Oxidation Equilibrium of the Electrolyte of Magnesium(Part2)

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Oxidation Equilibrium of the Electrolyte of Magnesium (Part3).

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

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On the oxidation equilibrium of the mixed electrolyte of magnesium chloride with sodium chloride by oxygen, no investigation could be found until the present paper will be published about it.

I. Material, Apparatus and Determination.

The apparatus and determination were quitely the same as used in the previous experiment[1)2)] in the case of the mixed electrolyte with potassium chloride, provided that the ratios of the molar constitution in the sample were 9 $MgCl_2$.NaCl, 5$MgCl_2$.NaCl and so on.

II. Experimental Results.

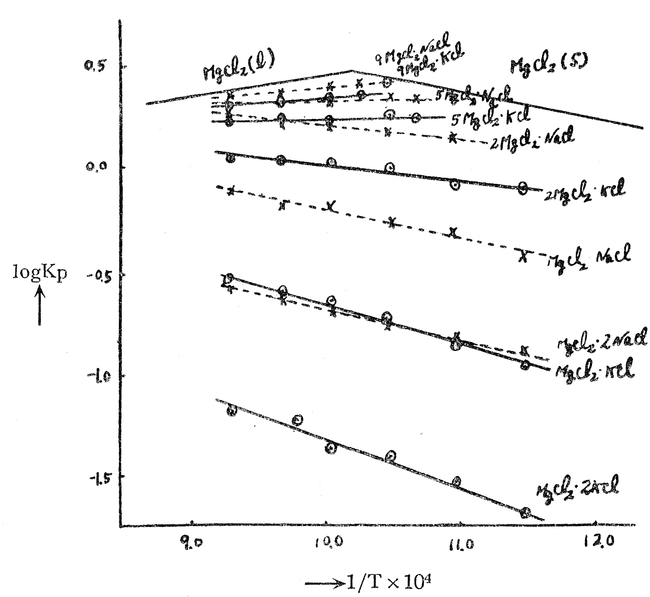


Fig. 1

The experimental results were listed in Table 1—5.

III. Discussion,

I. Relations between the Equilibrium Constant and Temperature.

Plots of the logarithm of the equilibrium constant versus the reciprocal temperature becomes linear in each electrolyte as fairly shown in Fig. 1, where the plots in the case

Table 1. $9MgCl_2$. NaCl

Temp.(°C)	Equilibrium Constant Kp	1/T+10⁴	logKp	logKp (calc.)
700	2.78	10.28	0.444	0.439
720	2.66	10.07	0.424	0.425
760	2.44	9.68	0.387	0.397
800	2.39	9.32	0.378	0.372

Table 2. $5MgCl_2$. NaCl

Temp.(°C)	Equilibrium Constant Kp	$1/T\times10^4$	logKp	logKp (calc.)
660	2.37	10.72	0.375	0.373
680	2.32	10.49	0.365	0.367
720	2.27	10.07	0.356	0.357
760	2.23	9.68	0.349	0.348
800	2.18	9.32	0.339	0.339

Table 3. $2MgCl_2$. NaCl

Temp.(°C)	Equilibrium Constant Kp	$1/T\times10^4$	log Kp	logKp(calc.)
640	1.50	10.95	0.177	0.173
680	1.56	10.49	0.193	0.196
720	1.64	10.07	0.215	0.218
760	1.73	9.68	0.238	0.238
800	1.81	9.32	0.258	0.257

Table 4. $MgCl_2$. NaCl

Temp.(°C)	Equilibrium Constant Kp	$1/T\times10^4$	log Kp	log Kp (calc.)
600	0.383	11.45	−0.416	−0.404
640	0.470	10.95	−0.328	−0.340
680	0.527	10.49	−0.278	−0.281
720	0.606	10.07	−0.217	−0.227
760	0.650	9.68	−0.187	−0.177
800	0.735	9.32	−0.133	−0.131

Table 5. $MgCl_2 \cdot 2NaCl$

Temp.(°C)	Equilibrium Constant Kp	$1/T \times 10^4$	log Kp	log Kp (calc.)
600	0.126	11.45	−0.901	−0.907
640	0.150	10.95	−0.825	−0.828
680	0.173	10.49	−0.762	−0.755
720	0.203	10.07	−0.693	−0.688
760	0.233	9.68	−0.632	−0.626
800	0.277	9.32	−0.557	−0.569

of the mixed electrolyte with potassium chloride[2] are drawn with the dotted lines for comparison each other at the same time.

As well seen in this figure, the sodium chloride can diminish the equilibrium constant of magnesium chloride in the mixed electrolyte less than the potassium chloride.

Their relation formulae obtained are mentioned below :

$$9MgCl_2 \cdot NaCl\,(l):\ \log Kp = \frac{699.83}{T} - 0.2802 \quad (1)$$

$$5MgCl_2 \cdot NaCl\,(l):\ \log Kp = \frac{240.82}{T} + 0.1147 \quad (2)$$

$$2MgCl_2 \cdot NaCl\,(l):\ \log Kp = -\frac{513.34}{T} + 0.735 \quad (3)$$

$$MgCl_2 \cdot NaCl\,(l):\ \log Kp = -\frac{1277.3}{T} + 1.059 \quad (4)$$

$$MgCl_2 \cdot 2NaCl\,(l):\ \log Kp = -\frac{1583.0}{T} + 0.906 \quad (5)$$

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

By the combination of the above formulae, (1)—(5), with Sano's formula for Deacon process, the formulae between the equilibrium constant of the mixed electrolyte with sodium chloride and temperature are obtained, which are plotted in Fig. 2 without their formulae. The dotted lines in it show the same relations in the case of the mixed electrolyte with potassium chloride, which are gained in the previous experiment.[2]

3. Heat of Reaction and Free Energy change.

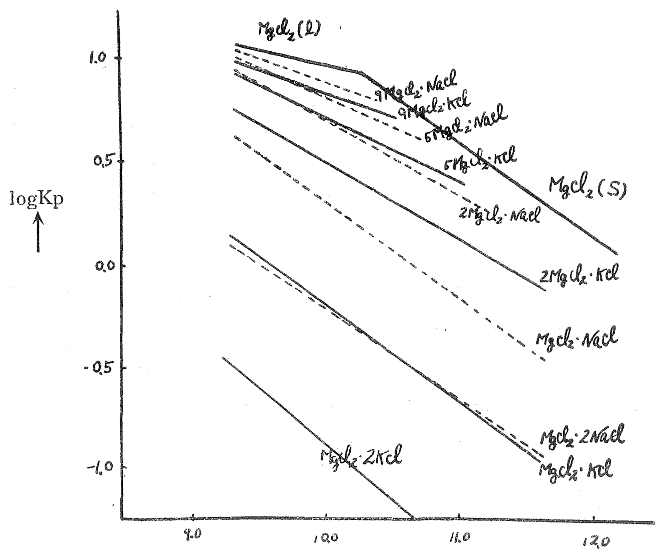
The heats of reaction and the free energy changes in the reaction of magnesium chloride mixed with sodium chloride in various proportions against oxygen are obtained from the molecular heats and the equilibrium constants determined in the same way as the previous paper.[2] They are similarly written such as,

$9MgCl_2 \cdot NaCl$: $\Delta H = 5920 - 12.16\,T + 0.002735\,T^2$

$\Delta F^\circ = 5920 + 12.16\,T\,ln\,T - 0.002735\,T^2 - 89.14\,T$

$5MgCl_2 \cdot NaCl$: $\Delta H = 8008 - 12.16\,T + 0.002735\,T^2$

$\Delta F^\circ = 8008 + 12.16\,T\,ln\,T - 0.002735\,T^2 - 90.92\,T$



$\longrightarrow 1/T \times 10^4$

Fig. 2

$2MgCl_2.\ NaCl$: $\Delta H = 11588 - 12.16\,T + 0.002735\,T^2$

$\Delta F^\circ = 11588 + 12.16\,T\,ln\,T - 0.002735\,T^2 - 93.89\,T$

$MgCl_2.\ NaCl$: $\Delta H = 14860 - 12.16\,T + 0.002735\,T^2$

$\Delta F^\circ = 14860 + 12.16\,T\,ln\,T - 0.002735\,T^2 - 95.15\,T$

$MgCl_2.\ 2NaCl$: $\Delta H = 16187 - 12.16\,T + 0.002735\,T^2$

$\Delta F^\circ = 16187 + 12.16\,T\,ln\,T - 0.002735\,T^2 - 94.37\,T$

The heats of reaction, the free energy and entropy changes are, therefore, enumerated in Table 6.

Table 6.

Composition	$9MgCl_2.\ NaCl$	$5MgCl_2.\ NaCl$	$2MgCl_2.\ NaCl$	$MgCl_2.\ NaCl$	$MgCl_2.\ 2NaCl$
ΔH_{298}	2539	4627	8207	11479	12806
ΔF°_{298}	−273	1319	4014	6910	8470
ΔS°_{298}	11.88	11.10	14.07	15.33	14.55

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

Since the heats of formation of the compounds between magnesium chloride and sodium chloride are unknown, the calculation for the purpose of looking for the above values has been given up.

5. Decomposition Voltage of Magnesium Chloride in the Mixed Electrolyte with Sodium

Chloride.

The decomposition voltage of the reaction,

$$MgCl_2(a)(l) \rightarrow Mg(l) + Cl_2,$$

in the electrolyte of magnesium chloride containing the sodium chloride at the several proportions, is also calculated from the ΔF° in the above reaction, id est,

$$9MgCl_2.\ NaCl:\ E = 3.2550 + 2.0456 \times 10^{-4}\,T\,ln\,T - 1.0835 \times 10^{-8}\,T^2 - 2.1323 \times 10^{-3}\,T$$

$$5MgCl_2.\ NaCl:\ E = 3.3003 + 2.0456 \times 10^{-4}\,T\,ln\,T - 1.0835 \times 10^{-8}\,T^2 - 2.1709 \times 10^{-3}\,T$$

$$2MgCl_2.\ NaCl:\ E = 3.3778 + 2.0456 \times 10^{-4}\,T\,ln\,T - 1.0835 \times 10^{-8}\,T^2 - 2.2352 \times 10^{-3}\,T$$

$$MgCl_2.\ NaCl:\ E = 3.4488 + 2.0456 \times 10^{-4}\,T\,ln\,T - 1.0835 \times 10^{-8}\,T^2 - 2.2625 \times 10^{-3}\,T$$

$$MgCl_2.\ 2NaCl:\ E = 3.4775 + 2.0456 \times 10^{-4}\,T\,ln\,T - 1.0835 \times 10^{-8}\,T^2 - 2.2456 \times 10^{-3}\,T$$

Table 7.

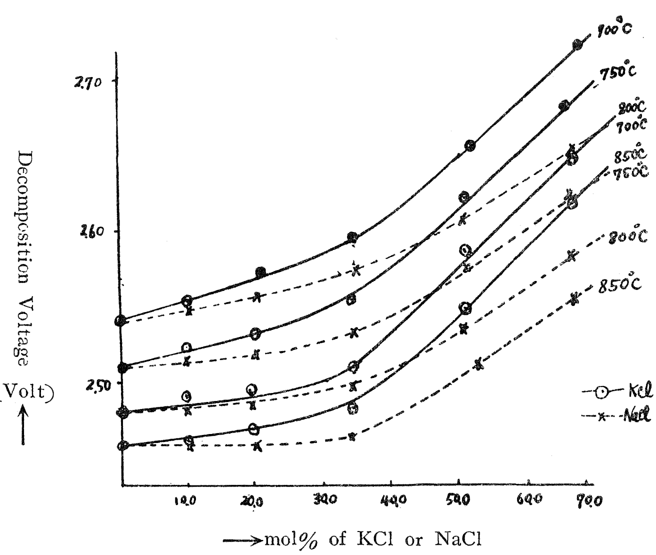


Fig. 3

Composition	$9MgCl_2.\ NaCl$	$5MgCl_2.\ NaCl$	$2MgCl_2.\ NaCl$	$MgCl_2.\ NaCl$	$MgCl_2.\ 2NaCl$
700°C	2.540	2.547	2.562	2.607	2.652
750°C	2.513	2.519	2.530	2.573	2.619
800°C	2.483	2.487	2.495	2.537	2.584
850°C	2.461	2.463	2.468	2.508	2.556

Their values at 700°C, 750°C, 800°C and 850°C are plotted in Fig. 3, being accompanied with those in the case of the mixed electrolyte with potassium chloride[2]. The former numerical values are summraized in Table 7.

IV. Summary

The oxidation equilibrium of liquid magnesium chloride mixed with sodium chloride by oxygen was studied.

The relations between the equilibrium constant and the temperature, the heat of reaction, the free energy change and the decomposition voltage magnesium chloride mixing into potassium chloride have been obtained.

It has been found that the addition of sodium chloride into magnesium chloride makes the equilibrium constant and the free energy change smaller and the decomposition voltage greater, but the degree of decreasing or increasing is less than potassium chloride.

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1) R. Tsuchiya, This Sci. Rep., **1**, 1 (1951).
2) R. Tsuchiya, ibid, **2**, 31 (1953).