + HgX_2, must be the same as for R_2PbPbR_2. With the alternate structure, $Hg{=}HgX_2$, it would seem that only one of the mercury atoms is free to take the metallic form unless there is a vibration of the X groups from one mercury atom to the other.

Methods of Fractionation

In order to determine whether there is any separation of isotopes in this simultaneous oxidation-reduction type of reaction, six series of fractionations were employed, the experimental conditions being varied widely. The mercury compounds used in the first five series were from the same source. No hesitancy was felt in starting the sixth series with material from a different source because the atomic weight of mercury is constant irrespective of geological origin,[9] and because a difference, if any, in the atomic weight of the initial mercury would not adversely affect the significance of the comparative density determinations of the fractionated samples. In the first four series the two samples of metallic mercury obtained by the chemical fractionation were converted to mercurous chloride, and each of these samples was refractionated, the extreme fractions being taken for analysis. Brief descriptions of the reactions used in the six series of fractionations are given below.

Series I. $Hg_2I_2 \rightleftharpoons Hg + HgI_2$.—Mercurous iodide was formed by the addition of a solution of potassium iodide to mercurous chloride. An excess of potassium iodide shifted the above equilibrium to the right, removing mercuric iodide through the formation of potassium mercuri-iodide, and leaving a heavy gray sludge of finely divided mercury. After decanting the solution and washing the precipitate, the mercury was coagulated to a globule by drying. The combined mercury in solution was reduced to the metallic form by heating with zinc and hydrochloric acid. The excess of zinc was removed by shaking with dil. nitric acid. In the following three series, the combined mercury was also recovered as metal in this way.

Series II. $Hg_2(CN)_2 \rightleftharpoons Hg + Hg(CN)_2$.—Mercurous chloride was added to an excess of potassium cyanide solution. In this way the mercurous cyanide was decomposed as rapidly as formed to give mercury and potassium mercuricyanide.

Series III. $Hg_2O \rightleftharpoons Hg + HgO$.—Mercurous chloride was added

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[9] Brönsted and Hevesy, *Nature*, 109, 780 (1922).

to an excess of dil. sodium hydroxide solution and allowed to stand for some days with frequent shaking. The precipitate of mercurous oxide was gradually heated out of contact with air to decompose it slowly into mercury and mercuric oxide. Finally potassium cyanide solution was added to dissolve the latter.

Series IV. $Hg_2Cl_2 \rightleftarrows Hg + HgCl_2$.—This method involved the use of an aqueous solution of ammonia to shift the above equilibrium to the right by the removal of mercuric chloride according to the equation $HgCl_2 + 2NH_3 = NH_2HgCl + NH_4Cl$. Several preliminary experiments, with the object of separating the mercury and the infusible white precipitate, were made. It was found that neither centrifugal sedimentation nor volatilization in a current of air was satisfactory. Extraction with a hot, concentrated solution of ammoniacal ammonium chloride was more efficient and so was adopted.

The formation of metallic mercury as one of the products of reaction of ammonia on mercurous chloride has not been universally accepted, the black precipitate being considered by some to be NH_2Hg_2Cl, a view persisting to the present day in some textbooks. The work of Barfoed and of Saha and Choudhuri[10] made it extremely probable that the precipitate was a mixture, but it seemed that their proofs were not rigid because of the possibility of secondary reactions. Therefore a purely physical method was devised[8] which depended on the difference in density between the two products. The freshly prepared precipitate made from pure mercurous chloride was suspended in cold glycerol and floated on a layer of colder glycerol in a test-tube. On centrifuging, the mercury settled out faster than the infusible white precipitate. There does not seem to be any possibility for secondary reactions in this treatment, so metallic mercury must have been one of the components in the black precipitate.

Series V. $Hg_2Cl_2 + 2C_2H_5MgBr = Hg + (C_2H_5)_2Hg + 2MgBrCl$.—, This method was selected because of its similarity to the Pfeiffer-Truskier reaction previously discussed. The organo-mercury derivatives differ from their lead counterparts in that the alkyl groups are not so firmly held in the former, as shown by the ease with which the "mixed" dialkyls and diaryls change into a mixture of the two simple compounds:[11] $2R\text{—}Hg\text{—}R' = R_2Hg + R'_2Hg$. Whether mercury isotopes differ in their power to hold alkyl groups is unknown. This was an additional reason for studying the reaction.

The directions of Marvel and Gould,[12] with certain modifications, were followed. In order to ensure as nearly complete reaction as possible

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[10] (a) Barfoed, *J. prakt. Chem.*, [2] **39**, 201 (1889). (b) Saha and Choudhuri, *Z. anorg. Chem.*, **67**, 357 (1910).

[11] Hilpert and Grüttner, *Ber.*, **47**, 177 (1914); **48**, 906 (1915).

[12] Marvel and Gould, THIS JOURNAL, **44**, 153 (1922).

the mercurous chloride in ether suspension was introduced by means of a dropping funnel directly into the mechanically stirred Grignard reagent. The proportion of reagents was altered so that the molar ratio of the Grignard reagent to mercurous chloride was 10:1. In the separation of the products, extraction with ether was attempted. A small amount of finely divided copper was added to prevent metallic mercury from passing through the filter. This method was not satisfactory, so the extraction was abandoned in favor of steam distillation. In the distillate, the layer of diethyl mercury, dissolved in ether, was heavier than the supernatant water. This was allowed to stand uncovered until the ether had evaporated. The diethyl mercury was then decomposed by long boiling with a reflux condenser. The product was finally distilled through a combustion tube containing hot copper oxide to complete the elimination of organo-mercury compounds. The two fractions thus obtained contained copper which was removed by dissolving the samples in nitric acid and precipitating mercuric sulfide from the solution of the nitrates in the presence of an excess of potassium cyanide. The filtered and washed sulfide was converted to bromide by the action of bromine and finally to metal by reduction with zinc and hydrochloric acid.

Series VI. $C_6H_5HgHgC_6H_5 = Hg + (C_6H_5)_2Hg$.—The reaction used in this fractionation is quite different from those employed in the previous five series, in that the initial material is not mercurous chloride. There was some doubt concerning the structural formula of calomel, which led to an uncertainty whether reactions involving that substance were really of the peculiar oxidation-reduction type desired. In the reduction of phenylmercuric acetate by sodium stannite, according to the equation $2C_6H_5HgOCOCH_3 + Na_2SnO_2 + 2NaOH = Hg + (C_6H_5)_2Hg + Na_2SnO_3 + 2NaOCOCH_3 + H_2O$, the intermediate formation of $C_6H_5HgHgC_6H_5$, which breaks down to form mercury and diphenyl mercury, is considered probable.[13] It would have been natural to suppose, from a general consideration of the properties of organo-mercury compounds, that diphenyl mercury was produced by the shifting of the equilibrium $2C_6H_5HgOCOCH_3 \rightleftarrows (C_6H_5)_2Hg + Hg(OCOCH_3)_2$ to the right by the reduction of mercuric acetate, were it not for the observation of Dimroth[14] that in this type of reaction no odor of organo-mercury was noticed until the black precipitate first formed turned gray from the separation of mercury. Kraus[15] prepared complex metals of the type R—Hg by the electrolysis of alkyl mercury halides in liquid ammonia. These substances were black solids which decomposed to form mercury

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[13] Whitmore, "Organic Compounds of Mercury," American Chemical Society Monograph Series, Chemical Catalog Co., New York, **1921**, p. 62.

[14] Dimroth, *Ber.*, **35**, 2853 (1902).

[15] Kraus, THIS JOURNAL, **35**, 1740 (1913).

and dialkyl mercury when heated to room temperature. They are in all probability similar to the intermediate product of the reduction of phenylmercuric acetate with sodium stannite.

The phenylmercuric acetate used in this series was prepared by the direct mercuration of benzene in the presence of ethanol according to the method of Maynard.[16] His directions for the chemical fractionation of this material into mercury and diphenyl mercury by means of sodium stannite were also followed. Only such modifications were made as were necessitated by the increased scale of production. The diphenyl mercury was converted to metal by the method used with diethyl mercury.

Series S. Standard Sample.—In addition to the fractions obtained in the above six series, a sample of ordinary unfractionated mercury was prepared from mercurous chloride by reduction with ammonium formate.

Table I

List of Samples

S, Ordinary mercury, unfractionated

Sample	Extreme fraction source of	Treatment	Sample	Extreme fraction source of	Treatment
I_a	Hg	Iodide	IV_a	Hg	Ammonia
I_b	K_2HgI_4	Iodide	IV_b	NH_2HgCl	Ammonia
II_a	Hg	Cyanide	V_a	Hg	Grignard
II_b	$K_2Hg(CN)_4$	Cyanide	V_b	$(C_2H_5)_2Hg$	Grignard
III_a	Hg	Oxide	VI_a	Hg	Stannite
III_b	HgO	Oxide	VI_b	$(C_6H_5)_2Hg$	Stannite

Purification of the Samples

Each of the samples enumerated in the above table was purified by a series of operations, both chemical and physical, summed up under the following headings. (1) Conversion of the metallic sample to mercuric chloride; reduction first to mercurous chloride and then to metal by ammonium formate. (2) Chlorination and three fractional volatilizations of mercuric chloride. (3) Reduction by ammonium formate and four distillations of the metal. All reagents used were carefully purified by methods customary in exact analytical work and adequate to remove deleterious impurities. The details, omitted here for lack of space, have been published elsewhere.[1]

In the first step of the purification, the sample was dissolved in nitric acid and converted to chloride by several evaporations with hydrochloric acid. The mercuric chloride was reduced to calomel by warming with an excess of ammonium formate solution. The pure white precipitate was filtered and washed well, before further reduction to metal. This second reduction was made more rapid and complete by boiling the calomel with an excess of ammonium formate solution to which from time to

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[16] Maynard, This Journal, **46**, 1510 (1924).

time portions of ammonium hydroxide were added. The finely divided mercury was well washed and coalesced into a globule. Surface contamination was removed by pouring the product through a fine glass capillary.

This reduction, carried out in two steps, resulted in a separation of the more electropositive elements, although silver and gold were not removed. To test this conclusion, the mixed chlorides of mercury and copper were reduced in the manner described above. Twenty-five-gram portions of the precipitated mercury were dissolved in nitric acid, evaporated to dryness and ignited. Silver was found in the almost invisible white residue but the hydrobromic acid test for copper[17] was negative.

The mercury obtained from the ammonium formate reduction was introduced into the first of a train of four Pyrex bulbs which was enclosed by an asbestos hot-air bath. Pure, dry chlorine was passed over the mercury until reaction was practically complete and the temperature was then adjusted so that the molten mercuric chloride gently volatilized. The vapor was carried by a stream of chlorine into the second bulb, where it condensed. A small portion of the sample was left behind. In the same way two more fractional volatilizations were made.

This manipulation resulted in a very complete removal of silver. After each volatilization each bulb was extracted with hydrochloric acid and ammonia; before reassembling they were well steamed out. The extracts from the first bulb contained traces of silver. None was found in the second bulb. The more volatile chlorides could not have been eliminated. Auric chloride, for example, volatilizes easily[18] in a current of chlorine at the temperature of these fractionations.

In order to recover the mercury in metallic form, the thrice volatilized mercuric chloride was dissolved in water and reduced to metal by the ammonium formate method. The process was the same as in the previous reduction except that mercurous chloride was not isolated. This metal was distilled four times in a partial vacuum in a current of air by Hulett's method.[19] Special care was taken in designing the still to prevent the passage of spray into the condenser. With this object in view, a fractionating column of zigzag form was inserted between the still and condenser.

Hulett has shown that by the distillation of mercury in a stream of rarefied air, all readily oxidizable metals, such as zinc, cadmium, bismuth, tin, copper, lead, etc., are completely oxidized in the vapor state. Three distillations are sufficient to reduce the concentration of silver, gold and platinum in the distillate to a non-detectable amount, silver being the

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[17] Endemann and Prochazka, *Chem. News*, **42**, 8 (1880).

[18] Rose, *J. Chem. Soc.*, **67**, 881 (1895).

[19] Hulett, *Phys. Rev.*, **33**, 307 (1911).

most difficult to remove. It is for this reason that the mercuric chloride was fractionally volatilized prior to the distillation of the metal.

The mercury samples, after passing through the various steps in the purification described above, were drawn by suction several times through extremely fine glass capillaries and collected in scrupulously cleaned weighing bottles.

Solution of gases from the atmosphere by the mercury, with consequent change of its density, has been shown by Hulett to be negligible. In any case, all samples would be similarly affected. It was realized that, in some step or steps in the purification, a partial separation of isotopes might take place. Therefore, all samples were treated as nearly alike as possible. In this way any such separation would be the same for all and without influence on the comparative densities determined.

Density Determinations

There is an accumulation of evidence upholding the view that the densities of isotopically different samples of the same element vary directly with the statistical atomic weights.[20] Although this relationship may not be exact, its deviation must be almost infinitesimal. For determining whether any separation has taken place, the density method is admirable. If the two extreme samples obtained by a process of fractionation do not differ in density, then that process does not effect any appreciable separation of isotopes.

For determining the density of the samples fractionated by chemical means and purified by the methods just described, three pycnometers were used. These pycnometers were made from the same length of Pyrex tubing nearly a year prior to the density determinations, in order to allow for the contraction of glass after fusion. Their dimensions were as nearly identical as possible. The weights of all three were the same to within 0.01 g. and the volumes to within 0.03 cc. The diameters of the capillary necks of two of these pycnometers were 0.2 mm. each. In the third one, used later as tare, this dimension was slightly larger, about 0.25 mm.

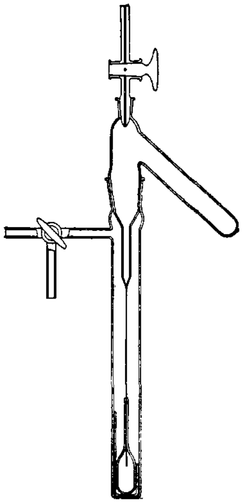
Fig. 1.

The pycnometers were filled by the use of an apparatus illustrated in Fig. 1. The mercury sample was introduced into the side arm of the stopper and the whole apparatus exhausted through both stop-

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[20] (a) Soddy, *Nature*, **94**, 1615 (1915); **107**, 41 (1921). (b) Richards and Wadsworth, This Journal, **38**, 221, 1658 (1916). Refs. 2e, 2f, 2g.

cocks. By tipping the apparatus the mercury was brought into the stem of the stopper. It is necessary to exhaust both stopper and pycnometer chamber prior to the transference of the mercury in order to prevent air from being carried into the pycnometer. Air so introduced is likely to form bubbles between the mercury and the glass, especially in the latter stages of the filling when the end of the capillary tube is submerged. When the vacuum in the stopper was broken, the mercury began to drop very slowly through the capillary into the pycnometer. After this had been filled, there still remained a portion of the mercury in the reservoir. Air was then admitted gradually, and the pycnometer removed.

The filled pycnometer was inserted into a long, thin glass test-tube and lowered into a padded and covered thermostat. The temperature was kept constant at approximately 29.0° to within 0.001° by a six-fingered toluene thermoregulator holding about 1 liter of toluene. After several hours the drop of mercury expelled was removed by drawing across the smooth top of the capillary a small sliver from a safety-razor blade cemented at right angles to the end of a wooden rod. The pycnometer was then removed. After coming to room temperature, the droplets of mercury on the surface of the pycnometer were brushed off with a camel's hair brush. Some trouble was experienced here because of the electric charge given to the glass. This was avoided by brushing the pycnometer inside a box in which a large quantity of radio-active uranium salt was strewn, the charge being dissipated by the ionized air.

One of the three pycnometers, filled with pure mercury from Sample S, served as a tare throughout the series of weighings. In each series of determinations (designated I, II, III, etc.) the two other pycnometers (designated by the prime numerals 1 and 2) were used. One was filled with Sample a and the other with Sample b, obtained from one of the series of fractionations. These two samples were brought to the standard temperature and the exuded drops of mercury removed at the same time. Thus, even if the temperature of the bath had varied slightly, the error would have been the same for both and consequently negligible. The samples were then weighed, one immediately after the other, against the tare. Since the tare and the two samples in their pycnometers were so nearly identical in composition, proportions and weight, errors due to temperature, surface adsorption and pressure differences were eliminated to a great extent. The tare and sample, during the weighings, rested on supports made from the same piece of glass rod and identical in weight to within 1 mg.

After this first weighing the pycnometers were emptied, filled again with the same samples reversed and adjusted to standard temperature. That is, if, in the first weighing, Sample a was in Pycnometer 1 and Sample b in Pycnometer 2 then, in the second set of weighings, Sample a was in Pycnometer 2 and Sample b in Pycnometer 1.

The balance used was a Troemner No. 10, which was purchased especially for this investigation and used for no other purpose. The sensitivity of the balance was adjusted so that 0.1 division of the scale was equivalent to approximately 0.015 mg. Three weighings and a measurement of the sensitivity were made for each determination. The averages are given in Table II.

Before weighing the fractionated samples, a set of determinations for comparison purposes was made using portions of the same standard sample S in each pycnometer. The weight of mercury in the tare was 72.0 g.

The data obtained, together with the densities calculated (assuming unity for the density of ordinary mercury), follow: tare = τ.

TABLE II

RESULTS OF DENSITY DETERMINATIONS

Sample	Wt., g.	Av. wt., g.
S^1	$\tau-0.35310$	$\tau-0.35308$
	$\tau-.35305$	
S^2	$\tau-.06911$	$\tau-.06915$
	$\tau-.06919$	

Sample	Weight, τ minus	Density	Av. density	Diff. in density, p.p.m.
I_a^1	0.35322	0.9999980	0.9999988	−0.6
I_a^2	.06917	.9999997		
I_b^1	.35314	.9999992	0.9999994	
I_b^2	.06918	.9999996		
II_a^1	.35309	.9999999	1.0000001	±0
II_a^2	.06913	1.0000003		
II_b^1	.35309	0.9999999	1.0000001	
II_b^2	.06913	1.0000003		
III_a^1	.35310	0.9999997	1.0000024	+1.9
III_a^2	.06878	1.0000051		
III_b^1	.35296	1.0000017	1.0000005	
III_b^2	.06920	0.9999993		
IV_a^1	.35300	1.0000011	1.0000010	+0.6
IV_a^2	.06909	1.0000008		
IV_b^1	.35319	0.9999985	1.0000004	
IV_b^2	.06899	1.0000022		
V_a^1	.35308	1.0000000	1.0000010	−1.8
V_a^2	.06900	1.0000021		
V_b^1	.35278	1.0000042	1.0000028	
V_b^2	.06904	1.0000015		
VI_a^1	.35303	1.0000007	1.0000006	+0.8
VI_a^2	.06912	1.0000004		
VI_b^1	.35315	0.9999990	0.9999998	
VI_b^2	.06911	1.0000006		

Discussion of Results

The average deviation of these weighings from the mean was 0.075 mg.

With two exceptions, III_a^2 and V_b^1, the maximum deviation from the average was 0.15 mg. In both these exceptional cases, the weights were high. This effect might have been due to an unseen droplet of mercury on the outer surface of the pycnometer or to incomplete removal of the expelled droplet of mercury after adjusting to standard temperature. However, we have included these figures. If they had been rejected, the difference in density between the two extreme fractions in the third and fifth series would have been —8 and —5 instead of +19 and —18 parts in 10,000,000. The difference in density between the two extreme fractions of a series was less than two parts in a million and probably less than one part in a million. The greatest change in the atomic weight of mercury in any one of the chemically fractionated samples was less than 0.0002 unit.

The failure of these chemical reactions to yield fractions of mercury differing in density does not necessarily indicate that mass has no influence in determining which of two isotopic mercury atoms is ejected from the molecule. The negative results indicate that the necessary irreversible conditions did not obtain. Hevesy and Zechmeister[21] found by the radio-active indicator method that a dynamic equilibrium existed between lead diacetate and tetra-acetate in glacial acetic acid solution, but that there was no such effect between lead chloride and tetraphenyl lead in pyridine or between lead nitrate and diphenyl lead nitrate in dilute alcohol. In the first four series of fractionations it is probable that the reactions employed were reversible to a sufficient extent to nullify any separation of isotopes otherwise possible. The products, Hg and R_2Hg, obtained in the last two series should not be capable of reacting together if the analogy between organo-mercury and organo-lead compounds holds. In these cases, one would expect irreversible conditions and evidence of a separation of isotopes. The fact that no such separation was obtained indicates that these compounds, when first formed, must be in a reactive state different from that existing afterwards.

Summary

Evidence is advanced indicating that a peculiar type of oxidation-reduction reaction, $M_2X_2 = M + MX_2$, should effect a partial separation of isotopes.

To test this conclusion, six reactions of this type, all involving mercury compounds, were studied.

Samples of mercury obtained by these six diverse chemical methods of fractionation were purified by both chemical and physical methods and their densities determined by the pycnometer method.

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[21] Hevesy and Zechmeister, *Ber.*, **53**, 410 (1920).

No difference in density between extreme fractions was found greater than 19 parts in 10,000,000.

HALIFAX, NOVA SCOTIA

NOTE

Monopotassium Phosphate.—The generally published value for the melting point of monopotassium phosphate is 96°. This value, unfortunately, appears in such standard reference books as the Handbook of Chemistry and Physics (published by The Chemical Rubber Company), Van Nostrand's Chemical Annual, the Smithsonian Physical Tables and the International Critical Tables. An investigation shows Tilden's determination to be the source of this datum. Gmelin-Kraut's Handbuch der anorganischen Chemie, Vol. 2, Part 1, p. 140, however, states "The crystals remain shiny at 204° (Graham). They melt upon heating to a clear, glassy potassium monometaphosphate which becomes opaque on cooling."

Reference to Tilden's paper, entitled "Note on the melting points and their relation to the solubility of hydrated salts"[1] reveals that he reports the melting points of 42 hydrated salts and the one anhydrous salt, KH_2PO_4. No explanation is given as to why this single anhydrous salt was used nor is it mentioned except in his list of compounds with their respective melting points. These melting points were determined in glass tubes, bent twice at right angles, into one leg of which moist filter paper had previously been inserted and that end sealed.

In connection with investigations carried on in this Laboratory, monopotassium phosphate was made by the neutralization of crystallized phosphoric acid of the highest purity[2] with pure potassium hydroxide. The salt was subjected to four recrystallizations and a 0.05 M solution had a PH value of 5.03 at 27.0°.

Pure monopotassium phosphate, prepared in the manner just stated, was not found to melt in contact with its boiling saturated aqueous solution Melting-point determinations were then made in melting-point capillaries. These were attached to a thermometer (Bureau of Standards No. 26387) and immersed in a bath of Crisco contained in a test-tube provided with a stirrer. This test-tube was in turn immersed in a bath of Crisco in a large tube also provided with a stirrer. Heating was carried on very slowly from 244° upward. No stem correction was necessary as the thermometer dipped into the bath beyond the points where the temperature readings were made. The melting point was not found to be sharp, fusion commencing at 252.6° and being complete at 254.3° (corr.) There is evidently no true melting point, fusion being accom-

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[1] Tilden, *J. Chem. Soc.*, **45**, 266 (1884).

[2] Ross, Jones and Durgin, *Ind. Eng. Chem.*, **17**, 1081 (1925).