

THE DEPENDENCY OF THE ELECTROMOTIVE FORCE OF Ag/AgCl ELECTRODE ON THE CHLORINE PRESSURE

MICHIO ISEKI and TOMOO KIRIHARA

Department of Nuclear Engineering

(Received 31, Oct., 1967)

Abstract

The influence of chlorine pressure on potentials of silver/silver chloride electrode have been studied for the cells of Ag/AgCl/Cl₂PmmHg (C) and of Ag/AgCl-KCl (70 : 30 mol.)/Cl₂PmmHg (C) below one atm. at 500°C and 600°C. The e.m.f. did scarcely depend on a half power of chlorine pressures below one atm. Corresponding to the color change of a melt three kinds of pressure dependency were essentially found for both salts. The relation between the e.m.f. and the pressure was generally explained by introduction of cation vacancies and anion vacancies in these melts.

I. Introduction

In the electrochemical investigation of a fused salt, the variation of a partial pressure of components of a melt generally have been neglected. It should not be disregarded in nature because an anion in the melt is equilibrium with a gas of the same element.

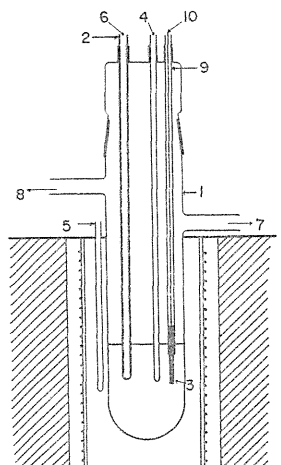
It seems probable that one reason why e.m.f. values of a reversible electrode in melts fluctuate and take a long time to become a constant value may be in the partial pressure change. It would considerably be expected that in a melt containing a transition element such as zirconium, uranium etc. a valence state of these elements should be influenced by a certain amount of partial pressure change of a gas of which ions are in the melt. Authors intend to investigate in near future the influence of partial pressures of chlorine on melts containing actinide chlorides. It is necessary for our purpose to clarify at first the behavior of a reference electrode under various partial pressures of a constituent of molten salt, *i.e.* chlorine.

The present investigation was thus undertaken to determine the effects of a chlorine pressure change on the e.m.f. of Ag/Ag electrode in AgCl and AgCl-KCl (70 : 30), because silver chloride electrodes were generally accepted as a good reference electrode in molten salts^{1) 4)}.

II. Experimental

II-1. Apparatus

The apparatus are shown schematically in Fig. 1. The cell was made of a pyrex glass tube of 4 cm in diameter and was 30 cm in length.



1. pyrex glass vessel
2. glassy carbon electrode
3. silver metal electrode
4. thermocouple sheath (1)
5. thermocouple sheath (2)
6. mixed gas inlet
7. mixed gas outlet
8. vacuum system
9. pyrex tube
10. silver wire

FIG. 1. Cell design for e.m.f. measurements: cell.
 $\text{Ag}/\text{AgCl}\cdot\text{KCl}(70:30)/\text{Cl}_2\{\text{PmmHg}-\text{Ar}(760-P)\text{mmHg}\}(\text{C})$

A glassy carbon* tube of 6 mm in diameter and 30 cm long was used for chlorine electrode on the bottom of which there was a hole about 1 mm in diameter to introduce gas through. A silver metal rod, 2 mm in diameter, 2 cm in length and 99.9% up in purity was used as a cathode. This electrode was connected to a silver wire of 0.6 mm in diameter which was inserted in a pyrex glass tube of 2 mm in diameter.

The electric furnace on the well of which were the window made of quartz glass was used for heating the cell to see the color change of a melt. The temperature controller (CHINO ET 1563) was used to regulate heating current through a reactor to the furnace. The melt temperatures were held constant within $\pm 0.5^\circ\text{C}$ for several hours.

The chlorine electrode of a glassy carbon tube and of spectroscopic carbon rod were heated for one hour in vacuum at 800°C and 500°C . And then dry chlorine gas was passed for one hour at that temperatures. As shown later the treatment at 800°C was sufficient to prepare a reversible electrode.

II-2. Procedures of purification

The chemicals of analytical reagent grade were used except silver chloride. Silver chloride of 99.9% purity was purified as follows: (1) It was washed by concentrated hydrochloric acid and dried at least for two days in a vacuum dryer at 300°C and 10 mmHg. (2) It was heated to melt in an atmosphere of dry argon and purified by passing dry chlorine gas for one hour at 500°C . Potassium chloride was also treated with chlorine for one hour at 800°C . This procedure give satisfaction to remove all traces of water vapor or other impurities²⁾. After that the dissolved chlorine gas in the melt was removed by bubbling argon gas for one hour. Cylinder chlorine dried and purified by passing through concentrated sulfuric acid, anhydrous magnesium perchlorate and anhydrous phosphorus pentoxide was used for purification of salts and others. Chlorine gas used on the measurement of electromotive force was further purified by condensation with a dry-ice and acetone trap.

* Synthesized carbon produced by Tokai Electrode Co.

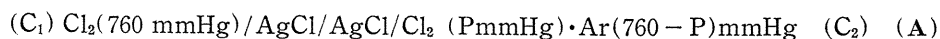
II-3. Pressure control of chlorine gas

The chlorine reservoir consists of a glass cylindrical vessel (about 20 mm long and 50 mm in diameter) closed at the bottom and having a side tube and a thermocouple sheath. The vessel set up in the dewer vessel and cooled by liquid nitrogen or dry-ice and acetone mixtures.

Cylinder argon which purified as described before was introduced to the chlorine reservoir at the flow rate of about 0.2 cc/min and mixed with chlorine gas. A partial pressure of pure chlorine gas was controlled by a temperature of chlorine reservoir. The reservoir temperature was measured by an iron-constantan thermocouple in a dewer vessel and was very slowly raised from -120°C to -36°C for about 24 hour.

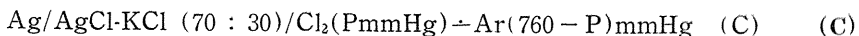
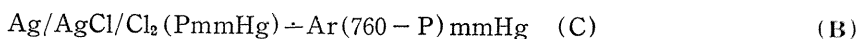
II-4. Cells for E.M.F. Measurement

At first to confirm the reversibility of a chlorine electrode of a glassy carbon the following concentration cell of chlorine gas with a spectroscopic graphite chlorine gas electrode, which was approved to be reversible, was constructed³⁾.



A graphite electrode (C_1) or chlorine gas at one atmosphere was separated with others by a thin pyrex glass wall. The e.m.f. of above cells were measured at various chlorine partial pressures below one atmosphere with a graphite electrode or a glassy carbon electrode which were denoted by (C_2).

Subsequently using a glassy carbon electrode the following cell without a diaphragm was constructed and the e.m.f. was measured at various chlorine pressures from 10^{-5} to 760 mmHg and temperatures from 500°C to 700°C .

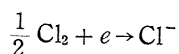


To maintain a constant partial pressure of chlorine gas the flow rate of argon should be slow as possible. Moreover, to obtain an equilibrium conditions e.m.f. measurements were carried out after stopping bubbles of a mixed gas through the hole of glassy carbon. The hole was settled under the surface of the melt about less than 1 mm in depth. A partial pressure difference between the reservoir and the cell was estimated about more than 1% below 20 mmHg. Therefore the reproducibility was not good below 30 mmHg.

III. Results and Discussion

III-1. E.M.F. of the concentration cell of chlorine gas

The relationship between the electromotive force of the cell (A) and the chlorine partial pressure (P) was shown in Fig. 2. If the following electrode reaction is adopted in the concentration cell (A).



the e.m.f. of a single chlorine electrode becomes

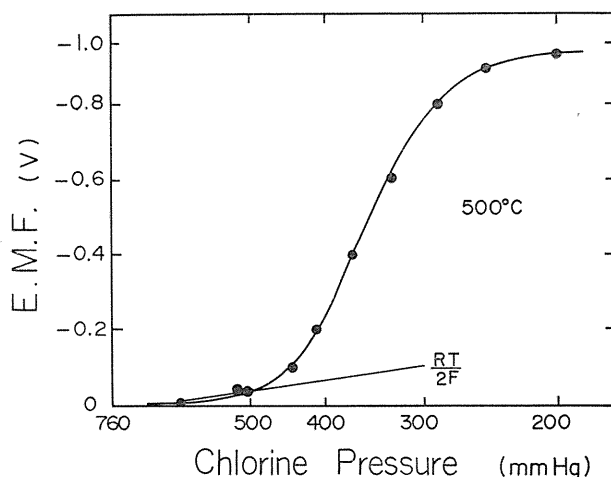


FIG. 2. E.M.F. of the cell
 $(\text{Cl})\text{Cl}_2\ 760\ \text{mmHg}/\text{AgCl}/\text{AgCl}/\text{Cl}_2\{\text{PmmHg-Ar}\ (760\text{-P})\ \text{mmHg}\}\ (\text{C})$

$$E_{\text{Cl}/\text{Cl}^-} = E_{\text{Cl}/\text{Cl}^-}^\circ + \frac{RT}{F} \ln P_{\text{Cl}_2}^{1/2}/a_{\text{Cl}^-}$$

where the $E_{\text{Cl}/\text{Cl}^-}^\circ$ is the standard electrode potential, a_{Cl^-} the corresponding activity of chlorine ion at PmmHg of chlorine. Accordingly the e.m.f. of the concentration cell without junction potentials are expressed,

$$E = \frac{RT}{F} \ln P_{\text{Cl}_2}^{1/2}/a_{\text{Cl}^-} \quad (1)$$

The dependency of the e.m.f. of the cell (A) on the chlorine pressure with a glassy carbon were the same as that of the e.m.f. with graphite. Moreover reversibility of the glassy carbon electrode treated with chlorine at 800°C as mentioned in section II-1 was rather superior than that of graphite. If the e.m.f. of the cell would follow Eq. (1), the deviation from straight line could be due either to a variation of the value of Cl^- activity, or to a junction potential arising from the permeability of ions in a pyrex glass membrane.

In the case where the deviation is due to chlorine ion activity a_{Cl^-} in Eq. (1) it must decrease with chlorine pressures and the e.m.f. decreases. This contradicts the result shown in Fig. 2. Therefore other ions of chlorine than Cl^- or anion vacancies are expectable in the melt below one atm. Further discussion on this point is beyond above results. It will be concerned with a following report.

On the other hand, if the deviation is due to junction potential, then modified form of the Nernst equation will apply on the assumption that conductance of the glass is due to permeability of cations only,

$$E_{\text{junction}} = \sum t_{M^+} \frac{RT}{F} \ln \frac{a_{M^+}(2)}{a_{M^+}(1)}$$

where the summation is over all the species of cations present, t_{M^+} is the transport number of the cation M^+ through the glass⁴⁾, and $a_{M^+}(2)$ denotes an activity of M^+ in the membrane on the side of chlorine high pressure and $a_{M^+}(1)$ that of lower side.

An observed potential (E) thus can be written in the form

$$E = E_{\text{conc}} - E_{\text{junction}}$$

where E_{conc} denotes an e.m.f. of a chlorine concentration cell. Since the E_{junction} involves only activities of cations in a glass membrane such as alkali, it does not change so much as E_{conc} with a variation of chlorine pressures. Therefore, the curve E vs. $\log P$ should be almost a straight line with the increment of a half.

Although from above consideration the electrode reaction of chlorine electrode was not $\frac{1}{2} \text{Cl}_2 \rightarrow \text{Cl}^-$ at low pressures, the reversibility of chlorine electrode was confirmed with a galvanic cell below one atm..

III-2. The effects of chlorine pressure on Ag/AgCl electrode

The relationship between the potential and the partial pressure of chlorine with the galvanic cell B and C are shown in Fig. 3. and 4.

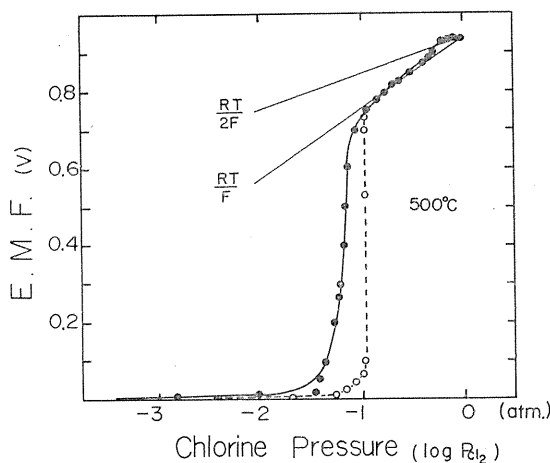


FIG. 3. E.M.F. of the cell.
Ag/AgCl-KCl (70 : 30)/Cl₂ {PmmHg Ar(760 - P)mmHg} (C)

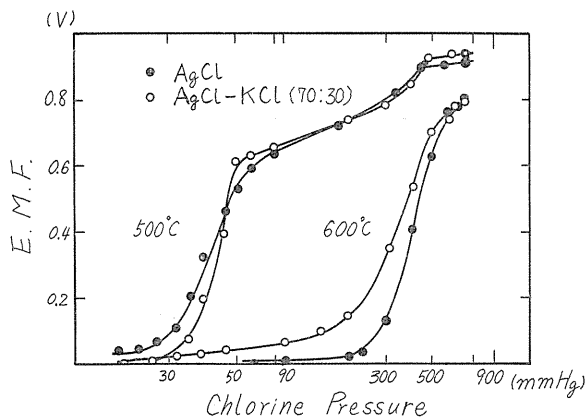


FIG. 4. Relationship between e.m.f. and $\log P_{\text{Cl}_2}$.

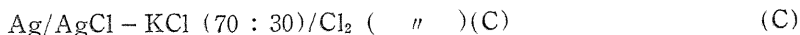
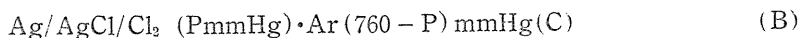


Fig. 3. shows the results of a series of experiments using a AgCl KCl (70:30) solution at 500°C. The potentials increased very slowly with a change in chlorine partial pressure up to 10^{-2} atm.. When the pressure reached about 10^{-1} atm., sharp rise occurred. After that the potential rose slowly with the increase of pressures and yielded about 930 mv at one atm.. The result obtained with an irreversible chlorine electrode are shown in dashed line in Fig. 3 for a comparison. As shown in the figure the sharp rise in potential was shifted to the higher pressures than that obtained by a reversible electrode.

A similar potential-chlorine pressure relationship for a change of AgCl concentration and of temperature are shown in Fig. 4. Although the rate of potential change was different to each other, they did not show a straight line with $\frac{1}{2}$ slope as the curve in Fig. 3.

The relationship between the e.m.f. and the temperature at 1 atm., 0.1 atm. and 0.09 atm. for AgCl are shown in Fig. 5. The entropy changes of these three pressures were calculated from the slope of this figure and have been listed in Table 1.

These different entropy changes suggest that there may be some structure change in the melt. Therefore it may be concluded that the three parts in Fig. 3 and 4 correspond to the phases of different liquid structures.

It was also observed that the color of AgCl at 500°C changed with partial pressures as follow: As chlorine pressures increased, red brown color below 10 mmHg changed to yellow and then it became dark yellow around 500 mmHg and finally deep red or black around one atmosphere. These color changes with chlorine pressures were reversible.

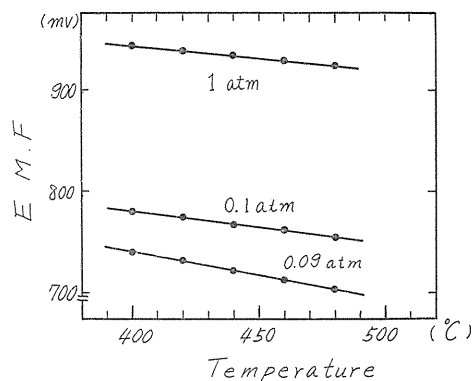


FIG. 5. Relationship between e.m.f. and temperature for AgCl.

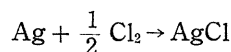
TABLE 1. The entropy changes with chlorine pressure for AgCl

P_{Cl_2} (atm.)	E.M.F. (mv)	dE/dT (v/°C)	S/n (e.u.)
1	927.6	2.69×10^{-4}	6.16
0.1	755.9	3.78×10^{-4}	8.66
0.09	701.9	5.35×10^{-4}	12.34

From the measurements of electrode potentials and the observations of colors of the melt, it seemed reasonable to assume that there may be at least three kind of structure changes in the melts below one atmosphere of chlorine pressures.

III-3. Discussion of a potential behavior of the cell B and C with chlorine pressures

In the case where the over all reaction in a cell B



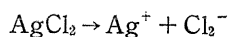
the electrode potential are expressed

$$E = E^\circ + \frac{RT}{F} \ln a_{\text{Ag}} P_{\text{Cl}_2}^{1/2} / a_{\text{AgCl}}$$

where E° are the standard electrode potentials, a_{Ag} , a_{AgCl} and P_{Cl_2} the corresponding activities and pressures, and R , T and F have usual significance. Since the activity of Ag and AgCl is equal to unity, the cell e.m.f. may be expressed as

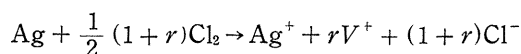
$$E = E^\circ + \frac{RT}{F} \ln P_{\text{Cl}_2}^{1/2}$$

This shows that the potential must depend on logarithms of a half power of a partial chlorine pressures. As the measured potentials depend on P rather than a half power of P above 0.1 atm., a cell reaction $\text{Ag} + \text{Cl}_2 \rightarrow \text{AgCl}_2$ was assumed where n is equal one. Therefore in the melt



might be considered. Since AgCl^+ ion was not recognized in the melt, the former type of ions will exist in the melt.

In order to explain the larger slope than one, cation vacancies were supposed in the melt. Then the cell reaction,

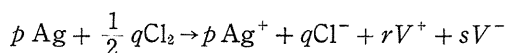


where V^+ is a cation vacancy.

Thus the e.m.f. of a cell B becomes

$$E = E^\circ + \frac{RT}{F} \ln P_{\text{Cl}_2}^{(1+r)/2}$$

Similar relation will be obtained for a cell C. Moreover if an anion vacancy was introduced, the cell reaction and e.m.f. are generally expressed as follow:



$$E = E^\circ + \frac{RT}{F} \ln \frac{1}{(a_{\text{Cl}^-})^q (a_{V^+})^r (a_{V^-})^s} + \frac{RT}{F} \ln p_{\text{Cl}_2}^{q/2}$$

where $q=(p+r-s)$ from electroneutrality and a_{Cl^-} , a_{v^+} , a_{v^-} , are the activity of Cl^- , v^+ , and v^- respectively. In this experiment (cell A and B) p is unity because silver metal is inserted in the melt as an electrode. The slope less than a half at low pressure shown in Fig. 3 and 4 are caused by anion vacancies, the existence of which was confirmed by absorption spectroscopy⁵⁾.

IV. Conclusion

Reversibility of chlorine electrode of a glassy carbon below one atm. was confirmed at 500°C by a concentration cell of chlorine composed by a graphite electrode and a glassy carbon. Pressure dependency of e.m.f. of this cell suggested that below 500 mmHg there must be some change in anions of this melt.

The e.m.f. of Ag/AgCl electrodes in AgCl and AgCl-KCl (70 : 30) under various chlorine partial pressures below one atm. were obtained to the chlorine electrode of the same partial pressure.

The results showed that dependency of the e.m.f. on chlorine pressures was not simple. It was, however, generally explained by introduction of vacancies of a cation and an anion based on the quasi-crystalline model.

Acknowledgement

The authors are indebted for skilled technical assistance of making electrodes to Mr. H. Shimizu.

References

- 1) K. H. Stern, J. Phys. Chem., **60**, 679 (1956).
- 2) D. L. Maricle, D. N. Hume, J. Electrochem. Soc., **107**, 354 (1960).
- 3) T. Nishi, N. Ichise, Denki-Kagaku, **32**, 155 (1964).
- 4) D. J. G. Ives, G. J. Janz, "Reference Electrode" Academic press, Inc. New York (1962).
- 5) M. Iseki, T. Kiriara Denki-Kagaku, **36**, No. 2 (1968) (in press).