$H_2$(gas)[19] and $S_2$(gas)[21] were used in computing values of $\Delta H_f^\circ$, $\Delta F_f^\circ$ and $\log_{10}K_f$ at selected temperatures from 0 to 1000°K. The calculated values of the eight thermodynamic properties are given in Table IX.

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION NO. 409 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

# A Laboratory Method for Separating Nitrogen Isotopes by Ion Exchange[1]

BY F. H. SPEDDING, J. E. POWELL AND H. J. SVEC

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Various aspects of the separation of $N^{15}$ and $N^{14}$ isotopes from each other by an ion-exchange process have been discussed. A number of experiments have been performed to establish the feasibility of using the process and to check the countercurrent theory of separation which has been developed. The separation factor for the exchange of $N^{15}$ and $N^{14}$ between a solution of dilute ammonium hydroxide and the ammonium form of Dowex 50-X12 was measured and found to be 1.0257 ± 0.0002. It was shown that an adsorbed band of ammonium ion must be eluted about 39 times its length in order to achieve separation of the isotopes. A method of continuous operation using a series of ion-exchange beds has been described and factors which influence the HETP at a steady state have been investigated.

## I. Theoretical Considerations

**A. Introduction.**—The remarkable success achieved in separating adjacent rare earths in high purity and good yields by ion-exchange methods suggested that isotopes might also be separated by a similar procedure. It was found[2,3] that, if a solution of mixed rare earth ions was adsorbed on the top of a column of sulfonated styrene–divinylbenzene copolymer in the hydrogen state, little separation occurred in the adsorption step. However, if the band was eluted with an eluent of citric acid, buffered with ammonia in an appropriate *p*H range, the individual rare earth ions separated to form sharp bands which traveled head to tail down the column. The individual rare earths could then be successively eluted off the resin bed in a pure state, with only a small amount of overlap between bands.

In order to obtain this type of elution,[4] the eluent had to contain one or more anions which complexed the rare earth ions strongly enough to compete with the resin in removing the triply charged rare earth cations from solution. It was found necessary that distinct chemical reactions occur at the front and rear edges of the adsorbed band so that the rare earths would be sharply confined between two boundaries. Under these conditions, the original rare earth band would spread out to a fixed equilibrium length which was determined solely by the composition of the eluent. Once this equilibrium was attained, the length of the band remained constant regardless of how far the band was eluted down a resin bed. As a consequence, all the boundaries of the individual rare earth bands moved at the same rate. It was also ascertained that, if the concentration of any ion in the eluate was plotted *versus* the volume of effluent solution while an individual rare earth band was passing off the column, a flat elution curve was obtained showing that the concentrations of all ions remained constant. When subsequent individual rare earth bands passed off the column the concentrations of all ionic species shifted slightly but remained at characteristic fixed values while each individual rare earth moved from the bed. The automatic adjustment, which arises primarily from the stability constants of the various complexed rare earth species, results in a self-sharpening of the bands.

It was hoped that the slight differences in the exchange constants of various isotopes of an element might also cause banding of the isotopes within a chemically constrained band, if the band was eluted under proper conditions.[5] While the chemical constraints at the ends of a band cause the over-all band to attain equilibrium in a short distance of travel, the much smaller exchange constants of the isotopes would require that the band travel a much greater distance before complete isotopic equilibrium would be approached.

Since the isotopic exchange constants for light elements are considerably larger than for heavier elements, the first experiments were carried out using nitrogen in the form of ammonium hydroxide in an attempt to separate $N^{15}$ from $N^{14}$.

**B. Chemical Conditions Required to Obtain a Sharp Adsorbed Ammonium Band.**—In order to develop and maintain a sharp adsorbed ammonium band it is necessary to have a uniformly packed resin bed. Under these conditions, as the solution percolates down the column, a horizontal boundary between two solutions can be maintained. In practice, if sufficient care is taken in preparing the resin beds, tilting and channeling can be kept less than a few millimeters for columns 2 to 6 inches in diameter. When one ion replaces another on the resin bed there is always some change in the volume of the resin. In small diameter tubes, bridging frequently occurs during expansion and contraction of the bed and results in uneven packing of the resin particles. This leads frequently to serious tilting of the band.

To separate nitrogen isotopes the resin beds are

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, THIS JOURNAL, **72**, 2354 (1950); (b) F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe, *ibid.*, **73**, 4840 (1951).

[3] F. H. Spedding and J. E. Powell, *Chem. Engr. Progr., Symposium Series*, **50**, No. 14, 7 (1954).

[4] F. H. Spedding and J. E. Powell, THIS JOURNAL, **76**, 2545, 2550 (1954).

[5] F. H. Spedding, J. E. Powell and H. J. Svec, *ibid.*, **77**, 1393 (1955).

first converted to the hydrogen cycle by passing a dilute mineral acid through the columns until the beds are saturated. The beds are then rinsed with water and a dilute solution of ammonium hydroxide is added until a band of ammonium ion of the desired length is obtained. When Dowex-50 resin is in the ammonium state it exhibits a somewhat different shade of brown than it does in the hydrogen cycle or the sodium cycle so that the boundaries of the ammonium band can be seen distinctly.

If a boundary is to remain sharp, a chemical reaction which goes virtually to completion must take place at the boundary. If ammonium ion from a salt solution such as ammonium chloride reacts with hydrogen resin the boundary will not be very sharp, because the reaction

$$H^+_R + NH^+_{4_S} \rightleftarrows NH^+_{4_R} + H^+_S \qquad (1)$$

has an apparent equilibrium constant

$$K' = K\,\frac{\gamma_{(NH^+_{4_S})} \times f_{(H^+_{4_R})}}{\gamma_{(H^+_S)} \times f_{(NH^+_{4_R})}} = \frac{C_{(NH^+_{4_R})} \times C_{(H^+_S)}}{C_{(NH^+_{4_S})} \times C_{(H^+_R)}} \qquad (2)$$

which does not differ greatly from one. While the forward motion of the solution sweeps the $H^+_S$ down-stream and tends to shift the equilibrium to the right, this alone is not sufficient to maintain a sharp boundary. On the other hand, when ammonium hydroxide is used the over-all reaction becomes

$$H^+_R + NH_4OH_S \rightleftarrows NH^+_{4_R} + H_2O \qquad (3)$$

For this reaction

$$K' = \frac{C_{(NH^+_{4_R})}}{C_{(H^+_R)} \times C_{(NH_4OH)}} \qquad (4)$$

has a value on the order of $10^9$. Here the equilibrium is far to the right, resulting in an extremely sharp boundary. It might be mentioned that considerable heat is liberated at the boundary by the above reaction and this limits the concentration of $NH_4OH$ which can be used conveniently.

The adsorbed ammonium band is driven down the column with an eluting solution of sodium hydroxide. Here the reaction is

$$NH^+_{4_R} + Na^+_S + OH^-_S \rightleftarrows NH_4OH_S + Na^+_R \qquad (5)$$

and the apparent equilibrium constant

$$K' = \frac{C_{(NH_4OH_S)} \times C_{(Na^+_R)}}{C_{(NH^+_{4_R})} \times C_{(Na^+_S)} \times C_{(OH^-_S)}} \qquad (6)$$

has a value of about $10^5$. This again produces a sharp boundary.

The adsorbed ammonium band is, accordingly, sharply confined between these two boundaries and is in equilibrium throughout its length with a solution of ammonium hydroxide. The concentration of ammonium hydroxide solution in contact with the ammonium band is constant throughout and is determined by the concentration of the sodium hydroxide used as the eluent.

The length of the adsorbed ammonium band is primarily determined by the amount of ammonia in the column and the capacity of the resin. The band length will depend to a certain extent upon the concentration of the ammonium hydroxide in the resin pores, which is fixed by the concentration of the eluent. Once the concentration of the sodium hydroxide has been chosen, the length of the ammonium band remains constant as it is eluted down the resin bed.

**C. Isotopic Equilibrium.**—If the ammonium hydroxide solution in the pores of the bed is maintained for a sufficient time in contact with a particular section of resin bed, the system will attain isotopic equilibrium according to the reaction

$$N^{14}H^+_{4_R} + N^{15}H_4OH_S \rightleftarrows N^{15}H^+_{4_R} + N^{14}H_4OH_S \quad (7)$$

The equilibrium constant is

$$K = K' = \frac{[N^{15}H^+_{4R}][N^{14}H_4OH_S]}{[N^{14}H^+_{4R}][N^{15}H_4OH_S]} =$$

$$\frac{[N^{15}_R][N^{14}_S]}{[N^{14}_R][N^{15}_S]} = \frac{R_R}{R_S} = 1.0257(8)^6$$

where $R_R$ and $R_S$ are the $N^{15}$–$N^{14}$ ratios in the resin and aqueous phases, respectively.

If the length of the ammonium band remains constant as the band is eluted down the resin bed, each time an equivalent of sodium ion is deposited at the rear edge of the band it displaces an equivalent of ammonium ion. The displaced ammonium ion comes to chemical equilibrium within the system very rapidly and isotopic equilibrium tends to be approached as the solution passes over the resin. When the ammonia in solution reaches the front edge of the ammonium band it is redeposited as ammonium ion on the resin bed. At all times, the ratio of $N^{15}$ to $N^{14}$ on the resin is greater than it is in the solution contacting it. From equation 7

$$R_R = KR_S = (1 + \epsilon)R_S = 1.0257R_S \qquad (9)$$

This presupposes that the solution remains in contact with an increment of resin of a given composition for sufficient time for equilibrium to be attained. In the case of the isotopic exchange for ammonia, the reaction is sufficiently rapid that, within our experimental error under the condition we have operated, equilibrium is attained at the critical points in the system even when the band is moving at the rate of 30 inches per hour down a bed. The band becomes richer in $N^{15}$ at the rear edge and richer in $N^{14}$ at the front edge as the elution proceeds.

Figure 1 shows a plot of how the isotopic ratio of the nitrogen varies across the band with different distances of travel. It can be seen that the maximum isotope enrichment or depletion occurs at the ends of the band. In the plateau region, the ratio of the isotopes in the resin phase and solution phase are not changing, although they differ from each other by the amount $\epsilon R_S$, where $\epsilon = (K - 1)$. The $N^{15}$–$N^{14}$ ratio on the resin, $R_R$, is equal to $KR_S$ from equation 9; therefore

$$KR_S - R_S = (K - 1)R_S = \epsilon R_S \qquad (10)$$

Since the solution is flowing past the resin in the plateau region carrying ammonia richer in $N^{14}$ and leaner in $N^{15}$ than the resin it contacts, there is a net transfer of $N^{14}$ toward the leading edge of the band. If the plateau region is sufficiently long that isotopic equilibrium is attained within this re-

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(6) See Part II, Section B.

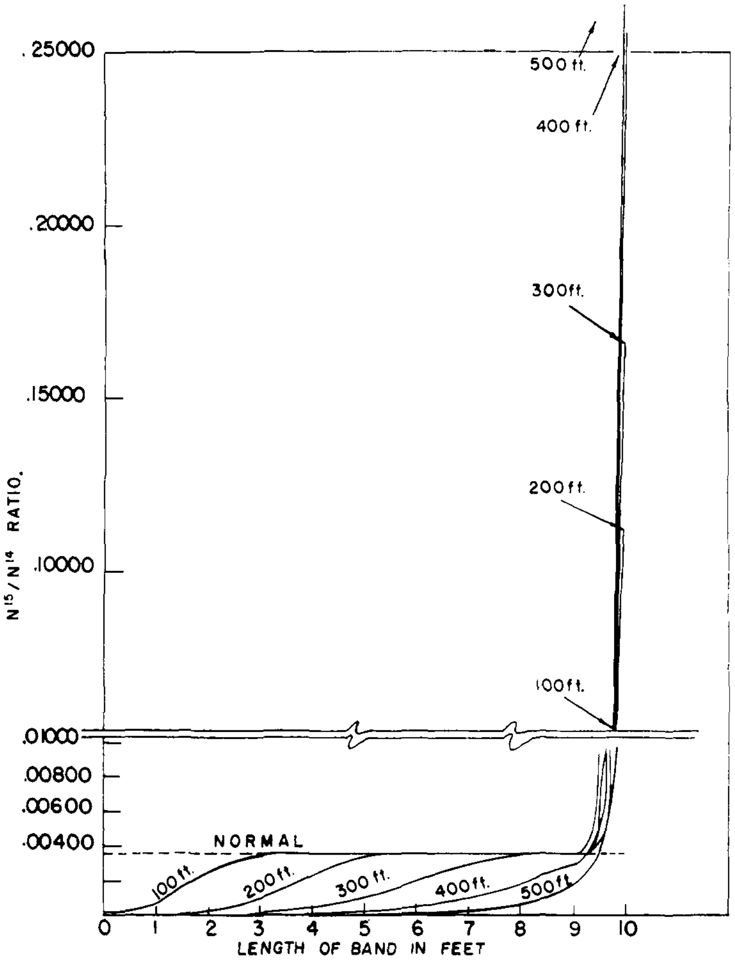

Fig. 1.—Profiles of an adsorbed ammonium band after various distances of elution. The plateau portion is magnified to illustrate the behavior in this part of the band. The depleted area increases at a constant rate up to about 40 times the length of the adsorbed band.

gion, the net transfer of $N^{14}$ per equivalent of ammonia passed over the plateau and redeposited is the same irrespective of the degree of equilibrium reached in the rest of band. It should be borne in mind that the rate at which ammonia is picked up and redeposited is not exactly the same as the rate at which the sodium ion is introduced into the column in equivalents, since some of the sodium ions must remain in the liquid which fills the pore spaces left behind as the ammonium band advances. The total amount of ammonia in the pore spaces of the ammonium band does not change, as this solution simply moves along at the same rate as the band advances. The percentage of the total ammonia in the pores is small, being on the order of a few per cent. when 0.6 *N* NaOH is used as the eluent and becomes increasingly smaller as more dilute NaOH solutions are used. It is apparent from Fig. 1 that the plateau region moves along with the band, but gets smaller and ultimately vanishes as the band progresses down the column. If a correction is made for the amount of sodium ion left in the pore spaces, then the rate at which ammonia is picked up and laid down can be calculated. Under these conditions, it is simpler to fix a plane of reference perpendicular to the moving band at a point within the plateau region. This plane moves with the band. Under these circumstances, each equivalent of ammonium ion picked up at the rear of the band flows through the reference plane and is redeposited at the front. Simultaneously, one equivalent of ammonium ion on the resin passes through the plane in the opposite direction, resulting in no net transfer of total ammonia across the plane of reference. In the case of the nitrogen isotopes, however, there will be a net transfer of $\Delta n$ equivalents of $N^{14}$ forward and $\Delta n$ equivalents of $N^{15}$ in the opposite direction across the reference plane for each equivalent of ammonia displaced from the resin and redeposited. This results from the difference in the isotopic ratios existing in the solution and resin phases which are moving past each other.

The transfer of $N^{14}$ and $N^{15}$ can be calculated, since $\Delta n$ for one equivalent of total ammonia transported is equal to $N_R - N_S$ where $N_R$ and $N_S$ are the mole fractions of $N^{15}$ in the resin and solution phases, respectively, in the plateau region. Since $R = N/(1 - N)$ in general, equation 9 becomes

$$\frac{N_R}{1 - N_R} = (1 + \epsilon)\frac{N_S}{1 - N_S} \tag{11}$$

Solving for $N_R$ and $N_S$

$$N_R = \frac{(1 + \epsilon)N_S}{1 + \epsilon N_S} \tag{12}$$

$$N_S = \frac{N_R}{1 + \epsilon(1 - N_R)} \tag{13}$$

Therefore

$$\Delta n = N_R - N_S = \frac{\epsilon N_S(1 - N_S)}{1 + \epsilon N_S} = \frac{\epsilon N_R(1 - N_R)}{1 + \epsilon(1 - N_R)} \tag{14}$$

In the plateau region $N_S$ is the mole fraction of $N^{15}$ in the solution originally fed to the column ($N_S = N_0 = 0.00365$). Since there is no net transfer of isotopic species between the resin and solution phases as they pass each other in the plateau region, $\Delta n$ moles of $N^{14}$ are transported into and distributed throughout the front section of the band, *via* the solution phase, for each mole of total ammonia displaced from the resin bed. Conversely, $\Delta n$ moles of $N^{15}$ leave the front section, are transported across the plateau, *via* the resin phase, and distributed throughout the rear section. In the front and rear sections, beyond the plateau region, a net transfer of isotopic species between the resin and solution phases will occur as the transported isotopes redistribute.

If it is desired to obtain the maximum rate of separation of isotopic species from a given feed material, one strives for the maximum mass transfer of the isotopes and adjusts the system so that an effectively continuous operation can be carried out.

It is convenient, when operating a fixed bed ion-exchange plant in a continuous manner, to have the resin bed in sections. This permits the injection of feed solution and the withdrawal of products from the band as it moves from section to section by simple valving operations. For this reason, a number of short columns connected in series are used rather than a single long column. This arrangement permits an adsorbed band to be eluted in a cyclic manner using only a few columns, since the spent resin can be regenerated for re-use before the band comes around the next time. Other advantages of such an arrangement are that it is simpler to maintain uniform resin beds in short columns, and the resistance to flow of the eluent and regenerant solutions can be minimized by having the solutions flow only through the desired portion of the bed system at any given time.

Experience has shown that it is only necessary to have a band of ammonia 7 to 10 feet long in order to provide a suitable plateau region and sufficient distance on either side to permit the concentrations of the isotopes to approach 100% $N^{14}$ at the front and 100% $N^{15}$ at the rear. After the ammonium band is adsorbed on the bed, it is eluted for a distance of 200–300 feet. This allows the system to approach the condition where continuous operation can be started. Feed solution can then be injected at the top of each column whenever the plateau region moves past this point. Similarly, products can be removed as the front and rear edges of the ammonium band pass the bottom of a column. In practice, since less valving is required, the feed is injected and the products withdrawn only once each time the band completes a circuit of the beds. Proportionately larger injections and withdrawals are made when the latter procedure is used.

Since the natural abundance of $N^{15}$ is low and the resin bed has an appreciable capacity, it is desirable to permit the $N^{15}$ to accumulate without withdrawal until its concentration has built up to the desired level. Withdrawal of $N^{14}$ can begin at the time feed injections are started. As the ammonium band is eluted from one resin bed with sodium hydroxide eluent, the front section is allowed to proceed down the next column until the plateau region is passing between columns. At this time, a valve between the two columns is closed and a quantity of ammonium hydroxide (say one mole) of the same normality as the sodium hydroxide eluent and containing a mole fraction of $N^{15}$ equal to $N_0$ is allowed to flow into the top of the leading column. At the same time, or at some prior or subsequent time $(1 - N_0)$ moles of ammonium hydroxide containing virtually pure $N^{14}$ is allowed to flow from the bottom of the column. In practice, the withdrawal can be made slightly before or after the injection so as to occur when the front of the band is moving off a column. This section of the band on the column will now be longer by $N_0$ moles. Further, since only $(1 - N_0)$ moles of $N^{14}$ were introduced in the mole of feed and $(1 - N_0)$ moles of pure $N^{14}$ were withdrawn, the gain in this section of the band is $N_0$ moles of $N^{15}$. However, since it was specified that the reference plane move at the same rate as the front edge of the band, it will have progressed down the column $N_0$ moles during this operation. Therefore, to restore the front section of the band to its original condition it is necessary to effect a net transport of $(N_0 - N_0N_R)$ moles of $N^{15}$ rearward across the boundary and a corresponding amount of $N^{14}$ in the opposite direction. The $N_0N_R$ moles of $N^{15}$ represent the amount of $N^{15}$ entering the rear section when the reference plane was shifted forward $N_0$ moles.[7] Since the net number of moles of $N^{15}$ or $N^{14}$ transported per mole of band displacement is $\Delta n$, defined by equation 14, the number of moles of displacement the band must undergo, is

$$\nu = \frac{N_0(1 - N_R)}{\Delta n} = \frac{(1 - N_R)(1 + \epsilon N_0)}{\epsilon(1 - N_0)} \qquad (15)$$

From equation 12

$$1 - N_R = \frac{1 - N_0}{1 + \epsilon N_0} \qquad (16)$$

Substituting for $1 - N_R$ in equation 15

$$\nu = \frac{N_0(1 - N_0)}{\Delta n(1 + \epsilon N_0)} = \frac{1}{\epsilon} = \frac{1}{0.0257} = 39 \qquad (17)$$

Therefore, the total advance of the band between subsequent injections of a mole of natural ammonium hydroxide is $(39 + N_0)$ moles. Since a mole of dilute sodium hydroxide solution advances the band about 1.75 inches on a 4-inch diameter resin bed and $N_0$ is normally small, the band would have to advance approximately 68 inches between one mole additions. It should be noted that a definite number of moles of sodium hydroxide are required to resolve one mole of nitrogen into its isotopes. Once the length of the band required to produce products of the desired purity is determined, increasing the cross-sectional area of the beds would result in a proportionate increase in the yield and would require only a proportionate increase in consumption of sodium hydroxide.

If the band is allowed to progress down a column system about 50 or 60 band lengths without addition or withdrawal of ammonia, it approaches very closely the condition known in countercurrent extraction as steady state in total reflux. Here the plateau range disappears entirely and the exchange between the resin and the solution reaches the steady-state equilibrium condition so that, if one examines the net transport of either chemical or isotopic species across an imaginary plane at any fixed arbitrary distance from the front of the band, the net transport is zero. Under these conditions, the concept of a theoretical plate height becomes unambiguous and the mathematics of a countercurrent system can be utilized, provided the equations used are those which apply to the case in which no product is withdrawn. Since there is no net transport into or out of a plate, the resin stream leaving the plate differs from the resin stream entering it by the factor $K$ and the same is true in reverse for the solution phase. Then if two points on the resin are chosen a distance, $L$, apart the isotopic ratios at the

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(7) This assumes that the ammonia in this section of the column is virtually all adsorbed on the resin bed. If it were all in solution phase the forward shift would be $N_0^2$ moles. Actually, with *dilute solution* $N_0N_R$ is the better approximation.

two points will differ by the factor $K^n$ where $n$ is the number of theoretical plates between the points.

$$R_n = K^n R \qquad (18)$$

or

$$\log \frac{R_n}{R} = n \log K \qquad (19)$$

Under these limiting conditions if the logarithm of the ratio of the isotopic ratios is plotted against $n$, the number of theoretical plates, a straight line is obtained whose slope is log $K$. The value of $n$ is not known, in general, but if the reasonable assumption is made that, under the conditions of steady state and total reflux, the height of a theoretical plate is constant across the band, then the plate height can be calculated, since

$$n = \frac{L}{\text{HETP}} \qquad (20)$$

giving

$$\log \frac{R_n}{R} = \frac{\log K}{\text{HETP}} L \qquad (21)$$

If the plot of log $R_n/R$ *versus* $L$ is linear, the above assumption is justified and the slope is log $K$ divided by HETP. Since $K$ can be determined independently, the height equivalent to a theoretical plate can be found. In our experiments, this has usually ranged from 0.15 to 1.5 mm. depending upon the flow rate, solution concentrations, etc.

When the columns are operated under plateau conditions, as is normally done, care must be exercised in utilizing equations derived for cascade or countercurrent extraction systems. Almost invariably, in deriving these formulas, simplifying assumptions have been made which are not applicable to the resin system as the operations are being carried out. Even in those cases where attempts have been made to adapt the equations to the type systems described here, the mathematics has become so complicated that the equations have not been solved. Frequently, terms have been introduced which not only have not been evaluated, but which are difficult to evaluate independently. Therefore, this theory has not yet been especially helpful in predicting quantitatively the shape of the curve preceding and following the plateau region. Nevertheless, it is clear that certain factors must be considered if the process is to be efficient: (1) the exchange reaction employed should have as large a $K$ as possible; (2) the band should be eluted as fast as practical to obtain the maximum transport per unit time, but not so fast that band boundaries become diffuse or the HETP excessively large; (3) the material should be eluted under conditions which permit maximum utilization of the active points on the resin bed by the ions being separated isotopically; (4) the length of the adsorbed band should be selected so that sufficient plates are included within the band to give the desired products at the steady state, but not so long that excessive resistance to flow is encountered.

## II. Experimental

**A. Preliminary Investigation of the Approach to a Steady State in the Elution of Ammonium Ion with Sodium Hydroxide** (in collaboration with S. A. Harmon and R. Harrington).—A series of ten ion-exchange columns were prepared. Each column consisted of a 5-foot section of 4-inch, i.d., flanged Pyrex pipe closed at the ends by type 316 stainless steel plates bolted to standard cast iron flange sets. The end plates of the columns were center-tapped and fitted with $^1/_8$-inch stainless steel nipples, two inches long. A circular baffle plate, two inches in diameter, supported by three $^1/_2$-inch long rods of stainless steel, was welded to the bottom side of each top plate to prevent the influent solution from disturbing the resin bed. The resin bed was supported by one thickness of Saran filter cloth backed up by a 30-mesh stainless steel screen. The circles of Saran and stainless steel gauze were rubber-cemented into a 5-layer sandwich between three 6-inch, o.d., 4-inch, i.d., by $^1/_8$-inch thick neoprene gaskets. The screen sandwich was supported an inch above the bottom plate by a Pyrex pipe spacer to prevent the screen from blocking the outlet in the bottom plate. Neoprene gaskets were used with both the column plates to obtain a water-tight seal. Individual columns of the series were interconnected by means of flexible $^5/_{16}$-inch Tygon tubing slipped over the $^1/_8$-inch pipe nipples which were screwed into the end plates. By using a binding of Scotch electrical tape over the junctions and $^1/_2$-inch brass tubing clamps, in addition, the system could be used up to an internal pressure of two atmospheres without leakage.

The resin beds of the columns consisted of 100–200 mesh spheres of Dowex 50-X12 and were 58–59 inches long in the $H^+$ cycle and 53–54 inches long in the $Na^+$ cycle. The resin beds were backwashed by removing the top plate and adding an auxiliary 5-foot section of Pyrex pipe. All exceptionally fine particles, which either did not settle readily after backwashing or which settled in a thin layer at the top of the resin beds, were removed by means of a siphon so that the finished beds offered a minimum of resistance to liquid flow. Under a 60-foot liquid head a flow rate of about a liter per minute could be obtained through a single unit.

The resin beds were given a preliminary treatment with 2 $N$ NaOH, rinsed with distilled water and restored to the $H^+$ cycle with 1 $N$ $H_2SO_4$. The excess $H^+$ ion was rinsed from the columns by means of distilled water, and five liters of 15 $N$ $NH_4OH$, diluted 30-fold with water, was passed downflow through three of the columns connected in series. This resulted in an adsorbed $NH_4^+$ band approximately 10 feet long.

The ammonia band was eluted down the series of columns with 0.6 $N$ NaOH at a flow rate of 120–180 ml. per minute. As the band progressed down the series, the eluent feed tube and the discharge tube were moved along so that only three columns were connected together at any one time. As the band passed, the resin left behind was reconverted from the $Na^+$ to the $H^+$ cycle, as before, and the columns were then ready to be reused. In all, the adsorbed band was eluted around the 10-column series ten times. Profiles were taken every twenty columns by withdrawing small samples of the solution periodically as the band passed between columns. Profiles B-20, 40, 60, 80 and 100 are shown in Fig. 2. It can be seen that the normal plateau is gradually removed by the transport of $N^{15}$ from the front to the rear of the band. Up to B-80, which represents about 36 displacements of the adsorbed band, the amount of $N^{15}$ transported was proportional to the distance the band was eluted. Beyond B-80 the plateau disappeared and the efficiency fell off markedly. At B-100 the band was approaching the steady state and very little improvement could be expected from this point on. However, the last 6 inches of the band containing practically all the $N^{15}$ was allowed to pass onto a series of 22 mm., i.d., by 4.5-foot resin beds and was eluted further until a mole fraction of $N^{15}$ of 0.81 was observed at the rear edge of the band. The 22 mm. diameter columns were closed at the bottom with fritted glass plates; the plates were not uniformly porous and, as a consequence, considerable channelling and tilting of the band boundaries were observed. The experiment did, however, show that separation would continue when steady-state conditions were destroyed by decreasing the diameter and increasing the length of the enriched portion of the band.

**B. Determination of the Equilibrium Constant for the Exchange of Nitrogen Isotopes between Ammonium Hydroxide Solution and Ammonium Ion Adsorbed on Dowex-50** (in collaboration with D. M. Provow and J. Capellen).—If one passes a dilute solution of $NH_4OH$ containing a mole fraction of $N^{15}$ equal to $N_0$ or a $N^{15}$–$N^{14}$ ratio of $R_0$ down a

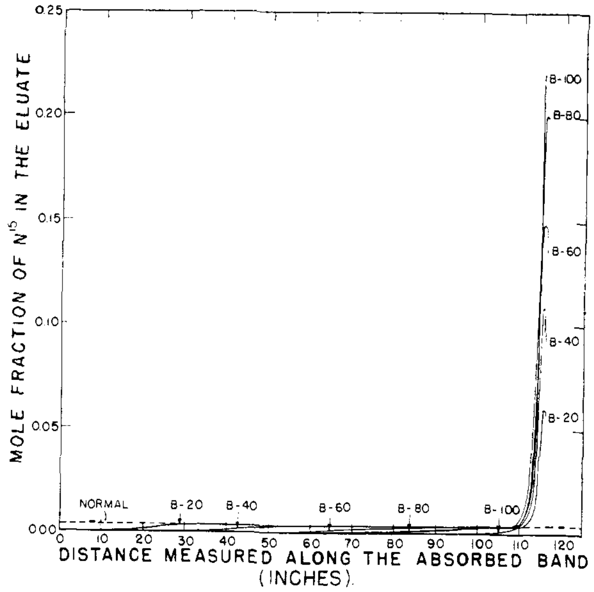

Fig. 2.—Profiles of a 10-foot long adsorbed ammonium band taken after traversing 20, 40, 60, 80 and 100 beds of 100–200 mesh Dowex 50-X12, each 4 inches in diameter and 58–59 inches long.

bed of cation exchanger in the $H^+$ cycle, the $H^+$ ion is completely displaced by $NH_4^+$ due to the large constant for the reaction which takes place at the front of the band.

When all the $H^+$ ion on the resin has been replaced by $NH_4^+$ ion, $NH_4OH$ solution will begin to flow from the resin bed. In the first fractions of $NH_4OH$ solution that are collected, the ratio of $N^{15}$ to $N^{14}$, $R$, will be less than the ratio $R_0$, which existed in the feed, due to the exchange reaction given by equation 7. The ratio $R$ will approach $R_0$ as more effluent solution is collected. When the ratio in the effluent solution becomes equal to $R_0$, the ratio of $N^{15}$ to $N^{14}$ in the resin phase must differ from $R_0$ by the factor $K$ due to the relationshp

$$K = \frac{R_R}{R_S} = \frac{R_R}{R_0} \tag{22}$$

Now equation 22 can be written in the form

$$K = \frac{N_R}{1 - N_R} \times \frac{1 - N_0}{N_0} \tag{23}$$

where

$$N_R = \mathrm{n}/Q \tag{24}$$

$Q$ is the total exchange capacity of the resin bed in equivalents and n is the total number of equivalents of $N^{15}H_4^+$ adsorbed on the resin bed.

If $K$ in equation 22 turned out to be exactly 1, then there would be no tendency for either enrichment or depletion of $N^{15}H_4^+$ in the resin phase when it is equilibrated with a solution of ammonia. That is, $\mathrm{n}_0/Q$ would equal $N_0$. However, if $K$ differs from 1, then n can be defined as

$$\mathrm{n} = \mathrm{n}_0 + \Delta\mathrm{n} \tag{25}$$

Therefore

$$N_R = \frac{\mathrm{n}_0 + \Delta\mathrm{n}}{Q} = N_0 + \frac{\Delta\mathrm{n}}{Q} \tag{26}$$

and

$$K = \frac{\left(N_0 + \frac{\Delta\mathrm{n}}{Q}\right)(1 - N_0)}{\left(1 - N_0 - \frac{\Delta\mathrm{n}}{Q}\right) \mathrm{N}_0} = 1 + \frac{\Delta\mathrm{n}}{\mathrm{N}_0 Q\left(1 - N_0 - \frac{\Delta\mathrm{n}}{Q}\right)} \tag{27}$$

and

$$\epsilon = K - 1 = \frac{\Delta\mathrm{n}}{N_0 Q\left(1 - N_0 - \frac{\Delta\mathrm{n}}{Q}\right)} \tag{28}$$

Solving for $\Delta\mathrm{n}/Q$, one obtains the relationship that

$$\frac{\Delta\mathrm{n}}{Q} = \frac{\epsilon N_0(1 - N_0)}{1 + \epsilon N_0} \tag{29}$$

If $\epsilon$ is small compared to 1, then $\Delta\mathrm{n}/Q$ is of the order of $\epsilon N_0 (1 - N_0)$ and is also much less than either 1 or $N_0$. Consequently, equation 28 can be written

$$\epsilon = \frac{\Delta\mathrm{n}}{QN_0(1 - N_0)} \tag{30}$$

Now $\Delta\mathrm{n} = \Delta\mathrm{n}$ resin $= -\Delta\mathrm{n}$ effluent, so $\Delta\mathrm{n} = \sum_{i=1}^{m} V_iC_i (N_0 - N_i)$, where $V_i$ is the volume; $C_i$, the ammonia concentration; and $N_i$, the mole fraction of $N^{15}$ in the ammonia of the $i$th fraction of the $m$ fractions which were collected before $R$, the ratio of $N^{15}$ to $N^{14}$ in the effluent, returned to the value $R_0$, the feed ratio. Equation 30 now becomes

$$\epsilon = \frac{\sum_{i=1}^{m} V_iC_i (N_0 - N_i)}{QN_0(1 - N_0)} \tag{31}$$

Since

$$N_i = \frac{R_i}{1 + R_i} \text{ and } N_0 = \frac{R_0}{1 + R_0} \tag{32}$$

then

$$\epsilon = \sum_{i=1}^{m} \frac{V_iC_i\left(\frac{R_0}{1 + R_0} - \frac{R_i}{1 + R_i}\right)(1 + R_0)^2}{QR_0} \tag{33}$$

Finally, since $R_0$ for normal nitrogen is 0.00365 $(1 + R_i) \cong (1 + R_0) \cong 1.00$ and

$$\epsilon = \sum_{i=1}^{m} \frac{V_iC_i(R_0 - R_i)}{QR_0} \tag{34}$$

If extremely high precision is desired and experimental accuracy warrants, $\epsilon$ can be determined from equation 28 at the expense of more involved computations.

For convenience, $NH_4OH$ solutions are oxidized with NaOBr to give $N_2$ gas prior to analysis on the mass spectrometer. The most sensitive determination at low concentrations of $N^{15}$ is the ratio of $N_2^{29}$ to $N_2^{28}$. For normal and below normal values of $N^{15}$, the ratio of $N_2^{29}$ to $N_2^{28}$ is, to a high precision, equal to twice the $N^{15}$-$N^{14}$ ratio. Since the ratio appears in both numerator and denominator of equation 34, it makes no difference whether one uses the $N_2^{29}$-$N_2^{28}$ ratios or the $N^{15}$-$N^{14}$ ratios for $R_0$ and $R_i$ in computing the value of $\epsilon$.

The value of $K = 1 + \epsilon$ has been determined in the manner described above and was found to be 1.0257 ± 0.0002.

**C. *The Investigation of Factors Which Influence the Theoretical Plate Height at the Steady State*** (in collaboration with J. Capellen).—In Part I it was shown that when an ammoniun band was eluted down a column 40 to 50 band lengths, a steady-state gradient of the isotopes was built up similar to that obtained in a countercurrent extraction system operating at total reflux (no product withdrawn). Under these conditions equation 21, written in the form

$$\log R_n = \frac{\log K}{\mathrm{HETP}} L + \log R \tag{35}$$

states that, if the logarithm of the isotopic ratio in any plate leaving the column is plotted against the length of the band which has progressed off the column, $L$, a straight line plot should be obtained. The slope of the line is equal to the logarithm of the equilibrium constant for the exchange reaction, $K$, divided by the height equivalent to a theoretical plate, HETP. Since $K$ is known from Section B, the HETP can be calculated from these data.

It is desirable in determining HETP's for a column that sufficient $N^{15}$ be present in the original mixture to allow a reasonably high mole ratio of $N^{15}$ to be attained in the $N^{15}$-rich end of the band. A 50-50 mixture of $N^{14}$ and $N^{15}$ would be ideal, but such a quantity of $N^{15}$ was not available. Since normal ammonia contains only one part of $N^{15}$ to 273 parts of $N^{14}$, enriched ammonia from several previous runs was adsorbed onto a 2-inch diameter resin bed to form a band 45 inches long for the following experiments.

The band was eluted down 60 2-inch by 5-foot columns of Dowex 50-X12, 100-200 mesh resin, at a flow rate of 125 ml. per minute with 0.6 *N* NaOH solution. This was more than sufficient to attain a steady state. Log $N^{15}/N^{14}$ *vs.* *L* is plotted in Fig. 3, curve A, and a straight line was obtained for a considerable portion of the band. It will be noted, for reasons given later, that deviations from linearity occurred at low $N^{15}$-$N^{14}$ ratios.

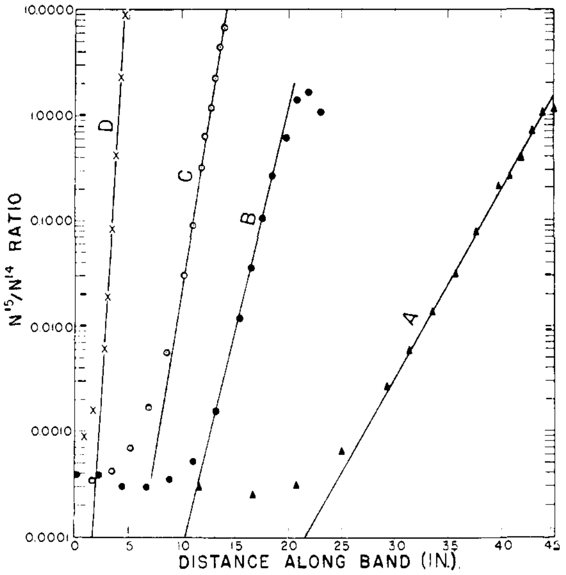

Fig. 3.—Profiles of adsorbed ammonium bands under various steady state conditions on 2-inch by 59-inch beds of 100-200 mesh, Dowex 50-X12 resin: A, 0.6 *N* NaOH at 125 ml. per minute; B, 0.6 *N* NaOH at 25 ml. per minute; C, 0.12*N* NaOH at 125 ml. per minute; D, 0.12 *N* NaOH at 25 ml. per minute. Some abnormal behavior is apparent at the ends of the bands, especially at low concentrations of $N^{15}$.

The last 23 inches of this band, containing most of the original $N^{15}$ adsorbed on the column, was next eluted with the same NaOH solution down 30 additional columns at one-fifth the original flow rate (25 ml. per minute). Since the length of the band was less, a shorter distance of elution was required to ensure the attainment of steady-state conditions. The results are plotted in Fig. 1, curve B.

The last 14 inches of this band were then eluted down 10 additional columns at the original flow rate of 125 ml. per minute, but with one-fifth the original concentration of NaOH, *i.e.*, 0.12 *N* (see curve C).

Finally, the last 5.5 inches of the band from the previous experiment were eluted down 3 more columns with 0.12 *N* NaOH at 25 ml. per minute (see curve D).

The HETP value for the linear portion of each of the curves in Fig. 1 was calculated and tabulated in Table I.

In general, it can be seen that a 5-fold change in concentration had a greater effect than a 5-fold change in flow rate by comparing experiments B and C, respectively, to experiment A. The apparent discrepancy between experiments A and E which had identical linear flow rates can be explained satisfactorily by the fact that the tubing used to connect consecutive four-inch and two-inch columns was identical and not scaled down proportionately. This would lead to greater re-mixing percentagewise in the case of the two-inch columns as the band passed from column to column during elution. The rates of band progress in B and C were equal and only one-fifth the rate of A or E. Experiment D represents an additional 5-fold decrease in the rate of band travel.

TABLE I

EXPERIMENTALLY DETERMINED VALUES OF THE HEIGHTS EQUIVALENT TO A THEORETICAL PLATE AT VARIOUS FLOW RATES AND CONCENTRATIONS WITH DOWEX 50-X12, 100-200 MESH RESIN

| Expt. | Flow rate (ml./min.) | Column diameter (in.) | *N* of base (equiv./l.) | Plate height (HETP in mm.) |
|---|---|---|---|---|
| A | 125 | 2 | 0.6 | 1.55 |
| B | 25 | 2 | .6 | 0.66 |
| C | 125 | 2 | .12 | 0.44 |
| D | 25 | 2 | .12 | 0.17 |
| E[a] | 500 | 4 | .6 | 1.24 |

[a] Data from a previous larger scale run not described here.

It will be noted that under the best conditions described above the nitrogen isotopic percentages would change from 99% $N^{14}$ to 99% $N^{15}$ in about 2.5 inches of resin bed.

In practice, straight line relationships are obtained in the log $N^{15}/N^{14}$ *vs.* *L* plots when the isotopic ratios lie between 0.002 and 50.0, provided one disregards ratios measured for plates that lie near the band boundaries. Tilted or channelled boundaries give erroneous data.

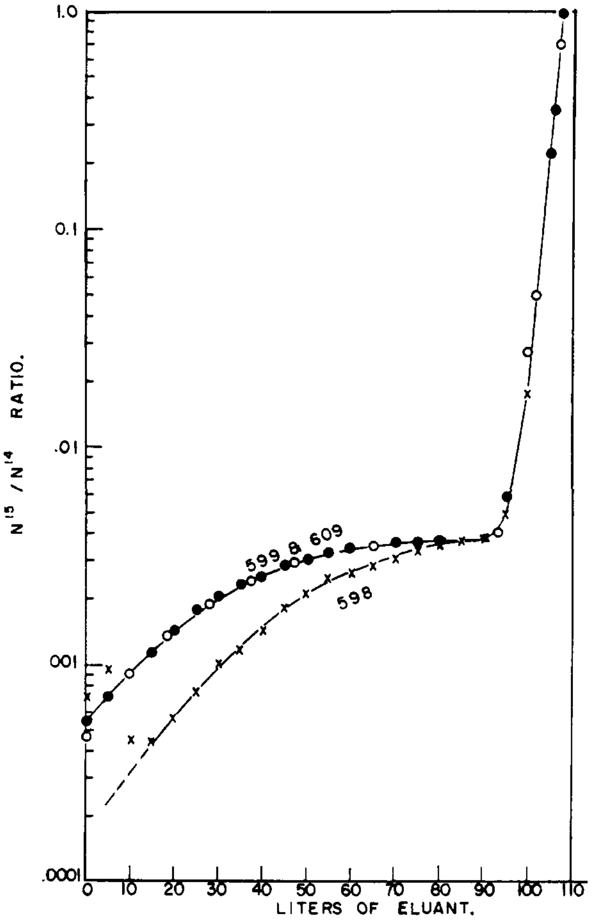

Fig. 4.—Profiles of the adsorbed ammonium band on a series of 4-inch by 59-inch, 100-200 mesh, Dowex 50-X12, resin beds. The adsorbed band was eluted in a semi-continuous manner by adding the equivalent of 550 ml. of 15 *N* ordinary $NH_4OH$ and withdrawing the same amount of $NH_4OH$ depleted in $N^{15}$ every circuit of the 10 column series. Profile 598 was taken just prior to, and profiles 599 and 609 were taken just after, an addition and withdrawal. Profiles 599 and 609 are exactly one cycle apart and are virtually identical.

Deviations will also be observed if any processes occur where part of the enriched $N^{15}$ is picked up at the rear in a form which does not exchange, but which does redeposit at the front edge of the band. For example, if there is carbonate in the sodium hydroxide, this might react with ammonia to give ammonium carbamate. If the carbamate hydrolyzes only slowly as it is swept across the adsorbed ammonium band, it may transport enriched $N^{15}$ from the rear to the front of the band without permitting equilibration. Acid conditions at the front boundary could bring about hydrolysis, redeposition and contamination of the $N^{14}$ at this point.

Deviations may also occur if the driving solution contains any nitrogenous impurities, or if the hydrogen-form resin bed contains nitrogen in a form which can yield ammonia. The latter case apparently occurs in our experiments and sets a lower limit for the $N^{15}$–$N^{14}$ ratio in the leading plates of the band. Any ammonia in the sulfuric acid or water used to recondition the resin will introduce ammonia into the resin stream and prevent the attainment of low $N^{15}$–$N^{14}$ ratios. An even more serious possible mechanism for resin contamination is that a small amount of the ammonia might react with the resin (perhaps with the sulfonic acid group) to give a compound which does not exchange rapidly or break down completely in cold caustic or the sulfuric acid regenerant solution. Such a compound might be broken down fairly completely by the heat generated by the reaction of the $NH_4OH$ with hydrogen-form resin at the front edge of the band during the next cycle of elution. Such an effect can be minimized by passing hot caustic over the resin after the band has passed. Analysis of hot caustic strip solution used for this purpose has shown traces of ammonia enriched in $N^{15}$ left behind on the resin. This effect is small and is not observed when the isotopic ratio at the front edge is high. The effect does become important, however, where the $N^{15}$–$N^{14}$ ratio to be measured is low, particularly, if the compound causing the trouble was formed sometime previously when the $N^{15}$–$N^{14}$ ratio was high.

Finally, deviations from linearity at very low and very high isotopic ratios may arise from analytical errors in the mass spectrograph as a result of background or air contamination of the gas samples.

D. **Continuous Operation with a System of Fixed Bed Ion-exchange Columns** (in collaboration with J. Capellen, D. M. Provow and H. Burkholder).—The theory of continuous operation with a system of fixed bed ion-exchange columns was discussed previously. The value of $\epsilon$ given in Section II-B indicated that a total of 39 moles of band displacement would be required to resolve each mole of nitrogen (added as ammonium hydroxide) into the individual nitrogen isotopes. Calculation showed that each 4-inch by 5-foot column of Dowex 50-X12, 100–200 mesh resin had an exchange capacity of about 32 equivalents. If an addition of ammonia were made once each cycle of ten columns, a total of 320 equivalents of resin would be traversed between injections. Consequently, 8.2 equivalents of ammonia should be added per cycle.

In order to test the validity of these calculations, a series of ten 4-inch diameter columns five feet long was prepared.

The original adsorbed band consisted of 3.5 liters of 15 *N* ammonium hydroxide (diluted 30-fold for loading). The band was eluted down 30 columns with 0.6 *N* NaOH at a flow rate of 400 ml. per minute before any additional ammonia was added or any $N^{14}$-rich product was withdrawn. Thereafter, 550 ml. of 15 *N* ammonium hydroxide in 15 liters of solution was added each cycle and a corresponding amount of $N^{14}$ product was withdrawn. No enriched $N^{15}$ product was removed, except when profiles of the adsorbed band were taken to determine its condition. Injections were initially made nine inches ahead of the tail-end of the band, but as the $N^{15}$ concentration in the rear part of the band increased, it became necessary to gradually move the point of injection forward in order to stay on the normal plateau. The injection point was 16 inches from the tail-end of the band by the 500th column.

The depleted product being withdrawn early in the experiment had a $N^{15}$–$N^{14}$ ratio of about 0.00012, but the ratio tended to increase gradually. When the $N^{15}$–$N^{14}$ ratio of the depleted product exceeded 0.00050, the length of the band was increased by making an addition but no withdrawal. In all, two such increases were made so that the band was about 100 inches long by column number 550 and contained the equivalent of 4.6 liters of 15 *N* ammonia or 69 moles. Figure 4 is a profile of the band taken as the band passed from the 598th to the 599th column just before an injection and withdrawal were made. Profiles were also taken at the bottoms of columns 599 and 609 just after additions and withdrawals were made. The fact that the data for profiles 599 and 609, exactly one cycle apart, fall on the same curve demonstrates that a more or less steady state had been achieved for this semi-continuous method of operation.

It is planned to operate these semi-continuously fed columns under conditions where 99.99% $N^{14}$ is withdrawn at the front and greater than 99% $N^{15}$ is bled slowly from the rear edge of the band. Before this can be done, however, sufficient $N^{15}$ will have to be accumulated in the band to fill the necessary $N^{15}$-rich plates. It would, of course, be possible to begin withdrawing highly purified $N^{15}$ from the present band, if it were eluted for a few cycles at a reduced flow rate with a lower concentration of NaOH. This would shorten the HETP and, thereby, decrease the amount of total $N^{15}$ required to fill the number of plates required to attain a mole fraction of $N^{15}$ equal to 0.99. This would not be especially desirable, since the decreased hold-up of $N^{15}$ would hardly justify the decreased rate of production caused by the slower rate of elution.

AMES, IOWA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CONNECTICUT]

# The Preparation of a Strontium–Niobium Bronze with the Perovskite Structure[1]

BY DANA RIDGLEY AND ROLAND WARD

RECEIVED APRIL 27, 1955

A study of the ternary oxide system of strontium and niobium has revealed the existence of a cubic phase of the Perovskite type which possesses the characteristics of the tungsten bronzes. The approximate limits of composition of this phase are $Sr_{0.7}NbO_3$ ($a_0$ = 3.981 Å.) to $Sr_{0.95}NbO_3$ ($a_0$ = 4.016 Å.). The color changes from deep blue to red with increasing strontium content. The compressed powder possesses a high electrical conductivity. Phases giving rise to complex X-ray patterns exist between the limits $Sr_{0.5}NbO_3$ (white) and $Sr_{0.65}NbO_3$ (black). With strontium content higher than $Sr_{0.95}NbO_3$, a blue phase which may be tetragonal was found. Evidence was obtained for the existence of similar phases in the ternary oxide systems of barium–niobium and barium–tantalum.

Only a few metallic oxide systems are metallic conductors. Most of these are the lower oxides of some of the transition metals which are usually considered to be in the same class as nitrides and carbides. The others appear to be confined to the tungsten bronzes which have the general formula $M_xWO_3$ where M is an alkali metal and $x$ is less than unity. The sodium and lithium tungsten bronzes have the cubic perovskite structure when the value of $x$ lies between 0.35 and 0.9 for sodium and 0.3 and 0.57 for lithium.[2] The lattice con-

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[1] Taken in Part from the Doctoral Dissertation of Dana Ridgley, 1955.

[2] M. E. Straumanis and S. S. Hsu, THIS JOURNAL, **72**, 4027 (1950); Arne Magnéli and R. Nilson, *Acta Chem. Scand.*, **4**, 398 (1950).