

Self-diffusion in molten copper(I) chloride*

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The self-diffusion coefficients of Cu(I) and Cl⁻ species in molten copper(I) chloride have been measured between 450 and 750°C. The capillary method [1] using ⁶⁴Cu and ³⁶Cl radiotracers has been employed. Attention has been paid to the analysis of experimental errors. The diffusion coefficient of Cu(I) is approximately two to three times higher than that of the chloride ion. This relation is in a qualitative agreement with the published results of neutron diffraction experiments, which indicates the possibility of associations between one copper cation and several chloride anions leading to the formation of CuCl_n⁽ⁿ⁻¹⁾⁻ ions in a "plasma" of Cu⁺ ions. The activation energy of diffusion of Cu⁺ in CuCl has been found to be 13.18 kJ mol⁻¹.

Были измерены коэффициенты самодиффузии частиц Cu(I) и Cl⁻ в расплавленном хлориде одновалентной меди в температурном интервале 450—750°C. Был использован капиллярный метод [1], применяющий радиоактивные ⁶⁴Cu и ³⁶Cl. Внимание уделялось анализу ошибок эксперимента. Найдено, что коэффициент диффузии частиц Cu(I) приблизительно в 2–3 раза больше коэффициента диффузии иона хлора. Это соотношение находится в качественном согласии с опубликованными результатами по экспериментам с нейтронной диффракцией, что индикует возможность явления ассоциации между одним катионом меди и несколькими анионами хлора, причем в „плазме“ ионов Cu⁺ возникают ионы CuCl_n⁽ⁿ⁻¹⁾⁻. Было найдено, что энергия активации диффузии ионов Cu⁺ в CuCl составляет 13,18 кДж моль⁻¹.

Experimental

Material

Copper(I) chloride (Merck, anal. grade) was further purified by mixing with concentrated H₂SO₄ in order to dissolve the Cu²⁺ main impurities. The mixture was then poured into

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a large volume of water, filtered under argon and washed with absolute ethanol, then diethyl oxide, and dried *in vacuo* at 150°C.

In order to prepare ^{64}Cu labelled CuCl , a copper wire was irradiated at the Grenoble "Centre d'Etudes Nucléaires", and oxidized with HNO_3 . The Cu^{2+} ions were then reduced to CuCl with copper turnings in HCl solution. The precipitate was filtered and dried as previously described.

Aqueous H^{36}Cl was obtained from the National Institute of Radioelements (MOL-DONK, Belgium). Cu^{36}Cl was prepared by neutralizing Cu_2O with this H^{36}Cl solution. About 10 μCi of ^{64}Cu and ^{36}Cl were used in each experiment. To prevent any oxidation of molten CuCl at high temperatures, the cell is bubbled through with argon previously deoxygenated by active copper at 150°C and dehydrated on zeolithes.

Apparatus and procedure

The apparatus is shown in Fig. 1. About 500 g of inactive CuCl are contained in a quartz crucible *A* (\varnothing 45 mm, *l* 100 mm). This crucible is placed inside a quartz tube *B* (\varnothing 60 mm, *l* 360 mm) closed at its upper end by a water-cooled brass head *C*. Quartz tubes can be held in position or slid through the brass head by means of 6 Crawford "Swagelock" Connectors fitted with teflon, so that all the operations can be done with a small argon overpressure (about 10 cm H_2SO_4) inside tube *B*.

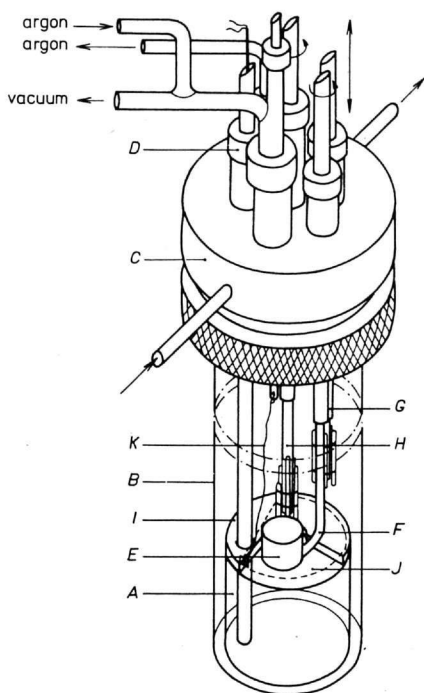


Fig. 1. Apparatus for determination of self-diffusion coefficients.

A, E — quartz crucibles; *B, F* — quartz tubes; *C* — cooled brass head; *G, H* — quartz tubes bearing capillaries; *J* — copper lid.

Active salt ($^{64}\text{Cu} + ^{36}\text{Cl}$) is contained in the quartz crucible *E* (\varnothing 12 mm, *l* 20 mm) welded to the quartz tube *F*.

Quartz capillaries are fastened with platinum wires around tubes *G* and *H*. Each of these tubes holds 5 flat-bottomed capillaries having the same bore diameter (about 1 mm) and different lengths (3, 4, and 5 cm).

The *G* capillaries are filled for initial activity determinations in the following way: they are slid down into crucible *E*, tube *B* is evacuated, then argon is let inside. This operation is repeated several times until the capillaries are completely filled with active CuCl. They are then slid up to the level of the brass head, where they remain till the end of the experiment, the salt inside their bores being solid. This filling operation is carried out at about 600°C.

The *H* capillaries are used for the determination of activity after diffusion. They are filled in the same manner as the *G* capillaries, then they remain in crucible *E* while the temperature is changed to the required value. When thermal equilibrium is established, both crucible *E* and capillaries *H* are slowly slid down into the inactive melt.

Crucible *E* is immediately slid out of the inactive melt to the top of the cell. The level of the mouths of the capillaries is adjusted at 1 cm from the bottom of tube *B*, and tube *H* is rotated (the linear velocity at the mouths of the capillaries is equal to 1 mm/s [2]).

In order to avoid excessive evaporation of CuCl during the filling operation and the time necessary to reach thermal equilibrium, the crucible *A* is closed by a quartz lid *I* and a thin copper lid *J* (dotted line), the latter being pulled apart by means of wire *K* before the introduction of crucible *E* and capillaries *H* into the inactive melt.

After a 16 to 24 h diffusion time, the *H* capillaries are raised out of the inactive melt. The outside of each capillary is carefully cleaned with HNO_3 , washed and dried with ethanol and diethyl oxide. The specific activity of each of the ten capillaries is then determined as follows:

- ^{64}Cu γ activity is measured through the walls of each capillary by means of a NaI (Tl) crystal and a 1024 channel "ZOOMAX" S.E.I.N. analyzer.
- ^{36}Cl β activity cannot be directly measured because electrons are stopped by quartz. The salt contained in the capillaries cannot be dissolved merely by immersion in an oxidizing solution. Therefore each capillary is crushed in a press, and the solid (quartz powder + CuCl) is transferred into a flask in which the salt is dissolved using hydrogen peroxide in acid solution. The activity of the solution is measured by means of an "ABAC-SL-40" INTERTECHNIQUE analyzer using the Cerenkov effect.

Analysis of the sources of error

The temperature, measured with a PtRh10—Pt thermocouple, is maintained constant within $\pm 0.5^\circ\text{C}$.

In order to minimize immersion effects, capillaries *H* and crucible *E* were jointly introduced into the inactive melt. We have verified that the immersion of crucible *E* into the inactive melt did not lead to any significant contamination of the latter (the activity of the inactive melt remained less than 1/1000 of the activity of the solutions contained in the capillaries).

When the H capillaries are raised out of the inactive melt, an adherent drop of inactive CuCl may be drawn into the capillaries during solidification. To reduce this effect, the walls of the capillaries have been bevelled next to their open ends.

Capillaries G were filled for initial activity measurements so that the γ countings of initial and final activities might be carried out under the same geometric and physical conditions. The reproducibility of these γ countings was 1%.

The reproducibility of the β countings of a given solution was 1%, but β countings of different solutions having the same activities gave discrepancies of the order of 10%.

The validity of the experimental conditions can be assessed for each determination since we used capillaries having different lengths. The value of the diffusion coefficient D is given in our case by the relation

$$D = \frac{4l^2}{\pi^2 t} \ln \frac{8}{\pi^2} \frac{A_0}{A_t} \quad (1)$$

where A_t denotes the final activity, A_0 denotes the initial activity, t is the diffusion time, and l is the length of the capillary.

If the values of D determined with 5 capillaries having different lengths (3, 4, and 5 cm) are equal, we can conclude that the experimental procedure is correct.

Results

Cu^+

The D_{Cu^+} values, calculated at each temperature from the results of 10 capillaries countings, are equal within $\pm 2\%$, and no systematic influence of the capillary length on the D value can be detected. The mean values of D_{Cu^+} are given in Table 1.

The analytical equation of the $\ln D_{\text{Cu}^+} = f(1/T)$ variations (Fig. 2), calculated using the least squares method is

$$D_{\text{Cu}^+} = 4.99 \times 10^{-4} \exp^{-(1583.5/T)}$$

Cl^-

The uncertainty on the D_{Cl^-} values is still much too high, because of the lack of accuracy of the β countings. Experiments are in progress to improve the accuracy

Table 1

Temperature dependence of the self-diffusion coefficients of Cu^+ and Cl^-

$T, ^\circ\text{C}$	450	483	535	598	650	723	750
$10^5 D_{\text{Cu}^+} \text{ cm}^2 \text{ s}^{-1}$	5.48	6.25	7.21	7.96	9.11	9.92	10.8
$10^5 D_{\text{Cl}^-} \text{ cm}^2 \text{ s}^{-1}$	1.28	2.35	3.0	2.97	3.40	4.36	4.93

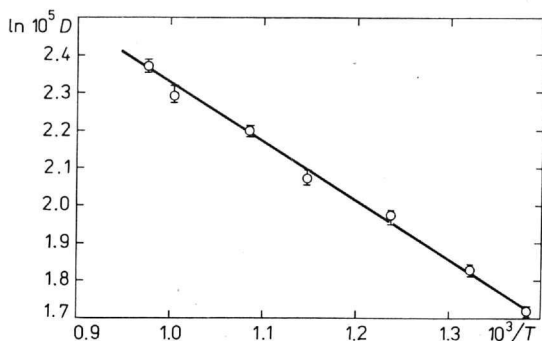


Fig. 2. Graphical representation of the dependence $\ln D = f(1/T)$.

of these countings. Moreover, we are carrying out new determinations using shorter capillaries and longer diffusion times in order to increase the A_0/A_1 value (eqn (1)) and thus to reduce the influence of the inaccuracy of the countings of the D_{Cl^-} values.

Nevertheless, we can observe that the D_{Cu^+} values are at least twice as big as the D_{Cl^-} values at arbitrary temperature.

Qualitative interpretation

Comparison between molten NaCl and CuCl should be meaningful because the Na^+ and Cu^+ crystalline radii (0.97×10^{-10} m and 0.96×10^{-10} m, respectively) are almost equal.

We can say that molten CuCl is mainly ionic, because the conductivities of both salts are similar (at 1000°C , $\kappa_{\text{CuCl}} = 3.916 \text{ S cm}^{-1}$ [3] and $\kappa_{\text{NaCl}} = 4.026 \text{ S cm}^{-1}$ [4]).

The difference between D_+ and D_- is much more pronounced in CuCl than in NaCl

$$\left(\frac{D_{\text{Cu}^+}}{D_{\text{Cl}^-}} > 2 \quad \text{vs.} \quad \frac{D_{\text{Na}^+}}{D_{\text{Cl}^-}} \approx 1.1 \quad \text{to} \quad 1.4 \quad [5, 6]\right)$$

This fact could be explained by the existence of $\text{CuCl}_n^{(n-1)-}$ associations in molten CuCl at the lower temperatures. This hypothesis is in agreement with several converging observations.

Comparison of the viscosities of molten CuCl and NaCl at 100°C above their melting points shows that the viscosity of CuCl ($2.54 \times 10^{-3} \text{ N s m}^{-2}$ [7]) is much higher than that of NaCl ($1.0 \times 10^{-3} \text{ N s m}^{-2}$ [8]).

The presence of partially covalent $\text{CuCl}_n^{(n-1)-}$ associations and of free Cu^+ ions has been postulated by Page and Mika [9] from neutron diffraction measurement

in molten CuCl at 500°C. *Murgulescu* [10] has suggested the existence of covalent bonds in molten CuCl to explain its low limiting molar volume ($25.5 \text{ cm}^3 \text{ mol}^{-1}$ for CuCl; $34.45 \text{ cm}^3 \text{ mol}^{-1}$ for NaCl).

The entropy of fusion of CuCl ($16.32 \text{ J mol}^{-1} \text{ K}^{-1}$) is much lower than that of NaCl ($27.20 \text{ J mol}^{-1} \text{ K}^{-1}$).

One can assume that with increasing temperature the proportion of the $\text{CuCl}_n^{(n-1)-}$ associations decreases. As a matter of fact, we have noticed that, at 800°C, the viscosity of CuCl ($1.44 \times 10^{-3} \text{ N s m}^{-2}$) becomes quite similar to that of NaCl ($1.38 \times 10^{-3} \text{ N s m}^{-2}$) at the same temperature.

This decomplexation would result in a decrease of the proportion of mobile Cu^+ ions, which could explain the fact that the activation energy of diffusion of Cu^+ in CuCl ($13.17 \text{ kJ mol}^{-1}$) is much lower than that of Na^+ in NaCl ($25.92 \text{ kJ mol}^{-1}$ [6]).

This decomplexation could also lead to the presence, at high temperatures, of molecular nonconducting species [3], which could qualitatively account for the low value of the conductance activation energy (2.72 kJ mol^{-1} for CuCl [3]; $10.03 \text{ kJ mol}^{-1}$ for NaCl [4]), and for the conductivity maximum found at 850°C for CuCl [3].

At the time being, we are carrying out migration experiments in order to confirm this hypothesis.

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