

## Electrolytic Separation of Lithium Isotopes in Aqueous Solutions of Lithium Chloride Using a Mercury Cathode

BENGT COLLÉN

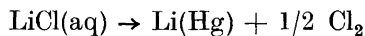
*Research Institute of National Defence, FOA 4, Sundbyberg 4, Sweden*

The separation factor,  $\alpha$ , for lithium isotopes in the electrolysis of aqueous solutions of lithium chloride at a streaming mercury cathode has been investigated as a function of temperature, current density and electrolyte concentration. The highest separation factor,  $1.056 \pm 0.004$  was obtained in 9.6 M LiCl at 5°C at a current density of 0.5 amp/cm<sup>2</sup>. From the temperature coefficient of the separation factor in 9.6 M LiCl, a difference in activation energy of about –75 cal/mole is found.

Several papers have been published on the isotope effect at the electrolysis of lithium salt solutions with a mercury cathode (see Table 1). The separation factor,  $\alpha$ , obtained for a single step of electrolysis, ranges from 1.020 to 1.074 (Refs.<sup>1–8</sup>). No explanation of the differing results has been given. These investigations were not made systematically under constant conditions; *e.g.* the electrolyte concentration was gradually decreased during the electrolyses. In the present investigation, a systematic study has been made of the effects of current density, concentration of electrolyte and temperature on the separation factor.

The Rayleigh distillation formula has been used<sup>3,5,6,8</sup> in calculating the true separation factor  $\alpha$ . However, by using a large volume of electrolyte and short time of electrolysis, the change in isotopic composition of the electrolyte is negligible and the simpler expression  $\alpha = R/R'$  can be applied, where  $R$  is the ratio between the mole fraction of <sup>7</sup>Li and the mole fraction of <sup>6</sup>Li in the electrolyte, and  $R'$  is the corresponding ratio in the amalgam formed at the mercury cathode during the electrolysis. Additionally, the separation factor is obtained at constant electrolyte concentration.

The over-all reaction in the process is:



By using streaming mercury, a continuously renewed cathode surface is obtained during the electrolysis.

The formation of amalgam instead of evolution of hydrogen at the cathode ( $\text{H}_2\text{O} \rightarrow 1/2 \text{H}_2 + \text{OH}^-$ ) is due to the high hydrogen overvoltage on mercury, especially at high current density according to the Tafel relationship. The various steps involved in the isotope separation will be discussed below.

### EXPERIMENTAL

**Apparatus.** The apparatus used is shown in Fig. 1. The electrolytic cell is made of Pyrex, closed on top with a lid of stainless steel, through which eight tubes of the same material pass. Since the atmosphere of the cell contains chlorine, evolved during the electrolysis, the exposed steel parts are coated with molten polyethylene. The stainless steel tubes fitted through the lid admit mechanical stirrer, thermometer, anode and capillary for the cathode as well as electrolyte and argon which also have outlet tubes. All seals were made with polyethylene packing sleeves.

The stream of mercury from the capillary acts as cathode. It is collected in the conical base of the cell under a layer of carbon tetrachloride and allowed to drain off by overflowing, as seen in Fig. 1.

The mercury is supplied to the capillary from a constant head system constructed in stainless steel. The amount of mercury flowing through the capillary is regulated by a needle valve. The mercury pump (Mono-pump, type B15; Mono Pumps Ltd, London, England) has a stator of neoprene and a rotor of stainless steel.

The anode consists of a cylindrical platinum net, which surrounds the capillary and reaches a few millimeters below the glass-tip.

The electrolyte is stored, as seen in Fig. 1, in a large bottle of polyethylene and is circulated through the cell by means of a double membrane-pump. It is injected at a constant rate and is sucked off at a fixed level in order to obtain both constant volume in the cell and a good circulation. The electrolyte is kept under an argon atmosphere.

The temperature in the electrolyte is regulated by circulating a thermostated liquid through the double wall in the cell and through a polyethylene tube in the large electrolyte bottle.

**Chemicals.** The mercury used was originally double distilled and before each run it was: (1) thoroughly washed with demineralized water for several days to remove dissolved

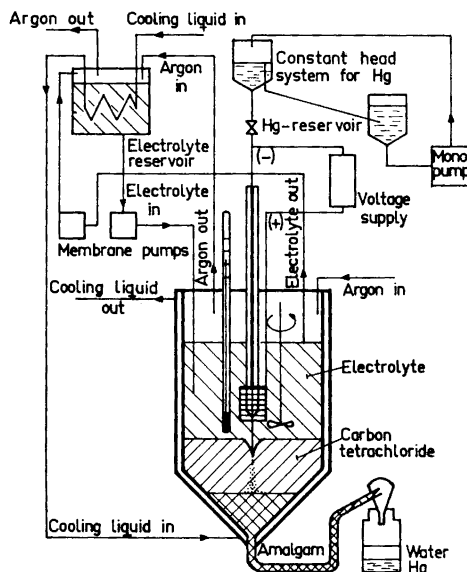


Fig. 1. The electrolysis apparatus.

lithium, (2) dried with filter paper, and (4) filtered through a glassfilter. The mercury was then kept in vacuum at 200–300°C for some hours, filtered again and stored.

This purification procedure is believed to be sufficient, as the mercury was not in contact with materials other than the electrolyte, carbon tetrachloride, pyrex, plastics, pure water and alcohol, from the time it left the capillary until it was brought into the mercury system again. As the mercury was always handled in the same manner and the reservoir in the apparatus held about 7 kg, it was assumed that the cathode was identical in every electrolysis.

The electrolyte was made up from lithium chloride (Malinekrodt A.R.) and demineralized water. During the electrolysis the solution was flushed with a large amount of argon in order to carry away the evolved chlorine.

*Electrolysis.* The electrolyses were performed keeping constant the speed of circulation of the 2–5 l of electrolyte (10 l/h), and of the mercury stream (4 kg/h). Current and voltage were constant during each run; only a small voltage fluctuation occurred. The temperature was held within  $\pm 1^\circ\text{C}$ . The stirring rate was also constant during the runs. In the amalgam the concentration of lithium varied, from about 0.0003 % by weight at low values, to about 0.007 % at high values of the current density.

The capillary tip ended 10 mm above the carbon tetrachloride surface. However, when mercury was flowing, a narrow cone, which was 10 to 15 mm in length, was formed in the carbon tetrachloride section of the cell. The total length of the mercury exposed to the electrolyte was approximately 22–25 mm. Although impossible to determine the cathode area exactly, it was calculated to be about 0.2 cm<sup>2</sup>. In the carbon tetrachloride the mercury stream was split up into fine drops, which fell through this liquid to the bottom of the cell, about 8 cm.

The current is set from a current stabilized voltage supply to the required current density. At the cathode, amalgam is formed, and after about 5 min the concentration is uniform in the collected mercury, the surface of which is kept at a constant level. The overflowing amalgam is then collected in a polyethylene bottle with water as seen in Fig. 1. The time, current, voltage and the temperature are read off every 5 min. The electrolyses are usually carried on for 15 min, after which the current is shut off, and the sample bottle is removed and closed. After some days most of the lithium in the amalgam has reacted with the water to form a lithium hydroxide solution. This is collected together with the solutions from repeated treatment of the mercury with water in order to get all the liberated lithium.

During the electrolysis chlorine is evolved at the anode, bubbles up through the electrolyte and is then carried away with the argon stream. From the amalgam surface some bubbles are also evolved and these pass through the carbon tetrachloride to the electrolyte.

*Chemical analysis.* The current efficiency is determined by titration of the lithium hydroxide solution with standard dilute nitric acid and comparing the result with what should have been obtained according to Faraday's law. The titrated solution is then evaporated in teflon cups and the dry lithium nitrate is kept in closed polyethylene tubes for mass analysis.

*Mass analysis.* Part of the lithium nitrate is dissolved in water in pyrex tubes and dried on the ion source of the mass spectrometer. The mass analyses have been carried out at the Dept. of Physics at Chalmers University of Technology, Gothenburg. For the analyses, a 60° deflector, 20 cm radius mass spectrometer was employed. Originally a commercial instrument (Atlas-Werke, Bremen, Type IS), it has been rebuilt and adapted for solid substances.<sup>9</sup>

The standard deviation of  $\alpha$ ,  $\sigma_\alpha$ , is calculated according to the relation

$$\sigma_\alpha = \pm \alpha \sqrt{(\sigma_R/R)^2 + (\sigma_{R'}/R')^2}$$

where  $R$  and  $R'$  are the relative abundances of the lithium isotopes, and  $\sigma_R$  and  $\sigma_{R'}$  are the corresponding standard deviations. From the mass analyses it is found that  $\sigma_R = 0.0025 R$  and  $\sigma_{R'} = 0.0025 R'$  where  $R$  and  $R'$  vary between 12.62 and 13.61, Refs.<sup>9,10</sup>. This gives  $\sigma_\alpha = \pm 0.004$ . However, one can find a slightly greater difference between measurements of the same sample made on different days, especially when the apparatus has been serviced or parts exchanged. Therefore, when calculating the separation factor, one must make the measurements of the isotopic composition of the standard and the corresponding sample on the same day. In addition, in order to eliminate the

Table 1. Summary of experimental conditions for electrolytic separation of lithium isotopes with a mercury cathode.

Separation factor $\alpha$	Salt	Current density amp/cm <sup>2</sup>	Temp. °C	Remarks	Reference
<1.07	Li <sub>2</sub> SO <sub>4</sub>	2		Starting with saturated solution.	1
<1.1	LiCl	3		Starting with 7 M solution.	2
1.020	LiOH	0.62	25	Starting with 5 M solution.	3
1.079 *	LiCl	0.06—0.08	38—40	Three steps, starting with 10 M solution. Current efficiency 30 %.	4
1.039	LiCl	0.62	36	Starting with 10 M solution.	5
1.055	LiCl	0.47—0.71	25—40	Current efficiency 25—65 %. $\alpha$ independent of temperature.	6
1.053	LiCl	0.21	42	LiCl dissolved in absolute C <sub>2</sub> H <sub>5</sub> OH.	6
1.06 *	Li <sub>2</sub> SO <sub>4</sub>			Pulsating voltage. Current efficiency 70 %.	7
1.055—	LiCl	0.05—0.28	30	The highest value obtained at constant current density.	8
1.074					8
1.043	LiOH	0.02—0.22	30		8

\* Single step factor not known exactly.

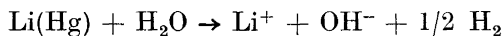
effect of an eventual drift in the mass spectrometer, the samples were not analysed in the same order, as the studied parameter was varied in the different experiments. As the isotopic composition of the electrolyte does not change measurably for a few electrolyses, the same standard could be used for a series of samples analysed on the same day; this appreciable reduces the number of analyses.

Some of the samples have been measured several times together with their standards and in other cases samples from identical electrolyses have been measured and compared. The results confirm the calculated error  $\pm 0.004$ . Most values lie within an error of  $\pm 0.003$ . Sometimes, however, the measurements fall badly off line, probably due to disturbances in the mass spectrometer. These irregularities often occur on particular days and are easily discovered from other comparable measurements. The extraordinary results are disregarded and new measurements made on the same samples or on samples from identical runs until reproducible results are obtained.

In two of the rejected results, it was found that the sample had been damaged during transportation, causing unknown isotopic effects.

## RESULTS

*Current efficiency.* The current efficiency is defined as the ratio of g-atoms of lithium in the amalgam to the number of faradays of electricity used in the electrolysis. Figs. 2 and 3 show how the current efficiency varies with temperature, current density and concentration of the electrolyte. A possible explanation of the deviation from 100 % is, that absorbed electrolyte starts a backreaction



when the amalgam drops have left the contact with the mercury cathode and are falling through the carbon tetrachloride section of the cell.

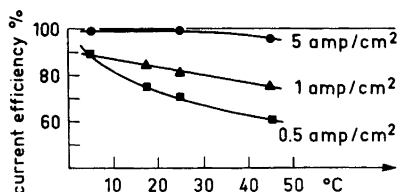


Fig. 2. Current efficiency in 9.6 M LiCl as a function of temperature.

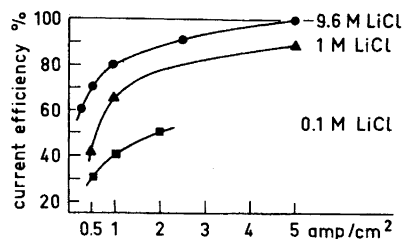


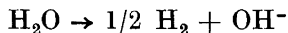
Fig. 3. Current efficiency at 25°C as a function of current density.

During the electrolysis bubbles are seen coming up from the amalgam surface. Some of these bubbles pass through the electrolyte indicating the presence of a gas. Even in the absence of current and lithium in the mercury, bubbles are seen leaving the mercury surface when the cathode is streaming. As these bubbles dissolve in the electrolyte, one can conclude that a small amount of the electrolyte follows the cathode down to the mercury surface, where it congregates in bubbles which return to the solution. No chloride ions could, however, be detected in the collected mercury or amalgam.

After the electrolysis the electrolyte is slightly acid and therefore the following reaction may also occur with the liberated chlorine



Another possible reaction, which could reduce the current efficiency (*i.e.* the yields of lithium), especially at low electrolyte concentration, is the evolution of primary hydrogen at the cathode



The present investigation does not, however, permit any detailed interpretation of the side or back reactions. Nor is it possible to determine if any back reaction occurs on the streaming cathode during the electrolysis due to highly concentrated spots of lithium or variations in the potential along the cathode.

Johnston and Hutchison,<sup>6</sup> who used a flowing unprotected surface of mercury as a cathode, found that the current efficiency increased from 36 % to 65 % when the mercury flow was increased from about 50 kg/h to about 100 kg/h.

The effect of these reactions on the separation factor has not been evaluated. However, as shown below, this effect does not screen other effects.

*Dependence of  $\alpha$  on current density at various electrolyte concentrations.* Fig. 4 shows the separation factor as a function of current density and electrolyte concentration. The irregularity at the lowest concentration may be due to the low current efficiency, which here could partly screen the expected increase of the separation factor at lowest current density. Fig. 5 shows the cell potentials used at the various current densities.

*Temperature dependence.* Electrolyses were carried out at temperatures between 5 and 45°C for several current densities and electrolyte concentra-

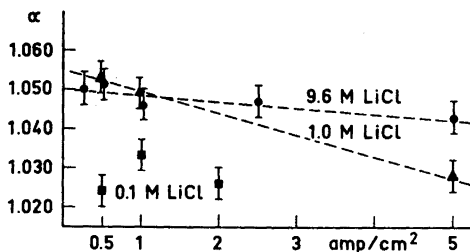


Fig. 4. Separation factor,  $\alpha$ , as a function of current density at 25°C. The limits of the standard deviation  $\sigma_\alpha = \pm 0.004$  are given.

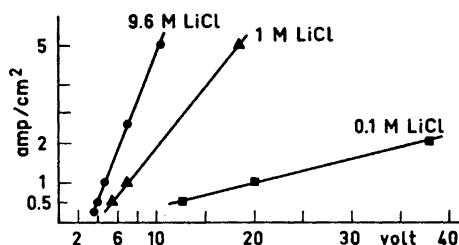


Fig. 5. Current density as a function of cell potential at 25°C.

tions. The results are shown in Fig. 6. One finds that at 5°C the separation factor is significantly higher than at 45°C. The mass analyses were made on the same day for samples obtained at 5 and 45°C from identical electrolytes; therefore, the error of  $\pm 0.003$  is used in Fig. 6. In addition, results from electrolyses at 25 and 17°C analyzed on different days have been marked. The three samples from electrolyses in 1 M LiCl at 1 amp/cm² at 17, 25, and 45°C are analyzed at the same time. Moreover the separation factors at 25 and 45°C were redetermined and the results fell within the calculated error. Consequently it can only be established that the slope of the temperature dependence between 45 and 25°C is greater than the corresponding slope for 9.6 M LiCl and tends to decrease at lower temperatures.

Fig. 7 shows the cell potentials used at various temperatures, current densities and concentrations.

#### DISCUSSION

The exact mechanism of the electrolytic isotope separation process for lithium with a mercury cathode in aqueous solutions is not known, though

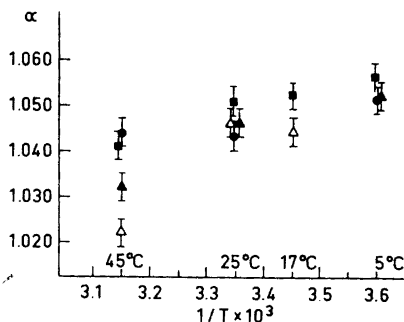


Fig. 6. Separation factor,  $\alpha$  as a function of temperature. 9.6 M LiCl: ● 5 amp/cm²; ▲ 1 amp/cm²; ■ 0.5 amp/cm²; 1 M LiCl: △ 1 amp/cm².

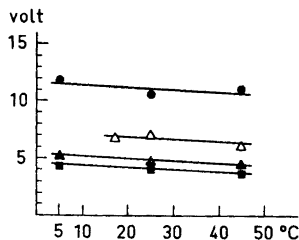


Fig. 7. Cell potential in 9.6 M LiCl as a function of temperature. ● 5 amp/cm²; ▲ 1 amp/cm²; ■ 0.5 amp/cm²; 1 M LiCl: △ 1 amp/cm².

it has been discussed by several authors.<sup>6, 11-13</sup> Two kinds of processes have been considered, on one hand involving rate-determining steps due to kinetic factors and on the other isotopic equilibrium exchange between the amalgam and the residual electrolyte.<sup>8,14</sup>

During electrolytic separation of hydrogen isotopes, it is found that different rate-determining steps occur at different cathode materials and that isotopic exchange probably can occur, especially at porous cathodes. The separation factor is also a function of temperature and electrode potential.<sup>15-17</sup>

The first step considered is the migration and diffusion of more or less hydrated lithium ions towards the cathode. The diffusion of unhydrated lithium ions through a diffusion layer will give <sup>6</sup> a separation factor of 1.08. But as lithium ions show a strong tendency to be solvated, it is probable that the ions are hydrated.

The primary hydration number of lithium is 4 according to Hindman,<sup>18</sup> who also found a small indication that lithium ions will attract water molecules outside the primary water sheet. It has also been estimated <sup>18-21</sup> that lithium ions can be attached to more than four water molecules when migrating in an electric field. Kunze and Fouss<sup>20</sup> estimated the relative mobility difference,  $\Delta v/v$ , between the isotopes to be 0.0036 in dilute LiCl-solution, which is in agreement with Arnikař's result.<sup>21</sup> This difference in mobility corresponds to a hydration number of about seven, as the mobility of an ion is an inverse function of the total weight of the ionic cloud undergoing movement.<sup>19</sup> The approximate calculation <sup>6</sup> will, in such a case, give a corresponding separation factor of only 1.004 with these hydrated ions.

In 9.6 M LiCl-solution the ratio of the number of water molecules to the number of lithium ions is 4.6. Assuming <sup>18</sup> a hydration number of zero for Cl<sup>-</sup>, the lithium ions can fill up the primary water sheet. In an electrolysis with high current density the solution in the vicinity of the cathode may be depleted of lithium ions, especially at low electrolyte concentrations, which means that the lithium ions may become more hydrated and the difference between the speeds of the isotopes will consequently decrease.

Therefore, if the rate-determining step in the isotope separation process is diffusion and migration of more or less hydrated lithium ions towards the cathode, the separation factor will decrease with increasing current density and decreasing electrolyte concentration. The lower separation factors obtained at higher current densities and 0.1 M LiCl can be explained in such a case, but not the high  $\alpha$ 's in 1 M LiCl, where the lithium ions can be highly hydrated even at low current density. As a consequence, the rate-determining step can not solely be the migration and diffusion of hydrated ions.

Bell<sup>11</sup> and Gurney<sup>12</sup> have based their quantum mechanical calculation of the separation factor on the assumption that the rate-determining step is the penetration of the hydration sheet surrounding the lithium ion by an electron. Johnston and Hutchison<sup>6</sup> have corrected Bell and Gurney's calculations and obtained a theoretical separation factor of 1.12. The calculations, however, involve several approximations, so this numerical value of  $\alpha$  can not directly be applied to experiments.

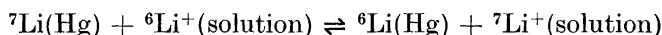
Effects on  $\alpha$  by other steps, such as dehydration and amalgamation, are not well known.

As seen from the temperature dependency, higher  $\alpha$ 's are obtained at lower temperatures. This effect is less pronounced at the highest current density, probably because the actual temperature in the vicinity of the cathode is higher than is noted in the solution, due to higher electrical resistance in the diluted cathode area. Therefore, the effects on the  $\alpha$  by current density and concentration may also involve a temperature factor.

Since probably all cathode reactions will show a temperature dependency, no process can be favoured on this basis.

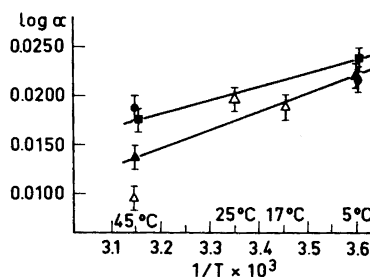
The amount of lithium released at the cathode represents a surface, if taken as monomolecular, which is 5 to 100 times the actual experimental cylindrical cathode surface of mercury. The diffusion coefficient of lithium in mercury is of the same magnitude as that of lithium ions in dilute solutions.<sup>22,23</sup> The concentration of lithium on the cathode surface and on the amalgam drops during the electrolyses is, however, difficult to determine due to non-stationary conditions on the electrode. The mercury is streaming with a speed of 170 cm/sec, which causes a forced motion of the solution as well as inside the mercury stream. Temperature gradients may also appear.

The exchange reaction



can occur between the formed amalgam and the electrolyte at least when the amalgam drops are falling through the carbon tetrachloride. For the equilibrium a separation factor of about 1.05 can be calculated.<sup>8,14</sup> It is not known to what extent this exchange contributes to the cathode reaction, but it will probably not play a major part in the separation process because (1) the amalgam is exposed to the solution only for a very short time, about 0.06 sec, during part of which it is in the form of drops. This time is presumably too short for the exchange to approach equilibrium. (2) Higher temperatures for the electrolysis should, in such a case, favour this approach, which is contradicted by the observed decrease in  $\alpha$ . The temperature dependence of the equilibrium could eventually interfere, but it is likely to be small. In addition, the side and back reactions at the cathode complicate the study of the results. Hutchison<sup>13</sup> found the corresponding separation factor for potassium isotopes to be independent of temperature, electrolyte concentration, amount of back reaction and current density, which led to the assumption that the kinetic mechanism was most probable.

Fig. 8.  $\log_{10}$  of  $\alpha$  as a function of temperature. 9.6 M LiCl: ● 5 amp/cm<sup>2</sup>; ▲ 1 amp/cm<sup>2</sup>; ■ 0.5 amp/cm<sup>2</sup>; 1 M LiCl: △ 1 amp/cm<sup>2</sup>.





From the temperature dependency it is possible to calculate the difference of activation energy for the rate-controlling step in the electrode process by means of the Arrhenius equation

$$\frac{d \ln \alpha}{dT} = \frac{\Delta E_a}{RT^2}$$

where  $\Delta E_a = E_6 - E_7$ .  $E_6$  is the activation energy for the over-all electrode process, *i.e.* transfer of a  ${}^6\text{Li}$ -ion to the cathode, its reduction and amalgamation, and  $E_7$  is the corresponding energy for  ${}^7\text{Li}$ -ions. An activation energy difference of about  $-75$  cal/mole is obtained as a mean value from measurements at 0.5 and 1 amp/cm<sup>2</sup> in 9.6 M LiCl-solution between 5 and 45°C; Fig. 8.

It may finally be added that the present investigation was not intended to elucidate all the separate steps in the complicated mechanism of the electrolytic separation process, but only to produce comparable results under controlled conditions. New experiments, giving more refined information, may be designed on the basis of this investigation.

*Acknowledgements.* I wish to express my sincere gratitude to Professor J. Rydberg for valuable discussions and continuous support, to Dr. A. Lundén for valuable discussions and facilities for mass analyses, and to Professor A. Ölander for his kind interest. The author is also indebted to Mr. H. Bäckström and Mrs. B. Stensland for technical assistance and to Mr. M. Lövenby for making the mass analyses. The English of this paper has been corrected by Mr. H. Peacock.

#### REFERENCES

1. Eucken, A. and Bratzler, K. *Z. physik. Chem.* **174 A** (1935) 269.
2. Champetier, C. and Regnaut, P. *Bull. Soc. Chim. France* **4** (1937) 592.
3. Taylor, T. I. and Urey, H. *J. Chem. Phys.* **5** (1937) 597.
4. Holleck, L. *Z. Elektrochem.* **44** (1938) 111.
5. Taylor, T. I. and Urey, H. *J. Chem. Phys.* **6** (1938) 429.
6. Johnston, H. and Hutchison, C. H. *J. Chem. Phys.* **8** (1940) 869.
7. Brit. Pat. 802,555, (1956).
8. Perret, L., Rozand, L. and Saito, E. A/CONF. 15/P/1267, 1958.
9. Lundén, A., Christofferson, S. and Lodding, A. *Trans. Chalmers Univ. Technol. Gothenburg* **221** (1959).
10. Lundén, A. *Private communication*.
11. Bell, R. *J. Chem. Phys.* **2** (1934) 164.
12. Gurney, R. *Proc. Roy. Soc. (London)* **A 134** (1932) 137.
13. Hutchison, D. A. *J. Chem. Phys.* **14** (1946) 401.
14. Lewis, G. and MacDonald, R. *J. Am. Chem. Soc.* **58** (1936) 2519.
15. Roy, L. *Can. J. Chem.* **40** (1962) 1452.
16. Conway, B. *Trans. Symp. Electrode Processes, Philadelphia, Pa.* **1959**, p. 267.
17. Lewis, G. and Ruetschi, P. *J. Phys. Chem.* **66** (1962) 1487.
18. Hindman, C. *J. Chem. Phys.* **36** (1962) 1000.
19. Ramirez, E. *J. Phys. Chem.* **62** (1958) 760.
20. Kunze, R. and Fuoss, R. *J. Phys. Chem.* **66** (1962) 930.
21. Arnika, H. *J. Inorg. Nucl. Chem.* **11** (1959) 248.
22. Samarin, A. and Svareman, L. *Izv. Akad. Nauk. SSSR, Otd. Tekhn.* **1947** 1649.
23. Harned, H. and Hildreth, C. *J. Am. Chem. Soc.* **73** (1951) 650.

Received June 18, 1963.