

## Migration of Lithium and Several Multicharged Ions through Quartz Plates in an Electric Field. II

George Gibson and Richard C. Vogel

Citation: *The Journal of Chemical Physics* **18**, 1094 (1950); doi: 10.1063/1.1747867

View online: <http://dx.doi.org/10.1063/1.1747867>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/8?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Stark parameters regularities within spectral series of several multicharged ions](#)

AIP Conf. Proc. **328**, 79 (1995); 10.1063/1.47444

[Heavyion migration through argon and helium in weak electric fields](#)

J. Appl. Phys. **69**, 6248 (1991); 10.1063/1.348822

[Optical waveguide formed by electrically induced migration of ions in glass plates](#)

Appl. Phys. Lett. **21**, 584 (1972); 10.1063/1.1654265

[Ag Ion Migration in  \$\alpha\$  Quartz](#)

J. Appl. Phys. **35**, 2364 (1964); 10.1063/1.1702864

[Migration of Sodium Ions through Quartz Plates in an Electric Field. I](#)

J. Chem. Phys. **18**, 490 (1950); 10.1063/1.1747667

---



relation occurring at  $w_j=0.04$  for the mixtures investigated, whereas the light scattering second coefficient appears to be most sensitive to traces of high molecular weight material. It has frequently been pointed out that the light scattering second coefficient is twice that occurring in the osmotic pressure rela-

tion; however, this will only be the case in general for well fractionated polymers. The ratio of  $2A_2'$  to  $A_2$  varies with heterogeneity. For normal degrees of heterogeneity this ratio will not differ much from two, but for an extreme heterogeneity the ratio may be appreciably greater or less than this value.

## Migration of Lithium and Several Multicharged Ions through Quartz Plates in an Electric Field. II

GEORGE GIBSON\* AND RICHARD C. VOGEL\*\*

*Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois*

(Received May 4, 1950)

The kinetics of the migration of lithium ions through crystalline quartz plates has been studied. The migration is induced by an electric field and probably takes place through tunnels inherent in the crystal structure and parallel to the principal axis of the quartz. It was shown that the rate-determining step is not the migration within the quartz plate, but is some step associated with the passage of the lithium ions into or out of the quartz plate. A previous investigation showed that the migration within the quartz plate is the rate-determining step for sodium ions.

It was demonstrated that neither magnesium, zinc, cadmium, nor bismuth ions will migrate through quartz plates under our experimental conditions. Copper ions migrated through the quartz plates but caused the plate to crack in each experiment.

### I. INTRODUCTION

IT has been demonstrated<sup>1</sup> that lithium and sodium ions in an electric field will migrate through crystalline quartz plates cut perpendicular to the  $Z$  or principal crystallographic axis. Gibbs,<sup>2</sup> in investigations of alpha-quartz, has indicated the existence of tunnels about an Angstrom in radius which are parallel to the principal axis. It has been suggested<sup>3</sup> that this tunnel-like structure is responsible for the anisotropic ease of sodium and lithium ion migration in quartz plates.

In the first paper of this present series<sup>4</sup> the authors have presented a kinetic study of the migration of sodium ions through quartz plates in an electric field. Liquid sodium amalgam anodes against one face of the plate served as the ion source, while pure mercury against the opposite face of the quartz plate was used as the cathode. A comparison of the behavior of lithium with that of sodium would be of interest. One might expect the smaller lithium ion to migrate more readily. Harris and Waring<sup>3</sup> studied the migration of lithium ions using fused lithium nitrate as the anolyte and fused ammonium bisulfate or mercury as the catholyte. Their system and apparatus were sufficiently different from that which we used in the study of sodium that it

seemed desirable to carry out the present investigation using lithium amalgams instead of fused lithium nitrate in the anode compartment.

Apparently, no studies have been made on the migration of the smaller multicharged ions. If such migration were to occur, some interesting correlations of ion charge and ionic radius might be observed. The results of an attempt to study the migration of magnesium, zinc, copper, cadmium, and bismuth ions through quartz plates are given below.

### II. APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus and experimental procedure were modified from those used in the sodium studies<sup>4</sup> in two ways found necessary during observations made during orientation runs with lithium. The Pyrex glass of the anode compartment of the cell used in the orientation runs with the lithium amalgam became dark red-brown throughout. In order to obviate this questionable behavior a quartz cell was substituted for the Pyrex one. The area of the plate exposed in the quartz cell was 3.048 cm<sup>2</sup>.

In order to prevent the formation of lithium nitride, an inert atmosphere of helium was used in preference to the atmosphere of nitrogen used in the sodium studies.

The lithium amalgams were prepared by adding small pieces of metal to purified hot mercury (160°C) in sufficient quantity to form a solid amalgam on cooling. The solid amalgam was then diluted with additional mercury to the desired concentration. The lithium

\* Present address: On leave of absence to the Chemistry Division, Argonne National Laboratory, Chicago 80, Illinois.

\*\* Present address: Chemical Engineering Division, Argonne National Laboratory, Chicago 80, Illinois.

<sup>1</sup> E. Warburg and F. Tegetmeier, *Ann. Physik* **35**, 455 (1888).

<sup>2</sup> R. E. Gibbs, *Proc. Roy. Soc. (London)* **A110**, 443 (1926).

<sup>3</sup> P. M. Harris and C. E. Waring, *J. Phys. Chem.* **41**, 1077 (1937).

<sup>4</sup> R. C. Vogel and G. Gibson, *J. Chem. Phys.* **18**, 490 (1950).

metal (Metalloy Corp., Minneapolis, Minnesota) contained 0.6 percent sodium, 0.02 percent calcium, 0.01 percent potassium, and 0.001 percent iron. The lithium amalgams were analyzed in the same manner as the sodium amalgams.

The amalgams of the other metals were prepared by adding weighed quantities of the pure metals directly to a weighed quantity of mercury. These amalgams were used without further analysis. All amalgams were prepared and stored in a helium atmosphere.

In the lithium runs, currents were measured for applied potentials of 20, 16, 12, 8, and 4 volts at four different temperatures between 200 and 170°C. It was necessary to lower the temperatures and the voltages from those used in the sodium studies. Under the sodium conditions (100 to 20 volts; 240 to 210°C) lithium gave such high currents that the lithium amalgam (whose concentration had a practical upper limit of about 0.014 mole fraction, the room temperature solubility) would be depleted before the end of a run. In addition to this difficulty, the high currents apparently caused cracks to form in the quartz plates on several occasions.

The quartz plates were 2.54 cm<sup>2</sup> and varied in thickness from 0.0492 to 0.1257 cm. They were the same plates that were used in the sodium studies. It was found in the sodium work that satisfactory reproducibility could not be obtained unless each plate was etched with a concentrated sodium amalgam. The etched surface was kept against the lithium amalgam. Before lithium runs were made, however, the crystals were pretreated by running a lithium ion current of about 1000 microamperes through the crystal for about sixteen hours.

### III. DATA

Since the current passing through the quartz plate was used to determine the amount of lithium migrating, it was necessary to show that all current passing through the cell was carried by lithium ions. To establish this a quartz plate, 0.0925 cm thick, was used with a concentrated two phase lithium amalgam in an extended run at 180°C with an applied voltage of 93 volts. The current was plotted against time and graphically integrated. The mercury in the cathode compartment was analyzed for lithium. Graphical integration showed that  $5.95 \times 10^{-4}$  mole of lithium was transferred while analysis of the cathode contents indicated that  $5.81 \times 10^{-4}$  mole of lithium had migrated. Thus, apparently all but 2.3 percent of the current was carried by migration of the lithium ions. This difference, also noted in the case of sodium, probably exists because of mechanical difficulties in quantitatively transferring the catholyte from the cell.

To further verify the anisotropic behavior of quartz, one run was made with a 0.0787-cm thick plate, cut with major faces parallel to the principal axis. At 140

TABLE I. Kinetic data for migration of lithium ions through quartz plates. (Mole fraction of lithium 0.0140.)

Run no.	Plate thickness (cm)	Potential gradient (volts cm <sup>-1</sup> )	"a"	Activation energy (kcal. mole <sup>-1</sup> )	"b"	Average percent deviation of calculated $i$ from experimental $i$
1	0.0492	407	4651.62	21.3	10.5276	0.9
		325	4616.62	21.1	10.2963	0.9
		244	4598.11	21.0	10.0536	0.7
		163	4658.49	21.3	9.9050	0.6
		81.3	5075.66	23.2	10.3750	0.9
2 <sup>a</sup>	0.0498	402	3883.46	17.8	9.1200	0.4
		321	3873.12	17.7	8.9231	0.5
		241	3859.93	17.7	8.6713	0.7
		161	3837.18	17.6	8.3118	0.7
		80.3	3922.73	17.9	7.9881	1.0
3	0.0744	269	4692.10	21.5	10.6702	1.2
		215	4780.58	21.9	10.7497	1.7
		161	4836.00	22.1	10.7244	1.4
		108	4874.58	22.3	10.6075	1.4
		53.8	4925.04	22.5	10.3926	1.3
4	0.0744	269	4695.19	21.5	10.6121	0.5
		215	4723.02	21.6	10.5394	0.3
		161	4771.28	21.8	10.4781	0.1
		108	4837.72	22.1	10.4002	0.2
		53.8	4876.33	22.3	10.1373	0.5
5 <sup>b</sup>	0.0744	269	4561.98	20.9	10.0955	0.5
		215	4566.19	20.9	9.9659	0.6
		161	4601.72	21.0	9.8719	0.7
		108	4689.51	21.4	9.8321	0.3
		53.8	4886.04	22.3	9.8897	0.1
6	0.0744	269	4708.10	21.5	10.7417	1.0
		215	4704.98	21.5	10.5916	0.9
		161	4734.50	21.7	10.4774	0.9
		108	4786.60	21.9	10.3508	0.7
		53.8	4877.13	22.3	10.1666	0.7
7	0.0925	216	3882.07	17.8	9.0943	1.3
		173	3861.76	17.7	8.8864	1.3
		130	3878.10	17.7	8.7081	1.3
		86.5	3994.60	18.3	8.6700	1.2
		43.2	4346.47	19.9	8.9515	0.5
8	0.1257	159	3771.27	17.2	8.7717	0.7
		127	3786.02	17.3	8.6510	0.3
		95.5	3871.37	17.7	8.6396	0.5
		63.6	4033.31	18.4	8.7235	0.6
		31.8	4485.77	20.5	9.2864	1.1
9	0.1257	159	3846.59	17.6	8.9190	0.5
		127	3869.06	17.7	8.8183	0.9
		95.5	3982.99	18.2	8.8757	0.6
		63.6	4126.02	18.9	8.9303	0.5
		31.8	4554.85	20.8	9.4513	1.3

<sup>a</sup> Crystal not etched with sodium amalgam before use.

<sup>b</sup> Lithium amalgam in both anode and cathode compartments of cell.

volts and 200°C, the equilibrium current was less than 0.01 microampere cm<sup>-2</sup>.

The kinetic data for the lithium ion migration were treated in much the same manner as in the sodium work. In each run five current readings were made at each of five potential gradients for a particular temperature. This procedure was repeated for four temperatures. The temperature dependence of the data for a given potential gradient and plate thickness is well represented by the Arrhenius equation,

$$\log_{10} i = -(a/T) + b, \quad (1)$$

TABLE II. Current in microamperes per  $\text{cm}^2$  at  $190^\circ\text{C}$  and a potential of 20 volts. (Mole fraction of lithium 0.0140.)

Run no.	Crystal thickness (cm)	Potential gradient (volts $\text{cm}^{-1}$ )	Current (microamperes $\text{cm}^{-2}$ )	Activation energy kcal. mole $^{-1}$ at 20 volts
2 <sup>a</sup>	0.0498	402	5.42	17.8
7	0.0925	216	5.15	17.8
8	0.1257	159	4.25	17.2
9	0.1257	159	4.10	17.6
6	0.0744	269	3.76	21.5
3	0.0744	269	3.45	21.5
1	0.0492	407	3.04	21.3
4	0.0744	269	2.97	21.5
5 <sup>b</sup>	0.0744	269	1.76	20.9

<sup>a</sup> Crystal not etched with sodium amalgam before use.<sup>b</sup> Lithium amalgam in both anode and cathode compartments of cell.

where  $i$  is the current in microamperes per square centimeter of exposed plate face,  $T$  is the absolute temperature and "a" and "b" are constants. By the method of least squares the best values of the constants were found for a particular potential gradient and quartz plate thickness. The data are presented in Table I. The mole fraction of lithium in the anode compartment was 0.0140. Column 3 gives the potential gradient calculated on the basis of plate thickness in volts  $\text{cm}^{-1}$ , column 5 gives the activation energy for the process and column 7 gives the average percent deviation of the experimentally determined currents at the four different temperatures from the corresponding currents calculated using Eq. (1). The data for a particular potential gradient generally fit Eq. (1) to about one percent.

The currents flowing through the quartz plates at  $190^\circ\text{C}$  with an applied potential of 20 volts are given in Table II. These currents are calculated from the data given in Table I. In the right column of Table II the activation energies at 20 volts are given.

The amalgams of the other metals used had the following mole fraction concentrations: magnesium 0.019, zinc 0.045, cadmium 0.018, bismuth 0.0096; the copper amalgam used was saturated at the temperature of the run. These latter runs were all exploratory in nature and were made using a 0.049 cm crystal, a temperature of about  $260^\circ\text{C}$  and an applied potential of 140 volts. With the exception of copper all the species studied showed no indication of ion migration. The currents observed were less than 0.01 microampere  $\text{cm}^{-2}$ .

When copper was studied, very interesting results were obtained. When the cell was brought up to temperature and the 140 volts applied, no current was observed for about an hour. Then the current rose erratically. Steady current readings were very difficult to obtain. When the cell was disassembled copper-colored stains and minute cracks were found which seemed to be beneath the surface of the crystal. The stains did not disappear on prolonged boiling of the plate with concentrated nitric acid or *aqua regia*. The experiment was repeated using a 0.0762 cm plate. With this crystal the current rose smoothly to 440

microamperes over a period of twenty minutes and then became very erratic. The same type of copper-colored stains were found in the crystal. It is suspected that copper will diffuse through quartz plates but that it cracks the plates in the process.

#### IV. DISCUSSION OF DATA AND CONCLUSIONS

A very striking difference in the behavior of sodium and lithium ions diffusing through quartz plates is that the rate for lithium is considerably greater. For example, with a potential of twenty volts across a plate 0.1257 cm thick at  $200^\circ\text{C}$ , the current due to lithium ions would be about thirty times greater than that in a similar experiment using sodium. This can be reasonably explained on the basis of the smaller ion size of lithium. The activation energies observed for lithium are also lower than those observed for sodium.

The data in Table II show that the current does not seem to depend upon the potential gradient. The currents vary from 1.76 to 5.42 microamperes  $\text{cm}^{-2}$  with no correspondence between current and potential gradient. This behavior is entirely different from that observed with sodium. In the case of sodium, the curves of current *versus* potential gradient at constant temperature and amalgam concentration for all different plate thicknesses almost superimpose upon one another.<sup>4</sup> The lithium data indicate that the diffusion within the quartz plate is not the rate-determining step. Since the diffusion rate is independent of the plate thickness, it appears reasonable that the rate-determining step is associated with the transfer of ions either into or out of the plate. This also would explain the fact that the data for lithium are not as reproducible from run to run as that for sodium. This irreproducibility can be seen in Table II, which gives data for four runs using the 0.0744 cm plate. The currents under presumably similar conditions vary by a factor of about two. When sodium was used in two similar runs, the maximum deviation was less than ten percent. The difficulty of reproducibility would be expected if the diffusion through a film or surface layer, either on the crystal face or within the amalgam, were the controlling factor since surface conditions are often difficult to reproduce from experiment to experiment.

The data in Table II are arranged in the order of decreasing currents rather than potential gradients to illustrate two important points. At high currents the activation energy is low as might be expected. The values of the activation energies fall into two groups. The activation energies from 17.2 to 17.8 kcal. mole $^{-1}$  are for three plates, the 0.0498, 0.0925 and the 0.1257 cm and the activation energies from 20.9 to 21.5 kcal. mole $^{-1}$  are for two plates, 0.0744 and 0.0492 cm thick. In no case does one plate give both a high and a low activation energy. This suggests that the slow step of the diffusion process is determined by the surface condition of the plate itself. It is not believed that this surface condition resulted from using the plates first

in the sodium studies. This is implied by Run 2 which was made with a plate (0.0498 cm) which had not been used (or etched) with sodium amalgam. It can be calculated from Table II that the resistance of this plate is only five percent less than that of the much thicker 0.0925 cm plate which was used in a number of sodium runs.

It is worth while to compare our data for lithium with that obtained by Harris and Waring.<sup>3</sup> The activation energies which they obtained using fused lithium nitrate in the anode compartment and ammonium bisulfate in the cathode compartment are around 17 kcal. mole<sup>-1</sup>. These values are in reasonable agreement with our lower set of activation energies. Their currents were much higher since they were not concerned with either lithium depletion or plate damage due to the high current. Thus, they were able to use temperatures from 250 to 300°C and applied potentials up to 125 volts. When their data were examined by plotting cur-

rent against potential gradient for five runs using five different plates, a closely grouped family of curves was obtained similar to our results obtained for sodium.

We conclude that the surface effect which appears to be the slow step in the lithium diffusion process in our experiments may be a property of amalgams not possessed by fused salts. There is a possibility that the surface effect would become negligible at temperatures higher than those we used although no such trend was observed in our temperature range.

The lack of diffusion shown by magnesium, zinc, cadmium, and bismuth suggests that these ions of higher charge interact with the oxygen atoms of the quartz and thus do not diffuse under the potentials which we applied. The cuprous ion (radius 0.96Å) is about the same size as that of the sodium ion (radius 0.95Å) so that the observed diffusion is reasonable; however, the plate damage by these ions is difficult to explain.

## The Reactions of Methyl Radicals. I. The Photolysis of Acetone

A. F. TROTMAN-DICKENSON\* AND E. W. R. STEACIE

*Division of Chemistry, National Research Council, Ottawa, Canada*

(Received May 2, 1949)

The photolysis of acetone has been investigated between 100°C and 300°C. The rates of production of carbon monoxide, methane and ethane have been measured over a range of acetone pressures from 3.9 to 100 mm and with a thirty-fold variation of light intensity. The methane and ethane formed can be quantitatively accounted for by the equations



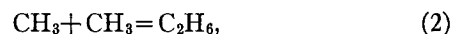
It is found that  $E_3 - \frac{1}{2}E_2 = 9.7$  kcal., where  $E_2$  and  $E_3$  are the activation energies of the above reactions. The photolysis of deuterated acetone has also been investigated, here  $E_3' - \frac{1}{2}E_2' = 10.3$  kcal. The collision theory "steric" or "P" factor for the second reaction is less than  $10^{-3}$  in each case.

### INTRODUCTION

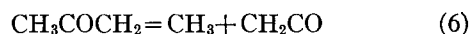
THIS paper is the first of a series which we hope to present on the quantitative study of the reactions of methyl radicals. Here is described the preliminary work which had to be carried out on the photolysis of acetone alone before it could be used as a source of methyl radicals for reaction with other hydrogen-containing compounds at high temperatures.

Acetone was chosen as the source of methyl radicals because its photolysis and the mechanism of the subsequent reactions are better understood than those of any of the alternative substances such as mercury dimethyl, acetaldehyde, or azomethane. This is largely owing to the very careful work of Noyes and his school, whose recent reviews<sup>1,2</sup> of the subject obviate the need for detailed discussion here.

The photolysis of acetone above 100°C may be fully described by the scheme,



which has been proposed by Noyes. Ferris and Haynes<sup>3</sup> have shown that ketene is a product at high temperatures and hence step (6) must be included above 250°C. This is also evident from the present



work. For the present purpose the important feature

\* National Research Council (Canada) Postdoctoral Fellow.

<sup>1</sup> W. A. Noyes, Jr. and L. M. Dorfman, *J. Chem. Phys.* **16**, 788 (1948).

<sup>2</sup> W. Davis, Jr., *Chem. Rev.* **40**, 201 (1947).

<sup>3</sup> R. C. Ferris and W. S. Haynes, *J. Am. Chem. Soc.* **72**, 893 (1950).