speed so expressed be defined as moles transformed in 1 mole of all components.

2. This interpretation offers a possible explanation of the salt effect on reaction speed. The expression of Brönsted must be modified for concentrated solutions.

3. An analysis of experimental work shows that it is of little value for determining the relation of reaction speed to viscosity. The kinetic theory, however, demands that reaction speed be independent of viscosity.

4. These conclusions lead to the formula for the inversion of sucrose previously presented when the concentration of electrolyte is unchanged.

5. The experimental measurements cannot serve as a criterion for choice between the various theories of the mechanism of the reaction, for the difference in agreement between the formulas is too small.

6. Any interpretation of the experiments depends upon the assumption that the liquid-junction potential with saturated potassium chloride is independent of the sucrose concentration.

7. Interpreted by the formula previously presented, the speed of inversion catalyzed by hydrochloric acid adds confirmation that 6 molecules of water react with each molecule of sucrose. The agreement is not quite so good as with sulfuric acid.

AMHERST, MASSACHUSETTS

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

THE SEPARATION OF ISOTOPES. APPLICATION OF SYSTEMATIC FRACTIONATION TO MERCURY IN A HIGH-SPEED EVAPORATION-DIFFUSION APPARATUS

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Introduction

Important Factors for Rapid Operation of Diffusion Methods.—In the separation of isotopes, the small separating power of the diffusion methods (including evaporation) must be compensated by very rapid operation, if large separations are to be obtained in a reasonable time. The apparatus described below was designed to accomplish this object for mercury. In the course of the work, systematic fractionation as applied to diffusion methods has been rather thoroughly studied.

The most important factors for maximum speed of separation fall into two classes: those of operating speed and those of operating efficiency.[2]

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[1] National Research Fellow in Physical Chemistry.

[2] By the efficiency of any given operation is meant the ratio of *actual* separation to the separation obtained under *ideal* conditions. The separation obtainable under ideal conditions by a process either of evaporation or of molecular diffusion, is given by Equations 7, 16 and 19 of a previous paper [(a) Mulliken, THIS JOURNAL, **44,** 1034 (1922)].

These two factors are usually opposed so that a compromise has to be sought. It will be shown later under "Systematic Fractionation" that about the best compromise is obtained, for the present apparatus,[3] at such a rate of output D and efficiency E that E^4D is a maximum.

The total rate of output is obviously proportional to the number of operating units, and to the output of each unit. For molecular diffusion the latter is proportional, other things being equal, to the diffusion area and to the permeability of the diffusion membrane. High permeability goes with minimum thickness. In the present apparatus filter paper is used to give maximum permeability.

Efficiency is needed both in each individual operation and in the mode of division and combination of fractions in systematic fractionation. Efficiency of the individual operation depends on the design of the units. The same effect as that of increased efficiency is secured when two different methods of separation can be combined as successive steps in one operation. This principle is used in the present apparatus by the superposition of an efficient molecular diffusion on an inefficient evaporation. Closely related to the efficiency factor is the variation from one element to another, or especially among compounds of a single element, in the degree of separation obtainable in a given operation.[4] The element mercury here used is decidedly unfavorable from this point of view, but is unusually good from the points of view of practicable speed of turn-over, and of general convenience of handling.

Description of Apparatus in Present Form

In the following paragraphs the apparatus as now set up, its operation, and the results obtained will be described. In a later section the subject of systematic fractionation will be discussed.

The method consists essentially in systematically repeated operations in each of which mercury vapor at low pressure (probably about 5 mm.), generated under such conditions that a partial separation of isotopes occurs, is diffused molecularly, giving a further separation. The chief advantage of the method is the relatively very high speed at which it can be operated without great sacrifice of efficiency, combined with the facts that the apparatus requires only tap water for perfect cooling, and that a high vacuum is not needed.

Vacuum System.—The apparatus consists of 6 similar upright units used independently[5] but in coöperation. They are set up on a table and

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[3] In general, maximum E^3D is a more appropriate criterion.

[4] See table of separation coefficients, Mulliken and Harkins, This Journal, **44,** 55 (1922).

[5] A set of connected units was at first considered, but was rejected for several reasons, one of which is that in such a set the evaporation effect would be nullified, as far as separation of isotopes is concerned.

each is connected through a 3-way stopcock to 2 vacuum lines, evacuated by a Cenco Hyvac pump. A McLeod gage is used to read the pressure. The units are ordinarily all connected to the same line. Any unit that needs to be repaired or emptied is switched to the other line, and air is admitted. To bring such a unit again into operation, the second line is opened to the pump and the first line shut off. As soon as the unit is evacuated, it is switched to the first line with the other units, and all are again connected to the pump. Several stopcocks are used to make these operations possible. Little trouble was experienced from leakage, especially since an air pressure of 0.2 mm. is as good as the highest vacuum, and even 0.5 mm. lowers the efficiency only slightly. There is little or no leakage in the units themselves, so that they can be shut off from the pump for considerable periods.

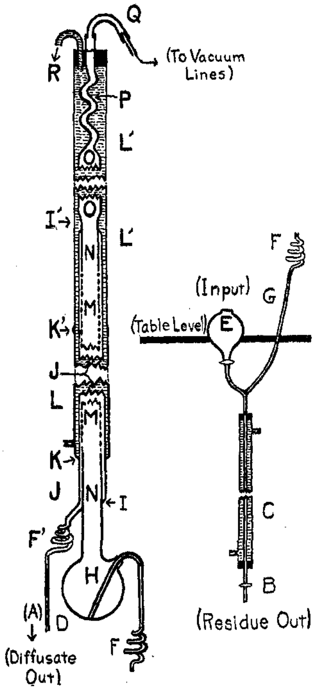

Fig. 1.—Section of type I unit

Design of Units.—The best design for the individual units, as now worked out, is shown in Fig. 1. They are made entirely of Pyrex glass.

In the operation of the apparatus the mercury is evaporated from the 500cc. flask H. A dirty evaporating surface improves the efficiency, as noted in a previous paper.[6] The mercury is fed into the evacuated flask from the 100cc. funnel E through the capillary tube G, the highest point of G being about 34 cm. above the stopcock on E. The inner end of tube G touches the bottom of the flask H, so that at the end of a run the entire residue in the flask can be removed except for a few drops. To remove the residue it is necessary to admit into the flask sufficient air pressure to drive the mercury over the highest point in G.[7] This is considerably more than 760 mm. above the exit stopcock B. so that a vacuum is automatically produced in the upper part of G if the mercury stops flowing. The flow of cold water in C completely cools the hot mercury on the way out.

The neck N of the flask H is sealed at I inside of a 40 mm. tube J, which is sealed in turn at K inside the 50mm. condenser jacket L. The distance IK, about 7 cm., is required for safety in making the seal I. Cold water flows continually between J and L, leaving by way of the tube R. For purposes of construction and repair, the tube L is in two sections, L and L', which are held together at K' by a thick sealing-wax joint. The tube N is continuous with the filter-paper membrane M, which has a diameter of 30 mm.

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[6] Mulliken, This Journal, **44**, 2388 (1922).

[7] It was originally hoped that the mercury would siphon out without interruption of the vacuum, but in practice the column in G usually breaks. The use of a capillary is to reduce to a minimum the volume of mercury not in action.

and a length of one meter.[8] M overlaps N for a distance of about 2 cm. at each end, and is fastened with water glass. The tube M is made by rolling a long strip of filter paper (one cross seam being needed if the paper is cut from a large sheet) and sticking the edges together, with a 3mm. overlap, by means of water glass. The paper turns brown on heating where it has been wet with water glass but this does not affect its strength. A number of small pieces of cork are fastened on the surface of the paper membrane to prevent it from coming into contact with the condenser wall.

Mercury vapor flows rapidly through N and M. Part of it diffuses through M, is condensed on the inner walls of J, and gathers into drops which collect in the exit from the inclined seal I. As soon as the height of the mercury in the 3mm. tube F exceeds 760 mm. the mercury flows when A is opened. The coils F reduce danger of breakage, but are perhaps unnecessary; they increase the volume of mercury not in action. The vapor which does not diffuse through M is directly exposed to condensation above I in the 20cm. residue condenser O, and falls back into the flask through the stream of rising vapor.[9] The coil P, 15 cm. long, is necessary to complete the condensation, because of the rapid upward motion of the vapor.[10]

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[8] Preliminary experiments showed that the rate of diffusion is, for a given evaporation rate, directly proportional to about the 1.3 power of the length, and *inversely* proportional to about the 1.3 power of the diameter. Decrease in diameter or increase in length of the membrane, especially the former, involves increased pressure inside the membrane, which decreases the operating efficiency as well as the life of the membrane, so as to neutralize the value of the increased rate of production. The dimensions given in the text represent a fairly good—doubtless not the best—compromise between speed and efficiency for the paper here used (Whatman No. 5). The best dimensions depend in general on the permeability and efficiency-speed curve (compare Fig. 3) of the paper used. The use of a similar paper half as thick, and so twice as permeable, would double the rate of production. Resistance to heat is an all-important consideration in the choice of paper; that here used was the best of several in that respect, although not the most permeable.

[9] It was thought that the efficiency could be improved by avoidance of this contact of the diffusion residue with undiffused vapor of different composition. Accordingly, a type of unit (Type 2) was constructed in which I was made with an annular catch, as shown in Fig. 2, by means of which the diffusion residue was led outside the unit on its way back to the flask. (Samples of the diffusion residue could be removed through suitably placed stopcocks, so that the fraction of vapor diffusing, as well as the separate efficiencies of the diffusion and evaporation processes, could be determined; this could not be done with the Type I unit.) As will be seen from Fig. 3, this type of unit gave a *lower* efficiency than the simpler Type I unit, except at low rates of evaporation. The most probable explanation of this result is that the falling drops of diffusion residue obtained in Type I units serve a useful function by slowing down and mixing the central core of the rising stream of vapor with the lateral portions, thus improving the diffusion efficiency, and that this beneficial effect more than compensates the bad effect of partial establishment of equilibrium between the condensed diffusate and vapor. Both causes of inefficiency are probably always present in Type I, that of imperfect vapor mixing increasing rapidly with increase in speed of operation, and nearly disappearing at low speeds.

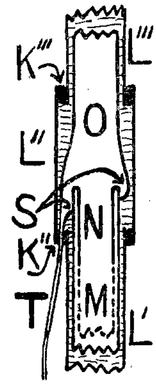

Fig. 2.—Diffusion residue catch of type II unit

[10] In constructing a unit, the 96cm. outer condenser tube L is first sealed at K to the inner tube J extending from I' to I. The end I is made with a slant and the en-

The flask H rests directly on a special iron tripod with a cup-shaped piece of Nichrome wire gauze. The tripod for each unit stands in an iron pan (30 x 20 cm.) which rests on a sheet of Transite asbestos wood that extends the length of the table. To secure effective heating without causing the burner to strike back, a rather roomy asbestos hood is built over the flask and tripod, provided with an ample opening at the back for admission of air, and another near the top at the front for the exit of the burner gases. A Transite asbestos board along the front of the table keeps the heat from E, so that the next lot of material for any operation can be kept there.

The units are supported (or guided) by a single clamp placed about at K′. They are easily taken down for repair or replacement by breaking the tubes D and G, and removing the U-shaped piece Q, which is fastened in place with sealing wax. The height of the top of the unit above A and B, which are just above the floor, is about 2.8 meters.

Conditions of Operation.—The most economical evaporation rate is about 450 cc. per hour per unit. This is equal to 36 kg. per hour for the entire 6 units. The rate of *diffusion* in each unit is then about 70 cc. per hour. Under these conditions the efficiency of the evaporation process[11] is about 21%, and that of the diffusion[12] about 80%, the combined efficiency being about 96%. The combined process is outwardly completely analogous to a simple distillation having an efficiency E, which may considerably exceed 100% (but cannot exceed 200%), given by, $E = E_e + E_d((1 - F_d)/F_d) \ln(1/1 - F_d)$. Here F_d is the fraction of the generated vapor which diffuses, and E_d and E_e are the individual efficiencies (compare Ref. 2) of the evaporation and diffusion processes, respectively.[13] The curve (Fig. 3) for Type I unit

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trance of F is attached to it. The paper tube M is next prepared and cemented at each end to a 16cm. section of 30mm. glass tubing, closed at the outer end which later forms part of the tube N. The paper tube with its glass end-pieces is now placed inside of J, so that each end piece projects for about half its length. The seals are now made at I and I′. The operations of sealing on the section OP, and the flask H are then fairly easily accomplished. L′ is attached with sealing wax at the top and bottom and the unit set up. The seals at K, I and I′ require very considerable care. A distance of 6–7 cm. from I or I′ to the junctions of M with N is sufficient to prevent seriously scorching the paper during the glassblowing.

[11] It is thought that the evaporation efficiency cannot be substantially improved at the stated speed of operation (Ref. 6).

[12] The diffusion efficiency is limited by the two factors referred to in Ref. 9, and also by the fact that the interstices between the fibers of the filter paper are, except at very low rates of evaporation, relatively too large as compared with the mean free path in the vapor (compare Ref. 4 for discussion). This of course varies with the paper used. The effect of back pressure, due to the vapor pressure of mercury at the temperature of the cooling water used, is negligible in all cases.

By using an apparatus somewhat like Type II (Ref. 9), a diffusion efficiency probably approximating 100% was obtained in several of the slower runs, where the pressure of mercury vapor is estimated to have been less than 2 mm. These runs have been used as the basis for a new value of the separation coefficient. This was reported in a previous paper (Ref. 6), and is here used as the basis for all calculations of efficiency.

[13] The adjustment of F_d is an important problem of design. Low F_d means increased E, but decreased D, and *vice versa*.

shows the relation of efficiency E to speed $\bar{D}$ for the present type of unit.[14]

With all 6 units operating effectively and continuously, a spread of 0.10 units of atomic weight, with a set of 50cc. fractions at equal intervals of about 0.004 units[15] between —0.05 and +0.05 could be produced in about 80 hours of diffusion. The time required for any spread (so long as complete separation of the individual isotopes is not approached) is about proportional to the cube of the difference between the atomic weights of the extreme fractions, as is shown by a study of the theoretical course of the fractionation. This will make a very slow process of obtaining a large separation, such as one unit of atomic weight. A complete set of intermediate fractions or working stock, of volume and distribution about as described above is *necessary* in increasing the separation of extreme fractions.[16] Any separation can, however, be readily increased by about 0.05 units by evaporating the final extreme 50cc. fractions to 0.5 cc. each in a small apparatus.

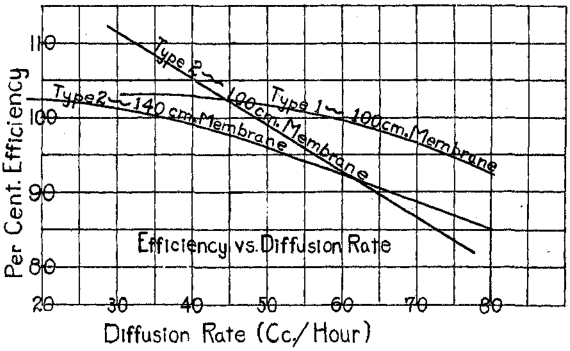

Fig. 3

The actual number of working hours required for any separation will be about twice or thrice the time of diffusion as given above. This is due to the considerable time needed for repair and replacement of units, to loss of time when the units are not in operation together, to time required

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[14] E is determined by determining the relative density of a sample of diffusate and one of residue for a run at the desired speed, and applying Equation 19 (Ref. 2). The difference in their densities is usually about 36 parts per million for 100% efficiency, and can be determined, if desired, to about 2%.

[15] This corresponds to $E = 0.92$, and a cut (see Ref. 4) of 2 in each operation.

[16] The time required for a given *extreme* separation is directly proportional to the size of the stock fractions. The minimum practicable size of fraction is determined chiefly by the falling off of efficiency with small volumes, and by the increased heating of the vapor and consequent effect on the life of the membrane. The loss of value by mixing during refilling also becomes increasingly important with small volumes. An improvement in the present apparatus which would permit smaller operating volumes without decrease of speed, would be most valuable.

in starting and stopping the apparatus and in emptying and refilling units, and to low efficiency in operation for various reasons.[17] The last two factors are particularly important in the case of the light fractions; a given amount of progress takes about 50% longer for them than for the heavy fractions. To avoid loss of time by too frequent replacement of units, the diffusion rate should not be allowed to exceed about 70 cc. per hour for any considerable period (a much lower speed limit is necessary at *small volumes;* compare Ref. 19), as the life of the membrane is limited by the temperature to which it is subjected.[18] The actual rate of progress is lowered very little if the diffusion rate falls as low as 60 cc. per hour, since the increased efficiency nearly compensates the decreased production rate, the E^4D curve being nearly flat for some distance near its maximum.

Method of Operation and Accounting System.—In filling a unit at the beginning of a run, the lightest fraction of sufficient size previously produced is introduced into the apparatus. As the diffusion proceeds, the density of the residue in the flask increases. Previously produced fractions of progressively increasing density are successively introduced at appropriate times, while the diffusate is removed in successive fractions equal in volume to about 30% of the flask contents (but compare below). The process continues until after the last of the earlier series of fractions has been introduced, and the residue in the flask has become too small for efficient operation. Air is then admitted to expel the residue through G. The unit can be emptied, re-evacuated and refilled in 30 minutes under favorable conditions. With each repetition of such a series of operations the lightest and densest fractions produced become more widely separated. At a given time the different units are in general at different states in their passage through the series.

An essential part of the operation is a method for rapidly calculating and recording the composition of each fraction as it is produced, for keeping account of the volume and composition of the material in the units, and for calculating the proper times to add more material. This last is done whenever the composition of a previously produced fraction is identical with that of the contents of a unit, except that the contents of a unit at any time is limited to 300–350 cc., or unless it is desired to reduce the volume of the contents before emptying a unit and starting on the retreatment of a lighter fraction. A pad of record sheets is kept on a

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[17] Efficiency is lost (1) by mixing of partly separated fractions (a) whenever the diffusion rate changes suddenly, as when the air pressure suddenly rises, (b) in the normal procedure of combining fractions on the shelves if they differ by less than 6 parts per million, (c) whenever a unit is emptied and refilled (about 2 cc. of diffusate and diffusion residue remains on condenser walls, etc., and a little in the flask); (2) when the volume in the flask is less than 150 cc. (See Ref. 19). Effects 1c and 2 influence the light more often than the heavy fractions.

[18] The reconstruction of a unit with a new membrane takes about 20 hours.

small shelf projecting from the front of each unit, and on this the "credits," "debits" and "balance," both volume and composition, are recorded. For rapid calculation of the composition of any diffused fraction, a table has been prepared showing the decrease in density of the diffusate over a range of efficiency of 72–110%, and over a range of the fraction of the balance diffused of 0–62%. In order to determine the composition of a given diffused fraction its volume is measured and divided by that of the previous balance to give the proportion diffused; the diffusion rate is calculated from the time, and the efficiency is then read from a previously determined plot (like those in Fig. 3) of efficiency against speed for that unit;[19] the density change (decrease) is recorded, and to it is added the composition figure (expressed as parts per million of density greater or less than that of ordinary mercury); the product is then transferred to a properly labeled bottle on a storage shelf. The change of density of the residue is read from another chart on which efficiency is plotted against diffused fraction, and the density and volume of the residue (balance) in the flask are recorded. The volume and density of the fraction newly added are at the same time recorded, together with the resulting new balance. The volume which must diffuse, in order to bring the contents of the flask to the composition of the next lightest fraction on the storage shelf, is then calculated, and diffusion allowed to proceed to this point, when the fraction in question is added, the diffusate removed, and the calculations described above are repeated. To avoid indefinite subdivision of fractions, any two fractions on the shelves differing by 6 parts per million or less are combined to give a single fraction. This means no great loss since the *value* of a separation between two fractions is proportional to the square of that separation (see Systematic Fractionation), and since a separation of about 35 p. p. m. between diffusate and residue is produced in normal operation. Similarly there is no great loss in value (only 1.3%) in the collection together of diffused fractions totaling as much as 30% of

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[19] The efficiency curve should be the same for all units of the same type. If the curve for that type has been determined, it is necessary only to determine 2 or 3 points for each new unit, to make certain that the unit has no defect or unusual characteristic. This can be done rapidly by comparing the densities of a diffusate and residue for each of 2 or 3 rates of diffusion. It is also necessary to check occasionally the results obtained with each unit to make sure that it is still in good condition.

The efficiency of a unit at any speed is lower, and the vapor temperature much higher, when the flask contains less than 100 cc.; the efficiency drop is roughly 2% at 100 cc. and 5% at 50 cc. Low volumes occur mostly with fractions near the extremes, thus increasing difficulties there.

High pressure (more than about 0.5 mm.) increases the fraction which diffuses. The loss in efficiency under such conditions is about the same as if the increased diffusion rate were due to an increase in the evaporation rate. (High pressure may be caused by air admitted accidentally through the stopcock below E, after a fraction has been added, or by breakage or leakage in the apparatus, etc.)

the previous balance (cut = 10/7), although the first and last portions of such a fraction differ in density by 10 p. p. m. The corresponding figures for a 50% fraction (cut of 2) are 4.0% loss, and 22 p. p. m. A great number of very small fractions would require an impossible amount of attention from the operator. The number of fractions removed per hour, at 70 cc. per hour per unit, is 6 × 70 divided by Q_d, or $420/Q_d$, where Q_d is the average size of the fractions as removed. The work of taking 10 fractions per hour, inspection of the apparatus, and occasionally emptying and refilling a unit, is enough to keep one man busy. When a unit is refilled, allowance has to be made, in recording the composition of the first fraction added, for the fact that about 2 cc. of the previous contents still remains in the units, chiefly adhering to the condenser walls.

Except in the early stages of operation, the best method is, all things considered, to make a series of cuts of 2, that is, diffusion of 50% of the flask contents between refillings. The changes of composition are thus equal and opposite for the two fractions produced in each stage of the operation. This method has the advantage of ease of arithmetical calculation; it involves the handling of a minimum number of fractions, and requires *no* mixing of fractions of differing composition except as a result of irregularities in operation.[20]

Results.—The work up to the present has been largely of a preliminary nature, but the features of design and operation have now been so far developed that additional radical changes are not to be anticipated. It seems desirable, therefore, to describe the method and apparatus at this time, as considerable time will be required to effect a large separation. The present preliminary separation, 0.01016 units of atomic weight on 22cc. (300g.) samples, was obtained in a few weeks of irregular operation with an incomplete set of units.[21]

Systematic Fractionation

A detailed study of systematic fractionation was found to be of prime importance in the design and operation of the apparatus. The most important results, given below, are applicable not only to the present

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[20] These factors are enough to offset the slightly greater loss of diffusion value during collection, and the 17% greater capital stock required, as compared with the use of 30% fractions. The advantage of the use of 30% fractions in regard to amount of stock needed can be obtained only by constantly mixing fractions. The separation into 50% fractions involves a higher average flask-content, and so a somewhat higher efficiency, than the use of 30% fractions for operation at a fixed minimum volume of the residue.

[21] The extreme samples consist of 22 cc. of material for which $\Delta M = +0.00504$ and 22 cc. for which it is -0.00512. The best result previously reported is that of Brönsted and Hevesy [*Z. physik. Chem.*, **99**, 189 (1921) and *Phil. Mag.*, **43**, 31 (1922)] who obtained 0.2 cc., $\Delta M = +0.0046$, and 0.3 cc., $\Delta M = -0.0052$. A far greater quantity has therefore been obtained in the present work although the quality of separation obtained in the two researches is about the same.

special method, but to all methods of the diffusion type (including evaporation).

Suppose a symmetrical fractionation procedure to be used for the division of an initially homogeneous sample into a set of fractions, all of size Q_0, spaced at equal ΔM intervals on both sides of the initial composition (atomic weight) M_0. The simplest procedure would consist of a series of individual or *unit* operations, in each of which a fraction of size $2Q_0$, and composition M, is divided into two fractions of size Q_0 and composition $M \pm EB\ ln\ 2$. It can be shown by a study of the fractionation procedure, that when the first $n-1$ pairs of fractions have already been produced, a total of n^2 *additional* unit operations will be required to produce the n^{th} pair of fractions without *permanently* using up or increasing in size any of the previously produced fractions. The corresponding time expended in producing the n^{th} pair is evidently $t_n = n^2(Q_0/D)$, where $D = dQ/dt$, the rate of diffusion (or, in general, of production) of the light fraction.

$$\text{Since } \Delta M = \pm nEB\ ln\ 2, \qquad (1)$$

$$t_n = (\Delta M)^2 Q_0/DE^2B^2\ (ln\ 2)^2, \qquad (2)$$

The time required to produce a pair of extreme fractions (or as can be shown, one of these) is thus proportional to the *square* of the difference between its composition and that of the original raw material, and *inversely* to the *squares* of the efficiency and of the separation coefficient. It can be shown that the same proportionalities hold for any type of fractionation procedure.

Since in the production of extreme fractions, intermediate fractions of sufficient size for efficient operation must be maintained (except as noted below) the time of production of any extreme fraction should be taken to include the total time of production of all intermediate fractions. Evidently,

$$t = t_1 + t_2 + \ldots\ldots + t_n = (1^2 + 2^2 + 3^2 + \ldots\ldots n^2)(Q_0/D) = n(n+1)(2n+1)(Q_0/6D) \qquad (3)$$

This equation can be used to calculate the operating time required to obtain any given fraction of composition ΔM, if the corresponding value of n is calculated from Equation 1. The *actual* working time required will be about three times this. For $n = 1$, t_n has the value n^3Q_0/D; for $n = 5$, $0.44\ n^3Q_0/D$; for $n = 10$, $0.38\ n^3Q_0/D$; for $n = \infty$, $n^3Q_0/3D$. Approximately, then, t is proportional to n^3, except for the smallest values of n. Then, approximately, from Equation 1 and the relation just deduced, $t = K\ (\Delta M)^3\ Q_0/DE^3B^3$ (4).

Equation 4 contains a great deal of information. The other factors being constant, in each case, it shows (1) the rapidly increasing difficulty of increasing ΔM, even by systematic fractionation, which is the most rapid way of applying any method of the diffusion type; (2) the great effect of the value of B (which depends on the element or compound used) on the possibility of obtaining a large separation ΔM in a moderate time;[22] (3) the importance of using a method and apparatus which can deal with small intermediate fractions (Q_0), yet operate at high speed (D).[23] Equation 4 also yields a criterion for the relative importance of speed, minimum operating volume (Q_0) and efficiency. Evidently for a given $\Delta M/B$, t will be a *minimum* if DE^3/Q_0 is a *maximum*. This criterion is of great value in both the design and the operation of any apparatus of the diffusion or of an analogous type. It was very useful in the development of the present apparatus.

The effect of the method of fractionation is not indicated by Equation 4, which was, in fact, developed above on the basis of a specific method consisting in a series of cuts of 2. It has already been stated, however, that, taking into account all practical factors, such a method of fractionation is probably more rapid than any other, and it is *certain* that no other fractionation procedure can have more than slight superiority. Equation 4 also does not take into account the possibility of using more than one type of apparatus in a single separation, that is, a rapid apparatus (one with large D) with large Q_0 in the earlier stages, and a slower, but also smaller, apparatus for the final stages. By such a method ΔM may be increased in a moderate time by a quite appreciable, although limited, amount with *small* quantities of material, the possible increase being proportional to B. In applying the criterion of the previous paragraph, the factors Q_0, E and D must be considered in relation to the amount of time required for repairs and reconstruction and in emptying and refilling the apparatus, and in relation to losses by mixing unlike fractions, such as occur especially at refilling operations, in which complete removal of previous contents is impossible. It may be noted that the heavy fractions are here, and usually, somewhat easier to separate than are the light fractions, because of the more frequent emptying and refilling required by the latter,[24] and for other reasons already noted. Although it is best to develop both fractions in equal amounts, either may be developed alone. In this case at least half the starting material must go into fractions which are left untouched after one or two operations.

Equation 2 or 4 may be made the basis of a criterion for the *value* of isotopic samples. The value of a fraction or set of fractions may perhaps best be considered as proportional to the time expended in producing it under standard, *optimum*, conditions of operation. On this basis, from Equation 2, the value of any individual fraction in a set of fractions may be defined as $V = (\Delta M)^2Q$. V, thus defined, is an additive function.

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[22] Note that B varies with ΔM, causing a progressive decrease in the separation as it approaches completion. Also see Ref. 4.

[23] The tendency is, of course, for E and D to fall with Q_0.

[24] This involves increased time and increased loss during mixing.

From a somewhat different point of view, which is particularly applicable to the *extreme* fractions, the value of an extreme fraction may be defined,[25] on the basis of Equation 4, as $V' = (\Delta M)^3 Q$. Really, $V' = C\Sigma V$, the summation being taken over all fractions in a complete set up to and including the extreme fraction to which it is desired to assign a value, in the case of a symmetrical fractionation.

Results of the application of the first of the above definitions to a study of the loss of value by the collection of fractions of 30% or 50%, and by mixing separated fractions, have already been indicated. The loss of value when two samples of respective compositions $M + \Delta_1 M$, and $M + \Delta_2 M$, and quantities Q_1 and Q_2, are mixed, is readily shown to be $-\Delta V = (\Delta_1 M - \Delta_2 M)^2 Q_1 Q_2/(Q_2 + Q_2)$. This equation also holds for the gain of value when two separated fractions of different composition are produced from a single uniform sample.

In conclusion, the writer wishes to express his appreciation of the assistance of Mr. B. R. Mortimer in the operation of the apparatus, and of Mr. F. A. Jenkins in the purification of the mercury. The further operation and development of the apparatus will be in the hands of Mr. Mortimer and Professor W. D. Harkins.

Summary

1. An apparatus is described for the rapid partial separation of mercury into isotopes by a combined process of distillation and molecular diffusion, at low pressure, the latter process being the major factor in the separation. The diffusion membrane in each unit consists of a tube of filter paper 1 meter long, this material being selected primarily because of its thinness.

2. The operation of the apparatus is carried on as a systematic fractionation, in which 6 units are used independently. A set of connected units was considered, but rejected for several reasons.

3. Preliminary operation of the apparatus has given a separation of 0.102 units of atomic weight between extreme fractions of 22 cc. A separation of 0.3 units with 50 cc. fractions should be obtained in a year of steady work.

4. The method by which the new value 0.0063 for the separation coefficient of mercury was obtained is described in connection with the preliminary studies on the design of the apparatus.

5. Systematic fractionation requires the maintenance of a permanent stock of intermediate fractions, of some minimum size Q_0, in order to extend the range of a separation. A thorough study of the course of systematic fractionation has yielded valuable results which are applicable to all methods of separation by diffusion or in an analogous manner.

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[25] Aston ["Isotopes," Edward Arnold and Co., London, **1922**, p. 139] has proposed the use of what is approximately $(\Delta M)Q$ as a measure of value; this has the disadvantage of not reflecting fully the difficulty of increasing ΔM.

The simple and symmetrical method of fractionation in which a cut of 2 is made in each individual operation is probably the most rapid for practical operation.

The time required for the production of any fraction, after the necessary preliminary or intermediate fractions have been produced, is given by the formula $t = C(\Delta M)^2 Q_0/DE^2B^2$, where E is the "efficiency," B the separation coefficient, D the rate of production of the light fraction, and C a constant. This serves to establish a criterion for the value (V) of any fraction, which may be defined as, $V = (\Delta M)^2 Q$. This criterion is applied to the calculation of loss of value by mixing, etc.

The time required for the production of any *extreme* fraction, taking into account the total time used in building up the intermediates, is given by $t = C'(\Delta M)^3 Q_0/DE^3B^3$. Study of this equation shows the difficulty of obtaining large values of ΔM, especially if B is low. It also shows the relative importance of Q_0, D and E, and this relation, somewhat modified by other practical considerations, was used in the design, and is also used in the operation, of the present apparatus. The optimum speed of operation is shown to be that for which $E^{3.5}D$ or E^4D is a maximum. The equation above can also be used as a basis for a criterion of value for extreme fractions, namely, $V' = (\Delta M)^3 Q$.

6. The approximate proportionality of the time required for a given separation to the *cube* of the degree of separation shows that while considerable separations can be effected by systematic fractionation, nothing approaching complete separation can be expected by methods of the diffusion type, unless in the most favorable cases and by factory-scale operation. It may be stated further that there seems to be little prospect that any other method or methods yet proposed will prove greatly superior to those of evaporation and molecular diffusion, although the centrifugal method may prove useful, especially for the elements of higher atomic weight.[26] For any particular element, the most favorable method depends greatly on the nature of the substance.

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[26] An ingenious method recently proposed by Hertz [*Physik. Z.*, **23**, 433 (1922)], while apparently very attractive in making possible an almost indefinitely large separation in one operation, can do so only at a rate of production that can be shown to decrease exponentially as the separation ΔM increases linearly. This, together with the relatively unfavorable ratio (Ref. 2, p. 1051) of the diffusion constants for gaseous, as compared with molecular diffusion, makes the apparent great superiority of the Hertz method extremely doubtful. The question reduces essentially to one of speed of production. The possibility of controlling the ΔM obtained in a single operation is however, certainly an advantage, as it gives a possibility of cutting down the volume of the intermediate fractions.