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Concentration of Isotopes of Potassium by the Countercurrent Electromigration Method[1]

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A new electromigration method for the separation of isotopes is described. This method is based on the principle of setting up a flow of electrolyte through a packed column in a direction countercurrent to the flow of the isotopic ions being separated and at a rate intermediate between the velocities of these ions. Under these conditions, the faster moving ions will make headway against the electrolyte stream, while the slower moving ions will be carried back. The separation coefficient $\epsilon-1$ in the case, for example, of cations, is given as equal to $FV_cC \ln S/1000\ I^+t$, where F is the Faraday constant, V_c is cathode volume in cubic centimeters, C is normality of the electrolyte, S is separation factor, I^+ is positive ion current, and t is time in seconds. Free space and temperature distribution in the packing, balance between ion transport and stream counter flow, and other factors which determine column efficiency are described. In a series of experiments for the concentration of ^{39}K in the cathode compartment of the electromigration cell, the abundance ratio $N={}^{39}\mathrm{K}/{}^{41}\mathrm{K}$ was increased from its normal value of 14.2 to a maximum of 24 in about 500 hours of operation and a maximum separation coefficient of 0.385×10^{-2} was obtained. Attempts to concentrate ^{41}K in the anode compartment resulted in a lowering of the isotope abundance ratio to a minimum of 9.1. A study of the distribution of ^{39}K in the packing in experiments carried out for the concentration of ^{39}K in the cathode compartment, showed that the abundance ratio decreases rapidly from the cathode to anode direction. A description is given of the mass spectrometer used in measuring the abundance ratio $^{39}\mathrm{K}/^{41}\mathrm{K}$, also, of the automatic control used in regulating the counter flow in some of the electromigration cells.

I. Discussion of Method for Concentration of Potassium Isotopes

By A. Keith Brewer and Samuel L. Madorsky

1. Introduction

The separation of isotopes by ion transport in solution was first suggested in 1921 by Lindemann [1].* A mechanism was proposed based on an intrinsic difference in the velocities of the isotopic ions. It was postulated that an ion of mass m retains a fraction $m/(M+m)$ of its momentum after collision with a solvent molecule of mass M. Lindemann suggested that the electrolysis should be carried out in a medium such as agar-agar to cut down diffusion. Mulliken and Harkins [2], in commenting on Lindemann's proposal, expressed the opinion that the slight differences in ionic mobility to be expected would be masked by diffusion and convection.

The first experimental test of the method was made by Kendall and Crittenden [3] on chlorine and lithium isotopes. Later Kendall [4] transported chlorine ions through 100 feet of agar-agar filled tubes, using the moving boundary method; an atomic-weight determination failed to show any

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*Figures in brackets indicate the literature references at the end of this paper.

[1] This paper will be included in volume 6, division III, of the Manhattan Project Technical Series.

[2] At present with the U. S. Navy Department.

isotope shift. Pilley [5], using the same technic, failed to detect an isotope shift for chlorine and magnesium. A further attempt by the same method led Jette [6] to conclude that "any difference in the mobilities of isotopic ions is exceedingly improbable."

A countercurrent reflux mechanism has recently been developed at the Bureau [7] which unquestionably establishes a difference in the forward transport velocities of isotopic ions of potassium. The basic principle of this method rests on an imposed flow of electrolyte through a packed column or capillary in the cathode to anode direction at a rate just sufficient to reduce the net forward transport of K^+ ions to zero. Under these conditions, the faster moving $^{39}K^+$ ions will make headway against the electrolyte stream, whereas the slower moving $^{41}K^+$ ions are carried back. This results in a concentration of ^{39}K being built up in the cathode compartment.

The concentrations that can be built up by this method are limited only by the number of theoretical plates that can be realized in the packing. The conditions that must be observed in order to obtain a short height of theoretical unit are essentially the same as in any conventional reflux column. A mathematical analysis of the mechanism is presented in RP1766 [10].

The experimental setup used in the separation of ^{39}K and ^{41}K is indicated by the following elementary arrangement. Consider a tube bent upward at the ends and filled with sand in the horizontal section. Let one arm serve as the cathode compartment and the other as the anode. The anode compartment is provided with a spillway to maintain a constant level in the system. When the tube is filled with a potassium sulfate solution and the current turned on, K^+ ions move toward the cathode and SO_4^{--} ions toward the anode. Conditions for total reflux are established by adding sulfuric acid to the cathode compartment at such a rate and concentration that the pH and concentration of the cathode solution remain unchanged. At the same time a solution of potassium hydroxide is added to the anode compartment at an equivalent rate. The result is a flow of electrolyte from the cathode to the anode, and from an overflow at a rate just sufficient to prevent a net forward transport of K^+ ions. The velocity of the electrolyte stream, in consequence, is equal to that of the average K^+ ion, and the current carried by the K^+ ions is reduced to zero. As $^{39}K^+$ has a slightly greater mobility than $^{41}K^+$, it will make headway against the electrolyte stream, whereas $^{41}K^+$ is washed back.

As the anode compartment is constantly being supplied with KOH, the ^{39}K concentration will remain at its normal value. As a result, this compartment serves as a constant-supply reservoir.

The point balance between ion migration and stream flow is confined to the uniform porous packing separating the cathode and anode compartments.

2. Separation Coefficient

The countercurrent reflux mechanism just outlined is dependent only on a difference in mobility for the isotopic ions. The basis for this difference in mobility is not pertinent. Nevertheless, it is interesting to speculate on the phenomena involved, which can give rise to a difference in forward transport. Several possibilities exist.

The forward motion of an ion in an electric field can best be considered as an unidirectional drift superimposed upon the random motion due to kinetic agitation; the ion receives a forward acceleration during the interval between collisions. The mean time between collisons is given by l/v_{th}, where l is the mean free path and v_{th} is the average thermal velocity. The velocity due to the electric field is equal to the force times the time between collisions divided by the mass, m, i. e., $v=Eel/(v_{th}m)$. Thus the average forward drift velocity is $v_a=Eel/2mv_{th}$. The mobility of the ion, $\mu=v_a/E$, is then

$$\mu=\frac{el}{2mv_{th}}=\frac{el}{2(3mkT)^{1/2}}, \qquad (1)$$

since $v_{th}=\sqrt{3kT/m}$.

On the basis of the above analysis, the electric field can be considered as imposing a drift velocity on the velocity of the thermal agitation, which is inversely proportional to the square root of the ion masses.

A further possible cause for a difference in isotopic ion mobility is a probable difference in the hydration of the ions. As ^{41}K has been shown to be held more tenaciously in a zeolite structure than is ^{39}K [8, 9], a difference in attachment to water molecules is to be expected.

A difference in forward transport of the isotopes may also exist if there is an isotope effect between ions and undissociated molecules. The isotope shift between carbonate ion and carbon dioxide is an example. This mechanism, however, may not apply to potassium salts, which are highly ionized.

The countercurrent ion-transport mechanism, although having much in common with conventional reflux columns used in adiabatic distillation, is different in that no single-stage or single-plate process exists. In consequence, it is impossible to define the height elemental theoretical plate for the column in an exact sense; for this reason it is preferable to use the term "height theoretical unit" to define the segment length of column required to produce a change in concentration, ϵ, where ϵ is the separation coefficient, defined as the ratio of the mobilities of the two isotopic ions. Assuming eq 1 to be correct, ϵ can be expressed according to eq 2 as the inverse ratio of the square root of the isotope-ion masses. The hydration of K^+ ions is not known with certainty, but $K^+.7H_2O$ is a reasonable value. The theoretical separation coefficient, therefore, has been given the arbitrary value of

$$\epsilon=\sqrt{\frac{{}^{41}.K7H_2O}{{}^{39}K.7H_2O}}=1.006. \qquad (2)$$

3. The Transport

The rate of transport of $^{39}K^+$ and $^{41}K^+$ ions across the tube is

$$AC_l\left(\mu_l\frac{P}{l}-v\right) \qquad (3)$$

$$AC_h\left(\mu_h\frac{P}{l}-v\right), \qquad (4)$$

Where A is the free cross-sectional area of the packing, C_l and C_h are the concentrations on the light and heavy ions in moles per cubic centimeter, μ_l and μ_h are the mobilities of the ions in centimeters second^{-1} volt^{-1}, P is the potential difference across the packing in volts; l is the length of the packing; v is the velocity of the liquid in centimeters per second.

As the velocity of the liquid, v, is adjusted so that the net transport of K^+ ions is zero, the sum of the transports of ^{39}K and ^{41}K are zero, hence

$$v=\frac{P}{l}\times\frac{C_l\mu_l+C_h\mu_h}{C_l+C_h}. \qquad (5)$$

The transports of light and heavy ions obtained by substituting eq 5 in eq 3 and 4 are

$$\pm A\frac{P}{l}C_lC_h\frac{\mu_l-\mu_h}{C_l+C_h}.$$

The initial change in concentration of the light and heavy isotopes at the cathode is given by

$$\frac{dC_l}{dt}\left[\frac{P}{l}\frac{dC_h}{dt}\right]=\frac{AP}{V_cl}C_lC_h\frac{\mu_l-\mu_h}{C_l+C_h},$$

so that

$$\frac{d}{dt}\ln\frac{C_l}{C_h}=\frac{AP}{V_cl}(\mu_l-\mu_h), \qquad (6)$$

where V_c is the cathode volume, and t is time in seconds.

Equation 6 can be rewritten

$$\ln S=\frac{AP}{V_cl}(\epsilon-1)\mu t, \qquad (7)$$

where μ is the mobility of the average K ion, ϵ is the separation coefficient, and S is the separation factor.

The separation factor, S, is defined as the ratio of the concentration of light to heavy isotopes at the cathode at time t divided by the normal ratio at time zero. Thus

$$S_{t=\infty}=\frac{R_c}{R_a}=\epsilon^n, \qquad (8)$$

where $R=C_l/C_h$, c and a refer to the cathode and anode, and n is the number of theoretical plates.

It is often more convenient to calcaluate ϵ in terms of the current rather than the voltage. In this case, the molar isotope transport can be considered as equal to the gain in concentration of the faster isotope in the cathode compartment. This can be expressed initially in terms of moles ^{39}K by the simple equation

$$\frac{I^+t(\epsilon-1)}{F}=\frac{V_c C\ln S}{1{,}000}, \qquad (9)$$

or more exactly by the equation

$$\frac{I^+t(\epsilon-1)N_1N_2}{F}=\frac{V_cC}{1{,}000}\times\frac{R_t-R_0}{(R_t+1)(R_0+1)}, \qquad (10)$$

where I^+ is the positive ion current in amperes before superimposing the counterflow: t is the time in seconds; N_1N_2 are the mole fractions of ^{39}K and ^{41}K, V_c is the cathode volume in cubic centimeters, C is the normality of the electrolyte, and F is the Faraday constant (96,500 coulomb/mole), R_t and R_0 are N_1/N_2 at times t and 0, respectively.

Neither the voltage nor the current equation can be considered to hold precisely except at initial stages of the experiment as both neglect the concentration built up in the packing. Likewise, both equations neglect back diffusion and remixing processes, which set in as soon as a concentration gradient is established. Both expressions anticipate that the process will continue until the gradient reaches the point where the forward transport is balanced by back diffusion.

4. Free Space and Packing Temperature

The reduction of remixing and back diffusion to a point below the forward transport necessitates that the ion-electrolyte reflux balance be established in a porous packing capillary, or thin sheet. In order to apply eq 7 to a packed column, it is necessary to know the free cross-sectional area, A, of the packing. In addition, a knowledge of the temperature distribution in the packing is required in order to evaluate μ.

(a) Free Space in Packing Materials

The free space in various packings was measured by the displacement of water. The values observed for several packings are

Material	Free space (percent)
Glass wool	75
Glass beads	38
Sand	34 to 36
Silicon Carbide	35

By comparison, the free space for perfect spheres of uniform size is 26 percent for close packing, where each bead is in contact with 12 others; and 48 percent for loose packing, where each sphere is in contact with 6 others. The glass beads used were No. 28, 48, 70, and 107 mesh. The free space was essentially the same for all sizes.

The electrical free space, which is not the same as the volume free space, was measured by comparing the conductivities of packed and unpacked columns. KCl, 1:60, was used as the electrolyte. The packings were carefully tamped in a glass U-tube, the electrodes being placed immediately above the packing surface. Care was taken to insure that the electrodes were replaced in exactly the same position in successive experiments. Measurements were made with 60-c a-c current over the range from 0.06 to 0.25 amp. The conductivity was independent of the current. The electrical free space obtained for various packings was

Material	Free space (percent)
Glass beads	28. 9
Sand	28. 1
Silicon carbide	27. 5

These values are appreciably lower than for the volume free space as the pores are not straight but have a tortuous path that is longer than the packing itself.

(b) Temperature in Packed Tubes

The temperature in the center of a diaphragm packing can be estimated by assuming that the heat leaving an element of volume within the tube is equal to the heat generated within that element.

The temperature was measured under operating conditions by inserting a thermocouple incased in a thin-walled glass envelope at various points within the packing. The diameter of the tubes used was 1.4 cm and the wall thickness 0.8 mm. The solution was 1:60 KCl. The cells were operated at the indicated current for 30 minutes prior to reading the temperature. The temperature reached its maximum at a point about 4 cm from the end of the packing. The maximum temperature for various packings immersed in a 25° C water bath is as follows:

Current	Temperature		
	Glass beads	Silicon carbide	Sand
amp	*°C*	*°C*	*°C*
0. 30	46	34	
. 40	59	40	44
. 50	73	45	50
. 60	86	51	61
. 70	Boiling	60	70

Two sizes of glass beads were tested, 60 and 107 mesh; no appreciable difference was observed; the sand and silicon carbide were 100 and 150 mesh, respectively.

5. Factors Determining Column Efficiency

The efficiency of the separation mechanism is determined by the power required to change the isotope ratio by one theoretical unit. As the conductivity of the column is independent of the isotope ratio the problem resolves itself into the number of theoretical units that can be realized in one centimeter of packing, i. e., the concentration gradient. It is obvious that a concentration gradient can be built up only to the point where the forward transport is balanced by back diffusion.

Back mixing in a reflux column can enter in a number of ways. Some of these can be eliminated by proper design of cell, but others are inherent in the mechanism.

The factors giving rise to back-mixing will be discussed in a qualitative manner in this report. A quantitative discussion of the problem is given in RP1766 [10].

(a) Diffusion

Back-mixing cannot be reduced below the limit set by diffusion in a stagnant liquid. The relation between the mobility, μ, and diffusion, D, is given by kinetic theory to be

$$\mu=\frac{e}{kT}D, \qquad (11)$$

where μ in a normal solution of K_2SO_4 for K^+ is 4.98×10^{-4} cm sec^{-1} volt^{-1}, e is the charge on the positive ion, k is Boltzman's constant, and D is in square centimeters per second. An evaluation of the constants gives $D=0.026\mu$ for singly charged ions in a gradient of 1 v/cm. As the gradient in most of the experiments to be described in this series ranged from 5 to 10 v/cm, the forward transport, μ, will exceed the back-diffusion coefficient by 200 to 400. From this it may be inferred that an upper limit for n in eq 8 could approach 200 theoretical units per centimeter, under ideal conditions.

(b) Balance Between Ion Transport and Stream Flow

Separation, as has been pointed out, is dependent on the establishment of an exact balance between stream flow and ion transport. For potassium the fractional difference in mobility of the two ions, as derived from eq 1 is taken to be $\epsilon-1=0.006$. The abundance ratio of the isotopes is $^{39}K/^{41}K=14.20$. In consequence, for zero current to be carried by the K^+ ions the stream velocity will be very close to the ^{39}K mobility. If the stream velocity falls below that of ^{41}K, then both isotopes will be carried into the cathode compartment. The tolerances are well defined, a decrease in rate of more than 14.2/15.2 of 0.6 percent from balance will admit ^{41}K to the cathode. An increase in rate of 1/15.2 of 0.6 percent will cause ^{39}K to be flooded out of the cathode compartment. The system will operate at moderate efficiency, however, if fluctuations in the stream flow do not exceed more than 1 percent of the balance velocity.

(c) Pore Size and Convection

The pore size is of importance, first, because it determines the length of the theoretical unit, and second, because it limits disturbances due to convection. The first is discussed in detail in RP1766 [10].

The effective pore size was determined by measuring the flow of water through vertical tubes packed with glass beads of various mesh sizes. The rates were determined over a range of pressure heads. The corrected results (cm/sec) gave the empirical relation

$$Q_s=0.28d^2h/l\eta, \qquad (12)$$

where Q_s is the flow in milliliters per second divided by the total cross section in square centimeters; d is the bead diameter in centimeters, h is the pressure head in centimeters of water, l is the length of packing, η is the viscosity in poises.

As the free space in the beads is 38 percent, the average lattice is more cubic than tetrahedral. In consequence, the number of beads per square centimeter of cross section is close to $(l/d)^2$. This is also the number of pores in 1 cm^2 of cross section. The volume rate of flow (ml/sec) through the average individual pore is

$$Q_p=0.28d^4h/l\eta. \qquad (12a)$$

If the bead packing is replaced by a bundle of straight capillary tubes equal in number to the number of pores and of the same length and operated under the same head, the two structures are hydraulic equivalents when the radius of each capillary is such that the flow is the same as the average pore.

The flow (ml/sec) through a capillary tube is determined in accordance with Poiseuille's law

$$Q=980\pi r^4H/8l\eta.$$

On equating the rate of flow it is found that, for 38 percent voids,

$$r=0.165d,$$

where r is the equivalent radius of the straight capillary. This radius, however, is smaller than the mean radius of the pore since the path is longer in the packing by a factor of about $\sqrt{2}$. The mean pore radius normal to the tube axis is in reality close to $38/29\times0.165=0.216d$.

Convection within the packing cannot be evaluated accurately, but can be approximated by considering the flow upward through the heated and downward through the cooled region to be comparable to that through hot and cold capillaries connected to a common reservoir at the top and bottom. The velocity flow through an individual capillary is given by Poiseuille's law to be $v_a=Pr^2/8\eta l$, where v_a is the average velocity in centimeters per second, P is the pressure in dynes per square centimeter, r is the radius in centimeters, η is the viscosity in poises, l is the length of capillary in centimeters.

The flow due to convection when the hot and cold capillaries are at 50° and 30° C, respectively, is

Diameter (mm)	v_c (cm/sec)
0. 02	1.5×10^{-4}
. 04	6.2×10^{-4}
. 08	2.5×10^{-3}

These values show that convection velocities are of the same order of magnitude as the ion mobility. Remixing due to convection is dependent on the direction of the convection stream with respect to the electrolyte stream. In the conventional horizontal tube, where the stream flow is in the axial direction, the convection flow in the radial direction will not be as disastrous as in vertical tubes, where both convection and ion migration are in the axial direction.

(d) Nonuniformity of Porosity

Nonuniformity of porosity and channeling are the principle sources of poor efficiency in operation. Their effect on the ion-stream balance follows from the fact that ion velocity is independent of the pore radius, whereas stream velocity varies with the square of the radius. In consequence, an excessively large pore need represent but a small fraction of the total cross-sectional area to throw the system out of point balance by more than 1 percent.

(e) Temperature Variation in Viscosity-Conductance ratio

An exact balance between ion transport and stream velocity at all points in the packing can be realized only if the effect of temperature on each is the same, i. e., the product of specific conductance, Λ, times viscosity, η, for KCl (1:60) must be constant. The values for several temperatures are

T	Λ	η	$\Lambda\times\eta$
°C			
0	0. 03345	0. 01713	0. 000574
25	. 05800	. 00890	. 000522
45	. 0810	. 00618	. 000500

A 5-percent difference is observed for a 20 degree difference in temperature. As the limits of tolerance are the same here as for difference in pore size, the effect of a temperature gradient across the tube on the value of h cannot be neglected.

(f) Potential Distribution Across Packing

Nonuniformity of potential across the packing is identical in its effect to nonuniformity in pore size. Probe measurements made on various cell designs showed that voltage deviations as large as 5 percent often existed between the top and bottom of horizontal packings. These irregularities can be eliminated by proper design of electrodes and by having the packing set back about the distance of one radius from the cathode compartment.

6. Cell Design

It is now possible to specify the prerequisites for successful cell operation. Maximum separation will be attained when the electrolyte stream velocity balances the average K-ion velocity. To approach this condition the following requirements must be satisfied: (1) The packing must be fine, 100 mesh or finer, if a height theoretical unit of 0.01 cm is to be realized. (2) The porosity of the packing must be uniform. As the difference in mobility of ^{39}K and ^{41}K is estimated at only 0.6 percent, the ideal limits of variation should be within this quantity. (3) Temperature distribution across the packing should be uniform. Variations in excess of a few degrees will seriously impair the efficiency since a temperature gradient not only gives rise to convective disturbances but disrupts the balance between ion and stream flow. (4) The potential distribution across the packing must be uniform to within a fraction of 1 percent.

On the basis of the above considerations, the highest efficiency should be expected in capillary tubes. A sheet capillary between closely spaced parallel plates placed horizontally should be as efficient, provided the spacing is accurate and the potential distribution and temperature uniform. Columns packed with uniformly grained material constructed so that the cooling is primarily at the ends should also possess a low value for h.

Part of the material presented in this report has been taken from a report by S. L. Madorsky, A. Keith Brewer, and Gregory Breit on file at the Bureau. The authors also express their appreciation for the cooperation of J. W. Westhaver throughout the course of this work. Above all, the authors express their thanks to Lyman J. Briggs for his continued interest and practical suggestions, which have been an inspiration throughout the progress of this research.

II. Experimental Development of Method for Concentration of ^{39}K

By Samuel L. Madorsky and A. Keith Brewer

1. Introduction

The successful operation of an electromigration cell depends primarily on (1) suitable cell design and packing, (2) suitable electrolyte, and (3) proper means for maintaining a balance between the ion transport and the electrolyte stream flow. Section I develops the general theory of electromigration, and this section describes a series of initial experiments designed to study the principal conditions for concentration of ^{39}K in an electromigration cell.

2. Cell Design and Construction

Two of the original designs of the electromigration cell are shown in figures 1 and 2. In figure 1 the packing consisted of well-rounded Ottawa sand of about 100 mesh. In order to pack the sand properly, the cell was placed in a vertical position, the cathode end plugged, and the sand introduced through the anode end with frequent tapping. In the apparatus shown in figure 2 the packing in one experiment consisted of Pyrex glass wool, as shown by the shading slanting from left to right and, in two other experiments, of

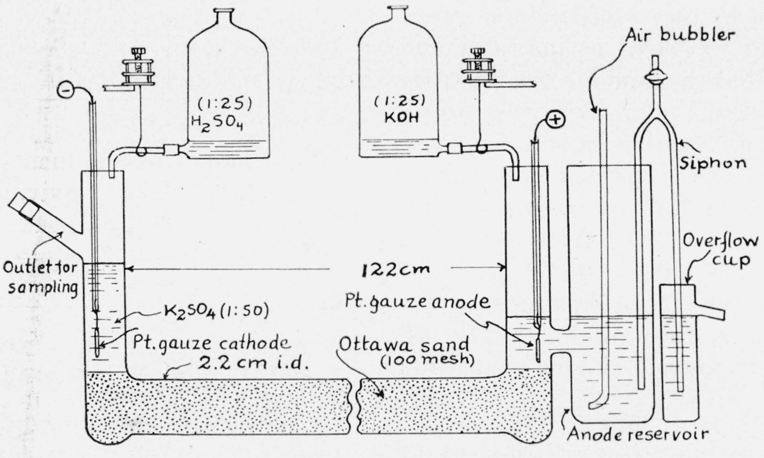

FIGURE 1.—*Electromigration cell packed with 100-mesh Ottawa sand.*

fritted Pyrex glass powder, as shown by the shading slanting from right to left. The glass wool was Corning standard No. 008 grade having a fiber diameter of 0.0002 to 0.0003 inch. It was cut into lengths of 1 to 2 cm and rammed into the cell through an opening at *A*, after which the opening was sealed. In preparing the fritted packing a straight tube was plugged with asbestos at the lower end and filled with glass powder 100 to 140 mesh. The tube was then packed in sand in a vertical position, heated in an electric furnace to 715° C and kept at this temperature for 1 hour. The anode and cathode compartments were then sealed on to the packed tube.

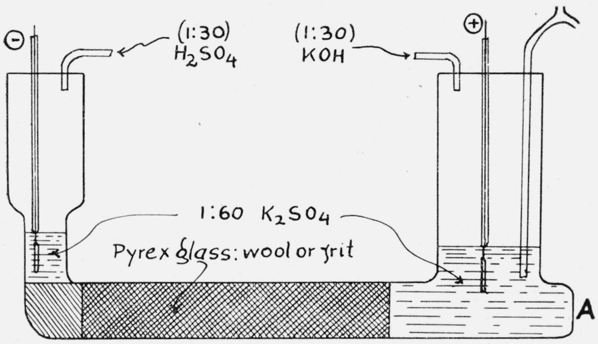

FIGURE 2.—*Electromigration cell packed with Pyrex glass wool (shading slanting from left to right) or fritted glass (shading slanting from right to left).*

The general arrangement of the electromigration cells is shown in figure 1. The restituent liquids[3] were added to the electrode compartments by means of droppers. These droppers were made from thick-walled capillary tubes bent at a right angle. The ends were ground flat to insure uniformity in the drop size. The drop rates were controlled by means of Hoffman screw clamps. Methyl red was used as indicator and the rates were such that the liquid in the electrode compartments changed color between drops. The anode was provided with a siphon and overflow cup. The electrodes consisted of platinum gauze 2 by 2 cm attached to platinum wires enclosed in glass tubes. In one experiment, when high voltage was used, a 2,000-v motor generator was employed. In the other experiments the source of current was a 220-v d-c line. The cell was kept in a bath to prevent sudden changes of temperature.

3. Electrolytes and Restituent Solutions

Potassium sulfate was the electrolyte used in all the experiments. The electrode reactions involved are $2K^+ + H_2SO_4 = K_2SO_4 + H_2$ at the cathode, and $SO_4^{--} + 2KOH = K_2SO_4 + H_2O + 1/2 O_2$ at the anode. Thus the anode receives a continuous fresh supply of K^+, and the initial ratio $^{39}K/^{41}K$ is kept constant in the anode compartment. In order to maintain the concentration of the electrolyte in the cell at its original value, the concentration of the restituent solutions, KOH and H_2SO_4, must be adjusted to the transport numbers of the respective cation and anion of the electrolyte. For the sake of simplicity, it is convenient to designate the electrolyte itself, as well as the restituent solutions, on the basis of equivalent ratios solute: Water, rather than on the basis of normality. In the experiments described in this paper, concentration ratios $1/2K_2SO_4 : H_2O = 1:50$ and $1:60$ were used. The transport numbers of K^+ and $1/2SO_4^{--}$ at the above concentrations are about equal, and the H_2SO_4 and KOH solutions were made up each in the equivalent ratios 1:25 and 1:30 for the 1:50 and 1:60 K_2SO_4 experiments, respectively.

Concentrations, densities, and normalities of all the solutions employed in this work are given in table 1.

TABLE 1.—*Solutions employed in the electromigration experiments*

Solute	Ratio solute: H_2O	Concentration	Density [a] at 25° C	Normality
		Percent		
$1/2K_2SO_4$	1:50	8.82	1.070	1.083
$1/2K_2SO_4$	1:60	7.46	1.059	0.906
$1/2H_2SO_4$	1:25	9.82	1.063	2.128
$1/2H_2SO_4$	1:30	8.32	1.053	1.785
KOH	1:25	11.07	1.102	2.176
KOH	1:30	9.40	1.086	1.821

Values for KOH are at 15° C.

The amount of restituents added, in grams per ampere hour (0.0373 equivalent) in the case, for example, of $1:60 K_2SO_4$ were as follows:

To cathode		To anode	
$1/2H_2SO_4$	1.830	KOH	2.092
$30H_2O$	20.164	$30H_2O$	20.164
Total	21.994	Total	22.256

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[3] "Restituent liquid" is a liquid that helps to restore the original chemical composition of the electrolyte in the cell.

4. Calculation of Separation Coefficient

The results obtained in the experiments on concentrating ^{39}K can be interpreted in terms of the separation coefficient ϵ by using eq 10, section I. Rearranging and substituting numerical values, eq 10 can be written

$$\epsilon-1=0.02882\frac{V_cC}{I^+t_1}\times\frac{R_{t1}-14.20}{R_{t_1}+1},$$

where t_1 is time in hours, and I^+ is positive current.

The cathode volume, V_c, is the free liquid in the cathode compartment down to the packing where it recedes into the horizontal tube, as in the case when fritted glass is used. However, where the packing extends into the cathode compartment, for example, when sand or glass wool is used, the cathode volume is the free liquid above the packing plus the liquid in the packing directly below the cathode cup, as the latter liquid is in thermal exchange with the free liquid due to the heat developed in the packing. Details of cells and experimental conditions are given in table 2.

TABLE 2.—*Experimental conditions*

Experiment No.	Packing [a]		Current		Ratio: 1/2 K_2SO_4: H_2O	Cathode volume	Bath temperature
	Type and mesh	Length					
		cm	*v*	*amp*		*ml*	° *C*
3	Ottawa sand, 100	122	800	0.5	1:50	30	25 to 30
7	do	10.3	78	.7	1:60	16	25 to 30
9	Pyrex wool	15.5	46	1.0	1:60	6.5	25 to 30
10	Pyrex frit, 100 to 140	12.0	96	0.7	1:60	6.5	4
13	do	6.0	54	.7	1:60	6.5	4

[a] The diameter of the packing was 2.2 cm in all the experiments.

5. Experiments

(a) Preliminary Experiments

Some preliminary experiments were carried out with normal K_2SO_4 as the electrolyte and 2 *N* H_2SO_4 and KOH as the restituents. In one experiment the packing was 2.1 cm in diameter, 27 cm long, and consisted of 60-mesh Ottawa sand. The cell was operated for 8 hours during the daytime with a current of 0.3 amp. At the end of this period, an approximately 1 ml sample was drawn from the cathode compartment for analysis and the operation discontinued overnight. This was repeated without renewing the electrolyte for a number of days. Analysis showed a value for *R* varying between 14.8 and 15. On continued operation, the concentration of ^{39}K in the cathode remained at this value. This must have been caused by too much sampling and too long intervals intervening between operating periods, which permitted the accumulated ^{39}K to diffuse from the cathode compartment into the packing.

A U-shaped tube of the same cross section and with the same kind and length of packing, and operated under similar conditions as the straight packed cell for four 8-hour periods, gave similar results.

A cell 30 cm long packed with parallel lengths of capillaries having bores 0.75 to 1 mm was operated with 1-amp current. The result was negative. A similar cell was packed with tubes of 2-mm inside diameter and 3-mm outside diameter, and the bores as well as the spaces between the tubes were filled with 60-mesh Ottawa sand. It was operated at 0.2 amp, the first day for 12 hours and the second day for 14 hours. The isotope ratios were 14.60 and 14.80, respectively, for the 2 days of operation. This experiment points to the necessity of having a packing in which the pores are small and uniform.

A cell of the same length and cross section was packed loosely with acid-washed asbestos wool and operated at 0.4 amp for 12 hours the first day and for 14 hours the next day. Analysis showed ratios of 14.70 and 14.85, respectively, for the two days.

(b) Ottawa-Sand-Packed Cells

Experiments 3 and 7 were carried out in a cell shown in figure 1. The packing was 122 cm long in experiment 3, and 10.3 cm in experiment 7. The bath temperature in both experiments was maintained at 25° to 30° C. In experiment 3 the operation during the first 272 hours was interrupted every night for periods ranging from 8 to 12 hours. The rest of the operation was continuous. The time counted was that of actual operation. Experiment 7 and the experiments described below were continuous throughout. Small samples for mass spectrometer analysis were drawn from the cathode compartments at about 50-hour intervals.

In order to check on the constancy of operation the cathode samples in experiment 3, before they were used for mass spectrometric analysis, they were analyzed for K_2SO_4 content. This was done by weighing the sample, evaporating it to dryness, and weighing the K_2SO_4 residue. The results of these analyses are shown in table 3. As seen from this table, the K_2SO_4 content in the cathode compartment varied little during 295 hours of operation.

Anode samples were analyzed similarly for K_2SO_4 in both experiments. The analyses, as seen from table 4, show little change in concentration of the electrolyte.

TABLE 3.—*Cathode analysis in experiment 3*

Time	K_2SO_4
Hours	*Percent*
0	8.82
52	8.61
102	8.65
152	8.61
244	8.33
295	8.83

TABLE 4.—*Anode analysis*

Experiment 3		Experiment 7	
Period of operation	K_2SO_4	Period of operation	K_2SO_4
Hours	*Percent*	*Hours*	*Percent*
0	8.82	0	7.46
107	8.79	19	7.84
176	8.70	42	7.51
		218	7.20
Experiment 10		Experiment 13	
0	7.46	0	7.46
45	7.98	45.5	7.76
91	7.74	92.5	7.97
139	7.73	144.5	7.70
211	7.78	188.5	7.70
260	7.89	212.5	7.65
309	8.18	254.5	7.68
354	7.70	309.5	7.73

The mass spectrometer analyses of cathode samples are shown in column 3 of table 5. In column 4, values of the separation factor, S, which is equal to R_T/R_o, are shown. Column 5 shows values of $\epsilon-1$ calculated by means of the equation shown above.

TABLE 5.—*Concentration of* ^{39}K *and separation coefficient*

Experiment No.	Time, T_1	Ratio: $^{39}K/^{41}K$, R_T	Separation factor, S	$(\epsilon-1)\times10^2$
	Hours			
3	52	14.70	1.035	0.229
	102	15.20	1.070	.227
	152	15.70	1.105	.221
	202	16.20	1.141	.215
	244	16.65	1.172	.213
	295	17.00	1.197	.197
	335	17.40	1.225	.194
7	50	14.95	1.052	.112
	150	16.50	1.162	.105
	250	16.70	1.176	.067
	300	17.00	1.197	.062
	350	17.35	1.222	.059
	408	17.75	1.250	.055
9	12.5	14.60	1.028	.070
	31.5	15.00	1.056	.054
	100.5	15.60	1.098	.028
	194.0	17.90	1.260	.034
10	94	14.60	1.028	.013
	152	14.90	1.049	.014
	203	17.50	1.232	.041
	259	20.50	1.443	.055
	360	17.20	1.211	.022
13	191	17.30	1.218	.043
	354	17.75	1.250	.026

(c) Glass-Wool-Packed Cell

Experiment 9 was carried out in a glass-wool-packed cell, as illustrated in figure 2. Details of design and operation are shown in table 2. No analyses were made of K_2SO_4 content in the cathode or anode liquids during operation. Cathode samples were analyzed for ^{39}K concentration, and the results are shown in table 5. The $\epsilon-1$ values are rather low, most likely because of channelling and nonuniformity of porosity in the packing.

(d) Fritted-Glass-Packed Cells

Originally four cells were started: Two cells, each having a 12-cm-long packing, were operated, one at 25° C (expt. 11) and the other at 50° C (expt. 12); two other cells, having packings 12 cm long (expt. 10) and 6 cm long (expt. 13) were operated at 4° C. The first two cells showed signs of rapid deterioration of the fritted packing at the cathode end soon after the operation was started, and the experiments were discontinued. The other two cells, operated at a lower temperature, stood up well, and the operation was continued for a number of days. Details of cells used in experiments 10 and 13 are shown in table 2.

Anode samples were checked for K_2SO_4 content, and the results are shown in table 4. These results indicate little change in the concentration of the electrolyte throughout the operation. Cathode samples were analyzed for concentration of ^{39}K, and the results are shown in table 5.

Figure 3 shows abundance ratio plotted against time for all five experiments.

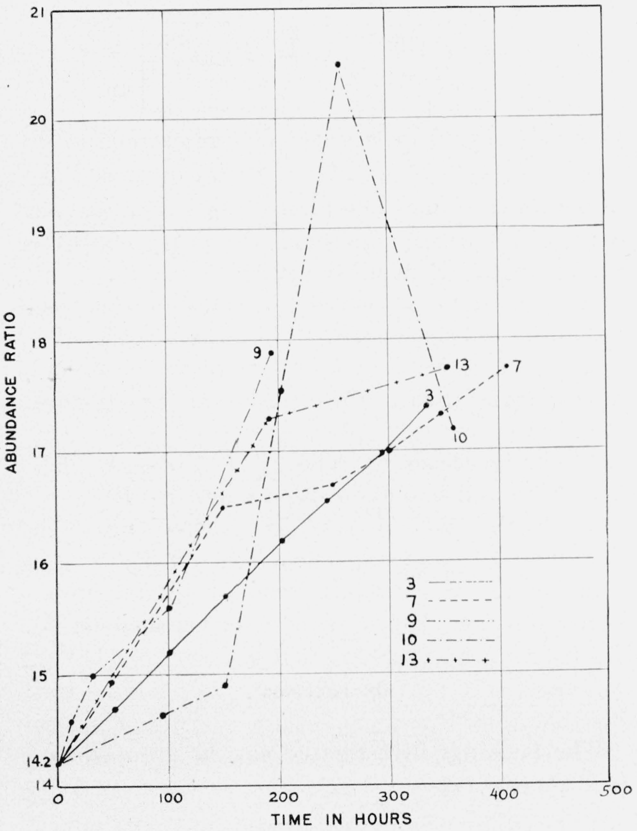

FIGURE 3.—*Change of ratio $^{39}K/^{41}K$ with time in five experiments.*

(e) Distribution of ^{39}K in Packing

Diffusion of ^{39}K from the cathode compartment into the packing and disturbances incidental to the operation, such as may be caused by irregularities in metering the restituents, would tend to lower the separation coefficient. Aside from this, the value of the cathode volume, V_c, cannot be measured accurately as it is not known how far it extends into the packing. In experiment 3, in which a very long packing was used, any losses of ^{39}K concentrate from the cathode volume into the packing could be recovered at the end of the operation.

When experiment 3 was discontinued after 335 hours of operation, 20 ml of liquid was first drawn from the cathode compartment, then the liquid was allowed to seep into this compartment, and successive samples of 25 ml each were drawn. The position of each sample in the packing near the cathode end before it was drawn is shown in figure 4. It should not be assumed that figure 4 gives a true picture of the distribution of ^{39}K concentrate in the packing, because of mixing of successive samples with some of the liquid left in the cathode compartment, as well as in the packing from the previous samples. However, it shows that the concentrate was mostly confined to the cathode end of the packing, and that all the ^{39}K concentrate was removed with the first four samples.

By adding the samples drawn at the end of the operation, as well as the samples drawn during the operation, we get a total of all the ^{39}K concentrate obtained in 335 hours of operation in experiment 3. Table 6 gives the volume and R_t values for all samples. All the samples add up to a total cathode volume of 96.65 ml of an average $R_{t_1} = 15.53$. On the basis of 0.5-amp, total current, or 0.25-amp, positive current used in this experiment,

$$\epsilon - 1 = \frac{0.0288 \times 96.65 \times 1.083 \times 1.33}{0.25 \times 335 \times 16.53} = 0.00290.$$

TABLE 6.—*Distribution of ^{39}K in the packing in experiment 3*

Period of operation	Volume of cathode sample	R_T
Hours	*ml*	
52	0.326	14.70
102	.222	15.20
152	.345	15.70
202	.243	16.20
244	.231	16.65
295	.283	17.00
335	20	17.40
335	25	16.30
335	25	14.73
335	25	14.35
Total and average	96.65	15.53

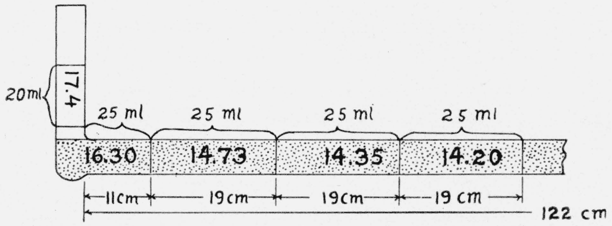

FIGURE 4.—*Distribution of ^{39}K concentrate in the packing.*

6. Conclusions

The data presented show the feasibility of concentrating ^{39}K by the electromigration method. Packings made of fine sand proved to be superior to those made of fritted glass, glass wool, asbestos, or glass capillary tubes. Concentration of the electrolyte in the electrode compartments remained practically constant through the entire operation of the cells. Experiment 3, which was carried out in a long tube packed with sand, gave the highest and longest sustained values of $\epsilon-1$. This is explained on the ground that the long packing held any losses of ^{39}K from the cathode compartment caused by irregularities in operation, such as those caused by variation in rates of addition of restituents, by loosening of the packing or by diffusion. The value of $\epsilon-1=0.0029$, obtained by taking into consideration the ^{39}K concentrate in the packing, at the end of experiment 3, should be taken as the best value for the experiments described.

III. Detailed Investigation of Method

By A. Keith Brewer, Samuel L. Madorsky, John Keenan Taylor, and Vernon H. Dibeler

1. Introduction

In view of the success attained in concentrating ^{39}K described in section II, a detailed investigation was initiated to test the various contributing factors described in section I. The results of some 170 experiments run under controlled operating conditions are summarized in this section.

2. Experimental Details

(a) General Assembly

A complete layout for a typical experimental setup is shown in figure 5. The cell illustrated is one using K_2SO_4 as the electrolyte. The cathode control is manually operated; the anode control is the constant pH flushed type.

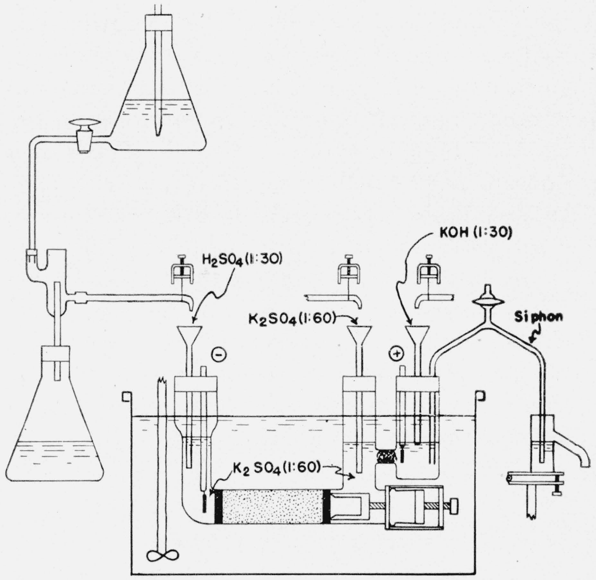

FIGURE 5.—*Experimental setup for the concentration of ^{39}K.*

A large number of modifications of the basic design have been tested. The cells illustrated in figures 5 to 10 are representative of the most common designs used. These cells can be classified as follows:

1. On the basis of type of control—pH (figs. 5, 6, 7, 9) and boundary (figs. 8 and 10, B).
2. On the basis of packing—packed (figs. 5, 6, 7, 8, 9, 10, A) and unpacked (figs. 10, B).
3. On the basis of direction of stream flow—horizontal (figs. 5, 6, 7, 8, 10) and vertical (fig. 9).

(b) Packings

The packings investigated can be grouped into four general types:

1. Granular: Sand, glass ballotini beads, silicon carbide.
2. Fibrous: Glass wool, asbestos, absorbent cotton, etc.
3. Rigid: Glass frits, Alundum, etc.
4. Close clearance: Concentric tubes.

The dimensions of the packings studied were varied over a wide range. A convenient size of cell used in testing the various pertinent variables was made with packings 14 mm in diameter and 8 cm long.

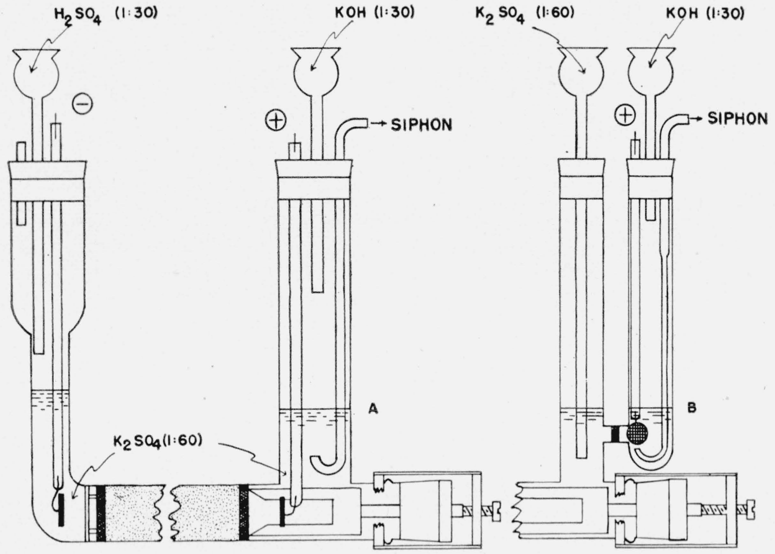

FIGURE 6.—*Cell used in* K_2SO_4 *experiments.*

A. Anode neutralized with KOH; *B*, anode neutralized with KOH and flushed with K_2SO_4 (1:60).

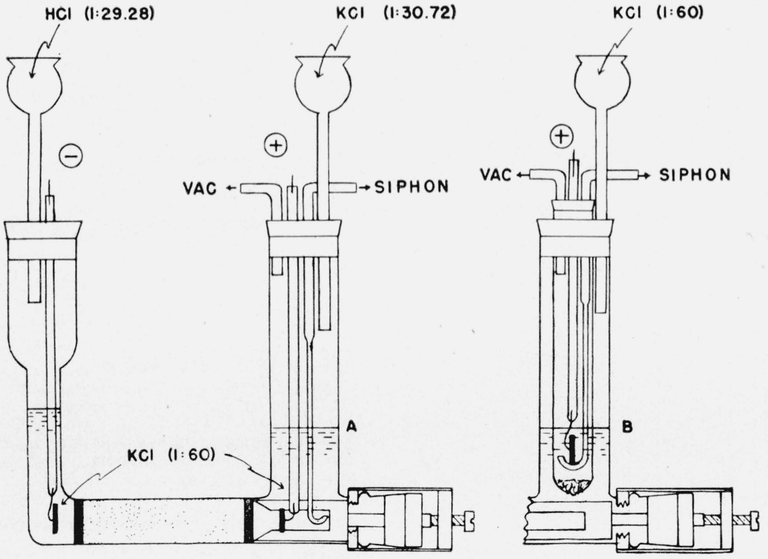

FIGURE 7.—*Cell used in* KCl *experiments.*

A, Single-cup anode flushed with KCl (1:30.72); *B*, double-cup anode flushed with KCl (1:60).

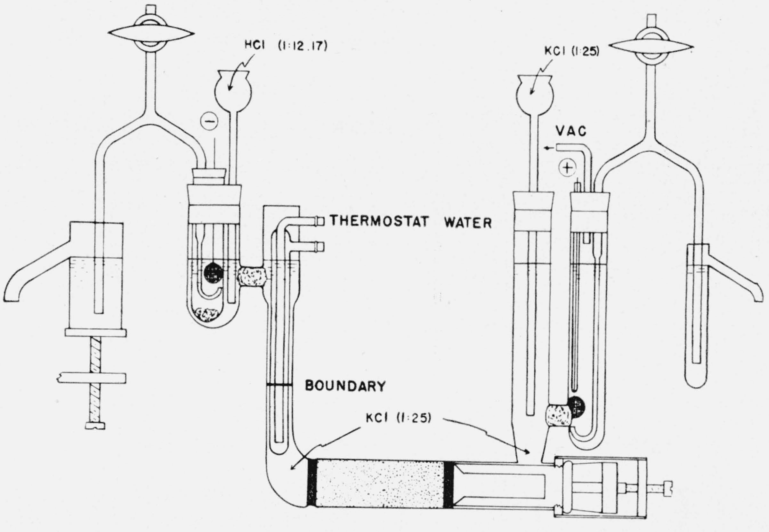

FIGURE 8.—*Cell used in boundary experiments with* KCl.

Anode is of the double-cup, flushed type.

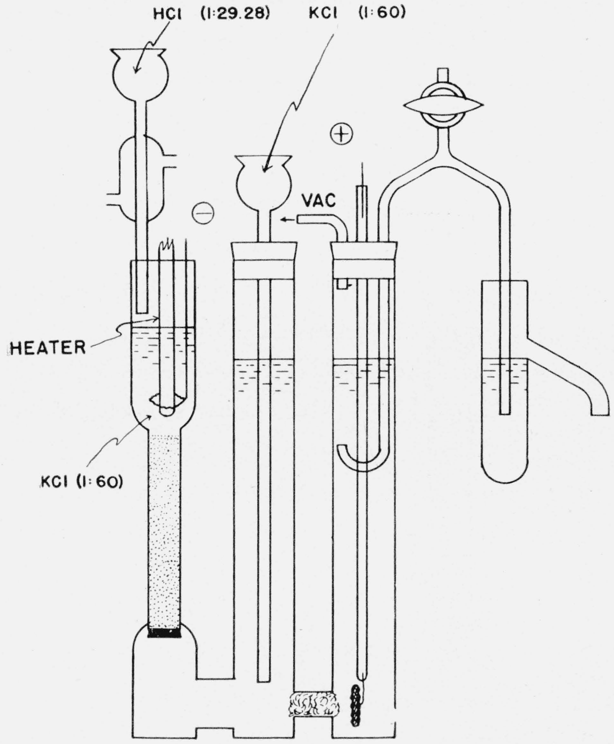

FIGURE 9.—*Cell with vertical packing and double-cup, flushed-type anode.*

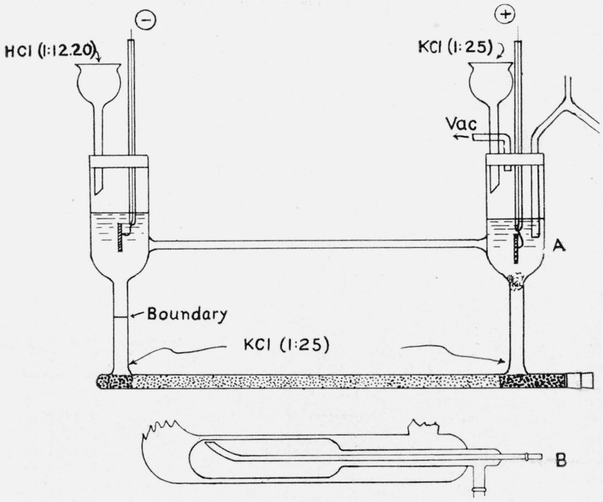

FIGURE 10.—*Cells designed to facilitate the dissipation of heat.*

A, Cell with small diameter of packing used in boundary experiments; *B*, cell with circular capillary space in place of packing.

(c) Packing Supports

The supports holding the packings in place are as critical as the packing materials themselves. The problem has been one of finding a thin, porous, rigid material to which sufficient pressure can be applied to prevent loosening or channeling of the packing during operation. Another requirement is that it should not distort the potential distribution across the face of the packing or cause an uneven electrolyte stream flow through the packing. Various supporting materials were tested, including sealed-in frits, Alundum plates, finely perforated Bakelite, and thin frits made from No. 47 ballotini beads; the latter proved to be the most satisfactory.

The ballotini frits were cast in graphite molds and heated to a point to insure rigidity without impairing the porosity. The best cathode frits were about 2.5 mm thick and were tapered slightly at the edge to fit tightly into the cell as shown in figure 8. The anode frits were about 5 mm thick and were calked at the edges with glass thread or glass cloth to prevent the fine packing from leaking out.

(d) The Electrodes

Platinum-gauze electrodes were used in all the experiments. Care was taken to place the electrodes in such a position that the potential distribution across the packing was uniform at all points.

(e) Source of Potential

A 100-volt storage battery was used. The battery was kept charged by floating on a d-c generator line, the generator current being slightly in excess of that drawn from the battery.

3. Electrolytes and Controls

(a) Electrolytes

Experiments were carried out with potassium chloride and potassium sulfate. The choice of electrolyte was based on the type of control mechanism used to maintain the counterflow. The concentrations were varied over a wide range; a 1:60 ratio was adopted as most convenient for general use.

The restituent solutions, i. e., the solutions that were added to the cathode and anode compartments in order to maintain the original composition of the electrolytes, were in the case of 1:60 K_2SO_4, 1:30 H_2SO_4, and 1:30 KOH for the cathode and anode, respectively. For KCl, more accurate values of the K^+ were used in the calculations, and the cathode restitutent for 1:60 electrolyte ratio was 1:29.28 HCl. The anode restitutent was either 1:30.72 KCl or 1:60 KCl, depending on the type of control used, as will be explained later. The concentrations, densities, and normalities of the varioussolutions are shown in table 7.

TABLE 7.—*Solutions employed in electromigration experiments*

Solute	Ratio Solute:H_2O	Concentration	Density [a] at 25° C	Normality
		Percent		
KCl	1:25	14. 20	1. 090	2. 077
KCl	1:30. 72	11. 87	1. 075	1. 711
KCl	1:60	6. 45	1. 038	0. 898
KCl	1:12. 20	14. 23	1. 067	4. 162
KCl	1:29. 28	6. 47	1. 029	1. 823
1/2K_2SO_4	1:60	7. 46	1. 059	0. 906
1/2K_2SO_4	1:30	8. 32	1. 053	1. 785
KOH	1:30	9. 40	1. 086	1. 821

[a] Values for KOH are given at 15° C.

The amounts of restituents added per ampere hour when the electrolyte is 1 : 60 K_2SO_4 are shown in section II. For 1 : 60 KCl, the amounts of restituents added were as follows:

To cathode		To anode	
	g		*g*
HCl	1. 362	KOH	2. 781
29.28H_2O	19. 680	30.72H_2O	20. 648
Total	21. 042	Total	23. 429

(b) Control of Cathode

The pH and the boundary controls used have been devised for both manual and automatic operation. The automatic-control system is described in section VII.

The pH controlled cells were equipped with droppers designed to supply acid to the cathode compartment at a constant rate. The droppers were attached to constant level spillways and were supported near the tips by adjustable screw clamps. Methyl orange and methyl red were used as the indicators to determine the dropping rate. The rate of dropping was adjusted to the point where the cathode solution turned from red to yellow between drops.

A boundary between HCl and KCl was also used as the index of reflux balance. An analysis of the boundary mechanism indicates that a stable boundary should exist when the concentrations C_1 of the HCl solution and C_2 of the KCl solution are in the ratio of their cation transport numbers, i. e., $C_1/C_2 = T_{H^+}/T_{K^+}$.

In the absence of a counterflow, the passage of 1 Faraday of current causes the boundary to move through a volume $V=T_{K^+}/C_2$. To maintain the boundary stationary a volume, V, of solution must be added to the cathode compartment. This volume must contain 1 equivalent of HCl to neutralize the electrode reaction.

The construction of the boundary cells is shown in figure 8. The internal cooler is desirable as large boundaries are inclined to become diffuse in the center. The height of the column of electrolyte controlling reflux rate is adjusted by a screw under the spillway. The rate of acid addition is not critical in the arrangement illustrated, provided it is sufficient to maintain a constant pH in the acid above the boundary.

(c) Control of Anode

Several types of anode controls have been tested. These are shown in the cells illustrated. In figure 6A, KOH is added to the anode at the stoichiometric rate. A precise regulation is necessary for the dropping rate. Cell 2B is designed to eliminate the need for drop control by employing a flushed-type anode. The electrolyte of the original concentration is added to the anode compartment at a rate sufficient to keep the pH at its initial value. KOH can be added at the anode cup if desired, to lessen the quantity of electrolyte required for flushing. This addition of KOH, when the electrolyte is KCl, is not necessary as chlorine is liberated at the anode.

4. Correlation of Experimental Data

The separation efficiency was determined in terms of the abundance ratio $^{39}K/^{41}K$ in the cathode compartment, as measured by the mass spectrometer. The experiments described in this report were all conducted under conditions where the abundance ratio in the anode compartment was maintained at the value for normal potassium, i. e., $^{39}K/^{41}K=14.20$.

In order to place individual experiments on a comparable basis, it is necessary to consider the current, the cathode volume, and the concentration of the electrolyte. The method chosen was to compare the amounts in milliequivalents of the light isotope ^{39}K transported into the cathode compartment per ampere. This value is designated by q/i, and is calculated from the expression

$$q/i=\frac{V_cC\Delta N}{i},$$

in which

q=milliequivalents of ^{39}K transport into the cathode compartment
i=current in amperes
V_c=volume of cathode liquid in milliliters
C=normality

ΔN is obtained from the abundance ratio as follows:

$$\Delta N=\frac{R_t}{R_t+1}-\frac{R_0}{R_0+1}=\frac{R_t}{R_t+1}-\frac{14.2}{15.2}=\frac{R_t}{R_t+1}-0.9342.$$

Here $R_t=^{39}K/^{41}K$ in the cathode compartment at time, t, and R_0=normal ratio 14.20.

The initial slope, q/it_1, obtained by plotting q/i against the time of sampling is related to the separation coefficient ϵ by the equation

$$\epsilon-1=0.876\times q/it_1,$$

where t_1 is time in hours.

5. Results

(a) General Operation

The $^{39}K/^{41}K$ ratio in the cathode compartment as a function of time of operation for six separate experiments is given in figures 11 and 13. These experiments were chosen from the types most regularly used in this research in order to illustrate normal cell operation as well as the effect of various disturbing factors. The separation efficiency (q/i vs t_1) for these same experiments is given in figures 12 and 14.

The pertinent data for the above experiments are given in table 8. The data for two boundary controlled experiments, 134 and 157, are included in table 8 and figures 13 and 14 for comparison.

Experiment 170 was run in a cell of the type illustrated in figure 7, using flushed anode 3B. The cathode was controlled by manual regulation of the drop rate; the indicator was methyl red. This type of cell was the easiest to keep regulated and, in general, represents the most satisfactory arrangement studied. It will be noted that the concentration of ^{39}K in the cathode compartment increases nearly linearly with time. The small deviation observed at the 113 hour is due to the cell becoming out of balance for a short period of time. The slight tapering off in rate is to be

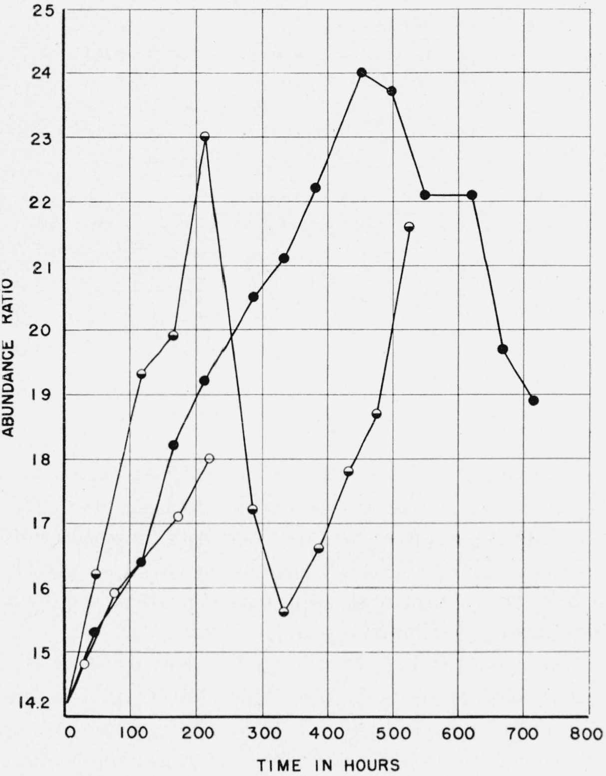

FIGURE 11.—*Ratio of* $^{39}K/^{41}K$ *in the cathode compartment, plotted against time, for three representative experiments.*
◒ 149 vertical; ● 170 horizontal; ○ 186 automatic.

expected as the concentration of light isotope in the packing is not taken into consideration in the efficiency curve.

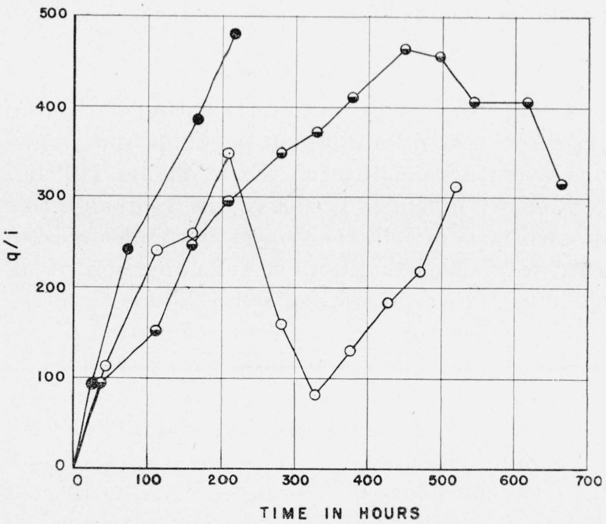

FIGURE 12.—*Milliequivalents of* ^{39}K *transported into the cathode compartment per ampere, plotted against time, for three representative experiments.*
○ 149 vertical; ◒ 170 horizontal; ● 186 automatic

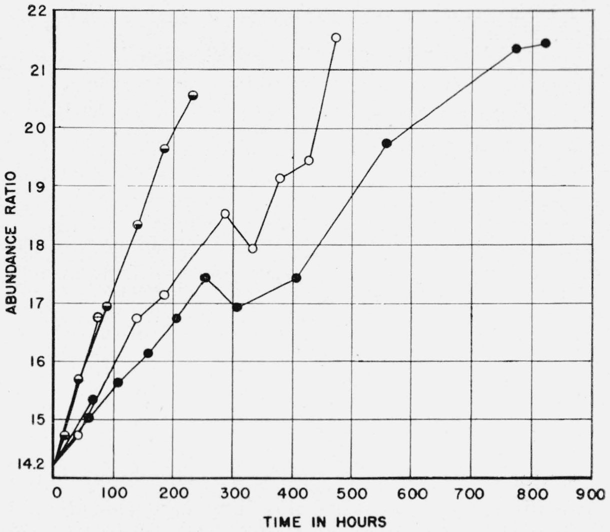

FIGURE 13.—*Ratio of* $^{39}K/^{41}K$ *in the cathode compartment, plotted against time, for five representative experiments.*
⊖ 134 boundary; ⊙ 157 boundary; ○ 158 indicator; ◒ 182 indicator; ● 184 automatic.

Experiment 186 was run under complete automatic control. The anode was the flushed type shown in figure 6, B. The cathode was provided with an automatic acid injector controlled by H_2 versus $PbSO_4$ electrodes in the electrolyte. The automatic arrangement is described in section VII.

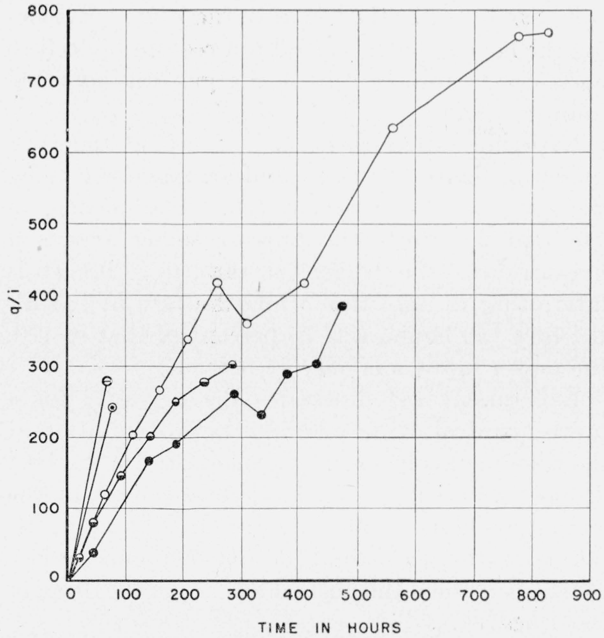

FIGURE 14.—*Milliequivalents of* ^{39}K *transported into the cathode compartment per ampere, plotted against time, for five representative experiments.*
⊙ 134 boundary; ⊖ 157 boundary; ● 158 indicator; ◒ 182 indicator; ○ 184 automatic.

TABLE 8.—*Experimental conditions and separation coefficient*

[H, horizontal. V, vertical. B, boundary. I, indicator. A, automatic. SiC, silicon carbide. S, sand. GB, glass beads.]

Experiment No.	Type of cell	Packing			Cathode volume	Current		Electrolyte		$(\epsilon-1)\times10^2$
		Mesh	Length	Diameter				Salt	Ratio salt: water	
			cm	*cm*	*ml*	*amp*	*v*			
134	H, B	SiC 150	10	0.4	0.75	0.06	80	KCl	1:25	0.286
149	V, I	S 100	10	1.4	8	.5	87	KCl	1:60	.221
157	H, B	GB 100	7	1.4	15	.5	32	KCl	1:25	.385
158	H, I	GB 100	5	2.5	12	.6	32	KCl	1:60	.080
170	H, I	GB 100	7	1.4	10	.5	93	KCl	1:60	.173
182	H, I	S 60	8	1.4	8	.5	90	KCl	1:60	.156
184	H, A	S 100	8	2.5	20	.5	80	K_2SO_4	1:60	.175
186	H, A	GB 60	10	1.4	16	.4	138	K_2SO_4	1:60	.318

Experiment 149 was run in a vertical cell of the type illustrated in figure 9. The cell was packed with sand held in place by gravity. The barrel of the tube was made from an extra-thin-walled Pyrex tube. The results indicate a rapid concentration at first, disturbed later by an accumulation of gas in the packing. Sometime after 200 hours a bubble of gas formed in the sand and slowly worked its way up and out during the next 100 hours; after this, the sand settled back in place, and the cell resumed its initial rate of operation. This particular cell was equipped with a degassing heater in the cathode compartment, and the gas accumulated after the heater burned out. Replacing the heater, however, did not restore the cell to normal operation until all the gas was expelled from the sand.

Experiment 158 was run in a cell of the type shown in figure 7, the general arrangement being the same as in experiment 170. The packing in 158 had 2.5 times the cross-sectional area and five-sevenths the length of that in 170. It is interesting to note that while the rate in 158 for the first 150 hours, was 75 percent of that in 170, the power input was only 41 percent.

Experiment 184 illustrates the necessity for a precise control of the required rate of addition of the restituent solutions. In this instance the HCl dropper was stopped up for about 1 hour at the end of 260 hours. This resulted in a break in the rate curve between the 250- and 320-hour period. The cell resumed the normal rate when the dropper was repaired.

Experiment 182 shows the results of loosening of the beads near the cathode. The effect began at about the hundredth hour; at the end of 300 hours the channel was of such a size that the entire concentrate in the cathode compartment was washed out. The development of channels in the packing represents the most common cause of cell failure. The slightest loosening of the beads results in a channel of sufficient size to prevent an efficient operation of the cell.

The general conclusion to be drawn from the above experiments is that the change in isotope concentration in the cathode compartment is very nearly linear with time over a wide range. The rate is sensitive to any factor that might disturb the precise point balance between the ion mobility and the countercurrent stream flow. Incorrect rate of addition of the restituent solutions and the accumulation of gas in the packing give rise to effects from which the cells will recover when the disturbance is corrected. Channeling in the packing results in permanent cell failure.

(b) Type of Cell

A large variety of both vertical and horizontal cells were tested for different packings under various operating conditions. Experiments 149 and 170, shown in figures 11 and 12, are representative of each type of cell when operating under reasonably favorable conditions. A comparison of all the data, however, showed some difference in the efficiency for the two types as a function of the packing size. For 100-mesh beads and sand packings the rates of separation were essentially identical; a large number of experiments of each type gave maximum q/i values between 0.35 and 0.40 for 200 hours of operation. In the case of 40- to 80-mesh beads, in contrast, the vertical cells showed very small separation, whereas the q/i value for the horizontal cells was about one-half that for 100-mesh beads.

The general conclusion to be drawn is that the efficiency of the two types of cells is essentially the same under conditions where convection has been reduced to a minimum. The effect of convection, however, is entirely different. In the horizontal cells the convection flow is at right angles to the stream flow. In addition, it is small at the ends of the packing where the surface is uniformly cooled by the cathode and anode solutions. In the vertical cells the convective flow is in the opposite direction to the stream flow, being in the anode to cathode direction through the center of the tube and in the opposite direction along the cooled walls. This necessarily results in a mixing of the solution in the two electrode compartments. In consequence, for successful operation it is essential to use either packings of such fineness that convection becomes negligible, or to adjust conditions so that convection will just counterbalance the excess electrolyte flow in the center of the packing, where the viscosity is lower because of the higher temperature.

(c) Grain Size

The effect of grain size on the separation efficiency of horizontal cells is shown in figure 11.

A number of comparison experiments were run under similar conditions except for the grain size in the packings. Five duplicates were run for each bead size. The type of cell used is illustrated in figure 6, B. The packings were 5 to 10 cm long and 1.4 to 2.4 cm in diameter.

Lines 1, 2, 3, and 4 represent the maximum slope for each set of duplicate runs. In each case a majority of the cells gave values at or near the line as drawn; deviations from the line were due either to imperfect packing or to faulty operation.

It was not found possible to sift beads to exact mesh sizes. Line 1 was taken with commercial 107-mesh beads sifted through a 140-mesh screen. Line 2 was taken with beads that passed a 100-mesh screen but were rejected by a 120-mesh screen. Line 3 was taken with commercial 70-mesh beads sieved between 80 and 100 mesh. Line 4 is for commercial 47-mesh beads sieved between 40 and 80 mesh.

The conslusion to be drawn from the data presented in lines 1, 2, 3, and 4 is that the rate of separation increases with the fineness of the beads, the rate for 140-mesh beads being about twice that for 60-mesh beads. Although the data are inconclusive, these results, combined with those obtained with fine fiber packings, indicate that the final separation to be obtained for various packings increases with the fineness of the pores.

(d) Packing Materials

The various types of packing materials were tested under similar conditions. The results however, are incomplete and to that extent are inconclusive.

Granular packings, in general, were the most satisfactory. Ballotini glass beads were the easiest to pack and were not affected by the electrolyte. Their poor thermal conductivity, however, resulted in a tendency for the cells to boil during operation; this necessitated the use of relatively low current densities. The free space and heating effects have been described in section I. Sand packed almost as well as glass beads; it was superior in that the cells ran slightly cooler. Silicon carbide of the type used in glass grinding did not pack well under pressure. In spite of the fact that it ran appreciably cooler than glass beads, it was more inclined to fill up with gas. In general, spheres are more satisfactory than sharp-edged particles.

Rigid packings were only moderately successful. Glass frits, on the whole, gave high initial rates, but they developed pores or cracks. Alundum plates behaved the same as glass frits, but they were more inclined to plug up with indicator or any suspended material in the acid. Rubber battery separators failed to show sufficient uniformity in porosity for satisfactory use. Filter paper cut in strips and pressed in packs gave rates comparable to the best bead packings. As these packings were difficult to support, their possibilities were not thoroughly investigated. Fiber packings gave high initial values but, in general, deterioration was rather rapid. The values for absorbent cotton shown in line 6 of figure 15 have a comparatively high rate. The length of packing was only 1 cm compared to 8 cm for the beads. The cotton was cut in disks and packed wet, care being taken to keep all the fibers lying in a radial direction. Unfortunately, fully half the tubes so packed proved defective because intimate contact between the cotton and the glass walls could not be obtained at all points. Line 7 is a typical run obtained with glass-wool packings. A number of glass fibers tested gave about the same results; these included very fine "*A* fibers" of alkali resistant glass, battery-separator fibers, and ordinary glass wool. In each case the fiber packings started off with a high separation rate, only to develop pores at the end of a few hundred hours. Apparently the systems became alkaline for sufficient time throughout the operation to cause the fibers to disintegrate. It is possible that glass fibers can be made to operate on the automatically controlled experiments, in which the pH variation can be reduced to a minimum.

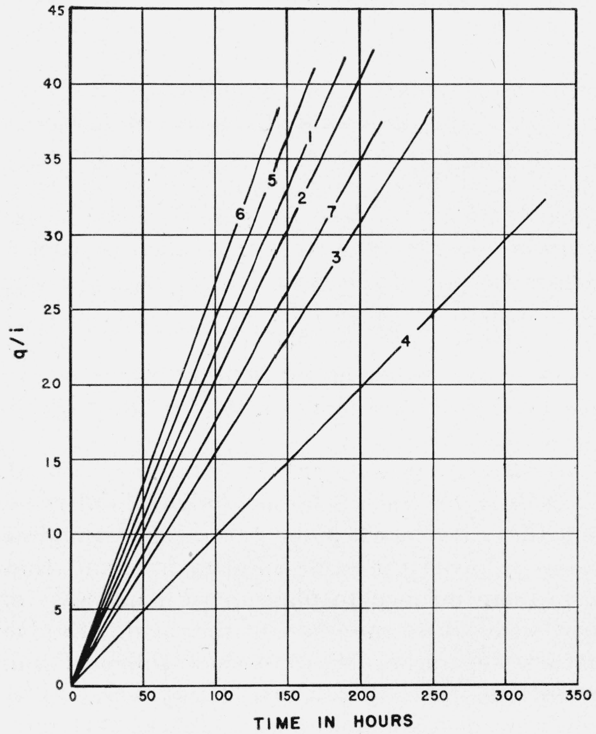

FIGURE 15.—*Comparison between various types of packings used in the electromigration experiments.*

1, Glass beads, 140 mesh; 2, glass beads, 100 to 120 mesh; 3, glass beads, 80 to 100 mesh; 4, glass beads, 40 to 80 mesh; 5, silicon carbide; 6, absorbent cotton; 7, glass wool.

From a consideration of all the packing materials studied it must be concluded that the material itself plays no direct part in the separation process. The choice of packing resolves itself into obtaining uniform porosity combined with mechanical and chemical stability.

(e) Length of Packing

Packing lengths from a few millimeters to 10 cm were investigated. In general, the longer packings gave the higher yields before breaking down. A study of the isotope distribution throughout the packing, however, revealed that high concentrations should be obtainable in very fine packings of 1 cm in length. The use of short packings necessitates a precise control at all times to prevent washing out of the material concentrated in the packing.

(f) Diameter of Packing

The diameter of the packings in horizontal cells was varied from 0.4 to 3.75 cm. The results showed the rate of concentration of ^{39}K to pass through a broad maximum between 1.2 and 2.5 cm. Results of this type are to be expected. For the small-diameter cells the contact between the glass walls and the beads constitutes an appreciable fraction of the free space. As this contact is not as intimate as between the beads themselves, a nonuniformity of porosity results. The loss of efficiency in large cells is doubtless due to the greater opportunity afforded for convective disturbances.

The packing in vertical tubes was investigated from 1 to 7 cm in diameter. The difficulties involved were confined largely to obtaining sufficient uniformity of porosity across the packing and also in arranging the electrodes to provide a uniform potential distribution while at the same time preventing the accumulation of gas on the under surface. When adequate precautions were taken, the large-diameter cells operated at an efficiency comparable with the horizontal tubes.

(g) The Anion

The effect of the chemical nature of the anion (Cl^- or SO_4^{--} on separation efficiency is shown in tables 7 and 8 and in figures 11, 13, and 15. These data were taken under similar conditions. Corresponding data have also been taken for other types of cells. Apparently no detectable difference in the efficiency of separation can be attributed to the chemical nature of the anion.

(h) pH of Anode Compartment

Experiments were run in which the pH of the anode was maintained as nearly as possible at 1.5, 3.5, and 6. No difference in the efficiency was detected. In practice, it was found more convenient to use the flushed type of control, in which the anode compartment remained at the pH of the original solution.

(i) Reflux Rate

The effect of the concentration of the HCl added to the cathode compartment was checked with KCl as the electrolyte, two experiments were run in which the restituent solutions were 1:28.28 and 1:31.72, respectively. The resultant rates were indistinguishable. This is to be expected as the cells will automatically adjust themselves to small differences in concentration.

(j) Concentration of Electrolyte

Experiments were performed in which the KCl:H_2O ratios were 1:25, 1:60, and 1:120. The differences in rate were no greater than usually observed between experiments run at the same concentration. For cells with equal cathode volumes, the rate of increase of the abundance ratio, for a given current, was greatest when the electrolyte was the most dilute.

(k) Type of Control

The results signify the necessity for the correct rate of addition of the restituent solutions at all times. Any system of control that permits a wide swing from low to high pH during the control cycle is objectionable. The pH swing is in general lower in the boundary and in the automatic-control experiments than is possible to obtain by manually regulated droppers. For this reason the q/i values for the latter are low on the average. This statement must be made with some reservations, however, because the cathode volume was kept small in most of the manually operated experiments, hence the pH swing is comparatively large. The results as a whole indicate a higher q/i value for the larger cathode volumes, although the rate of change in abundance ratio is in the reverse order.

(l) Potential Gradient

The potential gradient differed by a factor of about five for the various packings, being lowest in fiber packings, i. e., cotton, asbestos, and glass wool, and highest in the silicon-carbide and close-clearance cells shown in figure 10, B. The fact that q/i for cotton was as large as for silicon carbide does not indicate the absence of a potential gradient effect, because convection should also be less in the cotton. The only conclusion to be drawn from the limited data available is that if a gradient effect exists it does not make more than a first-power contribution.

(m) Current Density

The current density has been varied over a wide range without observing marked differences in the value of q/i. The interdependence of such factors as current, temperature, convection, and the like, prevent the drawing of any definite conclusions.

(n) Temperature

The cooling baths were operated at 15°, 25°, and 50° C. The temperature within the packings was measured in representative experiments by means of thermocouples incased in thin glass tubes inserted at various positions in the packing. The bath temperature had little or no influence upon the efficiencies observed. The temperature within the packing was just under the boiling point in experiment 149 and in the neighborhood of 50° C in experiment 186. Figure 12 shows no appreciable difference in rate.

6. Summary

The method of balanced electromigration has been shown to be very efficient for the concentration of the ^{39}K isotope. Its successful utilization rests upon the establishment of a local as well as an over-all balance between the electrolyte stream flow in one direction and the ion transport in the opposite direction, as a result of which the net transport of K^+ ions at all points is reduced to zero. When this has been realized, $^{39}K^+$ ions will make headway toward the cathode compartment, whereas the $^{41}K^+$ ions are washed back. To attain such a balance it is necessary to conduct the electrolysis through a packing of uniform porosity or through a capillary tube to reduce mixing to a minimum.

The separation efficiency has been found to be affected very little if any by the size and shape of the electrolytic cell, the composition of the packing material, the chemical nature of the anion, the electrolysis current, or the temperature of the cooling bath.

The most common causes of cell failure are channeling and nonuniformity of porosity in the packing. Other common causes of faulty operation are improper rates for the addition of the restituent solutions and gas-bubble formation in the packing.

The mechanism described in this paper should prove an effective means for the continuous separation of isotopes of most of the elements or of any two substances (i. e., Ra and Ba), whose ions have different transport velocities.

The authors express their indebtedness to Marvin Schwartz, Murray Nash, Thaddeus Sterling, Albert Lewis, and Ellen Dawson for their efforts in keeping the experiments under control; to H. W. Bond, Edward C. Wise, Dorothy Thompson, and R. J. Prosen, who prepared most of the solutions used in this research.

IV. Concentration of ^{41}K

By John Keenan Taylor and Vernon H. Dibeler

1. Method and Apparatus

A slight Modification of the apparatus and method used in the separation of ^{39}K can be utilized for the concentration of ^{41}K. In this case a stationary boundary is set up at the anode side of the packing. In an arrangement of this type the more mobile ^{39}K ions migrate toward the cathode, whereas the ^{41}K ions accumulate in the anode compartment between the packing and the boundary.

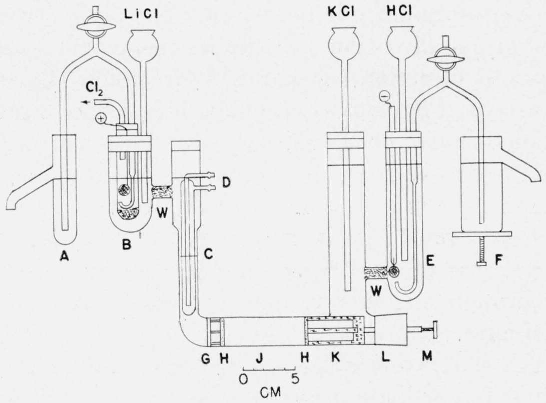

FIGURE 16.—*Cell for the concentration of* ^{41}K.

A, anode overflow; *B*, anode compartment; *C*, boundary; *D*, boundary temperature regulator; *E*, cathode compartment; *F*, reflux adjuster; *G, H, K*, packing supports; J, packing; *M*, screw device to apply pressure to packing; *W*, glass-wool plugs.

The cell is shown in figure 16. It is similar to that used in the concentration of ^{39}K, except that the cathode and anode are interchanged. The electrolytes were lithium chloride above the boundary and potassium chloride in the rest of the cell.

The cell was filled in the following manner. Potassium chloride solution that had been boiled to free it of gas was introduced while still warm until it stood at level *C* in both ends of the cell. Suitable rubber stoppers were placed in the openings, and the cell was evacuated with a water pump until no more bubbles of gas were evolved. The last traces of air were removed from the packing by pouring hot water over the cell. The vigorous boiling that took place at the reduced pressure effectively swept out remaining traces of trapped gas. The cell was then placed in a thermostated water bath, and lithium chloride and potassium chloride were introduced dropwise into their respective funnels. The former was made to seep through the glass-wool plug so that a fairly sharp density boundary resulted. This boundary became exceedingly sharp when the current was turned on.

A number of experiments were carried out with a 2.08 *N* potassium chloride solution containing 1 equivalent of salt to 25 moles of water (14.19% KCl). The lithium chloride solution used with the above solution was 1.22 *N* (5.03% LiCl). In later experiments a solution containing 1 equivalent of the potassium salt to 60 moles of water was used (0.90 *N*) with a lithium chloride solution of 0.55 *N* (2.31% LiCl).

Sodium chloride was tried in place of lithium chloride, but the boundary was difficult to observe because the refractive indices of the two solutions were so nearly identical.

The anode and the cathode compartments were continuously flushed with lithium chloride and potassium chloride solutions, respectively, of the above-mentioned concentrations to remove the products of electrolysis and maintain a constant composition of the solutions on both sides of the boundary. For a current of 0.5 amp, an addition rate of 100 g/hr was found to be adequate. It was also found advisable to add hydrochloric acid to the cathode at a rate sufficient to keep the electrode compartment neutral or slightly acid.

2. Results

(a) Single-Boundary Experiments

Four experiments were performed for the concentration of ^{41}K; the details are given in table 9.

TABLE 9.—*Specifications of cells used in concentration of* ^{41}K

Experiment No.	Concentration of electrolyte (equivalent of KCl per mole of H_2O)	Cathode volume	Current	Length of run	Minimum ratio $^{39}K/^{41}K$
		ml	*amp*	*hr*	
162	1:25	17	0.50	193	13.0
172	1:25	17	.50	1,061	10.9
177	1:60	8	.25	574	9.1
183	1:25	13	.40	338	12.1

Samples for mass spectrometric analysis were taken at approximately 50-hour intervals in the following manner. A thin-walled capillary tube was carefully inserted below the boundary, and the required amount of solution (about 0.2 ml) was withdrawn. The mass spectromatic technic and apparatus are described in section VI.

The treatment of the experimental data is similar to that used in section III. From the observed values of the abundance ratio $^{39}K/^{41}K$ and the constants of the cells, values of q/i were calculated and are plotted in figure 17. The irregularities of the curves are mainly due to mechanical difficulties, such as power failures, clogging of glass-wool plugs, loosening of the packing, etc. These produce disturbances that may result in the remixing of the isotopes. The maximum value for the slope is the one to be used in the calculation of ϵ for the separation process. The initial slope in experiment 183 gives, for the ratio of the mobilities, $\epsilon=1.0039$, a value in substantial agreement with that found previously for ^{39}K (sections II and III).

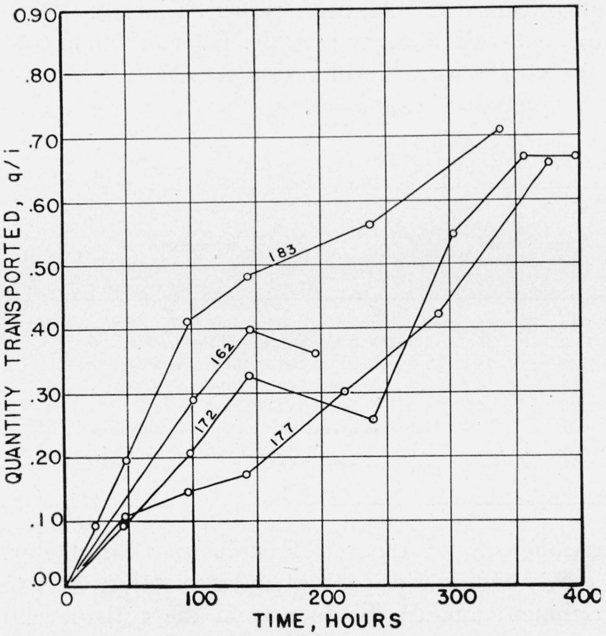

FIGURE 17.—*Performance of cells used to concentrate* ^{41}K.

(b) Double-Boundary Experiment

It is possible to construct a cell with both an anode and cathode boundary so that the simultaneous concentration of ^{39}K and ^{41}K is accomplished. Such a cell was set up, in which the anode boundary consisted of lithium chloride above potassium chloride, whereas the cathode boundary was composed of hydrochloric acid above potassium chloride. The potassium chloride was thus confined in the middle of the cell. It is evident that the concentrations of the solutions must be accurately adjusted to the theoretical values if both boundaries are to remain stationary. This was not attained, and the experiment had to be discontinued after 160 hours as the cathode boundary rose slowly while the anode boundary was held in a fixed position. Nevertheless, mass spectrometric analysis of the samples taken during the life of the experiment showed that the predicted isotope concentration changes took place. These values are plotted in figure 18. The method is thus practical and should prove useful for further isotopic concentration of small amounts of enriched potassium salts.

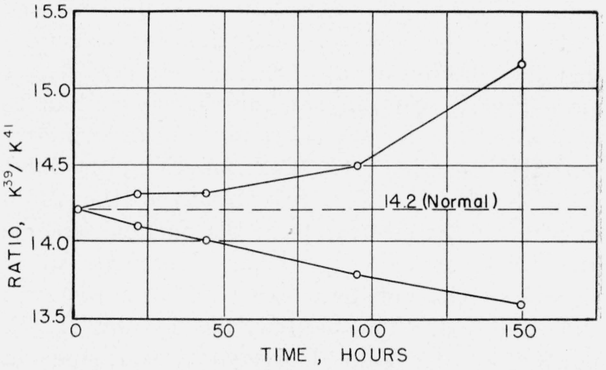

FIGURE 18.—*Performance of cell used to concentrate* ^{39}K *and* ^{41}K.

V. Distribution of ^{39}K in Packing

By John Keenan Taylor and A. Keith Brewer

1. Method

In section I it is pointed out that an ideal column packed with 100-mesh granuals could be expected to give up to 200 theoretical units per centimeter when operating at equilibrium under total reflux, and the various factors which affect the height of theoretical unit are discussed. A mathematical analysis of the problem is presented in RP1766 [10].

In practice, it is possible to determine the height of theoretical units of a reflux column from a knowledge of the distribution of the enriched material in the packing. A method for measuring this distribution is described in section II. A more precise sampling technic, however, had to be worked out for the short packing experiments reported in section III. Two sampling procedures were developed. The first involved the rapid freezing of the electrolyte in the packing with as little disturbance as possible. The material in various portions of the packing was then removed and analysed. The second, devised by R. G. VanName, of Yale University, consisted in placing rubber tips at various positions along the barrel of the tube, which could be punctured by a hypodermic needle.

In the first method the electrolyte of the cell was frozen by placing the vessel in a bath of dry ice and acetone. After the electrolyte had solidified, the glass envelop surrounding the packing was broken away to expose the packing as a solid plug. This plug was then sawed into thin disks with a clean hacksaw blade. The thickness of each disk, as well as the distance from its center to the cathode end of the packing, was measured as accurately as possible.

It is necessary to minimize flow of electrolyte from the cathode to the anode compartments during the freezing procedure. The method adopted was as follows: All clamps holding the apparatus in the bath were loosened while the electrolysis was still in progress. At the moment the current was shut off, a pipette was inserted in the cathode compartment, and the liquid level was adjusted as closely as possible to that in the anode compartment. The cell was immediately removed from the bath and placed in the freezing mixture. Some disturbance of the electrolyte in the packing undoubtedly took place during this process.

2. Results

Distribution studies were made on a number of the experiments described in section III. The pertinent data for the various cells are given in table 10. The free space for the packing material was computed by using 38 percent voids for the glass beads and 34 percent for the sand. Data for two cells designed by R. G. VanName, and operated under his direction at the Bureau are also included in table 10.

TABLE 10.—*Characteristics of the electrolysis cells*

Experiment No.	Packing				Current		Time	Cathode volume	Free volume of packing	Remarks
	Material	Mesh	Diameter	Length						
			cm	*cm*	*amp*	*v*	*hr*	*ml*	*ml*	
121	Glass beads	100 to 140	2.5	5	0.60	30	1320	15	9.9	800 hours past equilibrium value.
164	do	100 to 140	2.5	5	.50	34	748	15	9.9	200 hours past equilibrium value.
170	do	100 to 140	1.4	7	.50	93	713	10	3.9	300 hours past equilibrium value.
181	Sand	60 to 100	1.4	8	.50	90	332	5	4.2	100 hours past equilibrium value.
184	do	100 to 140	2.5	8	.50	80	874	20	14.1	150 hours past equilibrium value.
I (VanName)	do	80 to 100	3.75	18	.90	100	101	15	67.7	VanName equilibrium value not attained.
II (VanName)	do	100 to 140	3.75	16	1.00	105	100.5	14	60.1	Do.

The results obtained are summarized in table 11. The first column gives the distance, *d*, from the center of the packing slice to the cathode end of the packing; the second column gives the isotope abundance ratio, and the third column gives the number, *n*, of theoretical units per centimeter. This number was computed by plotting the enrichment against distance from the cathode end of the packing. A smooth curve was then drawn through the points, and the slope of the curve at various points was measured by graphically drawn tangents. From these slopes the equivalent enrichment per centimeter, S, was estimated. The number of theoretical plates per centimeter was computed by the equation $R_c/R_a=S=\epsilon^n$ (eq 8, section I), using $\epsilon=1.006$ for the separation coefficient. The values given in column four are the reciprocal of those in column three and represent values for the height of a theoretical unit for the various experiments.

TABLE 11.—*Efficiency of electrolysis cells*

d	$R={}^{39}K/{}^{41}K$	n (unit cells/cm)	Height of theoretical unit
EXPERIMENT 121			
cm			*cm*
0	18.6	63	0.016
.4	17.2	20	.050
1.3	15.9	11	.091
2.2	15.4	8	.125
3.1	14.7	6	.167
4.0	15.3	3	.333
4.9	14.2	0	
EXPERIMENT 164			
0	20.8	42	0.024
.4	19.4	29	.034
1.2	17.5	16	.063
2.0	17.1	11	.091
2.8	16.3	9	.111
3.6	15.0	9	.111
4.4	14.3	6	.167
EXPERIMENT 170			
0	18.9	34	0.029
.5	17.5	20	.050
1.5	16.0	11	.091
EXPERIMENT 181			
0.6	18.8	11	0.091
1.7	18.3	8	.125
2.8	17.2	6	.167
EXPERIMENT 184			
0	21.0	43	0.023
.5	19.6	12	.083
1.5	18.7	9	.111
2.5	18.3	8	.125
3.5	16.9	7	.143
4.5	16.2	6	.167
5.5	15.9	6	.167
6.5	15.0	5	.200
7.5	14.5	4	.250

TABLE 11.—*Efficiency of electrolysis cells*—Continued

d	$R={}^{39}K/{}^{41}K$	n (unit cells/cm)	Height of theoretical unit
EXPERIMENT I (VANNAME)			
			cm
0	16.7	14	0.071
2.9	15.16	2	.500
7.0	14.66	1	1.000
10.7	14.56	1	1.000
14.8	14.67	0	
EXPERIMENT II (VANNAME)			
0	16.63	9	0.111
2.5	15.28	4	.250
6.3	14.38	1	1.000
10.4	14.25	0	
14.5	14.2	0	

3. Discussion of Results

The data presented in table 11 show that the abundance ratio drops very rapidly with distance from the cathode end of the packing. In contrast, the gradient is small through the midportion of the packing and is negligible at the anode end. The height of theoretical unit computed from the abundance gradient increases rapidly from the cathode end of the packing. It is interesting to note that this is very low near the cathode, showing that a high value of n can be realized, as is pointed out in section I.

An exact interpretation of the data presented in table 11 should not be made at this time as it is probable that all the packings tested loosened slightly during operation. The steep gradient at the cathode end of the packing, and the negligible gradient at the anode reservoir end, are to be expected in a reflux column in initial stages of operation. If this were the case, the gradient adjacent to the cathode would be indicative of the equilibrium gradient to be expected across the entire packing. Thus experiment 184, for instance, would reach equilibrium when the abundance ratio in the cathode compartment was ${}^{39}K/{}^{41}K=112$. In reality, the cell failed to concentrate after reaching an abundance ratio of 21. This suggests that either the height of theoretical unit was not uniform through the packing or that the packing developed a defect when this ratio was reached. Without doubt, both conditions occurred. As the midportion of the packing has been shown to be materially hotter than the ends, the various controlling factors described in section I will tend to increase the height of theoretical unit in this region. This will account in part for the observed decrease in the number of theoretical plates per centimeter in the center of the packing, but it does not account for the absence of a gradient at the anode. The absence of an anode gradient, combined with the fact that the concentration in the cathode compartment increased linearly with time until a ratio of 21 was attained, when it suddenly ceased to increase, indicates that a packing defect developed at this stage in the operation.

In view of what has just been said, the results presented in tables 10 and 11 cannot be considered as defining the operation of an ideal packing. These data are important, however, in that they show conclusively that very small values for the height of theoretical unit are possible, and that the abundance concentration in the packing is in general analogous to that found in conventional reflux columns operating under total reflux.

The writers are particularly indebted to R. G. VanName for his interest in and contributions to this investigation, and to V. H. Dibler for constructing many of the cells used.

VI. Mass Spectrometric Analysis of Isotope Abundance Ratios

By Paul Bradt, O. Lee Parham, and A. Keith Brewer

1. Mass Spectrometer

The mass spectrometer used in measuring the isotope abundance ratios has been described previously [12]. A number of minor changes were made for the present work, the most conspicuous being the substitution of power packs for *B* batteries as a source of high potential. This, however, resulted in no improvement in the operation of the instrument.

The instrument, as modified, was of the 180-degrees type with a focusing radius of 3.6 cm. The side walls of the analyzing chamber were made of Swedish iron to serve as pole pieces. These were soldered into a brass block, as illustrated in figure 19.

The free space between the pole pieces was $\frac{3}{8}$ in. This space opened on three sides into a $\frac{3}{4}$-in. channel drilled in the brass block. The channel not only served as a well to prevent the reflection of ions, but facilitated evacuation. The faces of the pole pieces were chromium plated and burnished to minimize the formation of insulating deposits that might become charged and distort the resolved ion beams. The analyzing chamber was mounted between the pole pieces of a large electromagnet.

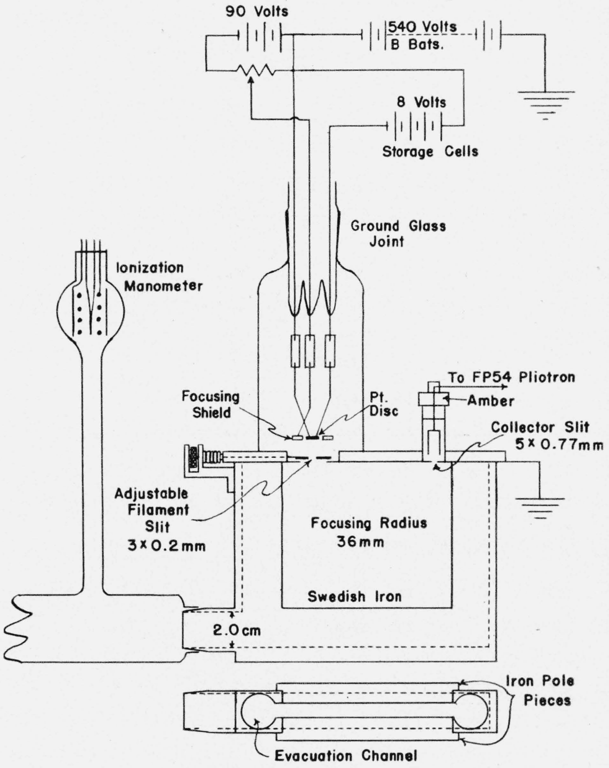

FIGURE 19.—*General outlay of the mass spectrometer.*

The resolved ion currents were measured with an FP54 Pliotron, using a balanced circuit hookup with a 4×10^{11} ohm grid shunt. Ion masses could be brought in by varying either the accelerating potential or the current energizing the electromagnet. The latter was used almost exclusively as positive-ion emission currents do not exhibit perfect saturation, hence it is preferable to keep the ion-acceleration potential constant.

2. Positive-ion Source

The ion source was of the thermionic type. The positive ions were emitted from a platinum disk impregnated with the sample. The disk, 2 mm in diameter, was spot-welded to a hairpin tungsten filament, and was mounted from 6 to 8 mm above the entrance slit to the analyzing chamber. Accelerating potentials from 500 to 600 volts were used.

In order to obtain precision results it was essential to bring the thermionic beam to focus on the entrance slit. This was accomplished by means of an electrostatic focusing shield in the form of a washer with the disk symmetrically located in the eye. In general, a positive potential on the washer of about 60 v with respect to the disk was required to bring the beam to a sharp focus on the filament slit. The slit was made movable to permit adjusting for maximum resolved ion currents. This position usually is identical to that for minimum background.

The platinum disk was prepared for impregnation by glowing at white heat in vacuum until all residual potassium was removed. Impregnation was accomplished by pasting a small quantity of a potassium containing material on the disk with distilled water and heating to redness for about 30 minutes. During the heating process the platinum absorbed sufficient potassium to serve as a positive-ion source. For high resolution, it is essential to remove all adhering deposits from the platinum by scraping it with a sharp knife. Salt or ash deposits on the platinum result not only in a nonuniform work function over the surface but become charged in operation, and consequently, introduce an appreciable background between the isotope peaks.

The positive-ion emission from impregnated sources always passes through a definite cycle with respect to time. The ion current at first increases with temperature until a fairly flat plateau is reached. Thereafter, the emissivity decreases, approaching zero when all the alkali is removed. Consecutive measurements of the heights of the isotope peaks taken when the emission is increasing slowly or when it has reached the plateau give the same abundance ratio. Measurements taken when the emission is decreasing usually give a ratio that is too low.

The mechanism resulting in a decrease in the abundance ratio when the source is near exhaustion has been discussed in a previous article [13]. In addition, it was pointed out that the emission of positive ions from impregnated sources can be expressed by an equation of the Richardson type having the form

$$N^+ = n(kT/2\pi m)^{1/2} e^{-e\phi/kT},$$

where N^+ is the number of K^+ ions escaping per unit surface at temperature T, n is the K atom density per unit volume at the surface, m is the atomic weight, and ϕ is the work function. The escape of positive ions at a given temperature is seen to be the product of two variable terms, the first, n, being a direct proportionality, and the second, ϕ, being a negative exponential. As positive ions on the surface behave as a positive grid to depress their own emissivity, it follows that the work necessary to remove an ion decreases rapidly with a decrease in n. Thus, the initial increase in emissivity can be explained as a result of a decrease in ϕ brought about by the concomitant decrease in n. When the surface in the final stages of exhaustion is largely denuded of potassium, ϕ will undergo little further change, and the emissivity will drop as n approaches zero.

3. Preparation of Samples

Although any potassium-containing material can be used to impregnate the platinum disks, crystalline salts like potassium chloride and potassium sulfate are difficult to use as the coatings are inclined to peel off during the initial heating. To overcome this difficulty, it has been found advantageous to convert such salts to phosphates.

As only 10^{-8} g of potassium is required for analysis, sample-taking becomes a problem of using a small quantity that can be handled conveniently. The smallest possible samples were preferred as the operation of the electromigration cells should be checked as nearly as possible under conditions of total reflux. The technic adopted was to remove a drop of solution from the cathode compartment and to place it in a 2-ml platinum crucible that had been boiled in nitric acid and washed in distilled water. A drop of dilute phosphoric acid and a little powdered quartz were added, and the mass was evaporated to dryness and heated to dull redness. The quartz, which had been boiled for 2 days in nitric acid, was used simply as a carrier for the potassium phosphate.

In preparing the sample for the mass spectrometer, a little quartz was scraped out of the crucible and placed on the platinum disk. The disk was then heated to dull redness in a vacuum, after which all the quartz and adhering phosphate were carefully removed. It was then spot-welded to the mass-spectrometer filament and placed in the instrument for analysis.

4. Potassium Isotope Abundance Ratio

The abundance ratio for the isotopes of potassium has been shown to be constant in nature, except where base exchange or perhaps certain vital processes have taken place. This ratio is $^{39}K/^{41}K=14.20 \pm 0.02$ [14]. As commercial salts all have the normal ratio, it was not necessary in the present experiments to check during the operations the solutions flowing through the anode compartment when ^{39}K was being concentrated or the cathode solution when ^{41}K was being concentrated. All isotope concentrations reported in the present paper represent a change in aboundance from the normal ratio of 14.20.

VII. An Automatic Reflux Control

By Roy J. Britten and J. Gilman Reid, Jr.

1. Introduction

In the electromigration method of isotope separation, conditions of reflux balance must be maintained over long periods of time. Manual control of operating conditions proved satisfactory when the cell was kept under continual observation. A virtually self-regulating system was controlled by the pH of the cathode solution. This provided greater convenience and reliability, and, in addition, reduced the amplitude of cyclic departures from conditions of exact reflux balance.

In potassium cells, the pH of the cathode solution was found to be a sensitive and reliable criterion of reflux balance. The rate at which restituent acid was added to the cathode volume proved an effective means of controlling the reflux rate. Here the pH was indicated by the emf of a hydrogen electrode against a lead-sulfate or silver-chloride reference electrode. This emf operated through a d-c amplifier to actuate an electric valve in the acid supply line.

The cathode compartment of a small K_2SO_4 separation cell with associated control elements is shown in figure 20. The hydrogen electrode and the lead-sulfate electrode were located side by side in a relatively field-free region above the cathode. Nascent hydrogen evolved in the cathode reaction saturated the hydrogen electrode. The feed line for the restituent acid (H_2SO_4, 1:30) entered the cathode solution and was curved to point up at the hydrogen electrode. The valve in the acid line, was attached to a Mariotte supply bottle and was held open or closed under control of the electric relay in the amplifier output circuit. Polarity of connections was such that an increase in cathode pH above a chosen reference value caused the valve to open and feed more restituent acid.

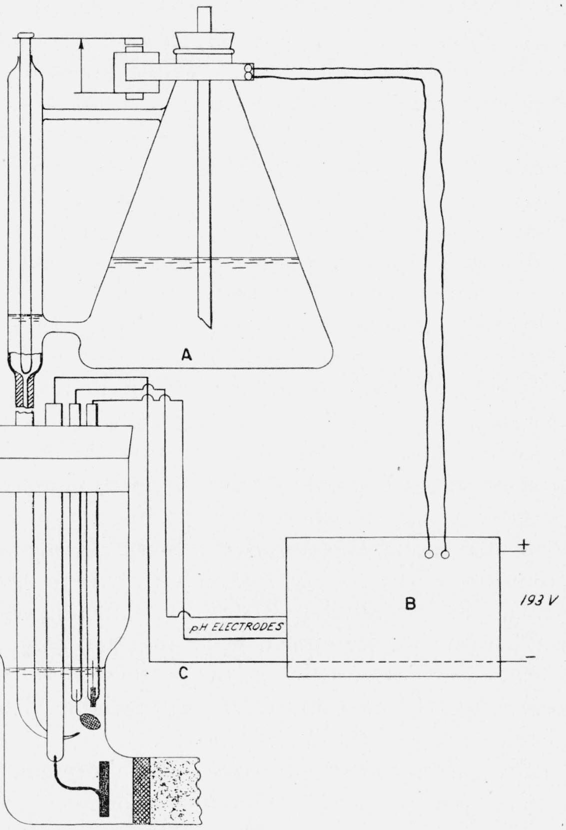

Figure 20.—*Cathode compartment and control equipment.*

A, Restituent acid; *B*, amplifier; *C*, cathode.

2. Control Electrodes

The reversible hydrogen electrode consisted of a 1-cm disk of platinized platinum gauze. This was located directly above the cathode of the cell so as to receive a plentiful supply of nascent hydrogen.

The reference electrode of lead-lead sulfate was a projecting length, about 0.3 cm^2 in surface area, of a pure lead wire waxed into the end of a protective glass sleeve. Previously, the wire had been anodized for about 15 minutes in a dilute sulfuric acid solution at a current density of 0.1 amp/cm,^{2}, and with several subsequent polarity reversals. Electrodes of this type were used in sulfate solutions.

In chloride solutions, the reference electrode was of silver-silver chloride with a built-in salt bridge. This electrode was housed in a 4-mm Pyrex tube with a porous frit sealed in one end. The tube was filled for several centimeters above the frit with an agar gel saturated with KCl. A silver wire with a drop of AgCl cast on its end was immersed in the gel. The open end of the tube was sealed with wax around the silver wire.

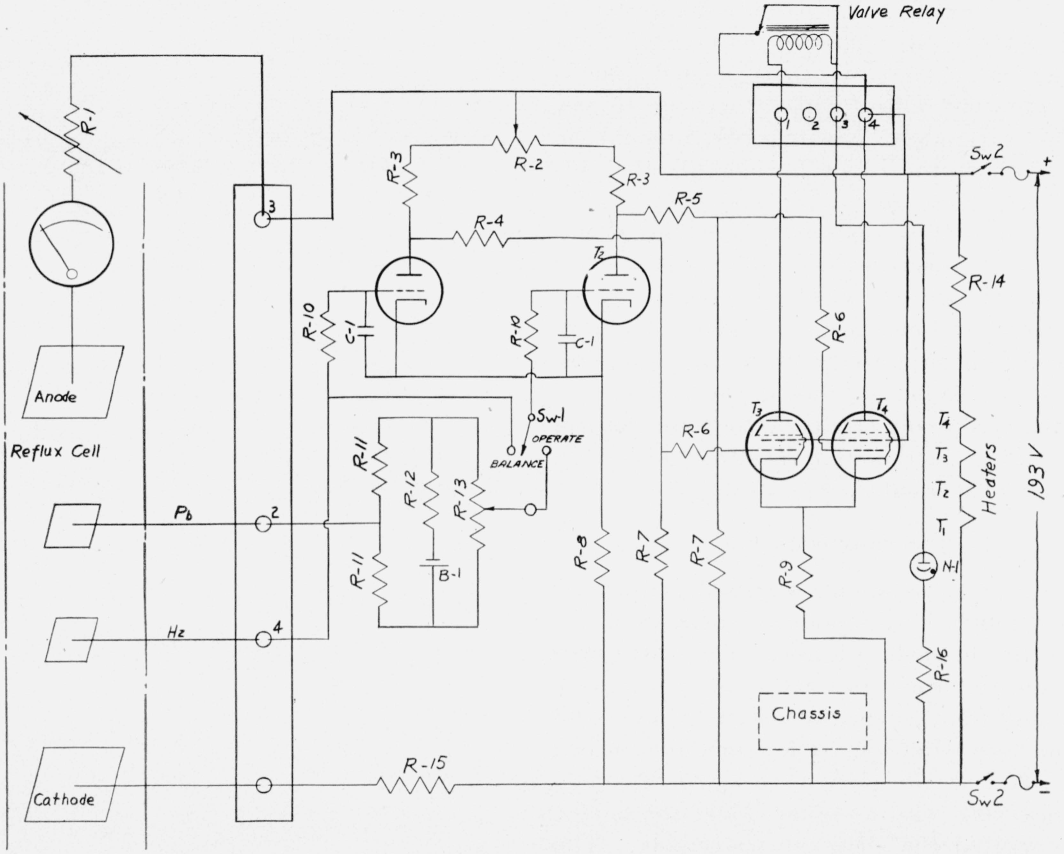

FIGURE 21.—*Amplifier.*

R-1, 2,000 ohm power rheostat (external to amplifier); *R*-2, 50,000 ohm potentiometer, *R*-3, 200,000 ohm resistor; *R*-4, 150,000 ohm resistor, *R*-5, 100,000 ohm resistor; *R*-6, 25,000 ohm resistor; *R*-7 1 megohm resistor; *R*-8, 35,000 ohm resistor; *R*-9, 2,000 ohm resistor, 10 watt, wire wound; *R*-10, 100,000 ohm resistor; *R*-11, 50,000 ohm resistor; *R*-12, 20,000 ohm resistor; *R*-13, 10,000 ohm potentiometer wire wound; *R*-14, 500 ohm resistor, 100 watt, wire wound, adjustable (adjusted to 440 ohms). *R*-15, 75 ohm resistor, 25 watt, wire wound, adjustable. (Adjusted for 20 to 25 volt drop at operating current of cell); *R*-16, 100,000 ohm resistor; all resistors ½ watt carbon, except where otherwise specified; *C*-1, 0.05 mf. Paper capacitor; *R*-1, neon lamp, 1/25 watt; *T*-1 and *T*-2, vacuum tubes 6SF5; *T*-3 and *T*-4, vacuum tubes 25L6.

The hydrogen electrode against either reference electrode developed a change in emf of about 60 mv per unit of pH. The electrodes operated without polarization into the 10-megohm input circuit of the amplifier. Random drift was a few millivolts and corresponded in all cases to an instability of less than 0.1 pH. Neither the hydrogen electrode nor the lead-sulfate electrode showed any deterioration during extended operation. Although the silver-chloride electrode was expected to be subject to deterioration due to the leaching of KCl from the gel, no such difficulty was encountered.

3. Amplifier

The amplifier is shown schematically in figure 21. It consisted of an input stage with 6SF5 triodes (T_1 and T_2) and a power stage with 25L6 beam tetrodes (T_3 and T_4). In each stage, reversed phase coupling of the two tubes was developed by the high resistance (R_8, R_9) in their common cathode circuit. The amplifier responded to potential variations between the two input grids but was only slightly affected by variations in their common potential relative to ground. The resistance offered by the input grids was about 10 megohms. The grid-circuit filters (R_{10}, C_1) provided a bypass of transient and alternating potentials picked up by the leads and electrode which could not easily be shielded.

The output load was the coil of a relay that actuated the acid valve. This was in the plate circuit of T_3. Between this point and the input grids the amplifier has a transconductance of 150 ma/v. Amplitude response was linear over an input range of 250 mv. R_{13} permitted application to the input emf of a positive or negative bias adjustable up to 250 mv. R_2 provided adjustment of quiescent output current between 15 and 35 ma approximately. Switch SW–1 could be thrown to short the input for making this adjustment.

The amplifier was operated from the power supply for the separation cell. This was a 180-v stack of heavy lead cells which were floated on the 220-v d-c line at a charge rate of about 0.2 amp. This gave a source of about 193 v with good stability. Alternatively it should be possible to operate the system directly on a 220-v line having good stability. In this case R–14 should have a value of about 550 ohms.

4. Acid Supply System

The acid supply system comprised a reservoir that fed through a ball-and-cone valve to an injector in the cathode volume. The valve was actuated by the armature motion of an ordinary electric relay from which the electric contact elements had been removed. The assembly is shown in figure 20.

The reservoir was a 4-liter Mariotte bottle, which supported the glass-valve assembly. The valve stem was a 32-cm length of 3-mm rod ground round at its lower end and with a head at its upper end for support by the lifting arm. The conical valve seat was ground in a length of heavy-walled capillary tube which was sealed into the lower end of the valve housing. The length of capillary tubing was adjusted to limit the acid flow to the desired maximum. The injector was a length of 5-mm tube curved and drawn into a nozzle at the discharge end.

The valve assembly is shown in greater detail in figure 22. The relay coil had a resistance of 850 ohms for normal actuation at about 20 ma. The relay was supported by a brass clamping strap from the neck of the Mariotte bottle. The lifting arm was a light brass strip, 15 mm wide and creased lengthwise for stiffness. It was attached with screws to the relay armature and projected 8 cm beyond the pivot axis. A notch in the open end engaged the valve rod just below its head. Two 4–40 machine screws threaded through the armature served as adjustable stops on closure.

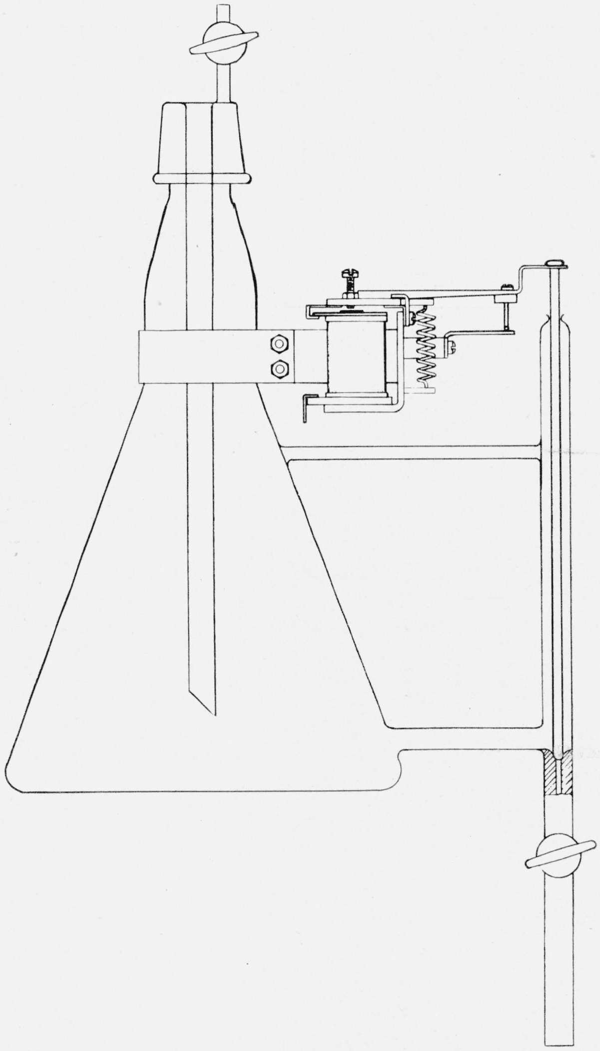

Figure 22.—*Acid bottle and valve.*

Mechanical adjustment of the relay was not critical. In a typical case, the stops for open and close position were set so that the relay closed to a 2-mm air gap at 30-ma current and opened to a 3-mm air gap at 25-ma current. The valve rod was lifted about 3 mm when the relay was energized. This adjustment maintained itself for an operation period of over 800 hours. The 5-ma difference in relay currents corresponded to 30 mv at the amplifier input. As the total instability of amplifier and pH electrodes was equivalent to less than ±10 mv at the input, the quiescent relay current could be set at 25 ma with no risk of actuation from a random surge.

Contacts consisting of short lengths of brass wire were attached to the valve lift arm and to the relay frame so as to close when the valve arm lifted. These were connected to a small neon lamp that served as an indicator of valve position.

5. Cathode Compartment

The character of the regulation was critically influenced by the shape of the cathode compartment and the placement of the cathode, of the pH electrode, and of the injector, as well as the rate of acid injection. The time required for the injected acid to mix completely through the cathode solution was determined by the compartment shape, the placement of the cathode, and the rate of hydrogen evolution through its mixing action. The dominant factor in establishing the period of the control cycle was the time interval between the opening of the valve and the contact of the injected volume of concentrated acid with the hydrogen electrode. This interval depended on the acid release rate and a placement of the injector relative to the hydrogen electrode.

During the part of the operating cycle when acid was not being added, the pH of the cathode solution continually increased as hydrogen was evolved in the cathode reaction. The emf from the pH electrode and the output current of the amplifier consequently increased. At the predetermined current level, the valve opened and then remained open until the concentrated acid circulated into the contact with the hydrogen electrode. During the ensuing interval, in which the hydrogen electrode was recovering from the contact of concentrated acid, the valve remained closed and the injected pulse of concentrated acid was thoroughly mixed through the solution. Upon recovery, the potential of the hydrogen electrode again represented the average pH of the cathode compartment, and the cycle was repeated.

In a typical case, the period of the operating cycle was maintained with stability at 10 seconds. Acid injection was at about three times the required average rate for approximately one-third of the cycle. The time required for thorough admixing of the injected acid was about 5 seconds. The emf of the hydrogen electrode indicated a total pH swing of from four to five units during the cycle.

The tip of the acid injector was located about 3 mm from the hydrogen electrode and was aimed directly at it from below. A closer placement of the injector reduced the period of the cycle, but this offered no particular advantage and decreased the stability of operation.

6. Adjustment Procedure

Initial adjustment of the self-regulating cell was made in the following manner: The current and the rate of addition of the restituent solution to the anode compartment were adjusted to the proper values. The control amplifier, which had meanwhile warmed up (with switch *SW*–1 thrown to short the input grids, was adjusted for a current output slightly below that for valve closure. Then, with *SW*–1 thrown to the operating position, a small quantity of a selected chemical indicator was added to the cathode solution and the potentiometer *R*–13 adjusted to open the valve coincidently with the indicator color change. Where necessary, acid was manually added to the cathode solution for bringing its pH into the chosen operating range. After the control cycle of operation had been established, *R*–13 was readjusted for more precise agreement of relay actuation and indicator color change. The neon lamp, *N*–1, was a pilot for valve operation and permitted easy observation of the cycle adjustment.

7. Results

Several potassium sulfate and potassium chloride cells were maintained in self-regulated operation for periods of, in some cases, more than 800 hours. Representative experiments are included in table 8. The automatic control was of principal value in making the operation of cells more convenient and reliable by eliminating their need for continual attention. From available data the separation efficiency of a cell was in no case impaired upon its conversion to self-regulation.

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