SEPARATION OF ISOTOPES OF CHLORINE IN CARBON TETRACHLORIDE BY EVAPORATIVE CENTRIFUGING

by

Charles Skarstrom, A.B., A.M.

A Dissertation Presented to the Graduate Faculty of the University of Virginia in Candidacy for the Degree of Doctor of Philosophy.

May, 1939.

TABLE of CONTENTS

FOREWORD

It is the purpose of this paper to describe in some detail the development of a machine and of a method whereby considerable quantities of carbon tetrachloride may be rapidly obtained, enriched with the heavy isotope of chlorine. For the first time, this should make available to chemists, physicists and biologists material with which to conduct experiments concerning the nature and effects of heavy chlorine. Just as the discovery and subsequent availability of heavy hydrogen opened up new fields of research, it is expected that the rapid concentration of heavy chlorine in large quantities will stimulate and enlarge these same fileds. While the material used in this work was chlorine (in the form of carbon tetrachloride) it is believed that the method will be equally successful with other isotopic elements, particularly the heavier ones which can exist in compounds readily vaporizable.

April 1939 C.S.

INTRODUCTION

The problem of separating the isotopes of the elements is one of the most baffling problems confronting experimental physicists and chemists. Ever since the discovery (1910-1912) that elements exist in several forms which are almost identical chemically but which differ in radioactive properties and in atomic weight, the persistent search for methods to isolate and concentrate these various forms (isotopes) of the same element has continued.

While almost complete separation has been effected for considerable quantities of some of the lighter elements because of large chemical and physical differences between the isotopes, only very samll changes have been obtained for the heavier elements. In the search for special methods to effect separation of isotopes of the heavier elements, a source of partially separated material would be very valuable. This would be particularly true if the partially separated material were inexpensive and available in relatively large quantities. The

The method of evaporative centrifuging whereby a vaporizable liquid is introduced into a rapidly rotating container from which the vapors are then withdrawn, appears on paper at least, to offer a method of producing the desired changes in the isotopic composition. This method also holds out possibilities of producing almost complete separation of isotopes if a way exists for making the process cumulative, analagous to a long fractionating column. The difference, however, between the theoretical changes to be expected [1] by this method and those actually acheived [2] is the difference between a practical industrial process and a laboratory demonstration of the existence of the phenomenon.

It is the purpose of this research to develop a practical method for achieving the partial separation of large quantities of isotopes of the elements by centrifuging. The isotopes of chlorine contained in carbon tetrachloride were chosen as the substance with which to work, partly because of convenience in handling and partly because some data had already been obtained with this particular material.

The work is divided roughly into three parts occurring in chronological order. The first part is concerned with the development of the technique of the production of large regions in which exists the maximum attainable centrifugal field. The second part is concerned with the proof of existence of an isotopic separation brought about by the centrifugal filed. The third part is a study of the efficiency with which the separation occurs under various modifications in the design and proceedure.

1) Mulliken, J.Am. Chem. Soc., 44, 1033, 1922
ibid. 45, 1592, 1923

2) Beams and Haynes, Phys.Rev., 50, 491, 1936
Beams and Masket, Phys. Rev. 51, 384, 1937
Masket, Doctor's Thesis, Univ. Va., 1938

THE MACHINERY

In order to produce rather large regions in which a centrifugal field existed, it was felt that the spinning hollow cylinder was ideal for this purpose, even though, because of its shape, it would be somewhat weaker than other structures of the same metal. The problem of spinning such hollow cylinders up to their bursting speed was undertaken.

DESIGN FEATURES

The Driving and Supporting Mechanisms.

A method already developed in this laboratory[1] for spinning small rotors for biological and other purposes, was adapted to spin the heavier cylinders. The driving mechanism was an air turbine, 1 inch diameter x 3/8 inches of solid pill-box shape and made of Duralumin. Air jets directed at flutes milled on its

---

1) Beams, Rev. Mod. Phys. 10, 245, 1938
Jour. Appl. Phys. 8, 395, 1937

outside edge produced the driving torque. Since the axis of rotation was vertical, the axial thrust due to the weight of the rotating system was borne by an air bearing. Several defects in this air bearing which were objectionable with light rotors become major problems with rotors weighing from 15 to 75 pounds. These difficulties were called the ' pile-driver effect ' and ' chattering '.

The pile-driver effect was the tendency for the whole rotating system to bounce up and down along the axis of rotation. When light rotors (less than 5 pounds) are supported on an air bearing there is often enough axial friction in the oil glands to damp out such bouncing, but with the heavier types of rotors used in this work this bouncing was a serious defect of the air bearing.

This difficulty has been removed[1] successfully by appropriate changes in the design. The guiding principle in making these changes was to keep the space immediately below the driver small. In this way the supporting air issueing from a constriction into the space immediately under the driver is able to build up pressure quickly. On the other hand, when the space immediately below the

---

1) Beams and Skarstrom, Phys. Rev., 53, 327(A), 1938

driver is large, the time required for the supproting pressure to build up becomes more nearly the order of magnitude of the natural period for vertical oscillation of the rotating system on its elastic support. Thus for an arbitrary upward displacement of the driver the air gap is increased, allowing the air to escape more rapidly. This in turn reduces the upward force on the bottom of the driver and increases the pressure drop across the constriction. If the supporting air is unable to fill up rapidly the space under the driver with air under pressure sufficient to cushion the fall, then the air gap is reduced to zero, i.e., the driver touches the bakelite collar. Since this collar is usually set on some springy material such as rubber, the whole system bounces, then repeats the up and down cycle.

This effect has also been eliminated in another way.[2] It was accomplished by using the bouncing of an inadequately designed air bearing to operate a piston pump forcing oil into dash pots, which effectively damped the bouncing motion. The additional complications in construction engendered by this solution for bouncing seem unnecessarily involved, in view of the satisfactory air bearing constructed here for rotors weighing from 15 to 75 pounds.

[2] E. G. Pickels, R.S.I., 9, 358-364 (1938)

The other difficulty was an high pitched chattering of the bakelite collar. Since the collar usually rests on an elastic material such as rubber, Neoprene, cork, etc., it is apt to chatter unless sufficient damping is provided. This may be done a number of ways as is shown in Fig. 1. A small disc of rubber or Neoprene sheeting is inserted in a groove cut in the collar. This fits fairly tightly over the brass base and serves to damp the chattering mation of the collar. Another method is to provide a number of elastic cushions separated by loosely fitting washers. Still another method is to snchor the collar to the elastic disc or ring by cement. For any particular collar and weight of rotor a combination may be found experimentally which is chatter-proof and in which bouncing is absent over a wide range of supporting air pressures.

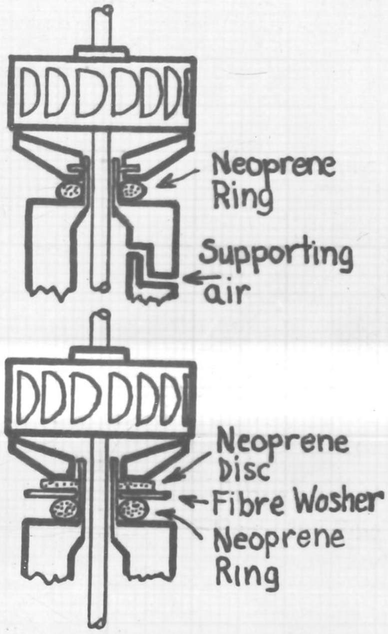

Neoprene Ring
Supporting air
Neoprene Disc
Fibre Washer
Neoprene Ring

Fig. 1

The Rotor

The first hollow cylinder which was spun was constructed of Dowmetal (a magnesium alloy) 3" diameter x 1/4" wall thickness x 12" long. At 800 R.P.S. it developed a longitudinal crack which unbalanced it sufficiently to break the supporting shaft.

Next, a cold rolled steel hollow cylinder was constructed 2 3/8" diameter x 1/4" wall thickness x 12" long. This was spun up to 1300 R.P.S. at which speed it slowed down to 1200 R.P.S. Under continued acceleration it burst upon reaching 1250 R.P.S.

The peripheral velocity at the bursting speed was 620 ft/sec which is in accord with that given by the formula for the bursting speed of a thin drum.[1] In view of this experience a new hollow cylinder was constructed of a stronger material,[2] Chrome Molybdenum Steel Alloy

[1] See Stodola, "Steam Turbines"

$$T = \rho v^2$$

$$\text{or } v = \sqrt{T/\rho}$$

T = tensile strength $= 36{,}000\ \mathrm{lbs}/\mathrm{in}^2$

ρ = density $= 490\ \mathrm{lbs}/\mathrm{ft}^3$

v = peripheral velocity

$$v = \sqrt{\frac{36{,}000 \times 12 \times 12 \times 32}{490}}$$

$$= 580\ \mathrm{ft}/\mathrm{sec}$$

[2] Obtained from the Summerill Tubing Co., Bridgeport, Mont C
Mont. Co., Pa.

4130x S.A.E. which was heat treated to show a yield point of 159,000 lbs/in^2. The cylinder was 12" long x 4" O.D. x 1/2" wall. This particular cylinder has been in operation for 14 months, having withstood severe usage during that time. At the present writing (March, 1939) 108 separate "runs" have been taken, during which this rotor has had 675 hours of rotation at 1000-1100 R.P.S. (2.5×10^9 revolutions). Cracks have developed at the ends of the rotor through screw holes, which made it necessary to reduce the length of the cylinder to 11 inches. On one occasion the speed was increased to 1200 R.P.S (v= 1250 ft/sec).[1] At this speed the rotor stretched radially causing the cylinder-head gaskets to leak. Upon examination, the internal diameter was found to have increased .02". After boiling in water for 30 minutes, new cylinder-heads were fitted to the enlarged rotor. It has been spun successfully ever since, taking care not to exceed 1100 R.P.S. This is one of the advantages of the softer of the steel alloys. A similar

1) Compare $v = \sqrt{T/\rho}$ $T = 159{,}000 \text{ lbs/in}^2$

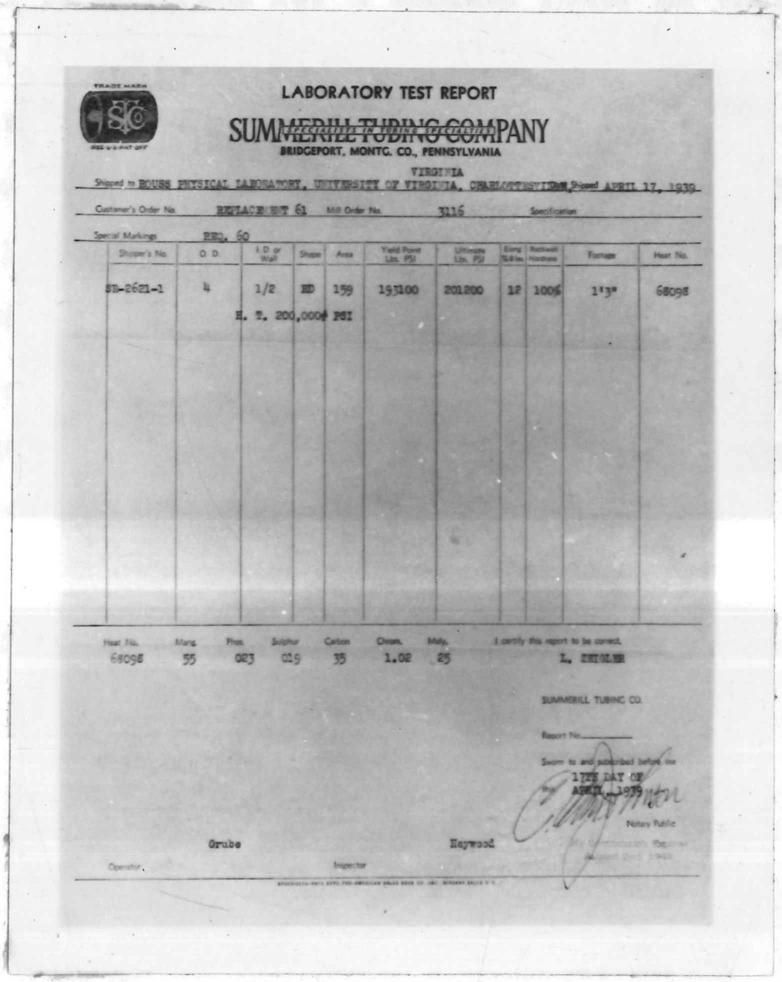
$\rho = 490 \text{ lbs/ft}^3$

$$v = \sqrt{\frac{159000 \times 12 \times 12 \times 32}{490}}$$

$v = 1220$ ft/sec

experience with a more brittle steel would very likely have resulted in an explosion. Of course, with a more brittle steel a higher peripheral velocity is possible. The selection of a material for the rotor is a compromise between the desire on the one hand for as high a peripheral velocity as possible (high tensile strength divided by density of material) and, on the other hand, the desire for permanent, consistent and explosion-free operation. Svedberg[1] sets the compromise at about 200,000 lbs/in^2 tensile strength in a hardened chrome-nickel steel. At the present writing a chrome molybdeum n tube 4130 x S.A.E. 24" long x 4" O.D. x 5/8" 1/2 (pp 15) wall, tensile strength 195,000 lbs/in^2 is being used to construct a rotor. The choice of this material rather than chrome nickel is based on the following factors: ease of machining, convenient availability and larger elongation (region between yield point and ultimate tensile strength). This 4130X steel was developed and is now often specified for use in aircraft engine frames and fusilage structure. Each piece of material carries with it a certified statement of the manufacturer as to its composition and physical properties. (See Fig. 2)

1) Boestad, Pederson and Svedberg, R.S.I., 9, 346-353, 1938



LABORATORY TEST REPORT

SUMMERILL TUBING COMPANY

SPECIALISTS IN TUBING SPECIALTIES

BRIDGEPORT, MONTG. CO., PENNSYLVANIA

Shipped to ROUSS PHYSICAL LABORATORY, UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VIRGINIA Shipped APRIL 17, 1939

Customer's Order No. REPLACEMENT 61 Mill Order No. 3116 Specification

Special Markings REQ. 60

Shipper's No.	O. D.	I. D. or Wall	Shape	Area	Yield Point Lbs. PSI	Ultimate Lbs. PSI	Elong. % 2 in.	Rockwell Hardness	Footage	Heat No.
SR-2621-1	4	1/2	RD	159	193100	201200	12	100$	1'3"	68098
		H. T. 200,000$ PSI								

Heat No.	Mang.	Phos.	Sulphur	Carbon	Chrom.	Moly.
68098	55	023	019	35	1.02	25

I certify this report to be correct.

L. ZEIGLER

SUMMERILL TUBING CO.

Report No.________

Sworn to and subscribed before me

this 17TH DAY OF APRIL, 1939

C. Lloyd Johnston

Notary Public

My Commission Expires August 2nd, [illegible]

Operator Grube

Inspector Heywood

Fig. 2

One other factor of importance to be considered in the choice of material for a tubular rotor is whether or not the rotor is to contain a material or structures which, when spinning, push against the walls of the rotor. For example, if the rotor is to contain a certain quantity of liquid, it must support the tremendous hydrostatic forces of the liquid as well as hold itself together. Thus, while certain aluminum alloys show a higher ratio of tensile strength to density, the absolute magnitude of the tensile strength is only 1/4 that of 4130X S.A.E.. Thus the other criterion, if the rotor is to contain liquid, is as large a tensile strength as possible.

Dynamical Balance:

While the method of spinning with a flexible shaft, as herein used, does not require that the rotor be exactly statically or dynamically balanced, it was found that, when considerable unbalance existed, the bearings of the oil glands wore rather rapidly.

When placed on parallel horizontal knife edges, tool marks and oxide on the outer surface of the rotor masked small static unbalance. Similarly, flotation of the rotor in mercury was relatively insensitive to small static unbalance due in part to adhesion of small droplets of mercury to the rotor. Both of these methods were unable to detect dynamic unbalances.

A simple and precise method of static and dynamic balancing was evolved, however, which is useful in determining the amount of unbalance of tubular rotors. A description and example of the use of this balancing apparatus is given below.

Two air bearings were constructed 9 inches apart in a 1/2" pipe into which air under pressure could be admitted. The bakelite collars were lapped to fit the inner surface of the 12" x 4" O.D. x 1/2" wall 18lb tube. The rotor was placed on the two air bearings as in the Fig.3 and the pipe was supported by laboratory stands and connected to the air supply. At about 50 lbs/in^2 pressure the air bearings were formed. Adjustment of the supports holding the pipe was necessary to make the bearings horizontal. Rotation of the pipe was necessary to direct the air jets vertically and prevent the rotor from spinning around under the oblique action of the air jet. When the pipe was carefully adjusted the rotor was observed to oscillate about the center of curvature of its inner surface with a period of 10 sec for small amplitudes. Addition of 22 grams in the screw-holes (radius of screw-hole center $\frac{9.3}{2}$ cm) caused the period of oscillation to become so long that the rotor appeared statically balanced. Calculation of the unbalanced mass from the observed period and from the weight of the rotor (18 lbs) showed that it was 16 gms, a fairly good check with that which was observed. (It was found later that the inner surface was .003" eccentric with the outer at one end of the rotor. Another machine cut was made on the inner surface. Static balancing again as described above showed 4 gms unbalance.)

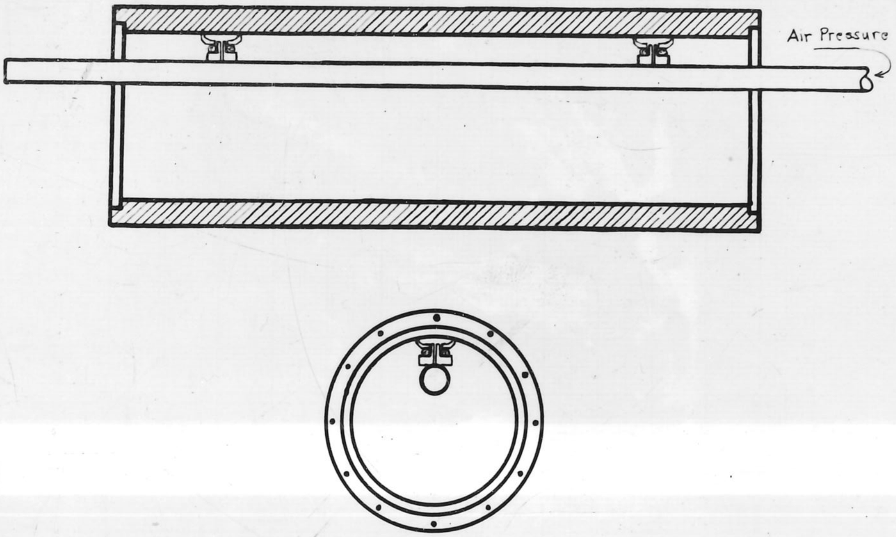


Fig. 3

To test the dynamic balance, the air bearings were tilted at a small angle causing the rotor to spin about an axis which was the center of curvature of the inner cylindrical surface. At about 4 revolutions per second a severe wobble developed (due to dynamic unbalance reacting on elastic supporting framework.) Appropriate placing of small weights in the screw-holes at each end reduced this wobble. Holes were drilled in the ends of the rotor to remove metal as indicated by the position of the balancing weights. With this accomplished the rotor appeared dynamically and statically balanced about its inner surface to within 2 gms at a radius of $\frac{9.3}{2}$ cm, the smallest additional weight for which any change could be detected, (2.5 parts in 10,000). It should be mentioned that the rotor was spun successfully both before and after the balancing process.

GENERAL DESCRIPTION OF CENTRIFUGE

The rotating system shown in Fig. 4 consists of the hollow cylinder just described, capped at both ends. The cylinder hangs from an air-supported air-driven turbine which is fastened to a hollow shaft (hyposermic needle gauge #14). The hypodermic needle is connected to the rotor by a pin chuck, which simultaneously clamps the shaft and imbeds itself into a lead gasket forming a vacuum- tight seal. To the other end of the rotor is fastened a short length of thick piano wire (1/8" dia.) which forms a shaft for the bottom of the rotor. Since the life of the babbitt bearings which guide these shafts is directly dependent upon the centering of these shafts, it is well to mount them within 0002" of the geometric axis of the rotor at the caps.

The centrifuge is housed in a vacuum chamber which consisted of an 18" length of cold rolled steel tubing (7" O.D. x 1/2" wall) which was closed at both ends by steel discs 5/8" thick, which had been lapped to fit. Cenco yellow vacuum wax (#11928) applied to the lapped joints made the chamber vacuum-tight. Three 1" tie rods were used to bolt the chamber together as an added precaution in case of explosion. An external view

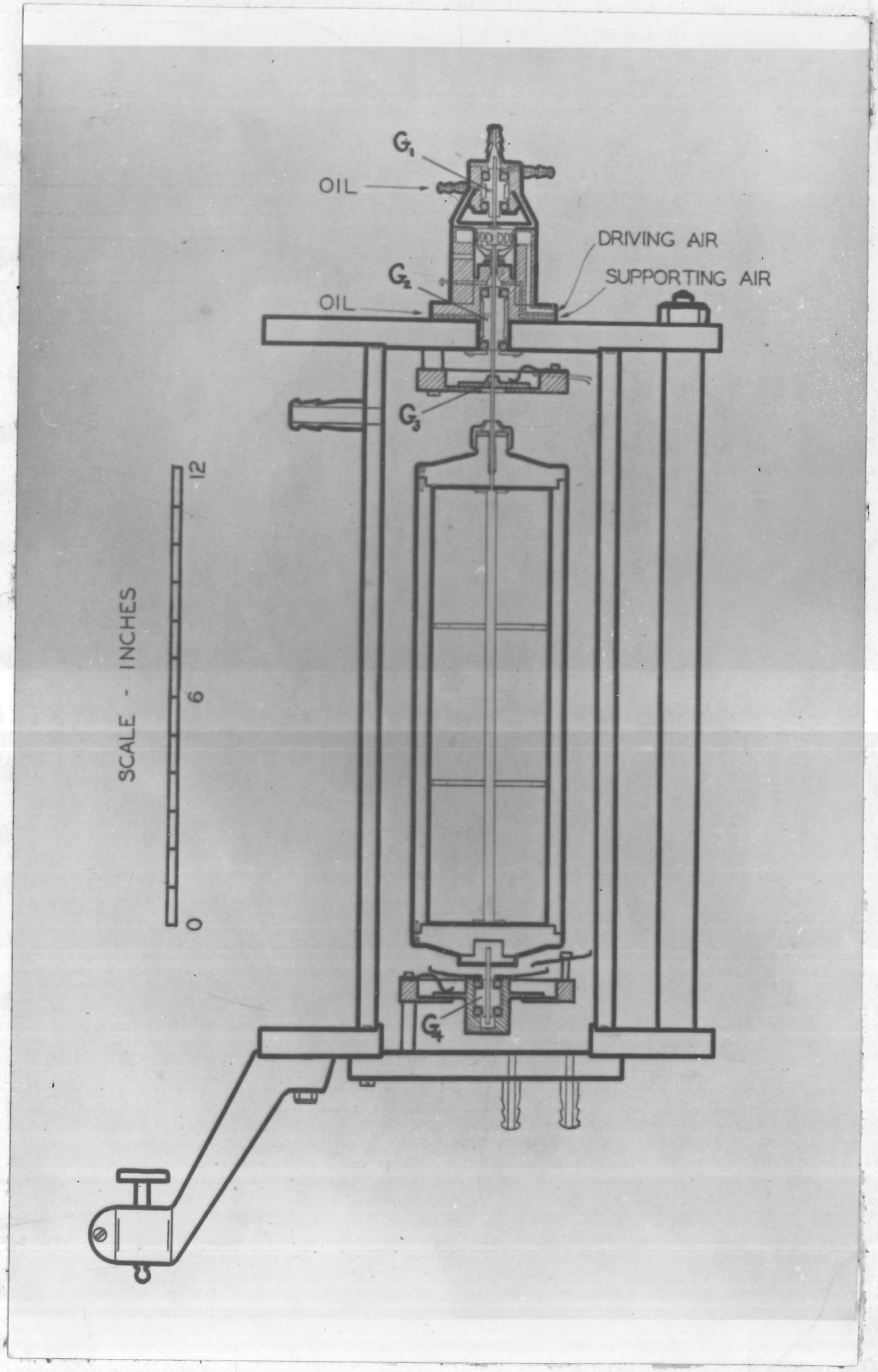

G₁
OIL
DRIVING AIR
G₂
SUPPORTING AIR
OIL
G₃
G₄
SCALE - INCHES
0
6
12

Fig. 4

of the chamber is shown in Fig. 5. A super structure of wood to support a pulley arrangement was necessary to facilitate assembly. This was conveniently mounted on the barricade which consisted of an 8" thickness of soft wood and which enclosed the machine when running.

The hollow drive shaft passed through the upper steel plate on a small babbitt bearing G_2, fed with oil under a pressure slightly greater than the supporting air pressure. Gaseous communication was maintained with the interior of the rotating system by the second oil bearing G_1 which isolated the open end of the drive shaft. This bearing made it possible to introduce and remove vapors from the rotating system.

Auxiliary bearings G_3 and G_4 were found necessary to reduce precessional motions which otherwise were apt to break the drive shaft if allowed to reach large amplitudes. Each of these bearings was set in a loose plate which was kept in contact with a fixed plate by heavy leaf springs. This construction supplied sufficient radial friction to inhibit the unwanted precession. These bearings were supplied with oil by drippings from the bearing G_2, the lower one receiving the overflow from the upper. Since in operation the average consumption of oil for the bearing G_2 was a quart every 5 hours, the

Fig. 5

bearings G_3 and G_4 were kept adequately lubricated and cooled.

This rather large consumption of oil was considerably reduced when G_2 was new. The figure given is about what may be expected after 5 months of almost daily operation of the centrifuge, the new bearing having had a chance to be well "broken in" during this time. The excess oil drains out of the vacuum chamber into a gallon container connected to the bottom chamber. At the end of a "run" the oil is filtered to make it again available for use.

The disadvantage of so large an oil flow into the vacuum chamber is that it brings in with it considerable quantity of dissolved air. (The oil is under 50 lbs/in^2 air pressure as it enters) This requires a fast pumping system on the chamber if the vacuum is to be maintained adequate (about 10^{-3}mm. Hg) to prevent excessive heating of the spinning rotor by air friction.

A four stage Leybold's Nachfolger Gaede mercury diffusion pump backed by a Hyvac, or a Megavac pump alone, have both been found adequate. A single stage all-glass Hg diffusion pump backed by a Hyvac has also been found satisfactory.

Operation

The rotor is fastened to the flexible drive shaft 7/8" below the upper auxiliary bearing G_3, which is attached to the top plate. The top plate is then slowly lowered, taking care that the short piano wire shaft on the bottom of the rotor passes into its guide bearing G_4. With the top plate bolted in place the vacuum chamber is complete. A fillet of vacuum wax around all joints insures freedom from leaks.

50 lbs/in^2 air pressure over the two oil tanks which supply G_2 is turned on. The reason for the use of two tanks is that one may be refilled while the other is in use, thereby insuring an uninterrupted pressure oil supply to G_2.

The backing Hyvac pump is started, and after it has reduced the pressure to a few tenths of a millimeter of Hg the mercury diffusion pump is started, making sure that it is supplied with cooling water and a cold trap to prevent Hg diffusion into the vacuum chamber.

The air for the supporting pressure is adjusted to be between 5 and 10 lbs/in^2 above that just necessary to form the air bearing. The total amount of this air pressure depends mainly upon the weight of the rotating system and the diameter of the bakelite collar. With the machine herein described, gauge pressures of 32 to 50 lbs/in^2 have been used for the supporting air.

The driving air is turned on and the barricades put in place. With the full pressure of the air supply, (95 to 115 lbs/in^2) from 1 1/2 to 2 hours is required for the 1" diameter driver to accelerate the rotor to 1000 R.P.S. The time required depends upon the condition of the bearings. Newly made bearings, (G_1, G_2, G_3, G_4) with small shaft clearances require a longer acceleration time than do well "broken in" bearings. About 30 hours operation at 1000 R.P.S. is sufficient to break in a bearing thoroughly, subsequent wear on the bearing being quite slow if the rotor is not seriously unbalanced.

The symptoms by which excessively worn bearings may be detected are: 1. Excessive oil flows to G_1 and G_2, and 2. Severe shaking and chattering of the whole machine at its operating speed which has been previously determined as <u>not</u> being at or near a vibration point. One set of bearings, G_1, G_2, G_3, G_4, made from high speed babbitt, withstood 4 months of daily operation before renewal became necessary.

As the rotor speeds up, data may be taken from the air compressor operation to determine power consumption.

Having attained a speed of 1000 R.P.S., a "run" is commenced. While runs lasting from 1 to 22 hours have been made, there is no time limit provided the machine is kept supplied with oil, air pressure and vacuum.

In order to maintain a constant speed of rotation it was found of great convenience to insert an adjustable pressure regulator in the air drive line. This served to smooth out the pressure changes due to intermittant operation of the compressor. This pressure regulator was by-passed during the acceleration period. Slight readjustment of the pressure regulator was necessary from day to day so that it would supply just the correct pressure to maintain a constant speed of the rotor. (Typical drive pressure = 40 lbs/in^2 for 1050 R.P.S.)

The run completed, the driving air pressure was shut off and the rotor allowed to coast. Deceleration measurements taken during this period allow calculations to be made on the power necessary to drive the rotor at different speeds.

With the vacuum pumps left on, it requires 8 hours for the rotor to coast to rest. Usually the pumps are shut off and small quantities of air are admitted to the vacuum chamber. With air friction acting as a brake, the minimum stopping time is 2 hours. The disadvantage of this method is that the rotor becomes quite hot which shortens the useful life of the artificial rubber (Neoprene) gaskets around the rotor caps.

Usually the rotor is brought to rest in 3 hours. In a newly designed air motor, not yet in use, reverse air jets have been provided, which, it is hoped, will materially shorten the deceleration time.

In the following tables is a set of data for a typical run from which various operational characteristics may be calculated.

TABLE A

Air support on: 39 lbs/in^2

The 15 H.P. air compressor delivers 63 cu ft/min N.T.P. operating intermittently as follows:

	ON	OFF	
	hr.min.sec.		Compressor on for
	2:23:45	2:24:02	17 seconds
4:42	2:28:27	2:28:43	16
4:43	2:33:10	2:33:27	17
4:44	2:37:54	2:38:11	17
4:45	2:42:39	2:42:56	17
cycle = 284 sec.			Av. 17 seconds

Compressor delivers $\frac{17}{60} \times 63 = 17.9$ cu ft every 284 secs.

Therefor air consumption for the air support alone is $17.9 \times \frac{60}{274} = 3.8$ cu ft/min N.T.P.

TABLE B

Acceleration period 1 hour 39 minutes.

8:21 a.m. Drive pressure on (95 to 115lbs/in^2)

Supporting pressure 39 lbs/in^2.

10:00 a.m. Reached 1000 R.P.S.

15 H.P. air compressor operating intermittently was:

	ON hr.min.sec.	OFF	Compressor on for
	9:55:32	9:55:56	24 sec.
1:11			
	9:56:43	9:57:06	23
1:09			
	9:57:52	9:58:16	24
1:11			
	9:59:03	9:59:26	23
1:10			
	10:00:13	10:00:37	24
cycle 70 secs.			23.6 secs.

Compressor delivers $\frac{23.6}{60} \times 63 = 24.8$ cu ft every 70 secs.
Therefor air consumption for whole machine is

$24.8 \times \frac{60}{70} = 21.3$ cu ft / min N.T.P.
Since the air bearing requires 3.8 cu ft / min N.T.P.
then $21.3 - 3.8 = 17.5$ cu ft / min N.T.PT is consumed during acceleration by the driver alone.

TABLE G

Having reached 1000 R.P.S. drive pressure is reduced to 42 lbs / in^2 to maintain this speed.

15 H.P. Compressor operating intermittently was:

	ON hr.min.sec.	OFF	Compressor on for
	10:38:19	10:38:38	19 secs.
1:44			
	10:40:03	10:40:22	19
1:44			
	10:41:47	10:42:06	19
1:44			
	10:43:32	10:43:51	19
1:44			
	10:45:16	10:45:35	19

cycle = 104 secs. Av. 19 secs.

Compressor delivers $\frac{19}{60} \times 63 = 19.9$ cu ft every 104 secs.

Therefor air consumption is $\frac{19.9}{104} \times 60 = 11.5$ cu ft/min N.T.P.

Since the air bearing requires 3.8 cu ft/min N.T.P. then $11.5 - 3.8 = 7.7$ cu ft/min N.T.P. air is needed on the driver to maintain the centrifuge at its usual operating speed.

TABLE D

Deceleration data with vacuum pumps left in operation.

	Time hr.min.	Speed R.P.S.	Δ R.P.S
	3:01	1056	
9 min			56
	3:10	1000	
20			100
	3:30	900	
21			100
	3:51	800	
20			100
	4:11	700	

9 minutes to lose 56 rev./sec in operation range, therefor, angular deceleration $\ddot{\theta}$ is

$$\frac{56 \times 2\pi}{9 \times 60} = .65 \text{ radian /sec}^2$$

Since the rotor weighs 18 lbs (= 8170 gms) and its mean square radius is

$$\frac{1}{4}\ \frac{\left[\left(\underline{\overset{\text{O.D.}}{10.08}}\right)^2 - \left(\underline{7.85}\right)^2\right] \text{cm}^2}{2} = \frac{101.5 - 61.7}{8} = \frac{163.2}{8}$$

$$= 20.4 \text{ cm}^2$$

then the torque necessary to balance the frictional drag in the range 1056 - 1000 R.P.S. is

$$\text{Torque} = I\,\ddot{\theta} = Mr^2\,\ddot{\theta}$$

$$= 8170 \times 20.4 \times .65 = 1.08 \times 10^5 \ \frac{\text{gm cm}^2}{\text{sec}^2}$$

TABLE D cont.

$$\text{Power used} = \frac{\text{work}}{\text{sec}} = \text{Torque } \dot{\theta}$$

$$\text{and since the average } \dot{\theta} = \begin{matrix} 1056 \\ \underline{1000} \\ 1028 \end{matrix} \text{ R.P.S.}$$

$$\text{the Power used} = 1.08 \times 10^5 n \ \frac{\text{gm cm}^2}{\text{sec}^2} \times 1028 \times \frac{2\pi}{\text{sec}}$$

$$= 7.0 \times 10^8 \ \frac{\text{dyne-cm}}{\text{sec}} = 7.0 \times 10^8 \ \frac{\text{ergs}}{\text{sec}}$$

$$= 70. \ \frac{\text{J}\overset{o}{\text{u}}\text{les}}{\text{sec}} = 70. \text{ watts}$$

Thus the power necessary to maintain the speed in the range 1056 - 1000 R.P.S. is 70 watts. Since all the work is being done against friction the overall efficiency is zero. This power is supplied by 7.7 cu ft/min driving air (Table C) . The power used during acceleration is $\frac{17.5}{7.7} \times 70 = 159$ watts, assuming that the power supplied to the driver is proportional to the volumetric air flow.

TABLE D concl.

The overall efficiency based on the approximate electrical input to the air compressor compared with the torque produced on the air turbine necessary to maintain the operating speed is:

$$\text{Efficiency} \quad \frac{70 \text{ watts}}{15 \text{ H.P.} \times \frac{19}{104} \times 746} = \frac{70}{2050} = 3.4\%$$

During acceleration the similar efficiency is:

$$\frac{159 \text{ watts}}{15 \text{ H.P.} \; \frac{23.6}{70} \times 746} = \frac{159}{3780} = 4.2\%$$

On any basis, the efficiency of the air driven turbine used in this machine is very low. Research to improve air turbines is recommended if operation of a large number of air driven centrifuges is contemplated.

The above description covers the typical mechanical aspects of the operation of the tubular centrifuge used for this work. The next problem is how best to utilize the spinning rotor to accomplish the separation of isotopes in CCl_4.

In different proceedured which have been tried and which will be described shortly, structures of various sorts have been mounted inside of the rotating system. Except in cases of serious unbalance, no difficulty has been experienced in spinning the rotor, the proceedure remaining the same except for slight increases in the supporting pressure to take care of the added weight of the rotating system.

It may well be added here that the greatest hazard has been the occasional failure of the electrical power supply, particularly during the thunder-storm season. It would be an excellent plan to have available either an auxiliary air compressor or a larger resevoir, able to supply sufficient compressed air to maintain the supporting pressure for several hours.[1]

---

1) The present (April 1939) resevoir capacity comprises 1 tank 10 ft^3 containing air at 110 lbs/in^2 and 1 tank 7 ft^3 containing air at 110 lbs/in^2, both of which will supply supporting air (3.8 cu ft/min N.T.P.) for about 45 minutes, in the event of failure of the air compressors.

SEPARATION OF ISOTOPES OF CHLORINE IN CARBON TETRACHLORIDE

The general problem to be undertaken, once the technique of spinning the large hollow cylinders had been developed, was the separation of isotopes. The separation of the isotopes of Cl in CCl_4 using the method of evaporative centrifuging had previously been reported.[1] The changes produced and the quantities obtained were, however, quite small. It was believed that the large cylindrical rotors would be better adapted to the method of evaporative centrifuging than the smaller rotors which had been used.

The specific problem, therefor, was to study and adapt the spinning tubes to the centrifugal concentration of isotopes. Described below are the various arrangements and proceedures which were investigated to this end.

---

1) Beams and Haynes, Phys. Rev., 50, 491, 1936

Beams and Masket, Phys. Rev., 51, 384, 1937

Masket, Doctor's Dissertation, Univ. Va., 1938

The Multi-stage Rotor

The isotopic separation effected by a single stage centrifuge as reported was exceedingly small. If the separation could be multiplied many times after the fashion of a fractionating column, it would be a worthwhile improvement. Toward this end a multi-stage centrifuge was designed and built.

The principles underlying its design were as follows:

If a spinning hollow cylinder containing a small quantity of a vaporizable liquid at the periphery were cooled at one end and heated at the other end, a flow of vapor would take place from the hot to the cold end. If the flow could be so directed as to pass from the periphery to the axis and back again many times in its passage from the hot to the cold end, and if the flow could be so regulated that it was slow on each trip toward the axis and rapid on each trip away from the axis, then a cumulative centrifugal separation would be obtained by the entire trip from one end of the rotor to the other.

The maze of passages was produced by stacking 19 discs in the rotor, so cut and drilled that the vapor followed the described path. (See Fig.6) In this way it was expected that in flowing toward the cold end of the

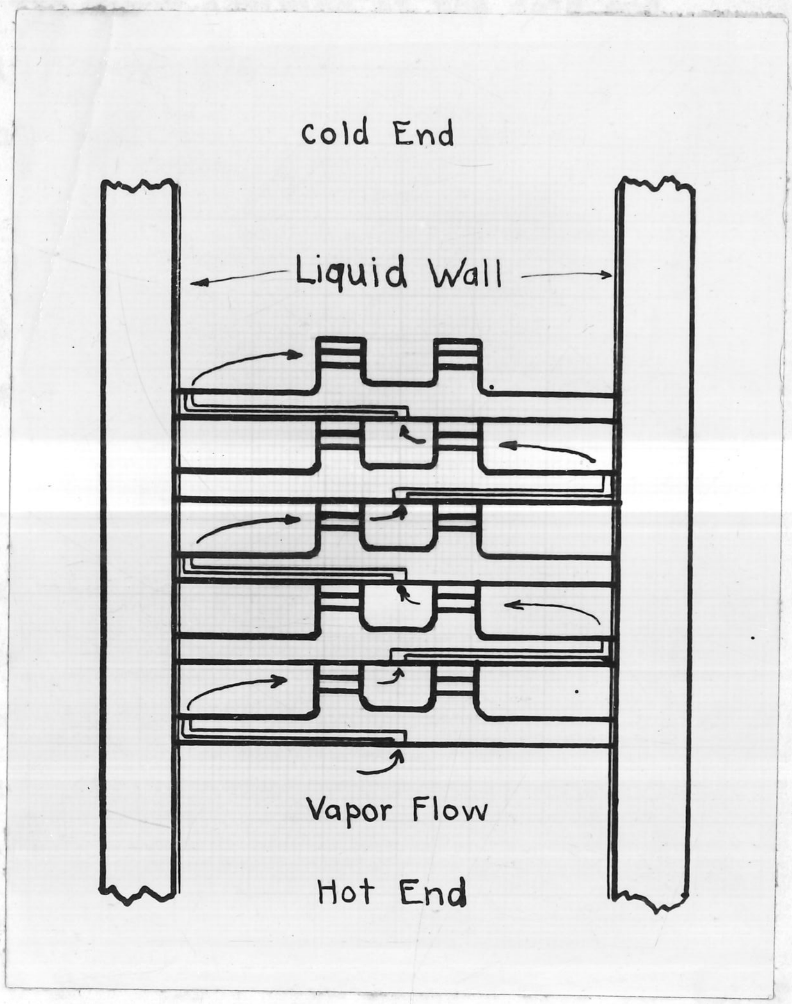


Fig. 6

spinning rotor each stage would be fed by vapor, the composition of which would be that obtaining at the axis, and thus the vapor arriving at the cold end would eventually be enriched 19-fold in the lighter isotopes. At the cold end the vapor was to be condensed and allowed to flow back toward the hot end in liquid form along the periphery. This process in comparable in part to that in a fractionating column containing 19 actual plates. In practice it would be necessary to provide and maintain a temperature difference between the two ends of the rotor for a time sufficiently long that equilibrimm be reached. Equilibrium could be acertained by noting no further increase in the separation measured between the ordinary material and samples taken from the cold end at various intervals.

In the experimental arrangement cooling was accomplished by allowing cold ethyl alcohol to pass through a dome shaped copper coil mounted over the upper end of the rotor. The cooling coil was kept within 1/2 inch of the spinning rotor. The refrigerant was pre-cooled by passage through a copper coil immersed in a slush of alcohol and solid carbon dioxide (dry ice). Flow of the refrigerant was maintained manually by returning the drain to a resevoir 7 feet above the outlet pipe. The temperature of the drain was -15°C. while that of the incoming refrigerant was estimated to be about -70°C..

The bottom end of the rotor was kept warm by radiation from an 18 ohm nichrome wire electric heater mounted 1 inch away from the bottom edge of the spinning rotor. Trouble was experienced in several runs by the melting of the Neoprene gasket in the bottom cylinder-head of the rotor. The maximum amount of heat which the gasket would stand was supplied by a 110 volt direct current source in series with an additional 250 ohms. Approximate calculations showed that the heater was supplying just about as much heat to the bottom end of the rotor as was being removed from the cold end, namely about 1 calorie per second.

The material used in testing the multi-stage rotor was carbon tetrachloride. 60 cc of liquid CCl_4 was introduced into the rotor by means of a long needled hypodermic syringe. The rotor was then brought up to and kept at a speed range of 1000-1040 R.P.S.. Air was pumped out of the rotor and the heating and cooling commenced. A series of runs of various lengths of time (6, 10 and 12 hours) were taken. At the termination of each run, small samples were withdrawn from the cold end. The process of withdrawal consisted in condensing the CCL_4 vapor in a cold trap after it had diffused out of the rotor through the hollow drive shaft. The traps were kept cold by immersion in a slush of dry ice and alcohol.

Comparison of the density of the smaples with that of ordinary CCl_4, as well as with that of the CCl_4 remaining in the rotor showed no change within the limits of measurement. (1 part in 20,000) Remeasurement of the densities again showed no change.

The method of measuring changes in densities will be discussed in detail in a separate section. In essence the method amounts to the comparison of weights of a "full" pyknometer, filled first with ordinary liquid and second with the changed material. Then the weight of equal volumes of 2 different liquids may be compared. Due precaution to keep the temperature constant and to remove water and other impurities must be observed before differential density determinations may be taken.

Each smaple to be measured was subjected to a vacuum fractionation from a slush of P_2O_5 and CCl_4, the middle third being used for the density measurement. The material used in this and in subsequent experiments was Baker's C.P. carbon tetrachloride.

Because no change in density of the samples and consequently no separation of isotopes occurred in the above procedure within the experimental error, it is well to examine here what change should be expected from elementary theoretical considerations. To simplify the problem, suppose a spinning rotor of interior radius R to contain a small quantity of liquid, held at the peripheral wall by centrifugal forces. Suppose further that the liquid ~~ia~~ in in equilibrium with its vapor at the temperature T of the spinning rotor. Because of the rotation, the pressure of the vapor will be less at the axis than at the periphery. The magnitude of this axial pressure reduction may be computed as follows:

In cylindrical coordinates r, θ, z, fixed to the cylindrical rotor which is revolving about the axis with an angular velocity ω, the pressure of the gas will be dependent only on the coordinate r. In the region between r and r + dr the contribution to the total pressure by the element of gas contained therein will be

$$dp = \rho \frac{v^2}{r} dr = \rho \omega^2 r dr$$

where ρ is the density of the gas at r.

The density of the gas is connected with the pressure by an equation of state, the simplest of which is that of an ideal gas:

$$p\bar{V} = \underline{R}T, \quad \rho = \frac{M}{\bar{V}}\,\underline{R}T$$

$$\text{or} \quad p = \rho\frac{\underline{R}T}{M}$$

Substituting this last relation in the differential expression above gives

$$dp = \frac{pM}{\underline{R}T}\,w^2 r\,dr$$

which integrates to

$$\ln p = \frac{M}{\underline{R}T}\,\frac{w^2 r^2}{2} + \text{const}$$

Putting in the boundary conditions that at the liquid surface r = R the pressure p_R is that of the saturated vapor at the temperature T, we get

$$\ln p_R = \frac{M}{\underline{R}T}\,\frac{w^2 R^2}{2} + \text{const}$$

From which

$$\text{const} = \ln p_R - \frac{M}{\underline{R}T}\,\frac{w^2 R^2}{2}$$

and thus

$$\ln p = \frac{M}{\underline{R}T}\,\frac{w^2 r^2}{2} + \ln p_R - \frac{M}{\underline{R}T}\,\frac{w^2 R^2}{2}$$

or again

$$p = p_R\, e^{\frac{Mw^2(r^2 - R^2)}{2\underline{R}T}}$$

This last is an expression for the equilibrium pressure established at various radii in a rotating cylinder of vapor. At the periphery the pressure is p_R while at the axis it is less than this. The ratio of the pressure at the axis to that at the periphery is

$$\frac{p_0}{p_R} = e^{-\frac{M\omega^2 R^2}{2\underline{R}T}}$$

For CCl_4 (mol. wt. 153.83) this ratio should have been about 1/6 in the experiment just described.

Since carbon tetrachloride is composed of four atoms of chlorine and one atom of carbon and since there are two isotopes of chlorine and two of carbon, there should exist ten distinct species of CCl_4 ranging in molecular weight from 152 to 161 gms. Because of the rarity [1] of C^{13} (0.7%) the number of

---

[1] International Table of Stable Isotopes, R.S.I., 7, 334, 1936

$$\frac{Cl^{35}}{Cl^{37}} = \frac{76}{24} \qquad \frac{C^{12}}{C^{13}} = \frac{97.3}{0.7}$$

Aston, "Isotopes", Ed. Arnold and Co., 1933

$$\frac{Cl^{35}}{Cl^{37}} = \frac{76}{24} \qquad \frac{C^{12}}{C^{13}} = \frac{99.75}{0.25}$$

Nier and Hanson, Phys. Rev. 50, 722, 1936

$$\frac{Cl^{35}}{Cl^{37}} = 3.07 \pm .03$$

Kallman and Lazareff, Zeits.f.Physik, 80, 237, 1937

$$\frac{Cl^{35}}{Cl^{37}} = \frac{6000}{1850} = 3.25$$

species is effectively reduced to five:

Molecular Type	Mol. Wt.	p / p_R
$C^{12}Cl^{35}_4$	152	1/5.90
$C^{12}Cl^{35}_3\ Cl^{37}$	154	1/6.05
$C^{12}Cl^{35}_2\ Cl^{37}$ Cl^{37}	156	1/6.20
$C^{12}Cl^{35}\ Cl^{37}_3$	158	1/6.36
$C^{12}\ Cl^{37}_4$	160	1/6.52

In ordinary CCl_4 these types are presumably mixed together in proportions to make the average molecular weight = 153.83 gms.

Each type of molecule exists in CCl_4 vapor, and since each has a different molecular weight, the pressure ratio p / p_R is different for each one. Because of this, the composition of the CCl_4 Vapor at the axis of the spinning rotor should be different than that existing at the periphery.

The composition of ordinary CCl_4 from the above molecular types may accur in a variety of ways with the same isotopic composition. The simplest assumption to make is that the isotopes are distributed at random throughout the various molecular species, i.e., that the fractional composition of each type is given by a term in the expansion of $(x_1 + x_2)^4$, where x_1 and x_2 are the fractions of Cl^{35} and Cl^{37} known to exist in ordinary chlorine. When this assumption is valid, the separation obtained in a centrifugal field occurs independently of molecular structure, as if only Cl^{35} and Cl^{37} were present.

It is to be recalled that an expression is being sought which will connect a measured change in density with the effect of a centrifugal separation on CCl_4 in the vapor state. Assuming that only the isotopes of Cl, I_1 and I_2 are present in the spinning rotor, the pressure ratios of each between the periphery and the axis will be proportional to the numerical density ratio in each region since

$$\left.\begin{aligned} p_{1R} &= \frac{\nu_{1R} m_1 \bar{c}_1^{\,2}}{3} \\ p_{2R} &= \frac{\nu_{2R} m_2 \bar{c}_2^{\,2}}{3} \end{aligned}\right\} \quad \frac{p_{1R}}{p_{2R}} = \frac{\nu_{1R} m_1 \bar{c}_1^{\,2}}{\nu_{2R} m_2 \bar{c}_2^{\,2}} ,$$

$$\frac{p_{10}}{p_{20}} = \frac{\nu_{10} m_1 \bar{c}_1^{\,2}}{\nu_{20} m_2 \bar{c}_2^{\,2}}$$

and the ratio

$$\frac{\dfrac{p_{1R}}{p_{2R}}}{\dfrac{p_{10}}{p_{20}}} = \frac{\dfrac{\nu_{1R}}{\nu_{2R}}}{\dfrac{\nu_{10}}{\nu_{20}}}$$

the masses cancelling out.

The right hand member may be written in terms of the fractional composition ratios as follows:

Fractional composition

at the periphery: at the axis:

$$x_{1R} = \frac{\nu_{1R}}{\nu_{1R}+\nu_{2R}} \qquad x_{10} = \frac{\nu_{10}}{\nu_{10}+\nu_{20}}$$

$$x_{2R} = \frac{\nu_{2R}}{\nu_{1R}+\nu_{2R}} \qquad x_{20} = \frac{\nu_{20}}{\nu_{20}+\nu_{10}}$$

therefor

$$\frac{\dfrac{x_{1R}}{x_{2R}}}{\dfrac{x_{10}}{x_{20}}} = \frac{\dfrac{\nu_{1R}}{\nu_{2R}}}{\dfrac{\nu_{10}}{\nu_{20}}}$$

and finally

$$\frac{\dfrac{x_{1R}}{x_{2R}}}{\dfrac{x_{10}}{x_{20}}} = e^{\frac{(I_1-I_2)\omega^2 r^2}{2\underline{R}T}} \equiv K$$

This is the expression for the composition ratios between the axis and the periphery.

The magnitude of the change $x_{1R} - x_{10} = \Delta x$, for one isotope I_1 may be computed as follows:

$$\frac{x_{1R}}{x_{2R}} = \overline{K}\,\frac{x_{10}}{x_{20}}$$

Transposing $\frac{x_{1R}}{x_{10}} = \overline{K}\,\frac{x_{2R}}{x_{20}}$

and subtracting unity from both sides

$$\frac{x_{1R}-x_{10}}{x_{10}} = \overline{K}\,\frac{x_{2R}-x_{20}}{x_{20}} = \frac{\Delta x_1}{x_{10}}$$

Remembering that $x_{10}=1-x_{20}$, $x_{1R}=1-x_{2R}$ and that from above

$$x_{20} = \overline{K}\,\frac{x_{2R}}{x_{1R}}\,x_{10}$$

$$= \overline{K}\,\frac{x_{2R}}{x_{1R}}\,(1-x_{20})$$

$$= \frac{\overline{K}\,x_{2R}}{x_{1R}+\overline{K}\,x_{2R}},$$

x_{10} and x_{20} can be eliminated from the expression for Δx_1 above to give

$$\Delta x_1 = \frac{x_{1R}\,x_{2R}\,(\overline{K}-1)}{x_{1R}+\overline{K}\,x_{2R}}$$

This last expression is equal to $-\Delta x_2$. Thus if the composition of I_1 is increased at the axis, the composition of I_2 is diminished at the axis by the same amount. For the spinning rotor discussed above the change is about 1/2 %; that is, if the isotopic composition at the periphery is $Cl^{35}/Cl^{37} = 76/24$ then at the axis it should have been 76.5/23.5. The ratio of these two ratios is 1/1.025 which is the value of K computed from the exponential.

This change in the isotope ratio at the axis should affect the density of a small sample of carbon tetrachloride removed from the axis as follows:

The molecular weights of CCl_4 computed for two different isotopic compositions of the Cl are

$$\bar{M} = 4I_1 x_1 + 4I_2 x_2 + C$$

$$\bar{M}' = 4I_1 x_1' + 4I_2 x_2' + C$$

The change in average molecular weight $\Delta\bar{M}$ is the difference

$$\Delta\bar{M} = \bar{M} - \bar{M}' = 4I_1 \Delta x_1 + 4I_2 \Delta x_2$$

and since $\Delta x_2 = -\Delta x_1$

$$\Delta x_1 = \frac{\Delta\bar{M}}{4(I_1 - I_2)}$$

Now it has been shown experimentally that for isotopic changes

$$\frac{\Delta d}{\bar{d}} = \frac{\Delta\bar{M}}{\bar{M}}$$

to within a few percent.

Substituting in this the value of $\Delta \bar{M}$ in terms of $\Delta \chi_1$, and of $\Delta \chi_1$ in terms of the isotopic composition change due to the centrifugal field results in the expression which has been sought:

$$\frac{\Delta d}{d} = \frac{\Delta \bar{M}}{\bar{M}} = \frac{4(I_1 - I_2)\Delta \chi_1}{\bar{M}}$$

$$= \frac{4(I_1 - I_2)\chi_{1R}\chi_{2R}(\underline{K} - 1)}{\bar{M}(\chi_{1R} + \underline{K}\,\chi_{2R})}$$

which for values of $\underline{K}$ close to unity becomes

$$\frac{\Delta d}{d} = \frac{4(I_1 - I_2)^2 \chi_{1R}\chi_{2R}\,\omega^2 R^2}{2\,\underline{R}\,T\bar{M}}$$

since $\chi_{1R} + \underline{K}\,\chi_{2R} \cong 1$

This gives $\frac{\Delta d}{d}$ = 2.5 parts in 10.000 for just one stage of the multi-stage centrifuge. Since no change was observed within 1 part in 20,000 for the 19 stages it was concluded that if the centrifugal separation had occurred it could have been easily detected with the proceedure used. The failure to observe any separation was attributed to insufficient circulation of the vapor through the various stages. That this was the cause was verified by the insertion of a second hollow shaft passing through the drive shaft, thence through each of the 19 discs, down to the bottom of the rotor. After 12 hours operation with 75cc liquid CCl_4 in the rotor, two 15 cc samples were simultaneously obtained, one from the top (cold) end and one from the bottom (hot) end of the rotor. The densities of the two samples differed by about 1 part in 10,000, the heavier sample having been obtained from the bottom (hot) end. Repetition of procecdure gave the came discouraging result.

The Single Stage Rotor

Owing to the negligible results with the multistage rotor, it was decided to study the separation obtainable in a single stage machine. For this purpose the discs were removed and the hollow steel cylinder itself was used as a single stage. A perforated steel pipe (3/8" dia x 1/32" wall thickness) was placed down the axis of the cylinder in an attempt to remove the vapor from points situated uniformly along the axis. It was discovered that the pipe braced at both ends was bowed out by the high rotational speed. Further bracing furnished by 2 evenly spaced duralinum discs was sufficient to keep the pipe in place at 1000 R.P.S.. Each disc had five 1/2" dia. holes drilled near its periphery in order to allow communication between the three resulting compartments. (See rotor in Fig. 4)

A run was made with this single stage rotor. 100 cc liquid CCl_4 was evaporated out of the spinning rotor at 1000 R.P.S. in 65 minutes. The first 15 cc and the last 11 cc to come out were analyzed, the first being 2 parts per 10,000 lighter, the last being 1 part per 10,000 heavier than the density of ordinary uncentrifuged CCl_4. The total difference between the two fractions was the order of magnitude, at least of the change which was calculated theoretically in the last section.

Another run was made with a bushing [1] in the hollow drive shaft which increased the time required to withdraw the initial 100 cc to 250 minutes. The first 11 cc and the last 7 cc showed a density difference of 6 parts in 10,000, the uncentrifuged material's density being midway between them.

Comparison of the 65 and 250 minute runs showed that considerably more separation was obtainable if the CCl_4 vapor was removed slowly. In order to check this conclusion, a series of 5 runs of each of the two types (A = 3 hr run, B = 1 hr run) just described were made. Analysis of the first (2A, 2B) and last (12A, 12B) composite samples from each series verified this conclusion.

At this juncture in the work it became increasingly evident that the observed changes in density might be due to the concentration of impurities as well

1) The 1/4" long bushing contained a hole .029" dia made by a #69 drill. The dimensions of the drive shaft were .109" O.D. x .012" wall thickness x 6 1/4" long.

as of the isotopes of chlorine. Due precautions were taken, of course, in the density measurements to treat all samples in a like manner. Each sample was thoroughly dried by a vacuum distillation at room temperature from a P_2O_5 — CCl_4 slush, the middle third of the distillation being used to fill the pyknometer. In spite of this, the only sure way to check the efficiency of separation of the centrifuge was by some direct measurement of the isotopic composition of the various samples. Since, at this time, a mass spectrograph[1] had become available it was decided to obtain a sample with as large a change as possible and compare the density measurement of it with the isotopic composition change as indicated on the mass spectograph. If the two methods checked each other reasonably well, then the method of density measurements could be used for subsequent investigations.

With this end in view a series of runs was undertaken to accumulate sufficient material for a second centrifuging.

[1] Patterned after the one described by Blewett, Phys. Rev., 49, 900, 1936

Type C' Runs.[1]

For the first centrifugings each of the 32 runs was of the following type: 105-106 cc CCl_4 liquid was introduced into the rotor. The machine was then accelerated to 1000-1030 R.P.S., At this speed range, which was maintained throughout the run, air was first exhausted from the rotor, 4 cc liquid CCl_4 being collected in the dry ice-ethyl alcohol slush traps in this process. The next 7 cc collected was put in a separate container (#2C'). The collection continued, combining all but the next to the last 7 cc (#11C') and the last 7 cc (#12C') which were kept in separate bottles.

The time required to remove the entire amount was 201 minutes. While this seemed to indicate that the rate of removal was 1.9 min. per cc liquid, in The actual case the rate of removal was variable, the material coming out slowly at first and more rapidly toward the end of the run. The curves (Fig. 7) which were typical, show this effect for several of the C' runs.

---

1) The results of this section were reported to the Am. Phys. Soc., see Skarstrom, Carr and Beams, Phys. Rev., <u>55</u>, 591, 1939

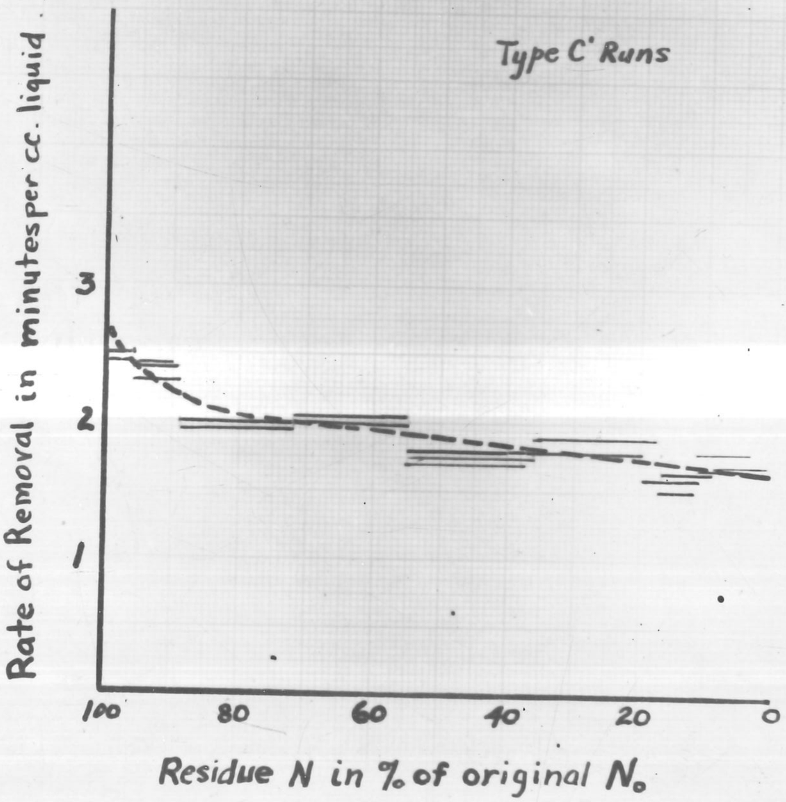
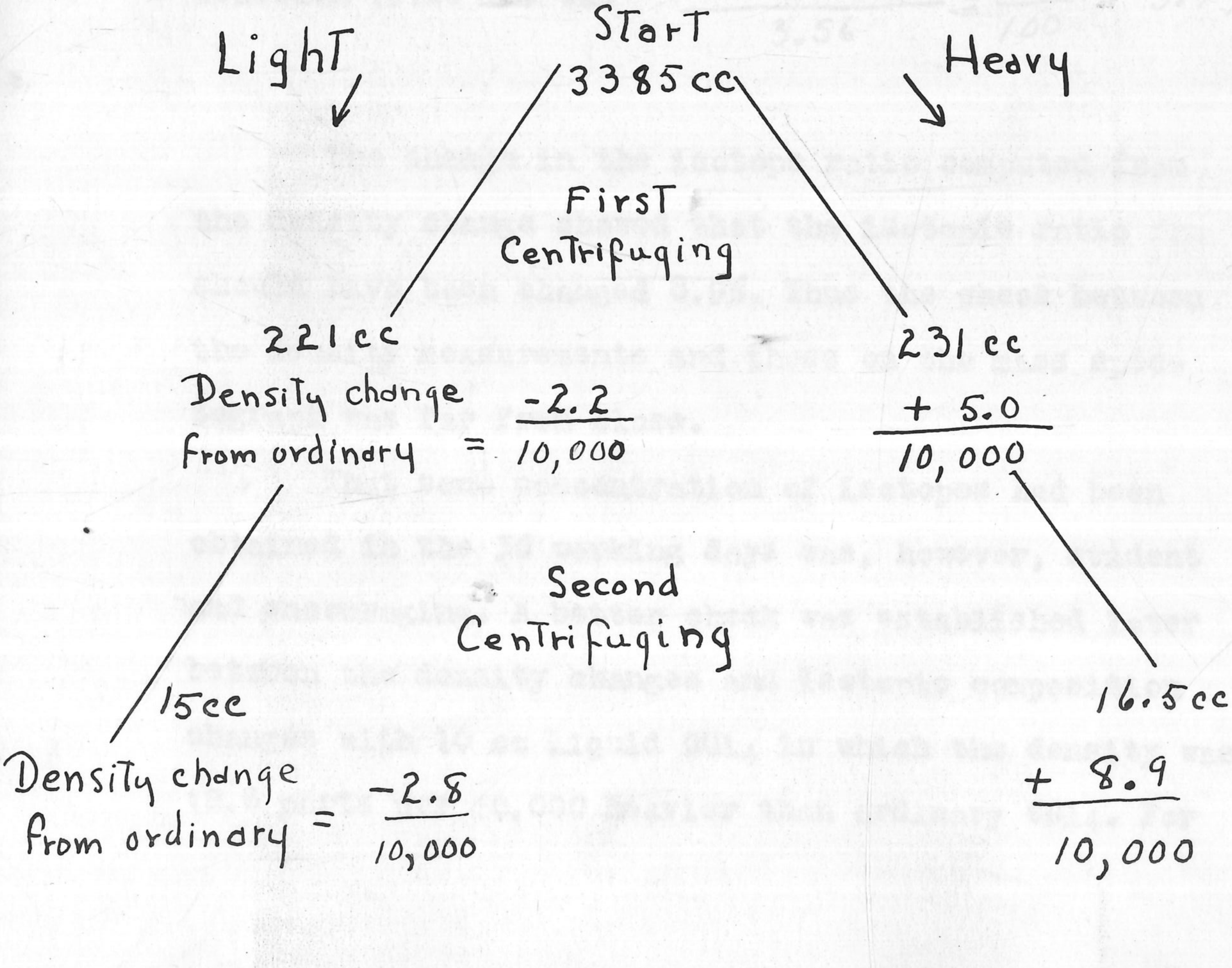

Type C' Runs
Rate of Removal in minutes per cc. liquid
3
2
1
100
80
60
40
20
0
Residue N in % of original N₀

Fig. 7

The effect was attributed to a net heating of the spinning rotor due to gaseous friction in the vacuum chamber.

From the 32 runs of the first centrifuging, 224 cc of light (#2C') and 231 cc of heavy (#12C') were obtained from a total of 3385 used. These two fractions were centrifuged again using the same proceedure. From the second centrifuging, 15 cc (#2C' II) light and 16.5 cc (#12C' II) heavy were obtained. All of the above fractions were analyzed for density change the results of which are summarized below:



The heavy fraction of the second centrifuging (#12C'II) was analyzed in the mass spectograph by Mr. H. E. Carr. The results of this analysis using Cl negative ions obtained from 100 volt electron bombardment of CCl_4 vapor were:

Ordinary CCl_4 $\frac{Cl^{35}}{Cl^{37}} = 3.56 \pm .06$ (35 readings)

Heavy (#12C'II) Fraction $\frac{Cl^{35}}{Cl^{37}} = 3.43 \pm .04$ (40 readings)

The measured change in the isotope ratio for the heavy fraction (#12C'II) was $\frac{3.56 - 3.43}{3.56} = \frac{3.7}{100} = 3.7\%$

The change in the isotope ratio computed from the density change showed that the isotopic ratio fro should have been changed 8.9%. Thus the check between the density measurements and those on the mass spectograph was far from close.

That some concentration of isotopes had been obtained in the 36 working days was, however, evident and encouraging. A better check was established later between the density changes and isotopic composition changes with 10 cc liquid CCl_4 in which the density was 12.8 parts per 10,000 heavier than ordinary CCl_4. For this sample (#13 E'III) the mass spectograph analysis gave:

Ordinary CCl_4 $\frac{Cl^{35}}{Cl^{37}} = 3.35 \pm .04$ (21 readings)

Heavy (#13 E'III) sample $3.03 \pm .04$ (14 readings)

The measured change in isotopic ratio was:

$$\frac{3.35 - 3.03}{3.35} = 9.6\%$$

whereas the change calculated from the densities was 12.8%

The material for this sample (#13 E'III) was obtained by re-centrifuging and combining intermediate fractions which had been accumulating from the various runs. The purpose was mainly to obtain material sufficiently changed that the methods of measuring the change might be validated. The methods were found to agree roughly within 25% of the change being measured.

Efficiency Studies of Single Stage Rotor.

The preceeding results obtained from the single stage rotor were estimated to be 60-70% efficient. This estimate was based on a calculation made from the following formula:

$$\text{Efficiency} = \frac{\frac{\Delta d}{\bar{d}}}{\frac{4(I_2-I_1)^2 x_1 x_2 \omega^2 R^2 \ln C}{2 \underline{R} T \bar{M}}}$$

where $\frac{\Delta d}{\bar{d}}$ = fractional density increase of residue over ordinary CCl_4

$\bar{M}$ = average molecular weight of CCl_4 whose isotopes are I_1 and I_2 inthe proportion x_1 and x_2 respectively

ω = angular velocity

R = radius of inner surface of centrifuged liquid

C = cut = fraction of original number of moles to residue

$\underline{R}$ = gas constant

T = absolute temperature

The use of this formula is justifiable if the separation obtained is independent of the molecular combination of the isotopes. This in turn may best be tested by re-arranging the conditions of the experiment until a maximum efficiency has been attained. Comparison of the maximum efficiency obtained with unity will then justify the formula's use.

It has already been observed that the rate of removal of the vapor had important bearing on the efficiency of the separation. The relationship was made more definite by a series of runs with different withdrawal rates. The various rates were obtained by inserting a bushing in the hollow drive shaft, thereby changing its cross-sectional area. The points in Fig. 8 show that not more than 1/5 cc liquid may be withdrawn per minute if maximum separation is to be expected.

The fact that there appears to be a maximum in the neighborhood of 100% is important, however, since it justifies the use of the theoretical formula at least within the experimental error (10%).

This observed reduction of efficiency when the vapor was removed rapidly is a serious handicap of the method.

At first glance (in Fig. 8) it might appear that because of the approximate linearity of the oblique portion of the curve, operation at less than maximum efficiency would produce the same or better result in a

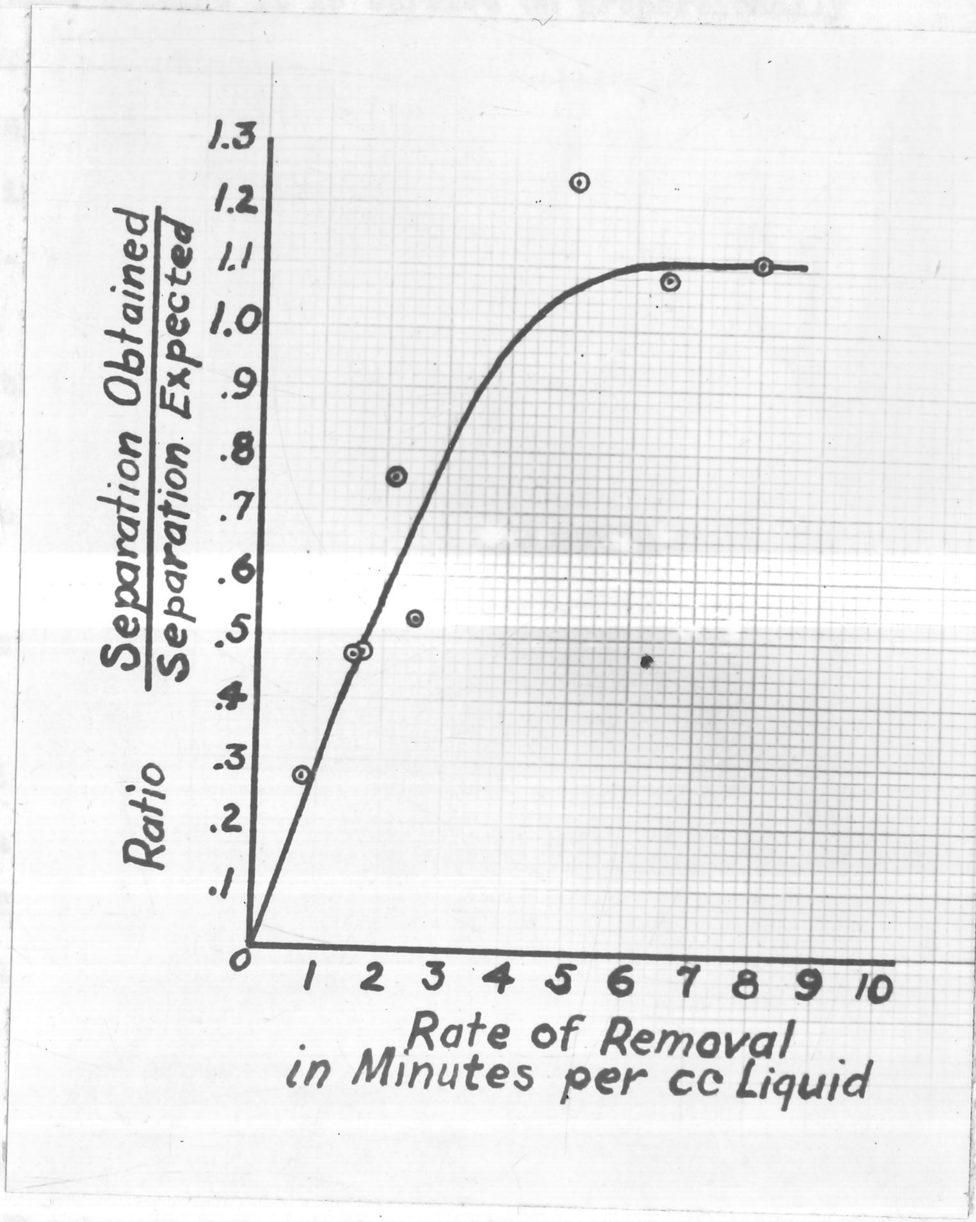

Ratio
Separation Obtained
Separation Expected
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
1
2
3
4
5
6
7
8
9
10
Rate of Removal
in Minutes per cc Liquid

Fig. 8

given time because it is carried on proportionally faster. Put another way, there might exist an optimum efficiency, less than the maximum, at which a given interval of operation would produce the best result. Qualifying the word "best", let it be required to produce the largest amount of material in which the isotope ratio is changed 10%. For CCl_4 in the centrifuge under discussion this would require a cut of about 55, operating at maximum efficiency. Starting with 100 cc of liquid CCl_4 in the rotor, the last 1.8 cc removed would have the required change in 500 minutes operation. On the other hand, operation at 50% of the maximum efficiency would require a cut of 3020 to produce the same 1.8 cc residue. This would necessitate handling 5440 cc which, even though transported twice as rapidly, would take 13,600 minutes, more than 27 times the operating interval in the first case. From this it appears that the optimum efficiency is the maximum efficiency.

The two cases may be represented symbolically by ~~(see appendix)~~

$$\Delta \bar{I} = Eff_1 B \ln \frac{N_0}{N}$$

and

$$\Delta \bar{I} = E'ff_2 B \ln \frac{N_0'}{N}$$

For the same size residue N containing the same change $\Delta\overline{I}$ the two above expressions may be equated to give

$$\left(\frac{N_0}{N}\right)^{E_{ff_1}} = \left(\frac{N_0'}{N}\right)^{E'_{ff_2}}$$

Thus if $E_{ff_1} = 1$ and $E'_{ff_2} = 1/2$, as in the example,

$$N_0' = N\left(\frac{N_0}{N}\right)^{\frac{1}{1/2}}$$

$$= 1.8\left(\frac{100}{1.8}\right)^2$$

$$= 5440\,cc$$

This 5440 cc is the quantity necessary to start with in order to obtain the same result at 50% efficiency as is produced from 100 cc at 100% efficiency.

All of which proves that if the separation process is to be carried on at all effectively it must be done at maximum efficiency. The remainder of the experimental work is directed toward discovering the cause and improving the efficiency, if possible, at rapid withdrawal rates.

The cause of the efficiency reduction at rapid transport rates was attributed to stirring and consequent mixing of various cylindrical layers of vapor in the rotor. This mixing prevented the maintenance of the radial composition gradient produced by the rotation.

In order to determine whether or not temperature gradients within the rotor were the cause of the stirring, an additional hollow shaft [1] was mounted in the rotor through which a constant supply of hydrogen could be admitted. In this way a pressure of H_2 at a few millimeters of Hg could be maintained within the rotating system. Because of the high thermal conductivity of hydrogen it was believed that any temperature gradients would be considerably reduced by the presence of hydrogen. No marked improvement resulted.

Next, a temperature gradient was introduced by inserting a Nichrome wire sheathed by a glass capillary into the newly installed auxiliary shaft. The 10 ohm wire was kept hot by 1/2 ampere of electricity supplied to it via two brushes. The vacuum chamber was imbedded in melting ice. It was hoped in this way to maintain a stabilizing temperature gradient, hot at the axis and cold at the periphery of the rotor. No marked improvement from this arrangement was observed.

Following this, a spiral of washed and ironed unbleached muslin cloth was wound and cut to fit inside the rotor. Difficulty was experienced in spinning the

1) Nickel tubing 21" long 1/16" O.D. x 1/64" wall

rotor because the cloth became displaced to one side, causing serious unbalance. To obviate this difficulty, several thousand 3" discs were cut from the cloth, stacked and pressed into the rotor. A 3/4" diameter hole in the middle of the stack provided an exit passage for the vapors. The idea of the cloth was to prevent stirring as the vapor was removed from the rotor. No marked improvement resulted, which was attributed to the spreading of the 3/4" hole which later was found to have been enlarged to 2 1/4" diameter due to the rotation. (1000 R.P.S.)

Next, the Duralumin discs which had been used in the multi-stage rotor were revised and drilled in such a way (see Fig. 9) that when stacked in the rotor they introduced a large surface tending to keep the angular velocity of the vapor equal to that of the rotor. A 1/2" diameter hole down the center of the stack provided an exit passage for the vapor. 9 short radial holes 1/8" long x 3/32" diameter were drilled in the grooved spacer hub of each disc. 18 discs filled the rotor and provided 19 compartments. This arrangement proved slightly successful in that the efficiency at rapid transport rates was markedly improved. The improvement was insufficient, however, to

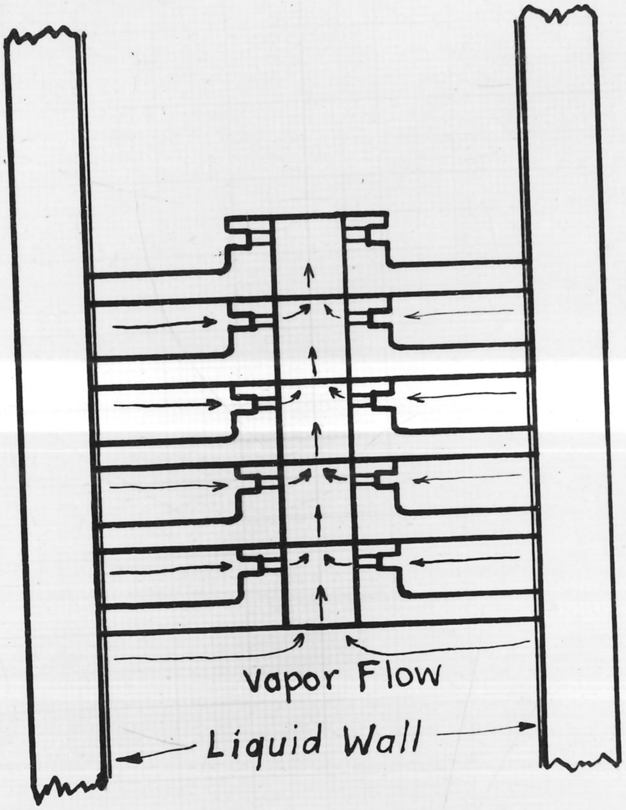


Fig. 9

warrant operating at these transport rates in view of the necessity for operating only under conditions of maximum efficiency (as has already been discussed.)

Nevertheless, the fact that the efficiency had been improved was important as it gave a hint as to the cause of the trouble. The discs were replaced as soon as possible by a star shaped column. (Fig. 10) This spider divided the rotor into 7 sector-shaped prismatic compartments which absolutely prevented any rotation of the vapor at speeds other than that of the rotor. The spider was turned and milled from a solid rod of forged Duralumin S T 14. A 3/8" dia. hole down the center provided exit passage for the vapor. This was fed by 10 .030" dia. holes drilled in the apex of each sector, making a total of 70 such holes spaced uniformly along the length of the spider.

With this arrangement the maximum efficiency was maintained at withdrawal rates as fast as 2cc per minute, an improvement in the optimum transport of 10 times.

In Fig. 11 all the points taken have been included and identified. The crosses refer to points taken with the rotor containing the spider. The circles, triangles, etc. refer to the points for the other ar-

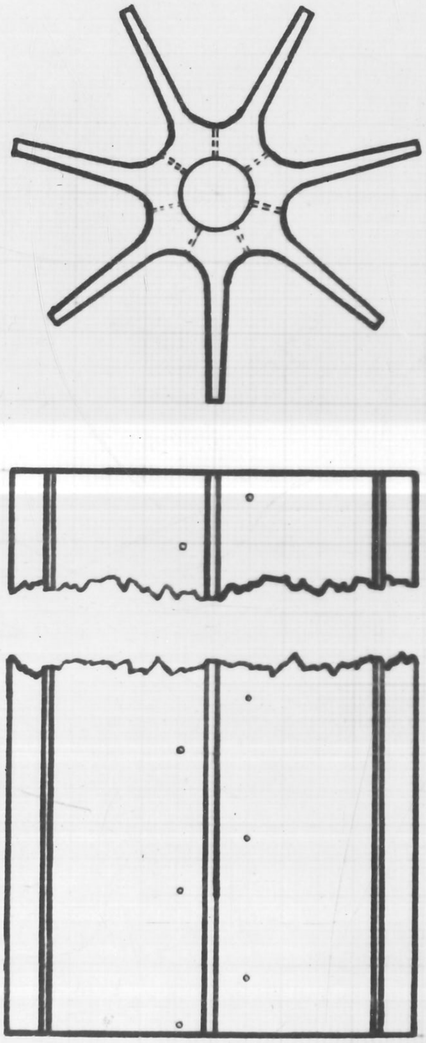


Fig. 10

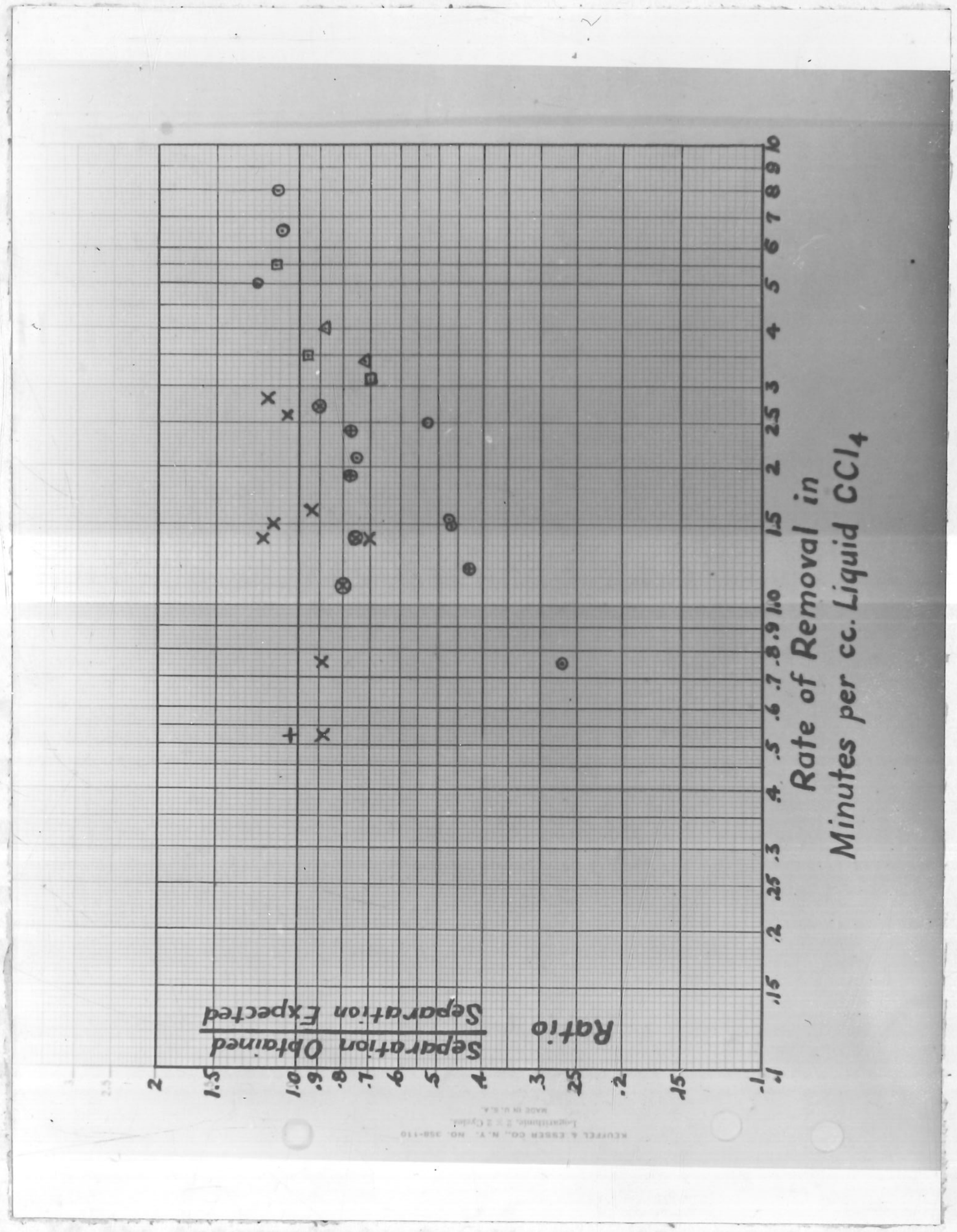

Ratio $\frac{\text{Separation Obtained}}{\text{Separation Expected}}$
2
1.5
1.0
.9
.8
.7
.6
.5
.4
.3
.25
.2
.15
.1
.1
.15
.2
.25
.3
.4
.5
.6
.7
.8
.9
1.0
1.5
2
2.5
3
4
5
6
7
8
9
10
Rate of Removal in
Minutes per cc. Liquid CCl_4
KEUFFEL & ESSER CO., N.Y. NO. 359-110
MADE IN U.S.A.

Fig. 11

rangements. A falling off of the efficiency as the material was removed more rapidly has not been observed over the range investigated. The range is to be extended by the provision of a hollow drive shaft with larger internal diameter. This will enable the vapor to be pumped out of the rotor more rapidly. As it stands, however, the single stage rotor is capable of reducing 100 cc to 1.8 cc CCl_4 liquid containing an increase of 10% in the ratio $\frac{Cl^{35}}{Cl^{37}}$ in 50 minutes operating time.[1]

The marked improvement due to the insertion of the spider allows the conclusion to be drawn that the cause of the reduced efficiency was stirring and mixing of the vapor due to its removal. Since on its way from the periphery in toward the axis the vapor tends to maintain its angular momentum, the angular velocity of the vapor near the axis tends to become larger than that of the rotor. Friction against the end walls of the rotor and against the liquid surface tends to limit this increase in angular velocity.

[1] If the intermediate fractions collected during this batch process are saved, to be centrifuged again, as in a systematic fractionation program, the yield of 10% change can be about doubled per unit time of operation.

Equilibrium is reached at any given removal rate when the moment of the frictional drag on the vapor is equal to the time rate change of angular momentum due to the removal. At rapid removal rates the large frictional drag of the rotor on the more rapidly spinning vapor produces turbulence between successive cylindrical layers which reduces the composition gradient. The introduction of the spider provides a means of absorbing the angular momentum as the vapor moves toward the axis and allows the maximum composition gradient to be realized. The limiting speed of removal with the rotor containing the spider has not yet been determined experimentally because of mechanical difficulties. It is hoped that these will be removed in the near future.

<u>Details of Measurement of the Separation</u>.

The following typical procedure was used to determine the separation factor of the evaporative centrifuging process.

Baker's CP carbon tetrachloride was doubly distilled slowly at atmosphere pressure to build up a supply of CCl_4 to be used in the experiment. The middle third of the first distillation was re-distilled to provide the middle fourth of the original amount to be used in the centrifuge and as a comparison liquid.

105 cc of this liquid CCl_4 was introduced into the rotor. This was done either by means of an hypodermic syringe with the rotor at rest or by distillation with the rotor spinning at 1000 R.P.S.. In the latter case air is pumped out of the spinning rotor. Communication is then established between the rotor and a flask containing 150 cc CCl_4. The spinning rotor acts as a pump, distilling the CCl_4 into the rotation system. When 105 cc. had entered the rotor the flask was cut off and the withdrawal commenced.

The removal of the CCl_4 from the rotor is accomplished by a vacuum pump preceeded by two cold traps each immersed in a slush of dry ice and alcohol, the one nearest the pump being used to trap any vapor which was missed by the first trap. This prevents contamination of the oil in the pump. The main collection trap condenses the vapor which diffuses out of the rotor through the hollow drive shaft. At intervals the process is stopped, this trap removed and another one substituted in its place. In this way separate fractions are collected for subsequent measurement. While measurements on 8 such fractions showed successive increases in density from the first to the last fraction removed, only the last fraction (usually 15 cc. liquid) showed a sufficient density increase over that of the ordinary material to be easily measurable. The rate at which the material collected in the trap could be used as a rough measure of the temperature of the rotor providing the speed of rotation was kept constant.

Having obtained the 15 cc. residue from a centrifugal evaporation of 105 cc. the next step was to determine its density increase. This was done the following way:

The residue and an equal volume of uncentrifuged CCl_4 were each vacuum distilled from a flask which contained anhydrous phosphorous pentoxide (P_2O_5). This process assured the elimination of most of the small amount of water dissolved in the CCl_4. Of this distillation the middle 5 cc. were collected in a cold trap.

If upon melting there appeared the slightest sign of cloudiness or small ice crystals visible in the liquid CCl_4, (M.P.-23°c) the whole process was repeated. In this fashion 5 cc. each of the residue and uncentrifuged CCl_4 were obtained.

The density measurements were made by determining the weight of a full pyknometer containing first the ordinary, then the centrifuged residue and finally the ordinary as a check. The difference in weight appeared in calculations only as the difference in position of a .006 gm platinum rider necessary to produce identical balance points.[1] This eliminated uncertainty in the absolute value of the weights used. In order to insure equality of temperature in the differential density measurements, the "fullness" of the pyknometer was determined when it was immersed in a large tub of water the surface of which was covered with machine oil. The tub resided in a sub-cellar which was sufficiently constant in temperature that the tub remained between 18°C and 21°C in temperature throughout the 18 months it has been in use. In the

1) Kohlrausch, Physical Measurements, D.Appelton & Co., 1874.

course of this time 26 density measurements on the ordinary CCl_4 over this 4°C range in temperature showed a rate of change of density with temperature within 2% of that given by the International Critical Tables. (.00194 $\frac{gms./cm^3}{°C}$ at 20°C) This provided an experimental temperature correction for each weighing. The temperature changes were read on a Beckman thermometer placed close to the pyknometer. Between any pair of density determinations, however, the change in temperature of the tub was small (never more than .01°C.)

The pyknometer itself (see Fig. 12) was constructed of Pyrex to hold 3.60 gms CCl_4. Two vertical glass stoppered capillaries attached to the bulb provided means for filling and emptying the pyknometer. A fine line scratched across each capillary served as a fiducial mark from which the displacements of the liquid levels were measured with a cathetometer. Frequent calibration of the capillaries giving weight versus cathetometer readings assured the correct calculation for the weight of a "full" pyknometer."

Having secured the cathetometer readings of the liquid levels in the capillary stems of the pyk-

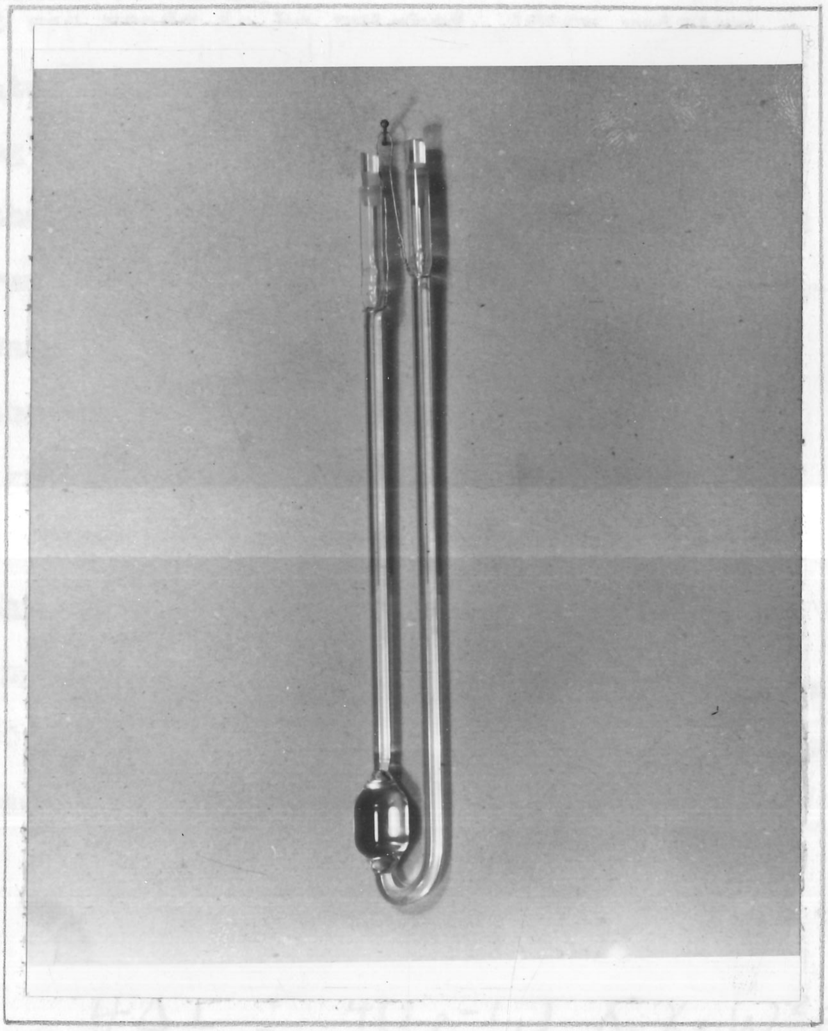


Fig. 12

nometer it was then removed from the bath, cleansed and dryed first with alcohol then with ether. Clean and dry, it was ready to be weighed. After waiting for temperature equilibrium in the beam balance case the weighing was made. The size of the difference in weight of the two samples was usually between 1.0 and 2.5 milligrams. Since the sensitivity of the beam balance used was 2 divisions per milligram and the only change in the weights used was change of position of the 6 milligram platinum rider, it is estimated that the above differences in weight were probably correct to within 0.2 milligrams.

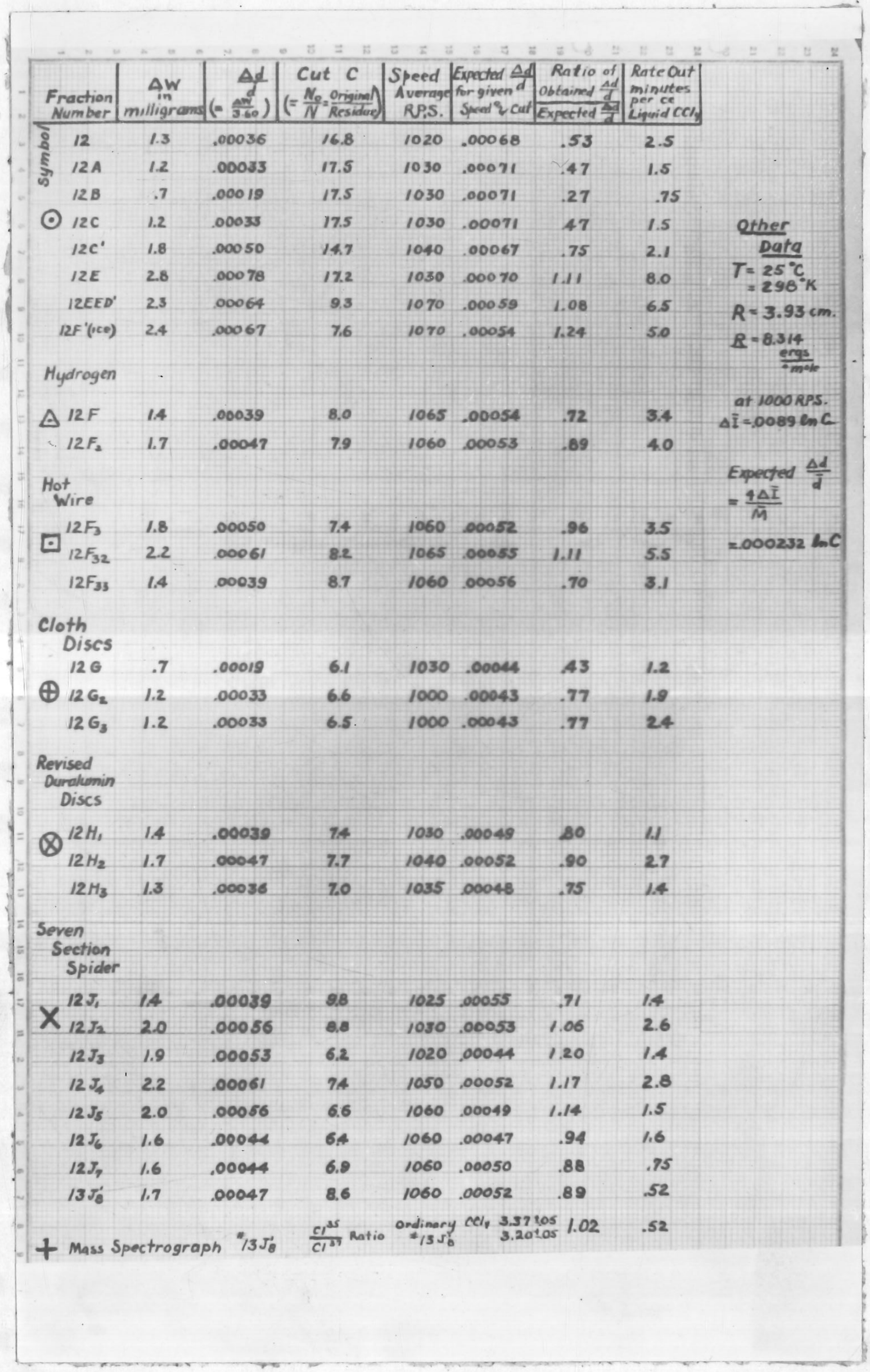
Having obtained the difference in weight, ΔW, between 3.60 gms of the ordinary and of the centrifuged CCl_4 the fractional change in density is $\frac{\Delta W}{3.60} = \frac{\Delta d}{\bar{d}}$

This may be compared immediately with

$$\frac{\Delta \bar{M}}{\bar{M}} = \frac{4\Delta \bar{I}}{\bar{M}} = \frac{4(I_2-I_1)^2 \chi_1 \chi_2 w^2 R^2}{\bar{M} \quad 2\underline{R}T} \ln C$$

to give a measurement of what fraction of the theoretical change to be expected has been observed. This is called for convenience, the efficiency of the centrifugal separation process. The word efficiency could be used in another sense, however, to connect the overall expenditure of energy of any separation process with the separation attained. This is sometimes convenient if comparison of entirely different separation processes is desired. The word is not so used herein.

Fig. 13 shows a table of all the density changes and other data taken from all the first centrifugings which have been made. Some of the points have been plotted in Fig. 8 (P.64) while all of them appear in Fig. 11 (P. 72).



Symbol	Fraction Number	ΔW in milligrams	$\frac{\Delta d}{d}$ $(=\frac{\Delta W}{3.60})$	Cut C $(=\frac{N_0}{N}=\frac{\text{Original}}{\text{Residue}})$	Speed Average R.P.S.	Expected $\frac{\Delta d}{d}$ for given Speed & Cut	Ratio of Obtained $\frac{\Delta d}{d}$ / Expected $\frac{\Delta d}{d}$	Rate Out minutes per cc Liquid CCl_4
	12	1.3	.00036	16.8	1020	.00068	.53	2.5
	12A	1.2	.00033	17.5	1030	.00071	.47	1.5
	12B	.7	.00019	17.5	1030	.00071	.27	.75
⊙	12C	1.2	.00033	17.5	1030	.00071	.47	1.5
	12C'	1.8	.00050	14.7	1040	.00067	.75	2.1
	12E	2.8	.00078	17.2	1030	.00070	1.11	8.0
	12EED'	2.3	.00064	9.3	1070	.00059	1.08	6.5
	12F'(ice)	2.4	.00067	7.6	1070	.00054	1.24	5.0
Hydrogen								
△	12F	1.4	.00039	8.0	1065	.00054	.72	3.4
	$12F_2$	1.7	.00047	7.9	1060	.00053	.89	4.0
Hot Wire								
⊡	$12F_3$	1.8	.00050	7.4	1060	.00052	.96	3.5
	$12F_{32}$	2.2	.00061	8.2	1065	.00055	1.11	5.5
	$12F_{33}$	1.4	.00039	8.7	1060	.00056	.70	3.1
Cloth Discs								
⊕	12G	.7	.00019	6.1	1030	.00044	.43	1.2
	$12G_2$	1.2	.00033	6.6	1000	.00043	.77	1.9
	$12G_3$	1.2	.00033	6.5	1000	.00043	.77	2.4
Revised Duralumin Discs								
⊗	$12H_1$	1.4	.00039	7.4	1030	.00049	.80	1.1
	$12H_2$	1.7	.00047	7.7	1040	.00052	.90	2.7
	$12H_3$	1.3	.00036	7.0	1035	.00048	.75	1.4
Seven Section Spider								
✕	$12J_1$	1.4	.00039	8.8	1025	.00055	.71	1.4
	$12J_2$	2.0	.00056	8.8	1030	.00053	1.06	2.6
	$12J_3$	1.9	.00053	6.2	1020	.00044	1.20	1.4
	$12J_4$	2.2	.00061	7.4	1050	.00052	1.17	2.8
	$12J_5$	2.0	.00056	6.6	1060	.00049	1.14	1.5
	$12J_6$	1.6	.00044	6.4	1060	.00047	.94	1.6
	$12J_7$	1.6	.00044	6.9	1060	.00050	.88	.75
	$13J_8'$	1.7	.00047	8.6	1060	.00052	.89	.52
+	Mass Spectrograph		#$13J_8'$	$\frac{Cl^{35}}{Cl^{37}}$ Ratio	Ordinary #$13J_8'$	CCl_4 $3.37 \pm .05$ $3.20 \pm .05$	1.02	.52

Other Data

$T = 25\,^{\circ}C$
$= 298\,^{\circ}K$

$R = 3.93$ cm.

$\underline{R} = 8.314 \frac{\text{ergs}}{^{\circ}\text{mole}}$

at 1000 RPS.
$\Delta\bar{I} = .0089 \ln C$

Expected $\frac{\Delta d}{d} = \frac{4\Delta\bar{I}}{\bar{M}}$

$= .000232 \ln C$

Fig. 13

THEORETICAL

In the experimental work of evaporative centrifuging, there were three main types of data taken: data concerning the operation of the centrifuge, data concerning the density and changes thereof and data concerningthe ratio of the isotopes and changes therein as measured in a mass spectograph. Three main equations connecting the types of data taken two at a time may each be put in two forms, for composition changes and for molecular weight (mass) changes. The welter of formulas resulting are apt to be confusing unless it is remembered that they all stem from one phenomenon.

Under conditions of no flow and equilibrium, the static composition change between the axis and the periphery of a spinning centrifuge is:

$$\frac{\frac{x_{1R}}{x_{2R}}}{\frac{x_{10}}{x_{20}}} = e^{\frac{(I_1-I_2)\omega^2R^2}{2\underline{R}T}}$$

as has already been derived. While this is exact for monatomic isotopes I_1 and I_2, it is also exact for molecules containing these two isotopes if they are distributed at random throughout the molecular structures.

This has been found to be approximately true for Cl in CCl_4 within 10%.

With a considerable supply of liquid CCl_4 at the periphery (100 cc), vapor drawn off at the axis enriches the material left behind with the heavier isotopes. The rate of enrichment of the residue is subject to exact formulation [1] as follows:

If a small number of molecules (moles) dN_1 leave the centrifuge, the number of this kind (N_1) which does so will be proportional to the pressure of this kind at the axis, which in turn, will be equal to the pressure of this kind (N_1) over the surface of the liquid at the periphery multiplied into $e^{-I_1\omega^2R^2/2\underline{R}T}$

$$dN_1 \sim p_{10} = p_{1R}\, e^{\frac{-I_1\omega^2R^2}{2\underline{R}T}}$$

Similarly for the second kind

$$dN_2 \sim p_{20} = p_{2R}\, e^{\frac{-I_2\omega^2R^2}{2\underline{R}T}}$$

Thus the ratio

$$\frac{dN_1}{dN_2} = \frac{p_{1R}}{p_{2R}}\, e^{\frac{(I_2-I_1)\,\omega^2R^2}{2\underline{R}T}} \equiv \frac{p_{1R}}{p_{2R}}\,k$$

---

1) Mulliken and Harkins, Jour.Am.Chem.Soc., 44, 44, 1922.

For the ratio of the pressure $\frac{p_{1R}}{p_{2R}}$ at the surface of the liquid, the ratio of the mole fractions $\frac{x_1}{x_2}$ in the liquid may be substituted providing the two isotopes exist as an ideal mixture [1] (and have the ? same vapor pressures when pure.[2])

We may then write that:

$$\frac{dN_1}{dN_2} = \frac{x_1}{x_2} k$$

where k = $e^{\frac{(I_2 - I_1)\omega^2 R^2}{2\underline{R}T}}$

If N_1 and N_2 denote the number of moles of each isotope in the residue at any instant and $N_1+N_2=N$, the total number of moles present in the residue, then by definition

$$N_1 = N x_1 \qquad dN_1 = N dx_1 + x_1 dN$$
$$N_2 = N x_2 \qquad dN_2 = N dx_2 + x_2 dN$$

---

1) An ideal mixture is one in which Henry's Law is true, viz., the partial pressures of volatile solutes p, are proportional to the mole fractions x, dissolved, p=ax where a is the vapor pressure of pure solute.

2) Some evidence exists that this is not quite true in CCl_4. See Stedman, Can. Jour. Res., 13B, 114, 1935.

Using these we may re-write

$$\frac{dN_1}{dN_2} = k\,\frac{x_1}{x_2}$$

as

$$\frac{dN_1}{x_1} = k\,\frac{dN_2}{x_2}$$

or

$$\frac{N\,dx_1 + x_1\,dN}{x_1} = k\;\frac{N\,dx_2 + x_2\,dN}{x_2}$$

On simplifying,

$$N\frac{dx_1}{x_1} + dN = kN\frac{dx_2}{x_2} + k\,dN$$

or

$$(1-k)\frac{dN}{N} = k\,\frac{dx_2}{x_2} - \frac{dx_1}{x_1}$$

Noting that $-dx_1 = dx_2$ the above becomes

$$\begin{aligned}(1-k)\frac{dN}{N} &= dx_2\left(\frac{k}{x_2} + \frac{1}{x_1}\right)\\ &= dx_2\left(\frac{k\,x_1 + x_2}{x_1 x_2}\right)\end{aligned}$$

Defining $\frac{N_0}{N}$ as the cut C then $\frac{-dN}{N} = -\frac{d\left(\frac{N}{N_0}\right)}{\frac{N}{N_0}}$

or $\frac{-d\left(\frac{1}{C}\right)}{\frac{1}{C}} = +d(\ln C)$ we get that

$$dX_2 = \frac{X_1 X_2}{(kX_1 + X_2)}(k-1)\, d(\ln C)$$

For small changes of the x's produced by k which is usually near unity $kX_1 + X_2 = 1$ approximately and

$$\Delta X_2 = X_1 X_2 (k-1)\Delta \ln C$$

$$= X_1 X_2 (k-1)[\ln 1 - \ln C]$$

$$= X_1 X_2 (k-1) \ln C$$

Since k was $e^{\frac{(I_2 - I_1)\omega^2 R^2}{2\underline{R}T}}$ which may be expanded into

$$k = 1 + \frac{(I_2 - I_1)\omega^2 R^2}{2\underline{R}T}$$

we finally obtain an approximate expression for the change in composition of I_2 in the residue of an evaporative centrifuging.

$$\Delta X_2 = \frac{(I_2 - I_1) X_1 X_2 \omega^2 R^2 \ln C}{2\underline{R}T} \quad \ldots ①$$

from which the change in atomic weight in the residue is [1]

$$\Delta \bar{I} = \Delta \chi_2 (I_2 - I_1)$$

$$= \frac{(I_2 - I_1)^2 \chi_1 \chi_2 \omega^2 R^2 \ln C}{2\underline{R}T} \dots ②$$

These two approximate equations ① and ② are important working formulae concerning the residue in a centrifuging process from which the following relations should be noticed:

A) The size of both the change in composition and the change in atomic weight are proportional to

1) $x_1 x_2$, the product of the fractional compositions (most favorable case 50%-50%)

2) $\omega^2 r^2$, the square of the peripheral velocity

1) That $\Delta\bar{I} = \Delta\chi_2(I_2 - I_1)$ is evident from the following:

$$\bar{I} = I_1 \chi_1 + I_2 \chi_2$$

$$\bar{I}' = I_1 \chi_1' + I_2 \chi_2'$$

$$\Delta\bar{I} = \bar{I} - \bar{I}' = I_1(\chi_1 - \chi_1') + I_2(\chi_2 - \chi_2')$$

$$= I_1 \Delta\chi_1 + I_2 \Delta\chi_2$$

But since

$$\Delta\chi_1 = -\Delta\chi_2$$

$$\Delta\bar{I} = \Delta\chi_2 (I_2 - I_1)$$

3) the reciprocal of the absolute temperature

4) lnC, the logarithim of the cut, $\frac{N_0}{N}$ in which N_0 and N are the number of mols. in the original amount and residue respectively.

B) The size of the change in composition is proportional to the difference in the atomic weights of the two isotopes,

C) The size of the change of the average atomic weight is proportional to the square of the difference between the weights of the two isotopes.[1]

These relations give the approximate dynamic properties of a centrifugal separation process providing, of course, it is operated so that the maximum separation occurs.

The efficiency of a single centrifuging of CCl_4 from which a residue was obtained which showed a density change Δ d may now be computed as follows:

---

1) More complicated expressions are available for more than two isotopes. See Harkins, Jour. Frank. Inst., 194, 783, 1922
195, 84, 1923
195, 67, 1923
195, 553, 1923

Since $\frac{\Delta d}{\bar{d}} = \frac{\Delta \bar{M}}{\bar{M}} = \frac{4\Delta \bar{I}}{4\bar{I}+12}$ is measured separately it follows from equation ② that the efficiency is

$$\text{efficiency} = \frac{\frac{\Delta d}{\bar{d}}}{\frac{4(I_2-I_1)^2 \chi_1 \chi_2 \omega^2 R^2}{2\underline{R}T}} \ln C$$

which is simply the ratio of the observed fractional density change to the calculated fractional density change.

Returning to equation ② which may be written

$\Delta \bar{I} = B \ln C$ where

B = $\frac{(I_2-I)\chi_1 \chi_2 \omega^2 R^2}{2\underline{R}T}$ it can be seen that for a cut of $e\left(= 2.718 = \frac{100}{36.8}\right)$, $\ln C = 1$ and $\Delta \bar{I} = B$ and for a cut of $e^2\left(= \frac{100}{36.8 \times \frac{36.8}{100}}\right)$, $\ln C = 2$ and $\Delta \bar{\bar{I}} = 2B$ Thus successive cuts of e on the residue increase its average atomic weight B atomic weight units at a time. Each increase of B units changes the isotopic ratio in the residue by a factor of approximately

$$1+\frac{B}{(I_2-I_1)\chi_1\chi_2}$$

since $$\frac{\chi_1'/\chi_2'}{\chi_1/\chi_2}=e^{\frac{(I_2-I_1)\omega^2R^2}{2\underline{R}T}}$$

$$\cong 1+\frac{(I_2-I_1)\omega^2R^2}{2\underline{R}T}$$

$$\cong 1+\frac{B}{(I_2-I_1)\chi_1\chi_2}$$

Thus in the experiments described wherein the maximum efficiency was attained, B was equal to .009 atomic units for Cl (4 x .009 = .027 molecular weight units of CCl_4) for a cut of e . For this cut the residue contained material in which the isotope ratio had changed by a factor of

$$1+\frac{.009}{(37-35).76\times\underset{24}{.26}}=1+.025$$

or roughly changed by 2.5%. Thus at 1000 R.P.S., it can be said that each separation factor B, by which the residue is reduced adds a 2.5% change to the isotope ratio.

It is desirable for many research purposes to obtain large quantities of Cl and other elements in which the isotope ratio has been altered by 15%. This change would require a reduction of volume such that the residue would be about 6 separation factors down, which corresponds to a cut of about 400. In the best arrangement of the single stage tubular centrifuge, such a cut could easily be taken on 400 cc to produce 1 cc liquid of this material in about 4 hours operating time. In this fashion Cl with atomic weight increased .054 units is readily available. Comparable changes and amounts by the method of diffusion of H Cl through porous pipes[1] requires a cut of the order of $(400)^2$, accomplishable in about 4 months.

For a cut of 400 the equations derived above are slightly in error since, for example, the product $x_1\ x_2$ changes by about 10%. It would be convenient therefor to have more accurate approximations. The simplest expedient is to use the average value of $x_1\ x_2$ for each cut of e (separation factor) as it is accomplished, summing for the total separation of the extreme residue.

There is another expression[2] which is useful if large cuts are to be taken which adds a small correction factor to B, namely that

$$\Delta \bar{I} = \left(B + \frac{dB}{d\bar{I}} \Delta \bar{I}\right) \ln C$$

1) As described by Harkins, Jour.Frank.Inst., 194, 783, 1922.

2) See Harkins, Jour. Frank. Inst., 195, 87, 1923.

or $$\Delta \bar{I} = \left(1 + \frac{dB}{d\bar{I}} \ln C\right) B \ln C$$

Evaluating $\dfrac{dB}{d\bar{I}}$:

Form definition $\chi_1 + \chi_2 = 1$ and

$$B = \frac{(I_2 - I_1)^2 \chi_1 \chi_2 \omega^2 R^2}{2 \underline{R} T}$$

and since $\chi_1 \chi_2 = (1 - \chi_2)\chi_2 = \chi_2 - \chi_2^2$

then $$\frac{dB}{d\chi_2} = \frac{B(1 - 2\chi_2)}{\chi_1 \chi_2} = \frac{B(\chi_1 - \chi_2)}{\chi_1 \chi_2}$$

and $d\bar{I} = (I_2 - I_1) d\chi_2$ or

$$\frac{d\chi_2}{d\bar{I}} = \frac{1}{(I_2 - I_1)}$$

then finally

$$\frac{dB}{d\bar{I}} = \frac{dB}{d\chi_2} \cdot \frac{d\chi_2}{d\bar{I}} = \frac{B(\chi_1 - \chi_2)}{(I_2 - I_1)\chi_1 \chi_2}$$

Thus the more exact expression sought is

$$\Delta \bar{I} = \left[1 + \frac{(\chi_1 - \chi_2)}{(I_2 - I_1)\chi_1 \chi_2} \cdot B \ln C\right] B \ln C$$

This expression is useful to check the averaging of $x_1 x_2$ as has been previously suggested. All of these formulae are amenable to simple calculation which is not true of the exact solution of the original differential equation.

Method of Utilizing Intermediate Fractions

In an extended fractionation where, because the size of each batch is limited, a large number of runs must be made to accumulate enough material for a second centrifuginh, an increased yield of the final residue may be obtained if the intermediate fractions are collected according to a pre-designed plan. Such a plan will be outlined below.

For two different sized residues N_1 and N_2

$$\Delta I_1 = B \ln \frac{N_0}{N_1}$$

$$\Delta I_2 = B \ln \frac{N_0}{N_2}$$

Multiplying the first by N_1 and the second by N_2 gives

$$N_1 \Delta I_1 = B N_1 \ln \frac{N_0}{N_1}$$

$$N_2 \Delta I_2 = B N_2 \ln \frac{N_0}{N_1}$$

For the intermediate fraction $(N_1 - N_2)$ the problem is to find the value for $\Delta \bar{I}_{int}$. Assuming that the resulting density of mixed fractions is additive, we get

$$(N_2 - N_1) \Delta \bar{I}_{int} + N_2 \Delta \bar{I}_2 = N_1 \Delta \bar{I}_1$$

or $$\Delta \bar{I}_{int} = \frac{N_1 \Delta \bar{I}_1 - N_2 \Delta \bar{I}_2}{N_1 - N_2}$$

$$\Delta \bar{I}_{int} = \frac{B\dfrac{\ln C_1}{C_1} - B\dfrac{\ln C_2}{C_2}}{\dfrac{1}{C_1} - \dfrac{1}{C_2}}$$

$$\text{or} \quad \Delta \bar{I}_{int} = \frac{B N_o \left(\dfrac{\ln C_1}{C_1} - \dfrac{\ln C_2}{C_2}\right)}{N_1 - N_2}$$

It is evident that an intermediate fraction collected between such values of residue N_1 and N_2 that $\frac{\ln C_1}{C_1} = \frac{\ln C_2}{C_2}$, will contain no change over the original material since $\Delta \bar{I}_{int} = 0$ for this particular fraction.

To make the importance of this last equation clearer, the function $\frac{\ln C}{C}$ has been plotted in Fig. 14 as a function of N as percent of N_o. The function has a maximum for a value of $C = e$, i.e., $N = 36.8\%$ of N_o. The limit of $\frac{\ln C}{C}$ as C approaches unity is zero which is likewise true as C becomes very large. Pairs of values of residues may be picked by inspection for euqal values of $\frac{\ln C}{C}$. This means that material collected between these residues N_1 and N_2 will contain no change $\Delta \bar{I}_{int}$.

Of particular interest in designing a systematic plan for the collection of intermediate fractions are two values N_1 and N_2, dividing the total quantity N_o into three parts such that the following relations hold:

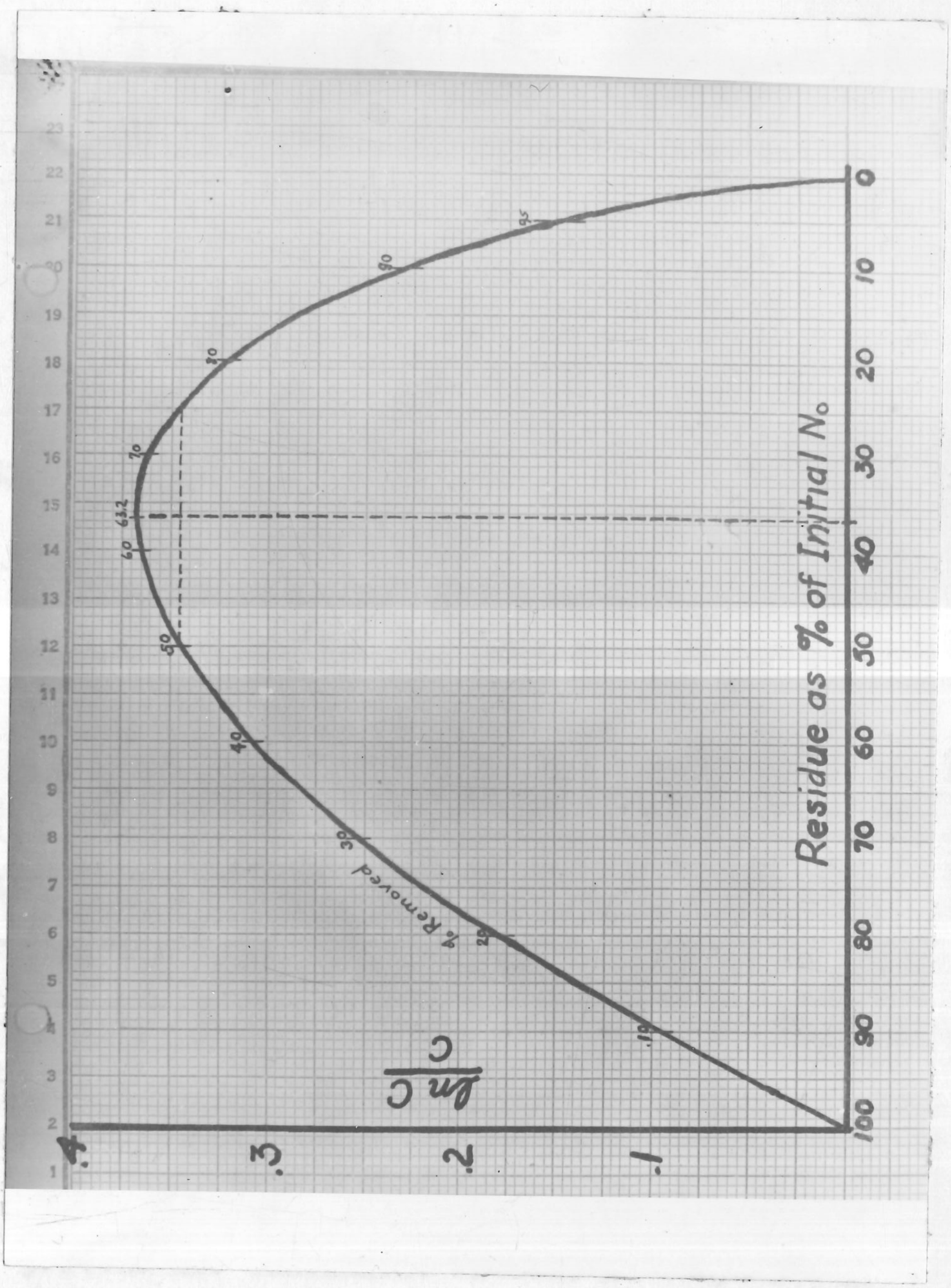

Residue as % of Initial N₀
0
10
20
30
40
50
60
70
80
90
100
$\frac{\ln C}{C}$
.1
.2
.3
.4
% Removed
10
20
30
40
50
60
63.2
70
80
90
95

Fig. 14

For fraction $N_o - N_1$, $\Delta\bar{I}_{int} = -X$ Light

" " $N_1 - N_2$, $\Delta\bar{I}_{int} = 0$ Middle

" " N_2, $\Delta\bar{I} = +2X$ Heavy

Calculations show that this can be realized uniquely if the first fraction is 50% N_o, for which $\Delta\bar{I}_{int} = -.693B$

" second " is the next 25% N_o " " $\Delta\bar{I}_{int} = 0$
" third " last 25% N_o" $\Delta\bar{I}_{int} = +1.386B$

In this way the heavy fraction would be two units (2 x .693 B) heavier than the ordinary while the light fraction would be one unit (1 x .693 B) lighter than the ordinary material.

Using this system for collection of fractions a network of centrifugings could be commenced as is shown in Fig. 15. The main features of this network are:

1) that the fractions from various stages of the process are combinable without loss by mixing,
2) that the necessary quantity of original material is considerably reduced,
3) that the network results in a set of evenly spaced fractions .693 B apart,
4) that the overall yield in the final heaviest

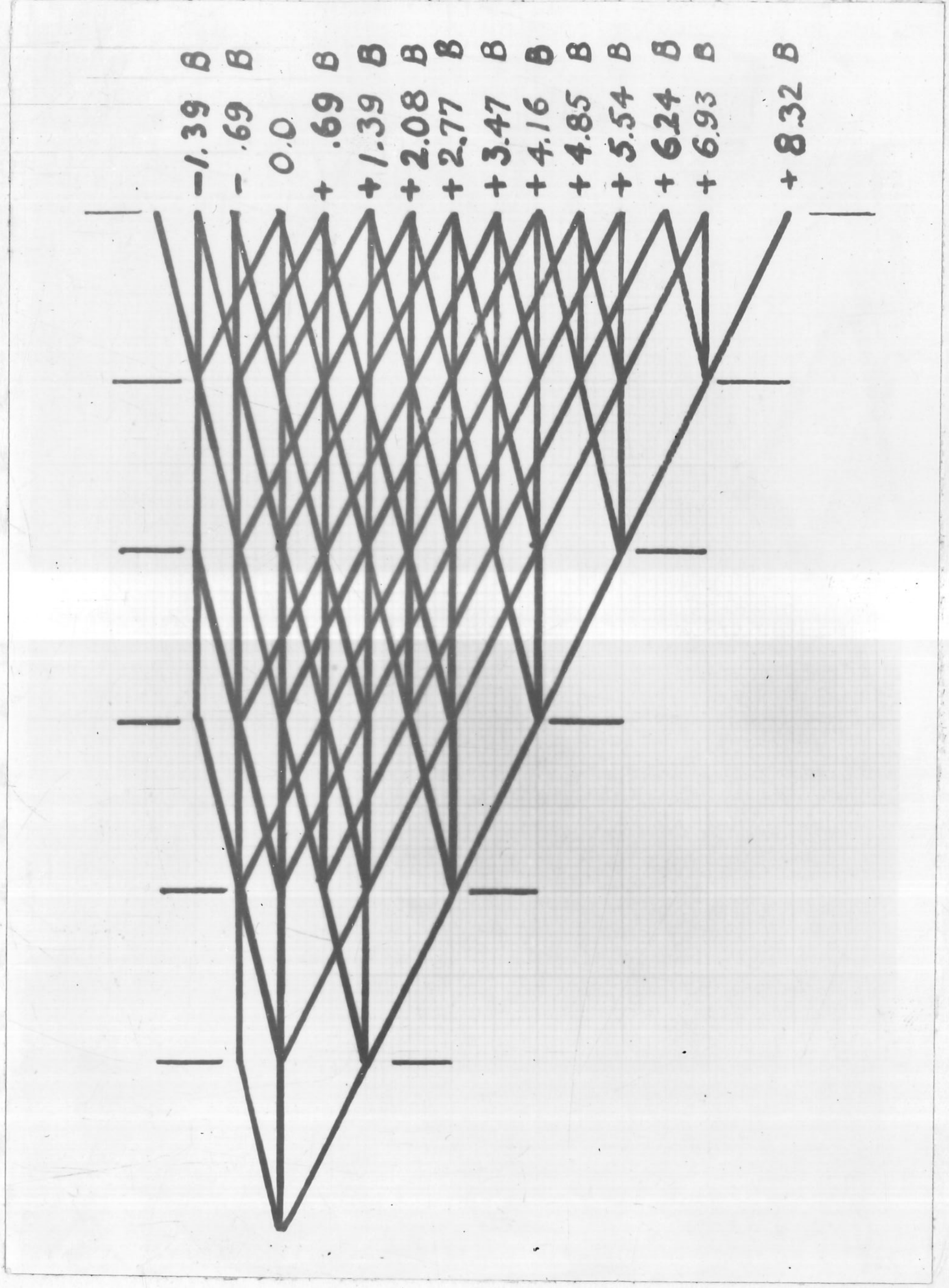

-1.39 B
- .69 B
0.0
+ .69 B
+1.39 B
+2.08 B
+2.77 B
+3.47 B
+4.16 B
+4.85 B
+5.54 B
+6.24 B
+6.93 B
+8.32 B

Fig. 15

fraction is considerably increased for a given total time of operation and original quantity of material.

In all this work attention has been directed to the heavy residue. This has been done simply because og practicality. In one operation a cut of e^2 has produced enough change ($\Delta I = 2B$ (to be conveniently measurable. If the light fraction had been wanted, at least two operations would have been necessary to obtain the same change for measurement purposes. As can be seen in Fig. 15 successive light fractions may be obtained spaced -.693 B apart. Each level corresponds to a change in the isotope ratio of about 1.8% for the operating conditions of the centrifuge described herein. The formula developed for intermediate fractions may be used to compute the changes produced in the light fractions.

CONCLUSION

Machinery, methods and formulae have been described for a process by which changes in the isotopic composition of Cl in carbon tetrachloride may be produced of sufficient magnitude and quantity to be useful for research in other fields. This process, while slightly cumbersome in its present experimental state, is a vast improvement over older methods. With minor procedural revisions, the method of evaporative centrifuging should find immediate application as an inexpensive source from which 15% or more change of the isotopic composition of many elements may be obtained.

BIBLIOGRAPHY

Mulliken, Jour. Am. Chem. Soc., 44, 1033, 1922

ibid. 45, 1592, 1923

Beams and Haynes, Phys. Rev., 50, 491, 1936

Beams and Masket, " " 51, 384, 1937

Masket, Doctor's Dissertation, Univ. Va., 1938

Beams, Rev. Mod. Phys. 10, 245, 1938

Jour. Appl. Phys. 8, 395, 1937

Beams and Skarstrom, Phys. Rev. 53, 327(A), 1938

E.G.Pickels, R.S.I., 9, 358-364, 1938

Stodola, "Steam Turbines"

Boestad, Pederson and Svedberg, R.S.I., 9, 346-353, 1938

International Tables of Stable Isotopes

Aston, "Isotopes" Ed. Arnold and Co., 1933

Nier and Hanson, Phys.Rev., 50, 722, 1936

Kallman and Lazareff, Zeits. f. Physik, 80, 237, 1937

Blewett, Phys. Rev., 49, 900, 1936

Skarstrom, Carr and Beams, Phys. Rev., 55, 591, 1939

Kohlrausch, "Physical Measurements", D.Appelton and Co., 1874

Harkins, Jour. Frank. Inst. , 194, 783, 1922

" " " 195, 87, 1923

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance and whole-hearted cooperation of the members of the Department of Physics of the University of Virginia.

To Dr. J.W.Beams, in particular, without whose guidance and unfailing interest and help this research could not have been undertaken, are tendered thanks and gratitude.

For funds with which to carry on this work, thanks are given to the Research Corporation and to the Dupont Fellowship Fund at the University of Virginia.

The various invaluable services of the staff of the Rouss Physical Laboratory are much appreciated.