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Concentration of N^{15} by Chemical Methods

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A study has been made on the application of chemical exchange reactions to the problem of the concentration of the nitrogen isotope of atomic weight 15. We have investigated the exchange reactions involving ammonia as the gas phase and solutions of ammonia in water and alcohol, and of ammonium nitrate and ammonium sulfate in water as the liquid phase. The apparatus used consists of an efficient type of fractionation column previously described. It is found that the exchange reaction between ammonium nitrate solution and ammonia is probably the best of all of these for this purpose, except that ammonium nitrate solutions corrode our steel column so badly that their use is impractical in the present apparatus. The exchange between ammonium sulfate solutions and ammonia gas is shown to be more satisfactory for the purpose than any of the other combinations, and has been used to secure a $6\frac{1}{2}$-fold increased concentration of N^{15}. Substantial amounts of nitrogen containing high concentrations of N^{15} have been produced and these together with the efficient mass-spectrometer method of analysis make possible a wide variety of studies.

THE problem of the separation of the isotopes of the elements other than hydrogen has been studied for many years.[1] The methods which were first used depended upon differences in physical properties related directly to the masses. The method of diffusion was early used by Aston and by Harkins[1] and depends upon the differences in the rates of diffusion of light and heavy molecules. These authors used diffusion to produce a slight change in the relative abundance of the isotopes and repeated the process many times to secure a measurable effect. Hertz and his co-workers,[2] using the diffusion method, arranged successive diffusion units in a cascade system so that the lighter isotope was displaced toward one end and the heavy toward the other. In this way they multiplied the effect of a simple diffusion process many-fold and have produced very large changes in the relative abundance of neon, hydrogen and oxygen. Others[3] have used essentially the same method to produce changes in the relative abundance of the carbon and nitrogen isotopes. The mass-spectrograph method has been used by Rumbaugh[4] to secure practically complete separation of the lithium isotopes in

very small amounts. Beams[5] using a centrifugal method has reported interesting and promising preliminary results. Huffman and Urey[6] have increased the concentration of H_2O^{18} by a factor of 4.5 by distillation of water. This method depends upon differences in vapor pressures of H_2O^{16} and H_2O^{18} discovered by Lewis and Cornish[7] and measured by Wahl and Urey.[8]

The marked differences in the chemical properties of hydrogen and deuterium, as well as the demonstration of differences in the vapor pressures of their compounds suggest the application of similar methods to the separation of other isotopes. Urey and Greiff[9] showed from theoretical calculations, that slight differences in the chemical properties of isotopic compounds of the lighter elements should exist, and Weber and Urey[10] have demonstrated that these theoretical calculations are confirmed in the case of the equilibrium between water and carbon dioxide with respect to the oxygen isotopic exchange. The separations that can be expected in the simple process equilibria of this type are very

[1] See Aston, *Mass Spectra and Isotopes* (Longmans, Green, New York, 1933), Chap. XVII.

[2] G. Hertz, Zeits. f. Physik 79, 108, 700 (1932); 91, 810 (1934); H. Harmsen, G. Hertz, and W. Schütze, Zeits. f. Physik 90, 703 (1934).

[3] D. E. Woodbridge and F. A. Jenkins, Phys. Rev. 49, 404, 704, 882 (1936); R. Sherr and W. Bleakney, Phys. Rev. 49, 882 (1936); D. E. Woodbridge and W. R. Smythe, Phys. Rev. 50, 233 (1936).

[4] L. H. Rumbaugh, Phys. Rev. 49, 882 (1936).

[5] J. W. Beams and F. B. Haynes, Phys. Rev. 49, 644 (1936); 50, 491 (1936).

[6] G. B. Pegram, H. C. Urey, J. Huffman, Phys. Rev. 79, 883 (1936); J. Chem. Phys. 4, 623 (1936); J. R. Huffman and H. C. Urey, J. Ind. Eng. Chem. 29, 531 (1937).

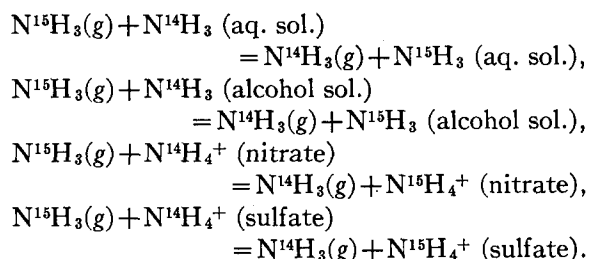[7] G. N. Lewis and R. E. Cornish, J. Am. Chem. Soc. 55, 2616 (1933).

[8] M. K. Wahl and H. C. Urey, J. Chem. Phys. 3, 411 (1935).

[9] H. C. Urey and L. Greiff, J. Am. Chem. Soc. 57, 321 (1935).

[10] L. A. Weber and H. C. Urey, J. Chem. Phys. 3, 129 (1935).

slight, and indeed are smaller than those secured in diffusion, so that it is necessary to devise means for multiplying the effect of a single separation. Methods were outlined by Urey and Greiff for accomplishing this and preliminary experiments by Urey, Aten and Keston[11] and by Urey and Aten[12] have demonstrated their feasibility. In this paper we wish to report more extensive experiments designed to concentrate the heavy nitrogen isotope, using exchange reactions in which ammonia constitutes the gaseous phase and solutions of ammonia in water or methyl alcohol or of ammonium salts in water, constitute the liquid phases.[13] The exchange reactions which have been studied in this research are:

$$N^{15}H_3(g) + N^{14}H_3 \text{ (aq. sol.)}$$
$$= N^{14}H_3(g) + N^{15}H_3 \text{ (aq. sol.)},$$
$$N^{15}H_3(g) + N^{14}H_3 \text{ (alcohol sol.)}$$
$$= N^{14}H_3(g) + N^{15}H_3 \text{ (alcohol sol.)},$$
$$N^{15}H_3(g) + N^{14}H_4^+ \text{ (nitrate)}$$
$$= N^{14}H_3(g) + N^{15}H_4^+ \text{ (nitrate)},$$
$$N^{15}H_3(g) + N^{14}H_4^+ \text{ (sulfate)}$$
$$= N^{14}H_3(g) + N^{15}H_4^+ \text{ (sulfate)}.$$

For convenience we shall refer to these reactions by the symbols, $NH_3 - NH_4OH$, $NH^3 - CH_3OH$, NH_3, $NH_3 - NH_4NO_3$ and $NH_3 - (NH_4)_2SO_4$, respectively. Lewis and Macdonald[14] using two liquid phases instead of the gas and liquid phases as described here, have used essentially this same method in concentrating the light isotope of lithium.

In considering a successful method of concentrating the rare isotopes we must keep two factors in mind. In the first place, an appreciable concentration is desired; but what is meant by an appreciable concentration depends upon the uses for which the isotopic mixtures are being prepared. If the principal purpose is to study the properties of pure isotopic compounds, a nearly complete separation is desired. On the other hand, if they are to be used as tracers or for studying many exchange reaction problems, the

extent of the separation is determined by the dilution factor in the experiments and the sensitiveness of the method of analysis. The method which we are describing in this paper has not as yet produced a concentration sufficient for convenient investigation of the physical properties of isotopic nitrogen but has produced concentrations which can be used for studies of many exchange reactions and biological problems.

The second requirement of a successful method for separating isotopes is that a sufficient amount of material be produced in a length of time which is not prohibitively long. The method of Hertz is able to produce highly concentrated materials, but only in amounts of the order of magnitude of a few cc of gas (S.T.P.) per 24 hours of operation. It is immediately obvious that no very extensive chemical or biochemical investigations can be made if only such small amounts of material are available. Thus the transport of heavy material per unit of time in the separating apparatus is of great importance. The method described in this paper has transported approximately 0.2 of a gram of N^{15} (100 percent) per 24 hours from natural nitrogen to nitrogen of a higher concentration. Even this is somewhat slow, when the production of sufficient amounts of material for the investigation of the physical properties of compounds of nearly pure N^{15} is undertaken.

The theory of the method used is essentially that of distillation in which a counter-flow of liquid and gas is maintained, condensation being used to convert the gas phase to the liquid phase and boiling to convert the liquid phase to the gas phase. Distillation columns have been used extensively for such distillation processes, and can be applied to the method of chemical exchange reactions in which we have a gaseous substance which can come to equilibrium with a liquid phase. The gaseous phase in the case of our problem consists of ammonia gas mixed with some water vapor or methyl alcohol vapor, and the liquid phase consists of a solution of ammonia in water or in alcohol, or of an ammonium salt in water. The process consists in a flow of the liquid phase downward through a fractionating column of high efficiency, liberation of the ammonia at the bottom of the column by boiling, or by the addition of sodium hydroxide and subsequent boiling, and the return of the ammonia upward

[11] H. C. Urey, A. H. W. Aten, Jr., and A. S. Keston, J. Chem. Phys. 4, 622 (1936).
[12] H. C. Urey and A. H. W. Aten, Jr., Phys. Rev. 50, 575 (1936).
[13] H. C. Urey, M. Fox, J. R. Huffman, H. G. Thode, J. A. C. S. 59, 1407 (1937).
[14] G. N. Lewis and R. T. Macdonald, J. Am. Chem. Soc. 58, 2519 (1936).

through the column. The maximum difference in concentration which can be secured in a distillation with total reflux is given by the formula

$$\frac{N_0}{1-N_0}\bigg/\frac{N}{1-N}=\alpha^k,\qquad(1)$$

in which N and N_0 are the mole fractions of one constituent, at the two ends of the column, α is the simple process fractionation factor (ratio of vapor pressures of the pure constituents) and k is the number of theoretical plates. This equation is really a definition of k, but general experience with distillation columns shows that k is proportional to the length of the column and that the distribution in the column at equilibrium is given by (1) if k is set equal to a constant multiplied by a distance from one end of the column. As we shall show, the value of α for the exchange reaction $NH_3-NH_4^+$ is about 1.02, and hence in order to produce a large ratio of the concentrations at the top and bottom, the value of k must be large.

The transport of a constituent in a column is equal to the quantity flowing in one direction multiplied by the mole fraction of the constituent in this phase minus the quantity flowing in the opposite direction multiplied by the mole fraction in that phase. When a steady state is reached the transport is the same at all points along the column. If there is no forward flow, i.e., no concentrated material removed, the transport, when in the steady state, is of course zero. Before the steady state is reached, the transport is not constant throughout the column, since a redistribution of material in the column is taking place. In the experiments which we are reporting, the column operates under these last conditions at the beginning; and at the end the steady state without forward flow exists and zero transport results. During the first part of the run a part of the column has very little or no variation in concentration along its length and hence there is adequate time for the two phases to come to equilibrium. Since the top part of the column is fed with natural isotopic ammonium salt or ammonia in water or alcohol solution, the transport can be calculated for this part of the column and is

$$T=w(N-n),$$

where w is the flow per unit time and N and n are the concentrations of N^{15} in the liquid and gas phases, respectively. Since equilibrium is established in this region,

$$\frac{N}{(1-N)}\bigg/\frac{n}{(1-n)}=\alpha\qquad(2)$$

and hence, when N and n are both small compared to unity and nearly equal as in the present case,

$$T=wN(\alpha-1).\qquad(3)$$

The question as to the effect of fluctuations in the rate of flow on the transport must be considered since we cannot keep the rate of flow constant to within better than about five percent. The transport when the upward and downward rates of flow are not the same is

$$T=WN-wn,$$

so that fluctuations in W, the downward rate of flow, and w, the upward rate of flow will cause fluctuations in the transport and may easily change its sign. However, since the mean values of W and w must be the same when operating without forward flow, the mean transport must be that given by Eq. (3).

Huffman and Urey[6] have shown that the approach to the steady state in a column operating without forward flow and with an infinite reservoir at one end is given by the formulae

$$(1-N)\ln\frac{1-N}{1-N_0}+N\ln\frac{N}{N_0}=Kt,\qquad(4)$$

$$K=\frac{wN(\alpha-1)k\ln\alpha}{H},\qquad(5)$$

where N is the mole fraction of N^{15} in natural nitrogen at one end of the column, N_0 the mole fraction of N^{15} at the other end, H is the hold-up i.e., the amount of material held in the column during operation, t is the time, and the other symbols have the meaning previously assigned. This formula is derived on the assumptions, (1) that the column may be divided into two regions, one toward the higher concentration end in which the distribution of the constituents is that for a column of that length in a steady state without forward flow and the remainder at the lower

concentration end, in which at any time the concentration is a constant (practically that of natural nitrogen) along this length, and (2) that the hold-up beyond the column at the high concentration end is negligible. If this hold-up, h, is not negligible, Eq. (4) becomes

$$(1-N) \ln \frac{1-N}{1-N_0} + N \ln \frac{N}{N_0} + k\frac{h}{H}(N_0-N) \ln \alpha = Kt. \quad (6)$$

Our experiments follow these formulae fairly closely and indicate that the assumptions used in their derivation are approximately correct.

EXPERIMENTAL

The distillation columns used in this work were suggested by Pegram[6] and were described by Huffman and Urey;[6] the reader is referred to this publication for a detailed description. The columns contain a succession of alternate stationary and rotating metal cones. We used a large steel column 35 feet high and 6 inches in diameter containing 621 pairs of cones and for control experiments a copper column $1\frac{1}{2}$ feet high, 6 inches in diameter containing 15 such pairs of cones.

The solution is pumped into the top of the column by means of a reciprocating piston pump with adjustable stroke driven by a synchronous motor and adjusted to pump the desired number of cubic centimeters of liquid per minute. See flow sheet in Fig. 1. The liquid draining from the bottom of the column is pumped to a mixing chamber at the top of a stripping column. This stripping column is placed on the upper floor, necessitating a pumping height of 40 feet. In order to minimize the hold-up at the bottom of the main column, the pump must have an excess capacity so that no accumulation of liquid takes place, and hence must be self-priming. In addition, this pump must handle any solid material such as iron oxide that drains from the column. After trying several types of pumps, a turbine pump was found to operate satisfactorily providing an additional 200 cc of water were fed into the pump per minute. This addition of water also decreases the hold-up in the pump and pump line. The packing gland of the turbine pump is kept wet by feeding water to it from a 500 cc reservoir of water; the water lubricates the gland and prevents air leaks. A solution of sodium hydroxide is fed by means of another piston type pump into the mixing chamber in order to liberate ammonia. This solution then flows into a small stripping column, consisting of a 7-foot length of 4-inch pipe packed with clay cylinders, $\frac{5}{8}$ of an inch in diameter. At the bottom of this column 200 cc of water are boiled per minute by means of a steam pot boiling at 45 lb. steam pressure in order to remove the last traces of ammonia from the solution. At the top of the stripping column and parallel to the mixing chamber there is a coil condenser to reflux the water boiled. The efficiency of this small column for removing the last traces of ammonia before the waste solution leaves the apparatus is very important. A loss of 20 parts of ammonia per million at the speeds we are using would be sufficient to limit the maximum concentration to 2.5 percent no matter how efficient the column. Tests on the waste solution from this stripping column made from time to time showed a content of 1 part of ammonia per million. The tests were made simply by warming without boiling a definite amount of the alkaline waste solution in a beaker covered with watch glass having a piece of wet litmus paper on its lower surface and noting the time for a color change. This was compared with similar tests using standard ammonia solutions. With reasonable care the test is quite reproducible. The spent solution of sodium sulfate runs to waste through a vertical pipe sufficiently long to permit drainage from the apparatus against the external atmospheric pressure. The liberated ammonia gas is returned to the bottom of the main column, and escapes at the top to be absorbed in water and wasted. This absorption chamber consists of a 3-foot length of 3-inch pipe packed with iron staples and furnished with an inlet for water and a vacuum leg to the sewer.

The small fractionating column is operated in much the same way. An ammonium salt solution pumped in at the top drains down through the column into a five liter flask containing an amount of sodium hydroxide sufficient to liberate the ammonia from its salt over the period of the run. The flask is kept boiling by means of a gas
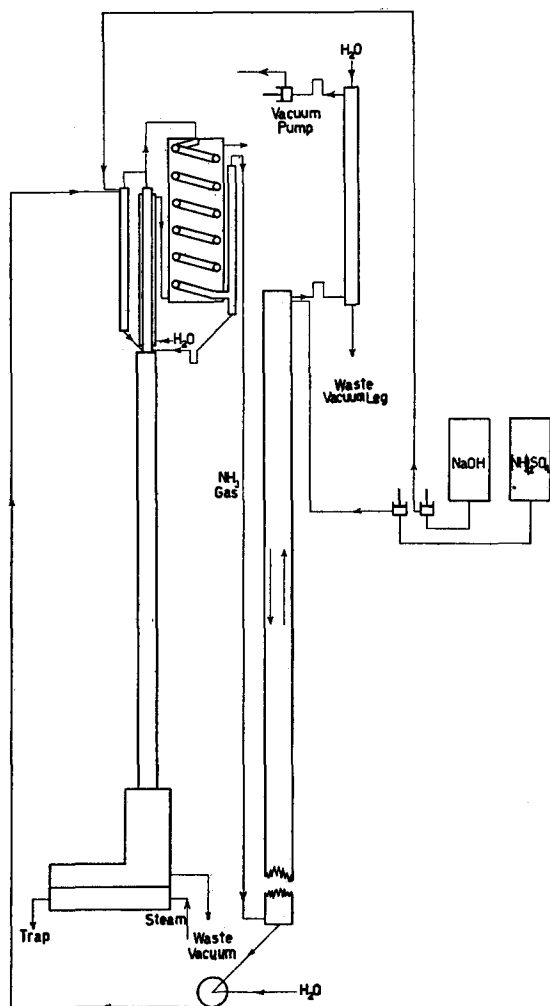
Fig. 1.

burner. A condenser is used above the flask to reflux the boiled water. In this way most of the ammonia is boiled out of the solution and the ammonia gas passes into the lower end of the column and escapes at the top. In all the small column runs equilibrium is established in from three to five hours. Since the column is not vacuum tight, nitrogen gas is led into the flask and passes through the system for the purpose of lowering the partial pressure of the ammonia gas. This decreases the hold-up of ammonia in the flask as well as the concentration of dissolved ammonia in the ammonium salt solution. The experiments are run under conditions of total reflux at the bottom until equilibrium is established.

ANALYSES

Analyses are made with the Bleakney[15] type mass spectrometer working with N_2 gas. Samples of NH_3 gas taken at the lower end of the column are dissolved in water and converted into nitrogen by the addition of a solution of sodium hypobromide. Air is removed by first freezing the separate solutions and pumping out the air with a mercury diffusion pump. Approximately 10 cc samples of nitrogen gas (S.T.P.) are used, though smaller samples would be satisfactory. The relative intensities of the mass 28 and mass 29 peaks are taken as the measure of the relative abundances of N_2^{14} and N^{15}. If this ratio is x then the mole fraction of N^{15} is easily seen to be $1/2x+1$.

The mass spectrometer is especially convenient for analysis since the mass 28 and mass 29 peaks are practically completely separated by our instrument. Since this is found to be true it is unnecessary to make corrections for overlapping of peaks. The determination of the relative abundance of the N^{14} and N^{15} isotopes in the same sample of nitrogen varies from day to day, ranging from 128.6 to 133.9 for the ratio of N_2^{14} to $N^{14}N^{15}$ for natural nitrogen. If we accept 0.38 as the percentage of N^{15} in nitrogen,[16] this ratio should be 131.0. The ratio is determined for ordinary nitrogen on each day that analyses are made, and the corresponding ratios for unknown samples are corrected for the deviation of natural nitrogen from the value of 131.0. Variations in the ratio $N_2^{14}/N^{14}N^{15}$ for natural nitrogen from day to day are due partly to experimental error and partly due to impurities which cause variations in the background intensity of mass peaks 28 and 29. The background intensity is small if the apparatus is well baked out before measurements are made and then the ratios run close to 131. An average value of 131.8 was obtained for this ratio in ordinary nitrogen over 34 different days. A potentiometric method is used to determine the peak intensities in order to avoid difficulties due to the nonlinearity of the amplifying circuit. The ion collector plate is connected through an approximately 10 megohm resistance to a potentiometer which is then connected to

[15] W. Bleakney, Phys. Rev. **40**, 496 (1932).
[16] *International Table of Stable Isotopes for 1936* (Paris, 1936).

ground. With no back potential from the potentiometer, the potential of the collector plate will be proportional to the ion current though due to nonlinearity of the amplifier the deflection of the galvanometer will not be proportional to the intensity. However, the potentiometer can be used to bring the potential of the collector plate when ions are coming to it to the potential it has when no ions arrive at the plate. The measurement consists in setting the mass spectrometer off a peak, noting the position of the galvanometer in the amplied current circuit, then moving to a peak and by means of the potentiometer bringing the potential of the collector plate to the same value it had when off the peak, i.e., the galvanometer swing is brought to the position it had when off the peak. The resistances in the potentiometer are then a measure of the peak intensity above that of the background and no question of linearity of the amplifying circuit is involved. In our measurements we have used the mass spectrometer settings at masses 26.5 and 30.5 to secure the background readings for the 28 and 29 peaks, respectively. Typical readings for natural nitrogen and one of our concentrated samples are given in Table I. It will be seen that the readings are very reproducible, and that the ratio can be determined within a probable error of about 1 percent.

RESULTS

A number of control experiments made with the small column from time to time are presented in Table II. In each run several samples were taken to make sure that equilibrium had been established but only the final concentrations are

TABLE I.

	ORDINARY NITROGEN		CONCENTRATED SAMPLE	
Mass Peak	Intensity in Arbitrary Units	Ratio	Intensity in Arbitrary Units	Ratio
28 29	0.01146 1.500	130.8	0.0672 1.360	20.25
28 29	0.01150 1.510	131.3	0.0695 1.395	20.08
28 29	0.01157 1.521	131.4	0.0705 1.418	20.08
		Av. 131.2		Av. 20.14

tabulated. If N_0 and N are small compared with unity, Eq. (1) can be written,

$$\log N_0/N = k \log \alpha.$$

The values of $k \log \alpha$ as given in the table are the experimental results, since both k and α cannot be determined from these experiments alone.

We use 1.006 as α for the exchange reaction $NH_3 - NH_4OH$ as found by Urey and Aten[12] and 1.021 for the exchange reaction $NH_3 - (NH_4)_2SO_4$, (31 percent solution), as found in the subsequent work reported below. For comparison it is assumed that α for the exchange reaction $NH_3 - (CH_3OH, NH_3)$ is 1.006. The values of k and α given in the last two columns are calculated by making various assumptions. The values of k for runs 1, 2, 3, and 4 are secured from $k \log \alpha$ by using the above values for α. Using 1.021 for α as given above the value 8 is calculated for k in run 7. This value of k is then assumed for runs 5, 6, and 8 and the values of α are calculated. Throughout the table the use of parentheses indicates assumed values.

Runs 1 and 2 give nearly the same result, indicating that for the $NH_3 - NH_4OH$ exchange the partial pressure of ammonia is unimportant. Run 3 shows that a methyl alcohol solution of ammonia is better than ammonium hydroxide for concentrating N¹⁵. Comparing run 4 with run 3 it is seen that the over-all fractionation factor is decreased by doubling the liquid velocity, keeping the partial pressure of N_2 about the same. This means the efficiency of our column or the number of theoretical plates will depend upon the feed velocity. Runs 5, 6, 7, and 8 show that high salt concentrations are desirable. In each case the solutions are saturated with dissolved ammonia under the conditions of the experiment, and thus the concentration of ammonia is about the same, though the total concentration of nitrogen as ammonia and ammonium ion increases from Run 5 to Run 8. The values of α increase in Runs 5, 6, 7 and 8 because the large α for the $NH_3 - (NH_4)_2SO_4$ exchange increases the experimental α above the low value of the α for the $NH_3 - NH_4OH$ exchange. It would be most desirable from the standpoint of operation and expense, to use NH_4OH in concentrating N¹⁵, since no sodium hydroxide would be necessary and a considerable fraction of the NH_3 could be

TABLE II.

RUN	FEED SOL.	LIQUID VEL. IN cc/min.	N_2 VEL. IN liters/min.	N_0	$k \log \alpha$	α	k
1	NH_4OH	6.0	0	0.00396	0.0179	1.006	7.
2	NH_4OH	6.3	2	.00399	0.0212	1.006	8.1
3	CH_3OH-NH_3	5.0	1	.00408	0.0309	(1.006)	11.6
4	CH_3OH-NH_3	10.2	1.4	.003966	0.0186	(1.006)	7
5	5% $(NH_4)_2SO_4$	4.4	2	.00401	0.0234	1.0067	(8)
6	14% $(NH_4)_2SO_4$	4.2	2	.00412	0.0351	1.012	(8)
7	31% $(NH_4)_2SO_4$	4.4	2	.00449	0.0725	1.021	8
8	34% $(NH_4)_2SO_4$	4.3	2	.00453	0.0763	1.022	(8)

TABLE III.

Run	9 60% NH_4NO_3 in water		10[a] 6.75% NH_3 in water		11 6.8% NH_3 in water		12 7% NH_3 in water		13 6.65% NH_3 in CH_3OH		14 15% $(NH_4)_2SO_4$ in water	
Feed Solution												
Pressure cm of Hg	18		40		18.1		15		27		20	
Feed Velocity cc/min.	108		75		98		10.4		12.2		10	
Temperature	Room		60°C		Room		Room		Room		Room	
Results	Hrs.	Conc. N^{15}	Hrs.	Conc. N^{15}	Hrs.	Conc. N^{15}	Hrs.	Conc. N^{15}	Hrs.	Conc. N^{15}	Hrs.	Conc. N^{15}
	0	0.38	0	0.38	0	0.38	0	0.38	0	0.38	0	0.38
	6	0.565	5	0.389	4	0.407	3.75	0.399	3	0.407	3	0.418
	10	0.632	10	0.405	7	0.424	7.25	0.418	6.25	0.422	6.5	0.446
			14	0.415	10	0.458[b]	10.25	0.429	9.5	0.437	10	0.468
			16	0.411	13	0.445			10.75	0.440		
					14.5	0.448						
K[d]	2.99×10^{-5}		0.456×10^{-6}		1.92×10^{-6}		1.58×10^{-6}		2.00×10^{-6}		4.25×10^{-6}	
α	1.021		—		1.006		1.006		1.006[c]		1.012[e]	
k	28.8		—		24.7		207		207		135	

[a] The plot of the results of Run 10 does not give an approximate straight line, hence the value of K is very uncertain and values of α and k cannot be given.
[b] This analysis is probably in error since this point alone does not lie on the straight line. It is ignored in securing the value of K.
[c] Since the value of α is a pure assumption the value of k is also. This is included only to indicate the superiority of Run 13 over Run 12.
[d] In drawing straight lines through the plots, we find that the best straight line does not pass through the origin. This we believe is due to some irregularity at the beginning of the run. In calculating k, the value of H is taken as 4480 cc as determined in the case of Run 10.
[e] This was taken from Table II.

refluxed at the top of the column. These advantages, however, are more than compensated by the much higher fractionation factor found for concentrated salt solutions. The methyl alcohol solution of ammonia used in Runs 3 and 4 gives a better fractionation than the water solution of ammonia of Runs 1 and 2, but it does not appear to present a better method of concentration than the use of water solutions of the ammonium salts.

A number of preliminary runs were made with the large column. The results and conditions of the experiments are summarized in Table III. The values of k listed in the table are secured by plotting the function

$$(1 - N) \log \frac{1-N}{1-N_0} + N \log \frac{N}{N_0}$$

against the time, drawing the best straight line through the points and taking the slope of this line as the value of K. The plots are shown in Fig. 2 and indicate how closely the relation of Eq. (6) is followed by our results. After Run 10, the column was drained, washed with water and the total hold-up of ammonia determined. This showed that the hold-up amounted to 4480 cc of the solution used. This value of H and the values of α given in the table are used to calculate k from the values of K secured from the plots. The value of α for the $NH_3 - NH_4OH$ exchange is that secured by Aten and Urey. The value of α ($= 1.021$) used for the $NH_3 - NH_4NO_3$ exchange is taken from subsequent experiments in which $(NH_4)_2SO_4$ is used, and may not be the correct value for this case. Finally, the value of k in Run 13 depends on the assumption of a value of α and may not be correct. The increase in concentration is small in all cases and due to

FIG. 2.
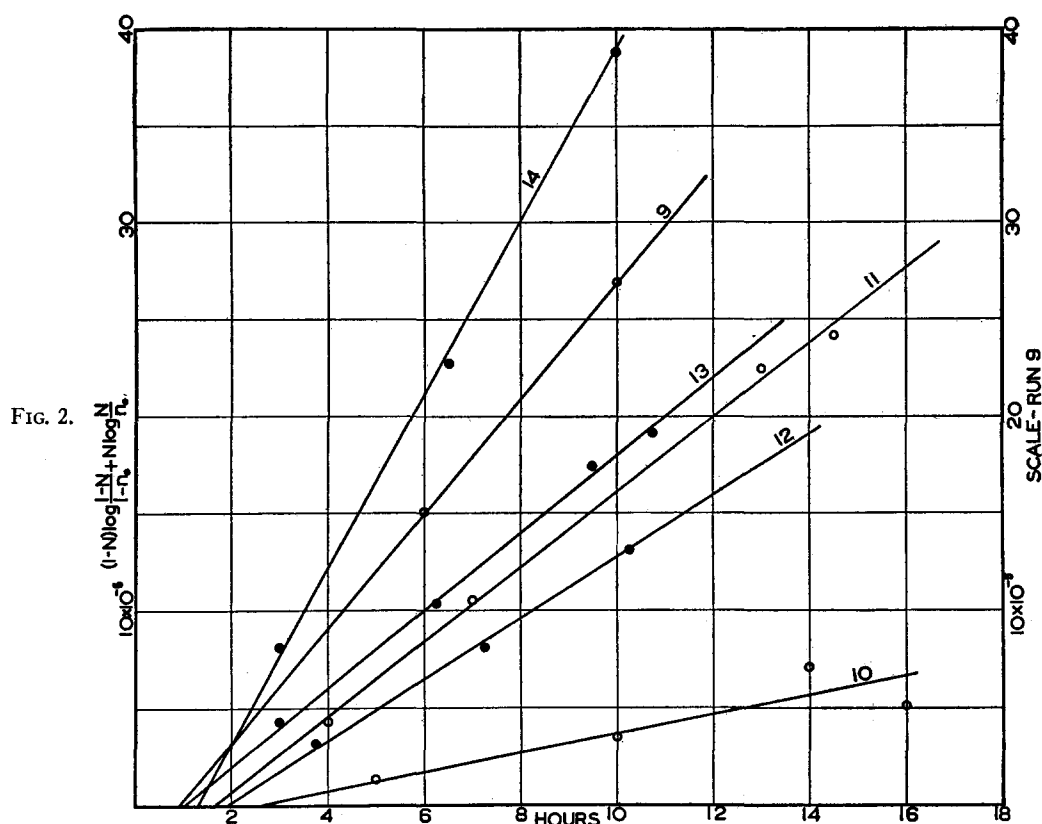
analytical errors, none of the derived constants can be regarded as very precise.

Ammonium nitrate was chosen in Run 9, because of its high solubility as well as the high solubility of sodium nitrate. The small value of k is very disappointing in view of the fact that the small column operates with 8 plates for $NH_3-(NH_4)_2SO_4$. However, the feed velocity used in Run 9 is more than 20 times that used in the small column runs. It was decided, therefore, to make a number of preliminary experiments to find out what liquid velocity should be used to give a reasonable number of plates with the large column. NH_4NO_3 had to be abandoned in these experiments because of severe corrosion. Although the fractionation factor for the exchange reaction NH_3-NH_4OH is much less, NH_4OH was more satisfactory in the test experiments. Runs 11 and 12 were run with feed velocities of 98, and 10 cc per minute, respectively. Decreasing the feed velocity, in-creased the number of plates, the number of plates being inversely proportional to the feed

velocity within the limits of error. Run 10 was made with 60°C with the hope that a higher temperature would speed up the exchange re-action and therefore yield a larger number of plates. It is evident from a comparison of Runs 10 and 11 that the higher temperature is not of advantage. There are compensating factors at work here since the value of the fractionation factor, α, probably decreases with temperature whereas the speed of the reaction increases. The solution of ammonia in methyl alcohol used in Run 13 was found to be more effective than NH_4OH, but it appears that the rate and degree of concentration are not sufficiently high to justify the use of ammonia-alcohol solutions instead of the ammonium salt solutions as is easily seen from a comparison of Runs 9 and 13. This checks the results from the small column. These results though qualitative show that the $NH_4^+-NH_3$ exchange must be used and that the rate of flow using ammonium nitrate might be as high as 40 cc per minute if 2 percent or 3 percent N^{15} is desired. However, because of the
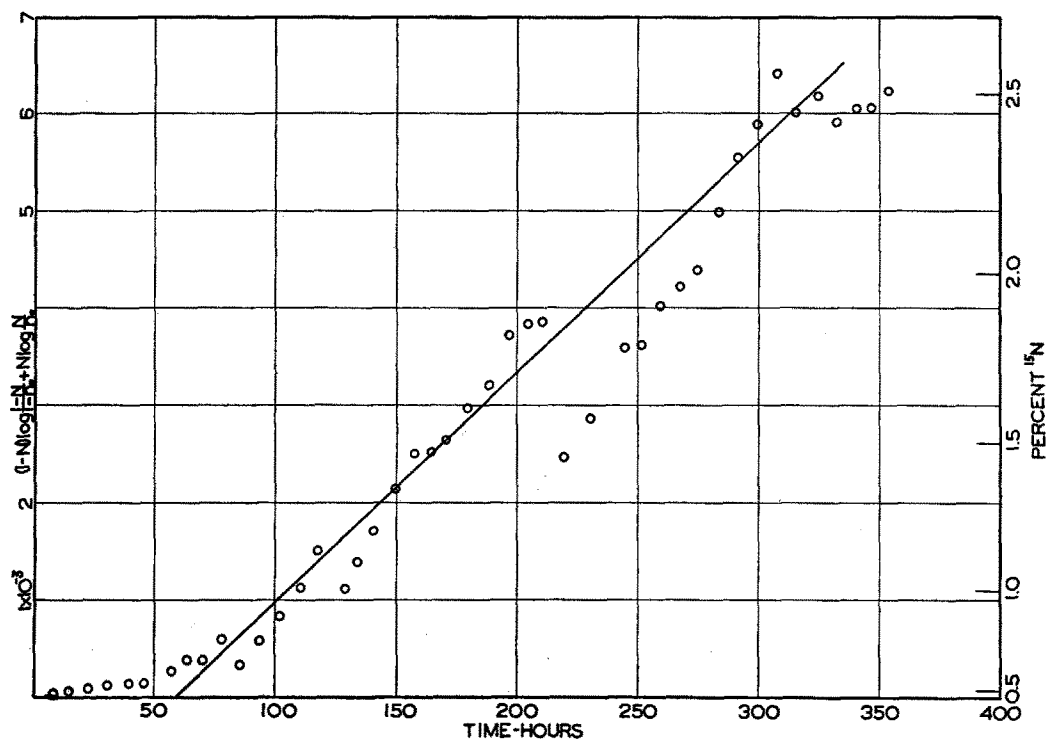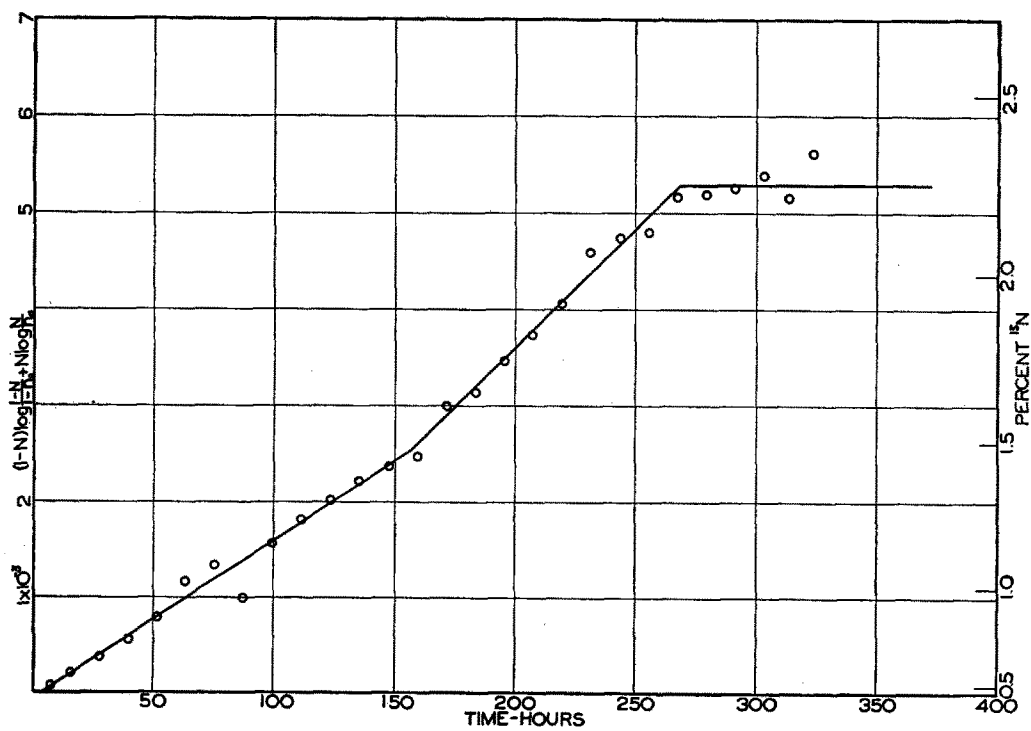
FIG. 3.

FIG. 4.

rapid corrosion we concluded that ammonium sulfate should be used in our column and that the rate of flow should be about 15 cc per minute as judged from Run 14.

Two final runs were made by feeding 15 cc/min. of a solution of ammonium sulfate (31 percent by weight) operating the entire apparatus at 8 cm of mercury pressure. Vacuum is used to cut down the concentration of dissolved ammonia and the amount of ammonia in the gas phase. Hence the working hold-up of the column is lowered so that less time is taken to effect a given separation. Low concentration of ammonia gas and low pressures are also important for the removal of ammonia from the solution in the stripping column. Ammonium chromate equivalent to 1 percent of the ammonium sulfate was added to the feed solution to decrease corrosion, and in Run 15 1 percent of methyl alcohol was added since this seemed to cause an oily film on the solution of the commercial ammonium sulfate to dissolve. During the first 150 hours of Run 16 we added no alcohol and for the remainder of the run, 5 percent of methyl alcohol.

In each of these runs the column was kept in operation until no further increase in the concentration of N¹⁵ was apparently obtained. A maximum concentration of 2.5 percent was reached in Run 15, and 2.34 percent in Run 16. The runs lasted about 12 days each. Ammonia gas samples were taken at the lower end of the column at intervals of from 8–12 hours, and the concentration of N¹⁵ determined on the mass spectrometer. The results are represented in Figs. 3 and 4. On the right-hand side of the figures the corresponding percentages of N¹⁵ are indicated.

The pressure in Run 15 was lowered from 20 to 15, to 10.8, and finally to 8 cm of Hg after 45, 85, and 280 hours of operation, respectively. Three interruptions occurred in this run; the steam pressure in the building was shut off, it was necessary to repair the small stripping column, and the feed pump gave trouble. A sharp break in the curve occurs at each interruption. However, the concentration increased until it reached 2.5 percent. The second run proceeded with but minor interruptions. The alkali pump was accidently shut off for twenty minutes. However, the ammonium sulfate lost in the waste from the stripping column was saved and fed back into the bottom of the column. The effect was to put one point off the curve at 87 hours. This curve follows the formula of Huffman and Urey rather well. The addition of 5 percent methyl alcohol after 150 hours increased the slope as can be seen from the curve indicating that the alcohol improved the operation somewhat though it did not increase the final concentration secured.

Knowing the total hold-up of the column and its average concentration, it is possible to calculate the amount of N¹⁵ transported during the run. On the completion of each of these runs the total hold-up of ammonia was determined by draining and washing the columns with water. A composite sample of all the drainings and wash waters was made up and analyzed. The hold-up in the pump, pump line, and condenser were also determined and analyses made. Table IV gives the results of these analyses and the amounts of NH₃¹⁵ transported. Using Eq. (3) it is possible to calculate α. The flow, w, in moles was calculated from the known rate of supply of ammonium sulfate including an estimate of the amount of ammonia dissolved in the solution. The duration of the run was taken as the time from the beginning of the run to the time at which the curves of Figs. 3 and 4 became approximately horizontal, namely, 320 and 268 hours for Runs 15 and 16, respectively. In this way we calculate α to be 1.013 and 1.021, respectively. It appears that considerable losses occurred in Run 15 due to the serious interruptions.

During Run 16 samples of the feed and of the ammonia gas escaping from the top of the column were taken at various times and the concentrations of N¹⁵ determined. Hence the value of α defined by Eq. (2) can be calculated since these concentrations should differ by one fractionation. The mean value of α secured from ten such analyses is 1.023. This is in satisfactory agree-

TABLE IV.

RUN	COLUMN HOLD-UP MOLES NH₃	ANALYSIS % N¹⁵	PUMP HOLD-UP MOLES NH₃	ANALYSIS % N¹⁵	MOLES N¹⁵H₃ TRANSPORTED
15	72.8	0.486	1.30	2.50	0.105
16	98	0.48	2.19	2.34	0.141

ment with the value calculated above though we believe that both values are uncertain because of the great difficulties involved in the determinations.[17]

The rate of attainment of equilibrium as given by the slope of the curve of Fig. 4, is greater than that to be expected from the final concentrations obtained. The slope

$$K = \frac{Nw(\alpha - 1)k \log \alpha}{H} = 2.36 \times 10^{-5}.$$

H thus calculated is 2479 cc, or about one-fifth the measured value of 13,050 cc for Run 16. This would be true if only one-fifth of the column at the lower end were working. We have no satisfactory explanation of this discrepancy since in all other tests of this relationship satisfactory agreement has been secured. It may be that the final steady state has not been attained in these runs in spite of the apparently horizontal character of the plots of Figs. 3 and 4 near the ends of the runs.

The hold-up was particularly large in both runs, amounting to approximately 10 liters in Run 15 and 13 liters in Run 16. In experiments on the distillation of water, and the bicarbonate-carbon dioxide exchange reaction, as well as for the exchange reaction $NH_3 - NH_4OH$, the hold-up was approximately 4 to 4.5 liters. It may be that the large hold-up in the ammonium sulfate runs was due to corrosion which produced a considerable amount of iron oxide in the column, but this does not explain the discrepancy between the measured and calculated values of H mentioned above.

Using the values of $k \log \alpha$ obtained from the maximum concentrations secured in these two runs and the values of α as given above, the numbers of theoretical plates for Runs 15 and 16 are 91 and 85, respectively. These are about

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[17] In the preliminary note which was based on Run 15, we reported a fractionation factor of 1.05 and 105 theoretical plates; this must be modified. We corrected the curve of Fig. 3 by eliminating the times apparently lost due to interruptions, giving a straight line or larger slope. In addition, two overhead samples gave us the large value of α, which on the basis of further work, was probably due to chance fluctuations in the rate of flow. Finally, an error in making the composite sample of the wash water gave too large transport. All these things gave consistent values for α and the number of theoretical plates.

what one would expect from the values secured in the shorter runs with the large column as recorded in Table III.

On the completion of each run 1500 cc of solution were drained from the column in 100 and 200 cc batches, in order to avoid mixing the concentrated material with the more dilute from higher up in the column. Samples from the two runs were analyzed for N^{15} and batches of nearly the same concentration combined. The ammonium sulfate solutions were boiled with alkali and the liberated ammonia absorbed in hydrochloric acid. The resulting solutions were evaporated to dryness. The two runs yielded 61 grams of ammonium chloride containing 2.5 percent N^{15}, 244 grams in which the concentration of N^{15} was better than 2 percent, and 1087 grams in which the concentration of N^{15} ranged between 0.7 percent and 1.5 percent.

CONCLUSIONS

The apparatus which we have described and used in these experiments has certain marked advantages over those previously used. It is capable of a very much larger transport than that of the Hertz method, the transport being approximately 100 times as great, so that appreciable amounts of material can be produced and in the two more successful runs described, substantial amounts of N^{15} of sufficiently increased concentration for many experiments have been produced. However, the increased concentration is not sufficiently high to enable us to investigate the physical properties of compounds of N^{15} particularly well. We should like to point out that modifications of our method may considerably increase the maximum concentration which can be secured. To accomplish this it is only necessary to use a fraction of the ammonia at the bottom of our column to feed another column of smaller diameter, a smaller hold-up, and a smaller rate of flow, in order to increase the concentration still further. The transport of this column would again depend upon the total flow in the column and the difference in concentration of the gas and liquid phases at the top of the column. Since the concentration of the material at the top of the second column would be $6\frac{1}{2}$ times higher, the difference in concentration would also be in-

creased by the same factor, and hence the total rate of flow could be decreased by a factor of $6\frac{1}{2}$ and yet maintain the same transport in the second column. This should, therefore, make possible a further increase in the concentration of N^{15} by a factor of $6\frac{1}{2}$ again if the second column were as efficient as the first. With smaller hold-up as would be expected for a smaller column, it should come to a steady state as rapidly as the first column, and hence the time required for the establishment of the maximum concentration should not be many times that required in our present experiments. Methods are being devised to carry out this extension of the method.

The transport when other apparatus, e.g. the Hertz type, is used, increases with the increased concentration of the starting material and hence our product can be used to advantage in such apparatus. The transport of a given apparatus using our product would be 6.5 times larger than when using natural nitrogen.

One of the disadvantages of the present method is the long time required for the apparatus to come to a steady state and the necessity of keeping it operating steadily during this time. One feature of our experiments is very encouraging in this connection. The interruptions which occurred during the course of our two most successful runs did not appreciably delay the time required for the establishment of the final steady state. A column of the rotating cone type does not drain if the rotor is stopped, and thus the distribution throughout the column is not changed if short shut-downs are required for repairs or to correct unavoidable accidents of the kind which we have encountered. This is a distinct advantage of this rotating type of column not present in the usual packed column which drains immediately if the process is interrupted, resulting in a mixing of most of the material throughout the column.

Previous experiments by Huffman and Urey on the distillation of water, led us to expect a much higher possible total rate of flow through the column than that we have been able to use. They used approximately 2 moles of total flow per minute in their most successful run, or 33 cc of liquid water per minute and secured 430 theoretical plates, while in these experiments we have been able to use only about 0.1 of a mole of ammonia per minute, or 15 cc of solution per minute and secured only 85 to 90 theoretical plates. The number of theoretical plates in a column must be determined by several factors. The rapidity of exchange of ammonia with the solution should increase the number of theoretical plates according to all experience. To accomplish this large surfaces are required. On the other hand, mixing processes such as back diffusion, or more probably turbulence in the gas, must occur which work against a large number of theoretical plates. It would appear that these mixing characteristics should be about the same in the case of the distillation of water and the exchange reactions which we have used here. Furthermore, the slow process in the exchange between the gas and the liquid phase would appear to be the rate with which mixing occurs in the liquid phase. We had anticipated that mixing would be as great in the liquid phase consisting of ammonium salt solutions, for example, as in the case of distillation of water. Such appears not to be the case. One would, of course, expect that ammonium ion would hardly diffuse as rapidly at ordinary room temperatures as water molecules at 60° to 70° as were used in the experiments of Huffman and Urey, but the difference could hardly be as great as that which we encountered.

Referring to Table III, we see from the values of k secured for Runs 9 and 11, that the number of theoretical plates is nearly the same when the exchange reaction $NH_3 - (NH_4)_2SO_4$ is used as when $NH_3 - NH_4OH$ is used. Hence the difficulty can hardly be that the reaction of NH_3 dissolved in water to form NH_4^+ is slow for if this were the case the number of plates should be markedly less in Run 9 than in Run 11 which is not true. It appears to us that the slow process is probably at the interface. Either ammonia does not condense readily on the surface of water, i.e. the accommodation coefficient is low, or the liquid surface under our conditions has a relatively impervious film of foreign material. An oily film is present when the commercial ammonium sulfate is dissolved in water. The methyl alcohol was added to remove this as it did judging from superficial observation. Ten percent of ethyl alcohol was

tried in some experiments to see whether the operation was improved but there appeared to be no marked improvement.

It should be noted that it is not necessary for the large ammonium sulfate molecule to diffuse through the liquid phase and hence cause much slower rates of diffusion than in the case of water, since the mixing processes in our problem consist only in an ammonium ion being transported from one part of the liquid to another and its position taken by a second ammonium ion.

A comparison of the results of Run 9 and of Runs 15 and 16 leads us to believe that the use of the $NH_3 - NH_4NO_3$ reaction would probably be more satisfactory for the concentration of N^{15} than that of $NH_3 - (NH_4)_2SO_4$ reaction, if the corrosion difficulties can be eliminated.

Evidence for Halogen Films on Tungsten in the Surface Ionization of Potassium Halides

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Molecular rays of the potassium halides were directed in high vacuum against tungsten and tungsten-oxygen surfaces, and the positive ion current to a collector cylinder was measured as a function of the surface temperature. Degrees of ionization on oxygen-free surfaces were calculated upon the assumption that each halide molecule produced one positive ion on striking a tungsten-oxygen surface. The high temperature results on oxygen-free filaments (1800°–2380°K) were interpreted as indicating surface dissociation of the potassium halide molecule, followed by partial ionization of the potassium atom and by the escape of the halogen as an atom. In the approximate temperature range 1800–1600°K a progressive change in the surface, with decreasing temperature, toward a higher work function was observed. This change led to surfaces of constant high work function, which were interpreted as due to the formation of halogen layers on the tungsten.

INTRODUCTION

THE surface ionization of the alkali metals on tungsten and tungsten-oxygen surfaces has been investigated by Ives,[1] Langmuir,[2] Becker,[3] Meyer,[4] and others,[5, 6] up to temperatures (about 1500°K) at which photoelectric currents become a complication in the type of ionization cell used by them. The range from 1500° to 2700°K was recently shown by two of the authors[7, 8] to be accessible to study by a molecular ray method. In this experiment a beam of potassium atoms of constant intensity

passed in a high vacuum through a hole in a cylindrical metal shell and struck a tungsten wire at the center. The cylinder was maintained at a negative potential with respect to the wire. Part of the potassium atoms lost their electrons to the tungsten surface, evaporated as positive ions, and were discharged on striking the cylinder. This positive ion current, i_+, was measured as a function of the temperature of the wire. Then, without disturbing the beam, the wire was coated with a layer of oxygen and a larger, temperature-independent current was observed. This current (designated as i_{WO}) was assumed, following Langmuir and Kingdon,[2] to represent 100 percent ionization of the potassium atoms striking the wire. The number of unionized atoms, i_a, leaving the wire at each temperature was calculated from the relation, $i_a = i_{WO} - i_+$.

[1] Ives, Phys. Rev. **21**, 385 (1923).
[2] Langmuir and Kingdon, Proc. Roy. Soc. **107A**, 61 (1925).
[3] Becker, Phys. Rev. **28**, 341 (1926).
[4] Meyer, Ann. d. Physik (5) **4**, 357 (1930).
[5] Killian, Phys. Rev. **27**, 578 (1926).
[6] Morgulis, Physik. Zeits. Sowjetunion **5**, 221 (1934).
[7] Copley and Phipps, Phys. Rev. **48**, 960 (1935).
[8] Copley and Phipps, Phys. Rev. **45**, 344 (1934).