# THE CONCENTRATION OF THE

## ISOTOPE HELIUM 3

Thesis by

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#### Abstract

The isotope He<sup>3</sup> was concentrated a factor of 10<sup>5</sup> times in a two stage apparatus. The first stage of the apparatus consists of five Clusius-Dickel Thermal Diffusion Columns, and the second stage is a twenty-nine unit Hertz Apparatus.

Gas well helium flowed continually through the Clusius-Dickel stage, but the product was removed only every eight days. This product was then introduced to the Hertz Apparatus in daily amounts. As the final concentration is linear with time, the product of the Hertz Apparatus was removed as the need demanded. A seven day product had a ratio of 0.008 of  $\text{He}^3/\text{He}^4$  as measured by a mass spectrograph. Another seven day product was used to fill a discharge tube. The isotopic shift of  $\lambda$  6678 was resolved by two methods: (1) 15 ft. Rowland mounting and (2) Fabry-Perot Interferometer. The calculated and observed shifts agree within the experimental error.

A table of performance ratings with other isotopic mixtures for the Clusius-Dickel Columns is given, as well as the experimental results of the separation of two different mixtures of gases:  $CO_2$ and  $N_2$ , and  $CO_2$  and He.

The separation factor for a three component mixture in the Clusius-Dickel Columns is derived.

#### I. Introduction

The isotope Helium 3 has long been of great interest. Its spectrum is of theoretical concern and its use as a projectile or a target in nuclear reactions is of obvious value. However its very low concentration in naturally occuring helium presents a difficult problem for the simple isotope concentration methods.

Isotope concentration methods fall into two classes, complete separation methods and concentration methods. The methods described herein fall in the latter class.

Attempts to concentrate gaseous isotopes by diffusion through porous tubes began soon after their discovery. This method, which is based on the fact that all gaseous atoms and molecules have the same kinetic energy at the same temperature, was quite inefficient until Hertz (1) designed his apparatus. Since the diffusion velocities of the atoms vary as the square root of their masses, this apparatus is well suited for increasing the Helium 3 concentration in a mixture of Helium 3 and Helium 4. The ratios of Helium 3 to Helium 4 in four different gas well samples are given as 0.6, 1.4, 1.4, and  $2.0 \times 10^{-7}$  by Aldrich and Nier (2). Hence for successful concentration the separation factor for the apparatus must be of the order of 10<sup>8</sup>. A forty unit Hertz Apparatus gives this factor but since it operates at a pressure of approximately 7 mm. of mercury the time required to obtain useful samples is excessive. The initial concentration stage should treat a large volume of gas at high pressure. This need is met by the thermal diffusion method which operates well with noble gases.

The fact that gaseous molecules of either different sizes or different weights diffuse differently in a temperature gradient was first discovered by Enskog (3) in 1911. The effect is so small however as to make separation by thermal diffusion alone impracticable. It was not until 1938 that Clusius and Dickel (4) combined the effect of thermal diffusion with the change in density of a gas at different temperatures to create a practical method of separation of isotopes and mixtures of different gases. Their apparatus was very simple, consisting of two concentric vertical tubes, one kept hot and the other cold, with the mixture between the tubes. The lighter isotope, because of the temperature gradient moves toward the hot tube while the heavier isotope moves toward the cold tube. At the hot wall of the tube the lighter isotope gets caught in the rising convection current and is swept up the tube; at the cold wall the heavier isotope is swept down by the downward convection current. This is true if the atoms or molecules attract one another according to some inverse power, greater than five, of the distance between them. If the inverse power is less than five the reverse takes place, i.e., the light mass moves toward the cold side and the heavy mass toward the hot side. If the inverse power is five no separation by thermal diffusion occurs. A similar effect takes place if the gas consists of two components of equal weight but with molecules of unequal size. The small molecule goes to the hot side and the large molecule to the cold side. These properties are described in detail by Jones and Furry (5).

The operating pressure of the Clusius-Dickel Columns is not critical as in the case of the Hertz Apparatus. It is possible to design a Clusius-Dickel Column with an operating pressure several hundred times that of the Hertz Apparatus. Accordingly we have designed the first stage of the helium concentrator to consist of five Clusius-Dickel Columns operating at a pressure of several atmospheres, and with an output rate equal to the input rate of the Hertz Apparatus. The final product of the two stages is then obtained at a low pressure. This faciliates handling the very small amount of product. II. Theory and Design of the Apparatus

A. The Clusius-Dickel Columns

The method of calculation of the most efficient Clusius-Dickel Column has been given in great detail by Jones and Furry (5). We require 0.036 grams per day concentrated about a thousand times. In order to get this rate of production it was decided to use four columns in parallel. High pressure operation reduces the tube cross sectional size required for optimum performance.

Using the method of Jones and Furry we have for the transport equation:

$$\mathcal{T}_{i} = HC_{1}(1-C_{1}) + \sigma C_{1} - K \frac{dC_{1}}{dz}$$

where

 $T_{l}$  is the transport of isotope 1 up the column, gm./sec.  $C_{l}$  is the concentration of isotope 1, mole fraction  $\sigma$  is the flow of gas per second through one column, gm./sec.  $H = H^{\circ} h'$ 

$$= \left(\frac{2\pi}{6!}\right) \left(\frac{\propto \varrho^2 g}{\eta}\right) \left(\frac{r_1 + r_2}{2}\right) \left(r_1 - r_2\right)^3 \left(2u\right)^2 h'$$

$$K = K_c + K_d$$

$$K_c = K_c^0 k_c^1$$

$$= \left(\frac{2\pi}{9!}\right) \left(\frac{\varrho^3 g^2}{\eta^2 D}\right) \left(\frac{r_1 + r_2}{2}\right) \left(r_1 - r_2\right)^7 \left(2u\right)^2 k_c'$$

$$K_c = K_c^0 k_c^1$$

 $K_d = K_d^0 k_d^1$ 

$$= 2\pi \rho D\left(\frac{r_i+r_2}{2}\right)\left(r_i-r_2\right) k_d'$$

 $\propto$  is the thermal diffusion coefficient

 is the density of the gas in the column (at the average temperature)

q is the acceleration of gravity

 $\eta$  is the viscosity of the gas (at the average temperature)  $r_1$  is the radius of the outer (cold) tube

 $\mathbf{r}_{2}$  is the radius of the inner (hot) tube

$$u = (T_2 - T_1) / (T_2 + T_1)$$

- T<sub>1</sub> is the temperature of the cold wall, or of the outer tube
- T<sub>2</sub> is the temperature of the hot wall, or of the inner tube

 $D = 1.37 \, \eta/\rho$  (the coefficient of self diffusion)

h', k' and k' are correction factors for cylindrical tubes. Let us assume a pressure of eight atmospheres and, to insure a large yield, the temperatures

$$T_1 = 300^{\circ} K$$
  
 $T_2 = 700^{\circ} K$ .

The data of Trautz and Binkele (6) give

$$\eta = 2.67 \times 10^{-4}$$
 poise

for helium at a temperature of  $500^{\circ}$  K. The coefficient  $\propto$  has been determined experimentally by McInteer, Aldrich, and Nier (7) and has the value

$$x = 0.059 \pm .005$$

In order to keep turbulence down  $K_d^o$  must not be less than  $K_c^o/25$ , and in order to secure the maximum separation factor for a given

length of tube  $K_c^o$  should be equal to  $2K_c^o$ . Hence a good value for the ratio  $K_c^o/K_d^o$  is 10.

Commercial stainless steel tubing comes in outside diameters of multiples of eigths of an inch. It turns out for a wall thickness of 0.035 inches that

> $r_1 = 0.3125$  inches  $r_2 = 0.590$  inches

satisfy the above conditions and result in a density

$$Q = 8.2 \times 10^{-4} \text{ grams/cc.}$$

This density at the temperature of  $500^{\circ}$  K corresponds to a pressure of

P = 8.45 atmospheres.

Substitution of the above values gives:

 $H^{\circ} = 3.26 \times 10^{-4} \text{ gm/sec.}$  $K_{c}^{\circ} = 1.83 \times 10^{-2} \text{ gm-cm/sec.}$  $K_{d}^{\circ} = 1.85 \times 10^{-3} \text{ gm-cm/sec.}$ 

These plane wall values must be modified for concentric cylinders. The corrections were first given by Furry and Jones (8) and are:

$$h' = f + h_{1} \ln (r_{1}/r_{2}) + h_{2} (\ln (r_{1}/r_{2}))^{2} + \dots$$

$$k_{c}' = l + k_{cl} \ln (r_{1}/r_{2}) + k_{c2} (\ln (r_{1}/r_{2}))^{2} + \dots$$

$$k_{d}' = l + u^{2}/3 + k_{d1} \ln (r_{1}/r_{2}) + k_{d2} (\ln (r_{1}/r_{2}))^{2} + \dots$$

Furry and Jones have calculated these values for  $T_1$  and  $T_2$  assuming no change of  $\propto$  with temperature. Thus we have

h' = 1.25 $k_{c}^{i} = 1.45$  $k_{d}^{i} = 0.97$  giving

H = 
$$4.08 \times 10^{-4} \text{ gm}/\text{sec}$$
.  
K<sub>c</sub> =  $2.66 \times 10^{-2} \text{ gm}/\text{sec}$ .  
K<sub>d</sub> =  $1.80 \times 10^{-3} \text{ gm}/\text{cm}/\text{sec}$ .

Assuming a parasitic convection current of 15% of  $K_c$  due to unavoidable construction defects we have

$$K = 1.15 K_c + K_d$$
  
= 3.24 x 10<sup>-2</sup> gm-cm/sec.

For continuous operation we have for the separation factor q

$$q = \frac{1+n}{\exp(-\frac{HL}{K}(1+n)) + n}$$

where

n = <sup>(T</sup>/H

L = length of the column in cm.

The maximum length of available Calrod heating unit is 540  $\rm cm_{\bullet}$ Thus we have

The time required to reach this concentration is given by

$$t_c = q (\mu K/H^2)$$
 seconds

where

 $\boldsymbol{\mu}$  is the mass of gas per unit length of column,

gm. per cm.

Substituting these values we have

If no parasitic current is assumed the values for the same n would be

q = 1550 t<sub>c</sub> = 12.5 days.

In computing the power consumption it is necessary because of the high conductivity of helium to consider only the heat transferred by conduction. Helium, because it is a noble gas, obeys the relation

 $\lambda = 15 \eta R/4M$ 

where

 $\lambda$  is the coefficient of heat conduction in cgs units

R is the gas constant per mole

M is the molecular weight

 $\eta = 2.67 \times 10^{-4}$  poise.

These values give

 $\lambda = 4.97 \times 10^{-4}$  cal/cm-deg-sec.

For the transfer of heat across a cylindrical cross section one uses the relationship

 $Q = 2\pi\lambda(T_2-T_1)/\ln(r_1/r_2)$  per cm. of length. Substitution in this equation gives for Q

Q = 1.96 cal/cm-sec.

and for a length of 540 cm. a total requirement of 4.5 kilowatts. In practice there are losses due to radiation so that one increases this value by 10% to 5.0 kilowatts per column.

The cross sections of one of the Clusius-Dickel Columns one to four are given in Figures 1 and 2. The heating element is a General Electric Calrod. It is 0.460 inches in diameter, 212 inches effective heating length (cold), and has a power rating of 5.0 kilowatts at 200 volts. The Calrod is centered in a stainless steel tube by means of wire rings placed every ten inches along the tube. The outside diameter of this tube is 0.625 inches and its outer wall forms the hot wall of the column. The elongation of this tube gives the temperature difference between the hot and the cold tubes. The hot tube is centered in the cold tube by means of seven thin monel spacers. These spacers contain 24 equally spaced holes to allow the gas to diffuse from one space in the column to another. The top spacer is placed 14 inches from the top of the 0.625 inch tube and the remaining 6 equidistant along the tube, approximately 3 feet apart. Some copper oxide is placed on this top spacer; the most effective location for the removal of hydrogen. The inside diameter of the cold tube is 1.180 inches; this tube is also stainless steel and has a wall thickness of 0.035 inches, the same as the thickness of the wall of the hot tube. A 2.00 inch galvanized iron tube forms the outside of the water jacket. It is centered about the cold tube by two spacers, studded so as not to interfere with the flow of the cooling water. A Sylphon bellows is inserted in this outer jacket to provide the small expansion necessary to prevent water leaks due to the difference in expansion coefficients of the iron and the stainless steel tubes of the water jacket. The Clusius-Dickel Column number 5 was constructed by W. R. Symthe in 1940 and is of similar construction. It is 280 cm. long and has a gas space between a 1.0 inch diameter hot tube and a 1.5 inch diameter cold tube.

The first stage of the complete apparatus consists of five Clusius-Dickel Columns. The block diagram is shown in Figure 3. Columns one to four are connected in paralled at the bottom; i.e., the entrance and exit tubes B and C are connected together. However, in order to stop all possibility of convection from one column to another due to small differences in the average temperature of each column the exit A is separate for each column. The tubes B and C of each column consist of concentric pipes and are connected by means of a small 24 volt motor pump serving to circulate the gas between columns one to four and column five. The housing for the pump is a 3.5 inch steel tube closed off with plates and rubber gaskets at the ends. The pump develops a static pressure of 3 cm. of water. The Clusius-Dickel Column number five is connected at its top to the pump by means of a 0.75 inch diameter tube 4 inches long. Finally the continuous leak at the bottom of column number five consists of a short section of porous tubing 3 mm. in diameter.

The complete Clusius-Dickel set-up is protected in the usual manner. As the cooling water is run at a pressure of 30 pounds per square inch a gauge makes contact and turns of the current if the pressure drops below a certain value, about 8 pounds per square inch. This same gauge also controls the continuous leak at the bottom of column number five, shutting it off in case of power or water failure and thus saving the enriched gas in the columns.

B. The Hertz Gaseous Diffusion Apparatus

The second and final stage is a 29 member Hertz Apparatus. This apparatus is now twelve years old and has been used in many isotope concentrations (9,10).

The individual members are very similar to those of Hertz' given in Figure 4, with only a change in the length of S. The change is such that the ratio of the length of S to the length of R is about one to twelve. If we let

$$1/f = 2 + R/S$$

and call the ratio of the mass of the heavy isotope to the mass of the light isotope  $v^2$  the separation factor for a single stage according to Harmsem (11) is

$$q = \frac{1 - (1 - f)^{v}}{f^{v}}$$

Various values for q as a function of f are given in Table 1.

Table 1						
f	1/11	1/14	1/20			
ą	1.64	1.75	1.78			

The total separation factor of 29 members thus is not less than

total q = q<sup>29</sup> = 1.8 x 10<sup>6</sup> The actual physical construction of the apparatus has been greatly improved. The present apparatus was originally constructed by Wooldridge (9) and in his thesis he states a number of possible improvements:

- 1. The use of larger tubing to connect the members
- 2. Shortening the leads to the members
- 3. Prevention of the circulation of mercury vapor in order to prevent clogging of the apparatus.

The first two of these improvements have been carried out and the circulation of mercury is no longer a matter of such great importance. Actually the one operation of changing the positions of the porous tubes on the supporting frames to facilitate drainage of liquid mercury back to the boilers of the pumps made it possible to carry out all of these changes simultaneously. Close scrutiny of Figure 4 reveals that all the connecting tubes are above the mercury boilers of the pumps; hence all the mercury that passes into the system drains back into the pumps when it liquifies. This is of importance in the actual operation for it means that the apparatus can operate indefinitely without any of the system becoming clogged with mercury as in the case of Wooldridge (9) and Townes (10).

The block diagram for the 29 member unit is given in Figure 5. The volume  $V_s$  for the heavy isotope end is a 22 liter flask and the volumn  $V_1$  for the light isotope end is approximately 30 cc. The flask  $V_1$  is a container for the storage of the enriched product.

The details of the equipment at the light end of the apparatus are shown in Figures 6 and 7. In order that samples can be removed without shutting down the complete apparatus and losing most of the enriched helium in the process an extra pumping system is installed between the flasks  $V_1$  and  $V_1'$ . This makes it possible to change  $V_1'$  without distrubing the equilibrium of the system. A liquid air trap filled with glass wool and a porous tube obstruction are also placed between  $V_1$  and  $V_1^{!}$ . The porous tube slows down the passage of the gas being transferred from  $V_1$  and  $V_1$ ; thus allowing the liquid air trap more time to remove the mercury from the enriched gas. A copper oxide tube is sealed into the system above  ${\tt V}_1$  . The stopcock below  ${\tt V}_1$  is a mercury valve. The details of construction are shown in Figure 6. It consists of a steel pin which is forced into a ground glass joint by the mercury from the reservoir shown below A in Figure 5. From side A (Figure 6) the valve will stand quite high pressures; thus allowing one to force the enriched gas from  $V_1$  to  $V_1'$ .

The stopcocks, with the exception of A and B (Figure 5), are all the mercury seal type; silicon vacuum grease is used as the temperature of the room is around  $110^{\circ}$  F. The pump (Figure 5) is a mercury diffusion pump and is used to circulate the gas out of the 22 liter flask V<sub>s</sub> into the main part of the apparatus. It was found that the mercury from this pump slowly made its way over into V<sub>s</sub> so an air trap with the bottom returning to the pump's boiler was placed in the system between the high pressure side of pump and V<sub>s</sub>. This device returns most of the mercury to the boiler of the pump, thus preventing the pump from going dry. The only seal other than glass in the system is a steel plate waxed on top of  $V_1$  at the heavy end. The two glass tubes which go through the plate into the flask are separated from the metal plate by rubber stoppers. The wax is the standard mixture of one-half beeswax and one-half rosin.

The Hertz Apparatus is protected in order that it can be operated continuously. The protection consists of an automatic shutoff in the gas main. It is actuated if the pressure of the gas in the apparatus rises to over 12 cm., or if the cooling water ceases to flow, or if the pressure in the gas main fails. A burner under a bimetallic strip actuates the latter device. III. The Operation of the Apparatus

As stated previously the Clusius-Dickel Columns shown in the block diagram of Figure 3 form the first stage of the apparatus. For a preliminary check of performance, two mixtures were run through the column with the results given in Appendix 1.

The helium gas (purity is at least 99.9%) is let out of the high pressure cylinder by means of a regulator valve in order to maintain a constant pressure in the apparatus. From the regulator valve it passes through a hot tube containing copper oxide wire to remove hydrogen impurity in the helium. From the copper oxide tube it flows into columns one to four at the tubes labeled A. After passing through the columns and the pump the gas leaks steadily out of the lower end of column number five. The small porous tube was shortened until the rate of leakage is about 500 cc. of helium per minute at room temperature and pressure.

The apparatus requires no attention except to replace the helium cylinder when its pressure falls too low, usually in a week or so. The elongation of the hot tube can be read through the gauge glass to an accuracy of 1/64th of an inch. This corresponds to 5° C change in temperature. The temperature of the different columns varies about 15°C (probably owing to small voltage changes) during a twenty-four hour period. The temperature of the cooling water increases about 12° C on going through the apparatus. This is the same order of magnitude as the daily change in the heating elements.

In order to remove the enriched sample from the tops of the columns one to four a brass reservoir of 225 cc. volume was constructed. If the weight of helium contained by this volume at 109 pounds per square inch and at room temperature is calculated, it takes about eight days for the columns to produce this amount. So the total time from the start to this point is about sixteen days. However the operating point is such that if it is taken out after fourteen days the separation factor has dropped from 775 to only 710.

This reservoir is placed at the top of columns one to four and evacuated simultaneously with the tubes leading to the valves on the columns. Then the valves on each of the four columns are opened and closed in such a manner that the enriched sample from each column contributes one-fourth of the total helium in the reservoir. The contents are then transferred through a hot tube containing a palladium sponge (to remove any hydrogen impurity) into a two liter flask. The pressure of the enriched helium in this flask is always less than one atmosphere, hence any leak in it merely prolongs the operation time of the Hertz Apparatus and none of the enriched helium is lost. This flask is then sealed into the Hertz Apparatus and constitutes the block labeled "helium supply" in Figure 5.

The Hertz Apparatus is operated as described in the paper of Wooldridge (9) and Townes (10). The apparatus is first evacuated to a pressure of one micron. Then after starting the gas burners under the diffusion pumps the enriched helium is allowed to flow through the hot copper oxide tube into the main part of the apparatus until a pressure

of about 6 to 7 mm. is reached, this pressure being measured by a mercury manometer at the heavy end near the 22 liter flask. The stopcocks at the heavy end are then closed to shut-off completely the helium supply and the copper oxide tube from the system.

The apparatus is allowed to run for 24 hours under these conditions. The pressure at the heavy end is 6 to 7 mm. on the high pressure side of the pumps and zero, as measured on the mercury manometer, on the low pressure side. Due to the pressure drop along the apparatus from the light end to the heavy end these two pressures are about 10 and 1 mm. respectively at the light end on the high and low pressure sides of the pumps. According to Wooldridge (9) the ratio of 1/10 will reduce the separation factor about 6% per stage or a total amount of 30% for the five stages next to the light end.

After running for 24 hours, the stopcocks which isolate the five stages at the light end are closed. Then the rest of the system is evacuated to a pressure of several microns and more helium is let in through the copper oxide tube from the helium supply. The apparatus runs under these conditions for 12 hours. At the end of this time it is assumed that the concentration is again similar to that at the time the light end was isolated, so the stopcocks isolating the light end are opened and the system continues to operate under these conditions for another 12 hours. Each succeeding 24 hour period is exactly like the second 24 hour period and this process is continued until the helium supply is exhausted.

To remove the enriched helium from  $V_1$  one turns the stopcocks which isolate  $V_1$  from the system and raises the mercury reservoir. The rising mercury forces the helium in  $V_1^i$  where it is then sealed off with a torch.

The glass wool liquid air trap removes mercury so thoroughly that it cannot be detected spectroscopically in the sample. The copper oxide tube also removes hydrogen so completely that it cannot **h**e detected spectroscopically either. IV. Results and Comparison with Theory

As no mass spectrometer with high enough sensitivity to measure the product of the Clusius-Dickel Columns was available it is difficult to compare the theoretically predicted result and the actual result. However if one assumes that the Clusius-Dickel Columns operate according to the theory, then one obtains a performance rating of the Hertz Apparatus.

The product taken from the first stage had, according to the theory, the following specifications:

1. 1000 cc. of helium at standard conditions

After processing by the Hertz Apparatus the analysis of Consolidated Engineering Corporation gave:

> 1. 0.24 cc. of helium at standard conditions 2.  $He^3/He^4 = 0.008$

To determine the concentration of the  $He^3$  in  $V_1$  of the Hertz Apparatus consider the following specifications:

1.  $V_1 = 30 \text{ cc.}$ 

2. Volume of each stage = 110 cc.

3. Separation factor per stage = 1.6.

Let

$$R = He^{3}/(He^{3} + He^{4})$$
 in  $V_{1}$   
k = total number of cc. of  $He^{3}$  in the last five stages,

then

k = 110 R 
$$\left(\frac{V_1}{110} + \frac{1}{1.5} + \frac{1}{1.5^2} + \frac{1}{1.5^3} + \frac{1}{1.5^4} + \frac{1}{1.5^5}\right)$$

and on solving this for R we have

$$R = k/(V_1 + 166)$$
$$= 7.6/(196)$$
$$= 3.9\%$$

If one compares this value with the sample analyized by Consolidated Engineering the ratio of the actual value to the theoretical value is 0.8/3.9 or 20%. If one divides this amount between the two stages the efficiency of each is about 45%. V. Isotopic Shift in the Helium Line Spectrum.

The mass difference of the nuclei of He<sup>3</sup> and He<sup>4</sup> produces a change in the energy levels of the different states of the extranuclear electrons. This effect can be divided into two parts, the normal effect and the specific effect. The former applies to all energy levels and its magnitude is given by

$$\Delta W_{T} = (m/M) W$$

where

m is the mass of the electron
M is the mass of the nucleus
W is the term value of the energy level for
a nucleus of infinite mass

For hydrogen-like atoms the normal effect accounts for the total change; however for more complex atoms the specific effect must be taken into account. This effect amounts to an additional change in the P levels only. Hughes and Eckart (12) have calculated this energy change to be

$$\Delta W_2 = \pm (128/3) (m/M) (R_{\infty}) (Z_1 Z_2)^5 n^3 (n^2 - 1) \frac{(Z_1 n - Z_2)^{2n - 4}}{(Z_1 n + Z_2)^{2n + 4}}$$

where

m is the mass of the electron M is the mass of nucleus  $R_{oo}$  is the Rydberg constant for infinite mass n is the quantum number of the p electron  $Z_1$  is the effective nuclear charge for the ls electron  $Z_2$  is the effective nuclear charge for the np electron. If one considers the spectrum line  $2^{1}P-3^{1}D$ ,  $\lambda$  6678 the normal effect is

$$\Delta \nu_{i} = (m/\lambda)(\frac{1}{M_{4}} - \frac{1}{M_{3}})$$

=-0.681 cm.-1

Eckart (13) has calculated the values of  $Z_1$  and  $Z_2$  and has found

 $Z_1 = 2.003$  for the ls electron

$$Z_2 = 0.965$$
 for the 2p electron.

The specific effect is

$$\Delta v_{2} = (128/3)(\frac{m}{M_{4}} - \frac{m}{M_{3}})(R_{00})(Z_{1}Z_{2})^{5} n^{3}(n^{2}-1) \frac{(Z_{1}n - Z_{2})^{2n-4}}{(Z_{1}n + Z_{2})^{2n+4}}$$
  
=-0.364 cm<sup>-1</sup>.

and the total change is

$$\Delta v = \Delta v_i + \Delta v_z$$
$$= -1.045 \text{ cm}^{-1}$$

or

$$\Delta \lambda$$
 = 0.466 Å

Using the 15 ft. Rowland mounting at the Mt. Wilson Observatory with a 5 inch concave grating and a dispersion of 3.60 Å/mm. in the first order we photographed the line  $\lambda$ 6678. From comparator readings, the average value of two different photographs shows

$$\Delta \lambda = 0.471 \pm .009 \text{ Å}.$$

The agreement is within experimental error.

The shift was also measured with a Fabry-Perot Interferometer. With a 3.0 mm. etalon we obtained photographs of two interference patterns of  $\lambda$ 6678. Measurements of the shift in six successive orders of the two microphotometer tracings (one is shown in Figure 8) give

$$\Delta \lambda = 0.467 \pm .004 \text{\AA}.$$

This also agrees very well with the calculated shift.

No other lines were examined as nearly all of them were either too weak, or were triplets, or were such that the specific and normal shifts were in opposite directions, thus making the total shift very small.

#### Appendix 1

Mixtures of Different Gases in the Clusius-Dickel Column

Before starting the helium through the first stages of the apparatus it was thought advisable to check its operation with some mixtures of gases that would separate rapidily and could be measured simply. Two mixtures were chosen:

1. Air (nitrogen) and carbon dioxide

2. Helium and carbon dioxide.

The mass difference in both cases is substantial and because of its high boiling point carbon dioxide lends itself to easy solidification through cooling by liquid air.

Jones and Furry (5) state that for most mixtures of gases  $\propto$  lies between 0.2 and 0.02. If one assumes

### $\propto = 0.1$

for air and carbon dioxide, a temperature difference of 280°C, and operates at a pressure of 94 pounds per square inch the separation factor q should be of the order of 1.5 and the time to achieve this of the order of 10 hours. Actually we measured

> q = 1.35 t<sub>c</sub>= 15 hours.

This is quite good as a substantial amount was removed from the top of the column for the analyses.

With the helium and carbon dioxide mixture we have

## a = 0.44

from the data of Elliott and Masson(14). With a pressure of 87 pounds per square inch and a temperature difference of 280°C the calculated values are

q = 6.0

tc= 1 hour

The actual results that were obtained are given in Table II.

Table II						
time (hrs.)	% He at top	q				
0	4.4	-				
6	40.	.9				
12	31.	7				
Heat turned off and allowed to stand for 24 hrs.						
36	2.2	12				

The results were better than expected. The reason for the final value of the helium percentage being lower than the initial is accounted for by the fact that a substantial amount of the helium was removed. for each of the two analyses at 6 and 12 hours.

The method of measurement consisted in drawing off 225 cc. of the gas at gauge pressure of 10 pounds per square inch from the top of one column. The reading of 10 pounds per square inch was due in each case to both components. The container was then submerged in liquid air and the resulting pressure was then due to the non-condensable component only. With proper corrections for the temperature the percentages of the air or the helium are in direct ratio to the resulting pressure at liquid air temperature and the initial pressure at room temperature.

## 26 Appendix 2

Other Isotopic Mixtures in the Clusius-Dickel Column.

It is of interest to determine how well this thermal diffusion apparatus would work with other isotopic mixtures. In calculating these results the same procedure is used as in the case of helium. The density of the gas is computed in order that the ratio of  $K_c$ to  $K_d$  would be 10. The temperature difference is  $300^{\circ}$  C.; however, this will affect only the rate of production and not the final separation factor. A parasitic convection current of 15% of  $K_c$  is assumed. The viscosity data are taken from the work of M. Trautz (15,16). The results are given in Table III.

Table III					
Gas	tc (hrs.)	q	Production rate gm./sec. x 10	$\propto$ x 10 <sup>2</sup>	
He <sup>3</sup> /He <sup>4</sup>	172	775	1.04	5.9	
$\frac{c^{13_{H_{\underline{4}}}}}{c^{12_{H_{\underline{4}}}}}$	50	2.0	4.16	0.77	
N <sup>15</sup> /N <sup>14</sup>	42	2.3	7.30	0.86	
017/016	35	2.0	8.32	0.65	
018/016	17	3.8	8.32	1.27	
A <sup>36</sup> /A <sup>40</sup>	15	7.2	10.4	2.06	

The results show clearly the advantage of helium over the other gases, even argon. It must be kept in mind that the columns were designed for helium; however, its high value of  $\propto$  is the most important factor as q varies with the exponential of  $\propto$ . Note also that the production rate would be the same for all the mixtures if it were measured in moles per second.

#### Appendix 3

Separation Factors for a 3 Component Mixture in a Clusius-Dickel Column

As many gaseous mixtures contain more than two components, it was thought desirable to develop the equations for the separation factors of a 3 component mixture. Following the method of Jones and Furry (5) we use an idealized apparatus consisting of the two walls a distance of 2w cm. apart and B cm. wide. The wall at -w is cold  $(T_1)$  and at +w hot  $(T_2)$  (see Figure 9).

The assumptions are the same as given by Jones and Furry and are:

- 1. The density  $\varsigma$ , the viscosity  $\eta$ , and the ordinary diffusion coefficient D are independent of temperature except in computation of the convection velocity  $\varsigma$  is represented by a linear function of T.
- 2. The model consists of two columns of gas, one moving upward and the other downward, and each have a constant velocity across its cross section.

To derive this average velocity consider the hydrodynamical equation for steady non-turbulent flow under the influence of gravity

$$\eta \frac{d^2 v_z(x)}{d^2 X^2} = (p - \overline{p})g$$

where

$$\rho = \overline{\rho} \left( 1 - \frac{T - \overline{T}}{\overline{T}} \right)$$

$$T = \overline{T} + \frac{X \Delta T}{2 w}$$

thus we have

$$\eta \frac{d^2 v}{d x^2} = - p g \frac{x \Delta T}{2 \omega T}$$

Here P is regarded as a constant. Integration gives

$$V = \frac{\rho q \Delta T}{12 \eta w T} \times (w^2 - x^2)$$

Since

$$\overline{\nabla} = \frac{1}{w} \int_{0}^{w} v \, dx$$

we have

$$\overline{V} = \frac{g g w^2}{48 \eta} \left( \frac{\Delta T}{\overline{T}} \right)$$

The equation for ordinary diffusion of a two component mixture is

$$C_{i}(\underline{\vee}_{i}-\underline{\vee})=C_{i}C_{z}(\underline{\vee}_{i}-\underline{\vee}_{z})=-D_{iz}\nabla C_{i}$$

where

ci is the fractional molar concentration of component i (i=1,2)

 $\underline{v}_i$  is the velocity of component i

 ${\tt D}_{12}$  is the coefficient of ordinary diffusion.

When one includes thermal diffusion the equation becomes

$$C_{1}(V_{1}-V)=-D_{12}(\nabla C_{1}-\alpha C_{1}C_{2}\nabla \log T)$$

where

 $\prec$  is the coefficient of thermal diffusion.

If we apply the foregoing to a 3 component mixture we obtain

$$C_{1} C_{3} (\underline{V}_{2} - \underline{V}_{3}) = - D_{13} (\nabla C_{1} - A_{13} C_{1} C_{3} \nabla \log T)$$

$$C_{2} C_{3} (\underline{V}_{2} - \underline{V}_{3}) = - D_{23} (\nabla C_{2} - A_{23} C_{2} C_{3} \nabla \log T)$$

assuming no interaction between  $\mathbf{c}_1$  and  $\mathbf{c}_2$  as they are both small. Since

 $C_1 + C_2 + C_3 = 1$ 

$$C_1 \underbrace{V_1}_{} + C_2 \underbrace{V_2}_{} + C_3 \underbrace{V_3}_{} = \underbrace{V}_{}$$

we can eliminate  $\underline{v}_3$  leaving

$$c_{1}c_{3}(\underline{V}-\underline{V}) = -(1-c_{1})D_{13}(\nabla c_{1} - \alpha_{13}c_{1}c_{3}\nabla \log T) + c_{1}D_{23}(\nabla c_{2} - \alpha_{23}c_{2}c_{3}\nabla \log T)$$

$$c_{2}c_{3}(\underline{v}_{2}-\underline{v})_{2}-(1-c_{2})D_{23}(\nabla c_{1}-\alpha_{23}c_{2}c_{3}\nabla \log T) + c_{2}D_{13}(\nabla c_{1}-\alpha_{13}c_{1}c_{3}\nabla \log T)$$

The transport equations are

$$\mathcal{T}_{1} = \rho \left( C_{1}^{\mathcal{I}} - C_{1}^{\mathcal{I}} \right) \overline{v} \omega B - 2 \omega B \rho D_{13} \frac{dc_{1}}{dz}$$
$$\mathcal{T}_{2} = \rho \left( C_{2}^{\mathcal{I}} - C_{2}^{\mathcal{I}} \right) \overline{v} \omega B - 2 \omega B \rho D_{23} \frac{dc_{2}}{dz}$$

where

 $c_1^{I}$  is the concentration of component one in region I  $c_1^{II}$  is the concentration of component one in region II. At equilibrium we have

$$\underline{\mathbf{v}} = \mathbf{0}_{\bullet}$$

As the velocity of the gas due to diffusion is in the x-direction we have

$$\underline{V}_{1} = V_{1X}$$
$$V_{2} = V_{ZX}$$

Also we can set

$$\nabla c_{1} = \frac{C_{1}^{T} - C_{1}^{T}}{W}$$

$$\nabla c_{2} = \frac{C_{2}^{T} - C_{2}^{T}}{W}$$

$$\nabla \log T = \frac{\Delta T}{2\omega T}$$

Thus we have

$$\begin{split} \rho c_1 V_{1X} &= -\rho \frac{1-C_1}{c_3} D_{13} \left( \frac{c_1^{\mathcal{T}} - c_1^{\mathcal{T}}}{w} - \frac{\mathcal{A}_{13} c_1 c_3 \Delta T}{2 \omega T} \right) \\ &+ \rho \frac{c_1}{c_3} D_{23} \left( \frac{c_2^{\mathcal{T}} - c_1^{\mathcal{T}}}{w} - \frac{\mathcal{A}_{23} c_2 c_3 \Delta T}{2 \omega T} \right) \end{split}$$

$$g_{C_{2}} V_{2x} = -g \frac{1-c_{2}}{c_{3}} D_{23} \left( \frac{C_{2}^{T} - C_{2}^{T}}{\omega} - \frac{A_{23} C_{2} C_{3} \Delta T}{2 \omega T} \right) + g \frac{C_{2}}{C_{3}} D_{13} \left( \frac{C_{2}^{T} - C_{2}^{T}}{\omega} - \frac{A_{13} C_{2} C_{3} \Delta T}{2 \omega T} \right)$$

At equilibrium the effects which tend to change  $c_1^{II} - c_1^{I}$  and  $c_2^{II} - c_2^{I}$  must add to zero. These effects are:

- 1. Movement of the columns of gas causes  $c_i^{II}$  to decrease by the amount  $\overline{v} (dc_i/dz)$  per second, and  $c_i^{I}$  to increase by the same amount.
- 2. Transverse flow of the lighter molecules, which is caused by ordinary diffusion and thermal diffusion; the magnitude of this effect is  $c_i v_{ix}/w$

The sums of these must be zero, thus

$$\frac{C_{i}V_{ix}}{\omega} - \overline{v} \frac{dc_{i}}{dz} = 0$$

$$\frac{C_z V_{zx}}{w} - \overline{v} \frac{d c_z}{dz} = 0$$

With the use of these two equations we can eliminate  $v_{1x}, v_{2x}$ , and  $c_i^{II} - c_i^{I}$ and the transport equations become

$$\mathcal{T}_{1} = H_{13} c_{1} c_{3} - \left(K_{c_{13}} + K_{d_{13}}\right) \frac{dc_{1}}{dz} + K_{c_{13}} \left(c_{2} \frac{dc_{1}}{dz} - c_{1} \frac{dc_{2}}{dz}\right)$$

$$\mathcal{T}_{2} = H_{23} c_{2} c_{3} - \left(K_{c_{23}} + K_{d_{23}}\right) \frac{dc_{2}}{dz} + K_{c_{23}} \left(c_{1} \frac{dc_{2}}{dz} - c_{2} \frac{dc_{1}}{dz}\right)$$

where

$$H_{13} = \frac{A_{13} p^2 q \omega^3 B}{96 \eta} \left(\frac{\Delta T}{\overline{T}}\right)^2$$

$$H_{23} = \frac{\mathcal{A}_{23} p^2 q \omega^3 B}{96 \eta} \left(\frac{\Delta T}{\overline{T}}\right)^2$$

$$K_{c_{13}} = K_{c_{23}} = \frac{p^3 q^2 w' B}{2304 \eta^2 D} \left(\frac{\Delta T}{\overline{T}}\right)^2$$

•

$$K_{dis} = K_{d23} = 2 \omega \rho B D$$

$$D_{13} = D_{23} = D$$

$$K_{c_{13}} = K_{c_{23}} = K_{c}$$

$$K = K_{c}$$

$$\mathcal{T}_{i} = H_{13}c_{i}c_{3} - K \frac{dc_{i}}{dz} + K \left[ c_{2} \frac{dc_{i}}{dz} - c_{i} \frac{dc_{2}}{dz} \right]$$

$$\mathcal{T}_{z} = H_{23}c_{2}c_{3} - K \frac{dc_{2}}{dz} + K \left[ c_{i} \frac{dc_{2}}{dz} - c_{2} \frac{dc_{i}}{dz} \right]$$

The separation factor is defined as the ratio of the concentrations when the transport reaches zero. Hence on setting

$$T_{1} = 0$$
$$T_{2} = 0$$

we have

$$H_{13}(1-c_{1})c_{1} - K \frac{dc_{1}}{dz} = H_{13} C_{1} c_{2} + K \left(c_{1} \frac{dc_{2}}{dz} - c_{2} \frac{dc_{1}}{dz}\right)$$
$$H_{13}(1-c_{2})c_{2} - K \frac{dc_{2}}{dz} = H_{23} C_{1} c_{2} + K \left(c_{2} \frac{dc_{1}}{dz} - c_{1} \frac{dc_{2}}{dz}\right)$$

To solve these we first rearrange them so that we have

$$\frac{dc_i}{dz} = f(c_i, c_z)$$

$$\frac{dc_z}{dz} = g(c_i, c_z).$$

Putting in the initial values of  $\mathbf{c}_1$  and  $\mathbf{c}_2$  and integrating we have

$$c_1 = z f(c_{10}, c_{20}) + c_{10}$$
  
 $c_2 = z g(c_{10}, c_{20}) + c_{20}$ 

This process is repeated until one attains the degree of approximation needed. With these two equations the series solutions become evident after several operations. The solutions are

$$C_{1} = C_{10} e^{\frac{H_{13} z}{K}} - C_{10} C_{10} \left( e^{\frac{H_{13} z}{K}} - 1 \right) - C_{10} C_{20} \left( e^{\frac{H_{13} + H_{23}}{K}} - e^{\frac{H_{13} z}{K}} \right)$$

$$C_{2} = C_{20} e^{\frac{H_{23}Z}{K}} - C_{20} C_{20} \left( e^{\frac{H_{23}Z}{K}} - 1 \right) - C_{10} C_{20} \left( e^{\frac{H_{13} + H_{23}Z}{K}} - e^{\frac{H_{23}Z}{K}} \right)$$

The separation factors are

$$q_{13} = c_{1z}/c_{10}$$
  
 $q_{23} = c_{2z}/c_{20}$ 

thus

8

$$q_{13} = e^{\frac{H_{13}Z}{K}} \left[ 1 - C_{10} \left( 1 - e^{-\frac{H_{13}Z}{K}} \right) - C_{20} \left( e^{\frac{H_{23}Z}{K}} - 1 \right) \right]$$

$$q_{23} = e^{\frac{H_{23}Z}{K}} \left[ 1 - \zeta_{20} \left( 1 - e^{-\frac{H_{23}Z}{K}} \right) - C_{10} \left( e^{\frac{H_{13}Z}{K}} - 1 \right) \right]$$

An example is the 3 component mixture of oxygen. We have  $c_{10}(0^{16}0^{17}) = 0.0004$   $c_{20}(0^{16}0^{18}) = 0.002$  $H_{13} = 6.11 \times 10^{-5} \text{ gm./sec.}$ 

$$H_{23} = 1.2 \times 10^{-4} \text{ gm}\text{./sec.}$$
  
K = 4.9 x 10<sup>-2</sup> gm-cm./sec.

then

$$q_{17} = 1.97(1 - 0.0004(1 - 0.51) - 0.002(3.82 - 1))$$
  
= 1.96  
$$q_{18} = 3.82(1 - 0.002(1 - 0.26) - 0.0004(1.97 - 1))$$
  
= 3.81

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Figure 3



Figure 4















Photometer Tracing of Fabry-Perot Pattern



