

The Separation of Isotopes  
by Thermal Diffusion

A Thesis

Submitted in Partial Fulfilment of the Requirements  
for the Degree of Master of Science  
to the Department of Chemistry  
of McMaster University

by

J. Gordon Lindsay, B.Sc.

Hamilton, Ontario.

September, 1948.



ACKNOWLEDGMENTS

The author wishes to thank Professor H.G. Thode for his guidance and inspiration during this project. The author also wishes to gratefully acknowledge the assistance of Mr. R.H. Mills during the Nitrogen run, and Mr. J. Macnamara who did the mass spectrometric analyses. The financial assistance provided under an Ontario Research Commission Scholarship is gratefully acknowledged.



Table of Contents

	Page
INTRODUCTION	1
General Introduction	1
Theoretical	2
Historical Review	7
EXPERIMENTAL	9
Description of Apparatus	9
Operation and procedure	9
Results and discussion	12
CONCLUSIONS	18
BIBLIOGRAPHY	19



## INTRODUCTION

### General Introduction

The phenomenon of thermal diffusion in gases consists in the fact that a temperature gradient in a mixture of two gases or isotopic forms of the same gas gives rise to a concentration gradient of the two gases. The effect in general is to concentrate the lighter molecule in the hot reservoir and the heavier molecule in the cold reservoir. The phenomenon was predicted by Enskog (1) in 1911 and independently by Chapman (2) in 1917. It was experimentally verified in 1917 by Chapman and Dootson (3). In the case of isotopes the separation was small compared to other separation methods and did not appear to be of any practical use (4). In 1938 Clusius and Dickel (5) developed a method of greatly enhancing the thermal diffusion effect. Their apparatus consisted of a long vertical tube closed at both ends and containing a gas at approximately atmospheric pressure; along the axis of the tube was suspended a platinum wire which could be electrically heated to a high temperature. The lighter molecules being concentrated near the hot wall were carried upward by convection currents, while the heavier molecules were concentrated at the bottom. Equilibrium is established when the thermal siphoning effect is balanced by self diffusion.

The separated stable isotopes of carbon, nitrogen, oxygen and sulphur are of considerable importance in isotope exchange and tracer work. The method of chemical exchange is particularly suited to the production of relatively large quantities of material of medium enrichment. Where high dilution of the tagged material is necessary, or in experiments designed to measure the physical and chemical properties of the enriched isotope, a higher concentration is desirable. Thermal diffusion provides a convenient method for the production of small quantities of highly enriched material. Considerable quantities of sulphur and oxygen enriched in



$S^{34}$  and  $O^{18}$  respectively were produced at McMaster several years ago and it seemed desirable to secure further enrichment of these isotopes by the thermal diffusion method.

Thermal diffusion columns set up previously (38) have been tested and used in the separation of the isotopes of nitrogen, oxygen and sulphur using  $N_2$ ,  $O_2$  and  $SO_2$  gases respectively. Nitrogen gas was used in the separation of the nitrogen isotopes due to its availability and its thermal stability. The simplest gaseous sulphur compound which is thermally stable in the temperature range necessary is  $SO_2$ . Calculations from viscosity data (7,10) indicate that  $SO_2$  would be a particularly poor gas to use. However, since several factors influence the separation it was decided to try  $SO_2$  before discarding the idea. In the separation of the oxygen isotopes the starting material was water whose  $O^{18}$  content was 7.5 normal. Of the common gaseous compounds of oxygen:  $O_2$ , CO and  $CO_2$ , the gas predicted to give the largest separation is CO with  $O_2$  next. Oxygen was used due to its ease of preparation and the fact that its predicted separation is only slightly less than that of CO.

### Theoretical

The fundamental equation of thermal diffusion is:

$$c_1(v_1 - v) = -D \text{ grad } c_1 + \frac{D_T}{T} \text{ grad } T \dots (1)$$

where  $c_1$  is the fractional molar concentration of the lighter isotope.

$c_2$  is the fractional molar concentration of the heavier isotope.

$v$  is the convection velocity of the gas as a whole.

$v_1$  is the convection velocity of the molecules of species 1.

$D$  is the coefficient of self diffusion.

$D_T$  is the coefficient of thermal diffusion.

The coefficient of thermal diffusion is proportional to  $c_1 c_2$  so we must introduce the constant  $\alpha$ , the thermal diffusion which is independent



of pressure, <sup>(20)</sup> and in general varies with temperature.

It is defined as:

$$D_T = D \alpha c_1 c_2 \dots \dots \dots (2)$$

Another constant found in the literature is  $k_t$ , the thermal diffusion ratio

$$k_t = \frac{D_T}{D} = \alpha c_1 c_2$$

In dealing with the theory of thermal diffusion, we are dealing with interactions between molecules involving transfer of momentum and it is important to know the nature of these intermolecular forces.

If the intermolecular force can be represented by an inverse  $v$ th power repulsion ie  $F = -kr^{-v}$ , it is interesting to note that in the special case of the Maxwellian molecule where  $v = 5$ , the coefficient of thermal diffusion vanishes. The use of the Maxwellian molecule in early calculations undoubtedly prevented the phenomenon of thermal diffusion from being predicted at an earlier date.

The theory of Thermal Diffusion has been developed by Furry, Jones and Onsager (6,&7) and much of their notation is used here. The theory of transport phenomena in gases is somewhat involved. A simplified treatment by Frankel (9) is useful in showing the direction of thermal diffusion and its dependence on the magnitude and size of  $\alpha$ .

Thermal diffusion tends to set up a partial pressure gradient of the lighter constituent which is parallel or anti-parallel to the temperature gradient. In order to do this there must be some force acting on the lighter molecules which prevents them from diffusing from the hot wall back to the cold wall. The only place this force can come from is from collisions between the lighter molecules (species 1) and the heavier molecules (species 2). There must be a continual net transfer of momentum from the molecule of one species to those of the other.

Consider the heavier molecules as stationary and the lighter molecules as consisting of two streams, each of uniform velocity coming from the hot



and cold walls respectively. The stream coming from the hot wall will have somewhat greater a velocity than the stream coming from the cold wall. Each light molecule with velocity  $V$  loses its momentum to the heavy molecules at a rate of  $V\sigma$  where  $\sigma$  is the cross section for complete dissipation of momentum. Since each stream must carry the same momentum / cm. (to make the net particle flux zero), the momentum transfer /sec of the streams is proportional to  $V\sigma$ . In order to determine the dependence of  $V\sigma$  on velocity, let the molecules interact with a force:

$$F = -kr^{-v}$$

Then  $\sigma$  may depend on  $k$ , on the mass of the light molecule, on  $V$  and on  $v$ . The only combination of these quantities which will give the dimensions of a cross section is

$$\left( \frac{k}{mV^2} \right) \frac{2}{v-1}$$

Consequently  $\sigma$  is proportional to  $V^{\frac{-4}{v-1}}$  and  $V\sigma$  varies as  $V^{\frac{v-5}{v-1}}$ .

Thus we see that  $V\sigma$  is directly proportional to the stream velocity if  $v > 5$  and inversely proportional if  $v < 5$ . For  $v > 5$  the resulting force is a net momentum transfer from species 2 to species 1, supporting a greater partial pressure of the light molecules at the hot wall; i.e.  $\alpha$  is positive.

For the case where the molecules behave as hard elastic spheres ( $v = \infty$ ), Furry, Jones and Onsager (6) have shown that to a first approximation

$$\alpha_{es} = \frac{105}{118} \frac{M_2 - M_1}{M_2 + M_1}$$

where  $m_1$  and  $m_2$  are the relative masses of the light and heavy molecules respectively.

In practice however, molecules do not behave as perfect elastic spheres. In general  $v$  varies from 3 to 15. A useful constant is  $R_T$  which measures the departure of the molecule from the elastic sphere model. It is defined as

$$R_T = \frac{\alpha(\text{calc. or expt'l})}{\alpha(\text{elastic sphere})} \dots(5)$$



$R_T$  may be calculated from viscosity data, (10) since the coefficient of viscosity varies as  $T^n$  where  $n$  is related to  $R_T$  by the approximate relationship

$$R_T \propto 1.7(1-n) \quad (7) \quad \dots\dots(6)$$

The constant  $\alpha$  consists of two factors, (11) one of which depends solely on the law of interaction between the unlike molecules. This factor and hence  $\alpha$  vanishes when the interaction is according to an inverse 5th power repulsion. The sign of the remaining factor in  $\alpha$  may change sign once as the proportion of either constituent increases from 0 to 1. This has been found to be the case with neon-ammonia mixtures, (12)

$\alpha$  has been measured experimentally for a number of gases. (13-17)

The gas is enclosed in a glass apparatus consisting of a hot and cold reservoir. After equilibrium has been established the concentration of the heavy isotope in the cold reservoir is determined and compared with the initial concentration.

From Eq. 1 it may be shown that

$$\alpha = \frac{(C_2^0 - C_2)}{C_2 C_1} \cdot \left[ \frac{T_1 - T_0}{T_0} \right] \cdot \frac{\ln T_0}{T_1}$$

Where  $T_1$  and  $T_0$  are the temperatures of the hot and cold reservoirs respectively.  $C_1$  and  $C_2$  are the normal concentrations of the light and heavy isotopes respectively.  $C_2^0$  is the concentration of the heavy isotope in the cold reservoir.

Also it is known that  $\alpha$  varies with temperature, (14-16) and a specific temperature must be assigned to  $\alpha$ . This temperature is defined by Brown (18)

as

$$T_r = \frac{T_1 T_0 \ln \frac{T_1}{T_0}}{T_1 - T_0}$$

For a unit thermal diffusion column the equilibrium separation factor is given as



$$\frac{(C_2^L) (1-C_2^U)}{C_2^U} = e^{2A_d L} / (1 - C_2^L)$$

where  $C_2^L$  and  $C_2^U$  represent the equilibrium concentration of the heavy gas in the lower and upper ends of the column.

$L$  is the length of the column.

$$A_d = \frac{A}{1 - K_d/K}$$

$$\text{where } A = \frac{252 \alpha \eta D p (\Delta T)}{\rho g d^4}$$

$$\text{and } K_d/K = 1890 (T_0^2 + T_1 T_0 + T_1^2) \times \left( \frac{g D \eta}{d^3 \rho g \Delta T} \right)^2$$

$\eta$  = coefficient of viscosity.

$D$  = coefficient of diffusion.

$p$  = pressure of gas in the columns.

$d$  = width of annular space.

$g$  = acceleration due to gravity.

$T_1, T_0$  = temperature of hot and cold walls respectively.

$\alpha$  = thermal diffusion constant

$\rho$  = gas density in the columns.

In the case of isotopes the equilibrium separation factor reduces to

$$\frac{C_2^L}{C_2^U} = e^{2 A_d L}$$

since  $C_2$  is small compared to unity.

Nier (19) has pointed out that since  $D$  varies as  $1/p$  and  $\rho$  varies as  $p$ , the equilibrium separation factor may be put in the form

$$e^{2 A_d L} = \exp. \frac{a}{p^2} / \frac{1 b}{p^4}$$

By obtaining the equilibrium separation factor of a column at two different pressures he was able to evaluate the constants  $a$  and  $b$  and calculate the pressure giving the maximum separation factor for the gas used.



## Historical Review

Chapman<sup>(20)</sup> first suggested the use of thermal diffusion for the separation of isotopes. However previous to the discovery by Clusius and Dickel of the separation column the separation produced was too small to be of any practical importance.<sup>(4)</sup>

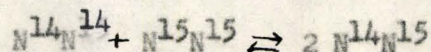
Several attempts have been made to formulate a theory of thermal diffusion (6,21,22) each meeting with a certain amount of success. The theory advanced by Furry, Jones and Onsager has been the one most generally accepted and considerable evidence has been advanced in support of the theory.

Certain modified types of columns have been constructed following the general principle of the Clusius and Dickel column, namely the concentric tube type used by Bramley and Brewer<sup>(23)</sup> and the all metal calrod heater type developed by Watson.<sup>(24)</sup> A number of isotopes of the light elements have been separated to a greater or lesser extent using these different types of column.

The rare gases have been used in many instances since their molecules approximate the elastic sphere model. Clusius and Dickel completely separated Ne<sup>20</sup> and Ne<sup>22</sup> (25) and also Kr<sup>84</sup> and Kr<sup>86</sup> (26). Krypton was partially separated by Groth and Harteck<sup>(27)</sup> Watson<sup>(24)</sup> obtained a separation factor of 8 for Neon. Nier<sup>(28)</sup> using a Clusius and Dickel column effected a 300 fold enrichment of He<sup>3</sup> in helium. It has been shown that the repulsive force indices of the rare gases decrease with increasing molecular weight, argon being the "softest" (29,30)

The chlorine isotopes have been separated using HCl gas. (31,32) Clusius and Dickel obtained 99.6% HCl<sup>35</sup> and 99.4% HCl<sup>37</sup>.

The nitrogen isotopes have been partially separated, Clusius, Dickel and Becker<sup>(35)</sup> having produced pure N<sup>14</sup>N<sup>15</sup>. No further enrichment was possible as the platinum wire does not catalyze the equilibrium.

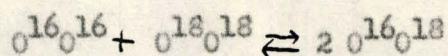


The carbon isotope C<sup>13</sup> has been concentrated using methane (19,33,34).



8

The oxygen isotopes have been separated by thermal diffusion. Using oxygen gas, Clusius, Dickel and Becker (35) effected a complete separation of  $O^{16}$  and  $O^{18}$  and showed that the isotopic equilibrium reaction



is catalyzed by the platinum wire. S.B. Welles (36) using 18 meters of column and maintaining a normal concentration of  $O^{18}$  in the top reservoir obtained  $O^{18}$  enriched from 0.2% to 14% and  $O^{17}$  enriched from 0.04 to 0.8%.

I. Lauder (37) produced oxygen containing 19.5%  $O^{18}$  and 1%  $O^{17}$  in a period of 24 weeks.



## EXPERIMENTAL

### Description of apparatus

The apparatus (38) consisted of 4 Watson type unit thermal diffusion columns mounted vertically in series in a light shaft. Each unit consisted of a General Electric 2000 watt Calrod heater of  $\frac{1}{2}$ " diameter and 9' long suspended concentrically in a copper tube of 1" I.D. leaving an annular space of  $\frac{1}{4}$ ". The cold wall was surrounded by a  $1\frac{1}{2}$ " I.D. copper jacket. The calrod heaters were kept centered along the whole length by stainless steel pins of 0.055" diameter which were placed 120° apart around the cold wall at intervals of 2' along the length of the column. The units were connected by means of a brass connecting sleeve and flange joints, providing an expansion chamber for the calrod heaters, whose expansion amounts to over an inch at the operating temperature of 530°. The calrod heaters were supported at the top of each unit by a perforated brass plug which allows the gas to pass freely between units. Electrical leads were brought out from the top and bottom of each unit through kovar glass seals. Two copper convection tubes one of which was electrically heated, connected the columns with the top and bottom reservoirs. A glass reservoir of 5 liters capacity or greater was attached to the top of the columns by a kovar glass seal and a glass reservoir of approximately 100 ml. was attached to the bottom by a housekeeper seal. Provision was made for removing small samples of gas from the top and bottom of the columns at suitable time intervals for mass spectrometric analysis.

### Operation and Procedure

The procedure involved in the operation of the columns was similar in many respects for the three gases. The columns were evacuated with a Welch duo seal oil vacuum pump to a pressure of 100 microns as measured on a Pirani gauge. Following this the copper surfaces were de-gassed by turning on the calrods for short periods at a time. The gas was then admitted to the evacuated columns through a drying agent to a known pressure.



The top reservoir consisted of a 5 liter flask for the nitrogen and sulphur runs. In the nitrogen run ordinary tank nitrogen dried by passage through a dry ice trap was used. Sulphur dioxide was prepared by the action of  $H_2SO_4$  on pure  $Na_2S_6O_3$ . Water vapor was removed by passing the gas through "Drierite" reagent.  $SO_2$  samples were removed from the top and bottom reservoirs of the thermal diffusion columns at suitable time intervals during the course of the run for mass spectrometric analysis of masses 64 and 66. It is important to note that mass 66 which is concentrated in the bottom reservoir consists of two molecular species  $S^{34}O^{16}O^{16}$  and  $S^{32}O^{16}O^{18}$ . Since we are interested primarily in concentrating  $S^{34}$  it became necessary to assure a normal  $O^{18}$  content in the samples before analysis. In order to do this each sample of  $SO_2$  was equilibrated with distilled water. The gas was dried by passage through  $CaCl_2$  and  $P_2O_5$  and subsequently analyzed for masses 64 and 66.

The oxygen was obtained by the electrolysis of water, water vapor and hydrogen being removed by passing the gas through dry ice traps and a platinized asbestos furnace. The oxygen was collected as liquid in a copper trap immersed in a dewar of liquid oxygen. The copper trap was connected to the glass system by means of a kovar glass seal. Fig. II shows the electrolysis cell. The water was 0.075 N. in NaOH and was cooled by means of a water condenser extending part way up the centre of the cell. The anode was platinum wire wound in a spiral around the condenser while the cathode was a sheet of platinum bent in the form of a cylinder around the condenser and a short distance from it. A glass tube connected to the top of the cell by a ring seal extended part way into the cell between the anode and the cathode. A cylinder of fiber glass paper was slipped up inside this tube and extended to the bottom of the cell serving to prevent any mixing of the hydrogen and oxygen.

Fig. III shows the complete apparatus. A mercury bubbler on the hydrogen side of the cell could be adjusted to maintain equal pressures on the hydrogen and oxygen sides.



In the actual preparation of the oxygen the system was flushed thoroughly to remove nitrogen by electrolyzing for  $\frac{1}{2}$  hour at atmospheric pressure. Stopcock T 2 was then closed and the oxygen allowed to condense in trap H which was immersed in a dewar of liquid oxygen. As the oxygen was produced faster than it could be condensed, causing an increase of pressure in the oxygen side of the cell, it was found necessary from time to time to lower the temperature of the cooling bath surrounding trap H, causing the oxygen to condense more rapidly with a resultant decrease of pressure. This was accomplished by passing a stream of compressed air over the cooling bath of liquid oxygen in the dewar surrounding trap H.

When it was calculated that sufficient oxygen had been produced, stopcock T 1 was closed and the trap and dewar removed from the line. The trap was then connected to the evacuated thermal diffusion columns and the oxygen allowed to evaporate, filling the columns and the 5 liter reservoir to a pressure of 32 cm. This pressure of oxygen was found to produce a maximum separation in columns similar to ours.<sup>(37)</sup> 8 Samples, 4 from the top and 4 from the bottom were removed at suitable intervals over a period of 106 hours. (Table III) At this time the electrolysis procedure was repeated and the columns filled to atmospheric pressure without stopping the run. 4 sets of samples were removed in the ensuing 8 days of the run.

Following this, the electrolysis apparatus was moved adjacent to the top reservoir. In order to increase the size of this reservoir another 5 liter flask was added. It was coupled to the first one by two arms, one of which was electrically heated to ensure circulation of the gas between the two reservoirs. (Fig. VI) It was then possible to electrolyze into the copper trap and allow the oxygen to vaporize directly into the reservoir system. The new 5 liter flask was filled with oxygen and the stopcocks between the flasks opened. Dry ice was placed in dewars around traps C and D to promote convective circulation and also to remove any traces of water vapor which may have leaked in from the water jacket. 2 sets of samples were removed during the following week. The new 5 liter flask was then



evacuated and filled with 7.5 normal O<sup>18</sup> as before. Unfortunately, shortly after this, one of the leads to the bottom calrod heater burnt out and the run had to be discontinued. One liter of gas was removed from the bottom of the columns as soon as this was discovered. An attempt to save the remainder of the gas was unsuccessful.

Results and Discussion

The analyses of all samples were made with 90° sector type mass spectrometer. (39) The results are tabulated as the isotopic ratio in the top and bottom reservoirs. The precision in all the ratios is better than 1%.

The separation factor was previously defined as  $\frac{C_2^L}{C_2^U}$

where C<sub>2</sub><sup>L</sup> is the concentration of the heavy molecule in the bottom reservoir and

C<sub>2</sub><sup>U</sup> is the concentration of the heavy molecule in the top reservoir.

In place of actual concentrations the abundance ratios of the light to the heavy isotope is taken as a measure of the concentration of the heavy isotope. The separation factor as here used becomes  $\frac{28/29 \text{ (top)}}{28/29 \text{ (bottom)}}$  for

nitrogen, and similarly for the other gases.

Nitrogen <sup>15</sup>

The mass spectrometric analyses of the samples removed from the top and bottom reservoirs are given in Table I. It is seen that a ten fold change in the ratio of the nitrogen isotopes has been effected in a period of 164 hours. Since the N<sup>14</sup>N<sup>15</sup> content of the bottom reservoir has been increased at the expense of the top reservoir, the enrichment factor relative to tank nitrogen is only 4.97 corresponding to an atom % N<sup>15</sup> of 1.77. From Fig. 1 it can be seen that the N<sup>14</sup>N<sup>15</sup>/N<sup>14</sup>N<sup>15</sup> ratio in the bottom



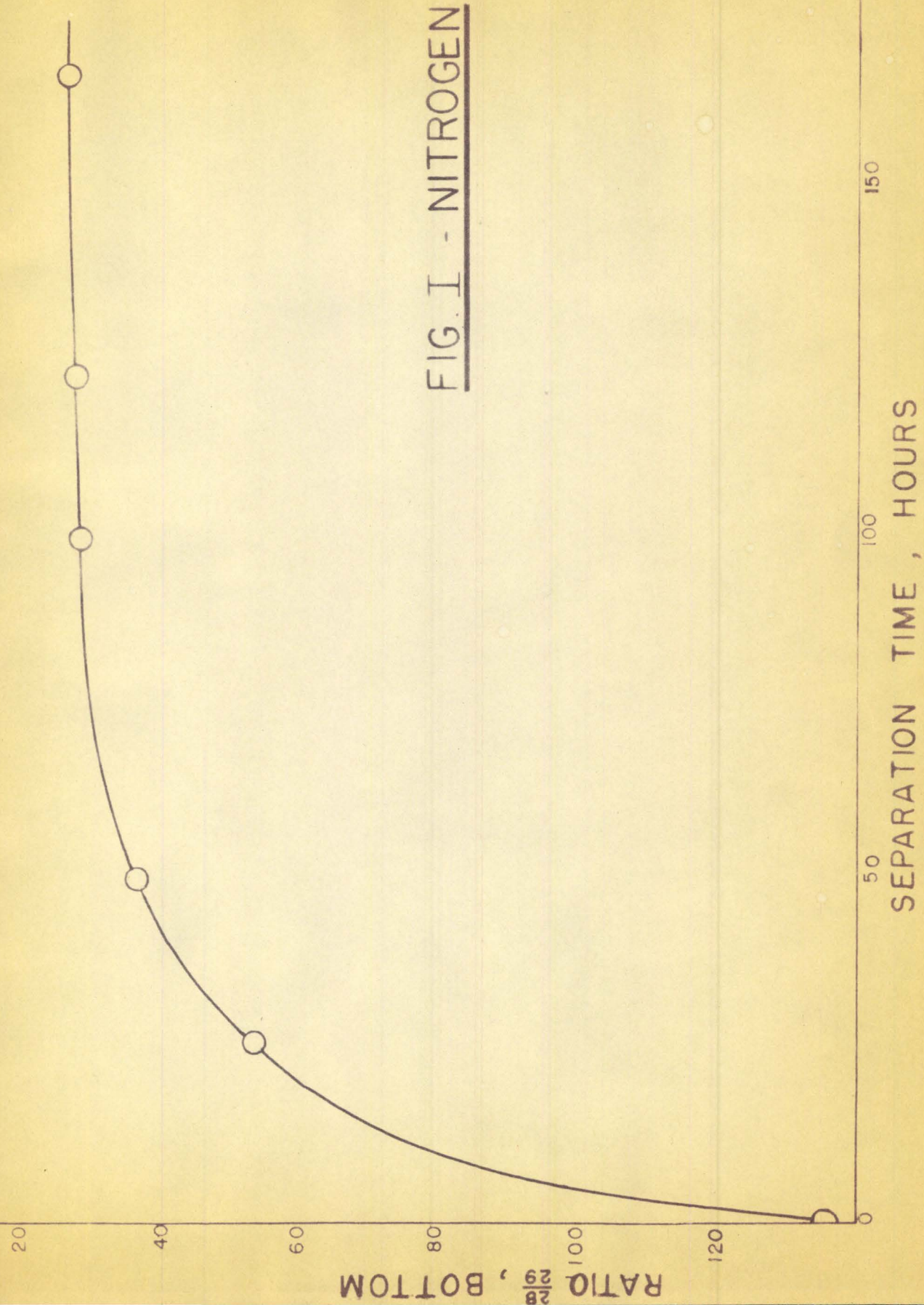


FIG. I - NITROGEN



Table I - Nitrogen

Time (hours)	Top	Ratio $\frac{28}{29}$	Bottom	Separation Factor
0	136		136	1
25.5	170		53.9	3.16
49	202		36.9	5.48
75	217		36.3	5.98
98	247		29	8.52
121	264		30.1	8.75
164.5	280		27.3	10.3

Table II - Sulphur Dioxide

Time (hours)	Top	Ratio $\frac{64}{66}$	Bottom	Separation Factor
0	20.50		20.50	1
24	20.67		19.95	1.036
48	x 20.56		19.88	1.034
72	20.63		19.78	1.043
93	xx		19.71	est. 1.049

x part of sample lost  
 xx sample lost



reservoir approaches equilibrium rapidly becoming 90% of its equilibrium value in 48 hours. These results compare very favourably with those obtained by others using similar columns.

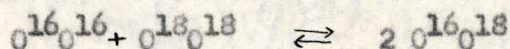
### Sulphur <sup>34</sup>

The mass spectrometric analyses of the SO<sub>2</sub> samples removed during the sulphur run are given in Table II. The 4.9% change produced in the 64/66 ratio of the sulphur isotopes indicates that  $\alpha$  is small but positive. This will give an  $R_t$  value which is also small but positive. This is in agreement with predictions of  $\alpha$  based on viscosity data. (7,10)

The results indicate that the sulphur isotopes can not be separated by the thermal diffusion process using SO<sub>2</sub> gas. This does not necessarily mean that sulphur in the form of some other gas such as SF<sub>6</sub> could not be concentrated by thermal diffusion. No thermal diffusion data has been secured with SF<sub>6</sub> and there is no viscosity data in the literature with which to make predictions. However there is always a disadvantage in using gases of high molecular weight in thermal diffusion columns due to the small mass differences involved and the correspondingly small .

### Oxygen <sup>18</sup>

It is of interest to note that as O<sup>16</sup>O<sup>18</sup> was concentrated at the bottom, an increase of O<sup>18</sup>O<sup>18</sup> was also observed indicating that the calrods catalyze the reaction

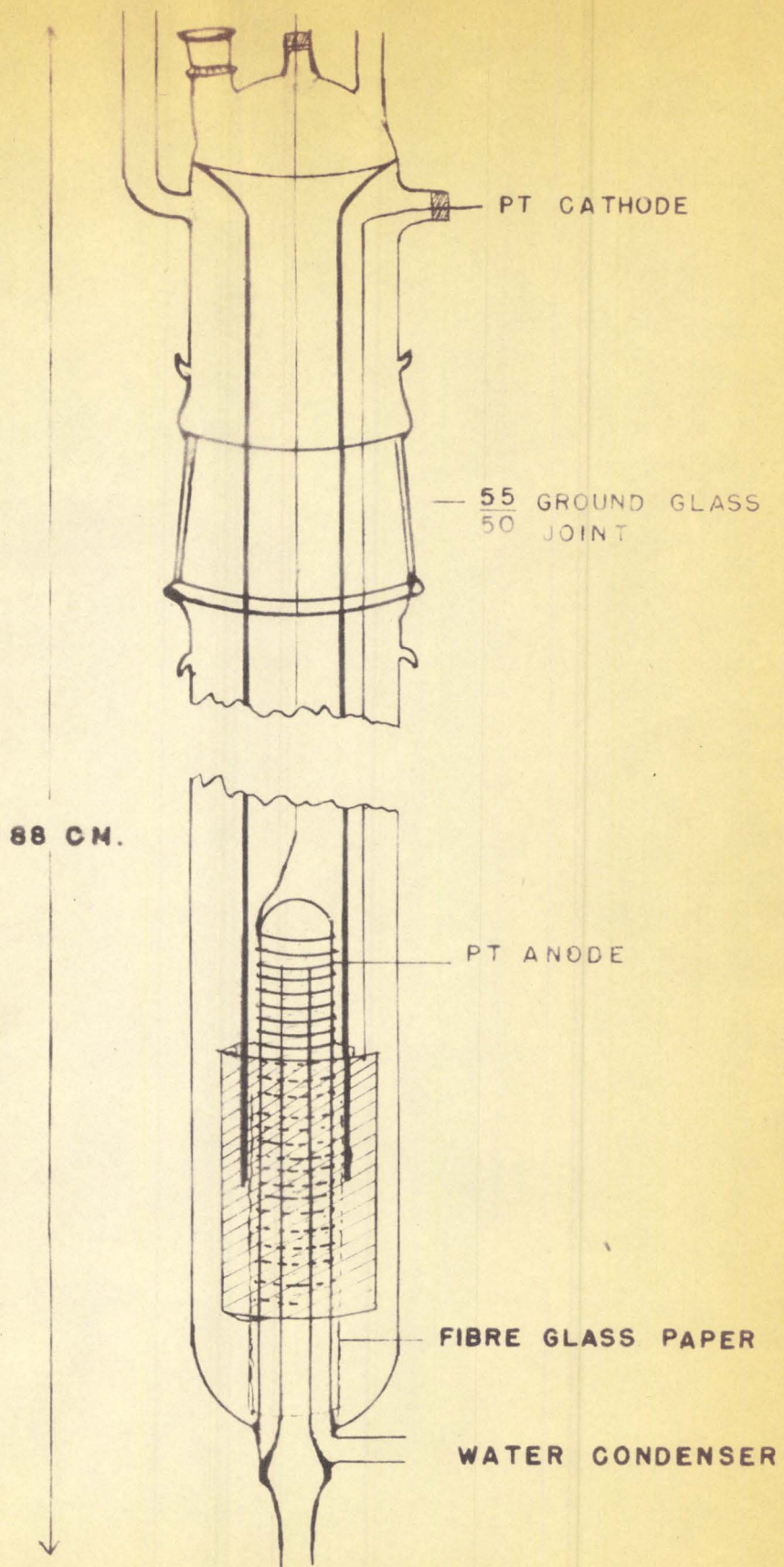


The equilibrium constant for this reaction is

$$K = \frac{[O^{16}O^{18}]^2}{[O^{16}O^{16}][O^{18}O^{18}]} \approx 4$$

if the formation of homopolar and heteropolar molecules is equally probable. The exact value of this equilibrium constant can be determined from an equilibrium mixture by measuring the relative ion currents for masses 32,





**FIG. II**

ELECTROLYSIS CELL FOR PREPARATION  
OF OXYGEN



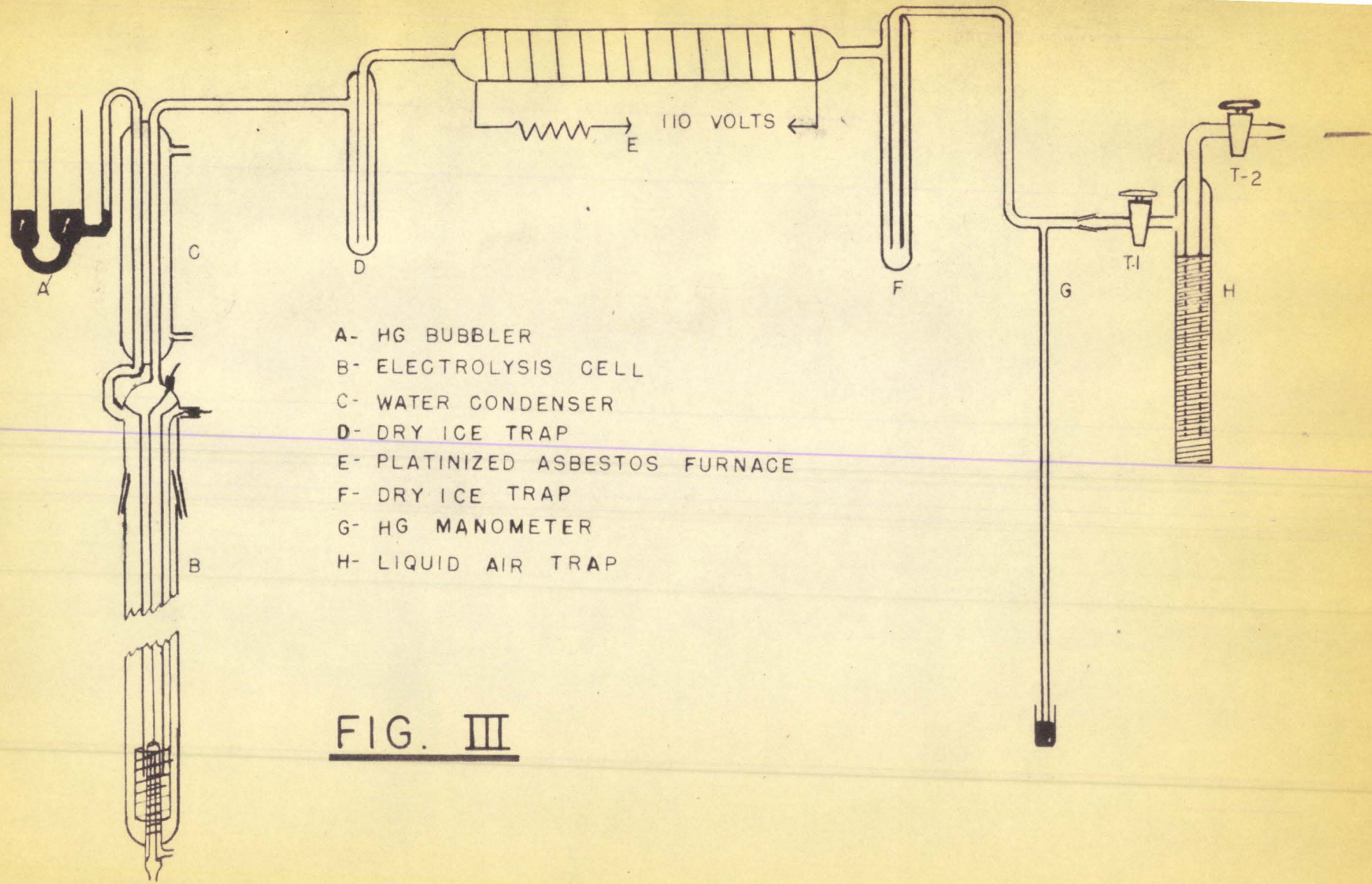


FIG. III

APPARATUS FOR PREPARATION OF OXYGEN

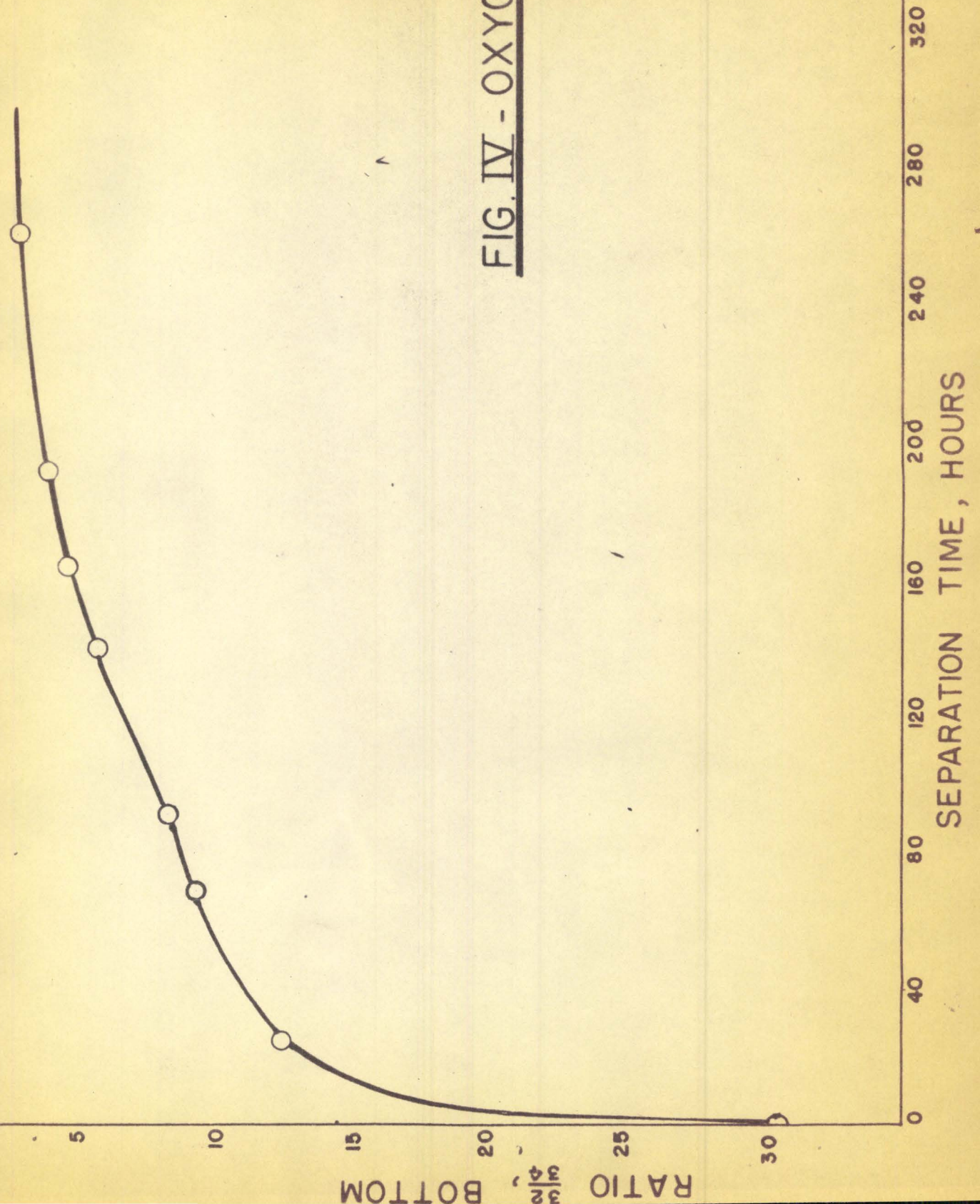


Table III - Oxygen

Time (hours)	Pressure	Ratio $\frac{32}{34}$		Separation Factor
		Top	Bottom	
0	32 cm.	30.5	30.5	1
24.5	32	37.5	12.3	3.05
68.0	32	49.6	9.36	5.30
90.0	32	56.2	8.13	6.91
139	At.	60.3	5.71	10.6
163	At.	85.6	4.64	18.4
190	At.	121	3.84	31.6
259	At.	238	2.89	82.6
283	At.	67.5	3.06	22.0
379	At.	93.6	3.27	28.6



FIG. IV - OXYGEN





34 and 36 in a mass spectrometer. Deviations of the ratio  $\frac{34}{32}^2$  from 4 measures the extent to which the system is displaced from equilibrium. Table 4 gives three sets of mass spectrometer ion currents obtained for the 259 hour sample removed from the bottom of the thermal diffusion columns. The average value of 3.9 for the ratio  $\frac{34}{32}^2$  means that equilibrium between the two kinds of oxygen atoms has been established on the calrod heaters in the thermal diffusion columns.

Table IV

		Mass Spectrometer Ion Currents		
		1	2	3
Mass	32	162.4	206	224
	34	56.13	69.12	75.1
	36	4.72	5.60	6.65
Equilibrium Constant K		4.02	3.78	3.80

$$\text{The Atom \% } O^{18} = \frac{2 \left[ {}_0^{18}O^{18} \right] + \left[ {}_0^{16}O^{18} \right] + \left[ {}_0^{17}O^{18} \right]}{2 \left[ {}_0^{16}O^{16} + {}_0^{17}O^{17} + {}_0^{18}O^{18} + {}_0^{16}O^{17} + {}_0^{16}O^{18} + {}_0^{17}O^{18} \right]}$$

or

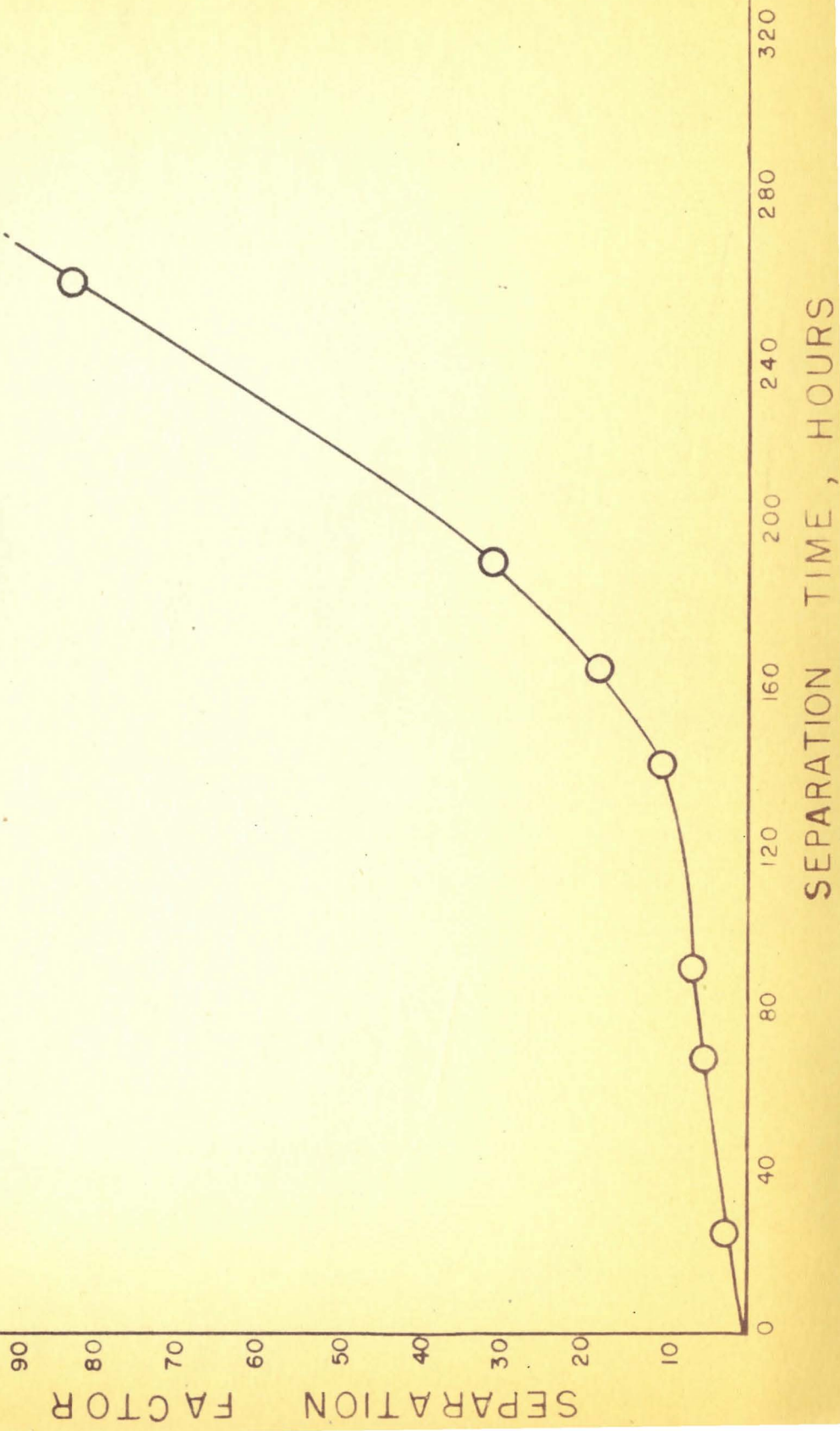
$$= \frac{2[36] + [34] + [35]}{2[32 + 34 + 36 + 33 + 35]}$$

where  $[34]$ ,  $[36]$  etc. are the concentrations of masses 34 and 36 etc. which are proportional to the ion currents produced by these masses in a mass spectrometer.

Table V gives the relative ion currents obtained for masses 32-36, in the mass spectrometric analysis of the 259 hour sample. The average %  $O^{18}$  thus calculated is 14.6. A small fraction of the mass 34 ion current will be due to  ${}_0^{17}O^{17}$  ions. However because of the low concentration of  ${}_0^{17}O^{17}$  this current can be neglected. The atom % of  $O^{17}$  can be calculated in



FIG. V - OXYGEN





a similar manner.

Table V

		Mass Spectrometer Ion Currents	
		1	2
Mass	32	224	162.4
	33	2.50	1.79
	34	75.1	56.13
	35	.41	.3
	36	6.65	4.72
Atom %	$O^{18}$	14.4	14.8
Atom %	$O^{17}$	.47	.46

For the 259 hour oxygen sample the  $O^{17}$  concentration turns out to be 0.46% or about 10 times normal. The liter of oxygen removed from the bottom reservoir at the conclusion of the run was analyzed and calculated to be 4.4%  $O^{18}$ .

Fig. IV shows the rate of approach to the equilibrium concentration of the oxygen isotopes in the bottom reservoir of the thermal diffusion columns during the oxygen separation. The break in the curve at 90 hours corresponds to the addition of a new supply of oxygen bringing the pressure up to 1 atmosphere. Only the values obtained while using one 5 liter flask are plotted; the addition of the second reservoir appeared to disturb the equilibrium at the bottom. Fig. V shows the change in separation factor with time for the oxygen isotopes.



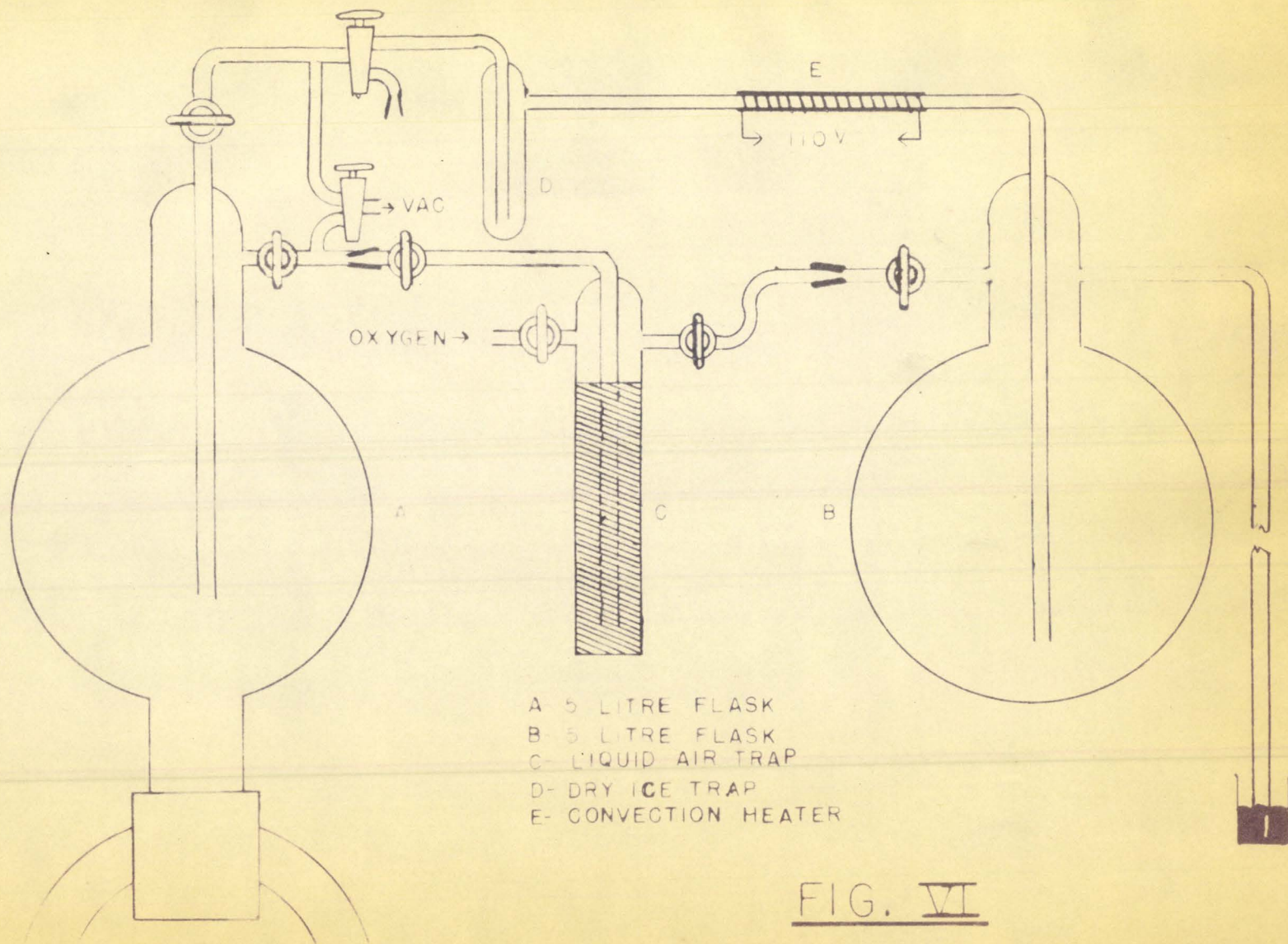


FIG. VI

TOP RESERVOIR USED IN OXYGEN SEPARATION



CONCLUSIONS

The thermal diffusion columns at McMaster have been tested and satisfactory separation factors obtained. A ten fold change in the ratio of the nitrogen isotopes has been effected corresponding to an atom %  $N^{15}$  of 1.77. Sulphur dioxide has been proven to be unsatisfactory for the separation of the sulphur isotopes by thermal diffusion. The oxygen isotopes have been partially separated. Starting with water containing a 7.5 fold enrichment of  $O^{18}$ , samples of oxygen containing a 72 fold enrichment over normal have been produced corresponding to an  $O^{18}$  content of 14.6%. Also one liter of oxygen gas containing 4.4%  $O^{18}$  has been produced.

For the case where we are attempting to concentrate the heavy and rarer isotope, the difficulty in any production is the depletion in the top reservoir of the heavy molecule. In order to utilize the full value of the separation factor an infinite reservoir at the top is necessary. This is effectively what is done when the concentration of the top reservoir is maintained constant by continuously supplying the gas at normal concentration and removing the gas depleted in the heavy isotope. The production of  $O^{18}$  could be greatly increased by electrolyzing into the top reservoir continuously and converting the oxygen depleted in  $O^{18}$  to water. This would ensure a much higher concentration of  $O^{18}$  in the bottom reservoir at equilibrium. Indeed with a separation factor of 82 as here obtained and starting with oxygen containing a 7.5 fold enrichment in  $O^{18}$  the final concentration of  $O^{18}$  in the bottom reservoir might be expected to approach 50%.



## BIBLIOGRAPHY

- (1) D. Enskog, *Physik. Zeits.* 56, 533 (1911) C.A. 5, 1697, (1911).
- (2) S. Chapman. *Phil. Trans.* 217 A, 115, (1917).
- (3) S. Chapman and F.W. Dootson. *Phil. Mag.* 33, 248, (1917).
- (4) R.S. Mulliken. *J. Am. Chem. Soc.* 44, 1033-1051 (1922).
- (5) K. Clusius and G. Dickel. *Naturwiss.* 26, 546, (1938). C.A. 33, 474<sup>B</sup> (1939)
- (6) W.H. Furry, R.C. Jones and L. Onsager. *Phys. Rev.* 55, 1083 (1939)<sup>2</sup>
- (7) R.C. Jones & W.H. Furry. *Rev. of Mod. Phys.* 18, 152 (1946).
- (8) R. Clark Jones. *Phys. Rev.* 58, 111 (1940).
- (9) S.P. Frankel. *Phys. Rev.* 57 661(1) (1940).
- (10) H. Brown. *Phys. Rev.* 57, 242 (1940).
- (11) S. Chapman. *Nature* 146, 431 (1940).
- (12) K.E. Grew. *Nature* 150, 320 (1942).
- (13) A.O. Nier. *Phys. Rev.* 56, 1009-13 (1939).
- (14) A.O. Nier. *Phys. Rev.* 57, 338 (1940).
- (15) L.G. Stier. *Phys. Rev.* 62, 548 (1942).
- (16) W.W. Watson & D. Woernley. *Phys. Rev.* 63, 181-4 (1943).
- (17) A.K. Mann, *Phys. Rev.* 73, 412 (1948).
- (18) H. Brown, *Phys. Rev.* 58, 661(L) (1940).
- (19) A.O. Nier. *Phys. Rev.* 57, 30-34 (1940).
- (20) S. Chapman. *Phil. Mag.* 38, 182-6 (1919).
- (21) L.J. Gillespie. *J. Chem. Phys.* 7, 530-35 (1939).
- (22) L. Waldman. *Naturwiss.* 27, 230 (1939) C.A. 33, 6672<sup>6</sup> (1939).
- (23) A. Bramley & A.K. Brewer. *J. Chem. Phys.* 7, 553-4 (1939).
- (24) W.W. Watson. *Phys. Rev.* 57, 899 (1940).
- (25) K. Clusius & G. Dickel. *Naturwiss.* 28, 461 (1940) C.A. 35, 3162<sup>B</sup> (1941).
- (26) K. Clusius. *Z. Physik Chem. B52*, 348-68 (1942) C.A. 37, 5907<sup>9</sup> (1943).
- (27) W. Groth & P. Harteck. *Naturwiss.* 28, 47 (1943) C.A. 34, (1940).
- (28) A.O. Nier. *Phys. Rev.* 72, 510 (1947).
- (29) B. Atkins, R. Bastick and T. Ibbs. *Proc. Roy. Soc.* A172, 142.



- (30) G.E. Harrison. Proc. Roy. Soc. (London) A181, 93-100 (1942). C.A. 37, 9<sup>8</sup>  
(1943)
- (31) K. Clusius & G. Dickel. Z. Physik Chem. B44, 451-73 (1939).  
C.A. 34, 673<sup>9</sup> (1940).
- (32) H. Akabori et al. Proc. Phys. Soc. Jap. 23, 599-604 (1941), C  
C.A. 36, 333<sup>5</sup> (1942).
- (33) T.I. Taylor & G. Glocker. J. Chem. Phys. 7, 851 (1939).
- (34) W.W. Watson. Phys. Rev. 56, 703 (1939)
- (35) K. Clusius, G. Dickel & E. Becker. Naturwiss. 31, 210, (1943). C.A. 38, 19<sup>9</sup>  
(1944)
- (36) S. B. Welles. Phys. Rev. 69, 586-90 (1946).
- (37) I. Lauder. Trans. Far. Soc. 43, 620 (1947).
- (38) D.L. Prosser, M.Sc. Thesis, (1946).
- (39) R.L. Graham, A.L. Harkness and H.G. Thode, J. Scientific Instruments  
24, 119, (1947).