[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE SEPARATION OF MERCURY INTO ISOTOPES IN A LARGE APPARATUS

BY WILLIAM D. HARKINS AND S. L. MADORSKY

Received September 25, 1922

Introduction

The object of the work of the present paper was to demonstrate the efficiency of a moderately large apparatus for the separation of the isotopes of mercury by vaporization in a vacuum. This apparatus is of a design such that it may easily be constructed as a part of a large multiple unit apparatus. It has been shown by Mulliken and Harkins[1] that the low pressure vaporization is essentially a diffusion through the surface of the liquid, which acts as a surface of molecular thickness, with apertures of the dimensions of a molecule. While the separation coefficient of mercury (0.0060) is considerably smaller than that of chlorine as hydrogen chloride (0.00950), the apparatus for the separation of the former may be made much more simple than that needed for the latter, so that the simplicity of the apparatus more than makes up for the smallness of the coefficient, provided a certain change in atomic weight is desired. However, for a certain change in the relative density—which is probably more important, if the object in view is to demonstrate differences in properties, such as the spectra, of the isotopes obtained—the separation coefficient of hydrogen chloride is nearly 9 times as great as that of mercury, so it is very difficult to overcome the theoretical advantage of the former by the use of any form of apparatus.

The advantage is, however, very greatly on the side of mercury when convenience of manipulation is considered, but is not inherent in the vaporization method, since Dr. Mulliken, working in this Laboratory, has secured an even more rapid separation by utilizing diffusion through a thin membrane, such as filter paper. The increase in the rate of separation was in this case due to the fact that it is easy to combine an efficiency of nearly 100% in the diffusion with a somewhat smaller efficiency in the vaporization utilized to obtain the vapor for diffusion.

A Large Apparatus for the Separation of Mercury into Isotopes by Vaporization

The apparatus used for the separation of the isotopes of mercury by Brönsted and Hevesy[2] is very simple, and consists merely of a Dewar

---

[1] Mulliken and Harkins, THIS JOURNAL, 44, 37–65 (1922).

[2] Brönsted and Hevesy, *Phil. Mag.*, 43, 31 (1922). These writers have failed to refer to the much earlier work on the separation of isotopes published from this Laboratory.

bulb, the outer jacket of which is used to contain the mercury, while the inner bulb is filled with liquid air, which acts as a cooling agent. Because the mercury is frozen by the liquid air it is difficult to collect the diffusate in several fractions. The difficulty was obviated by Mulliken and Harkins, who used an apparatus of an entirely different design, with ice as the cooling agent. This has been used almost entirely to study the efficiency of the process as related to pressure, speed of vaporization and form of apparatus, and no attempt has been made to obtain a separation of any considerable magnitude. It seemed advisable, therefore, to design a larger apparatus which would allow of the use of a considerable amount of material at one time. This was done early in 1921, and the first model was made of moderate dimensions in order that the efficiency of the process might be tested before the construction of a larger apparatus was undertaken. The general principle used is very similar to that made use of by Mullikens and Harkins in that the molecules which shoot out from the evaporating surface strike a roof, which has a slope such that the liquid mercury will adhere and run down the surface. The angle of the slope used is 45°.

The apparatus, Fig. 1, was cut from 2 large pieces of forged steel. Cast steel was not used since it is more likely to leak. The mercury is vaporized at a pressure between 0.001 and 0.0001 mm. from an annular steel trough D which holds 2600 g. of mercury. This amount could be easily increased in the same apparatus by the use of a wider trough. The trough is heated by an iron-encased calorized Nichrome wire F, insulated by magnesium oxide. This should be buried in a cast-iron jacket in order to give good contact with the trough, or it can be put inside the trough which affords better conduction of the heat, but does not give such free evaporation when the sample becomes very small. The coil may be cast into the base of the trough itself. The 4 supports for the heating wire are made from glass rods, though a poorer conductor of heat such as zirconium oxide would have been even better. The electric current is carried to the heating plate by 2 platinum wires, i, sealed in through the walls of the glass tube G which leads to the vacuum pumps. The wire is insulated from the inverted steel cone by 2 glass tubes, l. The joint, n, between the glass tube and the steel is long and very carefully ground, there is a second ground joint between the steel roof B and the inverted cone C. This is sealed by mercury, h, held in place by a thin hoop of steel, held on by friction. The cooling cylinder A is made of brass. It does not need to be as deep as the dimension given (36 cm.), but this depth is advisable in order to give a sufficient capacity for ice. The only materials, other than mercury, exposed on the inside of the apparatus are glass, steel and platinum, and the surface of the last is very small.

Operation of the Apparatus

The trough of the thoroughly cleaned apparatus is filled with 190 cc. of mercury which has been highly purified, and the roof B is carefully lowered. Mercury is run in at h to make the joint tight, and the vacuum pumps are then started. These consist of a Hyvac oil pump, and a large and very rapid Knipp mercury condensation pump. The current is then turned on, and as the heating plate rises in temperature considerable quantities of gas are evolved. The lower extremity of the glass tube G is sealed off with a long point, and in this the lighest fraction of the mercury begins to condense. If the pressure in the apparatus is sufficiently low, this has an atomic weight 0.006 unit

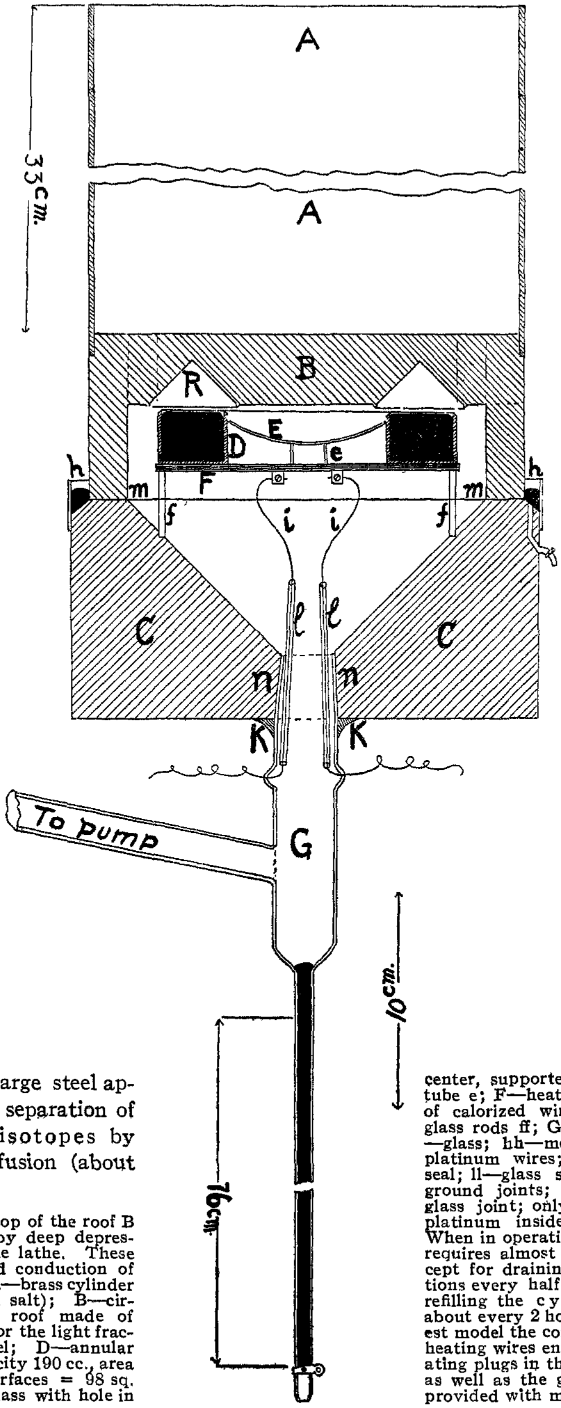

Fig. 1.—Large steel apparatus for the separation of mercury into isotopes by evaporative diffusion (about $^1/_2$ actual size).

Note: The top of the roof B was actually cut by deep depressions made on the lathe. These give a more rapid conduction of heat to the ice. A—brass cylinder for ice (or ice and salt); B—circular condensing roof made of steel; C—drain for the light fraction made of steel; D—annular steel trough, capacity 190 cc., area of evaporation surfaces = 98 sq. cm.; E—watch glass with hole in center, supported on short glass tube e; F—heating element made of calorized wire, supported on glass rods ff; G—collecting tube—glass; hh—mercury seal; ii—platinum wires; kk—sealing wax seal; ll—glass sleeves; mm—ground joints; nn—ground steel glass joint; only steel, glass and platinum inside the apparatus. When in operation the apparatus requires almost no attention except for draining the light fractions every half hour or so, and refilling the cylinder with ice about every 2 hours. In the newest model the connections ll to the heating wires enter through insulating plugs in the base and these, as well as the glass tube G, are provided with mercury seals.

lower than ordinary mercury, so it is lighter by 30 parts per million. This is 60 times the detectable difference since the pycnometer described by Mulliken and Harkins gives the density to 1 part in 2 million or better when only ordinary precautions are used. The lower part of this tube is a capillary in order that its volume may be small, and the mercury is run out against the pressure of the atmosphere after its height has risen above 760 mm. If small fractions are desired the mercury may be run into a vacuum flask or bottle at the lower end of G, but with too small fractions the work of determining the density becomes considerable.

In the experimental work the rate of evaporation was kept at 15 to 20 cc. per hour, or 0.15 to 0.2 cc. per square centimeter of surface. Thus a run in which all of the mercury is vaporized from the trough takes at least 9½ hours, provided the trough is full at the beginning.

The molecules of mercury which escape from the surface of the mercury in the trough D strike the roof above R. The temperature of this roof is kept low by the ice water in A, so very few molecules re-evaporate after condensation. The greatest distance which a molecule moving vertically upward has to travel between the top of the full trough and the peak of the roof, is less than 2.5 cm. and near the edges of the trough this distance diminishes to less than 1 cm. As the level of the mercury falls, the distance traveled by the molecules increases, and becomes considerable when it is nearly empty, since the depth of the trough is 2.40 cm. Furthermore, as the trough empties the molecules have more and more opportunity for condensation on and re-evaporation from the hot walls of the trough. These two factors serve to make the efficiency of the apparatus somewhat less toward the end of a run, or with small quantities of mercury, than at the beginning of a run with large quantities.

In order to obviate this evil a small conical roof has been cut from below in the center near B. A small circular dish of any capacity between 25 and 200 g. of mercury can be placed underneath this and heated by an independent hot plate. This is to be used when the samples become very small, but thus far it has not been put into operation since the glass apparatus of Mulliken and Harkins has been used for small samples. For this reason, and for the sake of simplicity, this unit is not shown in the drawing.

The mercury which collects on the surface of the steel gathers into drops, and these run down the 45° incline to a sharp edge which determines exactly where they shall drop. Those which fall from the outer edge drop directly into the conical hole in C, while those from the inner edge are collected by an inverted watch glass E, and fall through a hole at its center e, thus falling where there are no wires to be encountered.

Fractionation Scheme

Ten runs, I to V and XVI to XX of 190 cc. or 2600 g. each, using 26 kg. of mercury in all, were made on very pure mercury of the ordinary atomic weight. Each of these was collected in 8 fractions, as outlined in Table I. The process may be visualized by consulting Fig. 1 of the paper by Mulliken and Harkins.[3] The decrease of the atomic weight ($-\Delta M$) to be expected on the basis of the theory developed in this paper was calculated for the first fraction from the equation

$$-\Delta M = E.B\,\frac{\ln C}{C-1} \tag{1}$$

where E is the fractional efficiency, B is the separation coefficient, and $C = (N_0/N)$ is the cut. N_0 is the initial number of moles, and N is the number of moles in the *residue.*

For Fractions 2 to 7, that is, all of the intermediate fractions

$$-\Delta M = \frac{E.B}{C_2 - C_1}\,(C_1 \ln C_2 - C_2 \ln C_1) \tag{2}$$

Here C_1 and C_2 are the values of the cut at the beginning and end of the fraction which is taken.

For the end fraction (8)

$$-\Delta M = E.B \ln C \tag{3}$$

TABLE I

FRACTIONATION SCHEME FOR 190CC. OR 2600G. SAMPLES OF MERCURY OF ORDINARY ATOMIC WEIGHT. (RUNS I TO V, AND XVI TO XX)

Fraction	%	Cc.	Weight G.	Cut C or C_2-C_1	Change of dens. (Parts per million) Calculated 100%	90%	→ Actual	Change of at. wt. 100%	Actual
1	20	38	520	1.25	−25.4	−22.9	−22.8	−0.005	−0.0046
2	20	38	520	1.66–1.25	−18.2	−16.4		−0.0036	
3	15	28.5	390	2.22–1.66	−10.2	− 9.2		−0.0020	
4	15	28.5	390	3.33–2.22	− 0.4	− 0.36		−0.00008	
5	10	19	260	5–3.33	+10.9	+ 9.8		+0.0022	
6	10	19	260	10–5	+26.2	+23.6		+0.0052	
7	5	9.5	130	20–10	+45.9	+41.3		+0.0092	
8	5	9.5	130	20	+85.2	+76.7	V^a=+78	+0.0170	+0.016

[a] V designates that this particular figure was obtained in the fifth run, which gave about the average efficiency of 90%. II_8, that is the 8th fraction from the second run, showed an increase of only 51 parts per million, or an efficiency of 63%. This low efficiency was due to the high pressure, 0.060 mm., which was 60 times higher than the highest pressure in the other runs.

Table II gives the fractionation scheme used on the light fractions given in Table I.

TABLE II

FRACTIONATION SCHEME FOR THE LIGHT FRACTIONS OF TABLE I. (RUNS VI TO IX AND XXVIII TO XXXIII)

Fraction	%	Wt. G.	Cut C or C_2-C_1	Change of density Calculated 100%	90%	Actual	Density Actual	Δ (At. wt. increase)
1	25	650	1.33	−24.7	−22.2	−22.2	−44.4	−0.0089
2	25	650	2–1.33	−14.8	−13.3	..	..	....
3	25	650	4–2	0	0	..	..	....
4	25	650	4	+39.5	+35.5	..	..	....

---

[3] Ref. 1, p. 50.

The density change for Fraction 1 as given in the table is that for the sixth run. Runs VII to IX, inclusive, were made on combined light fractions. Run IX gave 55 cc., with $\Delta = -65.2$. Here Δ gives the increase of density in parts per million.

Runs X to XII were made on the basis of a 50% cut. Here the increase of density should be 17.7 parts, and the decrease also 17.7 parts per million. In the tenth run, the 55 cc. from Run IX was split into equal light and heavy fractions, with an estimated $\Delta = -(65.2 + 17) = -82.2$. In the eleventh run this was split in the same way again, with an estimated $\Delta = -(82.2 + 17.7) = -99.9$, and in the twelfth, $\Delta = -(99.9 + 15.9) = -115.8$. Two determinations were made of the density of the 8 cc., or 109 g. thus obtained, and it was found to be —112.4, which represents an efficiency of 93.3%.

The seventh fractions of Runs I to V were combined, giving 50 cc. with an estimated Δ of + 36 p. p. m. This was evaporated into 3 nearly equal fractions. The last fraction of 17 cc. was combined with the eighth fractions from Runs II to V, Fraction I_8 having been spoiled by accidental admixture of lower grade material. This 63 cc. with an estimated $\Delta = +64$ was evaporated to 12 cc. with an estimated Δ of + 106.5, while the value determined is 95.9 p. p. m.

In Runs XX to XXV a cut of 2 was used, and in Runs XXXIX to XLII, cuts of 2 or 3, upon the heavy fractions from previous work. This supplied 16 cc. of mercury with an estimated Δ of +175, and a determined Δ equal to 159 p. p. m. This small sample was then evaporated down to 0.2 cc. 7 times, at a rate of 4 cc. per hour, by the use of the small glass evaporator described by Mulliken and Harkins.[1] The combined heavy sample thus obtained, 1.4 cc., was then evaporated to 0.2 cc. with an estimated Δ of +310, and a determined value of 260 p. p. m.

Runs XXVI to XXXVIII were made on the combined light fractions, using the steel evaporator in the first 8, and the glass apparatus in the last 5. An intermediate density determination gave $\Delta = -112.5$ p. p. m. instead of the calculated 116. The final 0.4 cc. obtained in this way has a density such that Δ equals 220 p. p. m. instead of an estimated 240.

The total difference of density obtained in this work is equal to 480 parts per million, or 0.096 units of atomic weight, which is practically 0.1 unit. If it be assumed that the atomic weight of ordinary mercury is 200.600, then the heaviest specimen of 3.8 g. has an atomic weight of 200.652, while the lightest, 4.4 g., has an atomic weight equal to 200.556.

Density Determinations

The method and the pycnometers used for the density determinations on *large samples of mercury* have been discussed by Mulliken and Harkins,[1] so only a few examples will be cited here. The ordinary pure mercury used was compared with that of Mulliken.

Density of original material, $\Delta = 0$
Weight of pycnometer and stand
plus mercury (about 101 g.)
1st. detn. = 117.56360
2nd. detn. = 117.56356
3rd. detn. = 117.56357
Mean = 117.56358
Largest deviation from mean
= 2 parts in 10 million

Density of 8 cc. of light fraction
1st. detn. = 117.55233
2nd. detn. = 117.55235
Mean = 117.55234
Deviation from mean = 1 part in 10 million

$$\text{This gives } \Delta = -\frac{(117.56358 - 117.55234)}{101}$$

= —112.4 parts per million

Several slight changes were made in the pycnometer of Mulliken and Harkins, the principal one of which is the introduction of a small bulb in the upper part of the stem in order to hold the mercury when the temperature in the balance case is higher than that in the thermostat. At the suggestion of Dr. Mulliken the effect of changes of temperature and pressure of the air upon the buoyancy corrections was eliminated by the use of a glass cup of the proper volume, together with that of the glass of the pycnometer. A more accurate method would be to balance the pycnometer with a sealed-up pycnometer of the same area and weight, but this was found unnecessary.

In order to determine the density of fractions as small as 0.2 cc., a pycnometer of about this volume (Fig. 2) was constructed.

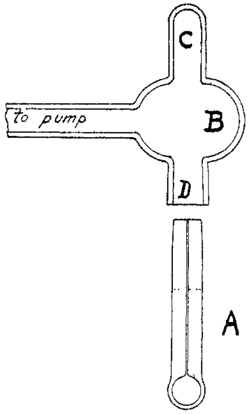

Fig. 2.—Small pycnometer for the determination of the density of mercury (volume = 0.2 cc.).

Since this differs in certain details from the larger pycnometers, its special features will be described. The capillary is about 0.1 mm. or even less in diameter, and the end of the capillary tube is very carefully ground into the filling device at D. Before using, part of the ground joint on this tube is covered with a thin coat of heavy vacuum grease, care being taken to keep this grease at a considerable distance from the tip, so that none can touch the mercury. The pycnometer is then carefully fitted into the joint at D, the mercury is put into the bulb B, and the filling device is attached to a tube from a mercury condensation pump by means of a greased ground-glass joint which allows the pycnometer and filling device to be rotated in a vertical plane. The apparatus is then evacuated fully while the mercury is in the bulb B, after which it is transferred to C by rotating the apparatus. After evacuating further, the apparatus is suddenly turned so that the mercury drops on the top of the capillary at D. The pycnometer fills completely, and a small amount of mercury is left. The pycnometer is then detached, the grease removed with great care by a solvent which does not spread too easily, and the pycnometer caused to overflow by setting it in a small thermostat at the proper temperature, which was 43.07° with the special pycnometer used. When this is placed in a thermostat at 25.000°, it is found that the mercury comes almost exactly to the mark. Any deviation is determined by a cathetometer or a measuring microscope.

The pycnometer was weighed on a high sensitivity analytical balance, which gave 1 cm. of deflection of a beam of light for 0.14 mg. The balance was made specially sensitive and stable for this work by Ainsworth and Sons.

The weights of the pycnometer and mercury as obtained in one set of determinations are given below.

Weight of small Pycnometer plus

Light isotopic mercury	Pure ordinary mercury	Heavy isotopic mercury
7.03083	7.03146	7.03217
7.03085	7.03144	7.03213
7.03085	7.03142	7.03211
7.03085	.....	7.03217
Mean=7.030845	Mean=7.03144	Mean=7.032145

While these results are very good, and sufficiently accurate for the purpose, it is believed that the principal cause of the variation which they show is due to the lack of a proper case for the balance, since the error seemed to be due to a variation in the temperature of the balance.

Other density determinations were made but are not listed in this paper, since this would add too greatly to the considerable amount of detail already included. These exhibit the close correspondence between the experimental results and the calculated. While the efficiency in some operations was much lower than in others, the lower efficiency always accompanied some apparent cause, and was usually due to working with smaller quantities of mercury than were required for the most satisfactory results.

Increase of the Density of the Heavy Fraction of an Isotopic Mixture with the Cut

The change in the density with the cut of either the heavy or the light fractions of *any isotopic mixture* may be calculated by the equations of Mulliken and Harkins, provided the composition of the initial mixture (present in the element) is known. The results may be expressed much more simply for the heavy than for the light fractions. It seems to be of value, therefore, to show the forms of the curves which result in the case of some of the most interesting elements. Fig. 3 gives the relative increase of density plotted against the logarithm of the cut. The values for lithium, zinc, and mercury were calculated by the writers, while those for neon and the compounds of chlorine were calculated by Professor A. C. Lunn of the Department of Mathematics of the University of Chicago for one of the writers. He has developed a set of equations which are more exact, but which give results practically indistinguishable from those given by the equations of Mulliken and Harkins.

The curve for zinc is only approximate, since the exact isotopic composition of this element is unknown. It has an abundant isotope of atomic weight 64, and less abundant ones of weights 66, 68, and 70, with a probable isotope of weight 67.

It is of interest that the curves for chlorine and methyl chloride have ordinates which are $^1/_2$, those for chloroform are $^1/_3$, and those for carbon tetrachloride $^1/_4$, of those for hydrogen chloride.

The most important feature of the diagram is that it shows curves of two seemingly different forms, those concave toward the X-axis, as for lithium, boron, etc., and those convex toward this axis, as in the cases of neon and the derivatives of chlorine. The former type of curve occurs when the mean atomic weight is nearer that of the heavier isotope, the latter when it is nearer the lighter isotope. It is evident that as the separation proceeds the curves for neon and the derivatives of chlorine will take on the form of that for lithium, and will finally become almost parallel to the X-axis, but at a height dependent on the initial composition of the element. Thus, the complete curves for the different elements have the same general form; but the part of the curve for lithium which is convex toward the X-axis occurs when there is less than 50% of the isotope of atomic weight 7 present, while the natural mixture contains about 94%

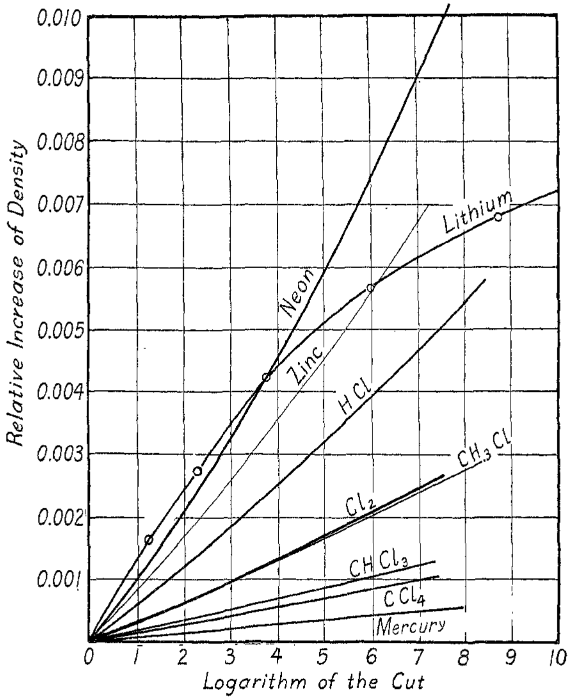

Fig. 3.—Increase in the relative density of various isotopic mixtures as the cut increases. The figure covers all of the region accessible to experiment at the present time, but it is of interest that the upper part of all of the curves is similar to that for lithium, which approaches as a limit the line 0.010. The limits approached by the other curves are much higher, but are all lines parallel to the X-axis.

of this isotope. Between these two parts of any curve there is obviously a point of inflection. When there are more than 2 isotopes present, there may be several points of inflection.

An apparatus having a capacity of 10 kg. of mercury, with a much increased area, has also been constructed. In this larger apparatus, which has not been used in the work described in this paper, the separation would be much more rapid.[4]

Furthermore, it is obvious that by the adoption of a rectangular instead of a circular cross section of the vacuum jacket, a number (conveniently 12) of troughs of mercury could be arranged side by side, each with its own slanting roof for the condensation of the mercury, and each with its own tube for draining off the fractions. By means of a hole in the roof, glass tubes could be used to supply mercury to each trough. In this way one apparatus would give the same amount of separation as would be produced by 12 units like that described above. On account of the expense of construction, such an apparatus has not been built as yet, but the successful operation of the evaporator described in the present paper demonstrates that the apparatus would operate successfully and rapidly with very little attention if it were provided with mercury seals at all joints, and were evacuated by the use of a rapid pump system.

The writers wish to thank the American Academy of Arts and Sciences for a grant of $500 from the C. M. Warren Fund. Of this $300 was spent for a high sensitivity balance, and the rest for apparatus now being used in the separation of the isotopes of mercury, zinc, and cadmium. The separation of mercury is being continued in this Laboratory by Mr. F. Jenkins, who is using the apparatus of 10 kg. capacity as well as those described in the present paper.

Summary

1. By evaporation in a vacuum in a large steel apparatus a separation of the isotopes of mercury has been obtained in which the density difference is 480 parts per million, and the difference of atomic weight is 0.1 unit. This has been secured, without other cooling than that given by ice, in 268 hours of operation of the apparatus, which holds 2.5 kg. of mercury, together with 37 hours of operation of the small glass apparatus used in earlier work in this Laboratory. The weights of the end fractions are 3.8 g. for the heavy, and 4.4 g. for the light. The increase in atomic weight obtained is 0.052, and the decrease 0.044 units. A multiple unit apparatus, which would give the same separation in about 30 hours of operation, has been designed.

---

[4] It is evident that the increase in the rapidity of separation secured by this larger apparatus is due to the increased area of the mercury surface rather than to the large volume. The apparatus is so built that the volume capacity of the trough may easily be made small without a reduction of its area.

2. A set of curves has been given to show the relation between the increase in density of an isotopic mixture and the cut. These curves exhibit one curvature when the amount of the heavier isotope is less than 50%, the opposite curvature when the amount is greater, and a point of inflection at this percentage. When several isotopes are present there may be several points of inflection.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

HYDROGEN HEXASULFIDE AND THE SOLUBILITY OF SULFUR IN THE PERSULFIDES OF HYDROGEN

BY JAMES H. WALTON AND EARL L. WHITFORD

Received October 2, 1922

Introduction

Since the time of Scheele, who first prepared the oily liquid usually known as hydrogen persulfide, much work has been done on the composition of this material. The results of analyses of various investigators gave empirical formulas varying from H_2S_5 to H_2S_9. Bloch and Höhn[1] have shown that the distillation of this oil yields two compounds of the composition H_2S_2 and H_2S_3. Their results were later confirmed by Walton and Parsons[2] who perfected a method for preparing the yellow oil in quantity, improved the method for distilling it and obtained the di- and trisulfides of hydrogen in a state of great purity. A new and extremely accurate method for the analysis of the persulfides was devised and their behavior towards a number of catalysts was investigated qualitatively.

Hydrogen disulfide and hydrogen trisulfide dissolve sulfur copiously, a fact that may be explained as a purely physical solution of the sulfur, a combination of the sulfur to form higher sulfides, or by these two effects operating simultaneously.

It is probable that the yellow oily liquid that separates when an excess of hydrochloric acid is added to a solution of a polysulfide of an alkali is a complex mixture of sulfides of hydrogen with dissolved sulfur. That sulfides higher than the hydrogen trisulfide do exist is evidenced by the existence of addition compounds. Among these are the strychnine compound, $(C_{21}H_{22}N_2O_2).H_2S_6$, prepared by Hoffman[3] and the brucine compound, $(C_{23}H_{26}N_2O_4)_3(H_2S_6)_2$, prepared by Schmidt.[4] Both of these were obtained by treating an alcoholic solution of strychnine or brucine with an alcoholic solution of ammonium polysulfide.

---

[1] Bloch and Höhn, *Ber.*, **41**, 1961 (1908).

[2] Walton and Parsons, THIS JOURNAL, **43**, 2539 (1921).

[3] Hoffman, *Ber.*, **10**, 1087 (1877).

[4] Schmidt, *Ann.*, **180**, 287 (1876); *Ber.*, **10**, 1289 (1877).