[CONTRIBUTION FROM THE UNIVERSITY OF ZÜRICH]

Enrichment of Rb^{85} by Countercurrent Electromigration[1]

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RECEIVED MARCH 24, 1954

A diaphragm countercurrent electromigration apparatus has been used to enrich Rb^{85}. The cell packing consisted of closely spaced diaphragms whose planes lie perpendicular to the flow of the countercurrent liquid. The enrichment took place in an aqueous medium with RbOH as the electrolyte. The voltage source employed in the experiment was 2300 v. The highest separation factor attained was 1.085. The Rb^{85} concentration was raised from 72.2 to 73.8% in 200 hr.

Introduction

The original idea that isotopes have different mobilities was first brought forth by Lindemann[3] in 1921. Lindemann postulated that the mobility of an ion was related to its ionic weight. This assumption led him to conclude that isotopes have different mobilities and that the isotopes could be enriched by differential electromigration methods. Although no one disputed his mathematical equations, scientists have spent more than 20 years in confirming the hypothesis.

The first article which confirmed the theory was published by Klemm[4] of Germany in 1944. In his research paper, Klemm was able to enrich the lighter isotope of silver by means of a countercurrent electrolysis of silver iodide.

Three years later, in 1947, a process of enriching isotopes in an aqueous medium was published by Brewer[5] and co-workers. In their article the authors reported an enrichment of K^{39} in a countercurrent electromigration apparatus. The apparatus of Brewer and co-workers consisted of a circular glass tube which served as the electromigration cell. The anode and cathode sections were situated at opposite ends of the tube. The solution flowed from the cathode section to the anode section. The migration of the K ions, of course, was from the anode to the cathode. In order to minimize convection, back diffusion and turbulence, the electromigration cell was filled with a packing. The choice of the packing was optional. The packings mentioned and tried by Brewer were granular, fibrous, rigid and concentric glass capillaries. The most serious objection in the mentioned packings is the channeling effect which so often sets in.

In this research, a completely new type of cell packing has been adopted, as described by Buehler,[6] consisting of closely spaced semi-permeable membranes. The plane of the membranes, which the author refers to as diaphragms, lies perpendicular to the countercurrent flow of the liquid.

Theory

The theory of the process has been reported by Westhaver,[7] Breit[8] and Brewer.[5] Although the authors do derive mathematical equations which describe the process of electromigration, there is still much left to be desired. The greatest objection raised with the mathematical calculations lies in the fact that these calculations had assumed that ideal conditions had existed in the electromigration cell throughout the process. The adverse effects of convection, turbulence, and channeling can at best be but crudely taken into account in the mathematical derivations.

The over-all principle of the process under ideal conditions is that the flow of the countercurrent liquid is faster than the heavier ion, but it should be slower than the velocity of the lighter ion. Under these conditions, the lighter ion will work its way against the liquid flow, while the heavier ion is slowly washed back to the anode section of the apparatus. Theoretically, the process is in equilibrium when the velocity of the countercurrent flow is equal to the velocity of the lighter cation.

It has been found that, for a binary system, the initial rate of separation of the light and heavy cations can be approximated by a material balance. Such a balance is given by equation I

$$\mathrm{d}C_lV_c = KAC_{ll}\left(\frac{P\mu_l}{L} - V_s\right)\mathrm{d}t \qquad \text{(I)}$$

The velocity of the countercurrent stream V_s under optimum conditions is equal to the average velocity of the ions in the solution. Thus V_s has the following value.

$$V_s = \frac{P}{L}\left(\frac{C_{ll}\mu_l}{C_T} + \frac{C_{lh}\mu_h}{C_T}\right) \qquad \text{(II)}$$

Upon substituting equation II in equation I, the following simplification can be made.

$$\mathrm{d}C_lV_c = KC_{ll}\frac{AP}{L}\left[\mu_l\left(1 - \frac{C_l}{C_T}\right) - \frac{\mu_hC_h}{C_T}\right]\mathrm{d}t \qquad \text{(III)}$$

The letters in the above three equations have the following interpretation

A, the cross-sectional area of the apparatus
L, the length of the apparatus
P, the potential drop (in v.) across the apparatus
t, time
μ_l,μ_h, the mobilities of the light and heavy ions
V_c, the volume of the cathode section
C_{ll},C_{lh}, the initial concn. of the light and heavy cations, respectively.
C_T, the sum of the concn. of the light and heavy ions
K, the cell constant, this also can be considered as the efficiency constant of the apparatus

The mobilities of similar ions are inversely proportional to the square root of their ionic weights

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[1] The material reported here is taken from part of the Dissertation for Doctor of Philosophy presented by the author to the Philosophical Faculty Section II of the University of Zürich, Zürich, Switzerland, in June. 1953.

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[3] A. Lindemann, *Proc. Roy. Soc.* (*London*), **A99**, 102 (1921).

[4] A. Klemm, *Naturwissenschaften*, **32**, 69 (1944).

[5] A. K. Brewer, S. L. Madorsky, J. K. Taylor, V. H. Dibeler, P. Bradt, O. L. Parham, R. J. Britten and J. G. Reid, *J. Research Natl. Bur. Standards*, **38**, 137 (1947).

[6] H. H. Buehler, Doctoral Dissertation, University of Zürich, Zürich, Switzerland.

[7] J. W. Westhaver, *J. Research Natl. Bur. Standards*, **38**, 169 (1947).

[8] G. Breit and F. L. Friedman, *ibid.*, **39**, 397 (1947).

as predicted by Lindemann. The ionic weight of Rb in water has been approximated by Washburn.[9] Although the results of Washburn do not agree with other data available on the subject, his values have been arbitrarily taken as true. The Rb ion is assumed to have five waters of hydration. The ratio of the mobilities of the two Rb isotopes is shown in equation IV.

$$\frac{\mu_{\mathrm{Rb}^{85}}}{\mu_{\mathrm{Rb}^{87}}} = \sqrt{\frac{\mathrm{Rb}^{87}\cdot 5\mathrm{H_2O}}{\mathrm{Rb}^{85}\cdot 5\mathrm{H_2O}}} = 1.0056 \qquad \text{(IV)}$$

The above calculation indicates that Rb^{85} is 0.56% faster than Rb^{87}. This difference is large enough to show an enrichment in the electromigration process.

Experimental

The apparatus has been both sketched and fully described by K. Clusius and E. R. Ramirez.[10] In short the apparatus consists of an electromigration cell 1.6 cm. in diameter and 100 cm. long. The cell is air cooled on the outside. Its center is cooled by a fast flow of water passing through a concentric glass tube 0.5 cm. in diameter. Dialysis paper is cut to the proper form and used as diaphragms. The diaphragms are circular and are snugly fitted on the concentric cooling tube, which runs through the center of the electromigration cell. The cooling tube together with the fin like diaphragms is then fitted into the electromigration cell. The diaphragms are spaced 0.25 cm. apart. They are sewed in place to assure that the proper spacing would be maintained throughout the experiment.

The diaphragms are so arranged that slow thermal convection currents are set up between the diaphragms. These thermal convection currents, for the most part, can only travel perpendicular to the flow of the countercurrent stream. Previous experiments have proved that these oval shaped thermal convection currents are helpful to the efficiency of the separating process.

Prior to working with isotopes, the electromigration apparatus was calibrated by separating various alkali-metal cations. In this operation, the rate of separation was considerably improved when slow thermal convection currents were present between the diaphragms. The voltage source for all the experiments herein described is 2300 v.

Procedure.—The source of Rb was C.P. RbCl. It was converted to the hydroxide before it was placed into the electromigration cell. A total quantity of 15 g. of the chloride salt was used for the enrichment. The concentration of the Rb in the electromigration cell was 0.006 *N*. The anode compartment was continuously washed with a 0.012 *N* RbOH solution which was kept in the anode reservoir. The countercurrent solution consisted of redistilled water which supplied the hydroxide ions.

The temperature of the electromigration cell could be adjusted to any value by controlling the countercurrent flow. After proper adjustment the temperature change of the apparatus over a 24-hr. period could be held to less than 10°. The control of the countercurrent liquid was automatically done by a self regulating mechanism. Once the apparatus has been properly adjusted, the experiment could be allowed to run for 75 to 100 hr. without readjustment. The apparatus was observed at least every 12 hr. to see that everything was in order.

The principle of the self-controlling mechanism of the apparatus was based on the conductivity of the cathode section of the electromigration cell. A conductivity cell was placed in the cathode compartment. The conductivity cell was connected in series with a gas coulometer of negligible resistance. The gas generated in the coulometer displaced an equivalent volume of water which was fed into the cathode section of the electromigration cell. This flow of displaced liquid is called the countercurrent stream.

The initial adjustment of the apparatus is such that the conductivity cell corrects the countercurrent flow as the need arises. The operating conditions of the apparatus when it is kept at 80° are as follows. The electromigration cell current is 110 m.a., and the average countercurrent flow is 280 cc./hr. At 40°, the cell current is maintained at 110 ma. and the average countercurrent flow is 190 cc./hr.

Results

During the first week the electromigration cell was operated at 80°. An analysis of the cathode section was then made. The analysis showed very little Rb was present. In its place Cs was found. The presence of Cs was confirmed by the use of the silico-tungstic acid test. It is conceivable that the C.P. RbCl had a trace of Cs present as an impurity. The fact that the Cs ion has a greater mobility than the Rb ion accounts for its accumulation in the cathode section. Successive samples were then taken from the cathode section until the last traces of Cs were removed. The apparatus was then allowed to run for 8 days at 80°. After this time two samples were taken from the apparatus, the first from the cathode section, while the second sample was taken 5 cm. from the cathode itself.

As a second part of the experiment it had been decided to see if the operating temperature would have any significant effect on the separating action. At this point the apparatus was readjusted to enable it to run at 40°. The experiment was then allowed to run for two weeks longer. A third sample was taken from the cathode section after the two weeks. The analyses of these samples are shown in Table I.

TABLE I

ENRICHMENT OF Rb^{85} BY COUNTERCURRENT ELECTROMIGRATION

Sample no.	Temp. of exp., °C.	Time. hr.	Position of sample in cell	Rb^{85}, %
0	..	0	Cathode compartment	72.2
1	80	200	Cathode compartment	73.8
2	80	200	5 cm. from cathode	73.6
3	40	530	Cathode compartment	73.6

Discussion

The enrichment of Rb^{85} has been carried out at two temperatures, namely, 80 and 40°. The results indicate that the enrichment is better at the higher temperature. From the outlook of back diffusion it would be expected that the enrichment could be poorer at the higher temperature. In spite of this the change of other factors as a result of the rise in temperature did favor a faster and better enrichment of the lighter isotope.

There appears to be two possible reasons for justifying the better enrichment at the higher temperature. The first is based on the ionic mobility as a function of the temperature. A rough rule of thumb is that the mobility of an ion increases about 2% for each temperature rise of one degree. The electromigration process of enrichment is based on differential mobility. The net result is that the differential mobility of two isotopes increases about 2% for each rise of 1°. This result obviously would give a faster separation at the higher temperature.

A second reason for the better enrichment at the higher temperature may be that the cations are less hydrated at these higher temperatures. A decrease in the hydration of the ionic isotopes would certainly increase the differential mobilities of the two isotopes.

Acknowledgments.—I am most thankful to

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[9] E. W. Washburn, THIS JOURNAL, **31**, 322 (1909).

[10] K. Clusius and E. R. Ramirez *Helv. Chim. Acta*, **36**, V, 1160 (1953).

Herr Prof. Dr. K. Clusius of the University of Zürich, Zürich, Switzerland, for his ever guiding advice during this research. I am obliged to Herr Dr. H. Hintenberger of the Max Plank Institut für Chemie of Mainz (am Rhein), Germany, for carrying out the analysis of the isotopes. I am grateful to my fellow colleagues Dr. E. Shumacher and Dr. M. Huber of the University of Zürich for their active discussions on isotope enrichment.

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[CONTRIBUTION FROM THE RESEARCH BRANCH, DIVISION OF CHEMICAL DEVELOPMENT, TENNESSEE VALLEY AUTHORITY]

Synthesis of Phosphorus Nitrides[1]

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RECEIVED JULY 12, 1954

The measured concentration of phosphorus mononitride vapor in equilibrium with an equiatomic mixture of phosphorus and nitrogen at 900°, together with the value 9.756 e.v. for the dissociation energy of nitrogen, leads to a value of 7.1 ± 0.05 e.v. for the dissociation energy of phosphorus mononitride. The calculated equilibrium constants range from 1×10^{-2} at 900° to 2×10^{-1} at 2000°. The apparent energy of activation for the homogeneous synthesis is about 31 kcal. per mole of PN. The observed rates of synthesis in the presence of tungsten (hot-wire method) show that the reaction at temperatures above 1800° is catalyzed by tungsten and is $^1/_2$-order with respect to concentration of P_2. The activation energy is 59 kcal. The formation of phosphorus atoms at the tungsten surface is advanced as the rate-controlling step in the synthesis mechanism.

The synthesis of phosphorus nitrides directly from the elements in the presence of a heated tungsten filament or an electrical discharge was reported by several investigators.[2-5] When Moureu and Wetroff[5] brought a gaseous mixture of phosphorus and nitrogen into contact with a tungsten filament at 1500 to 1800°, solid phosphorus nitride condensed on an adjacent glass wall at 500°. Since phosphorus vapor is predominantly in the diatomic form at 1500 to 1800°, they concluded that the process could be represented by the equilibria

$$nP_2(g) + nN_2(g) \rightleftarrows 2nPN(g) \rightleftarrows 2(PN)_n(s) \qquad (1)$$

Moureu and co-workers[6] later reported that phosphorus mononitride vapor (PN) heated at 800° "completely decomposes into its elements."

Equilibrium constants for the reaction

$$P_2(g) + N_2(g) = 2PN(g) \qquad (2)$$

as calculated by McCallum and Leifer,[7] indicated that the equilibrium is favorable for the synthesis in the temperature range 800 to 1000°. McCallum and Leifer observed that a difference of a few tenths of an electron volt in the dissociation energy of phosphorus mononitride could account for the inconsistency of their calculation with the experimental[6] results. Gaydon[8] concluded that the dissociation energy of phosphorus mononitride is not known more precisely than 6.0 ± 0.8 e.v.

Perhaps an even greater uncertainty clouded the dissociation energy of nitrogen until Douglas[9] recently reported measurements from which he concluded that the spectroscopic evidence strongly supports the value 9.756 e.v. Herzberg[10] agrees.

To aid in an evaluation of phosphorus nitrides as potential intermediates in the production of fertilizers, the controlling factors in the phosphorus–nitrogen reactions were studied in the laboratory. This paper describes a measurement of the concentration of phosphorus mononitride vapor in equilibrium with an equiatomic mixture of phosphorus and nitrogen at 900°, measurements of the rate of decomposition of phosphorus mononitride vapor, and a kinetic study of the synthesis of phosphorus nitrides from the elements in the presence of tungsten. A new value is given for the dissociation energy of PN.

Equilibrium Concentration of PN at 900°.—Respective sealed quartz tubes containing equiatomic mixtures of nitrogen and phosphorus were heated at 900° for 42 hours and at 950° for 44 hours. The tubes were quenched to 500° in about one minute. Although phosphorus nitrides will condense to the solid state at 500°, neither of the condensed products contained a significant amount of fixed nitrogen. This result indicated either that the equilibrium concentration of phosphorus mononitride is negligible at 900 to 950° or that the condensed products did not represent the equilibrium composition, possibly because of an inadequate rate of quenching.

The composition of the gas at equilibrium was evaluated *at the equilibrium temperature* by a static method in a quartz apparatus. The method was based upon a pressure–composition relation, and pressures were measured with a contact-making Bourdon gage as a null-point instrument. The volume of the apparatus, 288 ml., was determined with mercury.

The starting material was a laboratory preparation of phosphorus nitride containing 67.60% P, 31.36% N and 0.32% acid-insoluble material. It was degassed thoroughly at the beginning of each experiment. Three equilibria were involved.

$$(PN)_n(s) = nPN(g) \qquad (3)$$

$$2PN(g) = P_2(g) + N_2(g) \qquad (2)$$

$$P_4(g) = 2P_2(g) \qquad (4)$$

In a preliminary experiment, the phosphorus mononitride was vaporized into the system at 900° to a pressure of 391 mm. The capillary connecting the vaporizer to the equilibration flask was sealed, and the pressure was measured at intervals for 5 hours. A constancy of pressure showed that the vapor reached equilibrium forthwith. After the gas was pumped from the system at the end of the experiment, a check of the gage constant showed that it had drifted < 1 mm.

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[1] Presented before the Southwide Chemical Conference, October 1951, at Wilson Dam, Ala. Article not copyrighted.

[2] R. J. Strutt, *Proc. Roy. Soc.* (*London*), **A85**, 219 (1911).

[3] V. Kohlschütter and A. Frumkin, *Z. Elektrochem.*, **20**, 110 (1914).

[4] W. Moldenhauer and H. Dörsam, *Ber.*, **59B**, 926 (1926).

[5] H. Moureu and G. Wetroff, *Compt. rend.*, **207**, 915 (1938).

[6] H. Moureu, B. Rosen and G. Wetroff, *ibid.*, **209**, 207 (1939).

[7] K. J. McCallum and E. Leifer, *J. Chem. Phys.*, **8**, 505 (1940).

[8] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 212.

[9] A. E. Douglas, *Can. J. Phys.*, **30**, 302 (1952).

[10] G. Herzberg, letter, November 12, 1952.