

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

THE SEPARATION OF ISOTOPES. THEORY OF RESOLUTION OF ISOTOPIC MIXTURES BY DIFFUSION AND SIMILAR PROCESSES. EXPERIMENTAL SEPARATION OF MERCURY BY EVAPORATION IN A VACUUM.

BY ROBERT S. MULLIKEN AND WILLIAM D. HARKINS.

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Introduction.

In January, 1920, Harkins and Broeker obtained by the method of diffusion a separation of the isotopes of chlorine amounting to a difference of density of 1.55 parts per thousand.¹ About 6 months later Brönsted and von Hevesy reported a much smaller resolution of the isotopes of mercury, amounting to about 50 parts per million difference in density, obtained by an evaporation at low pressure.² The work of Harkins and Broeker has been confirmed by Harkins and Hayes in an entirely independent separation of the isotopes of chlorine by the use of the same method as before,³ a difference in density of 1.1 parts per thousand being obtained. In the work on chlorine very elaborate purifications were made with the materials obtained, before the density determinations were made. This makes the evidence for the separation conclusive.

Preliminary to more extensive work on the separation of isotopes, and as a guide to the choice of favorable substances for experimental work, the theory of the separation of isotopes by various types of diffusion or by non-equilibrium evaporation has been studied. Equations have been developed which show the rate of separation to be expected in such processes, for any given mixture of isotopes. A classification of methods which have been proposed for separating isotopes is also given. Molecular isotopes are discussed, and formulas are given for calculating the number and mol-fractions of the various molecular isotopes of a compound containing given isotopic elements. With the intention of comparing the efficiencies of the diffusion and evaporation methods, a partial separation of mercury into isotopes has been made, amounting to a difference in density of 133 parts per million. This is important in that it confirms the work of Brönsted and von Hevesy who, in their presumably preliminary note, give no special evidence that their mercury was entirely pure. Furthermore, the results agree completely with the theory which is developed in this paper.

¹ Harkins, *Phys. Rev.*, **15**, 74 (1920); *Science*, N. S., **51**, 289-291 (1920); *Nature*, **105**, 230-1 (1920).

² Brönsted and von Hevesy, *Nature*, **106**, 144 (1920).

³ Harkins and Hayes, *THIS JOURNAL*, **43**, 1803 (1921).

Notation.

(Letters preceded by a (*) in the following list are always used with one of the subscripts 1, 2, —*a*—*b*—*s*—*n*, each of which is used to refer to a particular molecular species; *a* and *b* refer to any molecular species, *s* and *n* to the last of a set or series. Letters preceded by a (+) may be used with the subscript ₀ to denote initial values of the quantities to which they refer, for example, N_0 , $(N_1)_0$, $(x_a)_0$.

- (*) N = rate of flow in mols per sec.
 (+) N = total number of mols of material in *residue* at any time during a diffusion
 (*+) N = number of mols of an individual component in the *residue*
 (*+) x = mol-fraction
 (*) x = increase in mol-fraction of a component over its initial value, in the residue; (*) $\Delta^c x$, in the *total condensate*; (*) $\Delta^{ic} x$, in the *instantaneous condensate*
 M = ordinary (average) molecular weight
 (*) M = molecular weight of a particular isotope
 ΔM , $\Delta^c M$, $\Delta^{ic} M$, increase in molecular weight of residue, total condensate, and instantaneous condensate, respectively
 k^1_a = $c\sqrt{M_1/M_a}$, where *c* is between 2 and 1; for example $k^1_3 = c\sqrt{M_1/M_3}$
 k^1_1 = $c\sqrt{M_1/M_1} = 1$
 R = gas constant
 T = absolute temperature
 (*) p = saturated vapor pressure (or, gaseous pressure in general)
 r = radius of capillary tube; l = length of same
 (*) λ = mean free path of gas molecules
 (*) \bar{c} = mean velocity of gas molecules
 (*) n = number of mols or molecules, per cc.
 (*) $\frac{\delta n}{\delta z}$ = concentration gradient
 (*) d_{1s} , d_{2s} , etc. = distance between centers of molecules 1 and *s*, or 2 and *s*, respectively, at impact; for example, d_{12} , d_{24} . Note that d_{11} or d_{12} become d_1 or d_2
 A , A' , B , B' = (see Equations 5, 5', 7 and 7')
 $C = N_o/N$ = "cut"
 D , D' , E , E' = (see Equations 6A, 6A', 7A, 7A')
 S = $\Sigma(x_a k^1_a) = x_1 + x_2 k^1_2 + \dots + x_n k^1_n$
 n_a = number of atoms of an isotopic element in a compound; e. g., for CCl_4 , $n_a = 4$

The Theory of Diffusion.

The Flow of a Gas Through Small Openings. Molecular Diffusion.—Graham⁴ in his work on the passage of gases through porous membranes, distinguishes (1), *effusion* through small apertures, in which there is practically no friction, different gases developing a mass motion whose velocity is inversely proportional to the square root of the molecular weight; (2), *capillary transpiration*, in which the rate of mass motion is greatly reduced by friction, and obeys Poisseuille's law, with a slip term added at low pressures; and (3), *molecular diffusion*, in which mass motion is absent

⁴ Graham, *Phil. Trans.*, 153, 385 (1863).

and the molecules pursue independent devious paths along the very fine pores, colliding repeatedly with the walls, but very seldom with one another. As with effusion, the rates of molecular diffusion of different gases are inversely as the square roots of their molecular weights. In the former case, however, the relation applies only to the gas as a whole, but in the latter, to each molecular species individually. For this reason molecular diffusion leads to a partial separation of mixed gases, while the other two processes do not. Knudsen⁵ has deduced theoretically and confirmed experimentally the relation, N (mols./sec.) = $\frac{4}{8}\sqrt{2\pi/MRT} (r^3/l) (p_1 - p_2)$ for a gas of molecular weight M flowing through a cylindrical pore of radius r and length l , from a partial pressure p_1 to a partial pressure p_2 . For pores of any shape, N is proportional to $(p_1 - p_2)/\sqrt{MRT}$. These relations begin to break down when the pore-diameter increases above 0.2 to 0.1 the mean free path in the gas at the maximum total pressure in the pore. Their failure is apparently not serious, however, until the pore diameter is about equal to the mean free path. If the pores are larger the phenomenon begins to pass into that of capillary transpiration.

To secure full efficiency in the separation of isotopes by molecular diffusion, all capillary transpiration must evidently be avoided. This can be done by the choice of membranes of sufficiently small pore diameter, or for a given pore size, by making the maximum pressure sufficiently low. If the efficiency is perfect, the rate of diffusion of any isotope (a) in a mixture will be $Kx_a/\sqrt{M_a}$, where K is the same for all such isotopes present, for any set of conditions. The efficiency of the separation will be cut down by back diffusion if there is any back pressure of the isotopic mixture on the vacuum side.⁶ Another important factor in efficiency is perfect mixing of the gas on the inner side of the membrane.

Molecular diffusion into a *vacuum* has been termed by Graham "single diffusion" or "atmolysis." When two gases (usually at equal total pressure) diffuse molecularly through a membrane from opposite sides, the phenomenon is called "double diffusion." This must be just as effective for the separation of isotopes as single diffusion, since the motions of the various molecular species are wholly independent. This method has also the advantage, provided a membrane containing fine enough pores can be secured, that it can be carried out at atmospheric pressure, the second gas being used in this case to sweep away the diffusate. If the pores are too large, relatively to the pressure, for double molecular diffusion, either capillary transpiration or ordinary gaseous diffusion, or a mixture of the two, will occur, depending on the magnitude of the pressure drop through the membrane.

Gaseous Diffusion.—When a gaseous mixture of isotopes and another

⁵ Knudsen, *Ann. Phys.*, [4] 28, 75 (1908).

⁶ See discussion on a later page, "Effect of Back Pressure on Efficiency."

gas interdiffuse through a porous membrane, a separation of isotopes should occur if there is a constant renewal of the two gases, as by flow along the membrane. This is the method used in the separation of the isotopes of hydrogen chloride by Harkins and his associates, who passed a stream of hydrogen chloride along the inside of clay pipes, and a stream of air along the outside. In their work the phenomenon was essentially gaseous diffusion, although there may have been some molecular diffusion.

Although gaseous diffusion as a method of separating isotopes considerably resembles molecular double diffusion, the theory is very much more complicated. The difference is due to the effects of collisions between molecules, which occur in the former case, but not in the latter. In the absence of mass motion, the rate of diffusion of one gas into another is given by N_1 (mols/sq. cm./sec.) = $(1/3) \lambda_1 \bar{c}_1 \delta n_1 / \delta z$. For the case under consideration, the relative rate of diffusion of 2 isotopes should be given by

$$\frac{N_2}{N_1} = \frac{\lambda_2 \bar{c}_2 \delta n_2 / \delta z}{\lambda_1 \bar{c}_1 \delta n_1 / \delta z} = \sqrt{\frac{M_1}{M_2}} \cdot \frac{\lambda_2 \delta n_2 / \delta z}{\lambda_1 \delta n_1 / \delta z}$$

The mean free path λ , of one molec-

ular species in a mixed gas is dependent on the molecular weights, mol-fractions, and molecular diameters of all the various components. According to Jeans,⁷ the value of λ_1 , taking into account persistence of ve-

locities, is given by $\lambda_1 = \frac{1}{\pi \sum [n_a d_{1a}^2 (1 - \theta_{1a}) \sqrt{1 + M_1/M_a}]}$ where $\theta_{1a} =$

$(m_1 - \alpha_{1a} m_a) / (m_1 + m_a)$, α_{1a} being a function of M_a / M_1 . In the summation, the subscript a applies to each type of molecule present, 1, 2, — a , — s , in turn. Neglecting the effect of the persistence term $(1 - \theta)$, it is found by considering several limiting cases, assuming always that the molecular diameters of isotopes are equal, that λ_2 / λ_1 has usually and on the whole a value equal to about $\sqrt[4]{M_1/M_2}$, so that the ratio N_2/N_1 is increased to about $(M_1/M_2)^{3/4}$. For a steady state, N_1 and N_2 have constant values, so that the concentration gradients must be uniform, except in compensation for the variation of λ_1 and λ_2 from point to point along the gradients. The concentrations of the isotopic substances and the corresponding gradients will of course decrease continuously along the length of the diffusion tube. This adds another complication to the theory of the operation as a whole. If the gradients are assumed uniform at a given point in the tube, and the concentration of both isotopes is zero at the lower ends of the gradients, we have $N_2/N_1 = (x_2/x_1) (M_1/M_2)^c$, where c is about $3/4$. On account of the various assumptions, this last figure cannot be considered very certain, but at least it is probable that the general relation stated, which is analogous to the relations for the other processes considered, holds good.

⁷ Jeans, "Dynamical Theory of Gases," The University Press, Cambridge, 1916, pp. 268, 330.

In the above treatment, mass motion has been assumed absent. Practically, this is an almost impossible condition, since the rate of gaseous diffusion does not exceed that of capillary transpiration unless the pressure drop is reduced to a fraction of a millimeter of mercury, even for openings as small as 0.01 mm. in diameter. Even with no pressure drop at all, there is normally some mass motion in gaseous diffusion, due to the unequal rates of diffusion of the two gases in opposite directions. This mass motion could of course be balanced by a suitable pressure drop (just sufficient to give rise to an equal and opposite capillary transpiration). In the diffusion of hydrogen chloride into air, the necessary mass motion is one of the former gas outwards; this could be prevented by a suitable slight excess of pressure on the air side.⁸ An *exact* balance could, however, hardly be obtained in practise. The actual relative rate of diffusion, when mass motion is present, will be given by

$$\frac{N_2}{N_1} = \frac{N_2 - x_2(N_1 + N_2 + N_s + N_{\text{cap. trans.}})}{N_1 - x_1(N_1 + N_2 + N_s + N_{\text{cap. trans.}})} = \frac{N_2 - Ax_2}{N_1 - Ax_1}$$

where $N_s = \frac{1}{3}\lambda_s \bar{c}_s \delta n_s$, $\delta z = -\frac{1}{3}\lambda_s \bar{c}_s \left(\frac{\delta n_1 + \delta n_2}{\delta z} \right)$, the term $N_1 + N_2 + N_s$ representing the mass motion necessary to overcome the inequality between $N_1 + N_2$ and N_s ; and $N_{\text{cap. trans.}}$ representing the added mass motion due to any drop in total pressure, and obeying Poisseuille's law. The values of x_1 and x_2 vary along the concentration gradient from their initial values to zero, hence N_1 and N_2 , and therefore $\delta n_1/\delta z$ and $\delta n_2/\delta z$ must vary, in order that N_1 and N_2 may be constant. If the mass motion, measured by the Ax term, is *positive*, its effect is clearly to *cut down* the rate of separation of the isotopes, although the detailed theory is complicated. (It may be noted that the gradual enrichment of the lighter isotope along the gradient reduces somewhat the effect of the Ax term.) If the mass motion is *negative*, the effect is apparently to *increase* the rate of separation of isotopes. A negative mass motion may however result in increased terminal pressure of the diffusing gas, which would again tend to decrease the rate of separation. A very rapid negative mass motion will of course practically prevent any diffusion.

A possible cause of loss of efficiency in gaseous diffusion is local convective action, due to unevenness in the texture of the membrane. In general, the theory of gaseous diffusion as applied to the separation of isotopes is evidently very complicated, but the relation $N_2/N_1 = (x_2/x_1)(M_1/M_2)^c$ is probably approximately correct on the whole, the value of c , however, being uncertain and variable but probably greater than $1/2$ in many cases.

⁸ In the work of Harkins and his associates the pressure was kept slightly higher on the air side.

Molecular Effusion and Non-equilibrium Evaporation.—The rate of effusion through minute orifices,—of diameter not greater than one-tenth of the mean free path, according to Knudsen,⁹ should from kinetic theory obey the law $N = (p_1 - p_2) / \sqrt{2\pi MRT}$, per square centimeter of opening. For larger openings, the phenomenon passes into that of mass effusion. As in the case of molecular diffusion, molecular effusion of two gases in opposite directions simultaneously can occur. The evaporation of a liquid in a vacuum, if no molecules return to the evaporating surface after they have once escaped, is equivalent to molecular effusion of the saturated vapor into a vacuum ($p_2 = 0$), and obeys the same law (see below). The field of force at the surface acts like a membrane with very fine pores and negligible interspaces. Molecular diffusion passes into molecular effusion when the length of the pores approaches their diameter. Both processes, as well as the mixed process, should be equally effective in the separation of isotopes.

Initial Diffusion Methods.—In the expansion of a gas or in effusion or evaporation into a vacuum, it would be expected that the lighter molecules would get ahead, due to their higher average velocity, so that there would be an enrichment of these in the front rank molecules, which could be utilized if the latter could be separated from the molecules that follow. The separation would not be complete or even large, however, because of the *distribution* of velocities about the mean, for each molecular species. A somewhat analogous effect must occur in the front rank molecules at the beginning of a gaseous diffusion. Although a considerable enrichment might occur as the result of such a process, the material would be small in amount and difficult to collect.¹⁰

Theory of Non-equilibrium Evaporation.

From kinetic theory, the number of mols of a vapor which strike one sq. cm. of the surface of a pure liquid in equilibrium with it, and so necessarily the number of mols of liquid which evaporate, per second, is $N = \frac{p}{\sqrt{2\pi MRT}}$.¹¹ For an ideal solution such as a mixture of isotopes, the re-

⁹ Knudsen, *Ann. Phys.*, [4] **28**, 999 (1909).

¹⁰ Kohlweiller's report (*Z. physik. Chem.*, **95**, 95-120 (1920)) of a considerable concentration of the lighter isotope of iodine is apparently an attempted application of this type of method. His theoretical treatment seems however to be unsound, and his experimental results are contrary to Aston's finding by positive-ray methods that iodine contains only one atomic species.

¹¹ For an excellent discussion of the derivation of this formula, first used by Hertz (*Ann. Phys.*, **17**, 177 (1882)), and tested for mercury by Knudsen (*Ann. Phys.*, **47**, 697 (1915)), see Langmuir, *Phys. Rev.*, [2] **2**, 329 (1913). Knudsen found that the rate of evaporation fell far below that calculated unless the mercury surface was kept

lation $N_a = \frac{px_a}{\sqrt{2\pi MRT}}$ should hold for each isotopic component (a), if the vapor pressure has the same value (p) for each such component when pure. That this is at least very closely true is shown by Aston's failure to obtain any separation of the isotopes of neon by 3000 fractionations, and by other evidence.¹² In an ordinary distillation, the rate of distillation is negligibly small compared with N , and there is practical equilibrium between liquid and vapor. Although lighter molecules evaporate faster from the liquid, they also return faster from the vapor, so that the two phases have practically the same isotopic composition. If, however, the pressure is made very low, and the condensing surface placed so close to the evaporating surface that practically all the evaporating molecules are condensed, it is clear that the condensate must be enriched in the lighter isotopes. This method of evaporation, as has already been seen, is really equivalent to molecular effusion.

The molecules leaving a liquid surface move forward with various velocities and in various directions. The farther a molecule has to travel before reaching a cold surface, the greater is its chance of collision with another molecule; and the greater the number of collisions it suffers, the more likely it is to acquire a backward component of velocity. If there are many collisions per molecule, the condition of a saturated vapor is approached, and the efficiency of the separation is reduced. The presence of air-molecules, which, being non-condensable, will be moving in all directions, will increase the number of unfavorable collisions. For maximum efficiency, (1) the apparatus must be thoroughly evacuated, (2) the rate of evaporation must be sufficiently low, and (3) the condensing surface must be as close as possible to the evaporating surface. Practically, at least in the case of mercury, as is shown by the present experimental work, the atoms can move through a distance equal to several times the mean free path for the saturated vapor, and can suffer a number of collisions, without much loss of efficiency.

In order that the theoretical efficiency shall be attained, the evaporating liquid must be kept at a uniform composition throughout, by diffusion, convection, or by artificial mixing. Otherwise the accumulation of heavy molecules in the surface will cause a corresponding increase in their proportion in the condensate. Approximate calculations indicate, however, that liquid diffusion alone is capable of preventing more than a slight loss of efficiency, even for fairly considerable rates of evaporation. This is very clean, as by constant renewal. The exact formula for the rate of evaporation is $N = (1-r) p \sqrt{2\pi MRT}$, but $r=1$, practically, for a liquid and its saturated vapor.

¹² In view of the thermodynamic relation between vapor pressure and solubility, the failure of Richards and Hall (*THIS JOURNAL*, 39, 531 (1917)), to secure any change of atomic weight by 1000 recrystallizations of lead nitrate from radioactive material, is additional evidence for the very close equality of the vapor pressures of isotopes.

in harmony with the experimental results. Because of the impossibility of rapid mixing, the separation of isotopes by evaporation from a solid surface is evidently impracticable. The range of application of the method may however be extended by the use of solvents.

Comparison of Methods.—The choice of elements suitable for separation by evaporation is limited to those forming suitable compounds or solutions or themselves existing as liquids having a small vapor pressure at a convenient temperature. To be suitable for a diffusion method, a substance must exist as a gas or have a considerable vapor pressure preferably at room temperature. The diffusion method probably has wider applicability than the evaporation method.

Development of Equations Showing Rate of Change of Composition and Atomic Weight in Diffusion Processes.

Change in Composition of Residue for the Case of Two Isotopes.—For a mixture of two isotopes having molecular weights M_1 and M_2 , and mol-fractions x_1 and x_2 , the relative rate of molecular diffusion, molecular effusion, or evaporation, is given by

$$-dN_2/-dN_1 = (x_2/\sqrt{M_2}) (\sqrt{M_1}/x_1) = (x_2/x_1) \sqrt{M_1/M_2} = k_2^1 (x_2/x_1). \quad (1)$$

N_1 and N_2 denote the respective numbers of mols of the two isotopes in the residue at any time. N will be used to denote $N_1 + N_2$, and N_0 to denote the number of mols initially present. For gaseous diffusion, the relation is the same, except that k_2^1 means $c\sqrt{M_1/M_2}$, where c is some number between 1 and 2. Rearranging Equation 1 and noting that $N_1 = N \cdot x_1$ and $N_2 = N \cdot x_2$

$$dN_2/x_2 = k_2^1 dN_1/x_1, \text{ or } \frac{Nd x_2 + x_2 dN}{x_2} = k_2^1 \left(\frac{Nd x_1 + x_1 dN}{x_1} \right).$$

$$\text{Then, } (1-k) dN/N = k \left(\frac{dx_1}{x_1} \right) - \frac{dx_2}{x_2}. \quad (2)$$

Integrating,

$$(1-k) \ln N/N_0 = k \ln (x_1/(x_1)_0) - \ln (x_2/(x_2)_0).$$

Or, denoting N_0/N , the "cut," by C ,

$$(1-k) \log C = k (\log (x_1)_0 - \log x_1) - \log (x_2)_0 + \log x_2. \quad (3)$$

This equation can be used to calculate the cut necessary to obtain any desired change in the composition of the residue, the initial composition being known. The change in atomic weight of the residue for a given change in composition may be obtained from the relation, $\Delta M = (M_2 - M_1) \Delta x_2$.¹³

¹³ In general, for a mixture of (n) isotopes, if the atomic or molecular volumes are equal, as the work of Soddy (*Nature*, **94**, 615 (1915)), and of Richards and Wadsworth (*This Journal*, **38**, 221 (1916)) shows to be true in the case of the atomic volume of solid lead, $\Delta M = (M_2 - M_1) \Delta x_2 + (M_3 - M_1) \Delta x_3 + \dots + (M_n - M_1) \Delta x_n = \Sigma (M_a - M_1) \Delta x_a$. This relation applies to mixtures of isotopic atoms or of isotopic molecules, *i. e.*, molecules differing only in containing atoms which are isotopes of each other, *e. g.*, HCl_{35} and HCl_{37} ; $\text{CH}_2(\text{Cl}_{35})_2$, $\text{CH}_2\text{Cl}_{35}\text{Cl}_{37}$, and $\text{CH}_2(\text{Cl}_{37})_2$; Mg_{24}O , Mg_{26}O , and Mg_{28}O .

For the diffusate, the change, $\Delta'M$, is exactly $-\Delta M/(C-1)$ (see Equation 14 p. 49). In connection with his work on the separation of the rare gases, Rayleigh¹⁴ developed a less direct but simpler equation, which is rather more convenient for calculation than Equation 3. He uses the term enrichment ratio, symbolized by r , for $\frac{x_2/(x_2)_0}{x_1/(x_1)_0}$. Using

the symbols of the present paper, Rayleigh's relation can be reduced¹⁵ to

$$C = [x_1/(x_1)_0] \cdot r^{1/(1-k)} \quad (4)$$

This is readily obtained from (3). If r is near unity, Equation 4 becomes, very nearly, $C = r^{1/(1-k)}$. In making calculations of C in terms of ΔM or Δx , the easiest method is to calculate $1/(1-k)$ (compare the table p. 55) once for all for the compound under consideration, then to calculate the value of r corresponding to the assumed value of ΔM or Δx , and finally to apply Equation 4. $\Delta'M$, the decrease of atomic weight for the diffusate,

equals $-\frac{\Delta M}{C-1}$.

Simple Equations for Change of Composition of Residue for Small Cuts.—The use of the exact relations (3) and (4) involves much calculation. For small cuts, or approximate calculations with larger cuts, a very simple relation, which shows clearly the factors governing the rate of separation, can be derived from Equation 2. Noting that $dx_1 = -dx_2$, Equation 2 becomes $(1-k) dN/N = (-k/x_1)dx_2 - dx_2/x_2$. Noting that $-dN/N = \frac{-d(N/N_0)}{N/N_0} = d \ln C$, this reduces to

$$dx_2 = -dx_1 = \frac{(1-k)x_1x_2}{x_1+kx_2} \cdot d \ln C = A d \ln C. \quad (5)$$

This quantity A is really the slope, at the point $(x_2, \ln C)$, of the curve obtained by plotting x_2 (or $-x_1$) against $\ln C$, starting with $C=1$ for $x_1 = (x_1)_0$ and $x_2 = (x_2)_0$. As the composition changes only very slowly with the cut, A is nearly a constant, so that

$$\Delta x_2 = \frac{(1-k)x_1x_2}{x_1+kx_2} \cdot \ln C, \text{ nearly.} \quad (6)$$

By taking average values of x_1 and x_2 this equation will hold rather closely even for a large cut. For the change in atomic weight of the residue,

$$\Delta M = (M_2 - M_1) \Delta x_2 = \frac{(1-k)x_1x_2(M_2 - M_1)}{x_1 + kx_2} \cdot \ln C = B \ln C. \quad (7)$$

¹⁴ Rayleigh, *Phil. Mag.*, [5] 42, 493 (1896).

¹⁵ Harkins and Hayes (Ref. 3) use a similar form of Rayleigh's equation. The (negative of the) quantity $1/(1-k)$ of this paper, which is the exponent of r in Equation 4, is termed the "diffusion coefficient" in their paper, and a rule is given for calculating this quantity. This rule and the relations of the quantities mentioned are discussed in a note on a subsequent page, under the head of "Useful Approximate Forms of Simple Equations."

Note that C is strictly a ratio of mols, or of volumes. Unless C is extremely large, however, it may without much error be considered a ratio of masses. From Equations 6 and 7 it is seen that the increase in the mol-fraction of heavy isotope and in the atomic weight of the residue proceed arithmetically as the quantity of the latter diminishes exponentially.

Relation of Rate of Separation to Composition of an Isotopic Mixture.—The rate at which A and B change with the composition or atomic weight of the residue during a diffusion or evaporation can be obtained to a close approximation as follows. Since $x_1 + kx_2$ is always nearly unity, we can write

$$A = \left(\frac{1-k}{x_1+kx_2} \right). \quad x_1x_2 = Fx_1x_2, \text{ and } B = \frac{1-k}{x_1+kx_2} (M_2 - M_1)x_1x_2 = Gx_1x_2, \quad F \text{ and } G$$

being regarded as essentially constant. Then

$$\frac{dA}{dx_2} \left(= \frac{dB}{dM} \right) = F \frac{d(x_1x_2)}{dx_2} = F \frac{d(x_2 - x_2^2)}{dx_2} = F(1-2x_2) = F(x_1 - x_2) = \frac{A(x_1 - x_2)}{x_1x_2}. \quad (8)$$

If values of A or B are plotted as ordinates against values of x_2 (or $-x_1$) as abscissas, a portion of a parabola is obtained, corresponding to the equation $A = Fx_1x_2 = F(x_2 - x_2^2)$, or $B = G(x_2 - x_2^2)$. This begins at the point ($x_2 = 0$, A or $B = 0$), rises to a maximum at ($x_2 = 0.50$, $A = 0.25F$ or $B = 0.25G$), and falls again to ($x_2 = 1$, A or $B = 0$). Thus the most favorable mixture for the separation of two given isotopes is that for which $x_1 = x_2 = 0.50$. Between $x_2 = 0.25$ and $x_2 = 0.75$ the value of B is still nearly as favorable, but if x_2 falls below 0.05 to 0.10, or rises above 0.90 to 0.95, the rate of separation is much reduced. If x_2 (or M) is plotted against $\ln C$ for the residue, the slope A (or B) of this curve thus approaches zero, and the curve itself approaches asymptotically the line $x_2 = 1$ (or $M = M_2$), as $\ln C$ continues to increase; the curve is terminated abruptly in the other direction at $C = 1$.

The slope dA/dx_2 of the A parabola is given by Equation 8. Since $B = (M_2 - M_1) A$, and $\Delta M = (M_2 - M_1) \Delta x_2$, it is evident that dB/dM is equal to dA/dx_2 . From Equation 8, then, dB/dM is zero when $x_2 = 0.50$, has a maximum positive value when $x_2 = 0$, and a maximum negative value when $x_2 = 1$. Thus B (and A) increase for the residue (and decrease for the diffusate), during a separation, if x_2 is less than x_1 ; and *vice versa*.

Modifications of Simple Equations for Large Cuts.—The quantity $\frac{dB/B}{dM}$ is useful as a measure of the error in B when ΔM is large.

$$\frac{dB/B}{dM} = \frac{F(x_1 - x_2)}{B} = \frac{x_1 - x_2}{x_1x_2(M_2 - M_1)}.$$

Call this last quantity $2H$. For a moderately large change ΔM of atomic weight we have, approximately,

$$\Delta M = \left[B + \frac{1}{2} \left(\frac{dB}{dM} \right) \Delta M \right] \ln C = B \left[1 + \frac{1}{2} \left(\frac{dB/B}{dM} \right) \Delta M \right] \ln C = B(1 + H \Delta M) \ln C. \quad (9)^{16}$$

For the case that $M_2 - M_1 = 2$, if $x_2 = 0.01$, the value of H is 24.8; if $x_2 = 0.10$, $H = 2.22$; if $x_2 = 0.25$, $H = 0.67$; if $x_2 = 0.50$, $H = 0$; if $x_2 = 0.75$, $H = -0.67$; etc. The correction term $H \Delta M$ is evidently not large unless ΔM is considerable, or x_2 is near zero or unity. For ordinary hydrogen chloride, $x_2 = 0.23$, $B = 0.00950$, and $H = +0.76$. Without using the correction term, we have, for $\Delta M = 0.05$, $\Delta M = 0.05 = 0.00950 \ln C$. By putting in the correction term, $\Delta M = 0.05 = 0.00950 (1.038) \ln C$. The value of C calculated from the former expression (Equation 7) is 192.7; that from the latter (Equation 9) is 158.9. The *correct* value of C , calculated by means of Equation 4, is 159.8. For $\Delta M = 0.10$, the respective values of C obtained by the three methods are 37,140; 17,630; and 18,530. The discrepancies between the results of Equation 4 and Equation 7 are not large, especially from the point of view of the change of atomic weight secured by a given cut, and are in fact much less than would normally result between theory and practise due to unavoidable inefficiency of operation. Equation 9 evidently gives a very close approximation to the results of the exact Equation 4, and is much simpler than the latter, once the values of B and H have been calculated for the compound under consideration. Values of B are given in Table I p. 55. Equation 10 which likewise gives a very close approximation, is useful for calculating ΔM if C is given.

Useful Approximate Forms of Simple Equations; Relation of Rate of Separation to Molecular Weights of Isotopes.—The term $(1-k)$ in Equations 6 and 7 can be calculated very quickly and accurately by means of the approximate empirical relation $(1-k) = (4/c) (M_2 - M_1) / (3M_2 + M_1)$. This is correct to within about 0.1% for the lightest elements, and is *still more exact* for the heavier elements. For example, the exact value of $1-k$, for $c=2$, and $M_1=6$ and $M_2=7$, is 0.074180, while that calculated from the above relation is 0.074074, or 0.14% too low. For $M_1=36$, $M_2=38$, the exact value of $1-k$ is 0.026672, and the approximate value 0.026667; the latter is only 0.018% low. Using the relation just given, Equation 6 becomes

$$\Delta x_2 = \frac{(M_2 - M_1)x_1x_2}{(c/4)(3M_2 + M_1)(1 - (1-k)x_2)} \ln C = A \ln C \text{ (practically)}. \quad (6B)$$

and Equation 7 becomes

$$\Delta M = \frac{(M_2 - M_1)^2 x_1 x_2}{(c/4)(3M_2 + M_1)(1 - (1-k)x_2)} \ln C = B \ln C \text{ (practically)}. \quad (7B)$$

A and B can be calculated with sufficient accuracy in accordance with these equations, the term $(1 - (1-k)x_2)$ being readily calculated by the help of

¹⁶ Since $\Delta M = B \ln C$, nearly, this can also be written,

$$\Delta M = B(1 + BH \ln C) \ln C. \quad (10)$$

the relation given. This term can be neglected entirely for neon and heavier elements, when an accuracy of 1% is sufficient, giving simplified forms of Equations 6B and 7B which may be called Equations 6BB and 7BB. These can be still further simplified to¹⁷ the still less exact forms,

$$\Delta x_2 = [(M_2 - M_1)x_1x_2/cM_2] \ln C = D \ln C \quad (6A)$$

and

$$\Delta M = [(M_2 - M_1)^2x_1x_2/cM_2] \ln C = E \ln C \quad (7A)$$

This form of Equation 7 brings out the dependence of the "separation coefficient" B on the total molecular weight and on the interval between the molecular weights of the two isotopes. For calculations of the separation coefficient, Equation 7B is practically as exact as Equation 7; and Equation 7BB gives results which are very little in error, except for the lightest elements. The very simple approximation given by Equation 7A gives results at worst 3% low, for elements above neon, but in general Equation 7B or 7BB should be used.

Change of Composition for Diffusate.—While the residue is being enriched in the heavier isotopes, the diffusate or condensate is being enriched in the lighter isotopes. For the "instantaneous" diffusate or condensate coming from material of a given composition (x_1, x_2) we can write

¹⁷ $(1-k) = 1 - \sqrt[c]{M_1/M_2} = 1 - \sqrt[c]{1 - (M_2 - M_1)/M_2} = 1 - \sqrt[c]{1 - c(M_2 - M_1)/cM_2} = 1 - \sqrt[c]{1 - (M_2 - M_1)/cM_2}$ (nearly) $= 1 - [1 - (M_2 - M_1)/cM_2]$ (nearly) $= (M_2 - M_1)/cM_2$ (nearly). The usual case is $c=2$, but the relation holds for any value of c (it is of course exact for $c=1$), provided $M_2 - M_1$ is small compared with M_2 . The empirical relation $(1-k) = (4/c) (M_2 - M_1)/(3M_2 + M_1)$ holds very closely even when $M_2 - M_1$ approaches M_2 in magnitude. This relation reduces to $2(M_2 - M_1)/(3M_2 + M_1)$, for $c=2$. This can be used for calculating B of Equation 7.

The quantity $(1-k)$ is closely related to the "diffusion exponents" (k) and (k') of Harkins and Hayes.³ (k) is equal to $-1/(1-k)$, and (k') to $-1/(1-(1/k)) = +k/(1-k)$. The "diffusion exponent" is the same (except for the sign) as the exponent

of r in Equation 4 of this paper. The rule of Harkins and Hayes that $\frac{(k) + (k')}{2} =$

$(M_1 + M_2)/(M_1 - M_2)$, (k) and (k') being respectively 0.50 unit greater, or less, than $(M_1 + M_2)/(M_1 - M_2)$, agrees with the above empirical relation for $1-k$. [The relation $(k) - (k') = 1$ is an exact and necessary one, for $(k) = \sqrt[c]{M_1/c\sqrt{M_1} - c\sqrt{M_2}}$, and $(k') = \sqrt[c]{M_2/c\sqrt{M_1} - c\sqrt{M_2}}$.] The approximations $(1-k) = (M_2 - M_1)/cM_2$ [1], and the analogous $(1-1/k) = (M_1 - M_2)/cM_1$ [2], are less exact than the approximations $(1-k) = (4/c) (M_2 - M_1)/(3M_2 + M_1)$ [3], and $(1-1/k) = (4/c) (M_1 - M_2)/(3M_1 + M_2)$ [4].

For, using [1] and [2], while $\frac{(k) + (k')}{2} = (-1/2)[(1/1-k) + 1/(1-(1/k))]$, $= \frac{M_1 + M_2}{M_1 - M_2}$,

comes out as it should, the result $(k) - (k') = 2$ is obviously wrong. Using Equations [3] and [4] for $(1-k)$ and $(1-(1/k))$, $(k) + (k') = (M_1 + M_2)/(M_1 - M_2)$, and $(k) - (k') = 1$, as it should. The relation of Equation 3, and the corresponding relations, $(k) = (3M_2 + M_1)c/4(M_1 - M_2)$, and $(k') = (3M_1 + M_2)c/4(M_1 - M_2)$, prove to be so nearly exact that they can be used for calculations by the exact Equation 4.

$$(x_1)^{ic} = \frac{dN_1}{dN_1 + dN_2} = \frac{x_1/c \sqrt{M_1}}{x_1/c \sqrt{M_1} + x_2/c \sqrt{M_2}}.$$

From this can be obtained¹⁸ the *exact* equations

$$(\Delta^{ic}x_1) = \frac{(1-k)x_1x_2}{x_1 + kx_2} = +A \quad (11)$$

and

$$\Delta^{ic}M = -(\Delta^{ic}x_1)(M_2 - M_1) = \frac{(1-k)x_1x_2(M_2 - M_1)}{x_1 + kx_2} = -B. \quad (12)$$

The composition of the instantaneous diffusate or condensate always keeps pace with that of the residue, x_1^{ic} being just A units ahead of x_1 , and M^{ic} just B units behind M (see Fig. 1). The composition of the *total* diffusate is an average of a series of continuously-changing instantaneous diffusates. It obviously approaches that of the original material as the *quantity* of residue approaches the vanishing point. For a mixture of two or any number of isotopes the mol-fraction x_a of *any* component (*a*) in the total diffusate is necessarily

$$x_a^c = \frac{(N_a)_o - N_a}{N_o - N} = \frac{(x_a)_o N_o - x_a N}{N_o - N} = \frac{(x_a)_o C - x_a}{C-1},$$

and

$$x_a^c - (x_a)_o = \Delta^c x_a = \frac{(x_a)_o C - x_a}{C-1} - (x_a)_o = \frac{(x_a)_o - x_a}{C-1} = \frac{-\Delta x_a}{C-1} \quad (13)$$

where Δ^c , x_a^c , etc., refer to the diffusate, x_a , Δ , etc., to the residue. Correspondingly,

$$\Delta^c M = \Sigma(M_a - M_1)(\Delta^c x_a) = \frac{\Sigma(M_a - M_1)(-\Delta x_a)}{C-1} = \frac{-\Delta M}{C-1}. \quad (14)$$

Equations 13 and 14 must hold independently of the nature or efficiency of the diffusion process, and depend only on the assumption that isotopes have equal atomic or molecular volume. By means of these relations, for a 100% efficient process, we have at once,

$$\Delta^c x_a = -A \frac{\ln C}{C-1} \quad (15)$$

and

$$\Delta^c M = -B \frac{\ln C}{C-1}, \quad (16)$$

¹⁸

$$\frac{x_1/c \sqrt{M_1}}{x_1/c \sqrt{M_1} + x_2/c \sqrt{M_2}} = \frac{x_1^c \sqrt{M_2}}{x_1^c \sqrt{M_2} + x_2^c \sqrt{M_1}} = \frac{x_1}{x_1 + kx_2}$$

Then

$$\begin{aligned} x_1^{ic} - x_1 &= \Delta^{ic}x_1 = \frac{x_1}{x_1 + kx_2} - x_1 = \frac{x_1 - x_1^2 - kx_1x_2}{x_1 + kx_2} = \\ &= \frac{x_1 - x_1^2 - kx_1(1-x_1)}{x_1 + kx_2} = \frac{(1-k)x_1x_2}{x_1 + kx_2} \end{aligned}$$

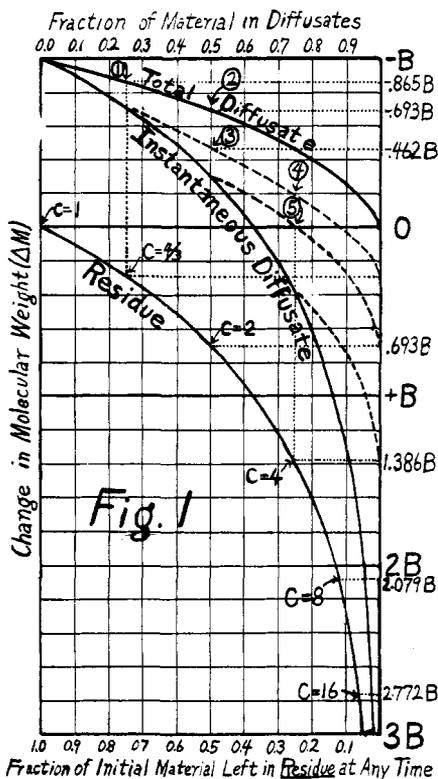


Fig. 1. Generalized plot showing atomic or molecular weight of fractions obtained during a 100% efficient diffusion or irreversible evaporation of a mixture of isotopes.

The curves are based on Equations 7, 12, and 16, of the text. The ordinates are expressed in terms of the "separation coefficient" B as a unit; this has a different numerical value (usually about 0.003 to 0.02) for each element (see Table I, and text). The value of B changes slightly with ΔM . The symbol C stands for the "cut" or ratio of quantity of material in the residue at any time to the initial quantity; for any abscissa on the lower scale, the "cut" is merely the reciprocal quantity. The "instantaneous diffusate" curve gives at any point the composition of the material which is at any instant diffusing or evaporating from residual material corresponding to the same abscissa. Note that this curve has exactly the same form as the residue curve, and differs only in an upward displacement of the ordinates by B units. Each point on the "total diffusate" curve gives the average composition of the material which has diffused or evaporated from the beginning up to that point. The various dotted curves give the composition of fractions of the total diffusate beginning at various points after the beginning of the operation. The meaning of the total diffusate curves can be made clearer by a few examples. Thus, Point 1 gives the composition of the diffused or condensed fraction for the interval 0-25%; Point 2, for the interval 0-50%; 3, for 25-50%; 4, for 25-75%; 5, for 50-75%. Taken in connection with the residue curve, the total diffusate curves show how the original material can be divided efficiently into isotopic fractions. For example, the curves show that the diffusate might be collected in fractions as follows: 0-25%, $\Delta M = -0.865B$; 25-50%, $\Delta M = -0.462B$; 50-75%, $\Delta M = 0$. If the operation were stopped here, the residue would have the atomic or molecular weight $M + 1.386B$, if M is the original atomic or molecular weight.

and corresponding approximate relations with D and E . By putting $C=1$ and noting that the limit of $\ln C/(C-1)$ is unity, as C approaches unity, Equations 13 and 14 reduce to 11 and 12. For the result of n successive identical operations on the light fraction, equations analogous to 9 and 10 can be written, *viz.*,

$$\Delta^c M = -nB(1+H\Delta^c M) \ln C/(C-1), \quad (17)$$

and

$$\Delta^c M = -nB[1-BH \ln C/(C-1)] \ln C/(C-1), \quad (18)$$

where C is the cut in *each* operation.

Systematic Fractionation.—Large *decreases* of atomic weight can evidently be secured only by repeated operations, a nearly equal decrease being secured in each similar operation. With the residue on the other hand, large *increases* can be secured in a single operation by starting with sufficient material and making a large cut. A good practical compromise for systematic fractionation is a cut of 2. Here — $\Delta^c M = \Delta M = \ln 2 = 0.693 B$. The use of such a method has been discussed by Lord Rayleigh¹⁴ who developed approximate formulas giving the size and quality of the various fractions. The collection of the whole diffusate together, especially for a cut as large as 2 or greater, involves considerable avoidable loss of efficiency. If it is collected in successive fractions as suggested by the plot (Fig. 1), successive cuts can be made on the *residue* in one operation. The total diffusate coming through between $C=2$, and $C=4$ has practically the composition of the original material, and in quantity is 25% of the latter. In systematic fractionation, the actual changes in atomic weight will be less than the calculated if any of the causes of inefficiency previously discussed operate. The values of Δx and ΔM given by Equations 6, 7, 11, 12, 15 and 16, etc., must be multiplied by an empirical efficiency factor which depends on the experimental conditions. Equations 3 and 4 are of course subject to a similar limitation. Equations 13 and 14 always hold (p. 49). The variation of Δx and ΔM with large cuts has already been discussed under "Modifications of Simple Equations for Large Cuts." In general, efficiency and speed will be opposed. On this account, it may not be desirable to aim at the highest efficiency at the beginning of operations, when dealing with large quantities of material, but high efficiency becomes more and more worth while as the cut increases.

Effect of Back Pressure on Efficiency.—In molecular diffusion and molecular effusion, the fractional loss of efficiency due to back pressure is equal to the ratio of the back pressure to the initial pressure. This is shown by the following considerations. The *actual* increase, $\overline{\Delta x}$, in the mol-fraction of any isotope in the diffusate, may be considered as the net result of two processes, forward and backward diffusion, which can be treated as independent (see earlier discussion). Letting Δx denote the

increase for a 100% efficient process, and N_1 and N_2 the quantities of material which diffuse forward and backward, respectively, we can write,

$$\overline{\Delta x} = \frac{N_1 \overline{\Delta x} - N_2 (\overline{\Delta x} + \Delta x)}{N_1 - N_2}.$$

Simplifying,

$$\overline{\Delta x} = \left(\frac{N_1 - N_2}{N_1} \right) \Delta x = \left(\frac{p_1 - p_2}{p_1} \right) \Delta x.$$

The efficiency of the process is $\overline{\Delta x} / \Delta x$, and is thus equal to $\frac{p_1 - p_2}{p_1}$; and the loss of efficiency is p_2/p_1 . Analogous considerations apply to non-equilibrium evaporation, if p_1 and p_2 now stand for rate of evaporation and rate of return of molecules, respectively. With gaseous diffusion the case is more complicated, but analogous effects are to be expected.

General Relations for Any Number of Isotopes.—For the general case of a mixture of n isotopes, exact and approximate slope equations analogous to (5), (6), and (7) can be obtained in the following way. N separate equations of the form of Equation 1 can be written, *viz.*,

$$dN_a/x_a = k^1_a dN_1/x_1 \quad (1')$$

and correspondingly, n equations of the form of Equation 2, *viz.*,

$$(1 - k^1_a) dN/N = k^1_a dx_1/x_1 - dx_a/x_a. \quad (2')$$

The equation for which $a = 1$ is included for the sake of generality in the subsequent development. It is convenient to write all the equations in terms of the lightest component, (1), although any other component could have been chosen. From the a^{th} equation of the form of (2'), one can get $dx_a = k^1_a (x_a/x_1) dx_1 - x_a (1 - k^1_a) dN/N$. Now it is evident that $\Sigma dx = 0$. Then

$$\Sigma dx_a = \Sigma [k^1_a (x_a/x_1) dx_1 - (1 - k^1_a) x_a dN/N] = 0.$$

Or,

$$(dN/N) \Sigma (x_a - x_a k^1_a) = (dx_1/x_1) \Sigma x_a k^1_a.$$

Or,

$$(dN/N) (1 - \Sigma x_a k^1_a) = (dx_1/x_1) \Sigma x_a k^1_a.$$

Denoting $\Sigma x_a k^1_a$ by S , this becomes $\frac{1-S}{S} \cdot \frac{dN}{N} = dx_1/x_1$. By substituting

the value $dx_1/x_1 = (1/k^1_a) [(1 - k^1_a) dN/N + dx_a/x_a]$, obtained from equation (2'), and simplifying, the general expression for any isotope (a),

$$dx_a = \frac{x_a (k^1_a - S)}{S} \cdot dN/N = \frac{x_a (S - k^1_a)}{S} \cdot d \ln C = A'_a d \ln C, \quad (5')$$

is obtained. This is the general form of the slope Equation 5, and can be treated like the latter. Thus

$$\Delta x_a = \frac{x_a (S - k^1_a)}{S} \ln C, \text{ nearly.} \quad (6')$$

Since $\Delta M = \Sigma [(M_a - M_1) \Delta x_a]$,

$$\Delta M = \frac{\Sigma [(M_a - M_1) x_a (S - k^1_a)]}{S}. \quad \ln C = B' \ln C, \text{ nearly.} \quad (7')$$

This summation has n terms. It can be shown¹⁹ that the following relation also holds approximately

$$\Delta M = \frac{\Sigma x_a x_b (M_a - M_b)^2}{cM}. \quad \ln C = E' \ln C \quad (7A')$$

where a and b take independently every value from 1 to n , like terms, however, being taken only once. This summation has $\frac{n(n-1)}{2}$ different terms. The calculation of E' is simpler than that of B' if n is not too large; and E' usually approximates B' very closely (see table of separation coefficients). The equations for the condensate are very easily generalized. Equations 11 and 12 become

$$\Delta^{ic} x_a = -A'_a \quad (11')$$

and

$$\Delta^{ic} M = -B'. \quad (12')$$

Equation 13 holds as it stands for any isotope a , and Equation 14 for the case of n isotopes; Equations 15 and 16 become

$$\Delta^c x_a = -A'_a \frac{\ln C}{C-1} \quad (15')$$

and

$$\Delta^c M = -B' \frac{\ln C}{C-1}. \quad (16')$$

¹⁹ Since $1 = \Sigma x$, we can write $S - k^1_a = (x_1 k^1_1 + x_2 k^1_2 + \dots + x_n k^1_n) - (x_1 + x_2 + \dots + x_n) k^1_a = x_1(k^1_1 - k^1_a) + x_2(k^1_2 - k^1_a) + \dots + x_n(k^1_n - k^1_a)$. In general $k^1_b - k^1_a = (1 - k^1_a) - (1 - k^1_b) = (M_a - M_1)/cM_a - (M_b - M_1)/cM_b$, nearly, (see note on earlier page), $= (M_1/c) (M_a - M_b)/M_a M_b$. Applying this relation to the expression for $S - k^1_a$, the latter becomes $(M_1/c) (1/M_a) \Sigma [x_b (M_a - M_b)/M_b]$, where the subscript b , like a , stands for all numbers from 1 to n , to be chose, however, independently of the series of values for a . By application of this relation, Equation 5 can be written approximately, $\Delta x_a = (x_a/c) \Sigma [x_b (M_a - M_b)/M_b]$, $d \ln C$ (5A'), since S is very nearly unity.

The summation in Equation 7' can be simplified as follows. $\Sigma (M_a - M_1) x_a (S - k^1_a) = S \Sigma M_a x_a - \Sigma M_a x_a k^1_a - M_1 S \Sigma x_a + M_1 \Sigma x_a k^1_a = S \Sigma M_a x_a - \Sigma M_a x_a k^1_a - S M_1 + M_1 S = \Sigma (M_a - x_a) (S - k^1_a)$. Equation 7' then becomes $\Delta M = \frac{\ln C}{S} \Sigma (M_a x_a) (S - k^1_a)$. Applying the relation already obtained for $S - K^1_a$,

$$\Delta M = [(M_1 \ln C)/cS]. \Sigma ([M_a x_a (1/M_a)] \Sigma [x_b (M_a - M_b)/M_b]).$$

This readily reduces to $\Delta M = (M_1/c) \frac{(\ln C)}{S} \Sigma (x_a x_b (M_a - M_b)^2 / M_a M_b)$.

This gives the closely approximate relation

$$\Delta M = \frac{\ln C}{cM} \Sigma [x_a x_b (M_a - M_b)^2] \quad (7A'')$$

Factors Determining Rate of Separation and Table of Separation Coefficients for Natural Isotopic Mixtures.

Equations 6' and 7' show that the close proportionality between ΔM and $\ln C$ holds for a mixture of any number of isotopes as well as for two isotopes. The approximate constant B for any element or compound can thus be determined experimentally by means of a 100% efficient diffusion or evaporation, without knowing the isotopic composition. In the following table are given values of the exact coefficients B , or B' , and of the approximate coefficients E , or E' , calculated for $c=2$, for various naturally occurring isotopic mixtures. It should be noted that the approximation of E' to B' is much closer than that of E to B , so that while E' satisfactorily replaces the more complicated B' , B should be calculated, by one of the more exact equations 7B or 7BB, rather than to use E of equation 7A. The isotopic composition has been estimated from the results of positive-ray analysis combined with the chemical atomic weights. *The value for mercury has been calculated from experimental data obtained by the evaporation method.* The coefficient B or B' is the value of $-\Delta^c M$, or of ΔM when $\ln C=1$, where M is in general the molecular weight. In the case of molecules, such as that of chlorine, Cl_2 or carbon tetrachloride, CCl_4 , containing more than one atom of an isotopic element, ΔM or $-\Delta^c M$ must evidently be divided by the number, n_e of such atoms per molecule, in order to get the change ΔA or $-\Delta^c A$, in the atomic weight of the isotopic element. Hence the coefficient B' must be divided by n_e in such cases, although this is never necessary for B . The quantity $\Delta A/\ln C=B$ or B'/n_e , calculated for the usual case of $c=2$, will be called the "separation coefficient." It might be considered preferable to calculate the quantity $\Delta A/A$, but this has not here been done. The values of $\Delta A/A$ will of course be much less favorable to the heavier elements than are the "separation coefficients" given on the opposite page.

The diffusion or separation coefficient for a given isotopic mixture is proportional to the increase of atomic weight for a definite cut. Since the coefficients (B/n_e) in the table below are calculated from the initial composition of the isotopic mixture, they represent the rate of increase of the atomic weight at the beginning of the diffusion. If neon and hydrogen chloride, for example, are compared it is found that the latter has the higher separation coefficient. If the approximate equation

$$\Delta M = \frac{(M_2 - M_1)^2 x_1 x_2}{c M_2} \ln C$$

is considered, it is seen that $(M_2 - M_1)^2$ is the same for both of these elements, while the molecular weights give a factor of $\frac{36.46}{20.20}$ or 1.805 in favor of the neon. However, the product of the mol fractions is 0.0900 for

TABLE I
COMPOSITION AND SEPARATION COEFFICIENTS OF ISOTOPIC MIXTURES

Element or compound	At. wt. or mol. wt.	At. or mol. wts. of isotopes	Corresponding mol-percentages	$1 - k^2$	B or B'/n_e	E or E'/n_e
Li	6.94	6,7	6,94	0.0742	0.00450	0.00403
B	10.9	10,11	10,90	0.0466	0.00438	0.00409
BH ₃	13.9	13,14	10,90	0.0364	0.00339	0.00322
Ne	20.2	20,22	90,10	0.0466	0.00843	0.00818
Mg	24.32	24,25,26	79,10,11(?)	0.00868	0.00843
HCl	36.46	36,38	77,23	0.02668	0.00950	0.00932
CH ₃ Cl	50.46	50,52	77,23	0.01941	0.00690	0.00681
Cl ₂	70.92	70,72,74	59.3,35.4,5.3	0.00494	0.00499
CH ₂ Cl ₂	84.92	84,86,88	59.3,35.4,5.3	0.00413	0.00417
CHCl ₃	119.38	118,120,122, 124	45.7,40.9,12.2,1.2	0.00295	0.00296
CCl ₄	153.84	152,154,156, 158,160	35.2,42.0,18.8,3.7,0.3	0.00229	0.00231
Ni	58.68	58,60	66,34	0.01680	0.00758	0.00747
Ni(CO) ₄	170.68	170,172	66,34	0.00582	0.00262	0.00260
Zn	65.37	64,66,68,70	51.5,31,15,2.5(?)	0.02037
K	39.10	39,41	95,5	0.00232
Rb	85.45	85,87	77.5,22.5	0.00409
Kr	82.92	78,80,82,83, 84,86	6,15,18,16, 25,30	0.0306
HBr	80.92	80,82	54,46	0.01228	0.00614	0.00606
Hg	200.6	197-200,202,204	0.0057	(experimental)

neon and 0.1771 for hydrogen chloride, thus giving a factor equal to 1.970 in favor of hydrogen chloride. Though the initial diffusion coefficient is thus more favorable in the case of hydrogen chloride, if an extensive series of diffusions is carried out, it is found that in the case of the *heavy fraction* the diffusion coefficient for both substances increases as the diffusion proceeds, but much more rapidly for neon, so the diffusion coefficient of the latter soon becomes the larger. However, with the *light fraction* the diffusion coefficients of both become less favorable, and that of neon becomes less favorable even more rapidly than that of hydrogen chloride.

The compounds of chlorine listed in the table indicate that if Cl, Cl₂, Cl₃, and Cl₄ could be diffused, the rates of separation in terms of the change of atomic weight (separation coefficient) would be respectively 1, $1/2$, $1/3$, and $1/4$. The values given in the table are slightly different from what would be expected from these ratios, since all but Cl₂ are loaded with either hydrogen or carbon.

The highest rate of separation for an *element* of given isotopic composition is that for monatomic molecules of the pure element. The separation coefficient B/n_e , is very nearly inversely proportional to the total molecular weight (see table), whether the molecule contains one or more atoms of the isotopic element. When n_e is greater than 1, the mixing of isotopes

in a single molecule tends to reduce the separation coefficients, as pointed out by Harkins in connection with molecular chlorine. This is, however balanced by the effect of the large difference in molecular weight of the lightest and heaviest molecular isotopes, so that the effect of the total molecular weight, as indicated by Equations 7A and 7A', is alone effective. For the separation of the element chlorine, hydrogen chloride is evidently the most favorable compound. The separation coefficient of mercury is rather low, but this is more than compensated, from the experimental standpoint, by the chemical inactivity, volatility and ease of purification of the element, and the accuracy with which changes in atomic weight can be determined by density measurements. According to the theory of Harkins,²⁰ many or most of the *even-numbered elements* above nickel should contain numerous isotopes. In agreement with this, Aston has found 6 or 7 isotopes each for the elements krypton, xenon, and mercury. The wide separation of the extreme atomic weights tends to give such elements a large separation coefficient, if the extreme components are present in any considerable proportion, for the coefficient depends on the squares of the intervals in atomic weight between isotopes (see Equation 7A').

Such elements as selenium, cadmium, tin, and tellurium, should on this basis, and in the absence of specific information as to the isotopic composition be favorable cases for separation. Experiments upon zinc and cadmium have been begun in this laboratory.

For elements or compounds containing more than two isotopes, it is possible to calculate from the coefficient E a virtual atomic or molecular weight interval corresponding to the case of only two isotopes. For example, the mixture of isotopes in mercury is equivalent to an equimolar mixture of two isotopes having an atomic weight difference of 3.0 units.

This is obtained by putting $\frac{(\Delta M)^2 x_1 x_2}{2M} = E = 0.0057$, setting $x_1 = x_2 = 0.50$,

and solving for ΔM : $(\Delta M)_v = \sqrt{8EM}$. For magnesium, $(\Delta M)_v = 1.32$; for hydrogen chloride, 1.68; for chlorine, 2.44; for carbon tetrachloride, 3.4; for zinc, 3.3, etc.

Isotopic Molecules and Isomeric Molecular Isotopes.

The mol-fractions of the various molecular species of a given chemical formula, in the table preceding have been calculated by assuming the molecules to have been built up from their atoms according to chance.²¹ If an element containing mol-fractions x_1 and x_2 of two isotopes is combined into molecules containing n_e atoms each of this element, there will be $n_e + 1$

²⁰ Harkins, *THIS JOURNAL*, 37, 1367 (1915).

²¹ Soddy (*Nature*, 105, 516, and 642 (1920)) gives the formula for the relative proportions of the isotopes of the chlorine molecule, whose existence had been pointed out previously by Harkins (*Science*, Ref. 1).

isotopic molecular species, whose mol-fractions can be shown to be given by the successive terms of the expansion of $(x_1+x_2)^{n_e}$. If the element has (s) instead of only two isotopes, the corresponding expression is

$(x_1+x_2+\dots+x_s)^{n_e}$, which gives $\frac{(n_e+s-1)!}{n_e!(s-1)!}$ terms, corresponding

to an equal number of molecular isotopes. If the compound contains atoms of several elements E, E', E'', \dots , each having a set of isotopes, as E_1, E_2, \dots, E_s , for element E ; E'_1, E'_2, \dots, E'_s , for element E' ; etc., and if each element contains mol-fractions $x_1, x_2, \dots, x_s; x'_1, x'_2, \dots, x'_s$, etc., of its isotopic atomic species, then the mol-fractions of the various possible molecular species will be given²² by the terms of the complete expansion of $(x_1+x_2+\dots+x_s)^{n_e} (x'_1+x'_2+\dots+x'_s)^{n'_e} (\dots) (\dots) \dots$. The total number of terms, and so of molecular isotopes, is $\frac{(n_e+s-1)!(n'_e+s'-1)!(\dots)!(\dots)! \dots}{n_e!n'_e! \dots (s-1)!(s'-1)!(\dots)!(\dots) \dots}$. The composi-

tion of the molecular species to which any term refers is given by the particular x 's occurring in that term, and their exponents. Thus $(x_1)(x_2)(x'_4)(x'_1)_2(x'_2)_4$ would be the mol-fraction of the molecular species $E_1E_2E'_4(E''_1)_2(E''_2)_4$. This might represent, for example, one of the isotopes of K_2PtCl_6 , as $K^{39}K^{41}Pt^{190}(Cl^{35})_2(Cl^{37})_4$. The number of isotopes of K_2PtCl_6 , if potassium has 2, platinum 6, and chlorine 2, is given by the formula above as $\frac{3!6!7!}{2!6!1!1!5!1!} = \frac{3!7!}{2!5!} = 126$. If tin has 6, and silicon 3

isotopes, then there are 30 molecular species of the formula $SnCl_4$, 54 of the formula $SnCl_2Br_2$, and 42 of the formula Si_2Cl_6 . If mercury has 6 isotopes, Hg_2Cl_2 has 63 isotopes under conditions where its molecules exist as individuals.²³ Similarly, $ZnCl_2$ should have 12 isotopes.

Among compounds containing more than one isotopic element, there will often be instances of isotopes of equal molecular weight. For example, $MgCl_2$, under conditions²³ where its molecules exist as permanent entities, would contain 9 isotopes having molecular weights 94, 95, 96, 96, 97, 98, 98, 99, 100. For both $Mg^{24}Cl^{35}Cl^{37}$ and $Mg^{26}(Cl^{35})_2$ the molecular weight is 96, and for both $Mg^{24}(Cl^{37})_2$ and $Mg^{26}Cl^{35}Cl^{37}$ it is 98 (isobaric molecules).

When an isotopic element appears in an organic molecule, its isotopism not only results in numerous isotopic molecular species, but also in many cases introduces new position isomers. For example, C_6Cl_6 must have 7 molecular isotopes, of which all but $C_6(Cl^{35})_6$ and $C_6(Cl^{37})_6$ must exist in sev-

²² These expressions take account of all elements present in a compound, even if some of them contain only one isotope ($s=1$). The factor $\frac{(n_e+s-1)!}{n_e!(s-1)!}$ reduces to 1 in the latter case ($0!=1$, by definition), so that it is necessary to consider only the elements in the molecule which contain isotopes.

²³ *I. e.*, in the vapor state, or in solution in non-ionizing solvents.

eral isomeric forms, due to the presence of the two different substituents Cl^{35} and Cl^{37} . Again, $\text{CH}_3\text{.CHCl.CH}_2\text{Cl}$ must consist of 4 molecular species, the isotopes $\text{CH}_3\text{.CHCl}^{35}\text{.CH}_2\text{Cl}^{35}$, $\text{CH}_3\text{.CHCl}^{37}\text{.CH}_2\text{Cl}^{37}$, $\text{CH}_3\text{.CHCl}^{35}\text{.CH}_2\text{Cl}^{37}$, and $\text{CH}_3\text{.CHCl}^{37}\text{.CH}_2\text{Cl}^{35}$, the last two being isomeric forms of the same isotope.

New optical isomers are possible as a result of isotopism, if isotopic atoms, by virtue of their different *masses* alone, can act as different substituents to make carbon or other atoms asymmetric.

Experimental Work with Mercury.

Purification.—The mercury used was purified by prolonged agitation with nitric acid, followed by 5 distillations in a current of air at low pressure according to the method of Hulett and Minchin,²⁴ who claim that a single distillation gives a completely pure product. The first and last portions were rejected in each distillation, and a final distillation *in vacuo* was made.

Evaporator.—The apparatus used in most of the runs was of Pyrex glass. It is shown in Fig. 2. The mercury was placed in the small basin B and was heated from

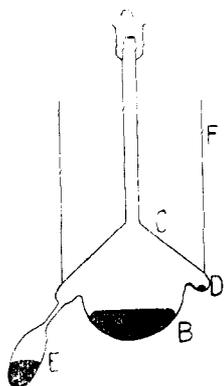


Fig. 2.

Cross-section of evaporator for the separation of isotopes (less efficient form).

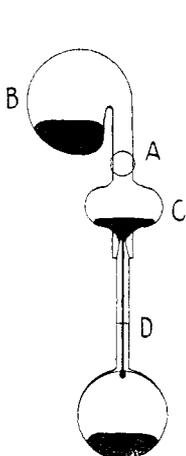


Fig. 3.—Pycnometer.

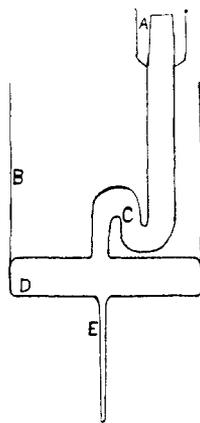


Fig. 4.—Section of efficient evaporator for the separation of isotopes.

below. Ice placed in the cylindrical jacket F caused the evaporating molecules to condense on the roof C whose slope was just sufficient so that the droplets ran down into the annular catch D, thence into the receiver E. The apparatus was filled through A and emptied by cutting off E, containing the condensate, and then pouring the residue out through the opening. The ground-glass joint A was connected to a mercury diffusion pump and oil pump, and to a McLeod gage. During the runs the apparatus was evacuated to a pressure of 10^{-4} to 10^{-5} mm. The efficiency was probably not much reduced until the pressure rose to about 10^{-3} mm., when the presence of air caused a

²⁴ Hulett and Minchin, *Phys. Rev.*, 21, 388 (1905).

considerable slowing up of the operation, and deflection of the mercury molecules so that some of them condensed on the roof of D.

The first runs were made with the form of apparatus shown in Fig. 4, which had the evaporating and condensing surfaces very close together, so that a high efficiency was to be expected. About 1000 g. of mercury was sucked into the apparatus at the beginning of the run, through the narrow tube at the bottom, which was then sealed off. The bottom of the apparatus was heated by a hot water bath fitted around it, and the evaporating molecules were condensed in the form of a solid on the roof of the apparatus, by the use of a mixture of solid carbon dioxide and toluene contained in an insulated cylindrical jacket fitted over the roof. After a run, air was admitted, and the residual liquid mercury allowed to run out through the tube at the bottom, which was cut open. The solid condensed mercury, after it had melted, was allowed to run out through the same opening. The use of this efficient form of apparatus had to be given up on account of the expense involved in supplying the necessary carbon dioxide or liquid air.

Pycnometer.—A special form of pycnometer was used in the density determinations. The pycnometer proper consisted of a glass bulb sealed to a thermometer capillary. This was fitted by means of a ground-glass joint to a filling device (Fig. 3). This consisted of two bulbs, and a side-tube A with a third bulb and a ground-glass joint through which the apparatus was evacuated. The mercury sample was placed in the upper bulb B and by rotating A, was caused to flow into the lower bulb C after the pycnometer was evacuated. Air was then admitted into the bulbs, which forced the mercury into the pycnometer. By filling at a low temperature, and then letting the mercury overflow at a suitable determined temperature, the meniscus was brought approximately to the mark (D) at 25.000°. Its distance from the mark was then measured by means of a cathetometer, and the observed weight of the filled pycnometer corrected accordingly. The correction was seldom over 0.1 mg. For a given sample in the same pycnometer, the corrected weights in successive fillings practically never varied among themselves by more than 0.3 mg., the extreme variation averaging about 0.2 mg., even when the weighings were made at intervals of days or weeks. The mean of three or more refillings was certainly correct to better than 0.1 mg. or about 1 part in 1,000,000, as can be judged from the table below. Two pycnometers were used in the determinations, one weighing when empty 13.4721 g. and holding 72.6375 g. of ordinary mercury, the other weighing 20.6576 g. and holding 106.9962 g. The air-buoyancy correction for the filled pycnometer was only 0.56 mg. in the first case and 0.95 mg. in the second, and therefore not appreciably dependent on the atmospheric density. The effects of pressure on the thermometer (0.002° per cm. of mercury), and on the pycnometers were also too small to require a correction, especially in view of the fact that the atmospheric pressure varied only from 741 mm. to 751 mm. during the whole series of determinations. No attempt other than filling the pycnometer at very low pressures was made to free the samples from dissolved gases, but this factor affected all the samples alike.

Results.—With a cut of 1.03, using the apparatus of Fig. 4, the combined condensates (Sample 1 of table p. 61) from two short runs showed a density 29 parts in 1,000,000 less than that of the original material. By Equation 7', this gives the value 0.0057 for the "separation coefficient" (B') of mercury. Brönsted and von Hevesy reported an increase of density of 31 parts per million for the residue for a cut of about 4, and a decrease of 20 parts per million for the condensate for a cut of about $\frac{7}{6}$. The average value of B' calculated from these data is 0.0042, so that their efficiency was about 75% assuming the above value of B' to correspond

to 100% efficiency. In the table below, the results of the present work are summarized. The same sample of pure mercury was used throughout as a standard of density and differences from this standard are expressed in parts per million. Using the apparatus of Fig. 2, which had an (initial) evaporating area of 17 sq. cm., and evaporating at a rate of 1 g. per sq. cm. per hour, at 40°, an efficiency of 93% was obtained (Sample 2 of table). In a run at 85°, with an evaporation rate of 2.6 g. per sq. cm. per hour, an efficiency of 83% was obtained (Sample 3).²⁵ After making these short runs, a systematic fractionation was undertaken, using successive cuts of 2. It was aimed to sacrifice efficiency somewhat to speed in the earlier stage, so that, allowing for various accidental causes of inefficiency, an efficiency of 80% was expected. One hundred and fifty g. of a light fraction (Sample 4) resulting from four successive cuts of 2, has been obtained, and shows a *decrease of density of 64 parts per million*, in exact agreement with that calculated for an average efficiency of 80% in each operation. Similarly, by making four cuts of somewhat more than 2, or a total cut of about 20 or 25, 140 g. of a heavy fraction (Sample 5) has been obtained which shows an *increase in density of 69 parts per million*, again completely in agreement with that calculated. A larger separation could undoubtedly have been obtained but the above results were considered convincing. Further work is being done on the separation of the isotopes of mercury by evaporation and diffusion methods.

Some of the purified mercury used in the above evaporations was subjected to distillation under reduced pressure, with the intention of showing the absence of impurities. The only possible impurities which could have been present are all much less volatile than mercury, and so should have become concentrated in the residue, if not wholly oxidized during the preliminary treatment, or by the air during the distillations. Most of these impurities (zinc, cadmium, lead, iron, etc.) are decidedly less dense than mercury, so that their presence in the residue would cause a decrease in its density. Only the very slightly volatile metals like platinum, gold, etc., which could not possibly be present in appreciable amount after the several redistillations, could have caused an increase in density. Actually, in every case, the residue from a distillation was found denser (4 to 7 parts per million) than the original material; and the first portion of distillate was if anything slightly less dense. While this cannot be accounted for by the presence of impurities, (unless by the presence of an undiscovered element similar to mercury, but denser and just a little less volatile) it is perfectly satisfactorily explained as due to a very inefficient separation

²⁵ For a perfectly clean surface (see Knudsen, *Ann. Phys.*, **47**, 697 (1915)); this rate of evaporation (2.6 g.) should be reached at 54°, while at 85° the rate should be about 19 g./sq. cm./hr., according to the Hertz formula. The *relative* rate of evaporation of isotopes should not be affected, however, by the reduced *total* rate of evaporation.

of isotopes as a result of incomplete equilibrium during the vaporization of the mercury. The relatively large changes of density of the residues, as compared with the distillates, are in harmony with the theory. The cut is very large (about 12) for the residues, thus producing a relatively large *increase* in density, while the corresponding *decrease* for the first fraction of distillate should be numerically equal (see theoretical discussion) to the increase for a cut of 2.7. The efficiency of the distillations, as compared with the method of evaporation, was about 6% for Sample 6, which was distilled rapidly, and about 10% for Sample 7, which was distilled slowly. Evidently there is a slight separation of isotopes every time mercury is distilled under reduced pressure. In fact, a similar effect must occur, to an extent usually negligibly slight, indeed, in every distillation of substances containing isotopes.

Aside from the indication of a slight separation of isotopes, the results of the distillations, in which conditions are as favorable as possible for impurities to show their presence, show conclusively that the changes of density resulting from the evaporations, which are made under conditions distinctly unfavorable to a separation of impurities, yet yield changes of density of a larger *order of magnitude* than the distillations, must be due to a separation of isotopes.

The results show that even a considerable number of collisions of molecules can occur before condensation without great loss of efficiency. The instantaneous molecular density in the space above the evaporating liquid should, according to calculations, be about $\frac{1}{3}$ that in the saturated vapor if no collisions occur. The vapor pressure corresponding to an

TABLE II
SUMMARY OF DENSITY RESULTS
Density Changes in Parts per Million

<i>Evaporations</i>		No. of	Mean change	Av. deviation
Sample	Cut	refillings	of density	(<i>a.d.</i>) of mean
		of pycnometer	(p. p. m.)	(p. p. m.)
1 Condensate.....	1.03	2	-29	± 0.7
2 Condensate.....	3	-20	0.4
Residue.....	2.22	2	+18	0.2
3 Condensate.....	2	-20	0.1
Residue.....	1.57	1	+ 9	...
4 Light fraction.....	4 cuts of 2	2	-64	0.7
5 Heavy fraction.....	20 or 25	2	+69	
<i>Difference in Density Between Extreme Fractions, 133 Parts per Million.</i>				
<i>Distillations</i>				
6 First fraction.....	2	-1.5	± 1.6
Residue.....	(?)	2	+3.5	0.4
7 First fraction.....
Residue.....	11.9	2	+4.0	0.8
8 First fraction.....	(6 cc. out of 85 cc.)	3	-1.5	0.9
Residue.....	13.0	3	+7.2	0.8

evaporation rate of 4 g. per sq. cm. per second is 0.025 mm., and the mean free path in saturated vapor at this pressure is about 1 mm. The actual mean free path was probably not over 3 mm. The average net distance any molecule had to travel before condensation was about 30 mm. in the apparatus used,²⁶ so that every molecule must have suffered a number of collisions on its way.

A Classification of Methods used for Separating Isotopes.

It seems worth while to classify, in outline form, the principal methods which might be used for separating isotopes.²⁷

- I. Methods using phenomena involving thermal motion of molecules and dependent on molecular velocities and their distribution. Separation necessarily incomplete.
 1. Equilibrium practically complete,²⁸—pressure and temperature constant throughout the system,—little or no separation.²⁹
 - A. Slow distillation, slow crystallization, chemical reactions in general.
 2. Equilibrium under a pressure or temperature gradient,³⁰—degree of separation proportional to logarithm of ratio of pressures or temperatures at ends of gradient, which ratio may theoretically be made indefinitely great, but practically is limited.
 - A. Equilibrium under a pressure gradient, due to gravity or rapid rotation,²⁷ or electron impact,³¹ etc.,—degree of separation proportional to the logarithm of the pressure ratio; or for centrifugal separation, to the square of the peripheral velocity, also to the product of the mol fractions and to the square of the interval between the atomic weights of the two isotopes, but *independent of the molecular weight*.
 - B. Equilibrium under a temperature gradient (thermal diffusion³²)—degree of separation approximately proportional to the logarithm of the temperature ratio; also to the product of the mol fractions, to the square of the difference of the molecular weights of the two isotopes, and *inversely proportional to the molecular weight*.
 3. Non-equilibrium processes. Flow under a gradient of partial pressure or concentration. The maximum efficiency of separation in A, B, and C, is given for zero partial pressure at the lower end of the gradient. The degree of separation in A, B, and C, is definite and limited for the light fraction, but proportional to

²⁶ In the more ideal apparatus shown in Fig. 4 this distance could be made as little as 5 mm. This apparatus was found to have a higher efficiency than that illustrated in Fig. 2. The use of the less efficient form as in the present work, is not advisable, since, in order to produce a given amount of material having a given change in atomic weight a multiplication of the number of operations is necessary.

²⁷ Compare Lindemann and Aston, *Phil. Mag.*, [6] **37**, 523 (1919), who discuss in particular, methods I, 1; I, 2, A; and II, 1.

²⁸ Compare Lindemann and Aston, Ref. 27; Lindemann, *Phil. Mag.*, [6] **38**, 173 (1919); Soddy, Ref. 21.

²⁹ A photochemical method of separation is being tried by Merton and Hartley (*Nature*, **105**, 104 (1920)).

³⁰ A fuller discussion of these methods of separating isotopes, including a comparison with the diffusion methods here discussed, will be given in a subsequent paper.

³¹ Skaupy, *Z. Physik*, **2**, 213 (1920).

³² Chapman, *Phil Mag.*, [6] **38**, 182 (1919).

the logarithm of the cut for the heavy fraction; while for both fractions it is proportional to the product of the mol fractions (as in thermal diffusion).

- A. Molecular effusion and non-equilibrium evaporation.³³
 - B. Molecular diffusion.
 - C. Interdiffusion of gases.
 - D. Liquid diffusion (separation probably small because diffusion coefficients in liquids depend on atomic or molecular volumes).
 - E. Rapid solution, precipitation, etc.³³
 - F. Initial effects in evaporation, diffusion, etc.
- II. Methods using phenomena in which molecules act as independent masses,—separation almost complete.
1. Positive ray methods,²⁷—yields very small, though products are, theoretically, almost pure.
 2. Possibly, electrolysis of ionized liquid or gas (separation probably difficult or impossible, because mobility of isotopic ions is probably practically equal; slight differences of mobility will be masked by diffusion and convection).³⁴

Summary.

1. The various phenomena of diffusion and effusion in gases are discussed in connection with the separation of isotopes. (a) It is shown that for the processes of molecular diffusion through a porous membrane, molecular effusion, and non-equilibrium evaporation, the relative rates of escape of isotopes are proportional to their respective mol-fractions and inversely proportional to the square roots of their molecular weights. In all the above processes the molecules (which may of course be monatomic, as in the case of neon or mercury) move independently. As collisions between molecules become more frequent, molecular diffusion passes into capillary transpiration, or mass motion, and non-equilibrium evaporation passes into ordinary distillation. In either case, practically no separation of isotopes occurs. (b) If a gaseous mixture of isotopes diffuses into another gas, with no convective mixing, the diffusion coefficients of any two isotopes are probably in the ratio $\frac{x_1}{x_2} \sqrt{\frac{cM_2}{M_1}}$, where c is a variable quantity

usually in the neighborhood of 1 or 2. The theory is complicated, but indicates a higher rate of separation than for molecular diffusion and evaporation, for which c is always 2. (c) Another possible method is that of "initial diffusion," which would take advantage of the fact that the front

³³ The method of irreversible condensation of a vapor or gas is a special case of the method of molecular effusion, and is thus somewhat similar to irreversible evaporation. J. J. Thomson's suggestion (*Proc. Roy. Soc.* 99A, 87 (1921) that the isotopes of chlorine might be separated by fractional absorption of hydrogen chloride in an alkaline solution would make use of this method. This would hardly be practical, however, due to the rapidity of the absorption and the consequent impossibility of good mixing. If air were admixed with the hydrogen chloride, there might be some degree of separation as a result of gaseous diffusion.

³⁴ See also Lindemann, *Proc. Roy. Soc.* 99A, 87 (1921).

rank of molecules diffusing into a gas or a vacuum should be enriched in the lighter isotopes.

2. The theory of non-equilibrium evaporation is discussed. If the vapor pressures of isotopes when pure are equal, a separation *must* occur when an isotopic liquid is evaporated *in vacuo* in such a way that practically all the evaporating molecules are condensed. For an efficient separation good mixing must take place in the surface and body of the liquid. This consideration bars the use of the method with solids, but solutions or liquid alloys might be used.

3. Simple and closely approximate equations are developed for the change in the mol-fraction of any isotope and for the change of atomic weight in a mixture of any number of isotopes, when the latter is separated into fractions by a diffusion or evaporation process. (See Equations 6 to 16 and 6' to 16'). These hold closely only for small changes in atomic weight, but by a second approximation, Equations 8, 9, 10, 17, 18 are obtained, which hold closely even for changes of considerable magnitude, Equations 3 and 4 permit exact calculations in the case of large changes, but apply only to the case of two isotopes. The *rate of separation* of two isotopes, as measured by the change in atomic weight for a given operation *is proportional to the square of the interval between the molecular weights of the two isotopes, inversely proportional to the ordinary molecular weight, and proportional to the product of the mol-fractions of the isotopes.* For a mixture of any number of isotopes, similar relations are shown to hold. For a given element, the *separation coefficient* (equal to the decrease of atomic weight of the isotopic mixture for the first small portion of diffusate or condensate) *is inversely proportional to the molecular weight of the compound* in which that element is combined. A table of separation coefficients is given, calculated from atomic weights and the results of positive ray analysis. The value given for mercury has been calculated from the present experimental data.

4. Most of the equations developed apply to the separation by diffusion of any gaseous mixture, whether or not it consists of isotopes. Equations 3, 4, 9, 10, 6, 7, 6B, and 7B are especially useful. Equations 6A, 6A', 7A, and 7A', are applicable only to the separation of a mixture of gases having very nearly the same molecular weight; Equations 6B and 7B fail only if the ratio of molecular weights is far from unity.

5. In systematic fractionation the diffusate (or condensate) being formed at any time has an atomic weight less than that of the corresponding residue, which becomes denser as the diffusion proceeds, by a constant amount. Thus *the enrichment of the light fraction is a maximum at the beginning. The atomic weight of the residue increases indefinitely, however, in proportion as the logarithm of its quantity decreases, while at the same time the atomic weight of the total diffusate approaches that of the original*

material. (Consult Fig. 1). The use of cuts of 2 gives equal and opposite enrichments for the two fractions, equal in magnitude to 0.693 times the separation coefficient, or initial enrichment for the light fraction. Efficiency conditions are discussed.

6. Formulas are given for calculating the proportions and numbers of isotopic molecular species in compounds containing several isotopic atomic species. Zinc chloride contains 12 molecular isotopes, and if, for example, tin has 6 isotopes, the compound SnCl_4 is a mixture of 30, and SnCl_2Br_2 , of 54, different molecular isotopes. The existence of many new isomers due to isotopism is also pointed out.

7. Experimental work on the partial separation of mercury into isotopes by non-equilibrium evaporation is described.³⁵ Calculation based on data for a very efficient evaporation gives a value of 0.0057 for the separation coefficient of mercury. Other runs with a less efficient apparatus gave concordant data. The results agree with those reported by Brönsted and von Hevesy, but the efficiency is better than theirs. By making four successive cuts of approximately 2, on both light and heavy fractions, a much larger decrease, of 64 parts per million, or 0.013 units of atomic weight, has been obtained on the lightest fraction, and a corresponding increase of 69 parts per million or 0.014 units on the extreme heavy fraction. The results are in complete agreement with the theory developed in this paper. *The total difference in density between the extreme fractions is thus 133 parts per million, and the difference in atomic weight, 0.027 units.* Data are given showing that a slight separation of isotopes occurs even in an ordinary distillation under reduced pressure.

8. A classification in outline of the possible methods for separating isotopes is given.

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³⁵ A larger separation has very recently been obtained by molecular diffusion of mercury vapor through filter paper at 150°. The results indicate that the separation coefficient of mercury is higher than 0.0057. A chemical method of separation and an electrolytic method have also been tried. All these will be described in a later paper.