Changes in Composition by Countercurrent Electromigration in a Gradient of Temperature and/or Composition

Alfred Klemm
Max-Planck-Institut für Chemie (Otto-Hahn-Institut), D-6500 Mainz

Arnold Lundén
Department of Physics, Chalmers University of Technology, S-41296 Göteborg

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Unexpected previous findings in countercurrent electromigration experiments are explained and a new measuring technique based on dual temperature or dual composition experiments is proposed.

In order to understand some unexpected previous findings during countercurrent electromigration experiments and to describe a new type of such experiments, the following situation shall be considered:

A tube is filled with molten salts consisting of different coions and a common counterion. In the tube there is a range of gradients in temperature and/or composition connecting ranges of uniform temperature and composition. The coions electromigrate with a velocity such that the average position of the coions does not move or moves only little with respect to the gradients. The mobilities of the different coions with respect to the counterion depend differently on temperature and/or composition.

Evidently, in this situation the composition of the melt in the range of the gradients changes with time even if diffusion is negligible. The following calculations are made in order to explain previous observations of this kind and to show how measurements of this effect can give information about the temperature – and composition – dependence of the internal mobilities of the coions.

Such measurements have to be made by determining after the electrolysis the overall composition of the melt between two cross sections on either side of the range of the gradients and comparing it with the original composition of the equivalents found between the two cross sections. If the composition at the two cross sections differs, the original overall composition of which was uniform throughout the tube before the electrolysis, usually isotopes are such groups, but also groups of elements can be made to fulfill this requirement.

Let \( y^{(k)} \) \((\sum y^{(k)} = 1)\) be the original equivalent fractions of the members \( i \) of a group \( k \), the composition of which was uniform throughout the tube before the electrolysis, and let \( y_k (\sum y_k = 1) \) be the equivalent fractions of all the coionic groups and non-grouped coions.

The quantities relating to the ranges of uniformity on either side of the range of the gradients shall be written without and with a prime, respectively.

Let \( S \) and \( S' \) be the cross sections in the two ranges of uniformity, respectively, the distance between \( S \) and \( S' \) changing in such a way that \( N_k \), the number of equivalents of the considered group \( k \) between \( S \) and \( S' \), remains constant:

\[
N_k = S c y_k v_{ks} - S' c' y_k v'_{ks} = 0 .
\]  

Here \( c \) and \( c' \) are the total equivalent concentrations and \( v_{ks} = \sum y_i v_{iS} \) and \( v'_{ks} = \sum y_i v'_{iS} \) are the equivalent velocities of \( k \) with respect to \( S \) and \( S' \), respectively. For simplicity, in the latter two and the following equations the superscript \((k)\) has been dropped.

The overall values \( y^* \) between \( S \) and \( S' \) change with time according to

\[
N_k y^*_k = S c y_k v_{ks} - S' c' y_k v'_{ks} .
\]

Reprint requests to Prof. Dr. A. Klemm, Saarstr. 23, D-6500 Mainz.

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The current \( I \) from \( S \) to \( S' \) can be expressed as
\[
I = \pm F S c^c y k v g, \tag{4a, b}
\]
or
\[
I = \pm F S' c' c y k v g, \tag{5}
\]
where the upper and lower signs correspond to the counterions \( g \) being anions or cations, respectively, and \( F \) is Faraday’s constant. By means of (4a, b), \( S c \) and \( S c' \) can be eliminated in (3) to yield
\[
FN k y k v t ^ 0 = \frac{FN k y k v t ^ 0 - y _ k v t ^ 0}{y _ k v t ^ 0} \pm I \frac{y _ k v t ^ 0}{y _ k v t ^ 0} - \frac{y _ k v t ^ 0}{y _ k v t ^ 0} \cdot \tag{6}
\]
On integrating the l.h.s. of (5) with introduction of the current time integral \( Q(t) \), and on introducing on the r.h.s. of (5) the internal mobilities \( b _ i \) and \( b _ k \) with respect to the counterions \( g \), one obtains from (5)
\[
FN k y k v t ^ 0 - y _ k v t ^ 0 = y _ k v t ^ 0 - \frac{\sum b _ k}{b _ k} \left( \frac{\sum y _ k b _ k}{\sum y _ k b _ k} - 1 \right) \tag{7}
\]
In the experiments to be discussed the groups were \( \text{Li}^+ + \text{K}^+ \) with the members \( {}^{6}\text{Li}^+ \) and \( {}^{7}\text{Li}^+ \), and \( {}^{39}\text{K}^+ \) and \( {}^{41}\text{K}^+ \), respectively. In these cases we can use molar fractions \( x \) instead of equivalent fractions \( y \) and have to apply the positive sign before \( Q(t) \). Putting \( k = A, B \) and \( i = 1, 2 \), (6) for member 1 of the group A can be written in the form
\[
\frac{FN A x _ 1 ^*}{x _ 1 x _ 2} = x _ A(1 + x _ B \varepsilon _ c) \varepsilon _ A - x _ A(1 + x _ B \varepsilon _ c) \varepsilon _ A' \tag{7}
\]
with
\[
\varepsilon _ c = \frac{b _ A - b _ B}{x _ A b _ A + x _ B b _ B}, \tag{8}
\]
\[
\varepsilon _ A = \frac{b _ 1 - b _ 2}{x _ 1 b _ 1 + x _ 2 b _ 2}, \tag{9}
\]
and corresponding definitions for \( \varepsilon _ c' \) and \( \varepsilon _ A' \). By interchanging A and B and/or 1 and 2 other formulas may be obtained.

For the case of a pure salt \((x _ A = x _ A' = 0, x _ B = x _ B' = 0)\), (7) reduces to
\[
\frac{FN A x _ 1 ^* (t) - x _ 1}{Q(t)} = \varepsilon _ A - \varepsilon _ A'. \tag{10}
\]

The proposed new type of experiments consists in getting values of the right hand sides of (6), (7) or (10) by measuring \( N_k \) (or \( N_A \), \( Q(t) \) and \( y _ k ^* (t) \) (or \( x _ k ^* (t) \)).

Phenomenologically, the process described by (10) resembles the usual dual temperature processes which make use of the change with temperature of the equilibrium constant of an isotope exchange reaction. A plant of this kind for the enrichment of deuterium, based on the \( \text{H}_2\text{S} - \text{H}_2\text{O} \) exchange reaction, has been in use in the USA [1].

It may be mentioned in passing that the above calculations are also valid if \( S \) is the surface of the anode or \( S' \) is the surface of the cathode. The electrodes being impermeable for the coions, the expressions \( b _ i / \sum y _ k b _ k - 1 \) and \( b _ A \) are zero if \( S \) is the anode, and the corresponding primed expressions are zero if \( S' \) is the cathode. Then there remains only one term instead of two on the right hand sides of (6), (7) and (10), and these equations become those valid for the usual arrangements of countercurrent electromigration experiments for the determination of internal mobility ratios.

Equation (10) shall now be applied for the explanation of the following previous results found in experiments on pure salts:

1. In an experiment on \( \text{KNO}_3 \), \( {}^{39}\text{K} \) was enriched near the mouth of the separation tube towards a large cathode compartment where the isotopic composition of K had practically remained unchanged [2]. Explanation: Due to Joule heating the temperature was higher in the separation tube than in the cathode compartment, i.e. the temperature was higher at \( S \) than at \( S' \). Now \( \varepsilon _ K (A = K, 1 = {}^{39}\text{K}, 2 = {}^{41}\text{K}) \) increases with temperature [3]. Thus \( \varepsilon _ A \) was greater than \( \varepsilon _ A' \), and therefore, according to (10), \( x _ 1 ^* \) was greater than \( x _ 1 \).

2. In a similar experiment on \( \text{LiNO}_3 \) this was true for the light isotope \( {}^{6}\text{Li} \) [4]. The explanation is similar: \( \varepsilon _ Li (A = Li, 1 = {}^{6}\text{Li}, 2 = {}^{7}\text{Li}) \) increases with temperature [4].

3. In an experiment on \( \text{KCl} \) with a negligible (5 mol %) admixture of \( \text{LiCl} \), \( {}^{39}\text{K} \) was depleted near the mouth of the separation tube towards a large...
anode compartment, where the isotopic composition of K had practically remained unchanged \[5\]. Explanation: The temperature was lower at \(S\) than at \(S\prime\). Now \(\varepsilon(A = K, 1 = ^{39}K, 2 = ^{41}K)\) increases with temperature \[6\]. Thus \(\varepsilon_A\) was smaller than \(\varepsilon_A\), and therefore, according to (10), \(x_1^*\) was smaller than \(x_1\).

Contrary to the above cases, \(\varepsilon(Tl = Tl, 1 = ^{203}Tl, 2 = ^{205}Tl)\) in TICl has been found to decrease with temperature \[7\]. This result could be checked with an experiment based on (10). The method being differential, its results would probably be more accurate than the comparison of two results obtained with an absolute method.

There exist also observations made in cases where the composition of the melt at \(S\) and \(S\prime\) was different, and these shall now be compared with (7). The experiments have been made on the following systems:

1. \((\text{Li}, K)_2\text{SO}_4\) with 81 mol\% \(\text{Li}_2\text{SO}_4\) at 625 °C \[8\],
2. \((\text{Li}, K)_\text{Cl}\) with 60 mol\% \(\text{LiCl}\) at 555 °C \[9\],
3. \((\text{Li}, K)_\text{NO}_3\) with 41 mol\% \(\text{LiNO}_3\) at 192 °C \[9\],
4. \((\text{Li}, K)_\text{NO}_3\) with 41 mol\% \(\text{LiNO}_3\) at 380 °C \[9\].

The observations concern the mouth of the separation tube towards a small anode compartment. In the anode compartment the heavy isotopes and the element with the smaller mobility are enriched. This element was K in experiments 1. and 3. and Li in experiments 2. and 4., the latter due to the Chemla effect. The cross section \(S\) must be imagined in the anode compartment, where the Li/K ratio is uniform though changing with time, and the cross section \(S\prime\) somewhere in the separation tube at a place of unchanged composition. In the range of the gradients, i.e. between \(S\) and \(S\prime\), an enrichment of \(^{39}\text{K}\) was found in experiments 1. and 3., and an enrichment of \(^6\text{Li}\) in experiments 2. and 4., i.e. the light isotope of that element, which was enriched at the anode, was enriched in the range where this element became less abundant then at the anode. This is what one would expect because in this range a fraction of the current, the fraction increasing with the distance from the anode, is taken over by the other cationic element. This has a similar effect as the taking over of the current by electrons at the cathode. Thus, as happens at the cathode, the light isotopes are enriched in this range. On the contrary, for the other cationic element, which is depleted at the anode, the range of the gradients acts like an anode, i.e. the heavy isotope of this element is enriched there. This, however, is not so easy to detect experimentally because the heavy isotope is simultaneously enriched at the true anode. The effect would only be showing up by the range of the enrichment extending farther into the separation tube than caused by mere diffusion.

Equation (7) tells us that this is not the whole story. If \(A\) is identified with the element that is enriched at the anode and \(I\) with the light isotope of that element, the result \(x_1^* > x_1\) has been explained above by \(x_A > x_A\). There are, however, the factors \((1 + x_B\varepsilon_c)\varepsilon_A\) and \((1 - x_B\varepsilon_c)\varepsilon_A\), which are positive but not equal. The experiments have shown that the difference between the two factors is too small for changing the qualitative result. From an accurate experiment done along the lines described in the beginning of this paper, however, it should be possible to determine \((1 + x_B\varepsilon_c)\varepsilon_A^*\) if \((1 + x_B\varepsilon_c)\varepsilon_A\) is known.

In \[9\] a numerical computation, taking diffusion into account, of the composition profile between \(S\) and \(S\prime\) in case of experiment 4. has been reported, which agrees well with the experimental profile.

Appendix

**Isotope Effects in a Countercurrent Electromigration Experiment on a Melt Consisting of 5\% LiCl and 95\% KCl**

A mixture of 5 mol\% \(\text{LiCl}\) and 95 mol\% \(\text{KCl}\) was electrolyzed in a U-shaped cell made of Vycor, see Figure 1. The inner diameter was 20 mm for the wide tubes and 4 mm for the narrow tube, the latter having been filled with quartz powder before the molten salt mixture was poured into the long wide tube. The total length of the “separation tube” (i.e. the narrow tube) was 26 cm. Carbon rods were used as electrodes, and the arrangement was such that the amount of salt above the separation tube was small on the cathode side but large on the anode side. The temperature was 800 °C on the anode side, but considerably higher in the separation tube due to Joule heating. The duration was 42 h and the total transported charge was 7.95 Ah.
Fig. 1. Electromigration cell. The light isotope $^{39}$K was enriched in the region marked 39, and an anomalous enrichment of $^{41}$K was found in the region marked 41.

The accuracy of the chemical analysis was not good enough to allow for an evaluation of the $\text{Li}^+$/K$^+$ mobility ratio. Also $^6\text{Li}/^7\text{Li}$ abundance ratios have not been measured. The $^{39}\text{K}/^{41}\text{K}$ abundance ratio was determined mass spectroscopically for 17 samples from different parts of the cell. As expected, the light isotope $^{39}$K was enriched in the cathode compartment and the adjacent part of the separation tube (at least a couple of cm's). This was followed by a long stretch without any significant deviations from the normal abundance ratio. However, the two last samples (with a total length of about 6 cm) before the anode compartment showed a slight but significant enrichment of $^{41}$K relative to the central part of the separation tube as well as to the large amount of salt on the anode side.

We have calculated the separation factor $Q = R_i/R_0$, where $R_i$ is the $^{39}\text{K}/^{41}\text{K}$ abundance ratio for a sample $i$ and $R_0$ is the normal ratio. We obtained $Q = 1 + 0.037$ for the salt in the cathode compartment and $Q = 1 - 0.009$ for the two samples with the anomalous enrichment of $^{41}$K.

Thus, the present experiment did show the same type of anomaly as found in the previous investigations on pure $\text{KNO}_3$ [2] and pure $\text{LiNO}_3$ [4]. The temperature gradient in the region of the anomaly was larger in the present investigation because the separation tube was not surrounded by molten salt, as was the case in the two previous investigations.