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Separation of Isotopes by Electrical Migration and Determination of Ionic Mobilities in Molten Salts

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Problems of the use of ionic migration for the separation of stable isotopes under laboratory conditions and in large-scale plant are considered. The phenomenological theory of the process, the apparatus, the mode of operation, experimental conditions, and results obtained for twenty elements are discussed in detail. Results obtained by countercurrent and zone electrical migration for the structure of molten salts and the mechanism of the migration of ions in an electric field are examined. A list of 341 references is included.

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I. INTRODUCTION

Electrical migration is the directed movement of ions in an electric field, which is superimposed on the random thermal motion of the particles. Study of the motion of ions in an electric field is important both for elucidating the internal structure of a substance and the actual mechanism of such motion and, in application, for separating mixtures of substances in an ionised state, in particular for the separation of isotopes.

Electrical migration has been the subject of several reviews [1-25], some of which have become out of date. Yet many experimental and theoretical papers are continually being published on this method, which indicates the unflagging interest of research workers. It therefore appears useful to review the present-day state of the problem.

Electrical migration can be accomplished in solids, liquids, and gases possessing ionic conduction. The present review considers aspects of the migration of ions in molten salts. Information on analogous processes in other media—solid salts, solutions, liquid metals—is given only in the historical survey or for comparison with corresponding data for molten salts. Reviews have been published fairly recently on the movement of ions in aqueous solutions [26,27] and in liquid metals [28,29].

II. HISTORICAL SURVEY

The separation of isotopes by the migration of ions in an electric field is based on the fact that the mobility of isotopic ions is greater the smaller their mass. This idea was first put forward in 1921 by Lindemann [30]. Milliken and Harkins [31], however, then expressed doubt concerning the feasibility of the process owing to possible masking of the isotopic effect by diffusion and convection. These misgivings appeared to be confirmed by a series of experimental papers [32-37], for no change could be observed in the isotopic composition of lithium, magnesium, or chlorine in attempts to effect the electrical migration of their salts in aqueous solution, and Eilert's experiment [38] evidently passed unnoticed. And although rare-earth metal ions were successfully separated by this method [37,39-42], Jette [43] concluded, from a comparison of deductions from hydrodynamic and kinetic theories, that "differences in the mobilities of isotopic ions are extremely small, and cannot be detected by existing methods". Attention was therefore switched to other processes, and even in 1942 Kendall [44] still asserted that the method was powerless to effect the separation of isotopes.

These failures are explained by the low sensitivity of the method of isotopic analysis—determination of the atomic weight of the element undergoing separation—employed at that time. An isotope effect was, of course, present, but it was too small. This was proved later, when mass-spectrometric and activation methods of analysis became generally available, and radioactive isotopes began to be used as tracer atoms: when the experiments were repeated under identical conditions, a change in isotopic composition was not only observed qualitatively but also measured quantitatively [45-49].

In the initial attack on problems of producing an atomic bomb a detailed study was made of many methods—including electrical migration—suggested earlier for separating isotopes. As early as 1942 several groups of investigators in the U.S.A. were developing this method [50-58], but the first publication appeared only in 1946. [59] Accounts appeared later of the method of operation based on the countercurrent principle, and experimental results on the separation of the isotopes of potassium [60,61], chlorine [62], copper [63], and uranium [64,65], as well as the theory of the process [66,67]. During the War interest in this method was taken also in Germany [68-72].

In the postwar period the method of electrical migration was developed in several directions. Countercurrent electrical migration in aqueous solution applied to the separation of isotopes was studied in the Soviet Union [73-84], the Federal Republic of Germany [4,85-90], Switzerland [91-100], West Berlin [27,101-114], and Israel [115,116]. Electrical migration combined with ion exchange in resin-filled columns or with the use of ion-exchange membranes has been studied in Japan [117-130] and in the Soviet Union [131-137]. The electrical migration of ions on a paper strip impregnated with an aqueous salt solution has been studied in France by the use of radioactive and stable isotopes [13,14,138-144].

Study of the diffusion of ions in salt crystals by means of a radioactive tracer [145-148] suggested conducting this

process with a superimposed constant electric field: in this way electrical migration was effected in single crystals or compressed powders of salts[148-155]. The production of high-temperature fuel cells with solid electrolytes enabled them to be used to enrich oxygen isotopes by the electrical migration method[156-158].

Molten salts, which, like aqueous solutions, permit the countercurrent principle to be applied and thereby the effect of the difference in mobility between isotopic ions to be magnified many times, have attracted great attention from research workers. Following the successful enrichment in 1947 of lithium and potassium isotopes in a mixture of their molten chlorides[159], more than a hundred theoretical and experimental papers have appeared on countercurrent electrical migration in molten salts: studies have been made of the separation of the isotopes of lithium[20,21,159-197], sodium[192,198], potassium[20,21,159,191,192,199-201], rubidium[179,192,200,202,203], caesium[192], copper[204], silver[205], magnesium[191,206,207], calcium[21,206-214], strontium[206,207], barium[206,207], zinc[215,216], cadmium[214,217,218], thallium[219-222], tin[223-225], lead[214,225-227], uranium[228], chlorine[166,167,200,229-233], and bromine[200,234,235]. The technique developed for molten salts has been used to investigate electrical migration in solid salts of lithium[236-239]. The electrical migration of isotopic alkali-metal ions has been examined also in their molten nitrates impregnating a strip of asbestos[10-14,240-243].

In 1953 Haeffner[244] detected a slight change in isotopic composition when a current was passed through a capillary filled with mercury. This phenomenon, named after him the Haeffner effect, was investigated not only in mercury[245-247] but also in molten lithium[248,249], potassium[250-252], rubidium[251-254], zinc[255], cadmium[255], gallium[256-259], indium[252,258,260], tin[255,258], and lead[258] and in solid uranium[245]. Sharp differences were observed in the behaviour of isotopic ions in metals and in salts. The fact alone that in metals light isotopes accumulate at the anode—not at the cathode as in all other media—suggests that the migration of ions takes place by different mechanisms in metals and in salts. Many theoretical papers have been published[263-277] on isotope effects in the electrical migration of ions in liquid metals.

III. SEPARATION OF ISOTOPES BY COUNTERCURRENT ELECTRICAL MIGRATION

1. Principles and Phenomenological Theory of the Method

The underlying principle of countercurrent electrical migration consists in producing a flow of electrolyte in the opposite direction to the movement of the isotopic ions in the separating apparatus. The velocity of the electrolyte is adjusted so that the faster light isotopes overcome the countercurrent and accumulate in the "head" electrode compartment and in the adjacent portion of the separating tube joining the two electrode compartments, while the slower heavy isotopes are washed back by the counterflow of liquid. If isotopic cations are being separated, the cathodic compartment is the head electrode compartment in this sense.

The mathematical description of countercurrent electrical migration is based on the assumptions[67,96,278] that the velocities v of the ions, their diffusion coefficients D, and the electric field strength E are in general constant at any point in the system at any instant t. A one-dimensional process is considered: i.e. the variables change only along the x-coordinate in the direction of the axis of the separating tube, whereas all parameters are invariable in a radial direction, perpendicular to x. All non-kinetic factors which may affect the separation (degree of dissociation of the electrolyte, association and complex formation by the ions, reactions involving precipitation of a solid phase or the evolution of gases, etc.) are disregarded by the general theory; if one or more such processes are superimposed on electrical migration, this is regarded as a more complex particular case and is considered specially. Electrode reactions are assumed not to affect the separation of isotopes, and the electrolyte in the electrode compartments is perfectly mixed.

Such idealisation of the conditions of the process makes the problem much simpler to solve, while introducing only minor errors into the final results. Furthermore, if particular details of this method are disregarded, other methods of separation—gaseous diffusion, thermal diffusion, chromatography, etc.—can be described by the same mathematics. The phenomenology of the countercurrent electrical migration of ions is the same, of course, in molten salts, aqueous solutions, and liquid metals.

Let the mixture of isotopes to be separated consist of mole fractions ${}^i\gamma$ of n components:

$$\sum_i^n {}^i\gamma = 1.$$

When the current is switched on, the components acquire velocities ${}^iv$ in the direction of the x-coordinate, the speed of each component being inversely proportional to the square root of its mass[279]. Thus directed movement in the electric field—electrical migration—is superimposed on the random thermal motion of the molecules of the liquid. The transport of components along the separating tube results in a concentration gradient $\partial {}^i\gamma/\partial x$, which leads to diffusion in the opposite direction to the movement of the ions. The relation between these two factors—migration in the electric field and diffusion and in the opposite direction—determines the total flux ${}^i\varphi$ of the component along the separating tube:

$${}^i\varphi = {}^i\gamma {}^iv - {}^iD\frac{\partial {}^i\gamma}{\partial x}. \qquad (1)$$

The more mobile components, overcoming the countercurrent of liquid, accumulate at the head of the tube, while the less mobile components are washed towards the other end. Since the rate of the countercurrent is equal to the mean speed of the ions, the mixture as a whole remains stationary with respect to the walls of the tube:

$$\sum_k^n {}^k\gamma {}^kv = 0. \qquad (2)$$

The concentration of the components undergo redistribution along the separating tube at the rates

$${}^iv = \sum_k^n {}^k\gamma ({}^iv - {}^kv). \qquad (3)$$

From the condition of continuity we can set up the differential equation

$$\frac{\partial {}^i\gamma}{\partial t} = -\frac{\partial {}^i\varphi}{\partial x} = -\sum_k^n ({}^iv - {}^kv)\frac{\partial {}^i\gamma {}^k\gamma}{\partial x} - \sum_k^n {}^i\gamma {}^k\gamma \frac{\partial ({}^iv - {}^kv)}{\partial x} + {}^iD\frac{\partial^2 {}^i\gamma}{\partial x^2}. \qquad (4)$$

for the process of countercurrent electrical migration.

Since the strength of the electric field and the speeds of the components are everywhere constant, the second term on the right-hand side of Eqn. (4) vanishes. The inevitable

mixing of the liquid in the cell as a result of convection and electro-osmosis can usefully be allowed for by introducing, instead of the molecular diffusion coefficients ${}^{i}D$, an effective diffusion coefficient or coefficient of intermixing $D' > {}^{i}D$. There is then no need to distinguish between the diffusion coefficients of the components, and Eqn. (4) simplifies to

$$\frac{\partial {}^{i}\gamma}{\partial t} = -\sum_{k}^{n} ({}^{i}v - {}^{k}v)\frac{\partial {}^{i}\gamma {}^{k}\gamma}{\partial x} + D'\frac{\partial^2 {}^{i}\gamma}{\partial x^2}. \quad (5)$$

For a system of n components we have thus established a set of n differential equations of type (5), which are mutually dependent.

No general method has been found for solving this set of equations, and therefore simplifying artifices are used. A particular case of an actual n-component system—a binary mixture of isotopes—is usually considered. Since a two-component model can be used to describe the separation of isotopes of polyisotopic elements [280], the method of solution is evidently applicable also in the general case. Denoting light and heavy components by the affixes "l" and "h", we obtain ${}^{h}\gamma = 1 - {}^{l}\gamma$, ${}^{l}\gamma = \gamma$, and ${}^{l}v - {}^{h}v = \Delta v$; and Eqn. (5) becomes [74,281]

$$\frac{\partial \gamma}{\partial t} = -\Delta v(1-2\gamma)\frac{\partial \gamma}{\partial x} + D'\frac{\partial^2 \gamma}{\partial x^2} \quad (6)$$

It can also be assumed [8,282] that all the isotopes in the mixture, with one exception, are so rare that their mole fractions remain very small at any instant, and we then have a set of n independent equations. When in particular $\gamma \ll 1$, we have instead of (6) the linear differential equation

$$\frac{\partial \gamma}{\partial t} = -\Delta v\frac{\partial \gamma}{\partial x} + D'\frac{\partial^2 \gamma}{\partial x^2} \quad (7)$$

Mason and Weaver [283] discovered a method for solving an equation of the type (7) in a study of the distribution of fine particles, suspended in a liquid, in a gravitational field. Konstantinov and Fiks [74] suggested a direct solution for countercurrent electromigration. A general solution of Eqn. (6) was first given by Majumdar [284] when developing a theory of the thermal diffusion column. The general principle of the solution of such equations, which has since been used by all authors, consists in introducing the dimensionless variables

$$\xi = \frac{\Delta v}{D'}x, \quad \tau = \frac{(\Delta v)^2}{D'}t \quad (8)$$

whose physical meanings correspond to a coordinate along the separating tube and the time, both expressed in terms of the process parameters Δv and D'. For example, substituting (8) in (6) and replacing variables

$$\gamma = \frac{1}{2} + \frac{1}{q}\frac{\partial q}{\partial \xi}, \quad (9)$$

where q is some function [281,284], will give an equation of the type

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial \xi^2}, \quad (10)$$

the method of whose solution is well known.

Solutions of equations of the type (6), (7), and (10) have been published for several actual cases of countercurrent electromigration. If the salt containing the separable isotopes is located entirely inside the separating tube and is bounded by other salts at both ends, the system is simulated by the problem of a tube of finite length L closed at both ends [67,74,265,266,283,284]. The initial condition represents uniform distribution of the components throughout the length of the separation zone $0 \leqslant x \leqslant L$ at $t = 0$. The boundary conditions correspond to the fact that the components remain within the separation zone throughout the experiment, i.e. that their fluxes are zero at both boundaries of the zone, which can be written e.g.

$$\gamma(x, 0) = \gamma_0, \ \varphi(0, t) = 0, \ \varphi(L, t) = 0, \quad (11)$$

where γ_0 is the mole fraction of the component in the initial isotopic mixture.

If one end of the separation zone is bounded by another salt inside the separating tube, while the other end expands into a sufficiently large electrode compartment, the zone can be simulated by the problem of a tube of finite length with one end closed and a reservoir of infinite capacity at the other end [246,284] or by the problem of a tube of semi-infinite length with one end closed [67,74,265,266,281,282]. In such a system the second boundary condition is that the isotopic composition of the salt at the point $x = L$ or ∞ respectively should at any time t be equal to the initial composition.

If the separation zone occupies the whole separating tube, terminating at one end in an electrode compartment of small capacity (from which an enriched product can be withdrawn), while the other end is joined to a large electrode compartment, as in the preceding case, the model problem involves a tube of semi-infinite length with a reservoir of finite volume at one end [67,285]. Initial and boundary conditions are the same as in the preceding system, but with the refinement that zero flux of the component occurs at the point $x = -L'$:

$$\gamma(x, 0) = \gamma_0, \ \varphi(-L', t) = 0, \ \gamma(L, t) = \gamma_0 \quad (12)$$

where $L' = V/A$ is the reduced length of the reservoir (electrode compartment) of finite volume V, and A is the cross-sectional area of the separating tube (if the tube is filled with a packing, A is the free cross-section). These problems in effect cover all concrete cases of the separation of isotopes in an electromigration cell.

A solution to the differential equation is in general found as a more or less rapidly converging series suitable for practical calculations:

$$\gamma = \gamma_0 f(\xi, \lambda, \eta, \tau), \quad (13)$$

where ξ and τ are defined by formulae (8), while λ and η are also dimensionless variables. Their physical meanings correspond to the length of the separating tube and the reduced length of the reservoir:

$$\lambda = \frac{\Delta v}{D'}L, \quad \eta = \frac{\Delta v}{D'}L' \quad (14)$$

For a tube of finite length terminating in a reservoir, for example, the solution is [67]

$$\gamma = \gamma_0 \exp\xi - \frac{8}{\lambda}\gamma_0\left(\exp\frac{\xi-\lambda}{2}\right)\sum_{s=0}^{\infty}\frac{\sinh\frac{r_s\lambda}{2}\sinh\frac{r_s\xi}{2}\exp\left[-\frac{1}{4}(1-r_s)^2\tau\right]}{\frac{2}{\lambda}-1+r_s+\frac{2}{\lambda}\frac{\frac{\eta}{2}\left(1+\frac{\eta}{2}\right)(r_s^2-1)}{\left(1+\frac{\eta}{2}\right)^2-\eta^2\frac{r_s^2}{4}}}, \quad (15)$$

where the rs are the roots of the equation

$$\tanh\frac{r\lambda}{2} = \frac{r}{1+\frac{\eta}{2}(1-r^2)} \quad (16)$$

Equation (15) enables the distribution of the isotopic components along the tube to be calculated for any instant. A similar type of solution is obtained for the other problems enumerated above.

It is sometimes convenient to choose the separation factor of two isotopes

$$S = \frac{\gamma(1-\gamma_0)}{\gamma_0(1-\gamma)} \qquad (17)$$

instead of the mole fraction γ of a component of the isotopic mixture, as the variable for which a solution to the differential equation is sought [281]. Equation (17) has been written for a binary mixture. If an element consists of more than two isotopes, the separation factor for any pair is a linear function of the difference between their masses [215-217,226,246]. A method has been given [280] for calculating the separation factors of all pairs of isotopes provided that the value of S for any one pair of the mixture is known. Solutions analogous to (15) are found for S.

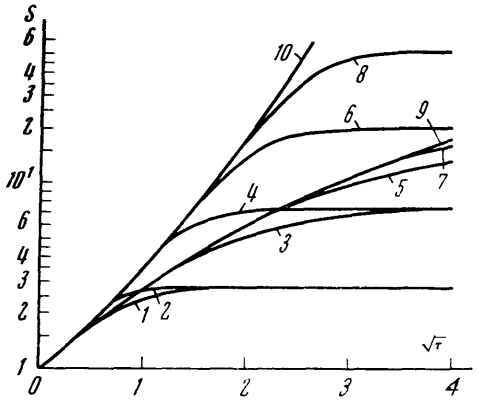


Figure 1. Dependence of separation factor S on time τ for separating tubes of different lengths λ with different initial mole fractions γ_0 of enrichable isotope [281]: 1) $\lambda = 1$, $\gamma_0 = 0$; 2) 1, 1; 3) 2, 0; 4) 2, 1; 5) 3, 0; 6) 3, 1; 7) 4, 0; 8) 4, 1; 9) ∞, 0; 10) ∞, 1.

Examination of expressions of the type (15) will give a theoretical description of the behaviour of an isotopic mixture during separation. Fig. 1 shows an example of such behaviour in separating tubes of various lengths, with one end closed and the other connected to an infinite reservoir [281]: it illustrates the dependence of S on $\tau^{1/2}$ for various reduced tube lengths λ. Initially enrichment follows an almost parabolic curve (Breit and Friedman [67] confirmed this by numerical calculations), and then it approaches a horizontal straight line asymptotically: it reaches a steady state.

For low values of τ the curve is described by the simple formula [281]

$$S = e^{2\sqrt{\tau/\pi}} \qquad (18)$$

i.e. initially the separation of an isotopic mixture is independent of the length of the separating tube. This holds provided that $L \geqslant 1.8(D'/|\Delta v|)\ln S$. Thus when τ is small we can put $\lambda = \infty$ in formulae of type (15), which greatly simplifies the calculations.

Fig. 1 shows that the rate of separation of the isotopes begins to diminish sooner the smaller is λ, i.e. the shorter the separating tube. If the closed end of the tube is replaced by a reservoir of limited volume, the overall rate of separation decreases: i.e. the corresponding $S-\tau^{1/2}$ curve is inclined at a larger angle to the horizontal axis than is the curve in Fig. 1. At $\tau = 0.002$, for example [67], the rates of accumulation of enriched isotope in the reservoir with $\eta = 0.1$ and 1 respectively are only one-third and one-tenth of the rate for $\eta = 0$.

An interesting feature is the dependence of the separation factor on the content of the enrichable isotope in the initial mixture: this is apparent in Fig. 1 in a "bifurcation" of the $S-\tau^{1/2}$ curves at quite large τ, but with the system still far from a steady state. Under otherwise similar conditions a given separation factor is attained more rapidly the richer was the initial mixture in the enrichable isotope [281,282]. For example, the time required to reach $S = 10$ with $\gamma_0 = 1$ is only one-third of the time required when $\gamma_0 = 0$. These are obviously limiting cases for the isotopic composition of a mixture, for in real materials $0 < \gamma_0 < 1$.

The "mean time" t_S required for a steady state to be established is given by the formula [74]

$$t_s = \frac{L^2}{\left(\pi^2 + \frac{\lambda^2}{4}\right)D'} \qquad (19)$$

Since $\frac{1}{2}\lambda \ll \pi$, we have [68,74] $t_S = L^2/\pi^2 D'$; a steady state is actually established [74,246] in the time $t \simeq 4t_S$. The maximum separation factor which can be achieved in the steady state is determined solely by the length of the tube [281]:

$$S_{st} = e^{\lambda}. \qquad (20)$$

Equations (18) and (20) are valid in the absence of withdrawals. If enriched material is removed at a rate p (in $cm^3\ s^{-1}$) from the head of the cell, the separation factor S_p is given by the formula [96]

$$\ln\frac{S_p}{S} = -\frac{v_p}{v_{cc}}(S-1)\frac{\gamma(0,t)}{\gamma(L,t)}, \qquad (21)$$

where $v_p = p/A$ (cm s^{-1}) is the speed of withdrawal, d_{cc} is the speed of the countercurrent of electrolyte in the separating tube, and $\gamma(0, t)$ and $\gamma(L, t)$ are the mole fractions of enriched isotope at the instant of withdrawal t at the head and at the opposite end of the tube. By integrating the equation of transport with continuous withdrawal

$$v_p\gamma_p = v'\gamma - D'\frac{d\gamma}{dx}, \qquad (22)$$

where γ_p is the mole fraction of the isotope in the product, while the rate of withdrawal of the isotope is related to its actual speed v' along the separating tube (i.e. v' is the rate of electrical migration minus the rate of diffusion in the opposite direction) by the expression

$$v_p = v'\gamma + (v' + \Delta v')(1-\gamma) \qquad (23)$$

(it is obvious $\Delta v' = \Delta v$), Klemm [167] obtained the formula

$$L = \frac{D'}{2\Delta v\sqrt{b^2 + \frac{v_p\gamma_p}{\Delta v}}}\ln\left[\frac{\gamma_p - b - \sqrt{b^2 + \frac{v_p\gamma_p}{\Delta v}}}{\gamma_p - b + \sqrt{b^2 + \frac{v_p\gamma_p}{\Delta v}}}\cdot\frac{\gamma_0 - b - \sqrt{b^2 + \frac{v_p\gamma_p}{\Delta v}}}{\gamma_0 - b + \sqrt{b^2 + \frac{v_p\gamma_p}{\Delta v}}}\right], \qquad (24)$$

where $b = \frac{1}{2}(1 - v_p/\Delta v)$. Substituting selected values for γ_p and v_p in Eqn. (24), together with values of Δv and D' determined by the actual conditions under which the process is conducted, we can find the length of tube L which is necessary for the withdrawal at a rate v_p of a product enriched to γ_p.

Accumulation of the enriched isotope is most rapid in the absence of withdrawal at the closed end of the separating tube or—rather slower—in a small reservoir. The content of the isotope also increases with time in the adjacent region of the tube, but a specified separation factor is reached here with some delay, which is greater the further the point from the end of the tube. In other words, the region of enrichment gradually extends from the end of the tube to its midpoint, reaching the latter in time $t_{1/2} = L^2/\pi D'$; at the same time impoverishment of the mixture with respect to this isotope takes place in the other half of the tube. The distribution of isotopes along the tube at time t is given by formulae of type (15). In particular, in the steady state

$$\gamma(\xi, \infty) = \gamma_0 e^{\xi} \tag{25}$$

It is easily seen that Eqn. (20) is a particular case of (25).

By time t the region of enrichment has extended to a distance

$$x' = \sqrt{\pi D' t}, \tag{26}$$

from the end of the tube[281,282], provided that the tube has no reservoir at its head. The presence of a reservoir of reduced length L' has little effect[285] on x', which remains proportional to $(D't)^{1/2}$, the coefficient of proportionality being $\pi^{1/2} = 1.77$ or $8/3\pi^{1/2} = 1.5$ according as $L' \ll$ or $\gg (D't)^{1/2}$.

Expanding Eqn. (18) as a series and neglecting powers higher than the first, we obtain for small values of τ the relation[278]

$$\gamma = \gamma_0\left(1 + 2\frac{\Delta v}{v} \cdot \frac{vt}{\sqrt{\pi D' t}}\right) \tag{27}$$

where v is the mean velocity of ions of the element in an electric field of strength E. Thus in the initial stage of the process the accumulation of the isotope $N(\gamma - \gamma_0)$ over the initial quantity, where N is the total number of equivalents of the element in the region of enrichment x', is proportional to the migration path vt and inversely proportional to the diffusion path $(\pi D't)^{1/2}$.

The quantity $\Delta v/v$ in Eqn. (27)—the relative difference in rates of migration of the isotopic ions—is independent of the operating parameters of the process and is directly related to the mechanism of separation. It represents the theoretical efficiency of countercurrent electrical migration, and determines the single-stage separation factor by this method

$$1 + \frac{\Delta v}{v} = 1 + \frac{\Delta w}{w} = 1 + \varepsilon = \alpha, \tag{28}$$

where $w = v/E$ is the mobility of the ions, i.e. their velocity in an electric field $E = 1$ V cm^{-1}.

Expressing the enrichment factor ϵ in terms of the relative difference between the mobilities of the isotopic ions $\Delta w/w$—not the difference in their speeds $\Delta v/v$—makes it unnecessary to allow for the effect of the variable E and enables an objective characteristic of the method ϵ to be assigned to standard conditions. In this respect a still more useful characteristic is the mass effect suggested by Klemm[68,282]

$$\mu = \frac{\Delta w}{w} \Big/ \frac{\Delta m}{m}, \tag{29}$$

where $\Delta m = {}^{j}m - {}^{k}m$ and $m = \frac{1}{2}({}^{j}m + {}^{k}m)$, which enables the efficiency of the method to be assessed independently of the number of atomic mass units distinguishing the isotopes j and k. If j and k are respectively a light and a heavy isotope, we have $\Delta w = {}^{l}w - {}^{h}w > 0$ and $\Delta m = {}^{l}m - {}^{h}m < 0$, so that the mass effect is always negative.

Taking into account the quantity of electricity transported in time t through a cross-section of the separating tube

$$Q = \frac{NF}{x'} vt, \tag{30}$$

where F is Faraday's constant, we obtain from Eqns. (26) and (27) the expression

$${}^{jk}\varepsilon = \frac{\Delta {}^{jk}w}{w} = -\left(\frac{{}^{j}\gamma}{{}^{j}\gamma_0} - \frac{{}^{k}\gamma}{{}^{k}\gamma_0}\right)\frac{FN}{Q} \tag{31}$$

for the relative difference in the mobilities of the two isotopes[282]. A method has been published[8,192] for assessing the accuracy of the calculation of ϵ by means of Eqn. (31).

Equation (31) is easily converted into a form which is convenient for practical calculation of the mass effect[200]:

$$\mu = \frac{Fz}{MQ} \cdot \frac{m}{\Delta m} \cdot \frac{1}{\gamma_0(1-\gamma_0)} \sum_r G_r(\gamma_r - \gamma_0), \tag{32}$$

where z is the valency of the isotopic ions, M the molecular weight of the salt, r the serial number of one of the specimens into which the separating tube is cut after electrolysis has ceased and the melt has solidified (see subsection 2), G_r is the weight of salt in the rth specimen, and the summation is made over all specimens r in which isotopic analysis has detected enrichment with a given isotope. This formula (32) applies to elements consisting of two isotopes. If an element comprises n isotopes, the mass effect can be calculated for the jth and kth isotopes by means of the equation[214]

$${}^{jk}\mu = \frac{Fz}{MQ^{j}\gamma_0} \cdot \frac{m}{\Delta m} \sum_r \frac{G_r({}^{jk}R_r - {}^{jk}R_0)}{\sum_i^n {}^{ik}R_r}, \tag{33}$$

where ${}^{ik}R_r = ({}^{j}\gamma/{}^{k}\gamma)_r$ is the ratio of the contents of these isotopes in the rth specimen, and

$$[m = \sum_i^n {}^{i}\gamma_0 {}^{i}m --$$

is the atomic weight of the element.

The overall and the single-stage separation factors, S and α, are related by the formula

$$S = \alpha^q \tag{34}$$

where q is the number of theoretical plates realised in the region of enrichment. The function q in Eqn. (9) has this physical meaning. The quantities x' and q are interrelated by the height of an equivalent theoretical plate:

$$h = \frac{x'}{q} \tag{35}$$

According to Westhaver[66] the physical meaning of h in countercurrent electrical migration is the length of the separating tube in which the isotopic ratio ${}^{jk}R$ changes by a factor α. This author discussed in detail[66] theoretical methods for estimating h and D'. The practical calculation of h can be based on data obtained when a steady-state is reached. Since α differs very little from unity, it follows from Eqn. (34) that $\ln S = q\ln(1+\epsilon) = q\epsilon$, when substitution for q in (35) yields for the steady state

$$h = \frac{L\varepsilon}{\ln S_{st}} \tag{36}$$

It follows from Eqns. (14) and (20) that $L/\ln S_{st} = D'/\Delta v$, and substitution in (36) gives

$$h = \frac{D'\varepsilon}{\Delta v} = \frac{D'}{v} \tag{37}$$

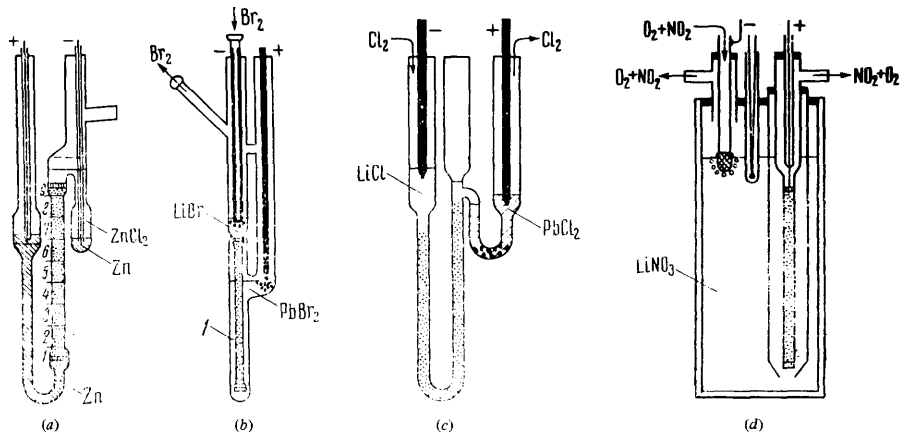


Figure 2. Cells used in the application of countercurrent electrical migration to the enrichment of: *a*) ^{35}Cl in molten $ZnCl_2$ (the numbering 1–9 indicates the specimens into which the separating tube is cut for chemical and isotopic analyses after the experiment)[8]; *b*) ^{7}Li in molten LiBr (*1* = boundary between LiBr and $PbBr_2$)[164]; *c*) ^{7}Li in molten LiCl;[162] *d*) ^{7}Li in molten $LiNO_3$.[192]

i.e. the height of an equivalent theoretical plate is smaller the smaller is D' and the greater the rate of migration of ions in the separating tube.

2. Apparatus and Method of Operation under Laboratory Conditions

Fig. 2 shows typical designs of cells for electrical migration under laboratory conditions. The cell is made of quartz or heat-resistant glass (Vycor, Supremax, Pyrex), the choice of material depending on the operating temperature and the corrosiveness of the molten salt. It consists mainly of a vertical cylindrical (*a*, *b*, *d*) or U-shaped (*c*) separating tube. Conical separating tubes have been suggested[192,203] to provide a better countercurrent and a higher current density transported by the enriched isotope; this increases the efficiency of separation of the isotopes provided that $(r_1r_2)^{1/2} < r$, where r_1 and r_2 are the radii of upper and lower portions of the conical tube, and r is the radius of a cylindrical tube of the same volume.

The separating tube is filled with a packing satisfying certain requirements—mechanical and thermal stability, chemical resistance to the molten salt, and the maximum possible thermal conductivity—in order to prevent mixing of the melt by convection currents. The packing materials usually employed are ground glass or quartz, from which the cell itself is made, and also alundum, steatite, zirconium oxide, zircon, and zirconyl phosphate. The packing should first have been carefully freed from traces of organic compounds and metallic particles by being boiled in acid or heated in a current of chlorine, washed with water, and dried. The free volume of a packed separating tube is 35–45% of the volume of the empty tube and depends on the uniformity of the particles with respect to shape and size, not on their coarseness. The "electrical free space" constitutes 70–80% of the geometrical free space, since the ions are unable to move in straight lines, but have to pass through pores between packing grains ("labyrinth effect"): in ignited asbestos, for example, the path traversed by the ions is on the average 30% longer than the straight line between the electrodes[14]. The efficiency of separation is independent of the material of the packing, but becomes higher as the latter becomes finer. Since at the experimental temperature the density of the packing may be comparable with that of the melt, the packing is placed between porous glass or quartz filters (frits) sealed into both ends of the separating tube, in order to prevent the packing from floating to the surface or being loosened by gases evolved from the melt with the formation of longitudinal channels. Details of the design of the cells and of the part played by the packing have been fully discussed by Lundén[8]. A theoretical analysis of the hydrodynamic flow of an electrolyte through a packed separating tube and of various effects on the separation factor was made by Westhaver[66].

A fundamentally different design of cell has also been proposed and studied for work with molten salts[20]: a horizontal separating tube without packing is divided by frits into a series of successive compartments, in which the melt mixes freely (Fig. 3). The advantages of such a design have been considered for aqueous solutions[27,91–93], and the conclusions reached are valid also for molten salts.

Intense movement of the liquid takes place in the separating tube during electrolysis. This results in a shift in the levels of the melt in the electrode compartments relative to their original position (Fig. 2*a*), and may even cause a break in contact between the salt and the anode[163]. Various methods are used to control the levels of the melt in the electrode compartments: the initial salt may be added to the anode compartment and excess of the melt overflows from the cathode compartment[200,219,233]; excess pressure is produced in the cathode compartment by means of an inert gas[160,214]; etc. With a correct choice of current density and in the absence of breaches in the packing, no displacement of the electrolyte relative to the cell is observed, although the components of the mixture undergo continuous separation as a consequence of mutual displacement of the molecules. This constitutes one of the advantages of the countercurrent method over

movement of a zone, e.g. in electrophoresis on a paper support: with a short distance between the electrodes the separable species, in overcoming the counterflow of electrolyte, traverse a very long path, which ensures high separation factors. Thus in an experiment with cadmium chloride in a tube ~ 20 cm long the displacement of the cations relative to the anions was estimated[217] to be 3 m, and in a prolonged experiment with thallium(I) chloride about 18 m[219].

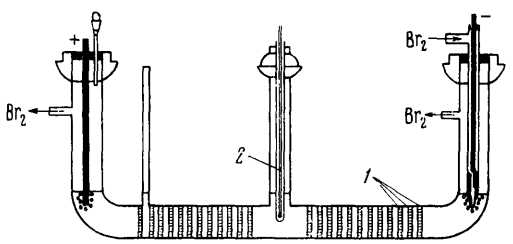


Figure 3. Horizontal cell[20] without packing: 1) porous sintered-glass discs; 2) thermocouple.

Electrical migration must be arranged in such a way that the components do not leave the separation zone, e.g. as a result of electrode reactions. This is ensured in two ways. The first method consists in neutralising the products of the electrode reaction and regenerating the original salt in the electrode compartment. Metals deposited on the cathode in molten halides are continuously oxidised by gaseous chlorine or by bromine or iodine vapour in a current of argon, entering the cathode compartment through either a special tube or a hollow cathode (special investigations have been made[8,20,163,184] to elaborate a cathode); a current of nitrogen dioxide, alone or mixed with oxygen, or of the vapours from fuming nitric acid is used for this purpose in molten nitrates. The quantity of oxidising gases supplied should always be considerably larger than stoichiometric to ensure saturation of the melt in the cathode compartment; otherwise, corrosive metals, especially alkali metals, will rapidly put the electrodes and the walls of the cell out of action. The results of many experiments have shown that the most corrosion-resistant materials for cathodes are graphite and carborundum with halides, and aluminium and stainless steel with nitrates; the most corrosion-resistant anodes are made of carbon and graphite for halides, and of platinum for nitrates, while gold anodes have been used with sulphates[193,236-238]. Data on the stability of various materials in molten salts and metals have been compiled in Ref. 286 and in standard tables[287].

Molten metal anodes can be used in the separation of isotopic anions, with tungsten wires as conducting electrodes (leads). Thus in the separation of chlorine isotopes[9,229,230] molten lead or zinc dissolves to form the corresponding chloride, so that chlorine does not leave the separation zone, and enrichment with the light isotope ^{35}Cl takes place gradually at the salt–metal interface. The same procedure is used in the separation of bromine isotopes[234,235]. If the opposite process—deposition of metal from the salt—takes place at the cathode, the molten salt remains held between two regions of molten metal—cathodic and anodic—and the only apparent result is the transport of metal from anodic to cathodic compartments (Fig. 2*a*), with no evident separation of isotopes. Liquid metals—lead, zinc, mercury—have sometimes been used as cathodes also in the separation of alkali-metal isotopes[8,193], but the alkali metal then underwent reduction and formed an alloy with the metal of the cathode, so that ions were removed irreversibly from the separation zone, and played no part in the subsequent process. Lundén has made a detailed study of this method[238,288,289].

The second method of retaining the components in the separation zone is to exclude any contact between the separable species and the electrode. This is accomplished by placing an ancillary salt, having the same gegenion as the working salt, between the latter and the electrode (Fig. 2*b*). A sharp boundary is formed between the two salts, which is especially noticeable when the salts differ in colour or have sufficiently differing refractive indices. The relative positions of the salts in the separating tube are determined by the ratio of their densities at the temperature of the experiment (to avoid mechanical mixing the denser salt should be below the boundary, which is the main factor governing the form of tube chosen) and by the relative mobilities of unlike ions (e.g. the salt having the more mobile cation should be located closer to the cathode). The common ion passes freely through the boundary, which is the only obstacle to the unlike ions: in fact, the more mobile the ions of the salt the higher its conductivity and the weaker the electric field on that side of the boundary; when, therefore, the "foreign" ion, which may be e.g. less mobile, penetrates the boundary into the zone occupied by the salt, it immediately begins to move more slowly than in its "own" salt, lags behind the ions of the first salt, and returns back through the boundary. However, this mechanism is not sufficiently effective with small differences in mobility between the ions, and the boundary between the salts remains blurred or "diffuse". If necessary the working salt can be bounded by other salts at both ends: relative densities and conductivities must satisfy the above requirements for both salt pairs forming the two boundaries. Conditions for the production of a boundary between molten salts and its behaviour have been surveyed[165]. A boundary is an excellent indicator of movement of the salts along the separating tube, and is often used to measure various characteristics of the salt systems.

Special precautions are necessary when filling the cell with the salts: no bubbles of air or other gases should remain in the separating tube; hygroscopic salts should absorb as little moisture as possible during filling; and the free surface of molten metal electrodes should not be oxidised before contact has been established with the molten salt. Filling is therefore conducted either under a vacuum or in an atmosphere of an inert gas; if necessary the initial position of the zone of the working salt in the separating tube is controlled by producing a difference in gas pressure between the electrode compartments.

The choice of conditions of electrolysis is dictated by the aims of the experiment. The design of the furnace should ensure that the thermal field inside it is as uniform as possible and is constant with time. The minimum working temperature is determined by the melting point of the most refractory of the salts used, and the maximum working temperature by the volatility of the salts and the temperature at which the glass of the cell begins to soften. In practice a vertical temperature gradient along the cell cannot be avoided, especially if the separating tube is not

immersed in a melt but is surrounded by air. Furthermore, the heating effect of the electric current produces a radial temperature gradient in the tube: special measurements have established that the difference in temperature between the centre of the tube and its outer wall may reach 200 deg in individual cases[231]. The electric field in the separating tube should be as strong as possible, but there is always an upper limit to the current, depending on the thermal conductivity of the salts and the materials of the cell: if the current density is too high, regions of local overheating appear in the packing, which may cause serious disturbances of the process and even the need to discontinue the experiment. In measurement of the electrical transport characteristics of salts the duration of an experiment is usually a few days, but with lithium salts 10–12 h is sufficient for isotopic effects to be measured by modern methods of analysis. Nevertheless, reliable means of measurement and automatic control have been developed which enable the process to be conducted continuously for several months or years in order to obtain the necessary quantity of enriched material.

The progress of electrical migration is monitored by means of electrical measuring instruments and also visually, by observing that no visible disturbances occur in the cell (a stationary boundary between the salts in the separating tube is often a convenient indication of the steady occurrence of the process), for which purpose the cell is placed in a vertical tubular electric furnace made of transparent fused quartz. The results of the separation are evaluated by studying the distribution of the components along the tube after the experiment. For this purpose the cold separating tube is divided into lengths of 1–1.5 cm, and chemical and isotopic analyses are made on every sample. Sometimes the accumulation of an isotope in the electrode compartment is observed by withdrawing after a certain time a sample of the molten salt for analysis.

3. Experimental Conditions for and Results of the Separation of Isotopes

Data on all published molten salt systems in which countercurrent electrical migration has been studied are compiled in Table 1. Certain data on electrical migration in solid salts, aqueous solutions, and liquid metals are included for comparison.

Table 1 shows that, for isotopes of the same element, the mass effect depends on the medium in which electrical migration is conducted: in solid and molten salts $\mu \simeq 10^{-2}$; in aqueous solutions it is usually 20–30% of its value in melts (for uranium isotopes the mass effect is larger in solutions than in melts, apparently because of the superimposition of the isotope effect of exchange between different species present in solution); in liquid metals $\mu \simeq 10^{-5}$; and in solid metals the mass effect is extremely small. Metals are clearly of no interest as media for the practical separation of isotopes. Solid salts will evidently also find no application, for it is impossible to accomplish a countercurrent process (but see Ref. 156 to 158). Solutions of salts in water and other solvents continually attract attention by the convenience and safety of their use for enrichment and by the simplicity of the apparatus, but a substantial defect is the considerable consumption of energy in the "useless" transport of the solvate sheaths together with the ions. Thus molten salts are the most suitable media for the separation of isotopes by the electrical migration of ions.

Despite several experimental difficulties (high temperature, restricted choice of materials resistant to the corrosive action of melts, and with several elements the absence of salts of sufficiently high electrical conductivity which do not undergo thermal decomposition), electrical migration in molten salts has definite advantages: maximum mass effects are accompanied by a far wider temperature range for molten salts, which makes artificial cooling of the separating tube unnecessary (with aqueous solutions this is required to avoid their boiling), while the heat produced by the passage of the electric current through the melt makes a substantial contribution to the thermal balance and may completely eliminate the need for additional heating of the melt[167]; a countercurrent of electrolyte is far easier to provide in molten salts than in solutions; and molten salts are liquids having the maximum concentration of separable isotopes (apart from liquid metals), which ensures a higher yield of product from apparatus of a given size.

4. Separation of Isotopes in Large-scale Plant

In laboratory apparatus, where working with small quantities of material involves a small consumption of energy, the tendency is to achieve maximum enrichment is as short time as possible, which determines the design of cells and the choice of experimental conditions. The organisation of large-scale production involves the solution of a large complex of engineering problems, consideration of which is beyond our scope, as well as economic problems. In the present subsection we shall deal only with a few questions of principle.

The design of industrial equipment is similar to that shown in Fig. 2*d*: vertical separating tubes, into which electrodes are inserted from above, are lowered into a molten-salt bath. The advantages of this design[192] are that the separating tube can be moved vertically to control the countercurrent of electrolyte (e.g. with very compact packing, of grain diameter < 0.1 mm, the rate of flow of the melt in the tube is so diminished that its level in the anode compartment should be 3–5 cm below the level of the melt in the bath in order to create additional hydrostatic pressure), the temperature gradient along the separating tube becomes negligible owing to the intense convection in the bath, and the separating tubes are easily replaceable and simple in construction. A substantial disadvantage, however, is the unavoidable diffusion of ions through the walls of the tube, intensified by the electric field (direct experimental evidence of such a process has been provided[101]), which may considerably diminish or even eliminate altogether the effect of separation of the isotopes, so that the choice of material for the separating tube and the thickness of its walls are of decisive importance. Thus in the separation of calcium isotopes the necessary enrichment was ensured only by use of tubes made of several varieties of alumina[213].

If light isotopes are to be concentrated, a cathode of suitable design is immersed in the electrode compartment of the separating tube, and several anodes are arranged symmetrically around the tube, in such a way that the bath forms the anode compartment of the installation[184]. When a steady state is reached, enriched material is withdrawn regularly from the cathode compartment of the tube, and an equivalent quantity of the initial salt is added to the

Table 1. Experimental conditions and results for the separation of isotopes by countercurrent electrical migration*.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
1	^{6}Li—^{7}Li MS	U, Supr 22, 5/4 quartz 0.1	— C | $PbCl_2$ | LiCl + KCl | $PbCl_2$ | C (Cl_2) + 98 mole %	62	500	$8.65\cdot10^4$	650	48	^{7}Li/^{6}Li 12.3 → 13.7/44.3	1.0208	0.135	159
2	^{6}Li—^{7}Li MS	U, Supr 27/5.5 quartz 0.13	— C (Cl_2) | LiCl | C (Cl_2) +	—	500	$1.82\cdot10^5$	650	101	% ^{6}Li 7.3 → 16.1/—	—	—	160
3	^{6}Li—^{7}Li MS	U, Supr 20/-	— C (Cl_2) | LiCl | $PbCl_2$ | C (Cl_2) +	—	730	$1.17\cdot10^6$	—	—	% ^{6}Li 7.3 → —/0.1 (2 cm^3)	—	—	162
4	^{6}Li—^{7}Li MS	U, Supr. 20/- ZrO_2 0.12—0.15	—C (Cl_2) | LiCl | LiCl + $PbCl_2$ | $PbCl_2$ | C (Cl_2) + 100 mole %	—	500	$3.96\cdot10^4$	650	22	% ^{6}Li 7.24 → —/3.81	1.0222	0.144	165
5	ditto	ditto	54 mole %	—	500	$8.32\cdot10^4$	650	46.6	% ^{6}Li 7.24 → —/4.68	1.0182	0.118	165
6	»	»	25 mole %	—	500	$3.96\cdot10^4$	650	22	% ^{6}Li 7.24 → —/1.77	1.0192	0.125	165
7	»	»	12.6 mole %	—	500	$2.27\cdot10^4$	650	12.6	% ^{6}Li 7.24 → —/3.20	1.0344	0.224	165
8	»	»	10.9 mole %	—	500	$1.98\cdot10^4$	650	11	% ^{6}Li 7.24 → —/1.39	1.0356	0.231	165
9	»	»	5.3 mole %	—	500	$1.80\cdot10^4$	650	10	% ^{6}Li 7.24 → —/5.78	1.0454	0.295	165
10	^{6}Li—^{7}Li MS	U, Supr.30/4 Al_2O_3 0.1	— C (Cl_2) | LiCl | C (Cl_2) +	—	—	$5.4\cdot10^4$	674	—	^{7}Li/^{6}Li 12.3 → —/17.4	1.0215	0.140	195
11	ditto	ditto	ditto	—	—	$7.2\cdot10^4$	732	—	^{7}Li/^{6}Li 12.3 → —/17.1	1.0194	0.126	195
12	»	U, quartz 30/4 Al_2O_3 0.1	»	—	—	$5.2\cdot10^4$	843	—	^{7}Li/^{6}Li 12.3 → —/16.6	1.0265	0.172	195
13	»	ditto	»	—	—	$5.8\cdot10^4$	895	—	^{7}Li/^{6}Li 12.3 → —/26.6	1.0293	0.190	195
14	^{6}Li—^{7}Li MS	V, Supr 30/8 Al_2O_3— 30/8	— C (Cl_2) | LiCl | C (Cl_2) +	100	2360	$3.74\cdot10^5$	650	44	% ^{6}Li 7.4 → 10.5/— (2.5 g)	—	—	184
15	ditto	ditto 30/18	ditto	100	7620	$1.83\cdot10^6$	650	67	% ^{6}Li 7.4 → 19.5/— (30 g)	—	—	184
16	»	» 30/12	»	100	4530	$3.96\cdot10^5$	650	24	% ^{6}Li 7.4 → 15.4/— (6 g)	—	—	184
17	»	» 30/15	»	100	6550	$2.74\cdot10^6$	650	116	% ^{6}Li 7.4 → 29.2/— (6 g)	—	—	184
18	»	» 30/30	»	100	13400	$2.63\cdot10^6$	650	55	% ^{6}Li 7.4 → 15.8/— (15 g)	—	—	184
19	^{6}Li—^{7}Li MS	V, Supr 25/3, 9 supr. 0.15–0.20	— C (Br_2) | LiBr | $PbBr_2$ | C (Br_2) +	110	239	$1.94\cdot10^4$	590	14.3	^{7}Li/^{6}Li 12.5 → —/45.30	1.0401	0.261	164
20	^{6}Li—^{7}Li MS	V, Supr 24/4 supr 0.15–0.20	— C (Br_2) | LiBr | $PbBr_2$ | C (Br_2) +	65	194	$4.9\cdot10^3$	565	7	^{7}Li/^{6}Li 12.32 → —/18.18	1.0214	0.139	173
21	ditto	ditto	ditto	155	239	$1.24\cdot10^4$	590	14.3	^{7}Li/^{6}Li 12.48 → —/45.30	1.0206	0.134	174
22	»	»	»	95	250	$1.48\cdot10^4$	565	164.7	^{7}Li/^{6}Li 12.09 → —/1162 ±26	—	—	174
23	^{6}Li—^{7}Li PC	U, Supr 24/4, 3 supr 0.20–0.25	— C | Pb | $PbBr_2$ | LiBr | $PbBr_2$ | C (Br_2) +	108	295	$8.56\cdot10^3$	580	81	^{7}Li/^{6}Li 12.28 → —/26.05	—	—	174
24	ditto	ditto	ditto	72	192	$3.66\cdot10^4$	560	53.1	12.35 → —/156.0	1.0242	0.157	173,174
25	»	»	»	120	172	$5.02\cdot10^4$	575	81	12.42 → —/41.24	1.0202	0.131	173,174
26	^{6}Li—^{7}Li MS	U, Pyrex 22/13 zircon 0.18	— C (Br_2) | LiBr | C (Br_2) +	20	480	$1.12\cdot10^5$	570	65	^{7}Li/^{6}Li 11.88 → —/14.54 (11.3 g)	1.0270	0.175	20
27	ditto	ditto	ditto	20	400	$1.10\cdot10^5$	570	77	11.84 → —/14.66 (10.2 g)	1.0263	0.171	20
28	^{6}Li—^{7}Li MS	U, Pyrex 16/- zircon 0.1	— C (Br_2) | LiBr + NaBr | C (Br_2) + 78 wt.%	25	600	$2.52\cdot10^6$	540	720	^{7}Li/^{6}Li 12.57 → 9.82/80.0 (7.6 cm^3) (5.3 cm^3)	—	—	178,180
29	ditto	ditto 26/8	— C (Br_2) | LiBr + KBr | C (Br_2) + 68 wt.%	70	700	$3.63\cdot10^6$	450	1008	^{7}Li/^{6}Li 11.7 → 6.6/3500 (8 cm^3) (1.14 cm^3)	—	—	178,180
30	^{6}Li—^{7}Li MS	U, Pyrex- zircon-	— C (Br_2) | LiBr + KBr | C (Br_2) +	—	—	—	500	4320	% ^{7}Li 92.7 → —/99.97	—	—	182
31	^{6}Li—^{7}Li MS	U, Pyrex 10/8 zircon 0.5	— C (Br_2) | LiBr + KBr | C (Br_2) + 70 mole %	—	165	$1.91\cdot10^5$	500	720	^{7}Li/Li^6 11.7 → —/22.4	—	—	183,186

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
32	^{6}Li—^{7}Li MS	U, Pyrex 21, 8/10 zircon 0.18	— C (Br_2) | LiBr + KBr | C (Br_2) + 51 wt.%	45	550	$4.32 \cdot 10^6$	450	2180	^{7}Li/^{6}Li 10.5, → 8/3000 (18.5 cm^3) (0.7 cm^3)	—	—	20
33	ditto	ditto 22/13	ditto	54	1600	$1.66 \cdot 10^7$	500	2880	0.50 → 0,33/35 (86 cm^3)	—	—	20
34	»	ditto	»	54	1600	$7.91 \cdot 10^6$	500	1200	1,94 → 0,053/40 (4 cm^3)	—	—	20
35	»	»	— C (Br_2) | LiBr + KBr | C (Br_2) + 50 wt.%	50	400	$5.72 \cdot 10^4$	450	40	12,07 → /13.68 (3.58 g)	1.0193	0.125	20
36	»	»	ditto	40	400	$9.38 \cdot 10^4$	450	65	11.85 → /13.72 (4.84 g)	1.0181	0.118	20
37	»	»	— C (Br_2) | LiBr + KBr | C (Br_2) + 57 wt.%	35	420	$1.32 \cdot 10^5$	570	88	11.70 → —/14.20 (6.22 g)	1.0200	0.130	20
38	^{6}Li—^{7}Li MS	V, Pyrex- ZrO_2-	— C (Br_2) | LiBr + KBr | C (Br_2) + 58.5 wt.%	—	165	$1.91 \cdot 10^5$	500	321.6	^{7}Li/^{6}Li 12.20 → —/46.9	—	—	197
39	^{6}Li—^{7}Li MS	H, Pyrex, 24 frits diam. 40 mm	— C (Br_2) | LiBr + KBr | C (Br_2) + 52.5 wt.%	39	8500	$2.34 \cdot 10^7$	510	1060	^{7}Li/^{6}Li 13.3 → 6.85/26 (212 g) (212 g)	—	—	20
40	^{6}Li—^{7}Li MS	U, Supr 24/4.3 supr 0.20–0.25	— C | Pb | PbI_2 | LiI | PbI_2 | C (I_2) +	112	191	$9.6 \cdot 10^3$	470	14.0	^{7}Li/^{6}Li 12.35 → — /22.14	1.0235	0.153	173,174
41	ditto	ditto	ditto	160	183	$8.11 \cdot 10^3$	475	12,3	ditto → — /18,01	1.0126	0,082	174
42	ditto	ditto 22/3.4	ditto	140	73	$8.10 \cdot 10^3$	480	30,8	ditto → — /26,14	1.0225	0.146 / 0,15[5]	174
43	^{6}Li—^{7}Li MS	Quartz membrane 0.2 mm thick	— Pt | KBr + NaBr | SiO_2 | LiBr | Pt (Br_2) +	30	2.5	225	770	5	^{7}Li/^{6}Li 14,4 → 13.3 / —	—	0.5[6]	181
44	ditto	ditto	ditto	5	2.2	40	810	5	ditto → 13.2 / —	—	0.5[6]	181
45	ditto	»	—Pt|KNO_3+$NaNO_3$| SiO_2| $LiNO_3$ |Pt(NO_3+O_2)+	2500	0.03	8	350	72	^{7}Li/^{6}Li 12,1 → 11.1 / —	—	0.5[6]	181
46	ditto	»	ditto	35	0.07	12	510	48	ditto → 11.05 / —	—	0.5[6]	181
47	^{6}Li—^{7}Li MS	V, Supr 26/4.5 quartz 0.1–0.12	— Fe (NO_2 + O_2) | $LiNO_3$ | Pt (NO_3 + O_2) +	76	173	$2.99 \cdot 10^4$	300	48	% ^{6}Li 7.40 → — /6.09	1.0087	0.057	163
48	^{6}Li—^{7}Li MS	V, Supr 22/4 quartz 0.2–0.25	— Fe (NO_2 + O_2) | $LiNO_3$ | Pt (NO_3 + O_2) +	150	243	$6.55 \cdot 10^4$	270	74	% ^{6}Li 7.40 → 7.68/6,05	1.0084	0.055	196
49	ditto	ditto	ditto	—	—	$2.03 \cdot 10^4$	320	28.8	—	1.0139	0,0906	196
50	»	»	»	—	—	$8.82 \cdot 10^3$	315	12.1	—	1.0119	0,0774	196
51	»	»	»	—	—	$2.04 \cdot 10^4$	320	21.2	—	1.0131	0.0848	196
52	»	»	»	—	—	$1.97 \cdot 10^4$	313	23.4	—	1.0135	0.0875	196
53	»	»	»	—	—	$1.72 \cdot 10^4$	326	23,2	—	1.0121	0.0789	196
54	»	»	»	—	—	$1.88 \cdot 10^4$	412	24,1	—	1.0127	0.0826	196
55	»	»	»	—	—	$1.75 \cdot 10^4$	429	24.0	—	1.0136	0.0880	196
56	»	»	»	—	—	$1.74 \cdot 10^4$	487	24.0	—	1.0070	0.0456	196
57	»	»	»	—	—	$7.56 \cdot 10^4$	339	9.5	—	1.0099	0.0643	196
58	»	»	»	—	—	$7.06 \cdot 10^3$	411	9.7	—	1.0138	0.0897	196
59	»	»	»	—	—	$4.61 \cdot 10^3$	488	6.5	—	1.0132	0.0856	196
60	^{6}Li—^{7}Li MS	U,quartz -/18 quartz 0.85	— Fe (NO_2 + O_2) | $LiNO_3$ | Rh (NO_2 + O_2) +	34	380	$5.5 \cdot 10^5$	280	402	^{7}Li/^{6}Li 12.69 → — /1349	—	—	161
61	ditto	U, quartz -/9 Al_2O_3 1.0	ditto	125	1000	$1,2 \cdot 10^5$	280	200	12,69 → 11.11/21.22	—	—	161
62	^{6}Li—^{7}Li MS	V, Vycor 12/4 quartz 0.1–0.15	— Fe (NO_2 + O_2) | $LiNO_3$ | Pt (NO_2 + O_2) +	60	60	$1,03 \cdot 10^4$	265	48	^{7}Li/^{6}Li 12.31 → — /28.80	1.0120	0.0782	192
63	ditto	ditto	ditto	40	100	$1.77 \cdot 10^4$	310	48	12.54 → — /30.34	1.0110	0.0713	192
64	»	»	»	48	90	$1.70 \cdot 10^4$	340	52	12.54 → — /21.62	1.0110	0.0712	192
65	»	»	»	42	95	$1.69 \cdot 10^4$	365	50	12.53 → — /26,06	1.0113	0.0733	192

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
66	^{6}Li—^{7}Li MS	V, Vycor 12/4 quartz 0.1–0.15	— Fe ($NO_2 + O_2$) | $LiNO_3$ | Pt ($NO_2 + O_2$) +	45	100	$1.75 \cdot 10^4$	365	47	12.40 → — /28.70	1.0112	0.0726	192
67	»	»	»	42	90	$1.64 \cdot 10^4$	415	52	12.53 → — /25.78	1.0103	0.0668	192
68	»	»	»	80	80	$1.37 \cdot 10^4$	460	48.5	12.31 → — /20.71	1.0103	0.0671	192
69	»	U, quartz 9/4 ZrPh 0.1–0.15	»	40	130	$1.16 \cdot 10^4$	300	25	12.40 → — /17.26	1.0089	0.0578	192
70	»	ditto	»	40	120	$1.29 \cdot 10^4$	290	30	12.40 → — /14.97	—	—	192
71	»	V, Vycor 12/4 quartz 0.1	»	85	59	$9.72 \cdot 10^4$	320	465	12.47 → — /473	—	—	192
72	»	ditto 12/5	»	100	72	$2.37 \cdot 10^5$	310	912	12.47 → — /250	—	—	192
73	^{6}Li—^{7}Li MS	U, Supr 24/4.2 supr 0.15–0.20	—Fe ($NO_2 + O_2$) | $LiNO_3$ | $RbNO_3$ | Pt($NO_2 + O_2$)+	—	207	$7.95 \cdot 10^4$	450	106.8	^{7}Li/^{6}Li 11.45 → — /15.24	1.0084	0.055	179
74	^{6}Li—^{7}Li MS	M, Pyrex 30/7 steatite 0.25–0.50	— Al (HNO_3) | $LiNO_3$ | Pt ($NO_2 + O_2$) +	20	50	$4.32 \cdot 10^4$	290	240	—	1.0046	0.030	171
75	ditto	ditto	ditto	80	200	$2.94 \cdot 10^5$	290	408	—	1.0088	0.057	171
76	»	» 3.5/5	»	23	250	$1.30 \cdot 10^5$	290	144	—	1.0035	0.023	171
77	»	» 27/12	»	38	260	$1.64 \cdot 10^5$	290	175	—	1.0087	0.057 0.050[9]	171 171
78	^{6}Li—^{7}Li MS	—	— Fe (HNO_3) | $LiNO_3$ | Pt ($NO_2 + O_2$) +	—	300	$7.77 \cdot 10^4$	280	72	^{7}Li/^{6}Li 11.35 → 10.8/11.95	—	—	187
79	^{6}Li—^{7}Li MS	— 25/— zircon —	—Ta (HNO_3) | $LiNO_3 + KNO_3$ | Pt ($NO_2 + O_2$) + 75 wt.%	88	450	$1.17 \cdot 10^6$	330	720	^{7}Li/^{6}Li 11.8 → — /28.2 (2.9 cm^3)	—	—	188, 190
80	ditto	ditto	—Ta (HNO_3) | $LiNO_3 + KNO_3$ | Pt ($NO_2 + O_2$) + 41 wt.%	92	500	$1.30 \cdot 10^6$	340	720	ditto /27.2 (2.9 cm^3)	—	—	188, 190
81	^{6}Li—^{7}Li SS	V, steel 5/10 in H_2 atm	— Zn | LiH | Fe +	30	900	$6.6 \cdot 10^3$	600	2	^{7}Li/^{6}Li 12.48 → — /12.71	1.00616	0.04	239
82	^{6}Li—^{7}Li SS	U, Vycor 30/10.4	— Mo | Zn | Li_2SO_4 | Au ($SO_2 + O_2$) +	—	255	$4.57 \cdot 10^3$	630	5	^{7}Li/^{6}Li 12.63 → — /13.08	1.0215	0.140	236, 237
83	ditto	ditto	ditto	—	775	$8.40 \cdot 10^3$	620	3	ditto → — /13.25	1.0228	0.148	236, 237
84	»	»	»	—	695	$1.26 \cdot 10^4$	600	5	ditto → — /13.64	1.0249	0.162	236, 237
85	^{6}Li—^{7}Li SS	ditto 30/7.4	— Mo | Zn | Li_2SO_4 | Au ($SO_2 + O_2$) +	—	345	$1.37 \cdot 10^4$	600	11	ditto → — /13.71	1.0168	0.109	236, 237
86	ditto	ditto	ditto	—	560	$2.0 \cdot 10^4$	605	10	ditto → — /13.98	—	—	236, 237
87	»	»	»	—	475	$1.89 \cdot 10^4$	660	11	ditto → — /14.10	1.0191	0.124	236, 237
88	»	»	»	—	430	$1.54 \cdot 10^4$	715	10	ditto → — /14.12	1.0215	0.140	236, 237
89	»	»	»	—	615	$1.99 \cdot 10^4$	740	9	ditto → — /15.04	1.0225	0.146	236, 237
90	»	»	»	—	485	$5.68 \cdot 10^3$	790	3.25	ditto → — /13.53	1.0169	0.110	236, 237
91	»	»	»	—	610	$1.32 \cdot 10^4$	790	6	ditto → — /13.96	1.0222	0.144	236, 237
92	^{6}Li—^{7}Li MS	V, Supr 21/4.5 supr 0.20–0.25	— Mo | Zn | $Li_2SO_4 + K_2SO_4$ | Pt ($SO_3 + O_2$) + 89.6 mole %	60	145	$6.84 \cdot 10^3$	685	13.1	—	1.00134	0.087	193, 194
93	ditto	ditto	80.4 mole %	100	215	$1.95 \cdot 10^3$	590	2.53	—	—	—	193, 194
94	»	»	80.4 mole %	140	175	$4.79 \cdot 10^3$	635	9.50	—	1.00120	0.078	193, 194
95	»	»	80.4 mole %	160	125	$3.32 \cdot 10^3$	760	7.50	—	1.00260	0.169	193, 194
96	»	»	81.0 mole %	110	180	$2.69 \cdot 10^3$	625	4.10	—	1.00182	0.118	193, 194
97	»	Pyrex 0.20–0.25	81.1 mole %	110	280	$2.75 \cdot 10^3$	635	2.75	—	1.00228	0.148	193, 194
98	»	Supr 0.20–0.25 ditto	79.8 mole %	35	200	$5.61 \cdot 10^3$	735	7.72	—	1.00194	0.126	193, 194
99	»	»	79.9 mole %	45	180	$5.14 \cdot 10^3$	745	7.98	—	1.00115	0.075	193, 194
100	»	»	79.9 mole %	60	215	$4.69 \cdot 10^3$	835	6.00	—	1.00238	0.155	193, 194

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
101	$^6Li—^7Li$ MS	Supr 0.20–0.25	59.8 mole %	70	200	$6.81\cdot10^3$	735	9.42	—	1.00177	0.115	193, 194
102	ditto	ditto	40.8 mole %	70	200	$7.36\cdot10^3$	745	10.20	—	1.00211	0.137	193, 194
103	$^6Li—^7Li$ AQ	H, Pyrex 75/16 paper membranes	— Pt (H_2) | CH_3COOLi | Pt (O_2) + 0.007*N*	2500	90	$3.25\cdot10^5$	41	1000	% ^6Li 7.31 → 7.61/ —	—	—	93
104	$^6Li—^7Li$ AQ	U, Pyrex 20/6 sand 0.03–0.04	— Pt (H_2) | HCl | LiCl | $CuCl_2$ | Pt (Cl_2) + 9*N*	150	110	—	37	140	% ^6Li 7.5 → 11.35/ —	1.0033	—	75
105	$^6Li—^7Li$ AQ	H, Pyrex 65/40 80 nylon membranes	— Pt (H_2) | CH_3COOLi | Pt (O_2) + 0.05*N*	1350	900	$2.55\cdot10^6$	40	786	$^7Li/^6Li$ 12.50 → 9.76/ —	1.00086	—	102
106	$^6Li—^7Li$ LM	H, steel 20/0.7 —	— Fe | Li | Fe +	—	37 amp	$1.65\cdot10^7$	300	159	% ^6Li 7.5 → — /9.4	—	$3.5\cdot10^{-5}$	248
107	$^{22}Na—^{23}Na$ MS	V, Pyrex 17/4 quartz 0.1–0.2	— Al ($NO_2 + O_2$) | $NaNO_3$ | Pt ($NO_2 + O_2$) +	45	80	$5.76\cdot10^3$	340	20	—	1.0023	0.051	192, 198
108	ditto	ditto	ditto	82	90	$2.22\cdot10^4$	380	67	—	1.0017	0.039 / 0.045[5]	192, 198
109	$^{39}K—^{41}K$ MS	U, Supr 22.5/4 quartz 0.1	— C | $PbCl_2$ | LiCl + KCl 2 mole % | $PbCl_2$ | C (Cl_2) +	62	500	$8.65\cdot10^4$	650	48	$^{41}K/^{39}K$ 0.0715 → — /0.0885	1.016	0.32	159
110	$^{39}K—^{41}K$ PC	U, Vycor 30.5 Al_2O_3 0.1	— SiC (Cl_2) | KCl | C (Cl_2) +	—	—	$9.72\cdot10^4$	824	—	—	1.0036	0.071	200
111	ditto	ditto	ditto	—	—	$1.26\cdot10^5$	882	—	—	1.0040	0.080	200
112	»	»	»	—	—	$1.26\cdot10^5$	893	—	—	1.0041	0.082	200
113	»	»	»	—	—	$7.05\cdot10^4$	918	—	—	1.0040	0.080	200
114	»	»	»	—	—	$8.45\cdot10^4$	943	—	—	1.0038	0.076	200
115	»	»	»	—	—	$7.5\cdot10^4$	1015	—	—	1.0046	0.091	200
116	$^{39}K—^{41}K$ MS	U, Pyrex 21.8/10 zircon 0.18	— C (Br_2) | LiBr + KBr 49 wt.% | C (Br_2) +	45	550	$4.32\cdot10^6$	450	2180	$^{39}K/^{41}K$ 15.0 → 17/6.5	—	—	20
117	$^{39}K—^{41}K$ MS	V, Supr 22/4.1 quartz 0.20–0.25	— Al ($NO_2 + O_2$) | KNO_3 | Pt ($NO_2 + O_2$) +	82	100	$5.26\cdot10^4$	360	146	% ^{41}K 6.7 → 6.68/7.64	1.00184	0.036	199
118	$^{39}K—^{41}K$ MS	V, Supr 22/4 quartz 0.20–0.25	—Al($NO_2 + O_2$) | $KNO_3 + KNO_2$ | Pt(NO_2+O_2)+	—	87.5	$4.72\cdot10^4$	360	149.5	—	1.0019	0.038	201
119	ditto	ditto	ditto	—	99.5	$8.53\cdot10^4$	360	248.0	—	1.0019	0.038	201
120	»	»	»	—	233	$2.43\cdot10^4$	354	29.0	—	1.0022	0.044	201
121	»	»	»	—	206	$3.54\cdot10^4$	370	47.8	—	1.0021	0.042	201
122	»	»	»	—	202	$3.38\cdot10^4$	375	46.5	—	1.0017	0.034	201
123	»	»	»	—	206	$1.78\cdot10^4$	388	24.0	—	1.0025	0.050	201
124	»	»	»	—	198	$2.55\cdot10^4$	442	35.7	—	1.0023	0.046	201
125	»	»	»	—	222	$2.56\cdot10^4$	454	32.1	—	1.0023	0.046	201
126	»	»	»	—	197	$4.10\cdot10^4$	470	57.0	—	1.0029	0.058	201
127	»	»	»	—	192	$2.88\cdot10^4$	496	41.6	—	1.0028	0.057	201
128	»	»	»	—	200	$2.02\cdot10^4$	541	28.0	—	1.0035	0.070	201
129	»	»	»	—	161	$1.35\cdot10^4$	562	23.3	—	1.0033	0.065	201
130	»	»	»	—	228	$2.46\cdot10^4$	586	30.0	—	1.0035	0.070	201
131	$^{39}K—^{41}K$ MS	V, Vycor 24/4 quartz 0.1–0.15	— Al ($NO_2 + O_2$) | KNO_3 | Pt ($NO_2 + O_2$) +	148	98	$3.37\cdot10^4$	388	100	$^{39}K/^{41}K$ 13.85 → — /8.57	1.0021	0.042	192
132	$^{39}K—K^{41}$ MS	V, Vycor 24/4 quartz 21/4	— Al ($NO_2 + O_2$) | KNO_3 | Pt ($NO_2 + O_2$) +	190	120	$7.63\cdot10^4$	380	177.5	13.86 → — /8.23	1.0020	0.040	192
133	ditto	ditto 14.6/4	ditto	145	150	$8.46\cdot10^4$	380	149	13.9 → — /5.22	1.0020	0.040	192
134	»	U, quartz 15/4 ZrPh 0.1–0.15	»	120	80	$2.06\cdot10^4$	380	70	13.85 → — /13.07	1.0017	0.034	192
135	»	ditto 9.5/4	»	45	90	$1.90\cdot10^4$	380	65	13.85 → — /12.68	1.0018	0.036	192

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
136	^{39}K—^{41}K MS	V, Vycor 14/4 quartz 0.1–0.15	—Al(NO_3+O_2) | $KNO_3+K_2SO_4$ | Pt(NO_3+O_2)+	55	130	$1.85\cdot10^4$	390	42	$^{39}K/^{41}K$ 13.85 → — /13.53	1.0027	0.054	192
137	ditto	ditto	ditto	95	55	$1.52\cdot10^4$	390	171	ditto /13.36	1.0021	0.042	192
138	»	»	»	80	50	$9.4\cdot10^3$	390	60	» /13.36	1.0018	0.036	192
139	^{39}K—^{41}K AQ	H, Pyrex 7/14 pyrex 0.15	— Pt (H_2) | KCl | Pt (Cl_2) + 0.898*N*	93	500	$1.81\cdot10^5$	27	450	$^{39}K/^{41}K$ 14.2 → 24.0/—	1.00385	0.077	60
140	^{39}K—^{41}K AQ	H, Pyrex 122/22 sand 0.15	— Pt (H_2) | H_2SO_4 | K_2SO_4 | Pt (O_2) + 1.083*N*	800	500	—	50	335	$^{39}K/^{41}K$ 14.2 → 17.4/—	1.0029	0.058	60
141	^{39}K—^{41}K AQ	V, Pyrex 20/6 sand 0.03–0.04	— Pt (H_2) | KCl | $CuCl_2$ | Pt (Cl_2) + 3*N*	—	—	—	—	—	—	1.0025	0.050	77
142	^{39}K—^{41}K LM	V, Pyrex 20/0.6	— W | K | W +	5.3	8250	$1.05\cdot10^7$	140	355	% ^{41}K 6.695 → 7.025/6.30	—	$9\cdot10^{-6}$	250
143	^{85}Rb—^{87}Rb MS	U, quartz 30/5 Al_2O_3 0.1	— SiC (Cl_2) | RbCl | C (Cl_2) +	—	—	$5.76\cdot10^4$	757	—	—	1.00121	0.052	200
144	ditto	ditto	ditto	—	—	$1.28\cdot10^5$	812	—	—	1.00109	0.047	200
145	»	»	»	—	—	$8.64\cdot10^4$	827	—	—	1.00119	0.051	200
146	»	»	»	—	—	$5.11\cdot10^4$	830	—	—	1.00114	0.049	200
147	»	»	»	—	—	$9.28\cdot10^4$	840	—	—	1.00135	0.058	200
148	»	»	»	—	—	$7.76\cdot10^4$	924	—	—	1.00132	0.057	200
149	»	»	»	—	—	$7.24\cdot10^4$	976	—	—	1.00140	0.060	200
150	^{85}Rb—^{87}Rb MS	U, quartz 39/5 Al_2O_3 0.1	— SiC (Br_2) | RbBr | C (Br_2) +	—	—	$5.26\cdot10^4$	745	—	—	1.00165	0.071	200
151	ditto	ditto	ditto	—	—	$7.20\cdot10^4$	768	—	—	1.00170	0.073	200
152	»	»	»	—	—	$4.57\cdot10^4$	852	—	—	1.00184	0.079	200
153	^{85}Rb—^{87}Rb MS	U, quartz 39/5 Al_2O_3 0.1	— SiC (Br_2) | RbBr | C (Br_2) +	—	—	$5.90\cdot10^4$	929	—	—	1.00168	0.072	200
154	»	ditto	ditto	—	—	$5.80\cdot10^4$	946	—	—	1.00184	0.079	200
155	^{85}Rb—^{87}Rb MS	U, Supr 24/4.2 supr 0.15–0.20	—Fe(NO_3+O_2) | $LiNO_3$ | $RbNO_3$ | Pt(NO_3+O_2)+	—	207	$7.95\cdot10^4$	450	106.8	$^{85}Rb/^{87}Rb$ 2.62 → 3.21/—	1.0011	0.05	179
156	^{85}Rb—^{87}Rb MS	U, Supr 22/4 quartz 0.20–0.25	—Al (NO_3+O_2) | $RbNO_3$ | Pt (NO_3+O_2) +	—	150	$4.68\cdot10^4$	354	120.7	$^{85}Rb/^{87}Rb$ 2.62 → — /2.47	1.00079	0.0345	202
157	ditto	ditto	ditto	—	150	$1.86\cdot10^4$	346	38.0	ditto → — /2.54	1.00079	0.0345	202
158	^{85}Rb—^{87}Rb MS	U, Pyrex 10/4 quartz 0.1–0.15	— Al (NO_3+O_2) | $RbNO_3$ | Pt (NO_3+O_2) +	80	120	$1.93\cdot10^4$	360	40	$^{85}Rb/^{87}Rb$ 2.612 → — /2.469	1.00064	0.028	192
159	ditto	ditto 13/4	ditto	60	80	$1.37\cdot10^4$	360	48	2.597 → — /2.380	1.00093	0.040	192
160	»	» 18/4	»	125	55	$1.75\cdot10^4$	360	77	2.597 → — /2.351	1.00068	0.029	192
161	^{85}Rb—^{87}Rb MS	V, quartz 16/5 quartz 0.075	— Al (HNO_3) | $RbNO_3$ | Pt (NO_3+O_2) +	120	120	$3.14\cdot10^5$	375	727	$^{85}Rb/^{87}Rb$ 2.60 → — /2.015	—	—	203
162	ditto	ditto 12/4–7	ditto	115	42.5	$6.35\cdot10^4$	365	415.5	ditto → — /2.126	—	—	203
163	»	V, quartz 16/4–9 quartz 0.075–0.1	»	141	125	$1.53\cdot10^5$	365	346	» → — /1.968	—	—	203
164	»	ditto	»	150	160	$2.52\cdot10^5$	365	442	» → — /1.807	—	—	203
165	^{85}Rb—^{87}Rb AQ	H, Pyrex 100/16 paper membranes	— Pt (H_2) | RbOH | Pt (O_2) + 0.006*N*	2300	110	$7.9\cdot10^4$	80	200	% ^{85}Rb 72.2 → 73.8/ —	—	—	92
166	^{85}Rb—^{87}Rb AQ	U, Pyrex 20/6 sand 0.03–0.04	— Pt (H_2) | HCl | RbCl | $CuCl_2$ | Pt (Cl_2) + 3*N*	—	—	—	—	—	—	1.0011	—	77
167	^{133}Cs—^{137}Cs MS	V, Vycor 11/4 quartz 0.1–0.15	— Al (NO_3+O_2) | $CsNO_3$ | Pt (NO_3+O_2) +	100	80	$6.3\cdot10^3$	450	23.5	—	1.00081	0.0218	192
168	ditto	ditto 9/5	ditto	55	130	$3.26\cdot10^4$	450	71	—	1.00115	0.031	192
169	^{63}Cu—^{65}Cu MS	V, Supr 17/3.8 quartz 0.15–0.20	— C (Cl_2) | LiCl + KCl | CuCl | $PbCl_2$ | C (Cl_2) +	54	194	$4.87\cdot10^4$	535	70	% ^{63}Cu 68.94 → — /65.1	1.0028	0.080	204

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
170	^{63}Cu—^{65}Cu MS	V, Supr 17/4.1 quartz 0.1–0.15	— C (Cl_2) | LiCl + KCl | **CuCl** | $PbCl_2$ | C (Cl_2) +	49	196	$5.65\cdot10^4$	530	80	% ^{63}Cu 68.94 → — /64.4	—	—	204
171	^{63}Cu—^{65}Cu AQ	H, Pyrex 10/10 sand 0.15–0.25	— Pt (H_2) | H_2SO_4 | **$CuSO_4$** | Cu + 0.923*N*	—	200	$2.8\cdot10^5$	29	429	$^{63}Cu/^{65}Cu$ 2.2045 → 2.2408/ —	1.00069	0.022	62
172	^{63}Cu—^{65}Cu AQ	V, Pyrex 1.5/1.2 sand 0.03–0.04	—Pt(H_2) | HCl | $MgCl_2$ | **$CuCl_2$** | $CdCl_2$ | Pt(Cl_2)+ 8.70*N*	—	25	—	50	35.3	$^{63}Cu/^{65}Cu$ 2.33 → — /2.08	1.0013	—	79
173	^{107}Ag—^{109}Ag MS	U, Supr 20/- supr 0.1–0.12	— C (Cl_2) | LiCl | **AgCl** | C (Cl_2) +	48	300	$4.89\cdot10^4$	650	50	$^{107}Ag/^{109}Ag$ 1.08 → 1.130/ —	1.00118	0.064	205
174	^{107}Ag—^{109}Ag SS	H, Pyrex 65/4 —	— Ag | α-**AgJ** | C (I_2) +	—	250	$1.8\cdot10^4$	230	20	% ^{109}Ag 48 → — /51	1.002	0.11	71.72
175	^{24}Mg—^{26}Mg MS	U, quartz 30/4 Al_2O_3 0.1	— C (Cl_2) | **$MgCl_2$** | C (Cl_2) +	—	262	$6.12\cdot10^4$	790	64.8	% ^{26}Mg 10.74 → — /12.50	1.00816	0.102	206.207
176	ditto	ditto.	ditto	—	288	$5.22\cdot10^4$	790	50.4	ditto /11.98	1.00825	0.103	206,207
177	^{24}Mg—^{26}Mg AQ	H, Pyrex 12/3 sand 0.1	— Pt (H_2)/HBr | **$MgBr_2$** | Pt (Br_2) + 4.65*N*	150	670	$3.2\cdot10^6$	25	1326	$^{24}Mg/^{26}Mg$ 0.1435 → — /0.1495	1.0009	0.0113	89
178	^{24}Mg—^{26}Mg AQ	V, Pyrex 1.5/1.2 sand 0.03–0.04	—Pt (H_2)/HCl | **$MgCl_2$** | $CuCl_2$ | $CdCl_2$ | Pt (Cl_2)+ 8.95*N*	—	25	—	50	35.6	$^{24}Mg/^{26}Mg$ 0.1435 → — /0.184	1.0031	—	79
179	^{40}Ca—^{48}Ca MS	U, quartz 30/4 Al_2O_3 0.1	— C (Cl_2) | **$CaCl_2$** | C (Cl_2) +	—	210	$5.8\cdot10^4$	850	76.8	% ^{48}Ca 0.187 → — /0.281	1.0093	0.052	206,207
180	ditto	ditto	ditto	—	125	$8.78\cdot10^5$	850	720	То же /0.294	1.0090	0.050	206,207
181	^{40}Ca—^{48}Ca MS	U, quartz 30/4 Al_2O_3 0.1	— C (Br_2) | **$CaBr_2$** | C (Br_2) +	—	205	$5.32\cdot10^4$	850	72	% ^{48}Ca 0.187 → — /0.481	1.0115	0.063	206,207
182	^{40}Ca—^{46}Ca MS	U, quartz 15/29 ZrO_2 —	— C (Br_2) | **$CaBr_2$** | C (Br_2) +	—	—	—	775	720	% ^{46}Ca 0.0032 → — /0.0064	—	—	213
183	ditto	V, Al_2O_3 15/29 ZrO_2 —	ditto	—	—	—	775	720	ditto /0.016 (200 g)	—	—	213
184	^{40}Ca—^{44}Ca MS	U, quartz 20/17 Al_2O_3 —	— C (Br_2) | **$CaBr_2$** + KBr | C (Br_2) + 50 mole %	14	400	$3.39\cdot10^6$	765	2352	$^{44}Ca/^{40}Ca$ 0.0216 → 0.0170/0.0261	—	—	209
185	ditto	U, quartz 17/14 zircon–	ditto	37	1000	$4.23\cdot10^6$	765	1176	0.0217 → 0.0173/0.0381	1.0057	0.06	209
186	ditto	ditto	»	78	2700	$5.14\cdot10^6$	765	528	0.0213 → 0.0194/0.0401	1.0057	0.06	209
187	^{40}Ca—^{44}Ca MS	U, quartz 12/6 zircon 0.15	— C (Br_2) | **$CaBr_2$** + LiBr | C (Br_2) +	—	1000	$3.9\cdot10^5$	—	100	% ^{44}Ca 2.06 → — /3.5	1.0057	0.060	211
188	ditto	ditto	— C (Br_2) | **$CaBr_2$** + $SrBr_2$ | C (Br_2) +	—	1000	$2.9\cdot10^5$	—	80	% ^{44}Ca 2.06 → — /3.7 % ^{48}Ca 0.185 → — /0.46	—	— —	211 211
189	^{40}Ca—^{44}Ca MS	U, quartz 26/3.5 Al_2O_3 0.1	— C (I_2) | **CaI_2** | C (I_2) +	150	205	$4.85\cdot10^4$	880	66	$^{40}Ca/^{44}Ca$ 0.0213 → — /0.0270	1.0067	0.072	214
190	ditto	ditto	ditto	168	235	$5.54\cdot10^4$	880	65.5	ditto /0.0248	1.0073	0.077 0.0745[9]	214 214
191	^{84}Sr—^{88}Sr MS	U, quartz 30/4 Al_2O_3 0.1	— C (Cl_2) | **$SrCl_2$** | C (Cl_2) +	—	250	$8.65\cdot10^4$	1000	96	$^{88}Sr/^{84}Sr$ 147.12 → — /214.46	1.00167	0.036	206,207
192	^{130}Ba—^{138}Ba MS	U, quartz 30/4 Al_2O_3 0.1	— C (Cl_2) | **$BaCl_2$** | C (Cl_2) +	—	318	$8.78\cdot10^4$	1080	76.8	$^{138}Ba/^{130}Ba$ 688.67 → — /875.99	1.00116	0.0195	206,207
193	ditto	ditto	ditto	—	260	$7.2\cdot10^4$	1075	76.8	688.65 → — /718.11	1.00111	0.0186 0.019[10]	206,207 206
194	^{64}Zn—^{66}Zn MS	V, Supr 18/4.1 supr 0.15–0.20	— C | Pb | $PbCl_2$ | **$ZnCl_2$** | C (Cl_2) +	300	230	$5.96\cdot10^4$	650	72	$^{64}Zn/^{66}Zn$ 1.76 → 2.62/ —	1.00239	0.0776	215
195	^{64}Zn—^{66}Zn MS	V, Supr 23/3.75 quartz 0.15–0.20	— C | Pb | $PbBr_2$ | **$ZnBr_2$** | C (Br_2) +	415	140	$2.9\cdot10^4$	500	57.5	$^{64}Zn/^{66}Zn$ 1.76 → 2,22/ —	1.00343	0.11	216
196	^{64}Zn—^{68}Zn LM	H, Pyrex 20/0.55	— W | **Zn** | W +	—	10,5amp.	$9.95\cdot10^6$	510	254	$^{64}Zn/^{68}Zn$ 2,655 → — /2,75	—	$0.58\cdot10^{-5}$	255
197	^{106}Cd—^{116}Cd MS	U, Supr 13/4 quartz 0.1	— C | $PbCl_2$ | LiCl | **$CdCl_2$** | C (Cl_2) +	95	550	$9.0\cdot10^4$	700	50	$^{106}Cd/^{116}Cd$ 0.205 → 0,308/ —	1.006	0.067	217
198	^{106}Cd—^{116}Cd MS	V, Supr 24/4 supr 0.15–0.20	— C (Br_2) | **$CdBr_2$** | C (Br_2) +	—	253	$1,18\cdot10^4$	610	13	$^{106}Cd/^{116}Cd$ 0.16 → 0.192/ —	1.00505	0.0560	218

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
199	^{106}Cd—^{116}Cd MS	V, Supr 24/4 supr 0.15–0.20	— C (Br_2) | **$CdBr_2$** | C (Br_2) +	—	225	$5.42\cdot10^4$	620	67	^{106}Cd/^{116}Cd 0.16 → 0.427/ —	1.00662	0,0735	218
200	^{106}Cd—^{116}Cd MS	ditto	— Cd (Br_2) | **$CdBr_2$** | C (Br_2) +	—	320	$5.77\cdot10^4$	620	50	^{106}Cd/^{116}Cd 0.16 → 0.402/ —	1.00628	0.0697	218
201	ditto	U, Supr 28/4 supr 0.10–0.12	— C (Br_2) | LiBr | **$CdBr_2$ + Cd** | C (Br_2) +	—	200	$3.62\cdot10^4$	630	50	ditto → 0.256/ —	1.00720	0.0800 0.075[11]	218 218
202	^{110}Cd—^{114}Cd MS	U, Supr 24/4 Al_2O_3 0.1	— W | Cd | **CdI_2** | C (I_2) +	278	230	$1.20\cdot10^5$	580	135	^{114}Cd/^{110}Cd 2,33 → — /3,25	1.00272	0.0762	214
203	ditto	ditto	ditto	268	225	$1.01\cdot10^5$	580	125	ditto → — /2.78	1.00266	0,0745	214
204	»	»	»	265	250	$7.20\cdot10^4$	580	84	ditto → — /2.62	1.00281	0.0786 0.0764[12]	214 214
205	^{106}Cd—^{116}Cd LM	H, Pyrex 20/0.55	— W | **Cd** | W +	—	12.5 amp	$1.6\cdot10^7$	540	360	^{116}Cd/^{106}Cd 6.14 → 6,73/5.43	—	$1.24\cdot10^{-5}$	255
206	^{113}In—^{115}In LM	V, quartz 20/0.987	— W | **In** | W +	—	16.3 amp	$2.0\cdot10^7$	820	360	^{115}In/^{113}In 22,00 → 22,19/21,36	—	$6\cdot10^{-5}$	260
207	^{113}In—^{115}In SM	V, Pyrex 20/0.566	— W | **In** | W +	—	9.1 amp	$2.5\cdot10^7$	123	768	—	—	$<5\cdot10^{-7}$	260
208	^{203}Tl—^{205}Tl MS	U, Supr 27/4 supr 0.3	— C | Tl | **TlCl** | **$ZnCl_2$** | C (Cl_2) +	244	250	$1.7\cdot10^4$	530	109	^{205}Tl/^{203}Tl 2.45 → — /2.81	1.0004	0.04	219
209	^{203}Tl—^{205}Tl MS	U, Supr 20/4 Al_2O_3 0.1	— C (Cl_2) | LiCl | **TlCl** | **$ZnCl_2$** | C (Cl_2) +	—	325	$1.16\cdot10^5$	680	98.4	% ^{205}Tl 29,59 → — 28.53	1.00035	0,0353	221
210	^{203}Tl—^{205}Tl MS	U, Supr 20/4 Al_2O_3 0.1	— C (Cl_2) | LiCl | **TlCl** | $ZnCl_2$ | C (Cl_2) +	—	380	$1.99\cdot10^5$	665	158.4	29.55 → — /28.25	1.00036	0.0366	221
211	ditto	ditto	— W | Tl | **TlCl** | $ZnCl_2$ | C (Cl_2) +	—	325	$1.14\cdot10^5$	555	96,5	29.62 → — /27,70	1,00041	0,0411	221
212	»	»	ditto	—	200	$1.58\cdot10^5$	535	214	29,49 → — /26,28	1,00042	0,0419	221
213	»	»	»	—	100	$1.64\cdot10^5$	475	455	29,54 → — /26.59	1.00045	0,0459	221
214	^{203}Tl—^{205}Tl MS	V,Vycor 13/4 quartz 0.1–0.15	— Al (NO_2 + O_2) | **$TlNO_3$** | Pt (NO_2 + O_2) +	100	102	$3.72\cdot10^4$	219	100	—	1,00031	0,032	222
215	ditto	ditto	ditto	127	70	$1.69\cdot10^4$	219	74,5	—	1,00031	0.032	222
216	»	»	»	90	90	$1.56\cdot10^4$	219	50	^{205}Tl/^{203}Tl 2.382 → — /2,540	1,00037	0,038	222
217	»	»	»	117	90	$1.59\cdot10^4$	219	50	—	1,00037	0,038	222
218	^{112}Sn—^{124}Sn MS	V, Pyrex 20/4 pyrex 0.2–0.3	— Mo | Sn | **$SnCl_2$** | $ZnCl_2$ | C (Cl_2) +	80	194	$4.51\cdot10^4$	590	64	^{112}Sn/^{124}Sn 0.163 → — /0.104	1.0064	0 065	223
219	ditto	ditto	ditto	90	210	$4.26\cdot10^4$	340	56	ditto → — /0.107	1.0065	0,066	223
220	»	U, Pyrex 12/4 pyrex 0.2–0.3	— Mo | Pb | $PbCl_2$ | LiCl + + KCl | **$SnCl_2$** | $ZnCl_2$ | C(Cl_2) +	110	188	$4,5\cdot10^4$	540	66	ditto → 0.227/—	1,0062	0.063	223
221	»	ditto	ditto	105	202	$3,85\cdot10^4$	450	53	ditto → 0,253/—	1,0065	0.066	223
222	^{112}Sn—^{124}Sn MS	U, Pyrex 20/4 pyrex 0.2–0.3	—SiC(Br_2) | LiBr+KBr | **$SnBr_2$** | $ZnBr_2$ | C(Br_2) +	110	154	$4.24\cdot10^4$	470	76	^{112}Sn/^{124}Sn 0.16 → 0.288/ —	1.0071	0.072	224
223	^{112}Sn—^{124}Sn MS	V, Pyrex 20/4 pyrex 0.2–0.3	— Mo | Sn | **SnI_2** | ZnI_2 | C (I_2) +	94	179	$2.06\cdot10^4$	470	32	^{112}Sn/^{124}Sn 0.16 → — /0.083	1,0079	0,080	224
224	^{112}Sn—^{124}Sn MS	U, Pyrex 17.7/4 pyrex 0.32–0.35	—SiC(Cl_2)|LiCl+KCl|**$SnCl_2$**+$PbCl_2$|$ZnCl_2$|C(Cl_2)+ 11.40 mole %	256	240	$1.19\cdot10^5$	575	161	—	—	0 012[13]	225
225	ditto	U, Pyrex 14.5/4 pyrex 0.35–0.4	58.83 mole %	224	150	$8.17\cdot10^4$	565	146	—	—	0,012[13]	225
226	»	ditto 17.8/4	78.84 mole %	196	200	$5.8\cdot10^4$	570	180	—	—	0,012[13]	225
227	^{112}Sn—^{124}Sn LM	H, Pyrex 20/0.55	— W | **Sn** | W +	—	10,3 amp	$1.52\cdot10^7$	285	408	^{124}Sn/^{112}Sn 6,19 → 7,22/5,43	—	$1,13\cdot10^{-5}$	255
228	^{204}Pb—^{206}Pb MS	V, Supr 0.22/3.8 supr 0.15–0.20	—C (Cl_2) | LiCl+KCl | **$PbCl_2$** | $ZnCl_2$ | C (Cl_2) +	110	220	$1.86\cdot10^5$	640	236	^{204}Pb/^{206}Pb 0,0570 → 0.0612/ —	1,000227	0,0233	226
229	^{206}Pb—^{208}Pb MS	V, Supr 17/- supr 0.20–0.25	— C (Cl_2) | LiCl+KCl | **$PbCl_2$** | $ZnCl_2$ | C (Cl_2) +	110	226	$1,38\cdot10^5$	530	169	^{08}Pb/^{206}Pb 2.148 → — /2.272	1,000232	0,0240	226

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
230	^{206}Pb—^{208}Pb MS	U, Supr 24/4 supr 0.20–0.25	— C | Pb | $PbBr_2$ | LiBr | $PbBr_2$ | C (Br_2) +	—	172	$7.42\cdot10^4$	590	120	$^{208}Pb/^{206}Pb$ 2.21 → 2.098/ —	1.000396	0.041	227
231	^{206}Pb—^{208}Pb MS	U, Supr 17/4 Al_2O_3 0.1	— W | Pb | PbI_2 | C (I_2) +	180	450	$1.15\cdot10^5$	600	81	$^{208}Pb/^{206}Pb$ 2.07 → — /2.17	1.000728	0.0753	214
232	ditto	ditto 24/4	ditto	285	425	$1.24\cdot10^5$	600	82	ditto → — /2.15	1.000685	0.0708 0.0731[14]	214 214
233	^{235}U—^{238}U MS	U, quartz 15/7.4 quartz 0.5–0.6	— C (Cl_2) | UCl_4 | C (Cl_2) +	65	130	$5.43\cdot10^4$	615	115	% ^{235}U 0.7205 → 0.7241/ —	1.00036	0.032	228
234	^{235}U—^{238}U AQ	H, Pyrex 20/30 pyrex 0.135	— Pt (H_2) | HCl | UCl_4 + UO_2Cl_2 | Pt (Cl_2) + 0.10*M* 0.10*M*	40	82	$4.16\cdot10^5$	18	1408	% ^{235}U 0.7111 → 0.7171/ —	1.0012	0.0945	64
235	^{234}U—^{238}U AQ	V, Pyrex 1.5/1.2 sand 0.03–0.04	—Pt(H_2)| HCl | UO_2Cl_2|$CdCl_2$+Cd(OH)$_2$|Pt(Cl_2)+	—	10	—	60	72	% ^{234}U 0.006 → 0.00602/—	1.0009	—	81
236	^{35}Cl—^{37}Cl MS	U, quartz 60/5 Al_2O_3 0.1	+ C (Cl_2) | KCl | KBr | SiC (Br_2) —	—	—	$3.64\cdot10^4$	825	—	—	1.00345	0.062	200
237	ditto	ditto	ditto	—	—	$3.24\cdot10^4$	938	—	—	1.00340	0.061	200
238	»	»	»	—	—	$3.6\cdot10^4$	974	—	—	1.00328	0.059	200
239	^{35}Cl—^{37}Cl MS	U, quartz 60/5 Al_2O_3 0.1	+ C (Cl_2) | RbCl | RbBr | SiC (Br_2) —	—	—	$4.68\cdot10^4$	781	—	—	1.00628	0.113	200
240	ditto	ditto	ditto	—	—	$3.42\cdot10^4$	881	—	—	1.00628	0.113	200
241	»	»	»	—	—	$4.0\cdot10^4$	959	—	—	1.00750	0.135	200
242	^{35}Cl—^{37}Cl MS	U, Supr 20.5 supr 0.1–0.12	+ Zn | $ZnCl_2$ | W —	415	215	$1.54\cdot10^5$	600	198	% ^{37}Cl 24.6 → — /17.55	1.00241	0.043	230
243	^{35}Cl—^{37}Cl MS	—	+ Cd | $CdCl_2$ + Cd | $CdCl_2$ | Cd —	—	—	—	—	—	—	1.00189	0.034	232
244	^{35}Cl—^{37}Cl MS	U, Supr 20/5.5 Al_2O_3 0.1	+ Tl | TlCl | Tl —	100	450	$8.0\cdot10^4$	565	50	% ^{37}Cl 24.6 → — 19.45	1.00433	0.078	231
245	ditto	ditto	ditto	100	350	$1.73\cdot10^5$	560	141.5	ditto → — /8.4	1.00472	0.085	231
246	»	»	»	100	500	$1.54\cdot10^5$	730	89	» → — /17.55	1.00310	0.056	231
247	»	»	»	100	500	$1.54\cdot10^5$	690	89	» → — /16.50	1.00305	0.055	231
248	»	»	»	100	500	$1.23\cdot10^5$	565	69	» → — /16.79	1.00422	0.076	231
249	»	U, Supr 30/5 Al_2O_3 0.1	»	100	600	$1.15\cdot10^6$	565	624	% ^{35}Cl 75.4 → 98.4] → (0.57 *z*)	—	—	231
250	^{35}Cl—^{37}Cl MS	U, Supr 20/5.5 supr 0.1–0.12	+ Pb | $PbCl_2$ | W —	130	523	$3.17\cdot10^5$	520	168.5	% ^{37}Cl 24.6 → — /14.1	1.0029	0.052	229
251	^{35}Cl—^{37}Cl MS	U, Supr 8.25/5.5 supr–	+ C (Cl_2) | $PbCl_2$| Pb —	110	400	—	520	73	% ^{37}Cl 24.6 → — /30.2	1.0020	0.036	233
252	^{35}Cl—^{37}Cl AQ	H,Pyrex 10/20 sand 0.15–0.20	+ Pt (O_2) | NaOH | NaCl | Pt (H_2) — 1,782*N*	80	500	$8.5\cdot10^5$	50	474	$^{35}Cl/^{37}Cl$ 3.12 → — /4.18	1.00207	0.037	61
253	^{35}Cl—^{37}Cl AQ	V, Pyrex 2.1/1.2 sand 0.03–0.04	+Pt(O_2) | LiOH | LiCl |$Li_2Cr_2O_7$|Li_2SO_4|Pt(H_2)— 7,5*N*	—	11	—	50	12.3	% ^{37}Cl 24.6 → — /26.6	1.0022	—	80
254	ditto	ditto 1.1/1.2	+Pt(O_2)| NaOH|NaCl |$Na_2Cr_2O_7$|Na_2SO_4|Pt(H_2)— 5,4*N*	—	20	—	50	6.8	ditto → — /28.8	1.0021	—	80
255	ditto	» 1.2/0.7	+Pt (Cl_2) | HCl | $H_2Cr_2O_7$ | H_2SO_4 | Pt (H_2) — 10*N*	—	60	—	50	7.4	ditto → — /26.5	1.0015	—	80
256	^{79}Br—^{81}Br MS	U, quartz 60/5 Al_2O_3 0.1	+ C (Cl_2) | RbCl | RbBr | SiC (Br_2) —	—	—	$4.68\cdot10^4$	800	—	—	1.00275	0.110	200
257	ditto	ditto	ditto	—	—	$3.42\cdot10^4$	889	—	—	1.00312	0.125	200
258	»	»	»	—	—	$2.95\cdot10^4$	935	—	—	1.00290	0.116	200
259	»	»	»	—	—	$4.0\cdot10^4$	967	—	—	1.00278	0.111	200

Table 1 contd.

Expt. No.	Isotopes and medium (Ref.1)	Construction of cell (Ref.2)	Electrodes and electrolytes (Ref.3)	Voltage, V	Current, mA	Quantity of electricity, C	Temp., °C	Duration, h	Isotope content before → after experiment (Ref.4)	α	−μ	Ref.
1	2	3	4	5	6	7	8	9	10	11	12	13
260	^{79}Br—^{81}Br MS	U, Supr 21/4.4 supr 0.1-0.12	+ Zn | $ZnBr_2$ | W −	400	171	$2.11 \cdot 10^5$	650	337	$^{79}Br/^{81}Br$ 1.024 → — /1.298	1.000875	0.035	235
261	ditto	ditto 20/3.9	ditto	—	159	$1.77 \cdot 10^5$	610	308	ditto → — /1.307	1.000875	0.035	235
262	^{79}Br—^{81}Br MS	U, Pyrex 20/5 pyrex 0.1-0.12	+ Pb | $PbBr_2$ | W −	182	447	$3.0 \cdot 10^5$	400	187	% ^{79}Br 50.414 → — /56.500	1.00111	0.044	234

[1]Isotopes for which the mass effect has been calculated. The abbreviations have the following significance: MS = molten salts; SS = solid salt; AQ = aqueous solution; LM = liquid metal; SM = solid metal.

[2]The structural characteristics of the cell are given in the sequence—form and material of separating tube, dimensions of tube (length (cm) in numerator, internal diameter (mm) in denominator) and material and grain-size (mm) of packing. Abbreviations: U = U-shaped tube of type illustrated in Fig. 2*c*; V = vertical tube as shown in Figs. 2*a*, 2*b*, and 2*d*; H = horizontal cell as in Fig. 3; Supr = Supremax glass; ZrPh = zirconyl phosphate.

[3]"Head" electrode on left-hand side (negative in the separation of isotopic cations, positive in the separation of anions). The salt containing the isotopes to be separated is printed in bold type; its content in the initial mixture or the concentration of the solution is indicated underneath.

[4]Results of isotopic analysis before → after experiment (in the numerator for the cathodic end of the separation zone, in the denominator for the anodic end): the values given are those which differ to the maximum extent from the initial values (for example, if maximum enrichment with a given isotope is observed not in an electrode compartment but in the adjacent portion of the separating tube, the latter value is cited). The quantity of enriched salt (in g or cm^3) is given in parentheses if electrical migration was conducted for preparative purposes.

[5]Mean value of μ for Expts. 40 and 42.

[6]Value of μ for Expts. 43–46 calculated in Ref. 279.

[7]Mean value of μ for Expts. 74–77.

[8]Mean value of μ for Expts. 107 and 108.

[9]Mean value of μ for Expts. 189 and 190.

[10]Mean value of μ for Expts. 192 and 193.

[11]Mean value of μ for Expts. 198–201.

[12]Mean value of μ for Expts. 202–204.

[13]Mean value of μ for Expts. 224–226.

[14]Mean value of μ for Expts. 231 and 232.

bath. When heavy isotopes are to be concentrated, on the other hand, the bath forms the cathode compartment, and enriched material is withdrawn from the upper space, not occupied by the packing, of the tube (the anode compartment)[20,213]. If, however, both cathodic and anodic separating tubes are immersed in the bath, both light and heavy isotopes can be concentrated in the same installation; an electrode at zero potential should be lowered into the bath to prevent disturbance of the electrical conditions in the individual tubes and the bath as a whole. Klemm[172] described the mode of operation of such an installation for separating the isotopes of lithium, in which the ratio of the numbers of cathodic and anodic tubes was 1 : 2, the quantity of material enriched with the light isotope ^{6}Li to 90 at.% was 8.2% of the total quantity of salt removed from the separating tubes, whereas 91.8% of the whole salt was enriched to 99.974 at.% with the heavy isotope ^{7}Li.

The choice of optimum dimensions for the separating tube is governed by the relation between the required separation factor S and the rate v_p of removal of the product from the plant, together with the mechanical and thermophysical properties of the materials of which the plant is made. Thus S is proportional to the current density, i.e. inversely proportional to the diameter of the tube; and the permissible rate of withdrawal, which is still insufficient to cause serious disturbance of the steady state, is directly proportional to the diameter of the separating tube. In the separation of lithium isotopes in the molten chloride with $S = 3-4$ and a very small withdrawal the optimum tube diameter has been estimated[184] as 10–15 mm; but with considerable withdrawal (several grams of lithium chloride per day) and $S = 2$, the diameter must be increased to 30 mm.

From Eqn. (24) and the requirement of minimum energy consumption Klemm[167] found that the optimum conditions for the concentration of ^{7}Li from 92.7% to 99.974% ($S = 310$) were a separating tube 22.8 cm long with the product removed at a rate of 2.8 cm day^{-1}. The electrical energy consumed was 11 kW h per gram of lithium enriched with ^{7}Li. The energy consumption for the concentration of ^{6}Li from 7.3% to 90% was[172] 60 kW h g^{-1}. Neubert and Klemm[208] calculated the energy consumption and the cost for calcium chloride enriched with the ^{48}Ca isotope: a single value of the separation factor, which must be achieved by electrical migration in order that the total cost of the product should be a minimum, corresponds to each value of the sum of overhead expenses in preliminary enrichment with ^{46}Ca by electrical migration followed by complete enrichment on an electromagnetic separator. In the equipment of Ménès et al.[211] 25 kW h of electrical energy was consumed per gram of calcium in which the initial content of ^{46}Ca had been doubled. Westhaver[66] estimated energy consumptions in the separation of potassium isotopes in aqueous solution: enrichment with ^{41}K from 14.2% to 21.3% in a tube 4.6 cm long requires 14 kW h g^{-1} potassium.

Equation (37) shows that the chief parameter of an actual tube as a separating device[74] is the ratio D'/v, so that its diminution is one of the most important engineering problems. Experience of the operation of large-scale installations[20,167,184,192] shows that under optimum conditions D' does not exceed D more than 3–4 fold: i.e. it is of the order of 10^{-4} cm^2 s^{-1}. Since the mobility of ions in a molten salt is $\sim 10^{-4}$ cm^2 V^{-1} s^{-1}, the quantity h is around 2–3 mm with a field of 3–5 V cm^{-1} in the tube: i.e. the dimensions of separating devices of this kind can be considerably smaller than in other methods for the separation of isotopes.

IV. APPLICATION OF ELECTRICAL MIGRATION TO THE STUDY OF THE STRUCTURE AND TRANSPORT PROPERTIES OF MOLTEN SALTS

1. Measurement of Ionic Mobilities by Countercurrent Electrical Migration

A cell with a separating tube can be used not only for applied purposes—for the separation of isotopes—but also as a scientific research tool. A large proportion of the experiments reflected in Table 1 were undertaken with the aim of measuring the relative difference in mobility between isotopic ions, a quantity which is necessary for theoretical conclusions and generalisations with respect to both the structure of the medium in which the ions move, in particular molten salts, and the mechanism of the actual movement of the ions.

Table 1 shows that the mass effect has a tendency to decrease with increase in the atomic weight of the separable element, which can be expressed by the empirical formula[290]

$$\mu_+ = \mu' \left(1 + \frac{m_+}{M}\right)^{-1} \qquad (38)$$

where μ' is a constant, $M = km_-$, and m_+ and m_- are the masses of the cations and anions forming the salt. Klemm[279,208], having published a summary of measurements of μ_+ for seventeen metal halides in the molten state, noted an interesting regularity: the mass effects of isotopic cations of salts having a layer lattice in the solid state conformed closely to the curve described by Eqn. (38) with $\mu' = -0.15$ and $k = 2.1$; but for cations of salts not having a layer lattice the appropriate values were −0.079 and 2.1 respectively. Both curves are shown in Fig. 4, from which it is evident that all halides have values of μ_+ grouped about these curves. Attempts to select other values of μ' and k had only partial success[8,200,227].

Klemm's suggestion[208]—that if the above rule is valid magnesium and cadmium bromides, the corresponding iodides, and the iodides of calcium, zinc, and lead, which have a laminar structure in the solid state, should when molten have values of μ_+ close to curve A, while those of strontium and barium bromides should be close to curve B—has since been verified for CaI_2, CdI_2, PbI_2,[214] and $CdBr_2$,[218] and also for $SnCl_2$,[223] $SnBr_2$,[223] and SnI_2.[224] The results made a more careful formulation of the rule necessary[214], the two types of salts being delimited by an empirical curve (the broken curve C in Fig. 4), for which an analytical expression was not found.

Experimental values of μ_+ for alkali-metal and thallium nitrates are also plotted in Fig. 4. Lundén and Ekhed[196] found that the variation in μ_+ for the alkali-metal nitrates is best represented by the equation

$$-\mu_+ = 0.0848(1 + m_+/46)^{-1}, \qquad (39)$$

provided that values of μ_+ are taken at temperatures 5% above the absolute melting points of the corresponding nitrates. It is evident that μ_+ for thallium(I) nitrate does not obey the rule. It is noteworthy that values of μ_+ for solid lithium sulphate and lithium hydride fit well on curve A.

Attempts to find a similar relation for isotopic anions were undertaken[229,235] in the absence of sufficient experimental results. Similar series of salts in the order of diminishing μ_-—RbCl > TlCl > KCl > $PbCl_2$ > $CdCl_2$ > > $ZnCl_2$ and RbBr > $PbBr_2$ > $ZnBr_2$—can be distinguished from the results in Table 1. If this type of relation does

exist for anions, it is obviously more complicated. In any case, the rule formulated by Herzog and Klemm[231]—that the isotope effect in ionic mobilities is larger the greater the number of the heaviest possible gegenions surrounding the separable isotopic ions in the melt—is well satisfied for cations, and with large exceptions for anions.

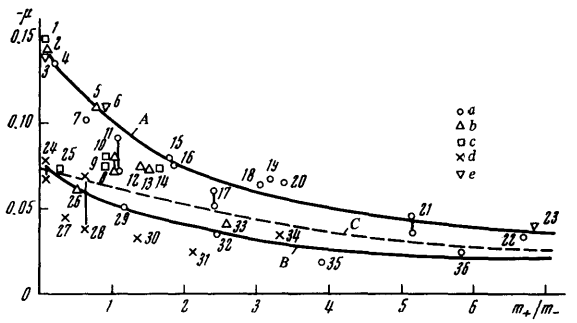


Figure 4. Graphical expression of Klemm's "halide rule"[279,208], where the curves represent: *A*) $\mu = 0.15(1 + m_+/2.1m_-)^{-1}$; *B*) $\mu = 0.079(1 + m_+/2.1m_-)^{-1}$; *C*) boundary between salts having layer and coordinated lattices in the solid state. The experimental points correspond to: *a*) molten chlorides; *b*) molten bromides; *c*) molten iodides; *d*) molten nitrates; *e*) solid salts: 1) LiI; 2) LiBr; 3) Li_2SO_4; 4) LiCl; 5) $ZnBr_2$; 6) α-AgI; 7) $MgCl_2$; 8) RbBr; 9) CdI_2; 10) SnI_2; 11) KCl; 12) $CdBr_2$; 13) $SnBr_2$; 14) PbI_2; 15) CuCl; 16) $ZnCl_2$; 17) RbCl; 18) AgCl; 19) $CdCl_2$; 20) $SnCl_2$; 21) TlCl; 22) UCl_4; 23) LiH; 24) $LiNO_3$; 25) CaI_2; 26) $CaBr_2$; 27) $NaNO_3$; 28) KNO_3; 29) $CaCl_2$; 30) $RbNO_3$; 31) $CsNO_3$; 32) $SrCl_2$; 33) $PbBr_2$; 34) $TlNO_3$; 35) $BaCl_2$; 36) $PbCl_2$.

Correlations of μ_+ with ionic radii are clearer than with ionic masses. For nitrates Okada and Saito[192,222] suggested a linear relation between μ_+ and r_+, but the empirical formula

$$-\mu_+ = 1/(20.9r_+ - 2.4) \qquad (40)$$

derived by Lundén and Ekhed[196] is a far better description of such correlation, which applies also to thallium(I) nitrate. With nitrates this formula (40) is satisfied better than (39)[196], and a still better correlation

$$-\mu_+ = 1/(9.91 + 1.51V_+) \qquad (41)$$

exists between μ_+ and the volume V_+ of the cation: thus the deviation in experimental values of μ_+ for the lithium isotopes from those calculated by means of Eqns. (39)–(41) is respectively 53%, 1%, and 0.4%. For halides Klemm[279] found that μ_+ is correlated more closely with r_+/r_- than with m_+/m_-.

The temperature variation of the mass effect has been studied for several salts. A linear relation is obtained in all cases, expressed by empirical formulae of the type

$$-\mu = a[1 + b(t - t_0)] \qquad (42)$$

where a and b are constant coefficients and t_0 (°C) is a fixed temperature. Table 2 gives values of these three parameters together with the temperature range for which formulae (42) have been derived. The mass effect is seen to decrease with temperature for thallium and chlorine isotopes in thallium(I) chloride and for tin and lead isotopes in tin(II) and lead(II) chlorides respectively; it is almost independent of temperature for lithium isotopes in solid lithium sulphate, chlorine isotopes in rubidium chloride, and bromine isotopes in the bromide; and in the remaining cases it increases with temperature. There are several discrepancies in the results of different workers: for example, μ_+ for lithium isotopes in the nitrate has been found to increase[196] and to decrease[14,172] with temperature (in Ref. 14 the coefficients in Eqn. (42) were not calculated). Lundén and Ekhed[196] suggested several reasons for such discrepancies, but also emphasised the strong influence of difficulty controllable parameters on experiments, which diminished reliability of the results.

Table 2. Values of the constant a, b, and t_0 in Eqn. (42). Elements for whose isotopes this relation has been found are indicated by **bold type** in the formulae of the salts.

No.	Molten salt	a	b	t_0	Temp. range, °C	Ref.
1	LiCl	0.111	+0.00237	610	670—900	195
2	$LiNO_3$	0.0718± ±0.0007	−0.00067± ±0.00024	360	265—460	192
3	$LiNO_3$	0.0860± ±0.0012	+0.00023 ±0.00024	375	313—488	196
4	^6LiCl—^7LiCl*	0.335	+0.000412	610	620—780	195, 291
5	$^6LiNO_3$—$^7LiNO_3$*	0.167	+0.000976	254	280—440	195
6	Li_2SO_4	0.139± ±0.009	−0.0003± ±0.0006	600	600—790	236—238
7	Li_2SO_4—K_2SO_4**	0.129	+0.000735	625	625—835	193
8	KNO_3	0.0385± ±0.0012	+0.00324± ±0.00039	337	354—586	201
9	KCl	0.071	+0.0013	820	820—1020	200
10	KCl	0.062	−0.0001	820	820—980	200
11	RbCl	0.048	+0.0012	750	750—980	200
12	RbCl	0.109	+0.0013	790	790—960	200
13	RbBr	0.072	+0.0003	740	740—950	200
14	RbBr	0.115	+0.0001	800	800—970	200
15	TlCl	0.045	−0.001	470	470—680	221
16	TlCl	0.077	−0.00192	565	565—730	231
17	$SnCl_2$	0.069	−0.0003	340	340—590	223
18	$PbCl_2$***	0.024	−0.033	530	530—640	226

*Calculated by authors from measurements of ratio of electrical conductivities for isotopically pure lithium salts.
**Calculated by Reviewer from results of Expts. 96–98 and 100 in Table 1.
***Calculated by Reviewer from results of Expts. 228 and 229 in Table 1.

Mass effects for the isotopes of five elements (shown in **bold type**) have been measured in the molten salt mixture LiCl–KCl,[159] LiBr–NaBr and LiBr–KBr,[20,178,180,182,183,186,197] Li_2SO_4–K_2SO_4,[193,194] $LiNO_3$–Li_2SO_4,[192] LiCl–$PbCl_2$,[165] $SnCl_2$–$PbCl_2$,[225] $CdBr_2$–Cd,[218] and $CdCl_2$–Cd.[232] In most cases measurements were made in a narrow range of compositions, which is probably why no clear dependence of μ on the chemical composition of the melt could be detected. The work of Chemla et al. showed that variation in the content of lithium and potassium bromides in the separating tube during electrical migration had no apparent effect on the separation of lithium and potassium isotopes. On the other hand, Klemm and Monse[165] studied the composition variation of μ in the LiCl–$PbCl_2$ system, and showed that the mass effect of lithium isotopes remains almost unchanged over the range 100–25 mole % of lithium chloride, but increases sharply at lower contents of this

salt (Table 1, Expts. 4–9), and $-\mu_+ = 0.296$ at 5.3 mole % LiCl. This rule is fully consistent with the value $-\mu_+ = 0.32$ for potassium isotopes in a mixture of 2 mole % of the chloride with lithium chloride[159] (Expt. 109). The abnormally high value of $-\mu_+ = 0.261$ obtained by Lundén[164] for lithium isotopes in the bromide (Expt. 19) is explained by considerable contamination of the lithium bromide melt with other salts, as has been established by control experiments[173,174] (Expts. 20–25). This relation is probably widespread: Klemm[216] showed that the mass effects in the diffusion of hydrogen in solid palladium, of lithium in molten lead, and of copper in solid silver sulphide are respectively −0.45, −0.47, and −0.44, of the order of ten times the values of μ for these cations in molten salts. A common feature of all these processes is the dilute state of the separable species. Nevertheless, over the range 10–80 mole % of tin(II) chloride in lead(II) chloride the tin isotopes have[225] $-\mu_+ = 0.012$ (Expts. 224–226), which is one-fifth of the mass effect in pure tin(II) chloride.

Klemm and Monse[165] proposed a method for measuring the absolute difference in mobility between the isotopic lithium ions in the $LiCl-PbCl_2$ system. The formula used for the calculations was

$$\Delta^{lk}w = -\frac{\varkappa}{Q}\left(\frac{^lN}{^lc} - \frac{^kN}{^kc}\right) = -\frac{\varkappa x' A}{Q}\left(\frac{^l\gamma}{^l\gamma_0} - \frac{^k\gamma}{^k\gamma_0}\right) \qquad (43)$$

where κ is the electrical conductivity, ^jc and ^kc are the molar concentrations of the components in the initial molten salt, and ^jN and ^kN are the numbers of moles of the components in the enrichment zone x' after the passage of Q coulombs of electricity through it, the remaining symbols having the same significance as in Eqn. (31). Variation in the mole fraction of lithium chloride from 1.0 to 0.053 is accompanied by an increase in $\Delta^{67}w$ from 3.93×10^{-5} to 7.10×10^{-5} $cm^2\ V^{-1}\ s^{-1}$.

Countercurrent electrical migration has proved extremely fruitful in studies of the transport properties not only of isotopic ions but also of ions of different elements in mixtures of molten salts. It has been used to measure the relative mobilities of Li^+ and Pb^{2+} in $LiCl-PbCl_2$;[165] Li^+, Na^+, and K^+ in various mixtures of their bromides[20,23,178,180] and nitrates[23,188,190,292,293]; Na^+, K^+, and Rb^+ in mixtures of their nitrates[294]; Li^+ and K^+ in $Li_2SO_4-K_2SO_4$;[193] Li^+, K^+, and Ag^+ in $LiNO_3-KNO_3-AgNO_3$;[294] Li^+ and Ca^{2+} in $LiNO_3-Ca(NO_3)_2$;[294] Li^+ and Ag^+ in $Li_2SO_4-Ag_2SO_4$;[193] Ca^{2+}, Sr^{2+}, and Ba^{2+} in mixtures of their bromides[211,295]; Li^+, K^+, and Ca^{2+} in mixtures of their bromides[211]; Sn^{2+} and Pb^{2+} in $SnCl_2-PbCl_2$;[225] Cl^- and NO_3^- in $AgCl-AgNO_3$;[296] NO_3^- in $LiNO_3-KNO_3$;[297] Cd dissolved in $CdCl_2$[232] and in $CdBr_2$;[218] and also Pb dissolved in $PbCl_2$.[298] The technique of measuring transport numbers of ions in individual melts was developed by Fischer and Klemm[299], and their temperature dependence in thallium(I) chloride and zinc chloride was measured. A general phenomenological theory of the measurement of transport in molten salts by this method was put forward by Klemm[300].

2. Measurement of Ionic Mobilities by the Electrical Migration of a Zone

The electrical migration of ions can be investigated also without production of a countercurrent of electrolyte, by the use of the classic principle of paper electrophoresis[301]. Fig. 5 illustrates the experimental arrangement[14] for molten salts: inside a tubular electric furnace *1* is fixed, in an exactly horizontal position, an asbestos strip *2* (typical dimensions 600 × 12 × 0.3 mm), the ends of which dip into small baths *3* and *4* containing melts of the same salt together with conducting electrodes *5* and *6*. The asbestos strip has previously been washed in acids, ignited, and impregnated with the molten salt solvent.

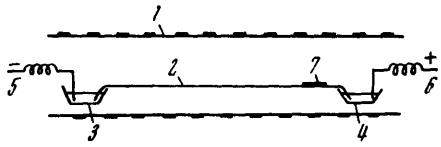


Figure 5. Experimental arrangement for studying electrical zone migration[14].

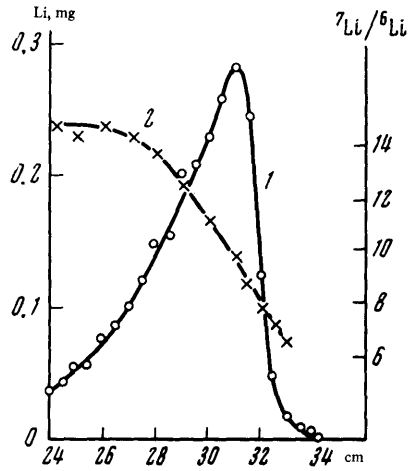


Figure 6. Distribution along migration path of zone after completion of experiment[12] for: 1) concentration of lithium; 2) isotope ratio $^7Li/^6Li$.

The method of investigation consists in applying to one end of the asbestos strip a few milligrams of the salt containing the isotopes, and passing through the system a constant current, under whose influence the initial spot (zone) of the salt *7* moves along the strip. If the zone contains radioactive isotopes, its movement can be followed conveniently by means of a counter. Owing to the difference between the mobilities of isotopic ions, their concentrations within the zone undergo redistribution in the direction of migration: the more mobile light isotopes accumulate at the forward edge of the zone, and the slower heavy isotopes at the rear. The experiment is continued for 2–4 h, after which the asbestos strip with the solidified salts is cut, in the region occupied by the zone, into transverse bands about 5 mm wide, in each of which the isotopic composition of the test element is determined, and if necessary a chemical analysis of the salt mixture is made. Typical results for the electrical migration of a zone in molten salts are illustrated in Fig. 6.

The phenomenological theory of electrical zone migration is simpler than that of countercurrent migration.

Chemla[10,13] showed that movement of the zone in the direction of the electrical field and extension of its boundaries by diffusion can be regarded to a first approximation as mutually independent processes. Substitution of variables $y = x - t\Delta v$ in Eqn. (7) then leads to the equation of Fick's law

$$\frac{\partial \gamma}{\partial t} = D\frac{\partial^2 \gamma}{\partial y^2}, \qquad (44)$$

in which the coefficient of molecular diffusion D (not the coefficient of mixing D') is used. In fact diffusion and electrical migration are not independent processes: Arnikar[48,49,302] showed that the final distribution of the components in electrical zone migration is not identical with their distribution in pure diffusion. The difference between the actual distribution curve for lithium isotopes along the zone and the symmetrical Gaussian curve is readily seen from Fig. 6. In order to calculate the relative difference between the mobilities of the isotopic ions we construct concentration distribution curves for each isotope along the zone, using curves *1* and *2* in Fig. 6. The curves obtained for the distribution of the isotopes are similar to curve *1* for the distribution of the element, but their maxima are displaced a distance $\Delta x'$, and it is easy to show that

$$\frac{\Delta w}{w} = \frac{\Delta x'}{x'} \qquad (45)$$

where x' is the distance traversed by the whole zone. This formula has been discussed critically[14,303]. Experimental conditions and measurements of the mobilities of isotopic ions by electrical zone migration in molten salts are collected together in Table 3, which includes for comparison some data on aqueous solutions with various kinds of paper as support.

Like countercurrent migration, zone migration is widely used to measure the electrical transport parameters of ions in molten salts. Besides asbestos, glass-fibre cloth and plates of sintered alumina powder are employed as substrates. This method has been used to measure the mobilities and the transport numbers of ions of alkali metals, silver, and thallium in pure alkali-metal nitrates[11,12,243,303-312] and in their mixtures[313-315], alkaline-earth metal ions in alkali-metal nitrates[11,12,303,313,314,316] and their mixtures with alkaline-earth metal nitrates[317,318], ions of multivalent metals—copper, zinc, cadmium, cobalt, chromium, cerium, lead, and thorium—in alkali-metal nitrates[313,314,319], in potassium thiocyanate[319], and in LiCl–KCl eutectic[313,320], and chloride, bromide, and nitrate anions in alkali-metal nitrates[11,12,243,303,306,315]. Radioactive isotopes have been widely used in these investigations as tracers in following the movement of the zone along the migration path.

3. Comparison of the Two Methods of Electrical Migration —Frame of Reference

Comparison of Tables 1 and 3 shows fairly close agreement between values of the mass effect determined by electrical zone and countercurrent migration for isotopes in the same salt. Lundén[321] made a detailed comparison of results obtained by the two methods for molten nitrates. Nevertheless, Table 3 shows that the mass effect varies in complicated fashion with the mass of the element, with the composition of the solvent medium impregnating the asbestos support, and also with the temperature. The effects of all these factors on the mobility of isotopic ions are closely interrelated, so that all the experimental results accumulated up to the present time (Tables 1–3) must be taken into account in order to establish general rules. Attempts at the interpretation of experimental results in the light of individual measurements (often only the interpreter's own) are considered below.

Table 3. Experimental conditions of and results obtained by electrical zone migration.

No.	Working salt	Solvent medium*	Potential gradient, V cm^{-1}	Path of zone, cm	Temp., °C	α	$-\mu$	Ref.
1	$LiNO_3$	$NaNO_3+KNO_3$	10	26.0	250	1.0137	0.089	14
2	ditto	ditto	10	23.4	300	1.0102	0.067	14
3	»	»	6	21.0	350	1.0090	0.0585	14
4	»	»	10	31	350	1.014	0.091	11, 12
5	»	»	16	20	300	1.03	0.19	240
6	$LiNO_3$	10% soln. NH_4NO_3	1.5	—	room.[4]	1.0036	0.023	10, 13, 45
7	ditto	ditto	4	56	room.[4]	1.0038	0.024	139
8	$NaNO_3$	$NaNO_3+KNO_3$	14	35	300	1.010	0.10	12, 241
9	ditto	$LiNO_3$	10	30	305	1.0040	0.046	243
10	»	ditto	10	30	355	1.0058	0.067	243
11	»	$NaNO_3$	10	30	358	1.0070	0.080	243
12	»	KNO_3	10	30	358	1.0088	0.101	243
13	»	$CsNO_3$	10	30	435	1.0057	0.0655	243
14	»	$NaNO_3+KNO_3$**	10	30	355	1.0071	0.0815	243
15	»	$NaNO_3+KNO_3$***	10	30	355	1.0080	0.092	243
16	»	$NaNO_3+KNO_3$	10	30	255	1.0053	0.061	243
17	$NaNO_3$	$NaNO_3+KNO_3$	10	30	304	1.0060	0.069	243
18	ditto	ditto	10	30	340	1.0076	0.086	243
19	»	»	10	30	374	1.0090	0.104	243
20	»	»	10	30	404	1.0076	0.086	243
21	»	»	10	30	434	1.0073	0.084	243
22	$NaNO_3$	0.04% soln. NaCl	12.5	—	room.[4]	1.003	0.035	138
23	ditto	soln. $NaNO_3$	17.5	—	1	1.0029	0.038	140
24	»	ditto	17.5	—	26	1.0048	0.055	140
25	»	»	17.5	—	38	1.0065	0.075	140
26	»	»	17.5	—	49	1.0083	0.095	140
27	KNO_3	$NaNO_3+KNO_3$	10	40	350	1.00274	0.0548	14
28	$RbNO_3$	$NaNO_3$	9.1	42	350	1.00158	0.0691	10, 12, 14, 242
29	$RbNO_3$	soln. $NaNO_3$	17.5	—	3	1.0011	0.047	141
30	ditto	ditto	17.5	—	28.5	1.0014	0.060	141
31	»	»	17.5	—	48	1.0017	0.073	141
32	$CsNO_3$	$NaNO_3+KNO_3$	10	41	350	1.0027	0.060	13, 14
33	ditto	$NaNO_3$	10	40	350	1.0036	0.080	10
34	»	soln. $NaNO_3$	—	40	35	1.0097	—	12

*The $NaNO_3 + KNO_3$ mixture always contains 45 wt.% $NaNO_3$.
**The mixture contains 75 wt.% $NaNO_3$.
***The mixture contains 25 wt.% $NaNO_3$.

In the comparison of mass effects obtained by different methods and the assessment of their reliability, it must be borne in mind that any determination of a velocity presupposes agreement on the frame of reference: in the present case this is an object, selected inside or outside the electrolyte, relative to which the speed of the ion is measured. A "convenient"[295] system is one in which the separation factor α is independent of the electric field strength in the electrolyte. Different frames of reference are chosen[279] depending on the medium in which the ions migrate: in solids the surface or the stationary crystal lattice is selected, in solutions the solvent, in molten salts the centre of gravity of the oppositely charged ions, and in liquid metals the flux of conduction electrons. In pure molten salts the choice is a fundamental question, involving controversy about the advisability of applying the concept of transport number to such salts[18,300,322-324]. If the gegenions are chosen as reference, the transport number of the test ions is unity: i.e. they alone are regarded as current carriers and move within the melt, while the gegenions are at rest (this gives rise to the concept of a quasi-crystalline lattice in molten salts).

Physically, however, it is also possible that both cations and anions may move relative to the walls of the vessel, which may also be chosen as stationary frame of reference: in such case both types of ions have fractional transport numbers. The possibility of displacement of the melt as a whole relative to the walls makes incorrect measurement of these quantities highly probable. The use of a porous diaphragm—packing in the separating tube or an asbestos support—tends to diminish the probability of such displacement, in the ideal case to zero (Eqn. 3).

Measurement of transport numbers and ionic mobilities relative to these two frames of reference—gegenions inside the molten salt and a porous diaphragm outside the salt—yields different values for these quantities, which Klemm [19,300] proposed calling "internal" and "external" respectively. Formula (29), which is a definition of the mass effect, shows that the choice of frame of reference affects only the one quantity

$$w = \frac{\sum_i {}^i w {}^i\gamma}{\sum_i {}^i\gamma} \qquad (46)$$

the mean mobility of the isotopic ions to be separated. According to this the internal mobilities of ions should exceed in absolute magnitude the external values, and therefore the internal mass effects, measured by counter-current electrical migration, should be smaller than the external mass effects, measured by electrical zone migration under identical conditions. Comparison of the values of μ for alkali-metal nitrates in Tables 1 and 3 shows general conformity to this principle.

4. Structure of Molten Salts and Mechanism of Ionic Migration

Among the numerous theoretical papers on the inner structure of molten salts and the mechanism of the movement of ions in them under the influence of an electric field, we shall consider only those relating to the problem of the mobility of isotopic ions and their separation. The reasons for the occurrence of an isotope effect in electrical migration have not been established unambiguously. Investigators usually choose the most soundly based (in their opinion) model for the structure of a molten salt and for intermolecular interaction, and compare with experimental results the macro-values calculated on the basis of this micro-model.

To explain the differences in the mobilities of isotopic ions in molten salts we suppose that the element can exist in several states (as free ions, ion-pairs, etc.). The mole fraction of the element in state l is $\Gamma_l = C_l/C$, where C is the molar concentration of the element in the melt, C_l is the concentration of a species in state l, and $\sum_l \Gamma_l = 1$. The mole fraction of the ith isotope in this state is ${}^i\gamma_l = {}^iC_l/C_l$, and $\sum_i {}^i\gamma_l = 1$. The mobility of the ith isotope in the electric field is

$${}^iw = \frac{\sum_l \Gamma_l {}^i\gamma_l {}^iw_l}{\sum_l \Gamma_l {}^i\gamma_l}. \qquad (47)$$

If the equilibrium constant for the exchange of isotopes j and k between states l and m

$${}^{jk}K_{lm} = \frac{{}^j\gamma_l {}^k\gamma_m}{{}^j\gamma_m {}^k\gamma_l} \qquad (48)$$

differs from unity, the difference between the mobilities of the two isotopes in the electric field is [325]

$$\Delta^{jk}w = {}^jw - {}^kw = \sum_l \Gamma_l \left[{}^jw_l - {}^kw_l + \left(w_l - \sum_r \Gamma_r w_r \right) ({}^{jk}K_{lm} - 1) \right]. \qquad (49)$$

Since the mobility of the element as a whole is composed of the mobilities of its species in different states $w = \sum_r \Gamma_r w_r$, it follows from formulae (29) and (49) that [290]

$$\mu \frac{\Delta_m}{m} = \frac{\Delta w}{w} = \sum_l \Gamma_l \frac{\Delta w_l}{w} + \sum_l \Gamma_l \left(\frac{w_l}{w} - 1 \right) ({}^{jk}K_{lm} - 1). \qquad (50)$$

Numerical estimates showed Klemm [215,231,290] that the effect of the isotope exchange equilibrium between different states is not significant in molten salts: i.e. the second summation in Eqn. (50) could be neglected. However, the precisely opposite view is also held [243]: isotopic exchange actually makes the chief contribution to $\Delta w/w$, and the first summation in formula (50) is negligible in comparison with the second.

If the "self-transport number" T is defined as the ratio of external u to internal w ionic mobilities of the element [19]

$$T = \frac{u}{w}, \qquad (51)$$

we can rewrite Eqn. (50), on the assumption that the second summation is close to zero, in the form

$$\mu = T \sum_l \frac{\gamma_l u_l}{\gamma u} \cdot \frac{\Delta u_l}{u_l} \cdot \frac{m}{\Delta m}, \qquad (52)$$

since $\Delta u_1 = \Delta w_1$. Only two states of the species—mobile and stationary—need be distinguished in ionic liquids [261,262]. In terms of the theory of rate processes, activated ions—i.e. those occupying interstitial sites, sites adjacent to holes, etc. in the quasi-crystalline lattice—can be regarded as mobile [167]. Thus mobile ions migrate through the quasi-crystalline lattice formed by the stationary species, by making spontaneous jumps between adjacent equilibrium positions with an average frequency z_S (s^{-1}). [216] This is proportional to the thermal vibration frequency ν of the ions, which is in turn proportional to $m'^{-1/2}$, where $m' = mM/(m+M)$, in which m is the mass of the ion making a jump and M is the total mass, arbitrarily concentrated at a point and vibrating together with the ion, of particles which surround this ion immediately before the jump [290]. Since the summation in Eqn. (52) is made only over the mobile states $l = b$, it follows that

$$\Delta u_l/u_l = \Delta u_b/u_b = \Delta\nu/\nu = -\tfrac{1}{2}\Delta m'/m',$$

and formula (52) becomes

$$\mu = -\frac{1}{2} T \frac{\Delta m'}{m'} \cdot \frac{m}{\Delta m} \sum_b \frac{\gamma_b u_b}{\gamma u}. \qquad (53)$$

The mean rate of migration u_b of mobile ions is proportional to their total number of jumps per second: $z = z_S + z_i$, where z_i is the frequency of jumps induced by processes in the immediate environment of the ion, e.g. by jumps by adjacent ions. Therefore

$$\sum_b \frac{\gamma_b u_b}{\gamma u} = \frac{\gamma_s u_s + \gamma_i u_i}{\gamma u} = \frac{z_s + z_i}{z}.$$

If we bear in mind that the frequency of induced jumps is independent of the mass of the isotopic ions and, passing from finite differences Δm and $\Delta m'$ to infinitesimals dm and dm', differentiate Eqn. (53), we obtain

$$\mu = -\frac{1}{2} T \frac{z_s}{z} \left(1 + \frac{m}{M} \right)^{-1}. \qquad (54)$$

Thus a theoretical basis has been found for formula (38), and the constant it contains μ' is interpreted as $-\frac{1}{2}Tz_S/z$.

It is also useful to introduce the concept of the intrinsic mobility w_0 of an isotopic ion—its mobility in the isotopically pure compound—when the molten salt contains only this isotope of the given element. Since $w = \Lambda/F$, where Λ is the equivalent conductance of the molten salt and F is Faraday's constant, the ratio of the intrinsic mobilities of two isotopic ions is equal to the ratio of the equivalent conductances of the isotopically pure molten salts, and since the difference between the molar volumes of such salts can be neglected[195], this ratio is equal to the ratio of their conductivities κ, which can be found experimentally. Values of this parameter have now been determined for the systems $^6LiCl-^7LiCl$,[195,291] $^6LiNO_3-^7LiNO_3$,[195] and $^6Li_2SO_4-^7Li_2SO_4$.[326]

In the absence of any interaction between the moving ions the mass effect attains the limiting value[279] of $\mu = -0.5$. But in an actual substance this interaction cannot be neglected. Even in an ionic gas, which may be so degenerate that only two-body collisions need be considered, and the effect of the charges of surrounding ions, i.e. the ionic atmosphere, can be neglected, the intrinsic mobility of the ions depends on the reduced mass of the component cations and anions of this gas[25,200]:

$$w_0 = A\left(\frac{m_+ \cdot m_-}{m_+ + m_-}\right)^{-1/2}, \qquad (55)$$

where A is a factor which is independent of the masses. The intrinsic mass effect then becomes

$$\mu_0 = \frac{\Delta w_0}{w_0} \Big/ \frac{\Delta m}{m} \approx \frac{\partial \ln w_0}{\partial \ln m} = -\frac{1}{2}\left(1 + \frac{m_+}{m_-}\right)^{-1}. \qquad (56)$$

Calculation by means of Eqn. (56) of μ_0 for lithium chloride, nitrate, and sulphate yields respectively −0.42, −0.45, and −0.47, whereas the corresponding values measured in the molten salt are −0.35, −0.18, and −0.28.[195,326] This indicates that the mass of the anions has a stronger effect on the intrinsic mobility of the cations in molten salts than in an ionic gas. The ratio $n = \mu_0/\mu$ is interpreted[195,326,327] as the mean number of cations involved in the elementary step of electrical migration by being bound into a single group. For the above lithium salts it has the values 2.39, 2.56, and 2.0. Whether these numbers can be linked with the number of spontaneous and induced jumps by ions and in what way is still being examined more closely; in any case these results reflect the fact that the ions in molten salts cannot move independently of each other.

Ionic conductivity, migration, and diffusion data do not yet enable us to suggest a more detailed model for the structure of molten salts. Thus Klemm[300] showed, when considering the phenomenology of the transport of ions in pure molten salts, that it was impossible to choose the best among models presupposing that a molten salt consists of two components (cations and anions), three components (cations, anions, and a quasi-crystalline lattice), or four components (cations, anions, lattice, and neutral complexes). Lundén[328] found that parameters calculated specially for molten alkali-metal nitrates on a basis of all three models agreed qualitatively with the experimental results. Attempts to apply similar models to solutions of cadmium in cadmium chloride[232] and of lead in lead(II) chloride[298] also showed the impossibility of selecting one of them unambiguously on the basis solely of data on the transport properties of the molten salts.

The theoretical concepts used to explain the temperature dependence of the mass effect have been modified and refined as experimental data have accumulated[25,167,200,231,279,303]. A model was suggested[25] taking into account the most recent measurements of the mass effect at different temperatures. With rise in temperature the structure of an ionic melt passes successively through three different stages (Fig. 7): a quasi-crystalline structure—a lattice with a few free ions within—predominates at low temperatures (stage I); then the lattice breaks down into electrically charged polyionic groups (stage II); and at very high temperatures the melt consists mainly of neutral ion-pairs with a small proportion of free ions (stage III). The situation is less favourable for a large mass effect in the second stage than in stages (I) and (III), in which a larger number of mobile groups of ions are present. Experimental results show larger mass effects in solid than in molten salts, and the above estimates indicate that they should also be larger in an ionic gas than in a melt. Thus on passing from a solid through the melt to the gas the mass effect has a tendency to pass through a minimum (the smooth variation in the function may be disturbed abruptly at the melting point and the boiling point[200]).

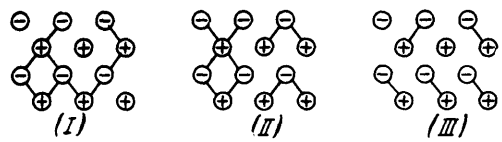


Figure 7. Model of change in structure of molten salt with rise in temperature[25].

From a comparison of this model with Table 2 it may be supposed that, for example, molten thallium(I) and lead(II) chlorides are located somewhere between stages (I) and (II), and molten alkali-metal halides somewhere between stages (II) and (III). The contribution of quantum-mechanical effects to isotopic differences in the mobilities of light elements such as lithium can be neglected at high temperatures[195,200], but in lithium nitrate electrical migration takes place at relatively low temperatures, and these effects may be appreciable: hence the difference between the temperature dependence of μ_+ for this salt and for other alkali-metal salts. The variation of the mass effect for sodium isotopes in the $NaNO_3-KNO_3$ eutectic (Expts. 16–21, Table 3), which is "unusual" in terms of this model, is explained[243] by the predominant effect at low temperatures of the proportion of combined displacements of ions, which increases with temperature, and by the predominant effect at high temperatures of the isotopic exchange constant (48) between ions and neutral complexes, which decreases with temperature. On the whole these views evidently do not contradict a three-stage model, and the above categorical statements on the relative contributions of the first and second summations in Eqn. (50) to the mass effect are refined. The most correct hypothesis is apparently that the separation of isotopes in the electrical migration of ions takes place by several parallel mechanisms[279], whose relative contributions to the overall effect varies with temperature.

APPENDIX

Since this paper was submitted for publication a monograph[329] and several papers have appeared on the electrical migration of ions in molten salts[330-339], aqueous solutions[340], and solid salts[341].

REFERENCES

1. J. Kendall, Proc. Roy. Soc. Edinburgh, 57, 182 (1937).
2. K. Westermark, Tekn. Tidskr., 78, 160 (1948).
3. Angew. Chem., 61, 108 (1949).
4. H. Martin, Angew. Chem., 62, 121 (1950).
5. A. Lundén, Kosmos (Stockholm), 31, 105 (1953).
6. J. V. Iribarne, Chemía (Argentina), 16, 41 (1955).
7. A. Klemm, Physikertagung Wiesbaden 1955, Physik-Verlag, Mosbach, 1956, p. 73.
8. A. Lundén, Thesis, Gothenburg, 1956.
9. A. Lundén, Proc. Internat. Symposium Isotope Separation, Amsterdam 1957, North Holland Publ. Co., 1958, p. 283.
10. M. Chemla, Proc. Internat. Symposium Isotope Separation, Amsterdam 1957, North Holland Publ. Co., 1958, p. 288.
11. H. J. Arnikar and M. Chemla, J. Appl. Radiation Isotopes, 2, 261 (1957).
12. Proc. Internat. Conf. Radioisotopes in Scientific Research, Paris, 1957, Pergamon Press, 1958, Vol. 2, p. 421.
13. M. Chemla, J. Chromatog., 1, 2 (1958).
14. H. J. Arnikar, Ann. Physique., 4, 1291 (1959).
15. H. C. Cole and H. London, in "Separation of Isotopes", G. Newnes Ltd., London, 1961, p. 381.
16. M. Gazith and A. Roy, Israel Atomic Energy Commission (Repts.), No. 832 (1963).
17. M. Gazith and A. Roy, Electrochem. Technol., 2, 85 (1964).
18. P. Gallone, in "Encyclopedia of Electrochemistry", Reinhold, New York, 1964, p. 747.
19. A. Klemm, in "Molten Salt Chemistry" (Edited by M. Blander), J. Wiley, New York, 1964, p. 535.
20. J. Périé, Thèse, Paris, 1965.
21. F. Ménès and G. Dirian, Bull. d'Inform. scient. et techn., No. 103, 89 (1966).
22. H. R. C. Pratt, "Countercurrent Separation Processes" Elsevier Publ. Co., 1967, p. 436.
23. M. Chemla, Bull. Soc. chim. France, 1457 (1967).
24. P. S. Baker, Survey Progr. Chem., 4, 90 (1968).
25. A. Klemm and K. Heinzinger, Advances in Chemistry Series 89, Amer. Chem. Soc. Publ., Washington, 1969, p. 248.
26. E. A. Kaimakov and N. L. Varshavskaya, Uspekhi Khim., 35, 201 (1966) [Russ. Chem. Rev., No. 2 (1966)].
27. H. D. Freyer and K. Wagener, Angew. Chem., 79, 734 (1967).
28. D. K. Belashchenko, Uspekhi Khim., 34, 530 (1965) [Russ. Chem. Rev., No. 3 (1965)].
29. D. K. Belashchenko, "Yavleniya Perenosa v Zhidkikh Metallakh i Poluprovodnikakh" (Transport Phenomena in Liquid Metals and Semiconductors), Atomizdat, Moscow, 1970.
30. A. Lindemann, Proc. Roy. Soc. A, 99, 102 (1921).
31. R. S. Milliken and W. D. Harkins, J. Amer. Chem. Soc., 44, 37 (1922).
32. J. Kendall, Phys. Rev., 21, 389 (1923).
33. J. Kendall and E. S. Crittenden, Proc. Nat. Acad. Sci. U. S. A., 9, 75 (1923).
34. E. Murmann, Österreich. Chem.-Ztg., 26, 14 (1923).
35. J. Kendall and F. White, Proc. Nat. Acad. Sci. U. S. A. 10, 458 (1924).
36. J. E. G. Pilley, Phil. Mag., (6), 49, 889 (1925).
37. J. Kendall, Science, 67, 162 (1928).
38. A. Eilert, Verhandl. deutsch. phys. Ges., 4, 5 (1923).
39. J. Kendall and B. L. Clarke, Proc. Nat. Acad. Sci. U. S. A., 11, 393 (1925).
40. J. Kendall and W. West, J. Amer. Chem. Soc., 48, 2619 (1926).
41. J. Kendall, W. West, and E. R. Jette, J. Amer. Chem. Soc., 48, 3114 (1926).
42. J. Kendall, Proc. Roy. Phil. Soc. Glasgow, 59, 1 (1931).
43. E. R. Jette, Phil. Mag., (7), 3, 258 (1927).
44. J. Kendall, Nature, 150, 136 (1942).
45. H. J. Arnikar, J. Inorg. Nuclear Chem., 11, 248 (1959).
46. C.-J. van Oss, N. R. Beyrard, S. de Mende, and M. Bonnemay, Compt. rend., 248, 223 (1959).
47. B. M. Shukla, and R. P. Gupta, Proc. Nucl. a. Radiation Chem. Sympos. 1964, Atom. Energy Establ., Trombay, India, 1965, p. 149; Nucl. Sci. Abstr., 20, 25 083 (1966).
48. H. J. Arnikar and R. Tripathi, Proc. Nucl. a. Radiation Chem. Sympos. 1964, Atom. Energy Establ., Trombay, India, 1965, p. 154; Nucl. Sci. Abstr., 20, 25 084 (1966).
49. H. J. Arnikar and R. Tripathi, Indian. J. Chem., 4, 1 (1966).
50. H. G. van Name, A-508, (19th Dec. 1942); see Ref. 17.
51. H. C. Urey, A-208, (27th July, 1942); see Ref. 17.
52. H. S. Harned, A-713, (19th May, 1942); see Ref. 17.
53. H. S. Harned, A-334, (2nd Nov., 1942); see Ref. 17.
54. H. S. Harned, Rept. No. OEM Sr-381, (2nd Nov., 1942); see Refs. 17 and 24.
55. L. G. Longsworth and D. A. MacInnes, A-164 (21st April, 1942); see Ref. 15.
56. D. A. MacInnes, L. G. Longsworth, and D. Taub, A-379, (24th Nov., 1942); see Ref. 17.
57. D. A. MacInnes and L. G. Longsworth, A-919 (15th June, 1943); see Ref. 17.
58. D. D. Wright and R. J. Best, A-164, (21st April, 1942); see Refs. 17 and 24.
59. A. K. Brewer, S. L. Madorsky, and J. W. Westhaver, Science, 104, 156 (1946).
60. A. K. Brewer, S. L. Madorsky, J. K. Taylor, V. H. Dibeler, P. Bradt, O. L. Parham, R. J. Britten, and J. G. Reid, J. Res. Nat. Bur. Stand., 38, 137 (1947).
61. S. L. Madorsky and A. K. Brewer, US P. 2 645 610 (14th July, 1953).
62. S. L. Madorsky and S. Straus, J. Res. Nat. Bur. Stand., 38, 185 (1947).
63. S. L. Madorsky and S. Straus, J. Res. Nat. Bur. Stand., 41, 41 (1948).
64. L. P. Twichell, R. D. Williams, and A. Clark, Y-488, (22nd Aug., 1949); Nucl. Sci. Abstr., 12, 3608 (1958).
65. A. Clark, US P. 2 813 064 (12th Nov., 1957); Nucl. Sci. Abstr., 12, 6984 (1958).
66. J. W. Westhaver, J. Res. Nat. Bur. Stand., 38, 169 (1947).
67. G. Breit and F. L. Friedman, J. Res. Nat. Bur. Stand. 39, 397 (1947).
68. A. Klemm, Z. phys. Chem., 193, 29 (1943).
69. A. Klemm, Naturwiss., 31, 205 (1943).
70. A. Klemm, Z. Physik., 123, 10 (1944).
71. A. Klemm, Naturwiss., 32, 69 (1944).

72. A. Klemm, Z. Naturforsch., **2a**, 9 (1947).
73. E. A. Bakulin and E. V. Stepin, Zhur. Fiz. Khim., **38**, 1655 (1964) [Russ. J. Phys. Chem., No. 6 (1964)].
74. B. P. Konstantinov and V. B. Fiks, Zhur. Fiz. Khim., **38**, 1647 (1964) [Russ. J. Phys. Chem., No. 6 (1964)].
75. B. P. Konstantinov and V. B. Fiks, Zhur. Fiz. Khim., **38**, 1904 (1964) [Russ. J. Phys. Chem., No. 8 (1964)].
76. B. P. Konstantinov and V. B. Fiks, Zhur. Fiz. Khim., **38**, 2255 (1964) [Russ. J. Phys. Chem., No. 9 (1964)].
77. V. B. Fiks, Zhur. Fiz. Khim., **38**, 2257 (1964).[Russ. J. Phys. Chem., No. 9 (1964)].
78. V. B. Fiks and E. V. Stepin, Zhur. Fiz. Khim., **38**, 2260 (1964) [Russ. J. Phys. Chem., No. 9 (1964)].
79. E. A. Bakulin, V. P. Troshin, and V. B. Fiks, Zhur. Fiz. Khim., **38**, 2262 (1964) [Russ. J. Phys. Chem., No. 9 (1964)].
80. B. P. Konstantinov and E. A. Bakulin, Zhur. Fiz. Khim., **39**, 3 (1965) [Russ. J. Phys. Chem., No. 1 (1965)].
81. B. P. Konstantinov and E. A. Bakulin, Zhur. Fiz. Khim., **39**, 592 (1965) [Russ. J. Phys. Chem., No. 3 (1965)].
82. B. P. Konstantinov, E. A. Kaimakov, and I. V. Basargin, Zhur. Fiz. Khim., **39**, 836 (1965) [Russ. J. Phys. Chem., No. 4 (1965)].
83. E. A. Bakulin, Zhur. Fiz. Khim., **39**, 1065 (1965) [Russ. J. Phys. Chem., No. 5 (1965)].
84. E. A. Bakulin and B. P. Aleksandrov, Zhur. Strukt. Khim., **7**, 174 (1966).
85. H. Martin, Angew. Chem., **61**, 302 (1949).
86. H. Martin, Z. Naturforsch., **4a**, 28 (1949).
87. H. Martin and E. Ruhtz, Z. Elektrochem., **54**, 560 (1950).
88. H. Martin, Proc. Internat. Symposium Isotope Separation, Amsterdam, 1957, Horth Holland Publ. Co., 1958, p. 285.
89. H. Martin and E. Harmsen, Z. Elektrochem., **62**, 152 (1958).
90. H. Martin and H.-J. Lübke, Z. Naturforsch., **19a**, 115 (1964).
91. K. Clusius and E. R. Ramirez, Helv. Chim. Acta, **36**, 1160 (1953).
92. E. R. Ramirez, J. Amer. Chem. Soc., **76**, 6237 (1954).
93. E. R. Ramirez, J. Phys. Chem., **62**, 760 (1958).
94. K. Clusius and M. Huber, Swiss P. 362 681 (1958); see Ref. 27.
95. K. Clusius and M. Huber, Swiss P. 374 367 (1959); see Ref. 27.
96. K. Wagener, Z. Elektrochem., **64**, 922 (1960).
97. K. Wagener, Z. Elektrochem., **64**, 1163 (1960).
98. K. Clusius and K. Wagener, Z. Elektrochem., **65**, 701 (1961).
99. K. Clusius and K. Wagener, Angew. Chem., **73**, 496 (1961).
100. K. Clusius, M. Huber, and K. Wagener, J. Chim. phys., **60**, 263 (1963).
101. E. Blasius and W. Neumann, Z. Elektrochem., **65**, 475 (1961).
102. W. Thiemann and K. Wagener, Z. Naturforsch., **18a**, 228 (1963).
103. K. Wagener, Dissertation, West Berlin, 1965.
104. D. Behne and K. Wagener, Ber. Bunsenges. phys. Chem., **69**, 378 (1965).
105. D. Behne and H. D. Freyer, K. Wagener, Ber. Bunsenges. phys. Chem., **69**, 893 (1965).
106. K. Wagener and B. A. Bilal, Z. Naturforsch., **21a**, 1352 (1966).
107. W. Thiemann and K. Wagener, Ber. Bunsenges. phys. Chem., **70**, 1170 (1966).
108. K. Wagener and U. Zimmermann, Ber. Bunsenges. phys. Chem., **71**, 898 (1967).
109. K. Wagener, Ber. Bunsenges. phys. Chem., **71**, 627 (1967).
110. W. Thiemann, Z. Naturforsch., **24a**, 830 (1969).
111. B. A. Bilal, Z. Naturforsch., **24a**, 1281 (1969).
112. B. A. Bilal, Z. Naturforsch., **24a**, 1791 (1969).
113. K. Reinert, W. Thiemann, and K. Wagener, Microchim. Acta, 709 (1969).
114. H. Gaus, Z. Naturforsch., **25a**, 1007 (1970).
115. M. M. Benarie, Bull. Res. Council Israel, **A6**, 280 (1957).
116. M. M. Benarie, Bull. Res. Council Israel, **A9**, 207 (1960).
117. I. Aoyama, K. Ishida, T. Aoyama, and S. Tamura, J. Atom. Energy Soc. Japan, **4**, 700 (1962) Ref. Zhur. Fiz., 8A, 247 (1963).
118. H. Kakihana, Y. Mori, and T. Hoshino, Bull. Chem. Soc. Japan, **35**, 2055 (1962).
119. H. Kakihana, Jap. P. 1965-20 000 (6th Sept., 1954); Nucl. Sci. Abstr., **21**, 3158 (1967).
120. H. Kakihana, B. P. 1 066 377 (26th April, 1967); Nucl. Sic. Abstr., **21**, 25 960 (1967).
121. H. Kakihana, Jap. P. 1968-7518 (21st March, 1968); Nucl. Sci. Abstr., **22**, 51 078 (1968).
122. H. Kakihana, B. P. 1 067 567 (3rd May, 1967); Nucl. Sci. Abstr., **21**, 25 967 (1967).
123. H. Kakihana, Y. Mori, and T. Hoshino, Nippon Genshiryoku Gakkaishi, **6**, 65 (1965); Chem. Abs., **62**, 2441f (1965).
124. H. Kakihana, Third U. N. Internat. Conf. Peaceful Uses Atomic Energy, 1964 (Preprint No. 439).
125. M. Okamoto, Tokyo Kogyo Daigaku Gakuho, 143 (1966); Nucl. Sci. Abstr., **22**, 4239 (1968).
126. M. Okamoto and H. Kakihana, J. Chem. Soc. Japan, **88**, 313 (1967); Nucl. Sci. Abstr., **21**, 22 018 (1967).
127. H. Kakihana, T. Kanzaki, M. Okamoto, S. Yokotsuka, and J. Hoshi, J. Chem. Soc. Japan, **88**, 313 (1967); Nucl. Sci. Abstr., **22**, 42 824 (1968).
128. H. Kakihana, M. Okamoto, and Y. Fujii, Isotopenpraxis, **4**, 232 (1968).
129. H. Kakihana and T. Kanzaki, Tokyo Kogyo Daigaku Gakuho, 77 (1969); Nucl. Sci. Abstr., **23**, 40 843 (1969).
130. M. Okamoto, Y. Fujii, M. Aida, and H. Kakihana, Isotopenpraxis, **6**, 69 (1970).
131. M. N. Kurin, I. A. Tikhomirov, and G. S. Tikhonov, Zhur. Fiz. Khim., **40**, 2177 (1966) [Russ. J. Phys. Chem., No. 9 (1966)].
132. G. S. Tikhonov, I. A. Tikhomirov, and V. A. Emel'kin, Elektrokhimiya, **3**, 93 (1967).
133. M. N. Kurin, I. A. Tikhomirov, and G. I. Mal'tsev, Zhur. Fiz. Khim., **43**, 2672 (1969) [Russ. J. Phys. Chem., No. 10 (1969)].
134. I. A. Tikhomirov, V. T. Doronin, A. P. Vergun, and V. V. Larionov, Zhur. Fiz. Khim., **44**, 751 (1970) [Russ. J. Phys. Chem., No. 4 (1970)].
135. I. A. Tikhomirov, V. T. Doronin, A. P. Vergun, and V. V. Larionov, Elektrokhimiya, **6**, 1467 (1970).
136. M. N. Kurin, I. A. Tikhomirov, and G. I. Mal'tsev, Zhur. Fiz. Khim., **44**, 1302 (1970) [Russ. J. Phys. Chem., No. 5 (1970)].
137. I. A. Tikhomirov and G. S. Tikhonov, Zhur. Fiz. Khim., **44**, 1504 (1970) [Russ. J. Phys. Chem., No. 6 (1970)].
138. A. Bonnin, M. Chemla, and P. Süe, Compt. rend., **241**, 40 (1955).
139. A. Bonnin and M. Chemla, Compt. rend., **243**, 1112 (1956).
140. A. Bonnin, Compt. rend., **244**, 2708 (1957).
141. A. Bonnin and M. Chemla, Compt. rend., **246**, 1189 (1958).

142. A. Bonnin, Thèse, Paris, 1967.
143. M. Périé, J. Périé, and M. Chemla, J. Chim. phys., 65, 1284 (1968).
144. M. Périé, J. Périé, and M. Chemla, J. Chim. phys., 66, 1379 (1969).
145. M. Chemla, Compt. rend., 232, 1553 (1951).
146. M. Chemla, Compt. rend., 232, 2424 (1951).
147. M. Chemla, Compt. rend., 234, 2601 (1952).
148. M. Chemla, Ann. Physique, 1, 959 (1956).
149. M. Chemla, Compt. rend., 234, 2064 (1952).
150. M. Chemla, Compt. rend., 236, 484 (1953).
151. M. Chemla and P. Süe, Compt. rend., 236, 2397 (1953).
152. J. R. Manning, J. Appl. Phys., 33, 2145 (1962).
153. R. Steiger, K. Boustany, and C. G. Boissonnas, Helv. Chim. Acta, 49, 787 (1966).
154. W. Dornelas and P. Lacombe, Compt. rend., 265C, 359 (1967).
155. V. B. Ptashnik and A. N. Naumov, Fiz. Tverd. Tela, 10, 880 (1968).
156. H. Tannenberger and H. Schachner, Swiss P. 428 671 (31st July, 1967).
157. H. Tannenberger and H. Schachner, US P. 3 451 911 (2nd Dec., 1964); Nucl. Sci. Abstr., 23, 45 377 (1969).
158. H. S. Spacil and C. S. Tedmon, Nature, 222, 662 (1969).
159. A. Klemm, H. Hintenberger, and P. Hoerness, Z. Naturforsch., 2a, 245 (1947).
160. A. Klemm, Z. Naturforsch., 6a, 512 (1951).
161. J. I. Hoover and C. E. Holloway, NRL-Report 3897 (2nd Nov., 1951).
162. A. Klemm, Z. Elektrochem., 58, 609 (1954).
163. A. Lundén, E. U. Monse, and N. G. Sjöberg, Z. Naturforsch., 11a, 75 (1956).
164. A. Lundén, Z. Naturforsch., 11a, 590 (1956).
165. A. Klemm and E. U. Monse, Z. Naturforsch., 12a, 319 (1957).
166. A. Klemm, Angew. Chem., 69, 565 (1957).
167. A. Klemm, Proc. Internat. Symposium Isotope Separation, Amsterdam 1957, North-Holland Publ. Co., 1958, p. 275.
168. E. Saito, Belg. P. 573 176 (5th Dec., 1957); Nucl. Sci. Abstr., 15, 15 935 (1961).
169. A. Kepes, Belg. P. 573 868 (20th Dec., 1957); Nucl. Sci. Abstr., 15, 15 939 (1961).
170. L. Perret, L. Rozand, and E. Saito, Second U. N. Internat. Conf. Peaceful Uses Atomic Energy, A/CONF 15/P/1267 (1958).
171. Vallet, Kepes, Beaufils, and Belilowski, Second U. N. Internat. Conf. Peaceful Uses Atomic Energy, A/CONF 15/P/1270 (1958).
172. A. Klemm, Angew. Chem., 70, 21 (1958).
173. A. Lundén, S. Christofferson, and A. Lodding, Z. Naturforsch., 13a, 1034 (1958).
174. A. Lundén, S. Christofferson, and A. Lodding, Chalmers Tekn. Högskolas Handl., No. 221 (1959).
175. French P. 1 190 099 (31st March, 1959); Nucl. Sci. Abstr., 14, 21 865 (1960).
176. French P. 1 207 421 (7th Sept., 1959); Nucl. Sci. Abstr., 15, 9313 (1961).
177. J. Périé and M. Chemla, French P. 1 216 418 (30th Nov., 1959); Nucl. Sci. Abstr., 15, 32 417 (1961).
178. J. Périé and M. Chemla, Compt. rend., 250, 3986 (1960).
179. A. Lundén, Ann. New York Acad. Sci., 79, 988 (1960).
180. J. Périé, M. Chemla, and M. Gignoux, Bull. Soc. chim. France, 7, 1249 (1961).
181. J. Pauly, Compt. rend., 252, 2407 (1961).
182. M. Chemla, Bull. Soc. chim. France, 7, 665 (1961).
183. M. Chemla, Israeli P. 13 582 (25th June, 1961); see Ref. 17.
184. M. M. Benarie, J. Inorg. Nuclear Chem., 18, 32 (1961).
185. A. Kepes, US P. 3 025 224 (13th May, 1962); Nucl. Sci. Abstr., 16, 17 958 (1962).
186. M. Chemla, US P. 887 052 (17th Jan., 1962); see Ref. 17.
187. B. P. 888 884 (7th Feb., 1962); see Ref. 17.
188. F. Lantelme and M. Chemla, J. Chim. phys., 60, 250 (1963).
189. G. J. Arkenbout, Third U. N. Internat. Conf. Peaceful Uses Atomic Energy, Rept. P/639, 1964.
190. F. Lantelme, Thèse, CEA, Saclay, France, 1965.
191. G. Dirian and F. Ménès, French P. 1 500 255 (25th Sept., 1967).
192. I. Okada, Thesis, Tokyo, 1966.
193. V. Ljubimov and A. Lundén, Z. Naturforsch., 21a, 1592 (1966).
194. A. Lundén and V. Ljubimov, Z. Naturforsch., 23a, 1558 (1968).
195. S. Jordan, R. Lenke, and A. Klemm, Z. Naturforsch., 23a, 1563 (1968).
196. A. Lundén and A. Ekhed, Z. Naturforsch., 24a, 892 (1969).
197. Y. Yamamura, J. Nuclear Sci. Technol., 6, 698 (1969); Nucl. Sci. Abstr., 24, 11 680 (1970).
198. N. Saito, I. Tomita, and I. Okada, J. Nuclear Sci. Technol., 6, 698 (1969); Nucl. Sci. Abstr., 20, 29 185 (1966).
199. A. Lundén, C. Reuterswärd, and N. Sjöberg, Z. Naturforsch., 10a, 279 (1955).
200. S. Jordan and A. Klemm, Z. Naturforsch., 21a, 1584 (1966).
201. A. Lundén and A. Ekhed, Z. Naturforsch., 23a, 1779 (1968).
202. A. Lundén, Z. Naturforsch., 21a, 1510 (1966).
203. N. Saito, A. Miyazaki, and I. Okada, Denki Kagaku, 36, 137 (1968); Ref. Zhur. Khim., 21B, 713 (1968).
204. A. Lundén and E. Berne, Z. Naturforsch., 9a, 684 (1954).
205. S. Floberg, A. Klemm, and C. Lang, Z. Naturforsch., 8a, 562 (1953).
206. A. Neubert and A. Klemm, Z. Naturforsch., 16a, 685 (1961).
207. A. Klemm, Discuss. Faraday Soc., 203 (1961).
208. A. Neubert and A. Klemm, Z. Elektrochem., 64, 1110 (1960).
209. F. Ménès, G. Dirian, and E. Roth, Rapp. CEA-2119 (1962); see Refs. 24 and 27.
210. F. Ménès, G. Dirian, and E. Roth, Kernenergie, 5, 295 (1962).
211. F. Ménès, G. Dirian, and E. Roth, J. Chim. phys., 60, 245 (1963).
212. F. Botter, P. Molinari, and G. Dirian, Rapp. CEA-2647 (1964).
213. F. Botter, P. Molinari, and G. Dirian, Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy (Geneva 1964).
214. J. Romanos and A. Klemm, Z. Naturforsch., 19a, 1000 (1964).
215. A. Klemm, H. Hintenberger, and A. Lundén, Z. Naturforsch., 6a, 489 (1951).
216. A. Klemm, E. Lindholm, and A. Lundén, Z. Naturforsch., 7a, 560 (1952).

217. A. Klemm, H. Hintenberger, and W. Seelmann-Eggebert, Z. Naturforsch., **3a**, 172 (1948).
218. I. Holmlid, Z. Naturforsch., **21a**, 270 (1966).
219. A. Klemm, H. Hintenberger, and W. Seelmann-Eggebert, Z. Naturforsch., **3a**, 622 (1948).
220. W. Fischer and A. Klemm, Z. Naturforsch., **16a**, 563 (1961).
221. W. Fischer, K. Heinzinger, and W. Herzog, A. Klemm, Z. Naturforsch., **17a**, 799 (1962).
222. I. Okada and N. Saito, Bull. Chem. Soc. Japan, **43**, 394 (1970).
223. S. I. Golyshev, V. N. Lyubimov, and I. A. Tikhomirov, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 12 (5), 3 (1969).
224. S. I. Golyshev, V. N. Lyubimov, and I. A. Tikhomirov, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 4 (2), 160 (1970).
225. V. N. Lyubimov, V. A. Fedotov, V. M. Grankin, and P. P. Semyannikov, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 12 (5), 24 (1970).
226. A. Lundén, G. Horlitz, and P. Signer, Z. Naturforsch., 11a, 280 (1956).
227. A. Lundén and G. Blomqvist, Z. Naturforsch., 15a, 950 (1960).
228. J. W. Grisard and S. S. Kirslis, K-1247 (28th Aug., 1958), see Ref. 17.
229. A. Klemm and A. Lundén, Z. Naturforsch., 10a, 282 (1955).
230. A. Lundén and W. Herzog, Z. Naturforsch., 11a, 520 (1956).
231. W. Herzog and A. Klemm, Z. Naturforsch., 13a, 7 (1958).
232. W. Herzog and A. Klemm, Z. Naturforsch., 15a, 1100 (1960).
233. A. Selecki and M. Czelej, Nukleonika, 11, 1437 (1966).
234. A. E. Cameron, W. Herr, W. Herzog, and A. Lundén, Z. Naturforsch., 11a, 203 (1956).
235. A. Lundén and A. Lodding, Z. Naturforsch., 15a, 320 (1960).
236. A. Lundén, Z. Naturforsch., 15a, 365 (1960).
237. A. Lundén, Z. Naturforsch., 17a, 142 (1962).
238. A. Lundén, J. Chim. phys., 60, 259 (1963).
239. B. Collén, Acta Chem. Scand., 18, 839 (1964).
240. M. Chemla, Compt. rend., 242, 1450 (1956).
241. M. Chemla and A. Bonnin, Compt. rend., 241, 1288 (1955).
242. C. Mangalo, H. J. Arnikar, and M. Chemla, Compt. rend., 244, 2796 (1957).
243. S. Wuhl, F. Lantelme, and M. Chemla, J. Chim. phys., 65, 488 (1968).
244. E. Haeffner, Nature, 172, 775 (1953).
245. E. Haeffner, T. Sjöborg, and S. Lindhe, Z. Naturforsch., 11a, 71 (1956).
246. I. V. Bogoyavlenskii, V. N. Grigor'ev, N. S. Rudenko, and D. G. Dolgopolov, Zhur. Eksper. Teor. Fiz., 33, 581 (1957).
247. I. V. Bogoyavlenskii, V. N. Grigor'ev, and N. S. Rudenko, Zhur. Eksper. Teor. Fiz., 37, 1241 (1959).
248. A. Lundén, A. Lodding, and W. Fischer, Z. Naturforsch., 12a, 268 (1957).
249. A. Maschka and G. Bauer, Allg. prakt. Chem., 18, 202 (1967).
250. A. Lundén, C. Reuterswärd, and A. Lodding, Z. Naturforsch., 10a, 924 (1955).
251. A. Lodding, Z. Naturforsch., 14a, 934 (1959).
252. A. Lodding, Z. Naturforsch., 16a, 1252 (1961).
253. A. Lodding, Z. Naturforsch., 14a, 7 (1959).
254. A. Nordén and A. Lodding, Z. Naturforsch., 22a, 215 (1967).
255. A. Lodding, Z. Naturforsch., 12a, 569 (1957).
256. G. Nief, and E. Roth, Compt. rend., 239, 162 (1954).
257. M. Goldman, G. Nief, and E. Roth, Compt. rend., 243, 1414 (1956).
258. P. P. Kuz'menko, E. I. Khar'kov, and V. I. Lozovoi, Dokl. Akad. Nauk SSSR, 160, 1343 (1965).
259. A. Lodding, J. Phys. and Chem. Solids, 28, 557 (1967).
260. A. Lodding, A. Lundén, and H. von Ubisch, Z. Naturforsch., 11a, 139 (1956).
261. A. Klemm, Z. Naturforsch., 8a, 397 (1953).
262. A. Klemm, Z. Naturforsch., 9a, 1031 (1954).
263. P. G. de Gennes, J. Phys. Radium, 17, 343 (1956).
264. N. S. Rudenko, V. N. Grigor'ev, D. G. Dolgopolov, and I. V. Bogoyavlenskii, "Trudy Sessii AN USSR po Mirnomu Ispol'zovaniyu Atomnoi Energii 1956" (Proceedings of a Session of the Ukrainian SSR Academy of Sciences on the Peaceful Uses of Atomic Energy 1956), Izd. Akad. Nauk Ukrain. SSR, Kiev, 1958.
265. S. E. Bresler and G. E. Pikus, Zhur. Teor. Fiz., 26, 109 (1956).
266. S. E. Bresler and G. E. Pikus, Zhur. Teor. Fiz., 28, 2282 (1958)
267. A. Lodding, Proc. Internat. Symposium Isotope Separation, Amsterdam 1957, North-Holland Publ. Co., 1958, p. 308.
268. A. Lodding, Thesis, Gothenburg, 1961.
269. A. Lodding, and A. Klemm, Z. Naturforsch., 17a, 1085 (1962).
270. A. Lodding, J. Chim. phys., 60, 254 (1963).
271. D. K. Belashchenko and G. A. Grigor'ev, Zhur. Fiz. Khim., 37, 929 (1963) [Russ. J. Phys. Chem., No. 4 (1963)].
272. A. Lodding, "Encyclopedia of Electrochemistry", Reinhold, New York, 1964, p. 491.
273. P. P. Kuz'menko, E. I. Khar'kov, and V. I. Lozovoi, Fiz. Metallov i Metalloved., 21, 414 (1966).
274. G. Bauer and A. Maschka, Monatsh., 98, 1066 (1967).
275. A. Lodding, Phys. Status Solidi, 22, 167 (1967).
276. D. K. Belashchenko, Izv. Vys. Ucheb. Zaved., Chernaya Metallurgiya, 20 (1968).
277. A. Lodding, Advances in Chemistry Series 89, Amer. Chem. Soc. Publ. Washington, 1969, p. 264.
278. A. Klemm, J. Chim. phys., 49, C 18 (1952).
279. A. Klemm, J. Chim. phys., 60, 237 (1963).
280. V. N. Lyubimov, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 12 (5), 18 (1970).
281. A. Klemm, Z. Naturforsch., 7a, 417 (1952).
282. A. Klemm, Z. Naturforsch., 1, 252 (1946).
283. M. Mason and W. Weaver, Phys. Rev., 23, 424 (1924).
284. S. D. Majumdar, Phys. Rev., 81, 844 (1951).
285. A. Klemm, Z. Naturforsch., 3a, 211 (1948).
286. A. Lundén, Corrosion Sci., 1, 62 (1961).
287. G. J. Janz, "Molten Salt Chemistry", Academic Press, New York, 1967.
288. A. Lundén, Z. Naturforsch., 16a, 326 (1961).
289. A. Lundén, Chalmers Tekn. Högskolas Handl., Gothenburg, 1964, No. 289.
290. A. Klemm, Z. Naturforsch., 6a, 487 (1951).
291. R. Lenke and A. Klemm, Z. Naturforsch., 20a, 1723 (1965).
292. F. Lantelme and M. Chemla, Bull. Soc. chim. France, 2200 (1963).
293. F. Lantelme and M. Chemla, Electrochim. Acta, 10, 663 (1965).

294. A. Lundén, Z. Naturforsch., **25a**, 1326 (1970).
295. F. Ménès, J. Chim. phys., **63**, 983 (1966).
296. E. U. Monse, Z. Naturforsch., **12a**, 526 (1957).
297. F. Lantelme and M. Chemla, Electrochim. Acta, **11**, 1023 (1966).
298. W. Herzog and A. Klemm, Z. Naturforsch., **16a**, 523 (1961).
299. W. Fischer and A. Klemm, Z. Naturforsch., **16a**, 563 (1961).
300. A. Klemm, Z. Naturforsch., **15a**, 173 (1960).
301. P. Munier, Uspekhi Khim., **26**, 568 (1957).
302. H. J. Arnikar, Nature, **194**, 271 (1962).
303. H. J. Arnikar, Compt. rend., **244**, 2241 (1957).
304. S. Forcheri and C. Monfrini, J. Phys. Chem., **67**, 1566 (1963).
305. A. A. Ketelaar and E. P. Honig, J. Phys. Chem., **68**, 1596 (1964).
306. E. P. Honig, Thesis, Amsterdam, 1964.
307. I. G. Murgulescu and D. Topor, Rev. roumaine Chim., **9**, 815 (1964).
308. I. G. Murgulescu and D. Topor, Studii si Cercetari Chim. (Acad. R. P. R.), **13**, 865 (1964).
309. V. P. Shvedov and I. A. Ivanov, Radiokhimiya, **8**, 373 (1966).
310. I. G. Murgulescu and D. Topor, Rev. roumaine Chim., **12**, 1279 (1967).
311. I. G. Murgulescu and D. Topor, Rev. roumaine Chim., **13**, 979 (1968).
312. J. C. T. Kwak and J. A. A. Ketelaar, J. Phys. Chem., **73**, 94 (1969).
313. G. Alberti, G. Grassini, and R. Trucco, J. Electroanalyt. Chem., **3**, 283 (1962).
314. A. Berlin, F. Ménès, S. Forcheri, and C. Monfrini, J. Phys. Chem., **67**, 2505 (1963).
315. E. P. Honig and J. A. A. Ketelaar, Trans. Faraday Soc., **62**, 190 (1966).
316. I. G. Murgulescu and D. Topor, Rev. roumaine Chim., **15**, 843 (1970).
317. V. P. Shvedov, I. A. Ivanov, and I. M. Barbashinov, Elektrokhimiya, **2**, 1108 (1966).
318. J. C. T. Kwak, J. A. A. Ketelaar, P. P. E. Meenaut, and A. J. H. Boerboom, J. Phys. Chem., **74**, 3449 (1970).
319. R. A. Bailey and A. Steger, J. Chromatog., **11**, 122 (1963).
320. G. Alberti, A. Allulli, and G. Modugno, J. Chromatog., **15**, 420 (1964).
321. A. Lundén, Z. Naturforsch., **14a**, 801 (1959).
322. B. R. Sundheim, J. Phys. Chem., **60**, 1381 (1956).
323. T. Førland and J. Krogh-Moe, J. Phys. Chem., **61**, 511 (1957).
324. C. Sinistri, J. Phys. Chem., **66**, 1600 (1962).
325. A. Klemm, Z. Naturforsch., **3a**, 127 (1948).
326. A. Kvist, Z. Naturforsch., **21a**, 487 (1966).
327. A. Klemm, Plenary Lectures Sympos., "Discussion on Molten Salts", 1964, EUR-2466, e, 1965, 31; Nucl. Sci. Abstr., **20**, 10 806 (1966).
328. A. Lundén, Z. Naturforsch., **15a**, 1019 (1960).
329. I. A. Ivanov, K. V. Kotegov, E. I. Maslov, G. F. Nichugovskii, A. V. Stepanov, and V. P. Shvedov, "Elektromigratsionnyi Metod v Fiziko-khimicheskikh i Radiokhimicheskikh Issledovaniyakh" (Electrical Migration Method in Physicochemical and Radiation-chemical Research), Atomizdat, Moscow, 1971.
330. R. Oyamada, J. Phys. Soc. Japan, **26**, 1068 (1969).
331. Y. Yamamura and S. Suzuki, J. Nuclear. Sci. Technol., **7**, 522 (1970).
332. Y. Yamamura and S. Suzuki, J. Nuclear. Sci. Technol., **7**, 631 (1970).
333. A. Klemm, Z. Naturforsch., **25a**, 1763 (1970).
334. N. Saito and H. Kanno, Bull. Chem. Soc. Japan, **42**, 2409 (1969).
335. H. Kanno, J. Inorg. Nuclear Chem., **33**, 1561 (1971).
336. V. P. Shvedov and V. N. Osipov, Radiokhimiya, **13**, 98 (1971).
337. V. N. Osipov and T. D. Negodaev, Khim. i Khim. Tekhnol., **14**, 53 (1971).
338. T. D. Negodaev and V. N. Osipov, Khim. i. Khim., Tekhnol., **14**, 213 (1971).
339. T. D. Negodaev and V. N. Osipov, Khim. i Khim. Tekhnol., **14**, 380 (1971).
340. B. A. Bilal, B. Mühlig, and B. Schwarz, Z. Naturforsch., **26a**, 267 (1971).
341. T. Morimoto, I. Okada, and N. Saito, Z. Naturforsch., **26a**, 300 (1971).

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