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Concentration of Potassium³⁹ by Countercurrent Electromigration: Some Theoretical Aspects of the Operation¹

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Equations are derived which describe the operations (A), for the early stages of the run, (B), after infinite time with no production, and (C), after infinite time at fixed production. The formulas under (A) enable evaluation of the elementary separation coefficient, ϵ . Those under (B) enable calculation of the maximum separation in terms of various channeling factors which determine the length of theoretical unit cell, h . The formulas under (C) enable calculation of optimum production conditions. When measured by the smallness of h , the analysis depicts the fractionator as one which is about 100 times more powerful than a modern laboratory distillation column.

I. Introduction

A mathematical analysis of various factors pertinent to the operation of countercurrent electrolysis [1, 2]³ in capillary tubes, packings, and sheets is presented. Special emphasis is given to the adverse effects of channeling. Although the discussion is applied to the specific problem of concentrating ³⁹K, it is applicable to open and packed reflux columns in general merely by changing the definition of terms.

The factors involved in the analysis are (1) The separation coefficient. This is defined as the ratio of the mobilities or velocities of the ³⁹K and ⁴¹K isotopes, $\epsilon = v_1/v_2$. The actual mechanism giving rise to a difference in mobility is not involved in the discussion. (2) The length of column, h , required to give a separation of ϵ . In the discussion the term h takes the place of the conventional height of elemental theoretical plate or height of theoretical unit. The various experimental conditions limiting h are considered individually. (3) Factors for continuous production. Calculations based on (1) and (2) are given

for the most efficient length of tube, the holdup, and the yield in grams per kilowatt hour, when the product is ³⁹K/⁴¹K=21.3.

1. Symbols and abbreviations

- A = cross-sectional area of packing, cm²
- a = lateral spacing between a velocity crest and a velocity trough, cm
- c_1, c_2 = concentrations of ³⁹K, and ⁴¹K, moles/cm³
- C = normality, moles/liter
- D, D_1, D_2 = isotropic, lateral and longitudinal coefficients of pure diffusion, cm²/sec
- D' = over-all or effective longitudinal coefficient of remixing by both pure diffusion and convection remixing, cm²/sec
- $\epsilon = v_1/v_2$ = elementary process separation factor
- F = Faraday constant = 96,500 coulombs/equivalent
- h = length of theoretical unit, as defined in text, cm
- η = viscosity of solution, poise
- I^+ = total current times positive-ion transference number, amperes
- l = length of packing or fractioning path, cm
- γ = equivalent conductivity of solution
- N_1, N_2 = mole fractional concentrations of ³⁹K and ⁴¹K

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³ Figures in brackets indicate the literature references at the end of this paper.

n = dimensionless exponent
 q = valence of positive ion = 1 for K
 r, r_0 = radial coordinate and radius of tube, cm
 $R = V_a/\Delta V_a$ = reflux ratio during production
 S_t, S_e = over-all separation factor at time t and at equilibrium
 t = time, sec
 v_1, v_2 = velocity of ^{39}K and ^{41}K relative to the solution, cm/sec
 V_a = mean countervelocity of solution for total reflux, cm/sec
 v = local point counter velocity of solution, cm/sec
 ΔV_a = mean departure from total reflux mean countervelocity, with reference to production, cm/sec
 Δv = local point departure from exact ion-velocity, solution-velocity balance under total reflux equilibrium, cm/sec
 V_c = cathode volume, cm^3
 x, w = thickness coordinate and semithickness between parallel walls, cm
 z = distance from anode face of packing, cm.

II. Significance of ϵ

In an electrolytic cell of the type discussed in RP1765 [2], the transport mole/cm²/sec of the light ^{39}K isotope due to the electric current before the liquid counterflow is superimposed is

$$\frac{c_1 v_1}{c_1 v_1 + c_2 v_2} \frac{I^+}{qFA},$$

in which c_1 and c_2 are mole concentrations of ^{39}K and ^{41}K per milliliter at time t ; v_1 and v_2 are their velocities; I^+ is the positive-ion current equal to the total current times the cation transference number; $F=96,500$ is the Faraday constant; A is the effective cross-sectional area; and q is the valence of the positive ion, being unity for K^+ .

When liquid counterflow is superimposed at a rate intermediate between the velocities of the ^{39}K and ^{41}K , these are transported in opposite directions and an isotope concentration gradient builds up. This gradient begins adjacent to the cathode and works its way to the anode, finally reaching an equilibrium value. When this equilibrium is reached, the stream flow plus the back diffusion and convection remixing just balances the ^{39}K ion current. If the potential is then removed, the flow of ^{39}K in the anode direction is

$V_a c_1 + D'(dc_1/dz)_{t=\infty}$ moles per square centimeters a second, where V_a is the mean liquid velocity, D' is the over-all or effective coefficient of remixing by both diffusion and convection processes, and z refers to length along the tube.

When the average K ion is static against the moving stream, as is the case during perfect operation, and when equilibrium is reached for the entire tube, conditions in the system are expressed by

$$\frac{c_1 v_1}{c_1 v_1 + c_2 v_2} \frac{I^+}{qFA} = V_a c_1 + D'(dc_1/dz)_{t=\infty}, \quad (1)$$

where $(dc_1/dz)_{t=\infty}$ represents the maximum attainable gradient.

The liquid countervelocity, V_a , is so adjusted at the cathode end that the net forward transport of positive ions by the current is balanced by the backward transport of the stream, so that $I^+/(qFA) = V_a(c_1 + c_2)$. Hence there is no net positive-ion current after this adjustment. The small currents of ^{39}K and ^{41}K that cause the tube to build up a gradient are equal and opposite, and finally disappear when the equilibrium gradient is reached. Hence, under proper conditions, the entire current is carried by the negative ions throughout the run. V_a is maintained constant throughout the run and has the value

$$V_a = \frac{I^+}{qFA(c_1 + c_2)}. \quad (2)$$

Substituting eq 2 in eq 1 and collecting

$$\frac{I^+}{qFA} \frac{c_1 c_2 (v_1 - v_2)}{(c_1 + c_2)(c_1 v_1 + c_2 v_2)} = D'(dc_1/dz)_{t=\infty}. \quad (3)$$

As v_1 and v_2 are nearly equal, it is sufficiently accurate to write $(c_1 v_1 + c_2 v_2) = (c_1 + c_2)v_2$ and, also, to express isotope concentrations as mole fractions by $N_1 = c_1/(c_1 + c_2)$, $N_2 = c_2/(c_1 + c_2)$, and $dc_1 = (c_1 + c_2)dN_1$. With these relations, eq 3 becomes

$$\frac{I^+(v_1 - v_2)}{qFAD'(c_1 + c_2)v_2} dz = \frac{dN_1}{N_1 N_2}. \quad (4)$$

As $N_1 + N_2 = 1$, and hence $dN_1 = -dN_2$, it follows that

$$dN_1/N_1 N_2 = dN_1/N_1 - dN_2/N_2 = d \ln(N_1/N_2),$$

and the integration of eq 4 over the length, l , of the tube, assuming uniform salt concentration, gives

$$\frac{I^+(v_1-v_2)l}{qFAD'(c_1+c_2)v_2} = \ln \frac{(N_1/N_2)_{z=l}}{(N_1/N_2)_{z=0}} \quad (5)$$

This is the equilibrium equation for the tube and applies only after the gradient ceases to rise in any part of the tube.

The elementary process separation coefficient is defined as the ratio of the mobilities or velocities, of the light to the heavy-isotope ions, thus

$$\epsilon = v_1/v_2 \quad \text{or} \quad \epsilon - 1 = \frac{v_1 - v_2}{v_2}$$

The over-all equilibrium separation factor is defined as the ratio of the abundance ratio at the cathode to the abundance ratio at the anode, thus

$$S_e = \frac{(N_1/N_2)_{z=l}}{(N_1/N_2)_{z=0}} \quad (6)$$

As ϵ is close to unity, $\epsilon - 1$ can be replaced by $\ln \epsilon$. Equation 5 therefore can be written

$$\ln S_e = \frac{I^+(\epsilon - 1)l}{qFAD'(c_1+c_2)v_2} = \frac{I^+l \ln \epsilon}{qFAD'(c_1+c_2)v_2} \quad (7)$$

or

$$S_e = (\epsilon)^{l/h} \quad (8)$$

where h is the height of theoretical unit and equals $qFAD'(c_1+c_2)/I^+ = D'/V_a$, and l/h is the number of theoretical units contained in the length l .

All quantities are measurable in eq 7 and 8 with the exception of the over-all remixing coefficient D' ; this can be calculated under certain simplified experimental conditions, for example, those prevailing in a single vertical capillary tube. Equations 7 and 8 thus make it possible to calculate the maximum separation attainable.

At the beginning of the run there is no remixing as $dc_1/dz=0$, and the total transport of light isotope is concentrated in the cathode compartment. The initial transport, in moles of ^{39}K per second, from eq 3 is

$$\frac{I^+ N_1 N_2 (v_1 - v_2)}{qF v_2} = \frac{I^+ N_1 N_2 (\epsilon - 1)}{qF} \quad (9)$$

The initial rate of rise in concentration at the cathode is inversely proportional to the cathode volume. When ΔN_1 is the mole fraction gain in concentration of the light isotope in t seconds; V_c , the cathode volume; and C , the normality; the moles of light isotope accumulated is $V_c C \Delta N_1 10^{-3}$ moles ^{39}K . This is equal to the rate given by eq 9 times the time. Hence

$$V_c C \Delta N_1 10^{-3} = \frac{I^+ N_1 N_2 (\epsilon - 1) t}{qF}$$

or

$$\epsilon - 1 = \frac{V_c C q F \Delta N_1}{1000 I^+ t N_1 N_2} \quad (10)$$

As ΔN_1 is small compared to N_1 during initial operation,

$$\frac{\Delta N_1}{N_1 N_2} = \Delta \ln(N_1/N_2) = \ln(N_1/N_2)_t - \ln(N_1/N_2)_{t=0} = \ln S_t$$

Equation 10 now becomes

$$\epsilon - 1 = \frac{V_c C q F \ln S_t}{1000 I^+ t} \quad (11)$$

With eq 11 it is possible to calculate the ratio of mobilities from the initial slope of the curve of $\ln S_t$ plotted with respect to t . If S_t is near unity, it is sufficiently accurate to write $\ln S_t = S_t - 1$ and plot this with respect to t . Also N_1/N_2 may be plotted, but in this case the initial slope must be divided by (N_1/N_2) (mean) in making the calculation of ϵ .

Equation 10 or 11 applies regardless of whether the light isotope is rare or abundant. In cases involving the concentration of the heavy isotope, N_1 and N_2 are interchanged, and S_t is defined as $(N_2/N_1)_t / (N_2/N_1)_{t=0}$. The definition of ϵ then remains the same, namely, the ratio of the light to the heavy-ion mobilities.

III. Calculation of h

The factor h is defined for the present process as that segmental length of tube or cell that will boost the abundance ratio by a factor ϵ when the concentration gradient has built up to a steady state under "total reflux", i.e., cathode sampling rate is zero. It is important that h be kept small as the power requirement, holdup, and time to reach equilibrium are each proportional to it. This section discusses conditions under which a small h can be realized, as well as other conditions that will lead to a large h .

According to eq 2, 7, and 8, the length h is given by

$$h = D'/V_a \quad (12)$$

where D' is the over-all longitudinal remixing coefficient, and V_a is the mean liquid counter-

velocity that balances the mean drift velocity of the K ions. In all cases met in practice the effective coefficient D' is made up of both pure molecular back diffusion and convective remixing. The latter is due to convection of K resulting from the fact that the point liquid countervelocity is not in exact balance with the point ion velocity over the entire flow cross section, being higher than the ion velocity in one region and lower than the ion velocity in another. It is necessary to evaluate this latter remixing effect to arrive at a value for D' or h . As convective remixing depends not only on the longitudinal velocity of the K but is diminished by the cross diffusion between the counterflowing streams of K , it is necessary to analyze the steady state in terms of the profiles of longitudinal velocity and lateral diffusivity. This can be done rigorously only for cases involving geometrical symmetry, in a manner now to be discussed.

Consider a round tube that may be either a single narrow capillary or a much larger packed tube. Assume that the mean liquid countervelocity is held in exact balance with the mean ion velocity, notwithstanding that the center of the tube has a liquid velocity greater, and the periphery a liquid velocity less, than the ion velocity in these regions. Assume further that the profile of the velocity departure is symmetrical to the center of the tube. Then, for the point difference between liquid countervelocity, v , and ^{39}K ion velocity v_1

$$\Delta v = v_1 - v, \quad (13)$$

where the point velocity departure, Δv , is a symmetrical function of r .

Also, as there is a net balance of transport with respect to average values,

$$\bar{v}_1 \bar{c}_1 + \bar{v}_2 \bar{c}_2 = V_a (\bar{c}_1 + \bar{c}_2), \quad (14)$$

where \bar{v}_1 and \bar{v}_2 are the averaged point ^{41}K ion velocities and the c 's are the averaged point concentrations of the two isotopes.

As by definition, $\epsilon = v_1/v_2$, which is closely \bar{v}_1/\bar{v}_2 , and as $\epsilon - 1$ is quite small compared to unity, eq 14 may be written

$$\bar{v}_1 - V_a = V_a \bar{c}_2 (\epsilon - 1) / (\bar{c}_1 + \bar{c}_2). \quad (15)$$

Equations 13 and 15 will be returned to, it now being necessary to consider the differential and

integral equations that describe the steady state operation of the tube.

Let $\partial \bar{c}_1 / \partial z$ be the longitudinal concentration gradient finally established after very prolonged running, \bar{c}_1 being the average ^{39}K concentration over the cross section at level z . This gradient is also the gradient for each point in the cross section because the distribution curves for concentration along the wall, along the axis, or along an intermediate cylinder, are closely parallel in all cases to be considered.

Consider an element of volume at a point r, z . Due to such lack of equality as may exist between ion and liquid velocity, the ^{39}K is removed longitudinal from the element at a rate $(v_1 - v) \partial \bar{c}_1 / \partial z$ moles $\text{sec}^{-1} \text{cm}^{-3}$. But as point concentrations in the tube have reached a steady state, this removal must be exactly compensated by a lateral diffusion of ^{39}K into the element at a rate $(d/dr) (D_1 r dc_1/dr)$ moles $\text{sec}^{-1} \text{cm}^{-3}$, in which D_1 is the radial coefficient of diffusion. Hence the steady state requires

$$\frac{d(D_1 r dc_1/dr)}{r dr} = (v_1 - v) \partial \bar{c}_1 / \partial z. \quad (16)$$

A second equilibrium condition, assuming zero sampling rate at the cathode, is that the integrated transport of ^{39}K is zero. This is expressed by

$$\int_0^r [(v_1 - v)c_1 - D_2 \partial \bar{c}_1 / \partial z] 2\pi r dr = 0, \quad (17)$$

where $(v_1 - v)c_1$ is the moles/ cm^2/sec transported at the point r, z due to the velocity departure, and $D_2 \partial \bar{c}_1 / \partial z$ is the moles $\text{cm}^{-2} \text{sec}^{-1}$ diffusing back, D_2 being the longitudinal coefficient of pure diffusion.

Equations 16 and 17 can be combined after suitable transformation as follows: Integration of eq 16 gives

$$dc_1 = \partial \bar{c}_1 / \partial z \left[\int_0^r (v_1 - v) r dr \right] dr / D_1 r, \quad (18)$$

whereas integration of eq 17 by parts gives

$$\bar{c}_1 \int_0^r (v_1 - v) 2\pi r dr - \int_0^r \int_0^r (v_1 - v) 2\pi r dr dc_1 = \pi r_0^2 \bar{D}_2 \partial \bar{c}_1 / \partial z. \quad (19)$$

For dc_1 in eq 19 is substituted the expression given by eq 18, giving

$$\bar{c}_1 \int_0^r (v_1 - v) 2r dr = \left[2 \int_0^r \left[\int_0^r (v_1 - v) r dr \right] \frac{dr}{D_1 r + \bar{D}_2 r_0^2} \right] \partial \bar{c}_1 / \partial z. \quad (20)$$

But

$$\int_0^r v_1 2r dr = \bar{v}_1 r_0^2 \quad \text{and} \quad \int_0^r v 2r dr = V_a r^2.$$

Hence returning to eq 13 and 15, and combining these with eq 20,

$$\frac{\bar{c}_1 \bar{c}_2 V_a (\epsilon - 1) r_0^2}{\bar{c}_1 + \bar{c}_2} = \left[2 \int_0^r \left[\int_0^r (\Delta v) r dr \right] \frac{dr}{D_1 r + \bar{D}_2 r_0^2} \right] \partial \bar{c}_1 / \partial z. \quad (21)$$

Now let $dz = h$. Then by definition of h the corresponding longitudinal increase in the abundance ratio is by a factor ϵ , where

$$\epsilon = \frac{\bar{c}_1 + d\bar{c}_1}{\bar{c}_2 + d\bar{c}_2} = \bar{c}_1 / \bar{c}_2.$$

As $d\bar{c}_1 = -d\bar{c}_2$, and is small, this last expression can be written

$$\epsilon - 1 = \frac{(\bar{c}_1 + \bar{c}_2) d\bar{c}_1}{\bar{c}_1 \bar{c}_2},$$

and substitution in eq 21 gives

$$h = dz = \frac{2 \int_0^r \left[\int_0^r (\Delta v) r dr \right]^2 \frac{dr}{D_1 r + \bar{D}_2 r_0^2}}{V_a r_0^2} + D_2 / V_a. \quad (22)$$

Equation 22 is the general result sought. It enables the calculation of h for any round tube whether packed or open, provided Δv and D_1 are known symmetrical functions of the radial coordinate, r .

In a similar fashion it can be shown that h for a long, thin packing or film, contained between parallel walls, where flow is lengthwise and a uniform balance can be assumed breadthwise, is given by

$$h = \frac{\int_0^w \left[\int_0^x (\Delta v) dx \right]^2 \frac{dx}{D_1}}{V_a w} + \bar{D}_2 / V_a, \quad (22a)$$

where Δv is the symmetrical velocity departure as a function of the thickness coordinate, x , the origin of the latter being midway of the walls, and w is the semispacing. In general, the upper and lower limits of x should be chosen such that $dc_1/dx = 0$ at both limits.

Five special cases under eq 22 and two under eq 22a will now be considered in detail.

Case I. The Isothermal Capillary.—Consider a single narrow capillary tube and assume an inappreciable rise in axial temperature relative to the wall temperature. Then the ion velocity is uniform over the cross section so that $v_1 = \bar{v}_1$. But the liquid countervelocity is a symmetrical parabolic function of r , and this is true even if the flow is aided or impeded by electro-osmosis, as it is known that the latter type of flow also has a parabolic profile [3].

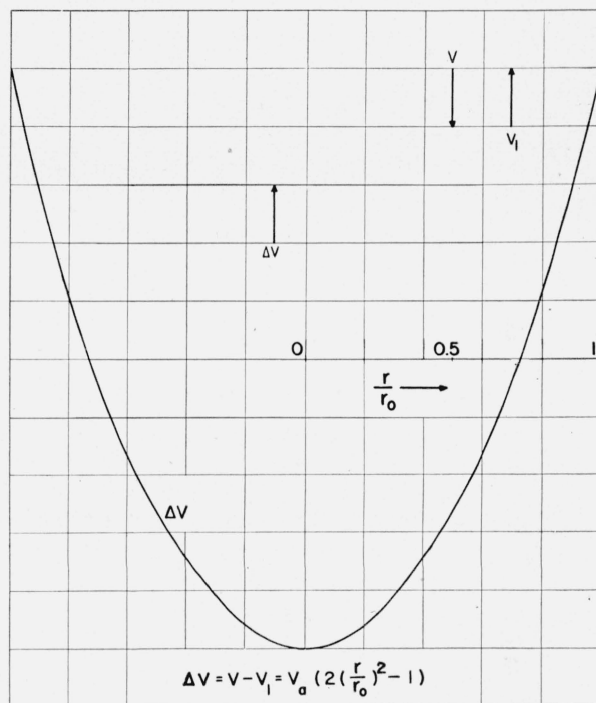


FIGURE 1.—Profile of isothermal capillary tube.

The profile of the velocity departure is illustrated in figure 1 and is given by

$$\Delta v = v_1 - v = v_1 - v = V_a [2(r/r_0)^2 - 1]. \quad (23)$$

This is to be substituted in eq 22. The profile of the radial diffusion coefficient D_1 is a horizontal line in this case, and hence D_1 may be brought outside the integral sign. The diffusion coefficient vertically will be the same as radially, and both will be designated D .

For the first operation indicated by eq 22,

$$\left[\int_0^r (\Delta v) r dr \right] = (V_a^2 r_0^4 / 4) [(r/r_0)^8 - 2(r/r_0)^6 + (r/r_0)^4].$$

The remaining integration with limits r_0 , and 0 leads to

$$h = (V_a r_0^2 / 2D) (1/8 - 1/3 + 1/4) + D/V_a = (1/48) V_a r_0^2 / D + D/V_a \quad (24)$$

From this result it is seen that the minimum value of h is $r_0/2\sqrt{3}$, and that the liquid countervelocity to achieve this minimum is

$$V_a = (D/r_0) 4\sqrt{3}.$$

The values of h for a 1.0-mm inside diameter isothermal capillary for several voltage gradients lengthwise of the tube are listed in table 1. The temperature is assumed to be 18° C throughout, for which the mobility in 1.0 N KCl [6] is 0.000498 cm sec⁻¹ volt⁻¹. The value of D in KCl solution up to 1.0 N is close to 1.55×10^{-5} cm²/sec.

TABLE 1.—Height of theoretical unit of 1.0-mm inside diameter isothermal capillary at 18° C

Potential	V_a	$(1/48) V_a r_0^2 / D$	D/V_a	h
r/cm	cm/sec			cm
1.....	0.000498	0.00168	0.03110	0.0328
4.31.....	.00215	.00722	.00722	.0144 min.
10.....	.00498	.0168	.00311	.0199

In practice, because of I^2R heating, the assumed isothermal condition is not realized. If the capillary is set vertically with cathode feed at the top, and say a 40° C axial rise in temperature is permitted, it is possible to so select the inside diameter that thermal convection up the center and down along the walls will partially balance the excess and deficiency of the countervelocity. The resultant profile, illustrated in figure 2, is a closer approach to ideal point balance than figure 1. In consequence, h will be less than the values indicated in table 1. Calculations indicate that a vertical capillary under perfect control with an inside diameter of 0.7 mm, and a gradient of 15 v/cm, can yield an h of 0.002 cm, or 500 theoretical units per centimeter length.

If the capillary is set horizontally, the effect of heating results in a lateral convective mixing. This increases the value of D in the first term of eq 24. Hence the value of h will be somewhat lower than indicated in table 1, provided the increased back diffusion represented by the term D/V_a is unimportant, as is the case for voltage gradients higher than about 10.

The foregoing calculations apply only to a single capillary tube. To be applicable to a bundle of tubes it would be necessary for the mean ion and liquid velocities to balance in each. The exactness of this individual tube balance will be realized when it is considered that maximum separation can occur in each tube only when the mean liquid velocity has a value lying between the velocities of the ³⁹K and ⁴¹K ions. As, for a given liquid head, the liquid velocity varies as the square of capillary bore, and as the two ions differ in veloc-

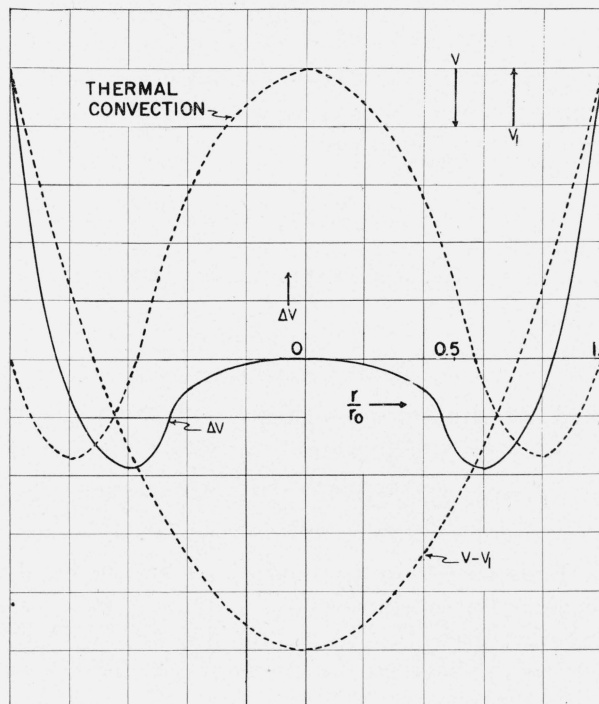


FIGURE 2.—Profile improved by thermal convection.

ity by only about 0.3 percent, a suitable bundle must consist of tubes with variations in bore of less than 0.2 percent. Such a requirement cannot be met by selection of ordinary glass tubing, although extruded tubes might have the required uniformity. However, a further requirement is that the tubes be at nearly the same temperature, and this is difficult to achieve as the solution has a negative temperature coefficient of resistance.

In contrast, if the above bundle is provided with numerous lateral communications between the tubes, the resulting cross diffusion will greatly compensate for lack of individual tube balance, and it becomes possible to achieve a reasonably low h . This action, though on a larger lateral

scale, is similar to the effect of radial diffusion in the single capillary, which partially compensates for the point lack of balance over the cross section and gave rise to the reasonably small first term in eq 24.

A tube packed with sand, beads, etc., is analogous to a capillary tube bundle having cross communication between passages. It will be clear, therefore, that isotope separation in other than an ideal packing is possible only because of cross diffusion. Various cases of nonideal packings will be treated hereinafter, but first it appears desirable to discuss the ideal, though as yet non-existent, packing in order to show the ultimate possibilities of this method of fractionation.

Case II. The Ideal Packing.—The perfect packing should have the properties of an ideal tube bundle. This requires that the pores be small and nearly identical in shape, cross-sectional size, and length. The ideal case must exclude the presence of a temperature gradient normal to the direction of liquid counterflow because fluidity of the solution increases with a somewhat greater temperature coefficient than does the mobility of the ions. This last consideration suggests that the ideal packing must be a face-cooled diaphragm.

In order to maintain maximum temperatures below 100° C, calculations indicate that the diaphragm should have a thickness not exceeding about 1 cm. Where one diaphragm is insufficient to give the desired separation factor, a series can be used with intermediate spaces for insertion of cooling elements.

A further requirement is that thermal convection across the thickness of the diaphragm must be eliminated. Consider a frit made from 50-mesh beads. With the faces vertical, a convection current will occur inwardly from both faces at the bottom, up the midsection, and outwardly toward both faces at the top. The convection at top and bottom will cause remixing. On the other hand, with the diaphragm horizontal, the upper half will comprise cool liquid overlying hot and the thermal instability will result in convection currents toward and away from the upper face. Calculations indicate that if thermal convections are to be reduced to negligible velocity the frit should be made from beads of about 200 mesh per inch or finer. This corresponds to a mean pore radius of 0.002 cm or less.

In summary, it appears that the ideal packing

should be a face cooled diaphragm of extremely uniform thickness and porosity with mean pore radius of less than 0.002 cm. For such a diaphragm the first term of eq 24, using for r_0 the mean pore radius, is negligible; hence, $h=D/V_a$, where D is the longitudinal diffusion coefficient of the free liquid and V_a the mean liquid counter-velocity in the pore. The following are the values of h under the ideal conditions assumed when V_a is taken as 0.00498 cm/sec, corresponding to a 1.0 N KCl solution and an applied gradient of 10 v/cm at 18° C:

Values of D at temperatures other than 18° C were estimated by assuming proportionality to absolute temperature times the fluidity of the water for that temperature [8].

At 18° C; $D=1.55 \times 10^{-5}$ cm²/sec; $h=0.0031$ cm.

At 40° C; $D=2.68 \times 10^{-5}$ cm²/sec; $h=0.0054$ cm.

At 80° C; $D=5.57 \times 10^{-5}$ cm²/sec; $h=0.0112$ cm.

The h at 18° C would apply to diaphragm regions close to either face. The h at 80° C would be encountered across the midplane of a frit having this maximum temperature. As the mobility increases toward the midplane, the voltage gradient across this plane will drop to a value such that the ion velocity and liquid counter-velocity are in balance.

Case III. Packed Tube With Uniform Porosity and Hot Core.—Assume first that the packing has a pore radius of about 0.002 cm or less, so that thermal convection is negligible. The value of h will be D/V_a at the cooled end faces of the packing just as in case II. At points remote from the ends, however, the ion velocity and liquid velocity are not in point balance over the cross section due to the fact that the temperature coefficient for fluidity is somewhat higher than for mobility. The bulk profile of the velocity departure will approximate the appearance shown in figure 3, and will be assumed to be parabolic, as given by the relation

$$\Delta v = \Delta v_m [2(r/r_0)^2 - 1], \quad (25)$$

where all velocities and diffusion coefficients are now to be considered as superficial. The superficial values are obtained by multiplying the mean pore values by the fraction voids.

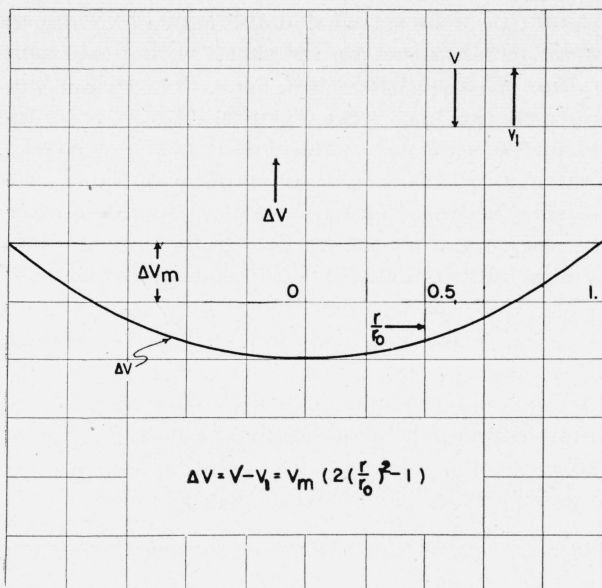


FIGURE 3.—Profile of packed tube, uniform porosity, hot core.

Equation 22 is applicable. A rigorous solution requires that the lateral diffusivity D_1 be expressed in terms of r , as D_1 increases with temperature and has its maximum value at the point of maximum temperature, $r=0$. It is sufficiently accurate for our purpose here to consider D_1 as having a uniform value based on the mean temperature between wall and axis. The result of the integration is then

$$h = (1/48) (\Delta v_m / V_a)^2 V_a r_0^2 / \bar{D}_1 + \bar{D}_2 / V_a, \quad (26)$$

where V_a is equal to the superficial mean ion velocity based on the mean temperature.

As eq 26 involves ratios of velocity to diffusivity, each of which is to be multiplied by the fraction voids to obtain superficial values, it is just as proper to use mean pore values. Further, as V_a is adjusted to balance the mean ion velocity, and as the latter is closely the same function of temperature as is the diffusivity, calculations can be based on KCl solution at 18° , for which, at 1.0 normal, $V_a = 0.000498 \text{ cm sec}^{-1} \text{ volt}^{-1}$, and $D_1 \cong \bar{D}_2 = 1.55 \times 10^{-5} \text{ cm}^2/\text{sec}$.

Consider a tube packed with 200-mesh sand and having an applied gradient of 10 v/cm. The maximum permissible temperature rise is assumed to be 80° C . For this rise, due to the fact that fluidity increases more rapidly with temperature than mobility, the ratio $\Delta v_m / V_a$ is calculated to be

0.10. Table 2 lists the values of h for various tube sizes.

TABLE 2.—Packed tube with uniform porosity, 80° C temperature (rise, 10 v/cm)

Inside diameter of tube	h
cm	cm
0.5	0.0073
1.0	.0198
2.0	.0701
4.0	.271
8.0	1.07

It should be emphasized here that the values in table 2 are for an extreme case, remote from the ends of the packing, and with no thermal convection. If the tube is set vertically, and instead of 200-mesh sand, a coarser packing of about 100 mesh is used, calculations indicate that thermal convection will largely overcome the lack of point balance indicated in figure 3. If a tube of 100-mesh sand is set horizontally, thermal convection will be sufficient to markedly increase the effective lateral diffusion coefficient, \bar{D}_1 . For these reasons it is possible to obtain lower values for h than are indicated by table 2. On the other hand, if the packing contains gas bubbles, the effective value of \bar{D}_1 is decreased; hence, h will be increased.

Case IV. Packed Tube With Wall Channeling.—Uniform porosity was assumed in case III. Actually, when a tube is packed with beads or sand, the porosity adjacent the wall, and for a width of about half a bead, is about 50 percent greater than elsewhere. This fact can usually be disregarded when the beads are very small and held under pressure. In the case of frits the higher porosity at the wall can be eliminated with suitable cement. It is of interest, however, to calculate the value of h for cases in which, due to failure of one kind or another, a wall channel makes its appearance.

Consider first a wall channel of uniform thickness over the entire circumference. A suitable function for Δv is

$$\Delta v = \Delta v_m - (\Delta v_w + \Delta v_m) (r/r_0)^{2n}, \quad (27)$$

where Δv_w is the maximum velocity departure near the wall. The parameter, n , determines the extent of the flat portion of the velocity profile and for large values of this parameter the profile

is flat over the major portion of the cross section, as illustrated in figure 4.

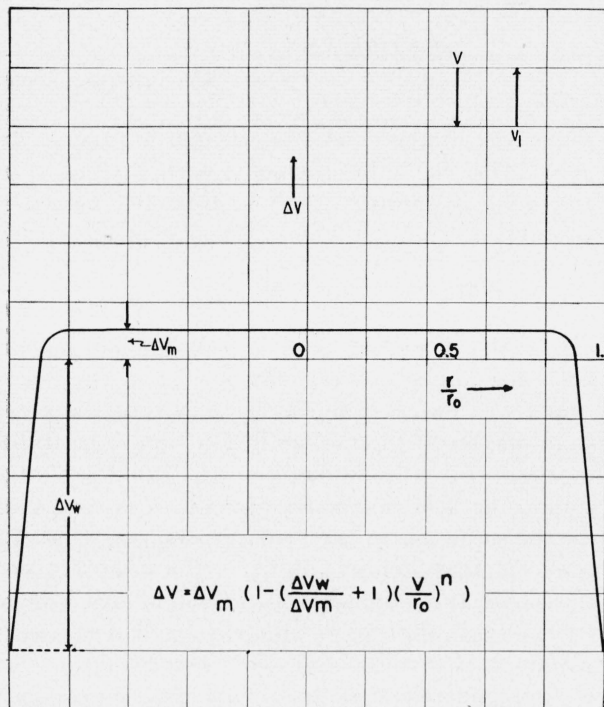


FIGURE 4.—Packed tube with symmetrical wall channeling.

Equation 27 must satisfy the condition for average balance,

$$\int_0^{r_0} (\Delta v) 2\pi r dr = 0,$$

from which it is found that

$$n = \Delta v_w / \Delta v_m.$$

From eq 22, neglecting the \bar{D}_2/V_a term, it is found that

$$h = (\Delta v_m^2 r_0^2 / 2 V_a \bar{D}_1) [1/4 - 1/(n+2) + 1/4(n+1)], \quad (28)$$

and for those cases in which the wall velocity departure is 10 or more times the departure in the packing, this becomes

$$h = 0.1 (\Delta v_m r_0 / V_a)^2 V_a / \bar{D}_1. \quad (29)$$

In terms of the channel thickness, d , this can be written

$$h = 0.1 (\Delta v_w d / V_a)^2 V_a / \bar{D}_1. \quad (29a)$$

It is seen from eq 29 that the values of h will be about five times those for case III for the same values of Δv_m , thus showing the adverse effect of abrupt as compared with gradual departure from point balance. A symmetrical wall channeling sufficient to cause a velocity departure in the packing of 10 percent will lead to a value of h of 0.12 cm for a 1.0-cm inside diameter tube operating with an applied voltage gradient of 10 v/cm.

From eq 29a it is seen that if the thickness of the wall channel is the same, the h for various tube sizes will remain the same. This is because the wall-velocity departure for a given head depends only on the channel thickness.

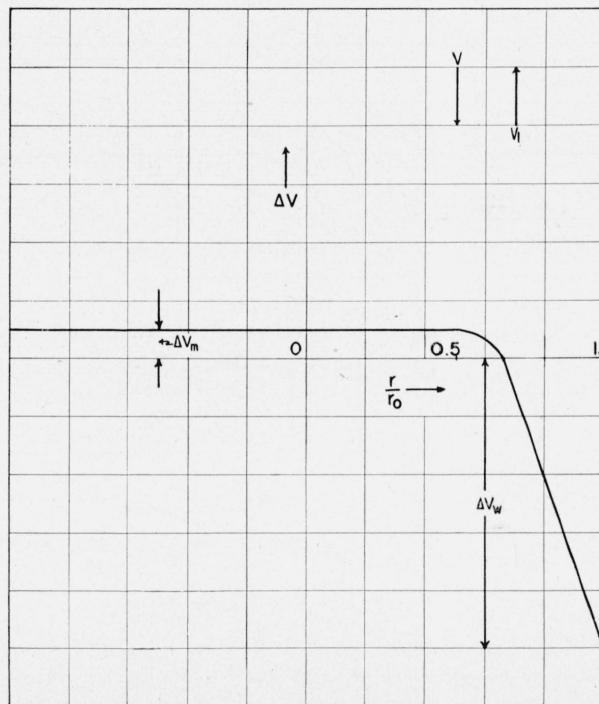


FIGURE 5.—Packed tube—unsymmetrical wall channeling.

Although a rigorous treatment cannot be given for cases involving unsymmetrical channeling, such as illustrated in figure 5, it can be stated that for the same Δv_m the value of h will be much higher than in the symmetrical case. Thus, in the general case, h varies as the square of the average diffusion distance between the channel and the interior of the packing and inversely as the lateral diffusion area between the channel and the packing. Hence, a wall channel due to a localized breakthrough may easily result in such

a large h that isotope separation for a 10-cm length of packing will be inappreciable.

Case V. Core Channeling.—Assume the formation of a single narrow round channel of radius r_1 and coaxial with the packed tube. The profile of the velocity departure will be parabolic in the channel and essentially uniform in the surrounding packing, as illustrated in figure 6. Hence

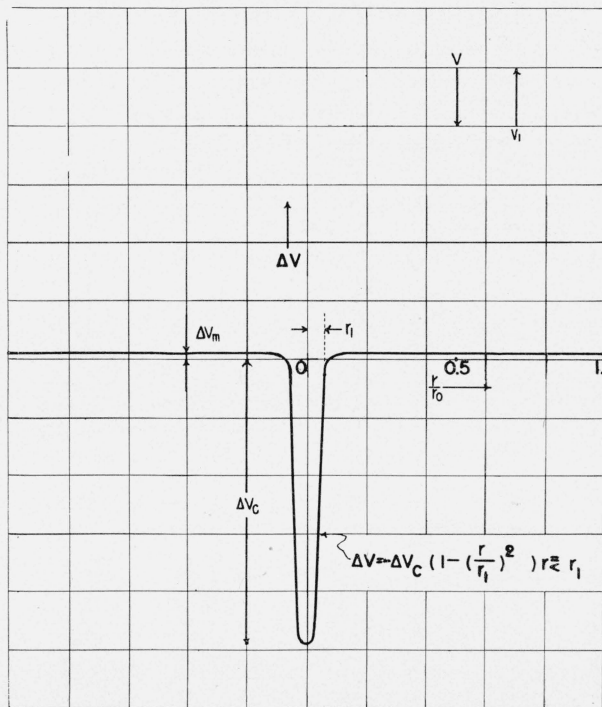


FIGURE 6.—Packed tube—symmetrical core channeling.

$$\Delta v = -\Delta v_c [1 - (r/r_1)^2], \quad 0 < r < r_1$$

and

$$\Delta v = \Delta v_m, \quad r_1 < r < r_0.$$

As an over-all balance is maintained,

$$\int_r^{r_0} (\Delta v) r dr = - \int_0^r (\Delta v) r dr,$$

and therefore eq 22, neglecting the \bar{D}_2/V_a term, and assuming uniform lateral diffusivity, can be put in the form

$$h = (2/\bar{D}_1 V_a r_0^2) \left\{ \int_{r_1}^{r_0} \left[- \int_r^{r_0} (\Delta v) r dr \right]^2 dr/r + \int_0^{r_1} \left[\int_0^r (\Delta v) r dr \right]^2 dr/r \right\}.$$

This is integrated after substitution of the above expressions for Δv , and the result is

$$h = (2/\bar{D}_1 V_a r_0^2) \left\{ (\Delta v_m^2 r_0^4/4) [\ln r_0/r_1 - 3/4 + (r_1/r_0)^2 - (r_1/r_0)^4/4] + (19/768) \Delta v_c^2 r_1^4 \right\}.$$

When the diameter of the channel is small compared with the tube diameter, such that $r_0 > 10r_1$ and $\Delta v_c r = 2\Delta v_m r_0^2$, this expression becomes, approximately,

$$h = 0.5 (\Delta v_m r_0 / V_a)^2 (V_a / \bar{D}_1) (\ln r_0 / r_1 - 0.7), \quad (30)$$

where the velocities and diffusivity are superficial and apply to the packing.

With a central hole having an inside diameter from one-tenth to one-hundredth that of the tube, $\ln r_0/r_1 - 0.7$ will lie between 1.6 and 3.9. On comparing this case with case IV, it is seen that for the same Δv_m in the packing, meaning that the total channel flow in milliliters per second is also the same, the h for axial core channeling is from 8 to 20 times that for symmetrical wall channeling. Although this result may seem surprising, it is to be remembered that the axial channel presents far less area to the packing through which the compensating effect of cross diffusion can occur.

From Poiseuille's law, the mean liquid velocity in the channel relative to the mean liquid velocity in the average pore within the packing is proportional to $(r_1/r_p)^2$, where r_p is the equivalent pore radius. Hence, for a bead packing with 38 per cent of void space,

$$\frac{V_a + \Delta v_c/2}{V_a/.38 - \Delta x_m} = (r_1/r_p)^2,$$

or, approximately,

$$\Delta v_c/2V_a = (\Delta v_m/V_a) (r_0/r_1)^2 = 2.63 (r_1/r_p)^2 - 1,$$

when $\Delta V_m/V_a < 0.1$.

The equivalent pore radius for a bead packing has been determined experimentally to be 0.165 × bead diameter [2].

Table 3 gives the values of h computed from eq 30 for a 2-cm inside diameter tube packed with beads of 100-mesh per inch, $r_p = 0.0042$ cm, assuming 1.0 KCl at 18° C and a voltage gradient of 10 v/cm. For these conditions, $V_a = 0.00498$ cm/sec and $\bar{D}_1 = 1.55 \times 10^{-5}$ cm²/sec.

TABLE 3.—Core channeling in 2-cm inside diameter tube, 100-mesh beads, 10 v/cm

Core channel radius Equivalent pore radius r_1/r_p	Core channel radius, r_1	h
cm	cm	cm
4	0.0168	0.068
6	.0252	1.6
8	.0336	15
10	.0420	92

Table 3 shows that when a single continuous core channel has reached a size about five times the mean pore size of the packing, the resultant h will be about 1.0 cm. In such a case isotope separation between ends of a 10-cm length of tube would be negligible. This result assumes, however, that the radial diffusion coefficient has the value indicated, this being the minimum value corresponding to molecular diffusion. Actually, when the tube is set horizontally, \bar{D}_1 will have a much larger effective value than assumed because of thermal convections in planes normal to the axis. Hence, the values of h in table 3 should be regarded as maximum. They show merely that very poor results can be due to a single relatively small core channel. It is for this reason that bead packings should be held under pressure.

Case VI. Face-Cooled Diaphragm, NonUniform Porosity.—The diaphragm of uniform porosity was considered under case II. When the diaphragm is not uniformly porous, various regions can be found in which the porosity is above or below a mean porosity. Two factors of equal importance determine the performance of the packing, the first being the magnitude of the velocity departure due to the porosity departure; the second is the lateral distance across the face of the diaphragm between a velocity crest and a velocity trough.

The general case does not permit a rigorous treatment. However, the order of magnitude of h can be gotten by assuming an equivalent diaphragm in which the regions of porosity departure are parallel, the mean velocity departure and the mean crest-trough spacing of the actual case and the equivalent case being the same.

The profile of the equivalent case is shown in figure 7 and is expressed analytically by

$$\Delta v = -\Delta v_m \cos(\pi x/a).$$

Equation 22a is applicable. As lateral diffusion vanishes at limits a and 0, as indicated in figure 5, the integration should be made between these limits. The result is

$$h = 0.0505 (\Delta v_m a / V_a)^2 V_a / \bar{D}_1 + \bar{D}_2 / V_a, \quad (31)$$

this being the h for each symmetrical pair of strips, and therefore the h for the entire diaphragm.

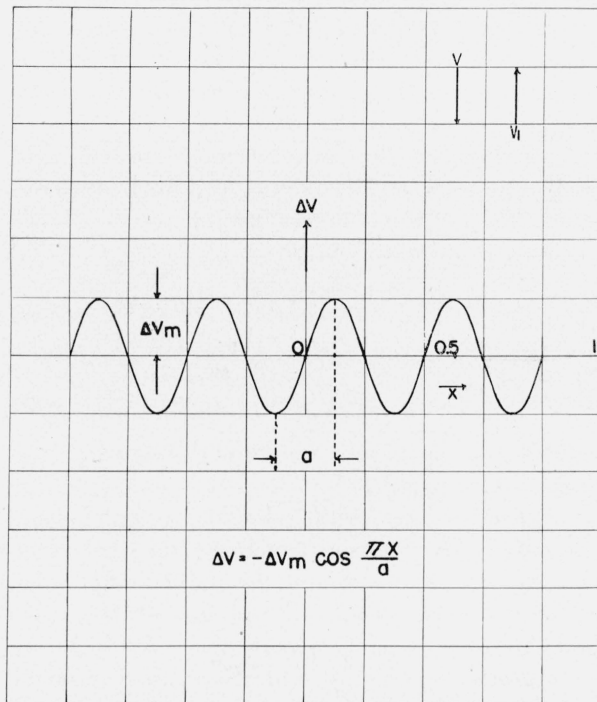


FIGURE 7.—Profile of a diaphragm with variable porosity.

From this result it is apparent that small values of h can be achieved only when the product, (velocity departure) times (crest-trough spacing), is small.

Consider two diaphragms wherein the velocity departures are 10 percent of V_a in one and 2 percent of V_a in the other. Assume a voltage gradient for each of 10 v/cm at 18° C, so that $V_a/\bar{D}_1 = 322$ and $\bar{D}_2/V_a = 0.0031$ for 1.0 N KCl solution. The resulting values of h are given in table 4 for various crest-trough spacings, a .

From the results in table 4 it can be seen that a nonideal diaphragm will enable appreciable isotope separation even though the centers of the regions of porosity departure are laterally a fraction of a centimeter apart, but, if several centimeters apart,

TABLE 4.—Diaphragms with variations in porosity, 10 v/cm

$\delta v_m/V_a$	a	h	$\delta v_m/V_a$	a	h
	cm	cm		cm	cm
0.10	0.5	0.044	0.02	0.5	0.0047
.10	1.0	.17	.02	1.0	.0096
.10	2.0	.65	.02	2.0	.029
-----	-----	-----	.02	4.0	.12
-----	-----	-----	.02	8.0	.48

only when the maximum velocity departure is less than about 2 percent of the countervelocity, V_a .

Case VII. Isothermal Capillary Film.—Consider the unobstructed passage formed between two elongated parallel walls that are closely spaced apart a distance $2w$, are extremely smooth, and strictly parallel. If temperature effects be neglected, the velocity departure in terms of the thickness coordinate will be

$$\Delta v = (V_a/2)[3(x/w)^2 - 1].$$

Equation 22a is applicable to this case and gives

$$h = (2/105)V_a w^2/D + D/V_a, \quad (32)$$

a result that is nearly identical to that for the capillary tube, case *I*.

In practice, the walls should be good heat conductors for external cooling, and the inner surfaces, at least, should be electrically non-conductive. The film will run hot at the mid-plane, but the fact that viscosity times conductance is not precisely constant will affect the numerical coefficient in equation 32 by only a few percent and can be disregarded. Calculations for h can be based on values of V_a and D at 18°C.

Thermal convection can be used to advantage to avoid a breadthwise velocity departure by arranging the walls so that length is horizontal and breadth vertical. A value of h calculated as in case *III* should be added to eq 32 when a breadthwise departure is present. The effective diffusion coefficient breadthwise can be found from eq 12 and 22a.

In a second arrangement the film can be confined by vertical concentric cylinders. In this case, one of the cylinders should be rotated to avoid circumferential variations in composition and temperature. By proper selection of spacing the profile would be analogous to figure 2, the theory permitting lower values of h than indicated by eq 32.

IV. Production Conditions

Economical production of enriched material depends primarily on the values of ϵ and h discussed in sections II and III of RP1765 [2]. The larger the ϵ and the smaller the h , the lesser will be the power requirement per unit rate of production. In general, the method is applicable, though not necessarily more economical than other methods, when ϵ exceeds unity by as little as 0.1 percent and when h is less than 0.1 cm. In the following discussion a specific example will be worked through for $\epsilon = 1.0030$ and $h = 0.020$ cm.

The simplest procedure for continuous production is to maintain constant anode composition by exchange with an unlimited supply of normal K. After a build-up period, material enriched in ^{39}K can then be very slowly bled from the cathode. Another procedure, analogous to continuous fractional distillation, is to feed normal material to a point intermediate to the ends and to withdraw from both anode and cathode compartments. In this case the apparatus provides a stripping section yielding material at the anode enriched in ^{41}K . The enriching section for ^{39}K may be treated as though an anode were located at the point of feed and is thus equivalent to the first procedure. The following treatment will be focused on the ^{39}K enrichment.

1. Build-up Period

In bringing the cathode to the desired enrichment, the procedure is to operate at zero sampling rate (total reflux) while maintaining at the cathode end an exact balance between counterflow of solution and K ion migration. Other factors remaining constant, it follows that the countervelocity must slightly increase as the enrichment increases; thus the maximum fractional increase in going from normal abundance to 100 percent ^{39}K would be $(\epsilon - 1)/15.2$, which is the difference between the mean ion velocity of normal K and the ion velocity of pure ^{39}K . This increase is well within the limits of the control and of no actual importance. However, assuming a uniform normality and a precise balance at the cathode, it follows that the countervelocity will be too high at the anode end by the same fraction. The result is a slight washing out of salt, the voltage gradient increasing slightly toward the anode, and the tube thus balances itself throughout. More important is

the tendency of increased temperature to increase ion speed and destroy the balance, but here also the balance throughout the tube is restored by a change in normality of salt and voltage gradient. Hence it is strictly correct to suppose an exact mean balance for all sections of the tube, but it is not correct to assume uniform normality of salt except when temperature effects at the ends of the tube may be neglected.

The velocity balance at any section requires $v_1c_1 + v_2c_2 = V_a(c_1 + c_2)$ or $v_1 - V_a = (v_1 - v_2)c_2/(c_1 + c_2)$. The net transport of light isotope across any section is $(v_1 - V_a)c_1 - D'\partial c_1/\partial z$ or $(v_1 - v_2)c_1c_2/(c_1 + c_2) - D'\partial c_1/\partial z$ mole $\text{cm}^{-2} \text{sec}^{-1}$. Each factor in the foregoing is an average for the cross section, distant z from the anode.

The exact differential equation governing the total reflux build-up of concentration as a function of time and distance, and applying to a tube having nonuniform temperatures lengthwise, is

$$\frac{\partial(D'\partial c_1/\partial z)}{\partial z^2} - \frac{\partial(v_1 - v_2)c_1c_2/(c_1 + c_2)}{\partial z} = \partial c_1/\partial t. \quad (33)$$

In a very long packed tube it would be permissible to neglect temperature nonuniformities at the ends. In this case the effective diffusivity, D' , the difference in the velocity of the ionic isotopes, $v_1 - v_2$, and total concentration, $c_1 + c_2$, can be considered invariant. Equation 33 in terms of mole fractions then takes the form

$$\partial^2 N_1/\partial z^2 - \frac{\epsilon - 1}{h} \partial N_1 N_2/\partial z = \frac{1}{D'} \partial N_1/\partial t, \quad (34)$$

which involves the close approximation $h = D'/V_a \cong D'/v_2$.

Attempts to obtain an exact solution of eq 34 in order to obtain the dependence of N_1 on distance at the time the cathode has reached a desired enrichment have not been successful. This solution is necessary to obtain the exact preliminary holdup of ^{39}K and the exact time at which production can be commenced. However, as it would apply only to a long tube, and since relatively short tubes or diaphragms are ample for ^{39}K concentration, this failure is of secondary importance to the present problem.

Returning to eq 33, which applies to a short tube, integration over the equivalent length V_c/A of the cathode volume gives

$$\partial c_1/\partial z = (v_1 - v_2)c_1c_2/D'(c_1 + c_2) - (V_c/AD')\partial c_1/\partial t, z=l, \quad (35)$$

showing that the concentration gradient at the front of the cathode volume is less than its maximum possible value at the concentrations by the amount $(V_c/AD')\partial c_1/\partial t$. This fact will be considered in the subsequent approximation for the build-up time of a short packed tube.

2. Production Equilibrium

When the cathode reaches the desired enrichment, withdrawal is begun at such a rate as to maintain the enrichment constant. Thereafter, the concentration distribution along the tube undergoes a further change until a steady distribution is reached.

Let ΔV_a be the departure from the "total reflux" countervelocity, V_a , this departure being due to continuous sampling at the cathode at a rate holding the cathode enrichment constant. When a steady distribution is reached a transport balance taken across the tube at distance z from the anode gives for the light component

$$(v_1 - V_a + \Delta V_a)c_1 - D'dc_1/dz = \Delta V_a c_{1-cath}, \quad (36)$$

and for the heavy component,

$$(v_1 - V_a + \Delta V_a)c_2 - D'dc_2/dz = \Delta V_a c_{2-cath}, \quad (36a)$$

where the c 's and D' refer to mean values for the cross section, and c_{1-cath} , c_{2-cath} refer to the moles per cubic centimeter of the two components in the product.

Equation 36 is divided by c_1 and eq 36a by c_2 , the latter is subtracted from the former, and the terms arranged to give

$$dz = \frac{D'(dc_1/c_1 - dc_2/c_2)c_1c_2}{c_1c_2(v_1 - v_2) - \Delta V_a(c_2c_{1-cath} - c_1c_{2-cath})}. \quad (37)$$

To proceed further, the approximation that temperature does not depend on z is assumed. The normality of salt is invariant and eq 37 can be written in terms of mole fractions as

$$dz = \frac{RhdN_1}{-R(\epsilon - 1)N_1^2 + [R(\epsilon - 1) + 1]N_1 - N_{1-cath}}, \quad (38)$$

where $v_1 - v_2 = v_2(\epsilon - 1) \cong V_a(\epsilon - 1)$, $h = D'V_a \cong D'/v_2$, and $R = V_a/\Delta V_a \cong v_2/\Delta V_a$. The integral of eq 38 is had by a well-known formula. The result is

$$z = \frac{hR}{\sqrt{q}} \ln \left[\frac{2aN_1 + b - \sqrt{q}}{2aN_1 + b + \sqrt{q}} \cdot \frac{2aN_{1-anode} + b + \sqrt{q}}{2aN_{1-anode} + b - \sqrt{q}} \right], \quad (39)$$

where $a = -R(\epsilon - 1)$, $b = R(\epsilon - 1) + 1$, $c = -N_{1-cath}$, and $q = b^2 - 4ac$. Equation 39 gives the relation between distance from anode, z , and mole fraction light, N_1 , when the distribution has reached a steady state after prolonged production at reflux ratio, R .

Example.—Consider the production of material having an abundance ratio greater than normal by 50 percent; $^{39}K/^{41}K = N_1/N_2 = 21.3$ at the cathode. Provided sufficient quantities can be produced, this enrichment would suffice for many purposes such as experiments for tracing potassium metabolism. It is desired to know (1) the length of packing and reflux ratio for maximum efficiency, (2) the efficiency of the yield in grams of total enriched potassium per kilowatt-hour, (3) the required build-up time under total reflux operation.

The case chosen is for a bead-packed tube, 1 cm inside diameter with anode abundance maintained normal at 14.2. The cathode volume, V_c is 1.0 ml, and the equivalent length of cathode volume based on a packing of 38 percent voids is 3.35 cm. The solution is taken as 1.0 N KCl. The temperature, normality, and voltage gradient will be assumed invariant with distance for purposes of this approximate calculation. The applied voltage is chosen to be 10 v/cm; the current is 0.50 amp and the input is 5.0 w/cm (a higher input would result in boiling).

The value of ϵ , based on the consideration of section II of RP1765 [2], together with experimental data reported in other papers of this series, is assumed to be 1.003. This is a conservative value.

The value of h is taken to be 0.020 cm, a value which appears conservative for the optimum conditions of operation discussed under case III of section III.

Equation 39, with the above values of ϵ and h , is shown plotted in figure 8, for various values of R and corresponding lengths of packing, l . The Rl versus l curve is also shown.

As seen in figure 8, the minimum packing length, l , required to give the assumed enrichment is 2.7 cm, under total reflux equilibrium, i. e., $R = \infty$ and $t = \infty$. The required reflux ratio for a packing of infinite length is 114.

The power requirement is proportional to length of packing whereas the production in grams of enriched material per unit time is proportional to $1/R$. Hence, maximum efficiency is had when

Rl is a minimum. The Rl versus l curve of figure 6 shows a fairly broad minimum at about 4.6 cm for which $R = 170$; these are the values of packing length and reflux ratio which will give the most efficient yield although the curve shows that considerable latitude is permissible in the direction of greater packing length and lower reflux ratio.

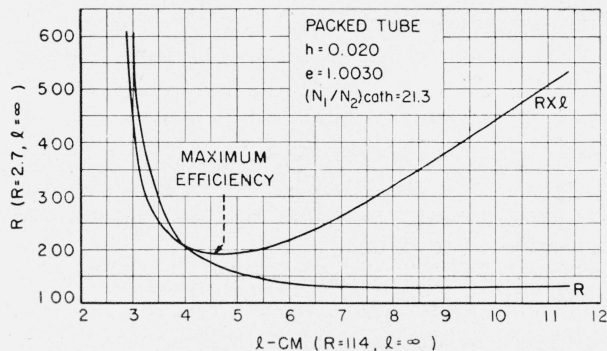


FIGURE 8.—Relation between reflux ratio, R , and length of packing, l , for fixed cathode enrichment.

The total potassium arriving at the cathode when counterflow is zero is I^+/F moles/sec, where I^+ is the total current times the transport number; the latter in this case is close to 0.50. At reflux ratio R , the production is (I^+/FR) moles/sec. For the present example the yield is

$$\text{yield} = \frac{0.50 \times 0.50}{96,500 \times 170} = 1.5 \times 10^{-8} \text{ mole of } 21.3 \text{ K/sec,} = 5.5 \times 10^{-5} \text{ mole of } 21.3 \text{ K/hr.}$$

The power input to the 4.6 cm-packing is $4.6 \times 5 = 23$ w. By allowing 7 w for electrode losses, the power, exclusive of that for the control equipment, is about 0.030 kw. Hence

$$\text{yield efficiency} = 5.5 \times 10^{-5} / 0.030 = 1.8 \times 10^{-3}$$

mole of 21.3 K/kwhr $= 7.2 \times 10^{-2}$ g of 21.3 K/kwhr. The corresponding energy requirement is 14 kwhr/g of 21.3 K. The energy charges against the production are thus seen to be quite nominal.

The solid curve, 1, of figure 9 shows the abundance ratio vs distance from the anode, z , as related by equation 39. This is the production equilibrium. Curve 2 is a rough sketch of the solution of eq 33 at the time the cathode reaches the production enrichment; this curve has a slope at $z=l$ that is less than curve 1, as was seen in eq 35. As at the time of curve 2 the build-up is still

diffusing toward the anode and is less near the anode than for curve 1, it follows that curve 2 must cross curve 1.

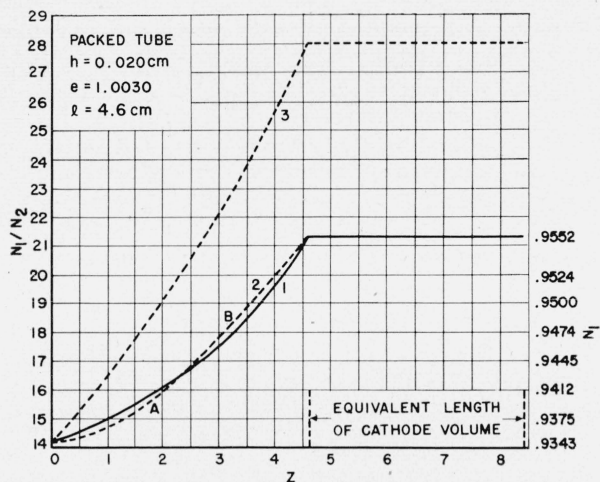


FIGURE 9.—Distribution of abundance ratio: 1, production equilibrium; ($R=170$, $t=\infty$); 2, end of build-up timer; ($R=\infty$, $t=13$ hr); 3, total reflux equilibrium; ($R=\infty$, $t=\infty$).

The difference between areas *A* and *B* of figure 9 represents the hold-up of ^{39}K yet to be accumulated in the packing after the production has begun. This difference is negligible in the present case because of the relatively large hold-up at the cathode. In consequence, the approximate hold-up for both curves 1 and 2 is given closely by graphical integration under curve 1. This proce-

dures gives: hold-up of packing plus cathode volume equals 2.2×10^{-5} mole of ^{39}K in excess of normal abundance.

As the concentration gradient at the anode remains zero for a large part of the build-up time, it is a good approximation to assume the hold-up of ^{39}K to have been transported at the maximum rate $I^+ (N_1 N_2)_{\text{anode}} (\epsilon - 1) / F$ moles $^{39}\text{K}/\text{sec}$, from the anode into the packing. This rate is in accordance with eq 9 of section I of RP1765 [2] and gives for the present example, $0.5 \times 0.5 (14.2/15.2) (1/15.2) \times 0.003/96,500 = 4.8 \times 10^{-10}$ mole $^{39}\text{K}/\text{sec}$. Hence total-reflux build-up time

$$\begin{aligned} &= 2.2 \times 10^{-5} / 4.8 \times 10^{-10} \\ &= 4.6 \times 10^4 \text{ sec.} \\ &= 13 \text{ hr.} \end{aligned}$$

V. References

- [1] A. Keith Brewer, S. L. Madorsky, and J. W. Westhaver, *Science* **104**, 156 (1946).
- [2] A. Keith Brewer, S. L. Madorsky, et al., The concentration of isotopes of potassium by the counter-current electromigration method, *J. Research NBS* **38**, 137 (1947) RP1765.
- [3] J. A. V. Butler, *Electrocapillarity*, p. 98 (Chemical Publishing Co., New York, N. Y., 1940).
- [4] *Int. Critical Tables* **6**, 234 and 310 (1929).
- [5] *Int. Critical Tables* **5**, 68 (1929).
- [6] R. E. Powell, W. E. Roseveare, and H. Eyring, *Ind. Eng. Chem.* **33**, 430 (1941).

WASHINGTON, July 29, 1946.