Attempts to Separate the Isotopes of Mercury by Chemical Means.—Prof. Harold S. King, Dalhousie University, Halifax, N. S.

Introduction.— Isotopes have been defined as substances chemically identical yet differing in atomic mass. For instance, chlorine is composed of two isotopic forms, one with atomic mass 35 and the other with atomic mass 37, but is completely free from any substance with atomic mass 35.46, the atomic weight of ordinary chlorine. The atomic weight of an element, therefore, is the statistical average of the atomic masses of its atoms. Chlorine, wherever found, in whatsoever kind of combination, nevertheless has the same atomic weight.[1]

It follows that the mixture of chlorine isotopes is remarkably uniform throughout nature. Iron and nickel, two other elements isotopically complex, from both meteoric and terrestrial sources, have invariant atomic weights within the limits of experimental accuracy.[2] Brönsted and Hevesy[3] have compared a large number of samples of mercury from a wide range of mineralogical, geological and geographical sources, and found no appreciable difference in the proportions in which its six isotopes are mixed. There is no evidence that any of the many chemical reactions, in which these elements must have taken part throughout geological eras, has produced a detectable change in the isotopic ratio.

Though isotopes have been separated by certain physical means that take advantage of their differences in mass, no laboratory method based on chemical fractionation has been successful even to the slightest degree. Much of the early work on the comparative chemistry of isotopes was done without a

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1. E. Gleditsch and B. Samdahl, Compt. rend. 174, 746 (1922); M. Dorenfeldt, J. Am. Chem. Soc. 45, 1577 (1923); A. W. C. Menzies, Nature 116, 643 (1925); W. D. Harkins and S. B. Stone, J. Am. Chem. Soc. 48, 938 (1926).

2. G. P. Baxter and T. Thorwaldson, J. Am. Chem. Soc. 33, 337 (1911); G. P. Baxter and L. W. Parsons, Ibid. 43, 507 (1921); G. P. Baxter and F. A. Hilton, Ibid. 45, 694 (1923).

3. J. N. Brönsted and G. Hevesy, Nature 109, 780 (1922).

knowledge of the extreme similarity of the structures of isotopic atoms.   According to modern theories of atomic structure, isotopes differ only in respect to their nuclei, the number of electrons about these nuclei being the same.   It has been shown in various ways that the outermost or valence electrons are chiefly responsible for the chemical properties of the atom as well as for most of the lines in the visible spectrum.   The similarity of spectral lines from isotopic atoms, therefore, indicates that the orbits of these electrons must be very nearly identical.

However, Aronberg,[1] in a comparison of the wave lengths of the line 4058Å from ordinary lead (at. wt. 207.2) and lead from Australian carnotite (at. wt. 206.3), found the latter to be 0.0044Å greater.   Merton and Perretta[2] have confirmed and extended this discovery.   Thus the mass of the nucleus has an effect, in this case of the order of one part per million, on the wave length of radiation from an electron.   Therefore the vibrations of the valence electrons can not be identical in isotopic atoms, though the difference may be too small to change the chemical properties appreciably.

Loomis and Kratzer,[3] independently, pointed out that much greater differences occur in the infra-red absorption bands of isotopic molecules, such as HCl^{35} and HCl^{37}, where the two vibrating masses, H and Cl, are more nearly equal in mass.   For instance, each line of the "first harmonic" band at 1.76μ has a satellite separated by an average interval of 14Å, the main lines being due to HCl^{35} and the satellites to HCl^{37}.   Thus the vibrations within a molecule, made up of two or more atoms, are much more affected by isotopic differences than are those of an electron in a single atom.

Lindemann[4] has discussed this same problem from the thermodynamic point of view.   He concludes that a change

1.   L. Aronberg, Astrophys. J. 47, 96 (1918).
2.   T. R. Merton, Proc. Roy. Soc. (London) 96A, 388 (1920); 100A, 84 (1921); B. Perretta, Compt. rend. 180, 1589 (1925).
3.   F. W. Loomis, Nature 106, 179 (1920); Astrophys. J. 52, 248 (1920); A. Kratzer, Zeit. f. Physik 3, 460 (1920).
4.   F. A. Lindemann and F. W. Aston, Phil. Mag. [6] 37, 523 (1919); F. A. Lindemann, Ibid. [6] 38, 173 (1919).

in the constant of the law of mass action, due to isotopic differences, would probably be imperceptible unless suitable equilibria were examined under favorable conditions. As he puts it, isotopes could not be separated by an ordinary precipitation reaction, any more than nitrogen and oxygen could be separated by dropping liquid air into a red-hot flask.

There is a highly speciallized type of reaction that seems to fulfill the conditions thus imposed for the separation of isotopes by chemical fractionation. 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. Though 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.

The action of a Grignard reagent on lead chloride, as discovered by Pfeiffer and Truskier[1], is an example of this type of reaction. The stoichiometrical relations are expressed by the equation

$$2PbCl_2 + 4RMgX = Pb + R_4Pb + 2MgCl_2 + 2MgX_2.$$
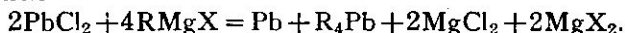
It has been shown[2] that R_2Pb is one of the intermediates in this reaction and that this compound is partially polymerized to R_2PbPbR_2. This latter compound, we assume, can break down with the production of metallic lead and the tetravalent organo-lead compound:

$$R_2PbPbR_2 = Pb + R_4Pb.$$
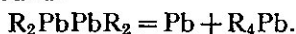
The use of this reaction to achieve a partial separation of isotopes has been investigated with conflicting results. Hofmann and Wölfl, Ebert and Dillon, Clarke and Hinchy[3] claimed that they obtained a change in isotopic composition while Staeh-

1.   P. Pfeiffer and P. Truskier, Ber. **37**, 1125 (1904).
2.   E. Krause and G. G. Reissaus, Ber. **55**, 888 (1922);   S. Möller and P. Pfeiffer, Ibid. **49**, 2441 (1916).
3.   K. A. Hofmann and V. Wölfl, Ber. **40**, 2425 (1907);   G. Ebert, Ion 2, 277 (1910);   T. Dillon, R. Clarke and V. M. Hinchy, Sci. Proc. Roy. Soc. (Dublin) **17**, 53 (1922).

ling and Brennen[1] reported negative results.   The author began his study of this reaction in his private laboratory in 1917[2].   More pressing duties interrupted the work until after the close of the war, when the investigation was resumed under the direction of Professor T. W. Richards at the Wolcott Gibbs Memorial Laboratory, Harvard University.   A sample of lead chloride was fractionated several times using the Grignard reagent, phenyl magnesium bromide.   It was hoped that a method of comparative density determinations could be developed that would indicate extremely small differences in isotopic composition.   After a year's unfruitful experimentation in this direction, this method of attack was dropped.   More recently the samples have been analyzed by determinations of the ratio $PbCl_2:2Ag$ by L. P. Hall[3].   He found that the atomic weight of the lead from the extreme metallic lead fraction was 207.217 and from the extreme tetraphenyl lead fraction 207.219, a difference of one part in a hundred thousand.   These results were 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.   In the author's opinion, the difference to be expected would be less than could be indicated even by these extremely accurate atomic weight determinations.

Methods of Fractionation.—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.   Aston[4] has proved the isotopic complexity of this element, his revised figures for the mass numbers of its isotopes being 198, 199, 200, 201, 202 and 204.

1.   C. Staehling, Compt. rend. **157**, 1430 (1913);   H. Brennen, Ibid. **180**, 282 (1925).
2.   T. W. Richards and W. C. Schumb, J. Am. Chem. Soc. **40**, 1409 (1918).
3.   T. W. Richards, H. S. King and L. P. Hall, J. Am. Chem. Soc. **48**, 1530 (1926).
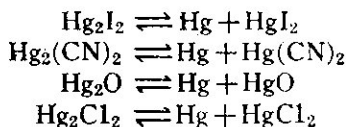4.   F. W. Aston, Nature **116**, 208 (1925).

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 Pfeiffer and Truskier previously discussed.   The basic equation for this type of reaction,

$$Hg_2X_2 = Hg + HgX_2,$$
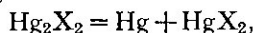
has been made the subject of a previous paper[1].   It was there pointed out that there were two possible structural formulae for mercurous compounds, X—Hg—Hg—X and $Hg = HgX_2$. If the first of these formulae is correct, then the course of the decomposition must be the same as for R_2PbPbR_2.   With the second, however, it would seem that only one of the mercury atoms is free to take the metallic form unless there is a shifting of the X groups back and forth from one mercury atom to the other.

In order to determine whether there is any separation of isotopes in this simultaneous oxidation-reduction type of re-action, five series of fractionations were employed, the conditions being varied as much as possible.   The mercury compounds used in these reactions were from the same source. No hesitancy would have been felt, however, in employing material from various unknown sources because, as has already been noted, the atomic weight of mercury from different sources is invariable, and because a difference, if any, in the atomic weight of the initial mercury would not affect adversely the significance of the comparative density determinations of the fractionated samples.

The reactions on which were based the first four methods of fractionation are represented as follows:—

$$Hg_2I_2 \rightleftharpoons Hg + HgI_2$$
$$Hg_2(CN)_2 \rightleftharpoons Hg + Hg(CN)_2$$
$$Hg_2O \rightleftharpoons Hg + HgO$$
$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$$

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1.   H. S. King, Trans. Nova Scotian Inst. Sci. 16, Pt. ᴏ, (1924).

In the fractionation by the iodide treatment, mercurous chloride was made to a paste with water and a solution of potassium iodide added gradually. Mercurous iodide first formed. The equilibrium between this compound on one hand and mercury plus mercuric iodide on the other was shifted by the addition of further portions of potassium iodide solution. This removed mercuric iodide by the formation of potassium mercuriiodide, leaving a heavy gray sludge of finely divided mercury. The solution was decanted from the residue. After washing first with potassium iodide solution and then with water, the latter was coagulated into a globule by drying. The combined solutions were digested with metallic zinc and hydrochloric acid until all mercury had been reduced to metal. This mercury was shaken with dilute nitric acid until a small amount of mercurous ions was found in solution, in order to remove the major part of the zinc. The two samples of mercury thus obtained were separately converted to mercurous chloride by the ammonium formate method described under the heading, —purification of samples. These two samples of mercurous chloride were treated as before, the complete system of fraction- ation thus being

$$Hg_2Cl_2$$
$$\downarrow$$
$$Hg_2I_2$$

$$Hg \longleftarrow \qquad \longrightarrow K_2HgI_4$$
$$\downarrow \qquad\qquad\qquad \downarrow$$
$$Hg_2Cl_2 \qquad\qquad Hg_2Cl_2$$
$$\downarrow \qquad\qquad\qquad \downarrow$$
$$Hg_2I_2 \qquad\qquad\qquad Hg_2I_2$$

$$Hg \longleftarrow \qquad \longrightarrow K_2HgI_4 \qquad\qquad Hg \longleftarrow \qquad \longrightarrow K_2HgI_4$$
$$\downarrow$$
$$Hg$$

[Sample I_a]   [Rejected].   [Sample I_b]
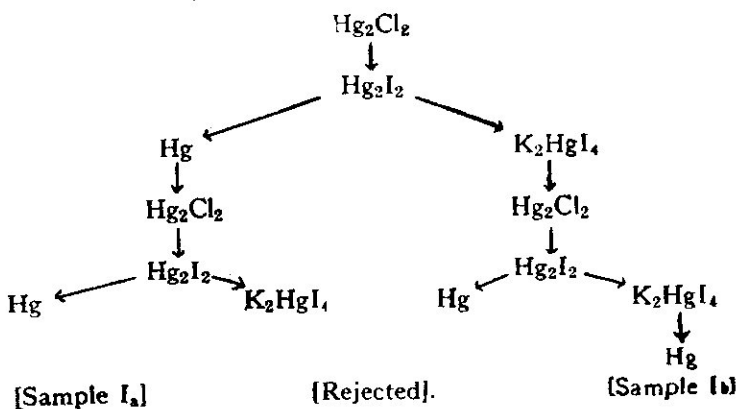
The fractionation by the cyanide method was the same as by the iodide except that mercurous chloride was added to an excess of potassium cyanide solution. In this way the mercurous cyanide was decomposed as rapidly as formed to give mercury and potassium mercuricyanide. The object of this method was to bring about as rapid a separation as possible.

In the case of the oxide fractionation, a very slow decomposition was desired. The mercurous chloride was added to an excess of dilute sodium hydroxide solution and allowed to stand for some days with frequent shaking. The precipitate of mercurous oxide, after careful washing, was gradually heated, out of contact with air, to decompose it into mercury and mercuric oxide. Finally potassium cyanide solution was added to dissolve the mercuric oxide.

The fourth method involved the use of aqua ammonia to shift the equilibrium

$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$$

to the right, the mercuric chloride reacting to produce infusible white precipitate. The mechanism has previously been discussed.[1] Several preliminary experiments, with the object of separating the mercury and the infusible white precipitate, were made. It was found that centrifugal separation was not complete and that volatilization of the mercury in a current of air was too slow. It was finally decided that extraction with a hot, concentrated solution of ammonium chloride was most efficient. By this treatment the infusible white precipitate was probably converted into fusible white precipitate.

$$Hg(NH_2)Cl + NH_4Cl = Hg(NH_3)_2Cl_2.$$

The two fractions obtained by each of these methods were converted to mercurous chloride and refractionated. The extreme metallic fraction in each case constituted the "a" sample itemized in the accompanying list. The mercury in solution in the other extreme fraction was reduced to the metallic state by means of zinc and hydrochloric acid. After removal of the excess of zinc by shaking with dilute nitric acid, these fractions were designated "b" samples.

1. H. S. King, Trans. Nova Scotian Inst. Sci. **16,** Pt. 3, (192'

The fifth reaction was similar to the Pfeiffer-Truskier reaction with the substitution of mercurous chloride for lead chloride.

$$Hg_2Cl_2 + 2C_2H_5MgBr = Hg + (C_2H_5)_2Hg + MgCl_2 + MgBr_2$$
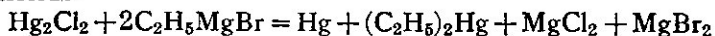
To bring about this reaction, the directions of Marvel and Gould[1], with certain modifications, were followed.   In order to insure as nearly complete reaction as possible the mercurous chloride in ether suspension was introduced directly into the Grignard reagent by means of a dropping funnel.   Mechanical stirring also aided in keeping the material in finely divided form. The proportion of reagents was altered so that, instead of about 4.5 moles of the Grignard reagent per mole mercurous chloride as directed, the ratio was 10:1.   In the purification of the products, the method used by Marvel and Gould, namely extraction with ether, was attempted.   There was some trouble with metallic mercury passing through the filter so a small amount of finely divided copper was added to prevent this. However the extraction method had to be abandoned because of the risk involved in working with such large quantities of so toxic a compound as diethyl mercury (over 200 grams).   Instead steam distillation was employed and found eminently satisfactory.   In the distillate, the layer of diethyl mercury, dissolved in ether, was heavier than the supernatant water. This was allowed to stand for a long time uncovered, the ether gradually evaporating.   The layer of diethyl mercury was then separated.   The yield was about 50% of theoretical based on mercurous chloride used.   By long boiling with a reflux condenser, the compound was decomposed into metallic mercury. The product was then distilled through a combustion tube containing hot copper oxide to ensure complete decomposition of the organo-mercury compound.   Because of the danger involved in working with organo-mercury derivatives the fractionation was not repeated.   The two fractions obtained in this way contained copper which was removed by dissolving the samples in nitric acid and precipitating mercuric sulphide from a solution of the nitrates in the presence of an excess of potassium

1.   C. S. Marvel and V. L. Gould, J. Am. Chem. Soc. 44, 153 (1922).

cyanide. The filtered and washed sulphide was converted to bromide by the action of bromine and finally reduced to metal with zinc. After the removal of excess zinc by shaking with dilute nitric acid, these samples were ready for the final purification.

In addition to the fractions obtained by the above five methods, a sample of ordinary unfractionated mercury was taken. This was prepared from the mercurous chloride by reduction with ammonium formate.

LIST OF SAMPLES.

S   = Ordinary mercury, unfractionated.
I_a = Mercury from extreme Hg fraction of iodide   treatment.
I_b =   "   " K_2HgI_4 "   "   "
II_a =   "   "   Hg   "   cyanide   "
II_b =   "   " $K_2Hg(CN)_4$ "   "   "
III_a =   "   "   Hg   "   oxide   "
III_b =   "   "   HgO   "   "   "
IV_a =   "   "   Hg   "   ammonia   "
IV_b =   "   " NH_2HgCl "   "   "
V_a =   "   "   Hg   "   Grignard   "
V_b =   "   " $(C_2H_5)_2Hg$ "   "   "

Purification of the Samples.— Each of the samples enumerated in the above table was purified in the same way by a series of operations, both chemical and physical, which is summed up under the following headings.

1.   Conversion of the sample to mercuric chloride and precipitation as mercurous chloride by the action of ammonium formate.

2.   Further reduction to metal by ammonium formate.

3.   Preparation of mercuric chloride by burning in chlorine and three fractional volatilizations of the product.

4.   Reduction to mercury by ammonium formate.

5.   Distillation of the metal four times in a stream of air under reduced pressure.

A discussion of the objects of these various steps together with the details of the technic follow.

All reagents used were carefully purified.   Ordinary distilled water of the laboratory was twice distilled, first from alkaline potassium permanganate and then with the addition of a few drops of sulphuric acid.   The condensers used were of block tin and had been thoroughly steamed out before use. The water was collected in pyrex flasks which had been filled with water and boiled for several hours before steaming out. Dust was excluded by suitable adapters.   The nitric and formic acids were redistilled, the first and last quarters being rejected.   In the case of hydrochloric acid the middle third only was collected for use.   The ammonia was distilled either directly into the diluted formic acid to convert it into the ammonium salt or absorbed in water.   The chlorine was prepared by dropping pure hydrochloric acid onto the "C. P." potassium permanganate of a reliable house.   The gas was first washed with water and then dried by two wash bottles of concentrated sulphuric acid and finally by a tower of solid glass beads down which a stream of sulphuric acid trickled.   With a few unimportant exceptions, all glass used throughout the investigation was of pyrex, which had been thoroughly cleaned and steamed out.

In the purification of the mercury, each sample (about 150 grams) was oxidized with nitric acid.   The mercuric nitrate, so produced, was converted into chloride by several evaporations with hydrochloric acid.   The solution was evaporated to dryness, and the residue dissolved in water.   An excess of aqueous ammonium formate was added, and the solution warmed. There was a copious evolution of carbon dioxide, and pure white mercurous chloride was precipitated.   The reaction was not quite quantitative.   The product was filtered, and the precipitate well washed.   This precipitate was treated with an excess of ammonium formate solution, and the mixture boiled. From time to time portions of aqua ammonia were added.   The reduction is much more rapid and complete in an alkaline medium.   Metallic mercury was precipitated in a finely divided form.   It was well washed by decantation.   On drying, the mercury coalesced into one globule.   There was a tendency for this globule to wet glass surfaces.   After pouring the product

through a fine glass capillary, the scum causing this wetting was removed.

This reduction, carried out first in a neutral or slightly acid medium, and then in an alkaline, must have effected a considerable purification. Though silver and gold were not removed the less electronegative elements must have been separated quantitatively. To test this conclusion, a solution of the chlorides of mercury and copper was reduced in the same way as described above. Five grams of the mercury precipitated were dissolved in nitric acid, evaporated to dryness and ignited in a pyrex beaker. Silver was found in the almost invisible white residue, but the ferrocyanide test for copper was negative. Since copper was known to be present in some of the initial samples, this result was reassuring.

The mercury, after the ammonium formate purification, was introduced into the first of a series of four pyrex bulbs. This first bulb was enclosed in an asbestos hot air bath. Pure, dry chlorine was passed over the mercury until the reaction was practically complete. Then the temperature was 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 residue, consisting largely of mercuric chloride, was left behind. In the same way two more volatilizations were made.

In a preliminary experiment with a sample of mercury known to contain traces of iron, there was a faint pink tinge to the mercuric chloride. In the fractionation of the pure mercury samples, the product was without a trace of color. This series of fractional volatilizations would not have removed the more volatile chlorides that might have been present. Rose[1] has shown that auric chloride volatilizes easily in a current of chlorine at temperatures ranging all the way from 180° to 1100°C. Thus this treatment would not have freed the product from gold. However the following tests show that silver must have been left quantitatively in the residue. The first bulb was extracted, first with hydrochloric acid and then with ammonia.

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1. T. K. Rose, Trans. Chem. Soc. (London) **67**, 881 (1895).

The combined extracts were evaporated to dryness and ignited. A faint white residue contained silver. By similar treatment no silver could be extracted from the second bulb. It might be noted here that, after each series of volatilizations, each bulb was extracted with hydrochloric acid and ammonia. Finally, before reassembling, they were well steamed out.

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 much 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.[1] 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 zig-zag 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 removed by oxidation in the vapor state. On the other hand, several distillations are necessary to reduce the amount of silver, gold and platinum to a point where their presence cannot be detected. After one distillation Hulett found 2 parts of silver, 0.027 part of gold and 0.001 part of platinum per million parts of the distilled mercury. A second distillation reduced the amount of silver to 0.03 part and of gold to much less than 0.01 part. A third distillation reduced these impurities to a non-detectable amount. Thus it is seen that silver is distinctly the most difficult to remove by this method. It is for this reason that mercuric chloride was fractionally volatilized prior to the distillation of the metal.

It is possible that part of the metallic impurity in the distillate found its way thither as spray. In the form of still used in our purification, the partial condensation of mercury in the fractionating column must have completely freed the vapor from any spray arising from the distilling flask. It is probable,

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1. G. A. Hulett, Phys. Rev. **33**, 307 (1911).

though no tests were made to prove this point, that the condensed mercury carried back with it any noble metal that may have volatilized.   In this way, one distillation should have been as efficacious in removing these impurities as several distillations without the fractionating column.

The mercury samples after passing through the various steps in the purification described above were drawn by suction several times through extremely fine capillaries and collected in scrupulously cleaned weighing bottles in order to remove every possible particle of dust.

If gases from the atmosphere are absorbed by mercury, an error would be introduced into the density determinations, though it would be more or less canceled out because there is no reason to suppose that one sample would absorb more than another.   Hulett[1] has discussed this possibility.   He referred to three barometers which had been under observation for over thirty years by the Weather Bureau at Washington.   After this period of time, they gave the same readings as new barometers to within 0.05 mm.   This very neat observation gives some idea of the insolubility of atmospheric gases in mercury.

It is recognized that, in some step or steps in the purification, a partial separation of isotopes might have taken 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[2].   Although this relationship may not be exact, its deviation must be almost infinitesimal.   For measuring the amount of separation effected by various processes, the exact ratio between density and atomic weight has been, perhaps, too implicitly relied upon.   For determining whether any separa-

1.   G. A. Hulett, Phys. Rev. **33,** 313 (1911.)
2.   F. Soddy, Nature **94,** 1615 (1915); **107,** 41 (1921); T. W. Richards and C. Wadsworth, J. Am. Chem. Soc. **38,** 221 and 1658 (1916); J. N. Brönsted and G. Hevesy, Z. physik. Chem. **99,** 189 (1921); W. D. Harkins and A. Hayes, J. Am. Chem. Soc. **43,** 1803 (1921); R. S. Mulliken and W. D. Harkins, Ibid. **44,** 37 (1922).
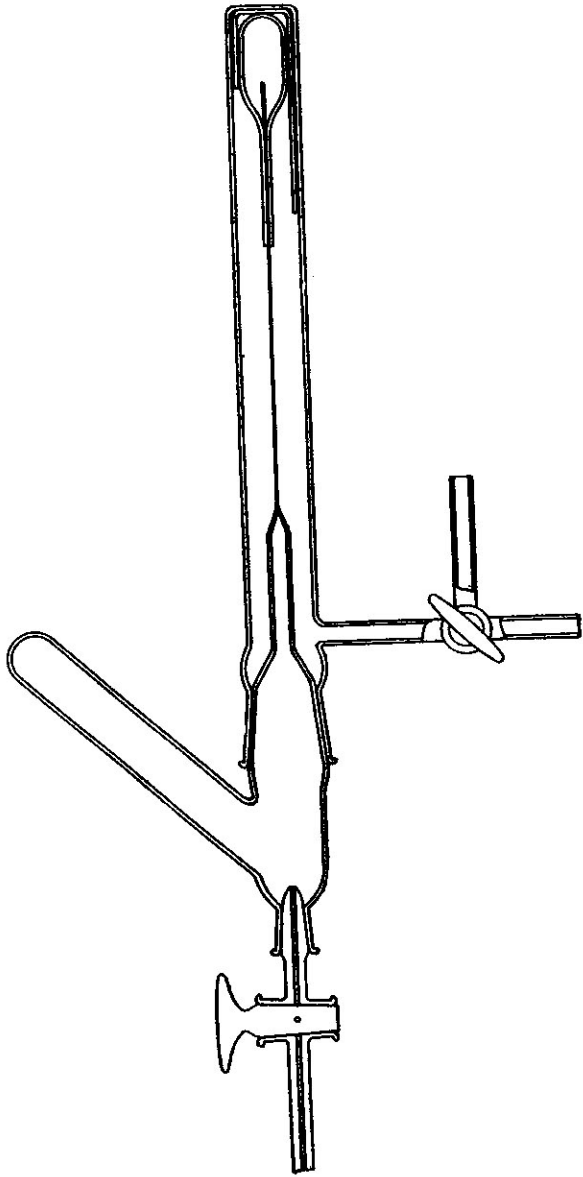
tion has taken place, the density method is admirable. If the two extreme samples obtained by a process of fractionation do not differ in density, then that process does not effect any appreciable separation of isotopes.

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

The pyknometers were filled in the manner to be described by the use of an apparatus illustrated in the accompanying cut. The pyknometer, resting in a holder, was lowered into the apparatus, care being taken to cover the greased glass joint with glazed paper to prevent contamination from this source. Then the extremely fine capillary on the stopper was inserted into the neck of the pyknometer. The mercury sample was introduced into the side arm of the stopper and the whole apparatus exhausted through both stopcocks. Then by tipping the apparatus the mercury was brought into the stem of the stopper. It is necessary to exhaust the stopper as well as the pyknometer chamber prior to this transference of the mercury in order to prevent bubbles of air from being carried into the pyknometer. Air so introduced is extremely hard to remove especially in the latter stages of the filling when the end of the capillary tube is submerged. When the vacuum in the stopper had been broken, the mercury began to drop very slowly through the capillary into the pyknometer. After this had been filled, there still remained a portion of the mercury in the reservoir. Air was then admitted gradually, and the pyknometer removed.

Since a change of 0.001°C in temperature changes the specific gravity of mercury by 0.000002 unit, the amount of

mercury in the pyknometer was adjusted at a definite temperature maintained as nearly constant as possible. The filled pyknometer was inserted into a long, thin glass test tube and lowered into a padded and covered thermostat tank. The temperature was controlled by a six-fingered toluene regulator holding about a liter of toluene[1]. At the suggestion of Dr. John Russell, while a student at Harvard, a roll of fine copper gauze was inserted in each of these fingers to bring about a more rapid heat transfer. Toluene itself is a poor conductor of heat. Ordinarily only the outer layer expands or contracts with changes of temperature. This modification was very satisfactory, the lag being less than with the ordinary type, as shown by the rapidity with which the electric light bulb, used for heating, flashed on and off. This regulator kept the temperature at approximately 29.0° to within 0.001°C. No change in the reading of a Beckman thermometer, on which a thousandth of a degree could be estimated, was noted. After several hours at constant temperature, 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. Then the pyknometer was removed. After coming to room temperature, the droplets of mercury on the surface of the pyknometer were removed by brushing the surface 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 pyknometer inside a box in which a large quantity of radioactive uranium salt was strewn, the charge being dissipated by the ionized air. It is hardly necessary to state that the pyknometers were never touched with the fingers, cork-tipped forceps always being used.

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1. The toluene was a sulphur-free sample which was further purified, washed with water and dried with sodium. Molten sodium was run into the hot toluene and the mixture shaken until the sodium solidified in the form of minute globules. Sodium in this form is much freer from surface oxidation than that exuded as wire from a press. The toluene was then distilled, the vapor passing through a trap containing liquid sodium-potassium alloy. These precautions were taken to eliminate the possibility of impurities reacting with the copper coils in the regulator.

When not being weighed, they were kept under a bell jar and carefully protected from dust or contamination of any kind.

It has been stated that three pyknometers were made. One of them 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 pyknometers (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 then 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.   These two samples were then weighed, one immediately after the other, against the first pyknometer as tare. Since the tare used was so nearly identical in composition, proportions and weight to the pyknometers plus samples, 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 one milligram.

After this first weighing the pyknometers were emptied and filled again with the same samples reversed and adjusted to standard temperature.   That is, if, in the first weighing, sample 'a" was in pyknometer "1" and sample "b" in pyknometer "2", then in the second set of weighings sample "a" was in pyknometer "2" and sample "b" in pyknometer "1".   In this way, it was felt, all irregularities introduced by temperature changes, etc., were eliminated.

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 0.015mg . Three weighings and a determination of the sensitivity were made for each determination.   The averages are given in the accompanying table.   The extreme variation between these weighings for any particular sample was 0.05 mg.   This extreme variation was rare.   Since in all six weighings (three in one pyknometer and three in the other) were made with each sample the error due to weighing was within 0.01 mg.

Before weighing the fractionated samples, a set of determinations for comparison purposes was made using portions of the same standard sample "S" in each pyknometer.   The result of this series shows that pyknometer "1" filled with mercury weighed 0.35308 gram and pyknometer "2", 0.06915 gram less than the tare.   The total weight of mercury in the tare was approximately 72.0 grams.

The data obtained, together with the densities calculated (assuming unity for the density of ordinary mercury) follow.
Tare $= \tau$.

Sample	Weight	Av. Weight.
$S^1\left\{\vphantom{\begin{matrix}a\\a\end{matrix}}\right.$	τ—0.35310$\left.\vphantom{\begin{matrix}a\\a\end{matrix}}\right\}$ τ—0.35305	τ—0.35308
$S^2\left\{\vphantom{\begin{matrix}a\\a\end{matrix}}\right.$	τ—0.06911$\left.\vphantom{\begin{matrix}a\\a\end{matrix}}\right\}$ τ—0.06919	τ—0.06915

Sample	Weight	Density	Av. Density	Diff. in Density. Parts in 10,000,000
I_a^1	τ—0.35322	0.9999980	0.9999988	
I_a^2	τ—0.06917	0.9999997		
I_b^1	τ—0.35314	0.9999992	0.9999994	—6
I_b^2	τ—0.06918	0.9999996		
II_a^1	τ—0.35309	0.9999999	1.0000001	
II_a^2	τ—0.06913	1.0000003		
II_b^1	τ—0.35309	0.9999999	1.0000001	±0
II_b^2	τ—0.06913	1.0000003		
III_a^1	τ—0.35310	0.9999997	1.0000024	
III_a^2	τ—0.06878	1.0000051		
III_b^1	τ—0.35296	1.0000017	1.0000005	+19
III_b^2	τ—0.06920	0.9999993		
IV_a^1	τ—0.35300	1.0000011	1.0000010	
IV_a^2	τ—0.06909	1.0000008		
IV_b^1	τ—0.35319	0.9999985	1.0000004	+6
IV_b^2	τ—0.06899	1.0000022		
V_a^1	τ—0.35308	1.0000000	1.0000010	
V_a^2	τ—0.06900	1.0000021		
V_b^1	τ—0.35278	1.0000042	1.0000028	—18
V_b^2	τ—0.06904	1.0000015		

The average deviation of these weighings from the mean is 0.08 mg.   With two exceptions, III_a^2 and V_b^1, the maximum deviation from the mean is 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 pyknometer or to incomplete removal of the expelled droplet of mercury after adjusting the temperature in the thermostat.   However we have included these figures.   If these two exceptions had been rejected, the difference in density between the two extreme fractions in the third and fifth series would be —8 and —5 instead of +19 and—18 parts in 10,000,-000.   The results show that certainly in none of the chemical methods of fractionation tried was there a difference in density between the extreme fractions of more than 2 parts in a million and probably none greater than 1 part in a million.   From these results the greatest change in atomic weight of mercury in any one of the samples analyzed must be less than 0.0002 unit.