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Ionic Migration in a Counter-Current as a Basis for Electrochemical Exchange Process

(isotope Separation by Counter-current Electrolysis)

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The principle and theoretical basis for an electrolytic counter-current process for the enrichment of isotopes is presented. The unit separation factor (q) is governed by a chemical exchange equilibrium between the ions and neutral particles (or between different types of ions) of a dissolved isotopic electrolyte. The counter-current which multiplies the unit separation effect to give the separation factor Q (q^n) is effected by means of ionic migration in a flowing liquid, the velocity of which is adjusted so that the element whose isotopes are being separated does not undergo any transference. The method is explained in terms of an exchange equilibrium of the type M+MI = M'+MI', illustrated by the electrolysis of a solution of MgSO4. As is to be expected, calculation gives exceedingly high values for the multiplication factor q obtainable by this method. The overall separation factor Q is calculated with and without consideration of the relaxation time of the exchange reaction. It turns out that Q goes through a maximum as the field increases. The optimum value of the field strength permits one to draw conclusions concerning the velocity of the underlying exchange reaction; this velocity can be measured under certain conditions. The results, which are also of interest in connection with investigations of the nature of ionic equilibria, are discussed briefly. A few statements of an orienting nature are made concerning the course of the separation process as a function of time. In conclusion, a few remarks are made concerning the mobilities of isotopic ions.

The chemical exchange process for the enrichment of isotopes, developed by Urey and co-workers<sup>1</sup> has since undergone many modifications. It is based on the fact that equilibrium constants for reactions involving isotopic species are not

1. H. C. Urey and L. Greiff, J. A. C. S. 27, 321 (1935); H. C. Urey, Rep. Prog. Phys. 6, 48 (1940)(contains bibliography).

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usually identical, and that differences between relative isotope concentrations may occur between the two phases in heterogeneous chemical equilibria such as  $^{14,15}\text{NH}_3^+ (\text{Aq}) + \text{OH}^- (\text{Aq}) = ^{14,15}\text{NH}_3 (\text{g}) + \text{Aq}$ . By using the counter-current method, this separation can, in principle, be multiplied in the same way as differences in the composition of liquid and vapor are multiplied in a rectification column. The two phases, containing the isotopes in different chemical compounds, can thus constitute the two opposing currents required by the counter-current principle. In order to hasten the attainment of equilibrium, these phases must be brought into as intimate and rapid contact as possible, but must be led past each other intact, in keeping with the state of chemical composition of the particles.

#### I. The Principle.

The distribution of the isotopic mixture into two phases which characterizes the Urey exchange procedure actually also serves a secondary purpose, namely the production of a directed counter-current. If the directed forces (usually gravity) which produce the transport are caused to act on the particles individually instead of on the phase as a whole in such a manner that those atoms which are in one chemical state will move in one direction and those in the other chemical state will move in the other direction, the counter-current principle can also be applied to homogeneous chemical exchange equilibria.

It is possible to create a counter-current of particles in the above sense in a single phase with relatively simple apparatus. This can be accomplished if the particles taking part in the equilibrium are ions, since in this case, the individual particles can be caused to migrate by means of an electrical field. One can distinguish between two cases: in the first case, only one of the species taking part in the exchange reaction is an ion; in the other, both species are ions, and can

have either the same or opposite signs. As an example of the latter case, let us consider the equilibrium  ${}^9\text{Cd}^{++} + [\text{CdI}_3]^- \rightleftharpoons \text{Cd}^{++} + [{}^9\text{CdI}_3]^-$ . In an electrical field, the  $\text{Cd}^{++}$  ions migrate in one direction, and the  $[{}^9\text{CdI}_3]^-$  ions, containing cadmium in a different chemical state, migrate in the other direction, thus giving rise to a counter-current. The above-mentioned exchange reaction between  $\text{NH}_4^+$  and  $\text{NH}_3$  can serve as an example of the first case if we describe it as a pure solution reaction:  ${}^{14}\text{NH}_4^+ (\text{Aq}) + {}^{15}\text{NH}_3 (\text{Aq}) \rightleftharpoons {}^{15}\text{NH}_4^+ (\text{Aq}) + {}^{14}\text{NH}_3 (\text{Aq})$ . The current of electrically neutral  $\text{NH}_3$  particles running counter to the  $\text{NH}_4^+$  ions can be maintained by causing the liquid to move in a direction opposite to that of the ion current.

The currents are set up in such a way that the particles taking place in a reaction are brought as close to each other as possible. When one considers that the time necessary to attain a distribution equilibrium between the current and the counter-current then becomes as short as the time required for an ion exchange reaction, one sees immediately, in a qualitative manner, that the electrochemical exchange method (hereinafter called counter-current electrolysis) has a tremendous initial advantage as to the space and time necessary to attain a given multiplication of the unit separation, compared with all previous methods of using the counter-current principle.

With these considerations in mind, we had already developed the theoretical aspect of the subject by the end of the war. Although working conditions were very difficult, the necessary apparatus was assembled at the institute, and an experimental development of counter-current electrolytic methods with suitable substances was undertaken with the aid of E. Rihls, W. Jach and E. Voss. We hope to be able to report on the experimental results soon<sup>2</sup>.

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<sup>2</sup> The theory of the method was presented in a lecture before the Physico-chemical Colloquium of the University of Kiel in December 1946.



Hamshile, Brewer, Madorsky, Westhaver et al., in the United States,<sup>3</sup> reported a separation of the K and Cl isotopes by a "counter-current electromigration" process in which the isotopic ions migrated against a liquid current. The currents were adjusted in such a manner that the more mobile light isotope barely managed to migrate upstream and the heavier isotope migrated downstream. This separation principle has more in common with ours than one might think in looking at the principles underlying the two processes.<sup>3a</sup> On the other hand, the following short discussion of our principle leads to results which are fundamental to all separation experiments<sup>21,22</sup> based on ionic migration. It will therefore be of general interest even though the abovementioned papers have been published.

## II. The Method

For the sake of simplicity, the following discussion will be given in terms  
p. 50 of a specific binary electrolyte, namely, magnesium sulfate.

In a concentrated aqueous solution of  $MgSO_4$ , some of the  $Mg^{++}$  ions are free, although hydrated, and some are bound to  $SO_4^{--}$  ions, thus constituting neutral ion

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J. A. K. Brewer, S. L. Madorsky, J. K. Taylor, V. H. Dibeler, P. Bratt, G. L. Parham, R. J. Britten and J. G. Reid, Jr., *J. Res. Nat. Bur. Standards* **53**, 157 (1947); J. V. Westhaver, *ibid.*, **53**, 169 (1947); S. L. Madorsky and S. Struss, *ibid.* **53**, 185 (1947).

3a. It can be seen from the original papers that the starting point for the American investigations was a supposition which was made some time ago<sup>17</sup>, but had not been verified up until that time<sup>18-20</sup>; namely, that two isotopic dissolved ions migrate at different rates in an electrical field. The method used to detect this effect, which can also be used for continuous isotope enrichment, is identical with the principle used by us. The chemical exchange equilibria which we have emphasized in our treatment were also mentioned in the American papers as a possible cause of the elemental effect, but not pursued further. See also footnotes 5a, 12a, and 32a.

dipoles or molecules, which we will write as  $MgSO_4 \cdot Aq^b$ . This question becomes important only when we are discussing the magnitude of the isotope effect. We then have the exchange reaction



where  ${}^0$  represents  ${}^{24}Mg$ , which is the more common isotope, and  $Mg$  represents  ${}^{26}Mg$ . We now must create a magnesium cycle within the solution such that the magnesium is continually transferred from one location in the solution to another in the form of  $Mg^{++}$  ions, and then back to the original location in the form of undissociated  $MgSO_4$ . Such a cycle can easily be realized in principle by means of the arrangement depicted very schematically in figure 1.

A solution is contained in an electrolytic cell consisting essentially of a long middle section or exchange region B (length L), a cathode chamber and an anode chamber (K and A, respectively). The various controls and means for introducing new chemicals and removing spent ones have been omitted from figure 1. In principle, the exchange region might be a large tube; actually, however, it consists of a bundle of smaller tubes which are cooled from the outside in order to remove the heat developed by the electrical current. In order to avoid convection currents, these tubes are filled with fine quartz wool or some such substance.

In an ordinary electrolysis,  $Mg(OH)_2$  would be formed at the cathode and  $H_2SO_4$  at the anode. Both of these difficulties can be overcome, as shown in figure 1, by continually introducing sulfuric acid into the cathode chamber at a suitable rate, and barium hydroxide solution into the anode chamber; the  $Ba^{++}$  ions will remove the excess  $SO_4^{--}$  ions (i.e., those introduced into the system as  $H_2SO_4$ ) in the form of

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b. It is unnecessary to specify whether we are dealing with an electrostatic ion pair ( $Mg^{++} \cdot Aq - SO_4^{--} \cdot Aq$ ) in the sense described by Bjerrum (without penetration of the hydration sheath) or with undissociated molecules ( $Mg^{++} \cdot SO_4^{--} \cdot Aq$ ).

of insoluble  $\text{BaSO}_4$ . We see that in this manner, the total quantity of  $\text{MgSO}_4$  present in the system remains constant in time. In a normal electrolysis, the  $\text{MgSO}_4$  would gradually be transferred from the anode chamber to the cathode chamber. In the arrangement shown in figure 1, water is continually flowing into the cathode chamber at such a rate that the  $\text{MgSO}_4$  concentration in the cathode chamber remains constant; the concentration of  $\text{MgSO}_4$  in the anode chamber is kept constant by continually evaporating water at the proper rate. The liquid in the exchange region R is thus caused to flow counter to the direction of migration of  $\text{Mg}^{++}$  ions at such a rate that on the average there is no transport of magnesium. The  $\text{Mg}$  atoms which swim with the current in the form of  $\text{MgSO}_4$  particles then form one particle stream, and the free  $\text{Mg}^{++}$  ions migrating in the electrical field form an equal and opposite

Figure 1. Principle of counter-current electrolysis. Suggested experimental arrangement for separating Mg isotopes.

counter-current, which is slowed down by the flow of liquid<sup>5</sup>. The rate of flow of the liquid and the quantities of water which must be added and taken off in order to maintain this flow can be derived as follows:

If  $V \text{ cm}^3$  of solution flow through a total cross section  $S$  of the separation region (R) in one second, the number of neutral particles (in moles) which will be

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5. This would also apply to the limiting case where only free ions were present. The cations would then have zero velocity relative to the apparatus if we disregard the fact, as we will in the present paper, that the isotopic ions themselves do not all migrate at exactly the same velocity (see concluding section).



transported through  $1 \text{ cm}^2$  of cross section by this current will be

$$(W/S) \bar{\alpha}; \quad (2)$$

where  $\bar{\alpha}$  is the degree of association of the solution at concentration  $c$  ( $\text{mol cm}^{-3}$ ), that is, the fraction of the salt which is not dissociated into free ions. The number of free cations ( $\text{Mg}^{++}$ ) migrating in the opposite direction in the potential gradient  $\Delta P/L$  is then (in  $\text{mol cm}^{-2} \text{ sec}^{-1}$ )

$$(w_+ - W/S)c(1 - \bar{\alpha}), \quad (3)$$

where

$$w_+ = \frac{1}{1 - \bar{\alpha}} \frac{\Lambda_+}{F} \frac{\Delta P}{L} \quad (3a)$$

represents the velocity of the cations with the solution at rest,  $\Lambda_+$  represents the equivalent conductance of the ion, and  $F$  is the Faraday. Equating the two particle currents and introducing the equivalent conductance  $\Lambda_0$  of the salt, the transference number  $\mathcal{J}t_+$  of the cation, the specific conductance  $\kappa$  ( $\Omega^{-1} \text{ cm}^{-1}$ ) and the equivalent concentration  $c_A$  ( $\text{val} \cdot \text{cm}^{-3}$ ) into the solution by means of the equations

$$\Lambda_+ = \mathcal{J}t_+ \Lambda_0 = \mathcal{J}t_+ \cdot \kappa / c_A, \text{ we obtain} \quad (4)$$

In the example outlined in figure 1, the sulfuric acid entering the anode chamber is removed by Ba ions. The operation could, of course, be carried out in other ways. For instance, it is also possible to vaporize the sulfuric acid, or, if there is no objection to an increase to a volume of liquid around the anode, this acid can be neutralized with magnesium carbonate, magnesium oxide or magnesium metal. These practical problems will differ from case to case, and will not be discussed here, since we are now concerned only with illustrating the principle.

### 1. The Degree of Enrichment

The theoretically obtainable degree of enrichment is given by the single stage enrichment factor  $q$ , which in this case is equal to the equilibrium constant  $K$  of the exchange reaction (1), and by the multiplication factor  $f$ . The isotope marked with an asterisk has the mole fraction  $Y_a$  among the neutral particles and the mole fraction  $Y_+$  among the free ions; we will define

$$q = \frac{Y_a}{1 - Y_a} / \frac{Y_+}{1 - Y_+} \quad (5)$$

If  $q > 1$ ,  $^{24}\text{Mg}$  becomes enriched in the anode chamber in counter-current electrolysis. The following considerations will indicate the multiplication effects which can be achieved in this manner.

We wish to find  $h$ , the rate of transport of the starred isotope, which is the one to be enriched, in mol/sec. That is, we wish to find the excess of particles of this isotope passing through the cross section  $S$  per second in the positive  $x$  direction at location  $x$ , compared to the number of particles of this same isotope passing in the other direction at the same location. We take it for granted that the exchange equilibrium is not noticeably influenced by the ionic migration, and thus that equation (5) holds at all times and places. We then have

(6)

where  $c_+$  and  $w_+$  are the concentration and translational velocity of the free cations, and  $c_a$  and  $w_a$  are the corresponding quantities for the neutral molecules. The last term takes account of the fact that the enrichment process in the  $x$  direction described



by the first two terms also produces an increase in concentration which causes partial back-diffusion.  $D$  is the diffusion constant of the salt, and  $\gamma_0$  the concentration of the starred isotope in the solution.

Total isotope current ( $Mg + Mg^*$ ) caused by the electrical field is equal and opposite to the isotope current caused by the flow of liquid  $W$ , thus

(7)

Furthermore, since  $\gamma_r \approx \gamma_a \approx \gamma$ , equation (5) may be replaced by

or

(8)

If we take equation (7) and (8) into account, the transport equation (equation (6)) simply becomes

(9)

Continuation of the electrolysis will result in a steady state in which the rate of separation by ionic migration is equal to the rate of re-mixing by diffusion, and thus  $n = 0$ . The differential equation

(10)

then holds. Solution of this equation gives the desired total separation factor

(11)

where  $\gamma_0$  and  $\gamma$  are now the mole fractions at the position  $x = 0$  and  $x = L$ ; i.e. in the cathode and anode chambers. If we use equation (4), and replace  $W$  by electrical

quantities, we obtain the following expression for the overall separation factor  $Q_0$  and the overall multiplication factor  $F_0$ .

5a, 5b

(12)

According to equation (12), the distance between the electrodes (length of separation chamber L) has no effect on the degree of multiplication ( $f$ ) of the exchange effect ( $q - 1$ ) obtainable by counter-current electrolysis with a given difference of potential  $\Delta P$ . The multiplication factor increases with the difference of potential.

The validity of this statement is dependent on an important assumption, which will be discussed below.

#### 4. Consideration of the Relaxation Time of the Exchange Reaction.

According to equations (11) and (12), the separation factor  $Q_0$  continues to increase indefinitely with the applied field strength  $\Delta P/L$ , i.e., with the circulating particle current. In all other applications of the counter-current principle, - rectification, chemical exchange processes, Clusius thermal diffusion, counter-current ultra-centrifuge, etc., - there is an optimum circulation velocity at which  $Q_0$  has the

5a. In place of  $\ln Q_0 = (\tau - 1) \frac{\Delta P}{D} \cdot \frac{v}{L}$  (equation 12), Westheimer<sup>3</sup> finds the expression  $(q - 1) \frac{\Delta P}{D}$  which is similar to our expression, but in which  $q$  does not represent an equilibrium constant as it does in equation (12), but the velocity ratio  $v_1/v_2$  of two isotopic ions.

5b. In the derivation of equation (12), it was tacitly assumed that translational velocities  $v_{1,x}$  and  $v_{2,x}$  do not vary with displacement perpendicular to the  $x$  direction. This conclusion cannot be realized completely in practice, so that the experimental values for  $q$  are somewhat lower than those calculated by equation (12). Experimental and theoretical treatment of questions of this type is given in the papers by Brewer, Madorsky, Westheimer and co-workers<sup>3</sup>.

maximum possible value  $q_0^0$ . The difference is quite characteristic, but of course depends on the validity of the assumptions made in deriving equations (11) and (12); namely, that exchange equilibrium can always be completely attained, regardless of ionic migration. We will now inquire as to the value of the field strengths at which we may expect incomplete attainment of equilibrium.

In previous counter-current processes, the upper limit of the circulation velocity has been determined by the fact that the exchange of particles between the current and counter-current has been slow because of the special separation of the two currents (average distance  $d$ ). The time necessary to attain distribution equilibrium (relaxation time  $\tau$ ) is thus determined by the time  $\tau_D$  required for diffusion through the distance  $d$ . It has been shown previously, however<sup>6</sup>, that if the maximum possible degree of separation is to be reached, a particle traveling along in the current must cover a distance equal to the diffusion path

(15)

within a period equal to the relaxation time  $\tau \approx \tau_D$ . The optimum translational velocity is therefore

(16)

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6. H. Martin and W. Kuhn. Z. Physik. Chem. 193A, 219, 517 (1941).



In counter-current electrolysis, the relaxation time  $\tau$  is the time necessary to attain equilibrium in the chemical exchange reaction. This quantity is determined by starting with the equation obtained by applying von Smolushowski's equation<sup>7</sup> for the rate of coagulation of colloidal particles to normal, unhindered bimolecular reactions. According to this equation, the number of collisions per second per cm<sup>3</sup> between two species of particles of concentration  $c_1$  and  $c_2$ , having equal radii  $r$  and diffusion constants  $D$ , is

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(15)

In our exchange reaction,  $c_1$  and  $c_2$  are replaced by the concentration  $c_a = c\bar{a}$  and  $c_b = c(1-\bar{a})$ , the concentrations of the element in its two different chemical states; instead of (15), we thus have

(16)

If we divide through by  $N_L c$ , the total number of particles taking part in the exchange equilibrium per cm<sup>3</sup>, we obtain the number of collisions which one atom of the element undergoes per second with another atom in the other chemical state:

(17)

The average time interval per collision is then:

(18)

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7. M. v. Smolushowski. Z. Physik. Chem. 92 129 (1927).

This is obviously the time required for attaining exchange equilibrium between current and counter-current, assuming that every collision is fruitful, i.e., leads to an exchange of isotopes.

Equation (15) states that the particles, on the average, diffuse a distance

(19)

in a given direction during the time  $\tau$ . According to optimum condition (14), this must be equal to the distance which an ion in an electrical field in counter-current electrolysis moves against its environment, i.e. against its reaction partner, in the time  $\tau$ . Back-diffusion and incomplete attainment of equilibrium will thus be adjusted best with regard to each other when the migration velocity  $W_{\pm} = |W_{+}| + |W_{-}|$  has the exact value

(20)

If this expression is inserted into the relationship between  $v_{\pm}$  and the field strength  $\Delta F/L$

(20a)

we obtain the following expression for the optimum diffusion, i.e. field strength at which the separation factor  $Q_{\pm}$  has its highest possible value  $Q_{\pm}^{\circ}$ :

(21)

The latter expression is attained by introducing the viscosity  $\eta$  of the solvent by means of Stokes' law, or by using

(20a)

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in place of (18).

This reaction, like many ionic reactions, is too rapid to measure; this does not mean, however, that we are always dealing with an activation energy ( $A$ ) which is negligible compared to the thermal energy ( $RT$ ), and that the diffusion of the particles toward each other is the sole rate-determining step.

We take account of the possibility that it is the reaction, rather than diffusion, which is the rate-determining factor, by replacing  $\tau$  in equations (18) to (21) by the longer relaxation time

(22)

where  $\lambda$  is the fraction of collisions which are fruitful, this in turn being given by  $\exp(-A/RT)$ . Thus,  $\tau$  in equation (19) must be replaced by a larger quantity

(19a)

In place of equation (21), we then obtain the following general expression for the optimum field strength:

(23)

Our question concerning the range of validity of equations (11) and (12) has been answered with the derivation of expressions (21) and (23): the overall multiplication factor ( $f_0$ ) is proportional to the electrolytic difference of potential ( $\Delta F$ ) as long as

(24)

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Near the optimum field strength, the ions migrate so rapidly into regions of other concentrations  $\gamma$ , that exchange equilibrium can no longer be completely attained.

The quantitative relationship between the optimum difference of potential and the relaxation time of the exchange reaction described by equations (21) and (25) is quite interesting. In principle, it makes it possible to measure the relaxation time ( $\tau_r$ ) of ionic reactions in condensed systems in terms of an optimum field strength  $(\Delta P/L)^0$ , and thus, under certain conditions, to measure the velocities of such reactions, which are usually quite high. It will not always be easy to determine which of the several reactions which may come into the picture is the critical reaction in a certain observed isotopic effect; however, we can obtain some indication from the fact that  $\beta$  and, as we will see below, the single stage effect  $(q - 1)$  both depend on the nature of the bands encountered by the reaction.

For the sake of completeness, it should be mentioned that equation (12), which is also valid in the region  $\Delta P/L \approx (\Delta P/L)^0$ , can easily be generalized by means of the equation

(25)

This expression was derived in another connection<sup>9</sup> and relates the overall multiplication factor at optimum circulation velocity ( $f_0^0$ ) to the overall multiplication factor at a times the optimum velocity ( $f_0$ ). If we use equation (25), we can replace (12) by the following general expression:

(26)

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9. H. Martin and V. Zahn<sup>6</sup>, pages 260 and 261.

where

(27)

3. Continuation of Discussion with Reference to Specific Experimental Data (MgSO<sub>4</sub> Solution)

For the counter-current electrolysis of a 1 M aqueous solution of magnesium sulfate at 100 V, with an interelectrode gap of 3 cm, and with  $\Lambda_{\infty} = 20$ ,  $\beta_{\pm} = 0.85$ ,  $D = 0.55 \times 10^{-5}$  and  $F = 96,500$ , equation (12) gives us, in round numbers,

$$f_{\infty} = 2500 \bar{a}.$$

If the degree of association is calculated by the method of Bjerrum<sup>10</sup> for  $c = 10^{-3}$  mol cm<sup>-3</sup>, we obtain  $\bar{a} \approx 0.86$ , which gives us  $f_{\infty} \approx 2,000$ . Now the isotope effect ( $q - 1$ ) in an exchange reaction between ions and merely associated ion pairs will be extremely small; since  $f_{\infty}$  is extremely large, however, one may obtain observable separations factors under certain conditions. In the present case, for instance,  $q_{\infty} \approx e^{0.2} \approx 1.2$  for  $q = 1.0001$ , that is, for the case in which the equilibrium constant  $K$  of reaction (1) differs from unity by only 0.1%.

Among the electrically neutral particles in electrolytic solution, there may exist not only associated ion pairs, but actual undissociated molecules<sup>11</sup> as well; the fraction of the ion pairs may vary from zero or almost zero to unity. Using G. W. Davies<sup>12</sup> value of  $6.5 \cdot 10^{-3}$  for the thermodynamic constant for the dissociation

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10. H. Bjerrum, Egl. Danske Vidensk. Selsk., Math. - Fysiske Medd. (7) 2 [1909].

11. See footnote 4.

12. See Handbook and Yearbook of Chemical Physics 6, II, W. Ulich, page 253 (In German); G. Kortum, Electrolytic Solutions, Leipzig 1941, page 252 (In German).

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of  $MgSO_4$ , we see that about  $1/3$  of the salt should be present in the undissociated state in a 1 M solution. If we were only taking account of the true molecules,  $\alpha$  would be approximately 0.33 instead of 0.86, and  $f_{\alpha}$ , according to (12), would be correspondingly smaller;  $Q_{\alpha}$ , on the other hand, might actually be larger, since undissociated molecules show considerably greater isotropy effects  $(q - 1) / \lambda$  exchange equilibria than do associated ion pairs.

The present investigation shows that counter-current electrolysis gives unusually high multiplication factors ( $f$ ) per unit length of the operating space, and that it will be possible, with an apparatus of reasonable size, to measure very slight isotopic effects in ionic equilibria, and, under certain circumstances, to achieve a practical separation of isotopes <sup>12a</sup>. More exact measurement of such effects will probably give information concerning the nature of the basic electrolytic equilibria, since different kinds of isotopic specificity are to be expected for different equilibria (for instance, ion - ion pair, ion - molecule).

We now wish to calculate the relaxation time ( $\tau$ ,  $\tau_R$ ) and the optimum field strength  $(\Delta P/L)^0$  for the above-mentioned practical example. We will assume that reactions of type (1) proceed practically unhindered, and that  $\zeta \sim 1$  (equation 22). Then if  $\alpha = 0.86$ ,  $c = 10^{-3}$ ,  $T = 300$ ,  $\eta = 0.01$ , equation (18a) gives us  $1.5 \cdot 10^{-9}$  sec; if we use the above-mentioned values of  $D$ ,  $\lambda_0$  and  $\beta L_+$ , equation (21) gives us  $10^3$  V/cm.

Field strengths this high cannot be realized in DC electrolysis, and we see that it was actually justified under the experimental conditions assumed ( $\Delta P/L = 20$  V/cm)

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12a. Brewer, Mikroski, Westhaver and co-workers<sup>3</sup> have achieved separation factors  $Q \sim 1.5$  for <sup>39</sup>K and <sup>41</sup>K in cases where the separation region was about 10 cm long.



to calculate  $Q_0$  and  $f_0$  according to equation (12), and not according to (26). It is worthy of note, however, that if  $\zeta = 10^{-6}$ , the exchange reaction thus having  $\tau_R \sim 10^{-3}$ , which would still be an immeasurably rapid reaction, the optimum field strength according to equation (25) would decrease to  $(\Delta F/L)^0 \sim 100$  V/cm. This is a range which is easily accessible experimentally<sup>13</sup>.

#### Velocity of the Separation Process

The general progress of the counter-current electrolysis in time will not be discussed in greater detail here, since the time-dependent variations in counter-current processes have been given detailed theoretical treatment in the literature in connection with certain specific separation procedures such as the Clusius thermal diffusion column,<sup>14</sup> the ultra-centrifuge<sup>6</sup> and others. Many of the results and lines of thought presented in these papers are of quite general validity<sup>15</sup>. For the sake of orientation, we will briefly mention a few expressions which are particularly applicable to electrochemical exchange processes.

For the case in which a rare isotope is enriched by a continuous process in such a manner that the initial concentration  $\gamma_0$  is kept constant in one electrode chamber and the enriched isotope is taken off continuously at the other at a concentration  $\gamma = Q \gamma_0$  ( $Q \gamma_0$  is still  $\ll 1$ ), integration of (9) with  $n \neq 0$  and  $1 - \gamma \sim 1$ , gives

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13. According to equation (21), low  $(\Delta F/L)^0$  values can also occur for  $\zeta \sim 1$  in the following cases (1) In strong electrolytes, when only the formation of actual molecules contribute to the isotropy effect, since the theory of electrolytes indicates very small values of  $\alpha$ , the degree of association, in many cases; (2) in weak electrolytes, since in this case very small values of  $(1 - \alpha)$  (degree of dissociation) occur; (3) at small values of  $c$  (concentration of electrolyte). Equation (28) shows that the yield ( $\Delta$ ) will be small in all three cases; equation (12) indicates that the degree of enrichment will also be small in cases 1 and 2).

14. See R. Fleischman and H. Jensen: The Thermal Diffusion Column, *Ergebn. exakt. Naturwiss.* **20** (1942); contains bibliography.

15. This is especially true, for example, in the cases of the following papers: W. Walcher, *Isotope Separation*. *Ergebn. exakt. Naturwiss.* **18** (1939); W. Ehm and H. Martin, *Z. Physik. Chem.* **189 A**, 317 (1941); A. Klamm, *Z. Physik* **123**, 10 (1944).

(28)

for the permissible take-off rate  $n$  in mol  $\text{sec}^{-1}$  or for  $\dot{V}$ , the quantity of solution which can be processed in one second ( $\text{cm}^3 \text{sec}^{-1}$ ). Evaluating this in terms of our experimental example for  $S = 1 \text{ cm}^2$ , if for instance  $q = 1.0001$ ,  $Q_0 = 1.2$  and  $Q = 1.1$ , we have  $\dot{V} = 10^{-7} \text{ cm}^3/\text{sec} \sim 0.01 \text{ cm}^3/\text{d}$ ; if  $q = 1.001$ ,  $Q_0 = 7.4$  and  $Q = 5.7$ , thus  $\dot{V} \sim 0.1 \text{ cm}^3/\text{d}$ .

The induction period which elapses before the separation factor builds up to  $Q$  must necessarily go by before one begins to take off any of the product; it is also necessary to know the length of this period when operation is not continuous. If  $Q$  is to come within  $1/3$  of its maximum value  $Q_0$ , i.e.,  $(Q_0 - Q)/(Q_0 - 1) \sim 1/3$  (attainment of steady state about  $2/3$  complete), the corresponding induction period will be of the order of

(29)

If the volume  $V_A$  of the storage chamber in which the rare isotope is being enriched is small compared with the volume  $V_R$  in which the separation is taking place,  $\theta$  will be about 25 days in the above case, where  $s \ll 1$ ,  $L = 5$  and  $D = 0.55 \cdot 10^{-5}$ . A more exact idea of the approach of  $Q$  to  $Q_0$  as time progresses may be obtained from the expression

(30)

p. 36 which was obtained by using (28). In (30)  $(Q_0 - 1) V_A / (q - 1) a W$ , like  $\theta$ , represents a relaxation time.

#### 7. Conclusion: Remark on the Mobility of Isotopic Ions.

According to the present investigation, the overall separation factor attainable by ionic migration in counter-current goes through a maximum as the electrolyzing field

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strength  $\Delta V/L$  increases, because of the finite time necessary for attaining exchange equilibrium<sup>16</sup>. An optimum field strength  $(\Delta F/L)^0$  cannot be expected to exist if the single stage separation effect  $(q - 1)$ , which always depends on small differences in the electrical conductivities of the isotopes, is an ion velocity effect, based on the differences in mobilities of the free ions, rather than an ion concentration effect, governed by chemical equilibria, as was assumed in the present case.

The question as to whether isotopic ions (in the same chemical state, including degree of solvation) in condensed systems has different migration velocities has been investigated theoretically by Lindemann<sup>17</sup> and has been answered in the affirmative. Subsequent unsuccessful attempts<sup>18,19</sup> to detect such a velocity defect in aqueous solutions threw some doubt on this prediction, although the blame was sometimes placed on such chemical processes (assumed to be isotopically unspecific) as molecule formation and hydration<sup>19,20</sup> or the extreme smallness of the mass effects which would be expected to exist according to the kinetic theory of ionic migration. A Klemm and colleagues<sup>21,22</sup> who were the first to succeed in detecting a migration effect, used

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16. On the other hand, see A. Klemm, *Z. Physik* **121**, 10 (1944).
  17. A. Lindemann, *Proc. Roy. Soc. London* **224**, 102 (1921).
  18. J. Kendall and co-workers, *Proc. Nat. Acad. Sci.* **2**, 75 (1925); **10**, 458 (1924).
  19. E. G. Pilley, *Philos. Mag. J. Sci.* **12**, 889 (1925).
  20. E. H. Jette, *Philos. Mag. J. Sci.* **3**, 258 (1927); J. Kendall *Nature (London)* **29**, 156 (1942).
  21. A. Klemm, *Naturwiss.* **32**, (1944); *Z. Naturforschg.* **22**, 9 (1947).
  22. A. Klemm, H. Hintsberger and Ph. Hoernes, *ibid.* **22**, 245 (1947).



*d*-silver iodide<sup>21</sup> and a lithium chloride melt (containing HCl)<sup>22</sup>, i.e., non-hydrated ions. Brewer, Madorski, Westhaver et al<sup>3</sup> who have also reported success with aqueous systems, found individual effects for the hydrated  $K^+$  and  $Cl^-$  ions which were of the order of magnitude which would correspond approximately to the diminution in relative mass difference of the ions which would be caused by association with  $H_2O$  molecules<sup>22a</sup>.

As far as any attempt to explain the observed separation effect as a velocity effect is concerned, it may be stated that this interpretation must be regarded as incomplete (if not incorrect) until it is proven that equilibrium effects are not concerned (or compensate each other).

From the standpoint of exchange equilibria, isotope effects would actually be expected in the case of hydrated ions: it would be sufficient to assume different degrees of hydration for different isotopes. In the case of the above-mentioned experiments by Klemm<sup>22</sup>, the observed enrichment of  $^7Li$  at the anode might be explained as follows in terms of exchange equilibria: if we assume that the melt contained negatively charged  $(LiCl)_x^-$  ions, as well as  $Li^+$  and  $Cl^-$  ions, then in Klemm's apparatus, in which the anode is a supported layer of fused  $PbCl_2$  (with carbon electrode), the  $(LiCl)_x^-$  ions as well as the  $Cl^-$  ions, can migrate to the  $LiCl - PbCl_2$  interface. The complex is destroyed there when the  $Cl^-$  ions pass through the interface and separate out, and the  $Li^+$  ions migrate back, forming a counter-current to the  $(LiCl)_x^-$  current. This process thus has all the characteristics indicated in figure 1 for the process

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22a. This agrees with the fact that the authors found that the primary effect in the case of  $K^+$  ion was not influenced either by the other ion ( $SO_4^{2-}$ ,  $Cl^-$ ) or by the salt concentration, within the reproducibility of the experiments. This reproducibility may well have been insufficient to permit complete exclusion of the possibility of exchange effects.



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process in the right hand part of our counter-current electrolysis set-up<sup>23,23a</sup>. This observation can also be extended to solid electrolytes, under certain conditions, an example of which would be the enrichment of <sup>109</sup>Ag at a carbon anode<sup>21</sup> pressed against  $\alpha$ -AgI, observed by Klemm from the standpoint of the carbon anode, (which is actually moving, in this case), we have an incoming particle stream consisting of Ag ions tightly bound in the AgI lattice, and a counter-current of particles consisting of Ag ions which are more or less free to move in the electrical field. In this case, one would probably speak less of a chemical exchange equilibrium than of a lattice defect (Fehlordnung) equilibrium in the crystal.

It would be an extremely difficult matter to make quantitative predictions concerning exchange equilibria in condensed systems, regardless of whether we were dealing with solvation equilibria, dissociation equilibria or perturbation equilibria<sup>24</sup>. It will therefore be necessary to determine in advance, experimentally, whether or to what degree an observed separation effect is an equilibrium effect (concentration effect) or a kinetic effect (velocity effect), or both. This must be done by varying the experimental conditions and substances. Such investigations will make use of the fact, demonstrated above, that in an exchange equilibrium, the magnitude of the separation factor is determined not only by the magnitude of the exchange constant  $K$ , but by the electrolyte concentration ( $c$ ,  $a$ ) as well as, under certain circumstances, the time necessary to attain equilibrium (relaxation time  $\tau$ ,  $\tau_R$ ).

23. In connection with their fusion electrolysis LiCl HDI, Klemm and co-workers<sup>22</sup> remarked that the primary effect measured in terms of relative mass, appeared larger in the case of K than in the case of Li. This can probably be regarded as an indication that exchange effects are also operating.

23a. A. Klemm has recently published a general expression for the single stage separation factor  $q$  in which the occurrence of both equilibrium effects and kinetic effects were considered (Z. Naturforschg. 3a, 127 (1948)).

24. H. C. Urey, J. Chem. Soc. (London) 1947, 562.

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**END**