

Oxidation Equilibrium of the Electrolyte of Magnesium(Part 2)

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Oxidation Equilibrium of the Electrolyte of Magnesium (Part 2).

Oxidation Equilibrium of the Mixed Electrolyte of Magnesium Chloride with Potassium Chloride.

Ryokichi TSUCHIYA.

(Received Sept. 29, 1952)

On the oxidation equilibrium of the mixed electrolyte of magnesium chloride with potassium chloride by oxygen, one report¹⁾ can be found, in which the circulation and flow methods were used. This equilibrium has been studied again in detail by means of the statical method as used in the previous experiment²⁾. It will be described in this paper.

I. Material, Apparatus and Determination.

With respect to the materials, their preparations were indicated in the first part of this report²⁾.

The ratios of the molar constitution selected in the present investigation were 9 MgCl₂, KCl, 5MgCl₂, KCl and so on, and the determinations were performed over the temperature range in which the mixed electrolytes were liquid according to the two component phase diagrams proposed by O. Menge.³⁾

The apparatus and determinations were the same as shown in the previous paper.²⁾

II. Experimental Results.

The experimental results were listed in Table 1—5.

The equilibrium constant owing to the calculation was indicated, without giving the initial and equilibrium pressure determined in each temperature.

III. Discussion.

1. Relations between the Equilibrium Constant and Temperature.

Table 1. 9MgCl₂, KCl

| Temp. (°C) | Equilibrium Constant K _p | 1/T × 10 ⁴ | logK _p | logK _p (calc.) |
|------------|--|-----------------------|-------------------|---------------------------|
| 700 | 2.43 | 10.28 | 0.385 | 0.385 |
| 720 | 2.38 | 10.07 | 0.376 | 0.373 |
| 760 | 2.21 | 9.68 | 0.345 | 0.349 |
| 800 | 2.13 | 9.32 | 0.328 | 0.326 |

Table 2. $5\text{MgCl}_2 \cdot \text{KCl}$

| Temp. ($^{\circ}\text{C}$) | Equilibrium Constant K_p | $1/T \times 10^4$ | $\log K_p$ | $\log K_p$ (calc.) |
|------------------------------|----------------------------|-------------------|------------|--------------------|
| 660 | 1.82 | 10.72 | 0.260 | 0.262 |
| 680 | 1.84 | 10.49 | 0.265 | 0.259 |
| 720 | 1.78 | 10.07 | 0.249 | 0.254 |
| 760 | 1.76 | 9.68 | 0.246 | 0.249 |
| 800 | 1.78 | 9.32 | 0.249 | 0.245 |

Table 3. $2\text{MgCl}_2 \cdot \text{KCl}$

| Temp. ($^{\circ}\text{C}$) | Equilibrium Constant K_p | $1/T \times 10^4$ | $\log K_p$ | $\log K_p$ (calc.) |
|------------------------------|----------------------------|-------------------|------------|--------------------|
| 600 | 0.855 | 11.45 | -0.058 | -0.055 |
| 640 | 0.913 | 10.95 | -0.040 | -0.034 |
| 680 | 1.009 | 10.49 | 0.004 | -0.006 |
| 720 | 1.059 | 10.07 | 0.025 | 0.020 |
| 760 | 1.111 | 9.68 | 0.046 | 0.044 |
| 800 | 1.146 | 9.32 | 0.059 | 0.066 |

Table 4. $\text{MgCl}_2 \cdot \text{KCl}$

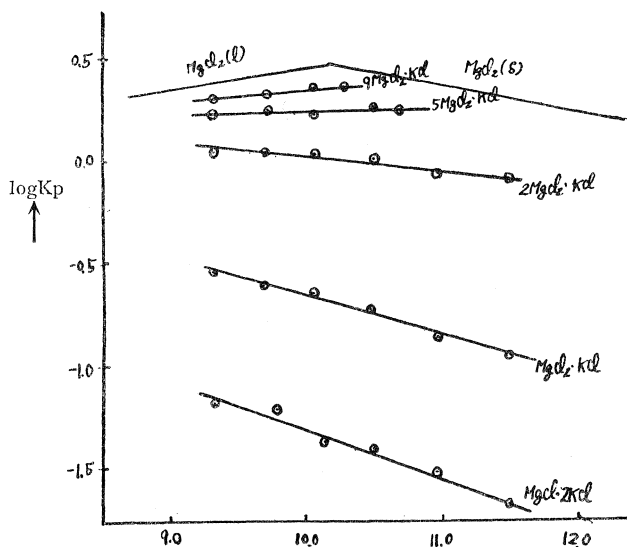
| Temp. ($^{\circ}\text{C}$) | Equilibrium Constant K_p | $1/T \times 10^4$ | $\log K_p$ | $\log K_p$ (calc.) |
|------------------------------|----------------------------|-------------------|------------|--------------------|
| 600 | 0.113 | 11.45 | -0.948 | -0.936 |
| 640 | 0.147 | 10.95 | -0.834 | -0.841 |
| 680 | 0.178 | 10.49 | -0.749 | -0.754 |
| 720 | 0.219 | 10.07 | -0.661 | -0.673 |
| 760 | 0.251 | 9.68 | -0.601 | -0.600 |
| 800 | 0.288 | 9.32 | -0.541 | -0.531 |

Table 5. $\text{MgCl}_2 \cdot 2\text{KCl}$

| Temp. ($^{\circ}\text{C}$) | Equilibrium Constant K_p | $1/T \times 10^4$ | $\log K_p$ | $\log K_p$ (calc.) |
|------------------------------|----------------------------|-------------------|------------|--------------------|
| 600 | 0.0206 | 11.45 | -1.687 | -1.682 |
| 640 | 0.0291 | 10.95 | -1.536 | -1.560 |
| 680 | 0.0381 | 10.49 | -1.419 | -1.448 |
| 720 | 0.0441 | 10.07 | -1.356 | -1.345 |
| 760 | 0.0609 | 9.68 | -1.216 | -1.250 |
| 800 | 0.0674 | 9.32 | -1.171 | -1.162 |

Plots of the logarithm of the equilibrium constant versus the reciprocal temperature almost give the straight line in each electrolyte respectively, which are shown in Fig 1, together with the result of liquid magnesium chloride. The relation formulae between

them are obtained by the method of least squares as shown in (1)—(5).



→ $1/T \times 10^4$

Fig. 1

$$9\text{MgCl}_2, \text{KCl} (l) : \log K_p = \frac{618.11}{T} - 0.2498 \quad (1)$$

$$5\text{MgCl}_2, \text{KCl} (l) : \log K_p = \frac{116.92}{T} + 0.1362 \quad (2)$$

$$2\text{MgCl}_2, \text{KCl} (l) : \log K_p = -\frac{615.61}{T} + 0.6401 \quad (3)$$

$$\text{MgCl}_2, \text{KCl} (l) : \log K_p = -\frac{1896.1}{T} + 1.236 \quad (4)$$

$$\text{MgCl}_2, 2\text{KCl} (l) : \log K_p = -\frac{2437.8}{T} + 1.110 \quad (5)$$

It is found that the calculated values of $\log K_p$ on the fifth column in Table 1—5 are in approximate agreement with the observed ones on the fourth column in them.

2. Oxidation Equilibrium of the Mixed Electrolyte of Magnesium by Water Vapour.

According to the combination of the above formulae, (1)—(5), with Sano's formula for Deacon process, the reaction isobar, namely the formulae between the equilibrium constant of the mixed electrolyte with potassium chloride by water vapour and temperature are obtained, which are plotted in Fig. 2 without their formulae.

3. Heat of Reaction and Free Energy Change.

In order to find the heats of reaction and the free energy changes in the reaction of

magnesium chloride mixed with potassium chloride in various proportions against oxygen, the molecular heats of each substance adopted from the literature and the equilibrium constants observed are used in their calculations in the same manner as the first paper.²⁾ They are given in the following formulae,

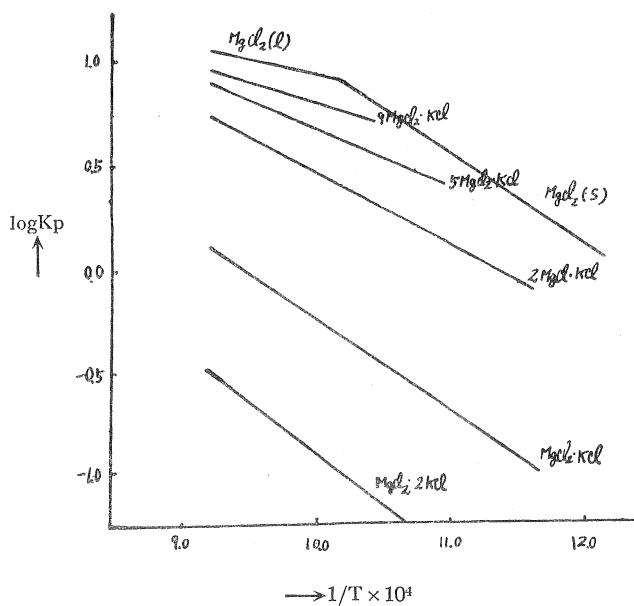
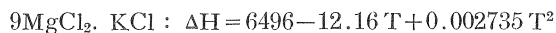
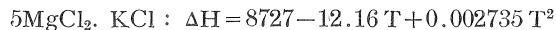


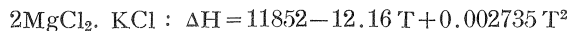
Fig. 2



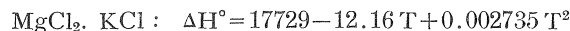
$$\Delta F^\circ = 6496 + 12.16 T \ln T - 0.002735 T^2 - 89.47 T$$



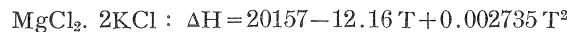
$$\Delta F^\circ = 8727 + 12.16 T \ln T - 0.002735 T^2 - 91.17 T$$



$$\Delta F^\circ = 11852 + 12.16 T \ln T - 0.002735 T^2 - 93.25 T$$



$$\Delta F^\circ = 17729 + 12.16 T \ln T - 0.002735 T^2 - 95.99 T$$



$$\Delta F^\circ = 20157 + 12.16 T \ln T - 0.002735 T^2 - 95.41 T$$

The heats of reaction, the free energy and entropy changes owing to the calculation using the former two values at 25°C are summarized in Table 6.

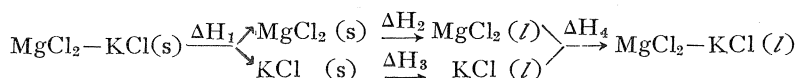
4. Heat of Fusion of Magnesium Chloride Mixed with Potassium Chloride.

It is thought that the heat of fusion of 1 mol of magnesium chloride mixed with potassium chloride consists of (i) the heat of decomposition, ΔH_1 , of the solid $\text{MgCl}_2\text{-KCl}$ compound (in which 1 mol of magnesium chloride is contained) to their components, (ii) the heat of

Table 6.

| Composition | 9MgCl ₂ . KCl | 5MgCl ₂ . KCl | 2MgCl ₂ . KCl | MgCl ₂ . KCl | MgCl ₂ . 2KCl |
|--------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------|
| ΔH ₂₉₈ | 3115 | 5346 | 8471 | 14348 | 16776 |
| ΔF° ₂₉₈ | 238 | 1963 | 4468 | 9529 | 12130 |
| ΔS° ₂₉₈ | 9.65 | 11.35 | 13.43 | 16.17 | 15.59 |

fusion, ΔH₂, of 1 mol of magnesium chloride, (iii) the heat of fusion, ΔH₃, of potassium chloride, and (iv) the heat of mixing or heat of formation of the two salts in the liquid state.

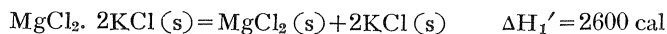
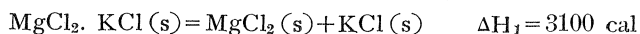


Heat of fusion is written such as ;

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

Each value is given as follows :

(i) ΔH₁ is obtained from the heat of formation by Berthelot,⁴⁾



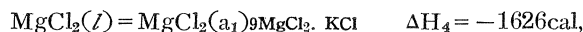
(ii) ΔH₂ is computed by using the molecular heat and H_{98b} already known,

$$\Delta H_2 = 4833 + 6.94 T - 0.001885 T^2.$$

(iii) ΔH₃ is calculated from the molecular heat and ΔH₁₀₄₉ (heat of fusion of potassium chloride) = 6290,

$$\Delta H_3 = 2310 + 6.1909 T - 3.598 \times 10^{-3} T^2 + 1.2517 \times 10^{-6} T^3$$

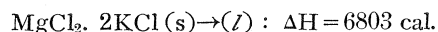
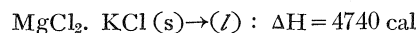
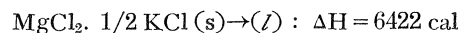
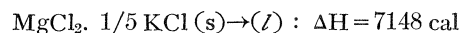
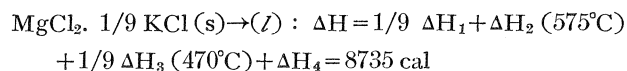
(iv) ΔH₄ is calculated by subtracting the heat of reaction of the liquid magnesium chloride with oxygen from that of the mixed electrolyte of magnesium,



etc.

where a, etc. express the activity of magnesium chloride in the mixed electrolytes such as 9MgCl₂. KCl and so on.

According to this method the heats of fusion of the mixed electrolyte are obtained as follows :

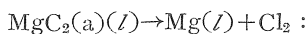


When the above four values exclusive of the final value are compared with the heat of fusion of magnesium chloride, 9840 cal, it is found that the heat of fusion of the mixed electrolyte decreases unexpectedly as the ratio of potassium chloride to magnesium

chloride increases. From this fact it is supposed that the exothermic reaction arises in the electrolyte, contributing greatly to the decrease of the heat of fusion in proportion to the increase of the ratio of potassium chloride. In order to confirm the reaction, it is very favourable to approve the assumption for the existence of magnesium complex ion proposed by V. M. Berenblit, W. D. Treadwell and Okuno.⁵⁾

5. Decomposition Voltage of Magnesium Chloride in the Mixed electrolyte.

The decomposition voltage of magnesium chloride in the mixed electrolyte being composed of the various proportions of potassium chloride, is also calculated from the ΔF° in the similar manner as in the first paper,²⁾ that is to say,



$$9\text{MgCl}_2 \cdot \text{KCl} : E = 3.2675 + 2.0456 \times 10^{-4} T \ln T - 1.0835 \times 10^{-8} T^2 - 2.1394 \times 10^{-3} T$$

$$5\text{MgCl}_2 \cdot \text{KCl} : E = 3.3161 + 2.0456 \times 10^{-4} T \ln T - 1.0835 \times 10^{-8} T^2 - 2.1763 \times 10^{-3} T$$

$$2\text{MgCl}_2 \cdot \text{KCl} : E = 3.3835 + 2.0456 \times 10^{-4} T \ln T - 1.0835 \times 10^{-8} T^2 - 2.2213 \times 10^{-3} T$$

$$\text{MgCl}_2 \cdot \text{KCl} : E = 3.5109 + 2.0456 \times 10^{-4} T \ln T - 1.0835 \times 10^{-8} T^2 - 2.2808 \times 10^{-3} T$$

$$\text{MgCl}_2 \cdot 2\text{KCl} : E = 3.5636 + 2.0456 \times 10^{-4} T \ln T - 1.0835 \times 10^{-8} T^2 - 2.2682 \times 10^{-3} T.$$

The decomposition voltages computed from the above formulae at 700°C, 750°C, 800°C and 850°C are shown in Table 7, which are plotted in Fig. 3.

Table 7.

| Composition | 9MgCl ₂ · KCl | 5MgCl ₂ · KCl | 2MgCl ₂ · KCl | MgCl ₂ · KCl | MgCl ₂ · 2KCl |
|-------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------|
| 700°C | 2.545 | 2.558 | 2.582 | 2.651 | 2.716 |
| 750°C | 2.523 | 2.529 | 2.550 | 2.617 | 2.683 |
| 800°C | 2.491 | 2.497 | 2.516 | 2.580 | 2.646 |
| 850°C | 2.465 | 2.472 | 2.489 | 2.550 | 2.617 |

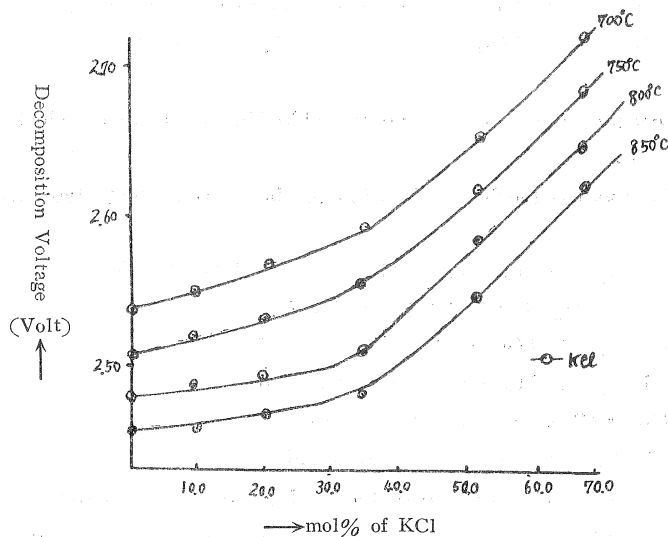


Fig. 3

IV. Summary

The oxidation equilibrium of liquid magnesium chloride mixed with potassium chloride by oxygen was investigated by the statical method.

The relations between the equilibrium constant and the temperature were obtained and the oxidation equilibria of the mixed electrolyte with potassium chloride by water vapour were computed. Furthermore, by the thermodynamic calculation the heat of fusion of the mixed electrolyte and the decomposition voltage were brought out.

From the result it has been surveyed that the more potassium chloride is added to liquid magnesium chloride, the greater the equilibrium constant, the free energy change and the heat of fusion are all diminished and the decomposition voltage of magnesium chloride is elevated.

In conclusion the writer wishes to express his hearty thanks to Prof. F. Ishikawa of Tohoku University for his kind guidance and also to Dr. I. Higuchi of the same university for his understanding help in the course of this study. In addition a debt of gratitude to Dr. S. Urano of Kanto-denka Co. Ltd. for his grants in aid of this research must be acknowledged.

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