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Tests of the Theory of Isotope Separation by Centrifuging

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INTRODUCTION

The possibility of separating isotopes by centrifuging was first suggested by Lindemann and Aston [1, 2] in 1919. Also, they worked out the equilibrium theory for the separation in an ideal gas and in an ideal incompressible liquid. This theory was critically discussed and extended by Mulliken,[3] Chapman,[4] Harkins [5] and others. A number of early attempts by several workers [6, 7, 3] were made to obtain the separation of different isotopes in specially constructed centrifuges. Unfortunately, each of these attempts was unsuccessful, probably because of convection, and the method was abandoned as impracticable. However, with the development of the convection-free vacuum type ultracentrifuge [8] in 1934, the method was tried again and the experiments were successful.[9–12] In most of these first successful experiments the so-called evaporative centrifuge method originally suggested by Mulliken [3] was employed to separate the Cl^{37} and Cl^{35} isotopes of chlorine in CCl_4. Also the bromine isotopes were concentrated. It was found that considerable separation could be obtained and the results were in good agreement with the theory when equilibrium conditions were approximately obtained in the centrifuge.[11, 12] The theory was tested further with a special type of centrifuge at dry ice temperature with different substances at different rotor speeds, and it was found to hold.[13] Humphreys [14] also used the same type of centrifuge as employed in some of the above experiments [11] to concentrate the isotopes of bromine and extended the theory of the evaporative centrifuge method to include the non-equilibrium condition. It was clear from elementary theory that the rate at which separation takes place in a centrifuge is proportional to the length or depth of the rotor. Accordingly, methods of spinning long tubular rotors were developed [11] and used not only in the evaporative centrifuge method [12] but in several other methods as well.[13] The purpose of this paper is to describe additional experiments which were designed to test the general theory of Cohen and his collaborators [15] for the separation of isotopes by the evaporative, the concurrent flow and the countercurrent flow centrifuge methods. Most of the tests were made on the separation of the uranium isotopes in uranium hexafluoride.

THE EVAPORATIVE CENTRIFUGE METHOD

The evaporative centrifuge method consists in partially filling a hollow centrifuge rotor with a liquid compound containing the element whose isotopes are to be separated. The centrifuge is then driven to running speed and the vapor is drawn off along the axis. The substance containing the isotopes evaporates near the periphery of the spinning rotor, diffuses along the centrifuge radius against the centrifugal field and passes out through a hollow shaft. The fraction drawn off along the axis has the lighter isotope enriched, while the residue in the rotor has the heavier isotope enriched. If the material is drawn off slowly so that equilibrium is approximately established throughout the vapor, the theory [1, 2] shows that for the case of a mixture of two isotopes of masses M_1 and M_2

$$\alpha = \frac{K_0}{K} = \exp \frac{4\pi^2 n^2 r^2 (M_2 - M_1)}{2RT} \qquad (1)$$

where K_0 = ratio of the quantities of light to heavy isotopes at the axis
K = same ratio at the periphery
n = number of revolutions per sec
r = centrifuge radius
T = absolute temperature
R = gas constant.

Mulliken [3] has shown that the theoretical value of α in Eq. (1) is independent of the state of combination of the elements being centrifuged, provided the isotopes have the same properties.

As the vapor is drawn off along the axis the residue in the spinning rotor becomes more and more enriched in the heavier isotope. As a result the isotopic ratio in the material drawn out at any instant during the centrifuging, called the "instantaneous diffusate", continues to change during the centrifuging process. It can be shown [3, 5] that the fractional change in the

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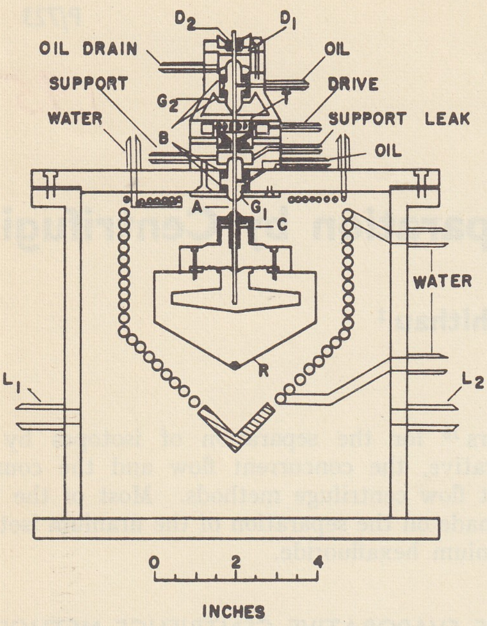

Figure 1. Evaporative centrifuge

isotopic abundance ratio in the residue f_r and the fractional change in the abundance ratio f_t in the total diffusate, the total sample drawn off along the axis, are given by the relations

$$f_r = (\alpha - 1)\ (\ln F) \tag{2}$$

$$f_t = \frac{(1 - \alpha)\ F \ln F}{1 - F}$$

where F is the ratio of the number of moles of material in the residue to the number of moles of material initially in the rotor or the " cut ".

Humphreys [14] and Cohen [15] have shown theoretically that when Q, the rate at which the vapor is drawn off along the axis, is great enough to disturb the equilibrium, then

$$\alpha = \exp\left[\frac{g4\pi^2 n^2 r^2\ (M_2 - M_1)}{2RT}\right] \tag{3}$$

where

$$g = \frac{4\pi hDd}{\overline{M}} \Big/ \left[\frac{4\pi hDd}{\overline{M}} + Q\right]$$

and

d = density
D = diffusion constant
h = height of the centrifuge chamber
$\overline{M}$ = average molecular weight of the gas or vapor being centrifuged.

The apparatus was essentially the same as that previously used [11] except that it was adapted for use with UF_6. A schematic drawing of the centrifuge is shown in Fig. 1. The rotating parts consist of the hollow Duralumin ST-14 rotor R, the flexible stainless steel tubular shaft A (0.083 in. od and 0.065 in. id) and the air turbine T. The outside radius of the rotor was 5.04 cm and the inside radius 4.12 cm while the effective height was 0.72 cm. In some experiments radial baffles were placed in the rotor chamber. The flexible oil glands G_1 and G_2 served both as bearings and as vacuum seals for the vacuum chamber. Vacuum pump oil was forced into the gland G_1 and a pure, carefully dried oil was forced into G_2. The flexible neoprene sheet diaphragms D_1 and D_2 which were clamped to the walls of the upper vacuum chamber prevented oil (droplets, film or vapor) from entering the UF_6 chamber above D_2. The rotor was heated by copper heating coils shown in Fig. 1 through which water above 69°C was circulated. The rotor spun in hydrogen at a pressure of 11 to 12 mm Hg. Experiment showed that the rotor temperature was approximately 5°C hotter than the coils and could be determined to within 2°C. Figure 2 is a diagram of the system used for evacuating the rotor and collecting the UF_6. The rotor designated R and S is a vacuum-tight chamber which is located just above G_2 in Fig. 1. The cold trap C is immersed in a dry ice-alcohol slush when UF_6 is to be trapped and K is a potassium fluoride trap for trapping any HF which was found unnecessary. Cold traps, I_1 and I_2, are for stopping diffusion pump vapors and P is a phosphorous pentoxide trap for keeping the system dry. An oil overflow trap O is used to catch oil from the gland G_2 of the centrifuge. The U bend shown between S and O fills with oil and seals the high vacuum on one side from the fore vacuum on the other.

Since the evaporative centrifuge method is a batch method the rotor is first carefully filled by distilling into it a known amount of UF_6. The rotor is then filled to atmospheric pressure with dry air and placed in the position shown in Fig. 1. It is next driven to running speed (1340 plus or minus 2 rps.) and the system (Fig. 2) evacuated. The heating coils are then quickly brought up to temperature. The high molecular weight of the UF_6 gives a large pressure ratio between the periphery and the axis (about 4.5×10^3). Consequently a good vacuum system was required to pump the UF_6 out of the axis of the spinning rotor. The cold trap C was made of thin aluminum so that the amount of UF_6 collected at any time during an experiment could be estimated by X-ray photographs. This was helpful in deter-

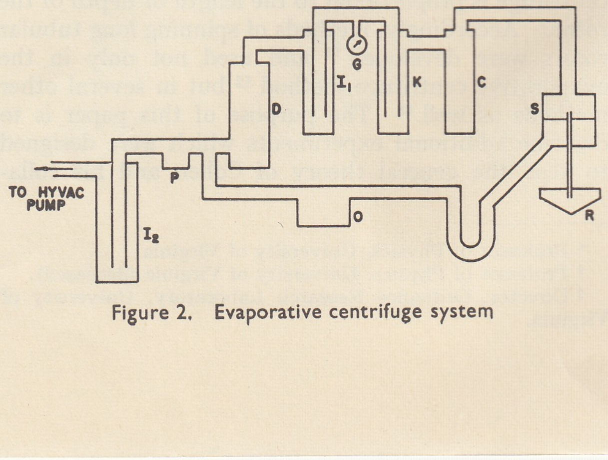

Figure 2. Evaporative centrifuge system

mining the proper " cut ". The isotopic separation was kindly determined by Prof. A O. Nier using a mass spectrometer. The results obtained are shown in Tables 1 and 2.

Table 1. Analysis of Samples Produced by a Single Centrifuging

Rotor temp., °C	*Weight of product gm*	*Rate of pumping Q, gm/sec*	*Increase in abundance ratio of U^{235}/U^{238}* Equilibrium theory, %	Humphrey-Cohen theory, %	Measured values, %
82	1.2	3.2×10^{-4}	5	4.3	4.0
81	0.6	1×10^{-4}	5.7	5.4	5.5
81–85	0.5	0.37×10^{-4}	5.3	5.2	4.6
81–83	1.0	0.7×10^{-4}	5.5	5.3	5.6
83	0.8	2.8×10^{-4}	5.0	4.4	5.3
81	1.1	3.1×10^{-4}	5.6	4.8	4.8
90	3.6	5.6×10^{-3}	3.0	0.8	0.7

In Table 1 the data are given for a single centrifuging of the UF_6. The first column gives the temperature of the rotor which could be determined with a precision of ± 2°C except where indicated. The second column gives the weight of the material in which the isotopic ratio is changed. The third column gives the rate of pumping Q. The fourth column gives the increase in abundance ratio of U^{235}/U^{238} in per cent as calculated by the Mulliken-Harkins equilibrium theory. This is $(\alpha - 1)$ of Eq. (1) multiplied by 100. The fifth column gives the same values calculated by the more exact Humphreys-Cohen theory (Eq. 2) and the sixth column gives the values measured by Nier with his mass spectrometer. The experimental values are believed to be in good agreement with the Humphreys-Cohen theory when the errors which may be introduced by the complicated weighings of products are taken into consideration.

Table 2. Analysis of Samples Produced by the Cascade Evaporative Centrifuging Method

Rotor temp., °C	*Weight of product, gm*	*Number of cascades*	*Change in abundance ratio of U^{235}/U^{238}* Humphrey-Cohen theory, %	Measured values, %
81–87	1	1	14	12.2
81–87	1	1	– 12	– 9.8
90–95	1	2	18	17.5
88–93	1	2	– 19	– 20 to – 28

Table 2 gives the values obtained when the product and/or stripped material is recentrifuged or cascaded. Here again the theory is in agreement with experiment when the possible errors introduced by weighings are taken into consideration.

THE CONCURRENT FLOW CENTRIFUGE METHOD

Although the above experimental results are in good agreement with the theory for the separation in a radial centrifugal field, the experimental conditions of the evaporative centrifuge method are somewhat restricted. Consequently, it is important to carry out additional tests where the experimental conditions can be varied over a greater range, and where axial flow as well as radial flow and diffusion takes place. At the same time the experiments should be designed so that the theory can be unambiguously applied.

The concurrent or " flow through " method of centrifuging consists in introducing the mixture to be separated into one end of a tubular centrifuge and collecting it in two separate fractions at the other end. This method was first used successfully for the separation of the isotopes of chlorine in ethylchloride[13] in a 7.62-cm id and 35.5-cm long tubular centrifuge[16] spinning at approximately 1060 rps. Essentially the same apparatus was used for separating N_2 and the CO_2 mixtures and H_2 and CO_2 mixtures.[11, 13, 16] The theory of the separation in the concurrent method was developed by Cohen and Murphree.[15]

Figure 3 shows a schematic diagram of the rotor and the assumed axial flow pattern inside the rotor. This design was chosen because the experimental results can be compared directly with theory.[15] The material to be centrifuged enters the rotor through a hollow shaft which is divided in such a way that two separate streams can pass through it. The end caps are constructed so that the material enters the rotor in two thin cylindrical coaxial streams of radius r_1 and r_2. These two thin cylindrical streams are supposed to flow through the tube as shown in Fig. 3 and be collected at distances r_1 and r_2 from the axis, respectively, at the opposite end of the spinning tube. The ratio r_1/r_2 was 0.534. Because of the centrifugal field, transport takes place between the two streams in such a way that the outer stream has the heavy component or isotope enriched while the

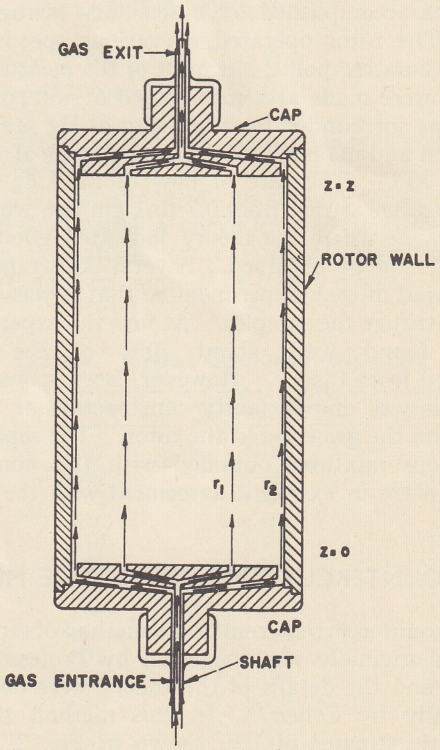

Figure 3. Concurrent centrifuge

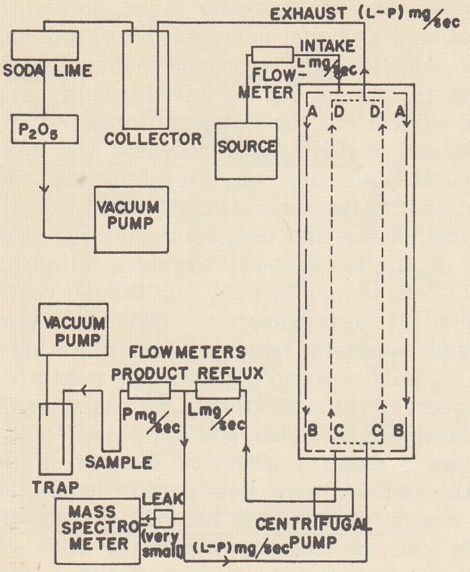

Figure 4. Type I countercurrent operation

inner stream has the light component or isotope concentrated.

The tubular Duralumin rotor was 16.6 cm id and 84.14 cm inside length between the Duralumin caps. The shafts were of steel but lined inside with divided stainless steel liners. The method of spinning the rotor was essentially the same as previously described in detail [11] except that a steam turbine drive was used instead of the air turbine. When UF_6 was used it was necessary to prevent the vapor from coming in contact with the oil in the vacuum oil seal bearings. This was accomplished by buffer (dry nitrogen) gas seals. The rotor operated at various speeds up to near its bursting point, but most of the measurements on UF_6 were made at a rotor speed of 450 rps. The rotor was surrounded by a few mm of Hg pressure of hydrogen and maintained at a temperature of approximately 70°C. The rate of flow of the UF_6 through the centrifuge varied from 0.7 to 1 gm/sec, which was in the range where the theory indicated good separation should be obtained. Several kilograms were centrifuged in each experiment so that it was possible to recentrifuge the samples. At first the experimental values found were about 70% of the values predicted from theory. However, later, it was found that this was due to faulty construction of the end cap where the gas entered the rotor. The separations of gaseous mixtures obtained with this concurrent method were in excellent agreement with the theory.

THE COUNTERCURRENT CENTRIFUGE METHOD

The countercurrent centrifuge method of separating isotopes originally was suggested by Professor H. C. Urey [15] and the details of the theory were developed principally by Cohen.[15] In this method the thin concentric streams of UF_6 shown in Fig. 3 flow in opposite axial directions instead of in the same direction. As a result the inner stream becomes enriched in the lighter isotope near its exit at one end of the spinning tube, and the peripheral stream becomes enriched in the heavier isotope near its exit at the other end. Because of the axial flow a concentration gradient is set up along the length of the tube which is limited only by back diffusion. Consequently, the separation may be many times that produced by the simple centrifugal process.

Figure 4 shows a schematic diagram of the countercurrent operation. UF_6 from the source at a measured rate of L mg/sec enters the spinning tube through the divided shaft and is directed downward near the periphery at AA in a thin cylindrical stream. At BB it emerges through the end cap and shaft into a centrifugal pump located on the shaft of the centrifuge. It next passes through a flow meter and is divided into two streams. One stream of P mg/sec is collected as product in a cold trap. The other stream, $(L-P)$ mg/sec, is returned to the centrifuge through the shaft and directed upward by the end cap in a thin cylindrical stream from CC to DD where it passes out of the end cap and shaft of the centrifuge and is collected in a cold trap. It will be observed that this type of operation enriches the U^{238} rather than the U^{235} in the product. This so-called "stripper" arrangement was used in these experiments rather than the enricher arrangement because of the greater reliability with which the flow and the product P could be measured under the experimental conditions. The theory and operation of the enricher and stripper are essentially the same and, if the experimental data are available for the stripper, the operation of the enricher can be reliably determined. Figure 5 shows another type of stripper operation which is essentially the same as that in Fig. 4, except that P mg/sec of ordinary UF_6 (called the "makeup") is introduced into the reflux system just beyond the

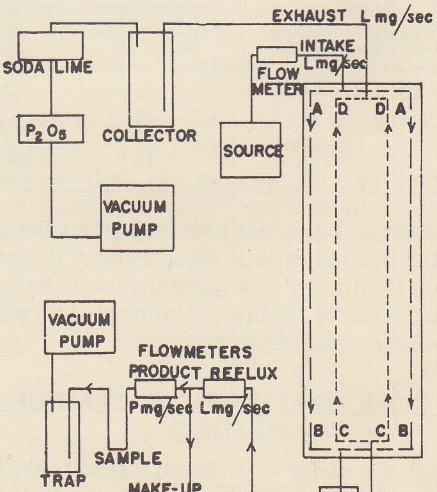

Figure 5. Type II countercurrent operation

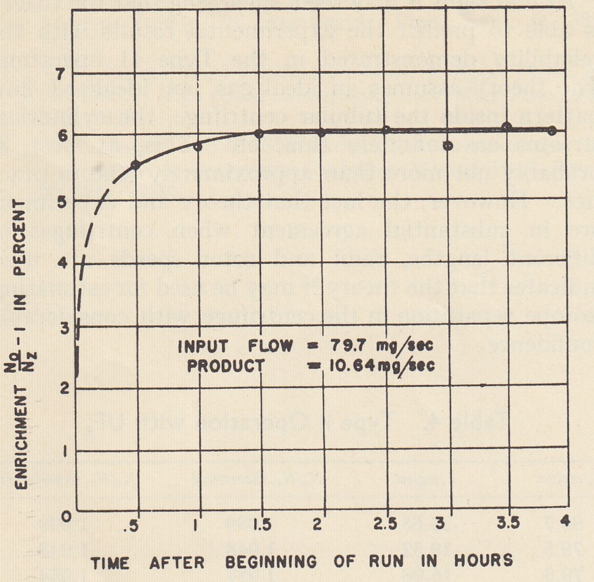

Figure 6. Measured enrichment vs. time after beginning of run

point of removal of the P mg/sec of product. This supposedly equalizes the flow in the two countercurrent streams inside the centrifuge. The operation in Fig. 4 will be called type I and that in Fig. 5 will be called type II.

Two different Duralumin tubular centrifuge rotors were used in the experiments. The first rotor was 7.62 cm id, and 81.3 cm long and the second was 21.2 cm od, 18.66 cm id, and 345.5 cm long. The general method of spinning the tubes was essentially an extrapolation of that previously described.[11] The rotors were, of course, balanced. The air turbine drive was replaced by a steam turbine. The temperature of the rotor was maintained constant at the desired value by surrounding the rotor with a vacuum-tight steel jacket containing hydrogen at about 3 mm Hg pressure. In the long rotor the heating tubes inside the jacket ran up and down parallel to the rotor axis. In this way, large temperature gradients in the long spinning rotor could be avoided. Also, the end caps were specially constructed to bring the entering gas to proper temperature. Dry nitrogen gas was used as a buffer gas to keep the UF_6 from coming in contact with the vacuum pump oil seal bearings. Both centrifuge tubes could be operated up to their bursting speed, but since the purpose of these experiments was to test the theory rather than to effect a large isotope separation, speeds of operation were chosen well below the bursting speeds. The smaller (81.3 cm) tube was operated at 1020±0.3 rps. Originally it was intended to operate the larger centrifuge tube (345.5 cm) between 450 and 470 rps but flaws were found in the Duralumin and it became necessary to limit the operating speed to 350±0.3 rps. The larger tube was tested for a short time at 420 rps.

According to the Urey-Cohen-Thompson theory[15] for a stripper as used in the experiments, the enrichment is given by the relation

$$\alpha - 1 = \frac{N_0}{N_z} - 1 = \frac{1 - e^{-y}}{\left[1 - \frac{P}{B(L-\Delta)}\right] e^{-y} + \frac{P}{B(L-\Delta)} - \frac{\Delta}{B(L-\Delta)}}$$

where

$$y = n_0 B \left[1 - \frac{\Delta}{B(L-\Delta)}\right]$$

$$B = \frac{(M_2 - M_1)V^2}{2RT}\left(1 - \frac{r_1^2}{r_2^2}\right)$$

$$n_0 = \frac{Z}{r_2[2 \ln (r_2/r_1)]^{1/2}}\left(\frac{2m}{1 + m^2}\right)$$

$$m = \frac{\sqrt{[L(L-P)]}\,[2 \ln (r_2/r_1)]^{1/2}}{2\pi r_2 D d} \qquad \text{(Type I)}$$

$$m = \frac{L[2 \ln (r_2/r_1)]^{1/2}}{2\pi r_2 D d} \qquad \text{(Type II)}$$

T = Temperature = 348 ± 2°K
Δ = product rate P minus make-up rate
L = flow rate
Z = length of centrifuge tube
r_1 = radius of inner flow stream
r_2 = radius of peripheral flow stream
r_1/r_2 = 0.534
d = density
D = diffusion constant
V = inside peripheral velocity of the centrifuge tube = 2.05×10^4 cm/sec.

For Type I operation $\Delta = P$.
For Type II operation $\Delta = 0$.

It is characteristic of countercurrent operation that it requires some time after starting up for the ratio N_0/N_z to reach a maximum steady value. Figure 6 shows such a curve for the operation of the 345.5-cm centrifuge for a Type II operation with $L = 79.7$ mg/sec and $P = 10.64$ mg/sec. It will

Table 3. Type I Operation with UF_6

L, mg/sec	*P, mg/sec*	N_0/N_z, *theoretical*	N_0/N_z, *experimental*
36.4	2.87	1.177	1.042
38.0	2.80	1.182	1.118
62.1	2.55	1.181	1.115
41.1	3.45	1.165	1.105
43.0	3.46	1.164	1.131
42.7	3.34	1.167	1.117
41.4	3.35	1.165	1.124
45.7	3.35	1.169	1.125
44.4	4.59	1.135	1.113
61.8	4.32	1.147	1.112
41.5	2.67	1.190	1.132
43.0	1.98	1.218	1.146
56.3	3.41	1.165	1.119
41.5	6.01	1.100	1.093

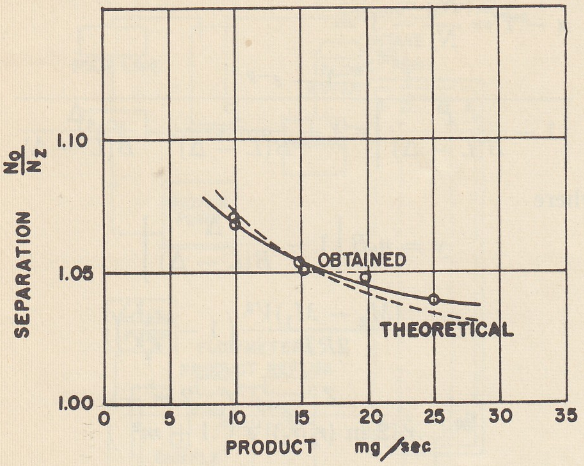

Figure 7. Separation vs. product

be observed that it is almost at equilibrium after one hour of operation. Figure 7 shows the separation versus product rate. Table 3 shows typical equilibrium values obtained with the 345.5-cm tube with Type I operation. The enrichments were measured by Drs. E. P. Ney and F. Armistead with a Nier type mass spectrometer.

Table 4 gives typical equilibrium values with Type II operation with the same centrifuge.

It will be observed that with Type I operation the enrichments obtained are slightly lower than those predicted by the theory. On the other hand the enrichments obtained with Type II operation are believed to be in excellent agreement with the theory within the experimental errors. It should be pointed out that the Type II operation was carried out with the same apparatus after the Type I operation was finished and some experience and improvements in the flow control were incorporated, which may account for the difference in the results. The enrichments obtained with the 81.3-cm long centrifuge also were in approximate agreement with the theory both for the isotopic separation in UF_6 and the H_2 and CO_2 gaseous mixtures.

At first sight it may seem surprising that the theory is able to predict the experimental results with the reliability demonstrated in the Type II operation. The theory assumes an ideal gas, an idealized flow pattern inside the tubular centrifuge, the cylindrical streams are infinitely thin, etc. This, at best, is probably not more than approximately true in practice. However, the fact that theory and experiment are in substantial agreement when centrifuges of different lengths, radii and rotor speeds are used indicates that the theory[15] may be used for estimating isotope separation in the centrifuge with considerable confidence.

Table 4. Type II Operation with UF_6

L, mg/sec	*F,mg/sec*	N_0/N_z, *theoretical*	N_0/N_z, *experimenta*
80.7	25.65	1.039	1.039
79.5	19.52	1.048	1.048
79.3	15.06	1.057	1.054
79.7	10.64	1.071	1.060
79.6	5.35	1.101	1.073
64.3	19.80	1.042	1.047
65.4	14.90	1.053	1.053
65.2	9.70	1.072	1.070
64.9	24.83	1.035	1.041
65.2	15.11	1.053	1.053
65.2	10.26	1.069	1.067
50.0	19.72	1.036	1.043
49.8	15.03	1.044	1.051
50.3	10.12	1.063	1.066

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