A Thesis

Submitted in Partial Fulfilment of

the Requirements for the Degree

Master of Science.

by

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at

McMaster University,

Hamilton, Ontario,

May 1946.

The Construction and Operation of

a Thermal Diffusion Column.

Introduction

The first observation of the phenomenon of thermal diffusion was made by Soret in 1878[1,2]. He found that a concentration gradient was set up in a liquid solution when a temperature gradient existed in the solution. Hence the lighter molecules or ions in the solutions moved toward the hotter part of the solution faster than the heavier particles, which distributed the homo-geneity of the solution. Two gases or gaseous isotopes were separated in the same way by a temperature gradient. A rigorous mathematical and theoretical treatment was given to thermal diffusion by Enskog in 1911, and independently by Chapman in England in 1917[1]. In 1918 first experimental data was obtained by Chapman and Dootson.

Mullikan discussed the use of the thermal diffusion process for the separation of gaseous isotopes, but concluded that other methods at that time superior[3]. However, he did not consider the new twist given to the application of thermal diffusion by Clusius and Dickel which consisted of thermal diffusion in conjunction with convection currents which increased the effect of thermal diffusion enormously. In order to produce this effect, they used a specially designed column consisting of two concentric tubes mounted vertically, the inner one of which was a hot wall and the outer one a cold wall. A temperature gradient was set up radially from the cold wall to the hot wall. Then the convection currents carried the light molecules, concentrating at the hot wall, up the tube and brought the heavier molecules, at the cold wall, down the cold wall[4]. This effect is sometimes called thermal syphoning.

The separated stable isotopes of hydrogen, carbon, nitrogen, oxygen and sulphur, are of considerable importance in isotope exchange and tracer work. These isotopes can be separated with relative ease by chemical exchange methods which are particularly suited for the production of relatively large amounts of material at medium concentrations. The thermal diffusion method, on the other hand, the method first used by Clusius and Dickel, is one of the best methods for producing small quantities of highly enriched isotopes. It would be most economical, therefore, to concentrate these isotopes by chemical exchange in a first stage in order to produce the large quantities of enriched material at medium concentrations, which will be required for most chemical and medical tracer work, and to enrich a much smaller amount of material still further by a second stage thermal diffusion unit for the few experiments where very high concentrations are desirable or necessary.

High concentrations of the isotopes will be required in experiments where high dilution of the "tagged" material is encountered and for experiments designed to study the physical and chemical properties of the separated isotopes. Thermal diffusion columns have been set up at McMaster University to make possible the further enrichment of the isotopes which have already been concentrated by chemical exchange methods. Several years ago the heavy isotopes of oxygen and sulphur were separated in this laboratory by distillation and chemical exchange methods, respectively. The latter involved the exchange between sulphur dioxide and bisulphite ion in solution. Our thermal diffusion columns will be used first to further enrich O^{18} samples now on hand. Of the elements mentioned above, deuterium has been an article of commerce for some time, and 75 percent N^{15} produced by chemical methods is now on the market. In the latter case, it might be of interest to produce a small quantity

of high concentrations. Further, the Houdry Catalytic Corporation has plans to produce C^{13} at two concentrations, twelve per cent and sixty per cent, in a two stage system, the latter stage being a thermal diffusion unit. Here again there may be experiments where higher concentrations are desirable. At the present time, however, the isotopes of oxygen and sulphur are not available commercially, but can be procured from several universities (McMaster) only at low concentrations.

Four thermal diffusion units have been completed. One of these units has already been tested on the separation of the nitrogen isotopes using nitrogen gas as a working substance. The results are most encouraging and indicate an enrichment factor of seven for the nitrogen isotopes using four units or 36 feet of column. Details of the thermal diffusion column and of the test runs made with one unit are discussed below.

Apparatus

Several designs of thermal diffusion columns have been built by Clusius and Dickel, Bramley and Brewer[4,5], and Watson[6]. The Watson type of column was used both because it was proved to be efficient, and because General Electric calrod heaters were obtainable.

The unit thermal diffusion column (see Figure I) consists of a General Electric 2000 watt calrod heater of $\frac{1}{2}$" diameter and nine feet long, suspended concentrically in a copper tube of one inch I.D. giving an annular space of $\frac{1}{4}$". The cold wall is surrounded in turn by a $1\frac{1}{2}$" I.D. water jacket. The assembled column is mounted vertically. The expansion of the calrod heater which operates at 530°C. amounts to over an inch, and this increase in length is taken up by a sylphon bellows silver soldered to the bottom of the 1" I.D. copper tube. The

convection tubes of 3/4" I.D. copper tubing, which are connected to the cold wall through a brass adapter, are in two halves silver soldered together by means of a coupling collar. At this junction another unit column can be connected in place of a reservoir. Thermocouple wires silver soldered to the calrod heater for indicating its temperature are brought out through the convection tube by means of Kovar glass seals which provide an air-tight joint and also insulate the wires from the metal column. All these details may be seen in Figure I. The calrod heater is kept centered along the whole length of the cold wall by stainless steel pins of 0.055" diameter which are placed 120 degrees apart around the cold wall at intervals of two feet along the wall. These pins have to be precision machined in order to center the calrod heater accurately in the cold wall, which is necessary to obtain satisfactory separation of the isotopes in the column. Glass flasks serving as gas reservoirs are attached at each end of the column by means of copper glass housekeeper seals.

The design of column worked satisfactorily but the following modifications, see Figure II, were made to facilitate the construction of additional units. The sylphon bellows of 0.005" phosphor bronze, which were very difficult to silver solder to the copper tubing, are replaced by an expansion chamber. Electrical contact with the bottom of the calrod heater is made through a Kovar glass seal in the side of the chamber by means of a flexible copper braid. For the connection between intermediate units, the convection tubes are replaced by a brass connecting sleeve which also allows for expansion of the calrod heater. Here again electrical contacts are brought out through Kovar glass seals. At the top of each unit, the calrod heater is supported by a perforated brass plug, which allows the gas to pass between units.
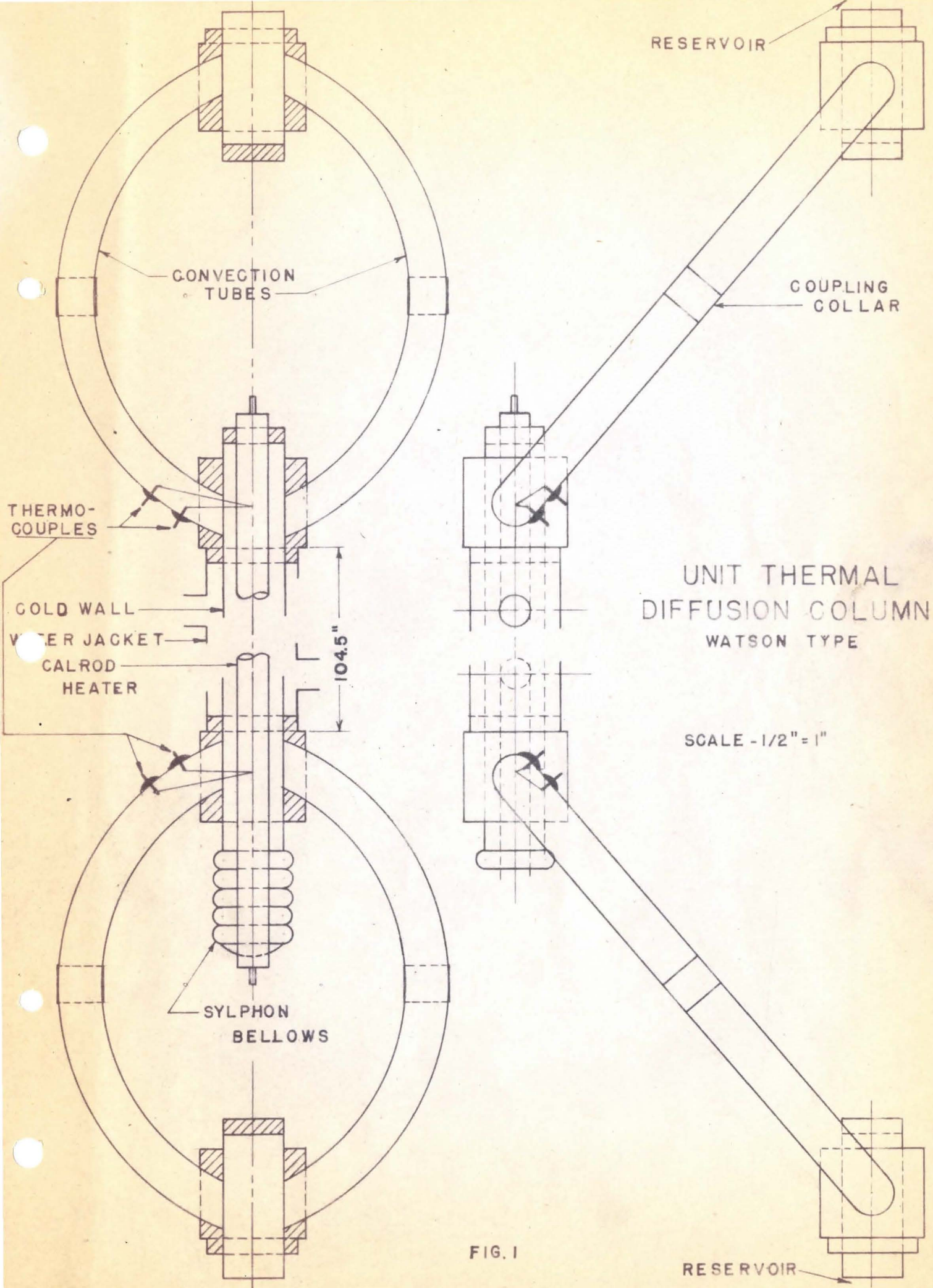
RESERVOIR

CONVECTION
TUBES

COUPLING
COLLAR

THERMO-
COUPLES

COLD WALL

WATER JACKET

CALROD
HEATER

104.5"

UNIT THERMAL
DIFFUSION COLUMN
WATSON TYPE

SCALE - 1/2" = 1"

SYLPHON
BELLOWS

FIG. 1

RESERVOIR

COLUMN OF
MODIFIED DESIGN

COLD WALL
WATER JACKET

CALROD HEATER

THERMOCOUPLES

KOVAR
SEAL

CONNECTING
SLEEVE
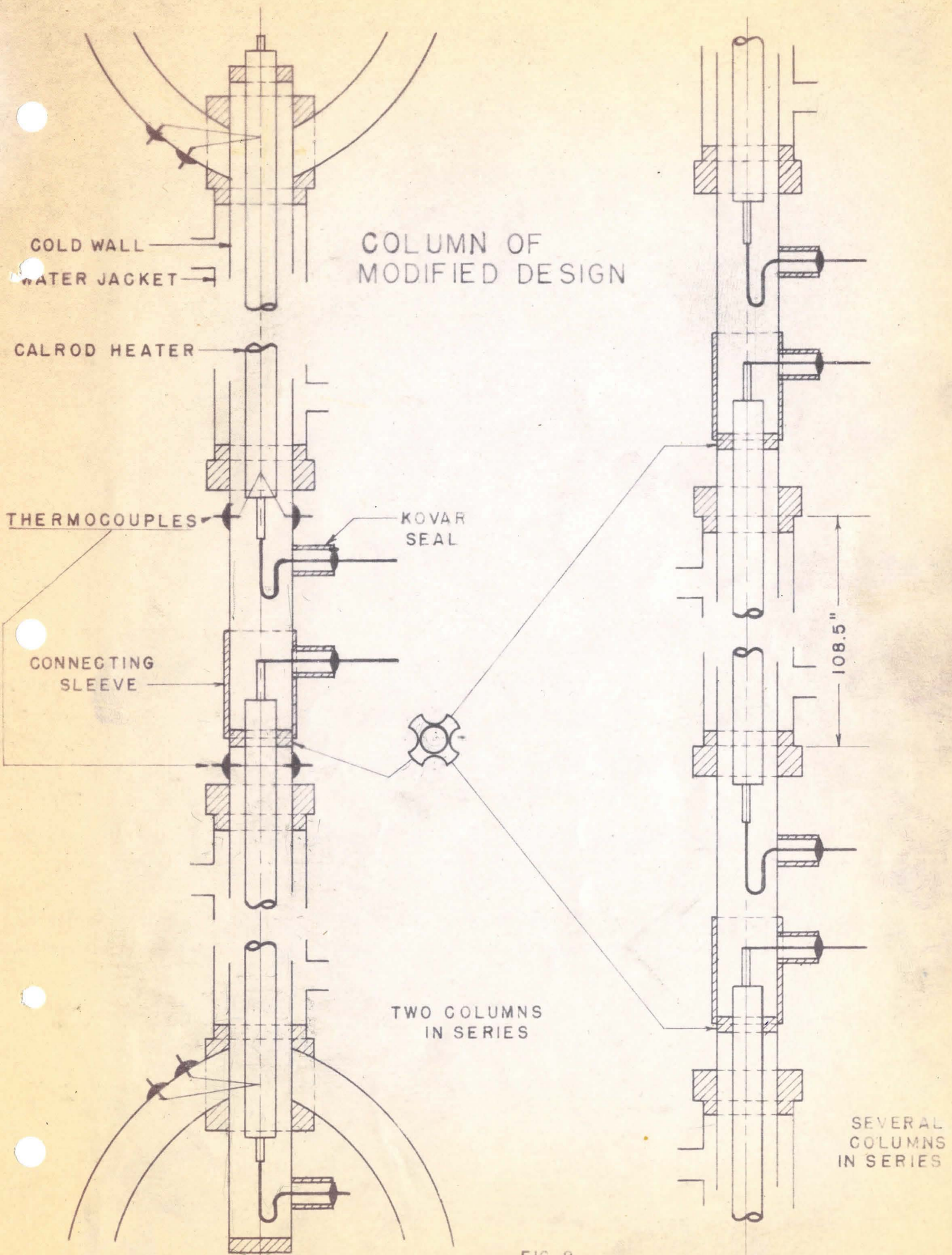
108.5"

TWO COLUMNS
IN SERIES

SEVERAL
COLUMNS
IN SERIES

FIG. 2

Convection tubes are used on the top and bottom units of several unit columns in series for connecting the glass reservoirs to the column.

All connecting parts are of brass which are all silver soldered in place to ensure an air-tight and strong mechanical connection.

The Theory of Thermal Diffusion.

The theory of the phenomena occurring in this type of tube under conditions necessary for its operation is not completely understood[2,7]. A knowledge of the kinetic energy of gases is a prerequisite which gives some knowledge of the equations of transport in gases which is the only way of knowing the phenomena of thermal diffusion[1]. The theory based on the transport of gases was treated quite mathematically by Enskog and Chapman.

The thermal diffusion process as occurring in the Clusius-Dickel type of column, results from the simultaneous action of a number of processes[8]. In such cases the simultaneous processes are thermal diffusion and swirling of the gas when the wall clearance is great enough to permit well defined swirls, or, if the clearance is not great enough, the operation is due to thermal diffusion and convection currents[4].

The lighter gas molecules upon heating have a higher average velocity[4] than the heavier gas molecules and rebound from the hot wall faster than the heavier ones. Hence they are in the front row of a gas front moving away from the hot wall. This gives a partial separation at the same time the swirling action of the gas up the tube set up by the gas rising at the hot wall and dropping at the cold wall (see diagram) takes up the lighter molecules and moves in continuing swirls up the column. The lighter ones are lifted more easily than the heavier ones which also enhances the separation. The swirls

moving down the cold wall catch the heavier molecules and give them momentum downward which, aided by gravity, carry them to the bottom of the column. In columns where the wall clearance is not great enough to allow well defined swirls to form, the convection current up the hot wall is the substituting factor and in conjunction with thermal diffusion picks up the light gases at the hot wall and carries them upward. At the same time, the convection current moving down the cold wall carries the heavy molecules toward the bottom. Ordinarily, a convection current counteracts the effects of thermal diffusion but in this type of column it aids the separation and in tall columns greatly multiplies the thermal diffusion effect.

With this mode of operation, the column is quite efficient in separating isotopes even where the concentration of one isotope is very small compared to the concentration of the other isotope present.

The fundamental equation of diffusion is

$$D \; grad \; C_1 = - \frac{DT}{D} \; grad \; T$$

which upon integration gives

$$c_2^1 - c_2^0 = \frac{D_T}{D} \; \ln \; \frac{T_1}{T_0}$$

where c_2^1 is the concentration of the light isotope at the top of the column

c_2^0 is the concentration of the light isotope at the bottom of the column

D^T is the coefficient of thermal diffusion or the amount of gas under the influence of a temperature gradient diffusing through one cm.[2] per second.

D is the coefficient of ordinary diffusion which in the case of isotopes is called the coefficient of self diffusion and is the amount of the

lighter isotope diffusing through one cm.[2] per second into the heavier
isotope at the same temperature

T_1 is the temperature of the hot wall in $^{\circ}$K.

T_2 is the temperature of the cold wall in $^{\circ}$K.

For hard elastic spheres $\dfrac{D_T}{D} = k_T$ [9] which depends on the relative concentration
of the two isotopes but not on the temperature or pressure.

In the case of isotopes k_T is greatly simplified since the mode of
interaction and the diameters of the two molecules are the same because these
properties are determined by the electronic configuration[3]. Then k_T depends
only on the difference in masses and

$$k_T = \frac{D_T}{D} = \propto c_1 c_2 \qquad [3,10]$$

where
$$\propto = \frac{105}{118} \left(\frac{M_2 - M_1}{M_2 \quad M_1} \right)$$

and $\propto$ is the thermal diffusion constant.

M_2 and M_1 are the masses of the heavier and lighter isotopes and

C_2 and C_1 are the concentrations of the heavier and lighter isotopes

where $C_2 + C_1 = 1$.

Discussion and Results

Several experiments were carried out with one thermal diffusion unit
of the Watson type to determine its efficiency in separating the nitrogen
isotopes using nitrogen gas as the working substance. The column was operated
with the gas at atmospheric pressure, the surface of the calrod heater at
530°C. and the cold wall at 15°C. The gas reservoirs at the top and bottom

of the columns were 3 liters and 100 mls. capacity, respectively.

The results obtained by the analysis of samples with a mass spectrometer show that a single 9 foot thermal diffusion unit will effect a 68 percent change in the ratio of the nitrogen isotopes. This means that four such units should give an enrichment factor of $(1.68)^4$ or an 8 fold change in the ratio of the nitrogen isotopes. These results are tabulated in Table I.

In the further concentration of O^{18} by thermal diffusion it is planned to use carbon monoxide gas enriched 6-7 fold in O^{18}. It is reasonable to assume that the enrichment obtained will be at least as good as that indicated in the test runs using nitrogen gas. Actually O^{18} enrichment may be a little better since the fractional mass difference between CO^{16} and CO^{18} is 2 in 28 as compared to 1 in 28 for $N^{14}N^{14}$ and $N^{14}N^{15}$.

Conclusions

This new method of isotope separation has received considerable attention since its discovery. Many papers have appeared to explain the quite complex theory, to present experimental data, and to compare the experiments with the theory. However, there is no universally accepted theory and not enough experimental work has been published to give definite corroboration between the theory and facts.

TABLE I

Thermal Diffusion Test Run
Using Nitrogen Gas.

Single Unit
Length of Column - 9 feet
Pressure of N_2 - 1 atmosphere.

Run	Time in hours	Mass Ratio (28/29) bottom	Mass Ratio (28/29) top	Enrichment Factor
1	0	133.4	133.4	1
	26	100.1	--	---
	98	86.7	--	---
	123	110.1	--	---
	126		135.4	---
	193	89.6	--	---
	200	90.0	151.2	1.68
2	0	135.1	135.1	1
	73	93.6	--	---
	91	91.1	--	1.65[#]

#Estimated.

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4. Bramley, A., and Brewer, A. K.   Science 90, 165-6 (1939)

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10. Chapman, S.   Nature 146, 431 (1940)

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The Separation of Isotopes

by Thermal Diffusion.

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D. L. Prosser and H. G. Thode.

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Introduction

The separated stable isotopes of hydrogen, carbon, nitrogen, oxygen and sulphur are of considerable importance in isotope exchange and tracer work. These isotopes can be separated with relative ease by chemical exchange methods which are particularly suited for the production of relatively large amounts of material at medium concentrations. The thermal diffusion method on the other hand, a method first used by Clusius and Dickel, is one of the best methods for producing small quantities of highly enriched isotopes. It would be most economical therefore to concentrate these isotopes by chemical exchange in a first stage in order to produce the large quantities of enriched material at medium concentrations which will be required for most chemical and medical tracer work, and to enrich a much smaller amount of material still further by a second stage thermal diffusion unit for the few experiments where very high concentrations are desirable or necessary.

High concentrations of the isotopes will be required in experiments where high dilution of the "tagged" material is encountered and for experiments designed to study the physical and chemical properties of the separated isotopes. Thermal diffusion columns are being constructed at McMaster University to make possible the further enrichment of the isotopes which have already been concentrated by chemical exchange methods. Several years ago, the heavy isotopes of oxygen and sulphur were concentrated in this laboratory by distillation and chemical exchange methods respectively. The

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latter involved the exchange between sulphur dioxide and bisulphite ion in solution. Our thermal diffusion columns will be used first to further enrich O^{18} samples now on hand. Of the elements mentioned above, deuterium has been an article of commerce for some time and 75 percent N^{15} produced by chemical methods is now on the market. In the latter case it might be of interest to produce a small quantity of high concentration. Further, the Houdry Catalytic Corporation have plans to produce C^{13} at two concentrations, twelve percent and sixty percent, in a two stage system, the latter stage being a thermal diffusion unit. Here again there may be experiments where higher concentrations are desirable. At the present time however the isotopes of oxygen and sulphur are not available commercially and can be procured from several universities (McMaster) only at low concentrations.

Two thermal diffusion units have been completed and two more are under construction. One of these units has already been tested on the separation of the nitrogen isotopes using nitrogen gas as a working substance. The results are most encouraging and indicate an enrichment factor of 7 for the nitrogen isotopes using 4 units or 32 feet of column. Details of the thermal diffusion columns and of the test runs made with one unit are discussed below.

Apparatus

The unit thermal diffusion column (see Fig. 1) consists of a General Electric 2000 watt calrod heater of $\frac{1}{2}$" diameter and nine feet long suspended concentrically in a copper tube of 1" I.D. giving an annular space of $\frac{1}{4}$". The cold wall is surrounded in turn by a $1\frac{1}{2}$" I.D. water jacket. This vertically mounted column is essentially the same as that used by W. W. Watson.

The expansion of the calrod heater which operates at 530°C. amounts to over an inch and this increase in length is taken up by a Sylphon bellows silver soldered to the bottom of the 1" I.D. copper tube. The convection tubes of $\frac{3}{4}$" I.D. copper tubing which are connected to the cold wall through a brass adapter are in two halves silver soldered together by means of a coupling collar. At this junction another unit column can be connected in place of the reservoir. Thermocouple wires silver soldered to the calrod heater for indicating its temperature are brought out through the convection tube by means of Kovar glass seals which provide an airtight joint and also insulate the wires from the metal column. All these details may be seen in Fig. 1. The calrod heater is kept centered along the whole length of the cold wall by stainless steel pins of 0.055" diameter which are placed 120° apart around the cold wall at intervals of two feet along the wall. These pins have to be precision machined in order to centre the calrod heater accurately in the cold wall which is necessary to obtain satisfactory separation of isotopes in the column.

Glass flasks serving as gas reservoirs are attached at each end of the column by means of copper glass Housekeeper seals.

This design of column worked satisfactorily but the following modifications, see Fig. 2, were made to facilitate the construction of additional units. The Sylphon bellows of 0.005" phosphor bronze which were very difficult to silver solder to the copper tubing are replaced by an expansion chamber. Electrical contact with the bottom of the calrod heater is made through a Kovar glass seal in the side of the chamber by means of a flexible copper braid. For the connection between intermediate units the convection tubes are replaced by a brass connecting sleeve which also serves as an expansion chamber. Here again electrical contacts are brought out

The Separation of Isotopes by Thermal Diffusion.

A seminar lecture given by D. L. Prosser in October, 1945, as partial completion of the work for the degree M.Sc.

The Separation of Isotopes by Thermal Diffusion.

Introduction

The first observation of the phenomena of thermal diffusion was made by Soret in 1878[1,2]. He found that a concentration gradient was set up in a liquid solution when a temperature gradient *existed across the* solution. Here the lighter molecules or ions in the solutions moved toward the hotter part of the solution faster than the heavier particles which disturbed the homogeneity of the solution. This phenomena where a temperature gradient produced a gradient of the relative concentration of two gases, when mixed, or gaseous isotopes was called thermal diffusion. A rigid mathematical and theoretical treatment was given to thermal diffusion by Enskog in 1911 and independently by Chapman in England in 1917[1]. In 1918 the first experimental data was obtained by Chapman and Dootson.

Mullikan discussed the use of the thermal diffusion process for the separation of isotopes but concluded that other methods at that time superior[3]. However, he did not consider the new twist given to the application of thermal diffusion by Clusius and Dickel which consisted of thermal diffusion in conjunction with convection currents which increased the effect of thermal diffusion enormously. In order to produce this effect they used a specially designed column consisting of two concentric tubes mounted vertically, the inner one of which was a hot wall and the outer one, a cold wall. A temperature gradient was set up radially from the cold wall to the hot wall. Then the convection currents carried the light molecules concentrating at the hot wall up the tube, and brought the heavier molecules, at the cold wall, down the tube[4]. This effect is sometimes called thermal syphoning.

Description of Apparatus.

In order to understand the theory of the thermal diffusion process more easily, it is best to know the construction of the apparatus. As stated before, the apparatus consists of a hot inner wall or tube which is concentric with a cold outer wall. The outer wall is kept cold by a water jacket. The heating of the inner wall has been achieved in various ways. Clusius and Dickel ran a wire, heated electrically, up the axis of a vertical hollow metal tube. Here the wire which was either chromel or platinum was the hot wall itself. In other columns used by Bramley and Brewer[4,5] the hot wall was a glass tube heated internally by a coil of chromel wire. The outer wall in this case is also a glass tube of larger diameter concentric with the inner glass tube with a glass water jacket around the outer tube along its full length. The columns built by Watson used a General Electric calrod heater for the inner wall. The calrod heater is a brass tube from 2 to 3 metres long and a half inch in diameter heated internally by a chromel coil, the brass tubing acting as the hot wall. The outer tube is of copper surrounded by a copper water jacket. Tubes as much as 30 metres long have been used. The radial distance between the inner and outer walls is of the order of 7 mm. which is called the annular space. Nevertheless this dimension varies depending on the pressure of the gas in the column during the process.

In the Clusius-Dickel type of column, the temperature difference between the hot and cold wall varies from 800-1500°C., whereas in the columns built of glass or using a calrod heater the temperature difference is about 300-400°C.

At each end of the column is a reservoir which leads directly to the annular space. If the heavier isotope in a gas is being concentrated, then a small reservoir is placed at the bottom and a large one at the top,

which is large to keep the concentrations of the isotopes in the gas the same before and after the run.

The accompanying diagram shows the column mounted in a vertical position and being used for the concentration of a heavy isotope.

The Theory of Thermal Diffusion.

The theory of the phenomena occurring in this type of tube under conditions necessary for its operation is not completely understood[2,6]. A knowledge of the kinetic theory of gases is a prerequisite which gives some knowledge of the equations of transport in gases which is the only way of knowing the phenomena of thermal diffusion[1]. The theory based on the transport of gases was treated quite mathematically by Enskog and Chapman.

The thermal diffusion process as occurring in the Clusius-Dickel type of column, results from the simultaneous action of a number of processes[8]. In such cases the simultaneous processes are thermal diffusion and swirling of the gas when the wall clearance is great enough to permit well defined swirls or, if the clearance is not great enough, the separation is due to thermal diffusion and convection currents[4].

The lighter gas molecules upon heating have a higher average velocity[4] than the heavier gas molecules and rebound from the hot wall faster than the heavier one. Hence they are in the front row of a gas front moving away from the hot wall. This gives a partial separation. At the same time the swirling action of the gas up the tube set up by the gas rising at the hot wall and dropping at the cold wall (see diagram) take up the lighter molecules and move in continuing swirls up the column. The lighter ones are lifted more easily than the heavier ones which also enhances the separation. The swirls moving down the cold wall catch the heavier molecules and give them momentum downward which, aided by gravity, carry them to the bottom of the column. In columns where the wall clearance is not great enough to allow well defined swirls to form, the convection current up the hot wall is the

substituting factor and in conjunction with thermal diffusion picks up the light gases at the hot wall and carries them upward. At the same time, the convection current moving down the cold wall carries the heavy molecules toward the bottom. Ordinarily a convection current counteracts the effects of thermal diffusion but in this type of column it aids the separation and in tall columns greatly multiplies the thermal diffusion effect.

With this mode of operation the column is quite efficient in separating isotopes even where the concentration of one isotope is very small compared to the concentration of the other isotopes present.

The fundamental equation of diffusion is

$$D \text{ grad } C_1 = -\frac{D_T}{D} \text{ grad } T \tag{1}$$

which upon integration gives

$$C_2^1 - C_2^0 = \frac{D_T}{D} \ln \frac{T_1}{T_0} \tag{2}$$

where C_2^1 is the concentration of the light isotope at the top of the column or in the upper reservoir

C_2^0 is the concentration of the light isotope at the bottom of the column or in the lower reservoir

D_T is the coefficient of thermal diffusion or is the amount of gas under the influence of a temperature gradient diffusing through one cm^2. per second.

D is the coefficient of ordinary diffusion which in the case of isotopes is called the coefficient of self diffusion and is the amount of the lighter isotope diffusing through one cm^2. per second into the heavier isotope at the same temperature.

T_1 is the temperature of the hot wall in ^oK.

T_0 is the temperature of the cold wall in ^oK.

For hard elastic spheres $\frac{D^T}{D} = k_T{}^9$ which depends on the relative concentration of the two isotopes but not on the temperature or pressure.

In the case of isotopes k_T is greatly simplified since the mode of interaction and the diameters of the two molecules are the same because these properties are determined by the electronic configuration[3]. Then k_T depends only on the differences in masses and

$$k_T = \frac{D_T}{D} = \alpha \, c_1 \, c_2 {}^{3, \, 10} \tag{3}$$

where

$$\alpha = \frac{105}{118} \left(\frac{M_2 - M_1}{M_2 + M_1} \right) \tag{4}$$

and α is the thermal diffusion constant

M_2 and M_1 are the masses of the heavier and lighter isotopes and C_2 and C_1 are the concentrations of the heavier and lighter isotopes where $C_1 + C_2 = 1$.

The coefficient of thermal diffusion vanishes and hence α also for Maxwellian molecules[3,10] (molecules where the force of interaction between them varies as the inverse fifth power of the separation). For molecules which interact with a force which varies with an inverse power of separation greater than five the lighter molecules move toward the hot wall and α is positive and for molecules which interact with a force which varies with an inverse power of separation less than five the lighter molecules move toward the cold wall and α is negative.

In isotopes, however, the mode of interaction and the diameters are the same so that α will depend only on the masses of the two isotopes and hence will always be positive.

Following upon Equation (1), the equation for diffusion with thermal diffusion included, as takes place in the Clusius Dickel type of column, is

$$C_1 (V_1 - V) = -D \text{ grad } C_1 + \frac{D_T}{T} \text{ grad } T_1 \qquad \qquad (5)$$

where V_1 is the convection velocity of the lighter isotope

and V is the convection velocity of the gas as a whole

and $V = (C_1 V_1 + C_2 V_2)$.

Experimental Data effecting Theoretical Values.

The above equations and deductions were based on a rigid elastic sphere as the molecule under examination. This is purely theoretical and correction factors must be applied to experimental results to make them compatible with theoretical calculations. Furry, Jones and Onsager[3], made allowances for this difference in the two sets of values when calculating the possible separation of an isotope and let $\alpha = 0.35 \left(\dfrac{M_2 - M_1}{M_2 + M_1} \right)$. Later experiments[11] proved this to be rather high for the isotope under consideration (heavy carbon) when the dimensions of the column were considered. Nier[8,12] determined a value for α for heavy carbon which is given in the following equation set up from experimental data. It is

$$\alpha = \frac{\dfrac{C_2^0 - C_2}{C_2} \cdot \dfrac{1}{C_1} \cdot \dfrac{T_1}{T_0} + 1}{\log \dfrac{T_1}{T_0}} \qquad \qquad (6)$$

where C_2^0 is the concentration of the heavy carbon (C^{13}) in the bottom reservoir

C_2 is the concentration of heavy carbon in the gas used in the column

C_1 is the concentration of light or normal carbon in the gas so that

$C_1 + C_2 = 1$,

and $\dfrac{C_2^0 - C_2}{C_2}$ is the fractional change in the relative abundance of the carbon isotope.

The ratio of the experimental α to the α calculated for elastic spheres is correction factor R_T [13,14,15] and

$$R_T \quad \frac{\alpha}{\alpha \text{ e.s.}} = \frac{K_T}{K_{T \text{ e.s.}}} = \frac{\dfrac{D_T}{D}}{\dfrac{D_T}{D} \text{ e.s.}} \tag{7}$$

Further experimental work by Gillespie produced a correction factor C which he found was better than R_T for fitting experimental values to theoretical values. This correction factor C is given as

$$C = \frac{c_2(M_2 - M_1)}{2(M_1 c_1 + M_2 c_2)} = \frac{d \ln c_1}{d \ln T}^2 \tag{8}$$

where M_1, c_1 is the mass and concentration of the light isotope and M_2, c_2 is the mass and concentration of the heavy isotope.

α is given a value of unity for rigid elastic spheres and so R_T for actual gases is a fraction of one, the lower the value of R_T the "softer" the molecule is, that is it rebounds from a wall with a greater loss of energy than a harder molecule[2]. The greater the value of R_T is the greater the possible separation. R_T for which C may be substituted is given by the following equation[16]

$$K_T = \frac{105}{118} = \left(\frac{M_2 - M_1}{M_2 \quad M_1}\right) R_T \quad c_1 c_2 \tag{9}$$

or

$$\frac{118}{105} \left(\frac{M - M}{M + M}\right) \ln \frac{(c_1/c_2)_1}{(c_1/c_2)_2} = R_T \ln \frac{T_2}{T_1} \tag{10}$$

where T_2 is temp. of hot wall in $^\circ K$.

and T_1 is temp. of cold wall in $^\circ K$.

and subscripts 1 and 2 designate concentrations of c_1 and c_2 in top and bottom reservoirs respectively.

It was also found by Brown[16] that the mean temperature $\frac{T_2 + T_1}{2}$ was not as satisfactory as the value of temperature he calculated which was to be used for calculating the viscosity, density, thermal conductivity and other factors used to determine the efficiency of a thermal diffusion and which are effected by temperature. The value of temperature he used was

$$T_r = \frac{T_1 T_2}{T_2 - T_1} \ \ln \frac{T_2}{T_1} \tag{11}$$

He also found this temperature T_r gave a better value of R_T in comparing experimental values with theoretical ones.

The Separation Factor.

The separation in the thermal diffusion column depends on $c_1 c_2$ which can be seen from the definition of the separation factor which is

$\dfrac{c_1 c_2 (\text{top reservoir})}{c_1 c_2 (\text{bottom reservoir})}$ for a light isotope. The reciprocal of this is

used for determining the separation factor of a heavy isotope.

The equilibrium separation factor may be expressed as

$$\frac{K_e}{C_1^0} \left(\frac{1 - c_1^0}{1 - K_e} \right) = e^{2Al} \text{[17]}$$

where

$$2Al = \frac{\dfrac{a}{p^2}}{1 + \dfrac{b}{p^4}} l \text{[12]}$$

and a and b are two constants,

and where K_e is the equilibrium concentration of c_1^0

c_1^0 is the concentration of the light isotope in the bottom reservoir

l in cm. is the length of the column used in producing the separation

p is the pressure in atmospheres

A is a constant given by $\dfrac{H}{2K}$ [18].

where H and K in turn are given by

$$H = -\frac{B}{Q^3} \int_{T_1}^{T_2} \left(\rho\frac{D\alpha}{\lambda T}\right) G(T)\ dT \quad [19] \qquad (13)$$

$$K = \frac{B}{Q^7} \int_{T_1}^{T_2} \left(\rho\frac{D}{\lambda}\right)\left\{G(T)\right\}^2 dT \quad [19] \qquad (14)$$

B is the mean circumference of the annular space in cm.

 is the thermal conductivity in cal./cm.deg sec.

Q is the heat flow in cal/cm^2. - sec. and $Q = \lambda dT/dx$ where x is radial ordinate from hot to cold wall and

G(T) is expressed in the differential equation

$$\frac{d}{dT}\cdot\frac{1}{\lambda}\cdot\frac{d}{dT}\cdot\frac{n}{\lambda}\cdot\frac{d}{dT}\cdot\frac{1}{\lambda\rho}\cdot\frac{d}{dT}\left(\rho\frac{D}{\lambda}\right) G(T) = g\ \frac{d\rho}{dT} \quad [19] \qquad (15)$$

η is the viscosity in poises

ρ is density

g is the acceleration due to gravity in cm/sec^2.

From these equations it is obvious that the physical properties of the gas being used are important in determining the separation factor.

As light a molecule as possible should be used to get a large speed for the separation where the speed is characterized by the following quantity $\frac{m_t\ f}{t_r}$ where f is the fraction of the molecular weight contributed by the element being separated, m_t is the mass of the gas in the top reservoir and t_r is the relaxation time or the time for the system to come to equilibrium. The relaxation time may be expressed in three ways depending on the concentration of c_1[20].

If c_1 is small compared to unity,

$$t_r \cong \left(\frac{m_t}{H}\right)\left(e^{2Al} - 1\right) \qquad (16)$$

If c_1^0 and K_e are about one half each,

$$t_r \cong \frac{2Alm_t}{H} \qquad (17)$$

If c_1 is always close to unity

$$t_r \cong \frac{m_t}{H} \left(1 - e^{-2Al} \right) \tag{18}$$

From the above equations we can conclude that the separation factor depends on

1. the pressure, the best range being between 0.3 and 0.7 atmospheres, depending on the gas used, for an annular space of 7 mm.,

2. the composition variables which are essentially the relative concentrations of the two isotopes present,

3. the difference in mass of the two components divided by their sum

$$\frac{m_1 - m_2}{m_1 + m_2} \quad ,$$

4. and most decidedly on the temperature gradient.[21]

Separation is helped

1. by having the diameter of the cold wall not too large (over 1") since back diffusion increases considerably with increase in diameter and counteracts the effect of thermal diffusion,[4]

2. by using the proper diameter allowing good swirls which increases the possible separation in the column,

3. by using washers or baffles[4,22] on the cold wall to help form good swirls. They also prevent a mass movement of the gas down the walls,

4. by having the pressure low enough so that the Reynolds number where turbulance begins is not exceeded since only lamellar flow is conducive to separation.[23,24] The larger the diameter the higher the pressure permissible, but is governed by 1,

5. by having symmetry in the column. The hot and cold walls must be concentric to give a constant temperature gradient in all directions in the same plane.[25]

6. by using as light a gas as possible[26] and using a third inert gas which gives initial 50-50 mass mixture[27,28],

7. by having a suitable pressure, usually less than 1 atmosphere depending on gas.[29]

The Continuous and Discontinuous Processes.

There are two methods for operating a thermal diffusion column. They are the discontinuous method and the continuous method. In the discontinuous method, the whole process is definitely a batch process. The proximity to the equilibrium condition can be determined by removing samples at various succeeding times and examining them in a mass spectrometer. When equilibrium is reached, there is no change in the concentration of the enriched isotope. Then the reservoir is sealed off from the column to prevent any remixing of the gas with that in the tube which may reduce the concentration of the desired isotope in the reservoir[17]. The predicted concentration can be more nearly attained the larger the reservoir used. If a small reservoir is used the normal gas is soon exhausted of all the desired isotope. A large reservoir within practical limits is then desirable.[12,17] The reservoir collecting the isotope should be quite small to get the isotope and yet keep out the more abundant isotope. In the discontinuous method a greater fraction of the equilibrium separation ratio can be obtained for a given speed.

In the continuous process, the gas of normal concentration is being continually admitted to the column at one end while the enriched mixture in small amounts of about 5-20 cc./hr., depending on the size of the column, are being withdrawn[9,12,27] at the other end of the column.

Although not as great a separation factor is possible by this method, a continuous supply of enriched mixture is available making the continuous process better suited for commercial processes.

If the enriched mixture from one column is fed into another column we have a multiple unit column operated in series. By having a number of these columns in series the concentration of the desired isotope is increased beyond that using one column[36]. Watson[30,31,32,33], using a two column set up, obtained a separation factor of 2.77 for the concentration of heavy carbon using methane as the gas. He predicted that by using six columns in series he may get $(2.77)^3$ or about 20 for the separation factor operating it continuously. To get increased production of moderate concentration the columns may be operated in parallel where the concentration will be the same as that for one column, but the production will be increased by a factor equal to the number of columns in parallel.

Uses

The thermal diffusion process is an efficient method[4] for separating isotopes when the isotopes are in a gaseous phase. Enriched mixtures of the isotopes produced in this way have been used for radioactivity experiments. Cl^{37} concentrated to a high degree from HCl gas has been used for this purpose[4,34,35]. Of course enriched concentrations of isotopes produced this way find the same uses as produced by other methods.

The thermal diffusion phenomenon as taking place in the thermal diffusion column is one of the few phenomena in a gas which depends essentially on the peculiar characteristics of the molecule. By studying this phenomenon, information about the intermolecular forces occurring in the gas in question may be obtained. The study of isotopes is particularly

valuable in this case since there is no intermixing of the characteristics of two dissimilar molecules.[3,8]

Conclusions

This new method of isotope separation has received considerable attention since its discovery. Many papers have appeared to explain the quite complex theory, to present experimental data, and to compare the experiments with the theory. However, there is no universally accepted theory and not enough experimental work has been published to give definite corroboration between the theory and facts. Meanwhile, the work goes on.

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