Some Electrochemical and Physical Properties on Molten BeCl_2 *

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Physicochemical properties of the granular BeCl_2 crystals have been investigated for the samples obtained by the fractional vacuum condensation. The melting point and boiling point were 392° and 474°C , respectively.

The crystal was proved to be far less deliquescent than the commercial BeCl_2 . When the crystal was let standing for 1100 hrs in air, stable $\text{BeCl}_2 \cdot 10\text{H}_2\text{O}$ was obtained.

Polarogram of BeCl_2 in CLCl-KCl-NaCl eutectic mixtures gave the half-wave potential of -1.95V at 460°C which corresponds to the redox couple of Be/Be^{++} .

Electric conductivity of the pure molten BeCl_2 increased linearly with the raise of temperature in the region between 412 and 473°C .

Specific conductivity at and below the melting point was found to be very small, indicating the strong co-valency of the crystal BeCl_2 .

The activation energy for the electric conduction in the molten BeCl_2 changed sensitively with the change of temperature.

The analysis of the data indicated that the electric conduction in pure molten BeCl_2 is purely ionic.

1. Introduction

In view of obtaining pure beryllium by the electrolysis in fused salt, we have prepared pure beryllium chloride by the fractional condensation. A new crystal thus obtained as granular form was found to be stable against the moisture as compared with the ordinary sample of acicular form¹⁾.

In the present investigation the various physicochemical properties of the granular BeCl_2 have been measured in an attempt to provide new data and mechanisms of ionic conductivity.

2. Experiment 1

2.1 Melting and Boiling Measurements

Pure crystal of BeCl_2 prepared by the fractional vacuum condensation was used. The

measurements were performed in the dried and purified Argon atmosphere. The temperature was measured by the Chromel-Alumel thermocouple which was calibrated with respect to the melting points of Sn (231.85°C), Pb(327.5°C), Zn(419.4°C) and Sb(630.5°C).

2.2 Deliquescence

About 10g of samples were placed in the atmosphere of 58% relative humidity at 14.5°C . The weight of the sample was measured every definite period.

2.3 Polarogram

Although many problems have remained unresolved in the polarography of fused salt, the solid micro-electrode developed in our laboratory shows satisfactory reproducibility. Cell used for obtaining polarogram is illustrated in Fig. 1.

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A : Electric furnace
B : Micro-electrode
C : Reference electrode
D : Thermocouple
E : BeCl₂ entrance

Fig. 1 Apparatus for fused salt polarography

The micro-electrode of Mo used in this experiment, however, had a surface area of only 0.80 mm² and it may well be called a point-electrode. Before each run, the electrodes were washed with dilute HCl, and Argon gas was bubbled for about 30 minutes to get rid of O₂ in the melt.

Universal Bridge (BV-Z-13B, 1000 c/s) manufactured by the Yokogawa Electric Works was used to measure the resistance of the conduction cell. Cell constant was determined by three standard solutions as reported by Bremner²⁾, the resistance being measured at 0.1 and 18°C for each solution. The cell constant was found to be 17.29, which is comparatively small indicating that the size of capillary is too big.

BeCl₂ is highly viscous and this cause the difficulty of balancing the surface levels at both sides of the cell, when narrow capillary was used.

3. Results and Discussion

3.1.

Obtained Results are Shown in Table 1. Sample B agrees with the result reported by

Table 1 Melting and Boiling Point of Pure BeCl₂

	mp(°C)	b.p.(°C)
A From Run 17 in Part I (Table 2) (granular, bluish)	392	474
B From Run 1 in Part I (Table 2) (acicular, white)	400	477
C Crude (Nippon Gaishi Co. Ltd, 95% up)	383	491

Furby and Wilkinson⁽³⁾ (i.e. melting point 399±1°C, boiling point 482.5±1°C).

Sample A gives the lowest values ever reported. But these are supported to be meaningful by the electric conductivity measurement (See. IV) and also by the visual observations.

Low melting point and high boiling point of sample C are probably due to the impurities included.

3.2. Deliquescence

The strong deliquescence of acicular BeCl₂ causes many troubles in industrial handling. The large granular crystals obtained in the preceding study have less surface area per unit volume than that of the regular needle crystals, hence, higher in bulk density.

Fig. 2 shows the rate of initial weight change of BeCl₂ of three different origins.

Fig. 2 Initial weight change of BeCl₂

In the initial stage, exposed to the moisture in the air, the commercial BeCl_2 deliquesces twice as quickly as the granular BeCl_2 . Whereas, the acicular BeCl_2 increases in weight more rapidly than that of the commercial one, indicating the difficulty of obtaining anhydrous BeCl_2 in such a form.

Fig. 3 Long term weight change of BeCl_2

Fig. 3 shows the long term deliquescent properties of BeCl_2 . Both samples reach to a certain saturated value after some 1100 hours exposure to the air. Although the plateau corresponds to $\text{BeCl}_2 \cdot 10\text{H}_2\text{O}$, it does not mean that such a component actually exists.

Crystal BeCl_2 dissolves itself into its own crystalline water after about 250 hours in the air to form $\text{BeCl}_2 \cdot 5\text{H}_2\text{O}$.

In the measurement of weight increase, no correction was made for the evaporation loss of BeCl_2 , because the vapor pressure of BeCl_2 at room temperature is less than 10 mmHg⁴⁾ and it is expected to be negligibly small.

It should be noted that the granular BeCl_2 obtained in the preceding investigation.

The micro-electrode was designed so as to avoid the influence of the following disproportionation reaction reported by Smirnov et al.^{5),6)}

As shown in Fig. 1, a large platinum reference electrode, with the surface area of 492 mm² was used in spite of its reactivity in molten chlorides.

Fig. 4 Polarogram of BeCl_2 in LiCl-KCl-NaCl (Mo Point electrode)

Fig. 4 shows a typical program of BeCl_2 in the alkali chlorides bath. To avoid the drawing over the same line, zero point of successive run is shifted above arbitrarily in Fig. 4 and Fig. 5.

Fig. 5 Polarogram of BeCl_2 in LiCl-KCl-NaCl (Mo micro-electrode)

Summary of the results are listed in Table 2.

Table 2 Half-wave Potential and the Wave-height of BeCl_2 in LiCl-KCl-NaCl Eutectic Mixture at 460°C

BeCl_2 in wt%	$-E_{1/2}$ (V)	Wave-height (Amp.)
0.323	1.91	7.3×10^{-4}
1.00	1.95	15.3×10^{-4}
1.72	1.99	28.0×10^{-4}

scanning speed: 0.167 V/min
 surface area ratio: Mo(cathode):Pt(anode)
 = 0.80:492 (mm²)

The theoretical calculation of the standard potential of the reaction

can be made using the following thermochemical data:

$$S^{298}_{\text{BeCl}_2} = 21.5 \pm 2.5 \text{ e.u.}^{7)}$$

$$S^{298}_{\text{Be}} = 2.28 \pm 0.02 \text{ e.u.}^{8)}$$

$$S^{298}_{\text{Cl}_2} = 53.5 \pm 0.02 \text{ e.u.}^{8)}$$

$$Cp_{1\text{BeCl}_2} = 18.7 + 0.68 \times 10^{-3}T + 0.30 \times 10^5/T^2 \text{ }^{9)}$$

$$Cp_{1\text{Be}} = 4.54 + 2.12 \times 10^{-3}T - 0.82 \times 10^5/T^2 \text{ }^{10)}$$

$$Cp_{1\text{Cl}_2} = 8.82 + 0.06 \times 10^{-3}T - 0.68 \times 10^5/T^2 \text{ }^{11)}$$

$$\Delta H_{\text{BeCl}_2\beta \rightarrow \alpha} = 1.490 \text{ Kcal/mol}^{12)}$$

$$\Delta H_{\text{BeCl}_2\alpha \rightarrow \text{melt}} = 2.07 \text{ Kcal/mol}^{12)}$$

$$\Delta H^{298} = -118.03 \pm 0.56 \text{ Kcal/mol}^{13)}$$

$$\Delta G \simeq -nFE$$

From these data, we get

$$E = -4.046/n \text{ (V) at } 733^\circ\text{K} = -2.023 \text{ V (for } n=2)$$

When the concentration of BeCl_2 is dilute enough and the diffusion coefficient D_0 of the solute in oxidation state and D_R in reduction state are nearly equal to each other, $E_{1/2}$ can be taken as E_o , if no other reaction occurs at the electrodes.

Although the anodic reaction on Pt is complicated and not certain, the theoretical calculation based on the Cl/Cl_2 reaction closely agrees with the experimental results, indicating that such is the case of above reaction. According to Delimarskii¹⁴⁾, polarization potential of large reference Pt electrode is about + 0.1 V or in most cases negligible. If we use the value 0.1V for the polarization, we can put $E_{1/2} \simeq E_o \simeq -1.99 - (+0.1) = -2.09\text{V}$, which is remarkably close to the theoretical calculation. Thus the wave observed at -1.99 V is concluded to correspond to Be/Be^{++} ($n=2$).

No other wave was observed with the point electrode. But, when Be metal existed in the melt (i.e., either by inserting a Be rod in the bath or

by once imposing a voltage above that of the decomposition of BeCl_2 between the micro-electrode (not the point-electrode) and the Pt-reference), a new wave as seen in Fig. 5 was found at -1.1V. With the assumption that the rate determining process is the diffusion of ions toward the electrodes, we carry out Ilkovič plot of the new wave.

Results shows that n should be half of that corresponding to Be/Be^{++} , namely, $n=1$.

This can either be $\text{Be}^+/\text{Be}^{++}$ or Be/Be^+ , but since the wave was not observed when Be metal was absent in the melt, it must be attributed to the latter, which supports the hypothesis presented by Smirnov et al^{5),6)}.

3.3. Electric Conductivity

The electric conductivity of BeCl_2 has been reported by many authors^{15),16),17)}, but most of them measured the conductivity of BeCl_2 in alkali chlorides and extrapolated it to BeCl_2 . At one atm, liquid BeCl_2 is stable only in the temperature range between 392 and 474°C. The vapor pressure being very high at elevated temperatures, many investigators have pointed out that it is difficult to keep the liquid BeCl_2 stable for a prolonged period. The granular BeCl_2 obtained by the fractional vacuum condensation, however,

Fig. 6 Apparatus for electric conductivity measurement

melts to form yellowish, transparent liquid which stays in the conduction cell (Fig. 6) for a few hours under Ar gas atmosphere. This enables ones to measure electric conductivity of pure liquid BeCl_2 . The conduction cell and apparatus used for this experiment is shown in Fig. 6.

Specific conductivity K and molar conductivity μ of BeCl_2 observed are listed in Table 3.

Table 3 Conductivity of Pure BeCl_2

$t^\circ (\text{C})$	$K (\Omega^{-1} \text{cm}^{-1})$	$\mu (\Omega^{-1} \text{cm}^2/\text{mol.})$
482	3.7694×10^{-3}	2.078×10^{-1}
475 (b.p.)	4.0518	2.224
469	4.0188	2.197
463	3.6847	2.008
459	3.3402	1.815
452	2.8141	1.523
446	2.4218	1.305
442	2.0742	1.115
436	1.7910	9.594×10^{-2}
427	1.2860	6.852
422	8.7012×10^{-4}	4.621
419	6.9968	3.708
415	4.4028	2.329
412	2.0711	1.093
407	7.7860×10^{-5}	4.099×10^{-3}
404	2.180	1.146
402	6.54×10^{-6}	3.43×10^{-4}
399	1.87	9.79×10^{-5}
395	3.11×10^{-7}	1.63
394	1.56	8.14×10^{-6}
393 (m.p.)	~ 0	~ 0

Fig. 7 shows the observed relation between μ and $t^\circ \text{C}$, from which the following equation is derived:

$$\mu = 0.1490 + 0.003663 (t - 451)$$

$$\text{or } \Lambda = 0.0745 + 0.007326 (t - 451) \quad (412 \sim 470^\circ \text{C}) \quad (1)$$

This shows a surprising agreement with the result reported by W. Biltz et al.¹⁵⁾ viz.

$$\Lambda = 0.087 + 0.0073 (t - 451) \quad (2)$$

But careful investigation of their results prove that (1) and (2) meet well only around 451°C . Drossbach gave the specific conductivity of BeCl_2 to be $0.0032 + 0.26 \times 10^{-3} (t - 451)$ (3)

This also agree with our results around 451°C . He reported the equivalent conductivity at the melting point (440°C).

$$\Lambda (m.p.) = 0.088$$

Our observation shows that $\Lambda_{m.p.}$ is nearly equal to zero ($m.p. = 392^\circ \text{C}$) or, at least, smaller

Fig. 7 μ vs. $t^\circ \text{C}$

than 1×10^{-6} mho-cm/equi.

It is clearly seen in Fig. 7 that molar conductivity approaches to maximum at 470°C .

Melting point and boiling point measurement

Fig. 8 $\log \mu$ vs. $1/T^\circ \text{K}$ (cf. Table 4)

Table 4 Activation Energy for Electric Conduction in Molten BeCl₂

Temperature Range (°C)	Activation Energy (Kcal/mol)
A. 474 (<i>b.p.</i>) ~ 452	9.31
B. 452 ~ 424	32.32
C. 424 ~ 413	88.13
D. 413 ~ 405	241.5
E. 405 ~ 392 (<i>m.p.</i>)	493.7

in Sec. I tells us that BeCl₂ melts at 392°C and boils at 474°C. Therefore the conductivity irregularity must correspond to the structural change which accompanies the abrupt change in chemical bonds.

From Fig.8 ($\log \mu$ vs. $1/T^\circ\text{K}$), the activation energy $E\mu$ for electric conduction of molten BeCl₂ is calculated as listed Table 4.

It is clear that $E\mu$ changes with temperatures; linearity is held only for a certain temperature range, showing the rapid change of the mechanism of electric conduction or of the structure of the melt.

Solid state BeCl₂ forms a strong covalent network between Be and Cl¹⁸⁾. Whereas the vapor structure is not certain, but recent investigations^{4),19)} are in favor of the existence of monomer prevailing over dimer.

No interpretation of the structure of liquid BeCl₂ has ever been proposed. The strong network will still exist even after melting. The electric conduction at this stage will be very difficult, for an ion must migrate by cutting through this network. Therefore the activation energy for the ionic migration will be as large as the lattice energy (*i.e.* ~200 Kcal/mol). Because of the strong covalency, few ionization will take place even through the electric field is applied, resulting in the low specific conductivity of the melt and high activation energy near melting temperature. As the temperature is raised, the number of activated Be⁺⁺ will increase and the network will also be loosened. This will make easy to move ion with smaller activation energy and the linear increase would occur in the electric conductivity. As this range, the observed conductivity will be the sum of cationic and anionic conductivity as mentioned by Eucken. Eucken.

$$\mu = A_1 \exp(-E_c/RT) + A_2 \exp(-E_A/RT) \quad (4)$$

where, E_c : activation energy for the cationic migration.

E_A : activation energy for the anionic migration

$$\gamma \text{ Be}^{++} : \gamma \text{ Cl}^- = 0.33 \text{ \AA} : 1.81 \text{ \AA}$$

If E_c and E_A are the function of temperature, the overall conductivity will not be expressed by a simple Arrhenius equation, but (4) can be applied to it. Therefore the relation, $\log \mu$ vs. $1/T^\circ\text{K}$ will not be a simple line, but will change gradually with temperature. This seems to be the case of molten BeCl₂ between 412 and 474°C. Near the boiling point, no network will exist any more because of the strong thermal agitation, hence the activation energy for the conduction will be used to overcome such agitation. But even at this stage, the covalency of Be-Cl bond will remain and not all of the molecules are ionized, this may be the main reason why BeCl₂ has such a small conductivity in comparison with other alkali and alkaline-earth chlorides even at its boiling point.

Thus the so far proposed mechanisms for electric conduction²¹⁾ or electronic conduction^{22),23)} can not simply be applied to molten BeCl₂.

Exchange of position between the ions and the sub-lattice requires larger activation energy for ionic conduction. Judging from the magnitude of $E\mu$ of BeCl₂, we consider that such exchange must be the main mechanism of electric conduction near the melting point. But at present, no quantitative interpretation of the activation energy change is possible, because the structure of fused salt is not well known to enable such calculations.

4. Conclusion

Using the pure BeCl₂ crystals obtained by the fractional vacuum condensation, the following results were obtained:

- (1) *m.p.* = 392°C, *b.p.* = 474°C.
- (2) Present crystal is superior in deliquency to regular acicular BeCl₂.
- (3) $E\frac{1}{2} = -1.99 \text{ V}$ for Be/Be⁺⁺ at 460°C was obtained by the molten salt polarography using a point Mo electrode.

$$(4) \mu_{m.p.} = 0 \quad \mu_{b.p.} = 0.224 \text{ [mho cm}^2\text{/mol]}$$

$$\mu = 0.1490 + 0.003663 (t-451) \quad (412 \sim 470^\circ\text{C})$$

(5) The activation energy for electric conduction of molten BeCl_2 is the function of temperature, and the mechanism of conduction, which is purely ionic, changes with the change in temperature.

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On the Cupric Oxalate Cell (1)*

Studies on the Immersion Battery Using Sea Water as Electrolyte.V.

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Cupric oxalate - magnesium immersion type battery was assembled and open circuit voltage, discharge characteristics and coulombic efficiency were measured in order to examine the utility of the battery using cupric oxalate as cathode depolarizer.

The open circuit voltage of the CuC_2O_4 - Mg cell was 1.71 - 1.79 V immediately after immersion and gradually decreased to stable voltage of 1.43 V. When this battery was discharged at 20°C through 20 ohms (average current density: 26 mA/cm²), 61% of the theoretical capacity was delivered to a cut-off of 1.0 V.

Though the cell has a disadvantage that the internal resistance increases gradually as discharge proceeds, this system can be used as single shot battery in emergency flares, air-sea rescue equipment and direction finding equipment etc.

* The original written in Japanese can be seen in *Denki-Kagaku* 35,493 (1967).