

for we have disregarded the effect of the inertia of the shaft, *i. e.* we have neglected the effect of wave motion along the shaft. The effect of this may be gauged by the following considerations:—

The velocity propagation of a simple wave of tension or compression is $\sqrt{E/\rho}$, where ρ is the density of the material of the shaft. The time for such a wave to pass along a length L of shaft will accordingly be $L\sqrt{E/\rho}$. For the calculations given in this paper to hold then, this time must be quite small compared with the time of vibration of the shaft as given by (xxv.). It will be readily seen that this is not always the case, particularly when the shaft is running at very high speeds.

§ 12. The general conclusions to be drawn from the paper are as follows:—

The presence of the excentric load does not alter the fundamental character of the vibrations (natural) of the shaft. The periods obtained are the same as those with the symmetrical load. At the same time, there is a state of steady deflexion, given by (xvii.), about which the natural vibrations take place. This steady state of deflexion becomes impossible when the whirling speed is attained; such whirling speed being given by (xviii.). It may also be noted that (xvii.) and a corresponding result for θ , will enable one to assign an inferior limit to the stresses due to the bending that takes place at any speed.

In addition, the effect of yielding at the bearing will cause the critical speed to become lower. The practical effect of this it is difficult to gauge. A calculation is given, depending on unknown constants.

XLVIII. *The Possibility of separating Isotopes.*

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AS the existence of elements of different atomic weights which occupy the same position in the periodic table but appear to be inseparable by chemical means seems now to be generally accepted, it is of interest to consider the various methods by which there may be some hope of separating them. These appear to fall into four main groups:—Distillation, to which chemical separation is closely allied thermodynamically, Diffusion, Density, and Positive Rays.

* Communicated by the Authors.

The second law of thermodynamics $A - U = T \frac{dA}{dT}$ may be written $\frac{dp}{dT} = \frac{\lambda'}{(v - V)T}$, where p is the pressure of the saturated vapour, v its molecular volume, V the molecular volume of the liquid, λ' the latent heat of evaporation, and T the temperature. At reasonably low pressures $v = \frac{RT}{p}$ and v is large compared with V . One may therefore write

$$\frac{d \log p}{dT} = \frac{\lambda'}{RT}.$$

Now
$$\lambda' = \lambda + \int_0^T C_p dT - \int_0^T c_p dT,$$

where C_p is the molecular heat of the vapour at constant pressure, and c_p the molecular heat of the solid or liquid.

Therefore

$$\log p = -\frac{\lambda}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T (C_p - c_p) dT + \text{const.},$$

the latent heat of fusion of course being included in $\int_0^T (C_p - c_p) dT$ if the temperature is above the melting-point.

If p is small C_p is constant so that

$$\log p = -\frac{\lambda}{RT} + \frac{C_p}{R} \log T + \int_0^T \frac{dT}{RT^2} \int_0^T c_p dT + \text{const.}$$

Now $C_p = C_v + \frac{9\alpha^2 v T}{\kappa}$, where v is the atomic volume, α the expansion coefficient, and κ the compressibility, whilst c_v , the atomic heat at constant volume, is given in the terms of the atomic frequency in the solid ν_m by

$$c_v = 3R \left[\frac{12T^3}{(\beta\nu_m)^3} \int_0^{\frac{\beta\nu_m}{T}} \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3\beta\nu_m}{e^{\beta\nu_m} - 1} \right] = f(\nu_m).$$

Therefore

$$\begin{aligned} \log p = & -\frac{\lambda}{RT} + \frac{C_p}{R} \log T - \int_0^T \frac{dT}{RT^2} \int_0^T f(\nu_m) dT \\ & + \int_0^T \frac{dT}{RT^2} \int_0^T \frac{9\alpha^2 v T}{u} dT + \text{constant.} \end{aligned}$$

It is clear that p cannot be identical over a wide range of T , *i. e.* that two substances must be separable by fractionation unless ν_m is identical for both as well as λ and C_p and $\frac{\alpha^2 v}{\kappa}$. All these constants may change with the atomic volume, *i. e.* they may and probably do depend upon the total pressure. Therefore if the theorem that the isotopes are not separable is mathematically true, at any rate λ and C_p must be identical over a finite range of atomic volumes. It has been shown by Soddy, at any rate in the case of lead, that the distances between the centres of the atoms in the solid state are identical. If this is so, it seems impossible for λ and ν_m to be identical.

Consider an atom at the surface of a plane of the isotope defined by $z=0$. Let the forces acting upon it have a component in the Z axis $\phi(z)$. The latent heat at the absolute zero λ is then proportional to $\int_r^\infty \phi(z) dz$. Since r is identical for two isotopes the condition that λ is identical means that $\int_r^\infty \phi(z) dz$ is identical. Further, they must be identical although r may be varied over a finite range.

Now imagine another plane of the same material placed in contact with the first. The force on the atom will be $\phi(z) - \phi(z)$, so that the quasi-elastic restoring force is by Taylor's theorem $2\Delta z \phi'(z)$. The frequency ν_m is therefore

$$\frac{1}{2\pi} \sqrt{\frac{2\phi'(z)}{M}}$$

If this is to be identical in two isotopes $\phi'(z)$ must be proportional to the atomic weight M .

Therefore if two isotopes are to be inseparable by fractionation, $\phi(z)$ must be a function such that $\int_r^0 \phi(z) dz$ is identical in both cases, whereas $\phi'(z)$ must be proportional to the atomic weight.

If $\phi(z)$ may be represented as a power series, say $a_n z^n + a_{n-1} z^{n-1} + \dots$ in the case of one isotope and $b_n z^n + b_{n-1} z^{n-1} + \dots$ for the other, one has

$$\begin{aligned} \phi_1'(z) &= n a_n z^{n-1} + (n-1) a_{n-1} z^{n-2} + \dots \\ &= \frac{M_2}{M_1} \phi_2'(z) = n b_n z^{n-1} + (n-1) b_{n-1} z^{n-2} + \dots \end{aligned}$$

This is only true over a finite range of z , if

$$b_n = \frac{M_1}{M_2} a_n, \quad b_{n-1} = \frac{M_1}{M_2} a_{n-1} \text{ etc.}$$

On the other hand, if this is so,

$$\lambda_1 = \int_r^\infty \phi_1(z) dz = \frac{a_n}{n+1} r^{n+1} + \frac{a_{n-1}}{n} r^n + \dots$$

and

$$\begin{aligned} \lambda_2 &= \int_r^\infty \phi_2(z) dz = \frac{b_n}{n+1} r^{n+1} + \frac{b_{n-1}}{n} r^n + \dots \\ &= \frac{M_1}{M_2} \int_r^\infty \phi_1(z) dz = \frac{M_1}{M_2} \lambda_1. \end{aligned}$$

Therefore if $\phi(z)$ is an analytical function, both λ and ν^m cannot be identical and the isotopes must be separable under appropriate conditions.

It is of course true that the separation may be minute. If, for instance, M only varies by 1 per cent. as in the case of lead, the percentage difference of pressure at the boiling-point would probably not exceed 1 per cent. and might be very much less if the first-order terms cancel one another.

A similar argument applies to the chemical separation of isotopes. For

$$A = U_0 - T \int_0^T \frac{dT}{T^2} \int_0^T \Sigma c_p dT + \Sigma i,$$

so that complete identity of the affinity A implies the identity of U_0 and c_p over a finite range of values of r . It is almost inconceivable that the values of U_0 should be identical unless the values of λ are identical, for U_0 is made up of the heat of reaction of one atom of the isotope with one or more atoms in the gaseous state plus the algebraic sum of the latent heats of the combination and of the reacting substances at the absolute zero. The possibility that there is a difference between different isotopes in the heat of combination of one atom with one or more atoms of some other substance which exactly balances the difference in $\Sigma \lambda$ seems sufficiently remote to be ruled out without further discussion. But if one may conclude that the values of λ are identical the same difficulty arises in assuming the values ν_m to be identical as was experienced above. Since the values of $\frac{U_0}{RT}$

are usually large compared with

$$\int_0^T \frac{dT}{RT^2} \int_0^T \Sigma cv dT$$

at all ordinary temperatures, the difference in the constant of the law of mass action would probably be imperceptible unless suitable equilibria were examined under favourable conditions. Thus isotopes could not be separated by an ordinary precipitation, *i. e.* what used to be called an irreversible reaction, any more than nitrogen and oxygen could be separated by dropping liquid air into a red-hot flask.

Fractional distillation was the first method used by Aston in attempting to separate the two hypothetical constituents of Neon ("Homogeneity of Atmospheric Neon," Brit. Assoc. Birmingham Meeting, 1913). The gas was fractionated over charcoal cooled in liquid air. The apparatus used

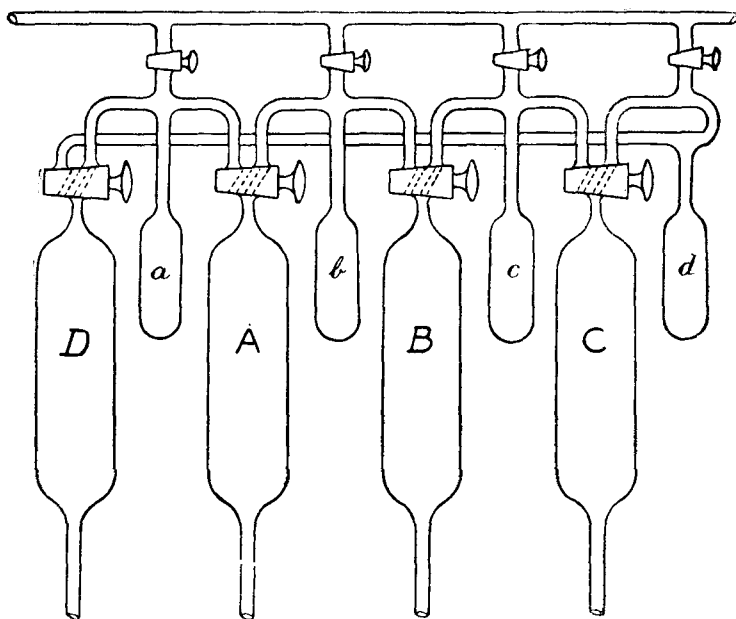


Diagram of Fractionation Apparatus.

is illustrated in the accompanying figure; the method of working was as follows:—

The gas was admitted in *a*, one of the small charcoal bulbs *a b c d* all cooled in liquid air. After a reasonable time had elapsed the first fraction was pumped off by lowering

mercury in gas-holder A and opening the connecting stop-cock between it and *a*. After another interval the stopcock was turned, the mercury raised in A and the gas forced into bulb *b*. The mercury was next lowered in both A and B, the former receiving the second fraction from *a* while the latter withdrew the first fraction of the gas now in *b*. The fundamental assumption on which this arrangement was made was that at this stage, if the vapour-pressures of the gases are nearly the same, the gas in A would have the same composition as that left in *b*, and that they therefore might be mixed. This was done by raising the mercury, which not only drove the gas from A into *b* but also the lightest fraction from B into *c*, where it again fractionated, each process driving the lower boiling gas forward and keeping the higher back.

The apparatus may contain any number of units, the whole system being made cyclical and continuous by joining the charcoal bulb at one end with the gas-holder at the other. Four such units were actually employed, and after four operations the liquid air was removed from *a* and the residue it contained was pumped off completely with an Antropoff pump as the first contribution to the heaviest fraction, in the same way that in D was also pumped off as that of the lightest. The bulb *a* was then immersed again in liquid air and the process continued.

After about two-thirds of the gas had been collected in this way as light and heavy fractions, that remaining was all pumped out as the middle fraction. The process was next repeated with the light and heavy fractions in turn, the intermediate ones being combined by a definite rule.

By this arrangement, which does many operations at once, the small quantity of helium contained in the original gas was removed in a remarkably short time, after which the neon was subjected to continual fractionation for three weeks. The gas had now been through about 3000 fractionations and was divided into seven main fractions; the density of these was determined by the quartz micro-balance (F. W. Aston, Roy. Soc. Proc. A, vol. lxxxix. 1914), the figures for the pressures giving the same zero as oxygen at 76·35 were as follows:—

(1)	(2)	(3)	(4)	(5)	(6)	(7)
121·05	120·95	121·05	120·90	121·00	121·05	121·05

The mean of these, 121·05, gives a molecular weight of 20·19, which is identical within experimental error with the accepted one of 20·200 determined by Watson (J. C. S. 1910).

It is evident that no appreciable separation whatever had been achieved, hence if neon is not homogeneous the vapour-pressure of its constituents at the temperature employed must be very nearly the same. It is, however, impossible to draw any definite conclusion from the above experiment as to the homogeneity of the gas until further fractionations have been performed at other and lower temperatures, preferably without the use of charcoal.

Diffusion.

Lord Rayleigh (*Phil. Mag.* xlii. p. 493, 1896) has investigated the problem of the separation of gases of different density by diffusion. He obtained as an expression for the effect of a single operation

$$\frac{x+y}{X+Y} = \frac{X}{X+Y} \gamma^{v_1/v_2-v_1} + \frac{Y}{X+Y} \gamma^{v_2/v_2-v_1},$$

where (X, Y) (x, y) are the initial and final volumes of the gases, v_1 v_2 the velocities of diffusion, and γ the enrichment of the residue as regards the second constituent.

After the failure of fractional distillation described above, an attempt was made to separate the hypothetical constituents of neon by diffusion through pipeclay. In this case, as the molecular weights given by positive rays are apparently 20 and 22 respectively, ν and μ only differ by 5 per cent., so the above equation may be written in the simple form

$$\frac{x+y}{X+Y} = \gamma^{-20} \quad \text{or} \quad \gamma = \sqrt[20]{\frac{\text{Initial Volume}}{\text{Residual Volume}}}.$$

The first apparatus was similar to that described by Ramsay and Collie (*Roy. Soc. Proc.* lx. p. 206, 1896). After an extremely laborious and prolonged series of diffusions a small but apparently real difference of density was detected amounting to about 0.7 per cent. A much more elaborate apparatus was designed and was started early in 1914. This apparatus is on the see-saw principle and the volume ratio is about 2000, so that given perfect mixing this should give an enrichment of 1.4. Rather more than 200 c.c. of enriched gas had been collected by the time the War interrupted the experiment. It is hoped that the apparatus will soon be

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started again, and when another 100 c.c. are collected the whole will be diffused again. This second operation should give a theoretical enrichment of 2, so that unless the mixing is very bad a definite increase of density might be obtained.

A very much simpler and better type of continuous diffusion apparatus would be one on the rotating principle used in the Gaede mercury pump, the difficulty being the manufacture of the rotating part of pipeclay or unglazed porcelain with a suitable device for withholding and collecting the small residual volume of less diffusible gas. Should diffusion methods prove sufficiently hopeful, an effort will be made to construct such an apparatus.

It will be seen from Rayleigh's equation above that there is not the least hope of getting approximately complete separation for a reasonable quantity of gas in a reasonable time by this diffusion method even under theoretically perfect conditions of mixing.

Another method that has been suggested consists in allowing the gas to diffuse through a column of heavier gas or liquid. Its practical difficulties are considerable, and its advantages over the other method by no means obvious.

Density.

There are two direct methods of separating isotopes by the effect of their different masses. The first of these, gravitational separation in the stratosphere, applies only to neon if this be really a mixture of two isotopes.

If M be the atomic weight, g the gravitational constant, p the pressure, and ρ the density, then if no mixing takes place $dp = -g\rho dh$, h being the height. In the isothermal layer convection is small. If it is small compared with diffusion the gases will separate to a certain extent. Since T is constant

$$p = \frac{RT\rho}{M} \quad \text{and} \quad \frac{dp}{\rho} = \frac{Mg}{RT} dh,$$

whence

$$\rho = \rho_0 e^{-\frac{Mg}{RT} \Delta h},$$

ρ_0 being the density at the height h_0 at which mixing by convection ceases, about 10 kilometres, and Δh the height above this level. If two isotopes are present in the ratio 1 to K_0 , so that the density of one is ρ_0 and of the other $K_0\rho_0$

at height h_0 , then their relative density at height $h_0 + \Delta h$ is given by

$$K = K_0 e^{-\frac{g\Delta h}{RT}(M_1 - M_2)}.$$

Putting $T = 220$ as is approximately true in England,

$$\frac{K}{K_0} = e^{-5.38 \times 10^{-3} \Delta h (M_1 - M_2)},$$

Δh being measured in kilometres. If $M_1 - M_2 = 2$, therefore

$$\frac{K}{K_0} = e^{-1.075 \times 10^{-2} \Delta h}$$

It might be possible to design a balloon which would rise to 100,000 feet and there fill itself with air. In this case the relative quantity of hypothetical metaneon would be reduced from 10 per cent. to about 8.15, so that the atomic weight of neon from this height should be 20.163 instead of 20.2. If one could get air from 200,000 feet, *e.g.* by means of a long-range gun firing vertically upwards, the atomic weight of the neon should be 20.12. Though the quantities are measurable they do not appear sufficiently striking to warrant the outlay and labour such experiments would entail.

The second method which suggests itself for separating isotopes by means of their different masses is to centrifuge them. In this case the same equation holds as above except that g varies from the centre to the edge. In a gas therefore

$$\frac{d\rho}{\rho} = -\frac{Mv^2}{RT} \cdot \frac{dr}{r} = -\frac{M\omega^2}{RT} r dr,$$

whence
$$\rho = \rho_0 e^{-\frac{Mv_0^2}{2RT}},$$

v_0 being the peripheral velocity. Here again, if K_0 is the ratio of the quantities present at the centre, the ratio at the edge will be

$$K_0 e^{-\frac{v^2}{2RT}(M_1 - M_2)}.$$

A peripheral velocity of 10^5 cm./s. or perhaps even 1.3×10^5 cm./s. might probably be attained in a specially

designed centrifuge, so that $\frac{K}{K_0}$ might be made as great as

$$e^{-0.205(M_1 - M_2)}$$

or even

$$e^{-0.37(M_1 - M_2)}.$$

If $M_1 - M_2$ is taken as 2 a single operation would therefore give fractions with a change of K of 0.65. Thus again, if neon is supposed to consist of 90 per cent. of gas of atomic weight 20 and 10 per cent. of a gas of atomic weight 22, the concentration of the heavier component at the edge would be 2.36 times that at the centre. The apparent atomic weight of the gas from the edge, however, would only be about 1.0065 greater than that of gas from the centre after one operation. By centrifuging several times, however, or by lowering the temperature the enrichment might be increased exponentially.

Centrifuging a liquid, *e. g.* liquid lead, would not appear to be so favourable, though it is difficult to form an accurate idea of the quantities without a knowledge of the equation of state. If compression is neglected and the one lead treated as a solution in the other, a similar formula to that given above holds. Provided the atoms occupy equal spaces, as they appear to do in the solid, the centrifugal force on the heavier component is $(M_1 - M_2) \frac{v^2}{T}$, and, as above, its concentration should increase from the centre to the edge in the ratio

$$e^{-\frac{v^2}{RT}(M_1 - M_2)}.$$

Again, putting $M_1 - M_2 = 2$ (*e. g.* thorium lead and uranium lead), $v = 10^5$ and $T = 600$, one finds that the concentration of the thorium lead would be nearly 50 per cent. greater at the edge than at the centre, after one operation. Separation by this method therefore seems possible though difficult and costly.

Positive Rays.

This method consists in allowing the parabolas corresponding to the isotopes generated by the use of electric and magnetic fields in the usual way, to fall through two parabolic slits into separate vessels containing *e. g.* charcoal cooled in liquid hydrogen. In this manner theoretically

complete separation would be achieved, so that it is worth while inquiring into the quantities of the gases obtainable in the case of neon.

The maximum separation of the parabolas corresponding to masses 20 and 22 (obtained when electric deflexion θ is half the magnetic) is approximately

$$2 \frac{1}{\sqrt{2}} \frac{M_1 - M_2}{M_1} \theta = \frac{\theta}{28}.$$

Taking a reasonable value of θ as $\cdot 3$ the maximum angular width of the beam for complete separation = $\cdot 01$. If the canal-ray tube is made in the form of a slit at 45° to axes, *i. e.* parallel to the curves, the maximum angular length of the beam might be say 5 times as great, which would collect the positive rays contained in a solid angle of $\cdot 0005$ sq. radian.

The concentration of the discharge at the axis of the positive ray bulb is considerable, and may be roughly estimated to correspond to a uniform distribution of the entire current over a $\frac{1}{4}$ sq. radian. One may probably assume that half the current is carried by the positive rays, and that at least half the positive rays consist of the gases desired. If neon is analysed by this method therefore the total current carried by the positive rays of mass 20 is

$$\cdot 0005 \times 4 \times \frac{1}{2} \times \frac{1}{2} \times i = \cdot 0005 i.$$

If i is as large as 5 milliamperes this = $1 \cdot 5 \times 10^4$ E.S.U.

or
$$\frac{1 \cdot 5 \times 10^4}{2 \cdot 7 \times 10^{19} \times 4 \cdot 77 \times 10^{-10}} = 1 \cdot 2 \times 10^{-6} \text{ c.c./sec.},$$

i. e. one might obtain about one-tenth of a cubic millimetre of neon and $\frac{1}{100}$ cubic millimetre of metaneon per 100 seconds run.

The chief difficulty is the excessive cold necessary in the receiving vessels which must be sufficient to fix the molecules even at the extremely low pressure of 10^{-4} mm. in the camera. This could be obtained by the use of liquid helium, but whether charcoal cooled by liquid hydrogen would suffice is at present uncertain. No such difficulty occurs of course in the separation say of the lead isotopes, but so far it has not proved possible to obtain lead positive rays quite apart from the difficulty of separating the parabolas when obtained.

Conclusions.

The following conclusions may be drawn from the above considerations and results :—

(a) Thermodynamic theory indicates that isotopes must be separable in principle even chemically under some physical conditions, though the separation may be small and these conditions may not be obtainable without great difficulty.

(b) None of the physical methods considered give hope of easy separation even for gaseous isotopes. When the quantities dealt with are reasonably large the enrichment is extremely small, and when anything like complete separation is hoped for the yield is microscopic. The most promising method appears to be the use of a centrifuge, provided the engineering problems can be overcome.

(c) The experimental results quoted so far as they have gone cannot pretend to be conclusive either as to the homogeneity of neon or to the separability of isotopes.

Summary.

Theoretical considerations are advanced to show that elements of different atomic weights must be separable in principle though possibly not in practice.

Various possible methods of separating such substances are discussed.

Fractional Distillation or Chemical Separation may be possible under suitable conditions.

Diffusion must lead to a positive result, but the technique is necessarily laborious.

Gravitational Separation is small. Centrifugal Separation appears promising, but would involve heavy outlay and elaborate preparations.

Electrical Separation, the only method offering hopes of a pure product, will only yield microscopic quantities even if the very serious difficulties indicated can be overcome.

Experiments to separate the hypothetical constituents of Neon are described, in which neither by fractional distillation nor by diffusion have conclusive results yet been obtained.

Farnborough,
Feb. 15th, 1919.