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Oxidation Equilibrium of the Electrolyte of Magnesium (Part 1).

Oxidation Equilibrium of the Electrolyte of Solid and Liquid Anhydrous Magnesium Chloride.

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On the oxidation equilibrium of anhydrous magnesium chloride, especially on the reaction between the chloride and oxygen, several reports⁽¹⁾⁻⁽⁶⁾ can be found in the past. But they are on the reaction not between the molten chloride and oxygen but between the solid chloride and oxygen.

So first of all the oxidation equilibrium of the liquid magnesium chloride by oxygen, which has never been able to be found up to this time, has been investigated. The present paper will be described about it.

However, on the oxidation equilibrium of the liquid magnesium chloride mixed with potassium chloride by oxygen only one report by W. D. Treadwell and A. Cohen⁽⁶⁾ has been published. The inspection about the same reaction has been repeated again and moreover the investigation on the equilibrium when mixed with sodium chloride has also been carried out, which shall be given out in the later paper.

I. Material, Apparatus and Determination.

Anhydrous Magnesium Chloride. — It was prepared by passing the gaseous hydrogen chloride for 5–3 hours dried by concentrated sulphuric acid and phosphorus pentoxide upon the guaranteed magnesium oxide which was being heated at about 650°C in the electric furnace after removing water and carbon dioxide by heating it for several hours at about 800°C.

KCl and NaCl. — Guaranteed potassium and sodium chloride was ignited.

Oxygen. — It was purified by removing manganous dioxide, carbon dioxide and water vapor by glass wool, solid potassium hydroxide, calcium chloride and phosphorus pentoxide from the oxygen which was evolved by heating potassium permanganate.

Apparatus and Determination. — The statical method was used, as shown in Fig. 1. After the sample was thrown into the reaction tube A made of quartz, the whole apparatus was produced a vacuum, raising the temperature of the electric furnace F_1 . It was regulated at constant within $\pm 1^\circ\text{C}$ by the another electric furnace F_2 . The refined oxygen, the volume

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of which was measured by gas buret B, was sent into the reaction tube A. The pressure in A increased gradually and it required about 5-6 hours for the pressure to get to the equilibrium. It was determined by mercury manometer M, after adjustment of spring manometer S.

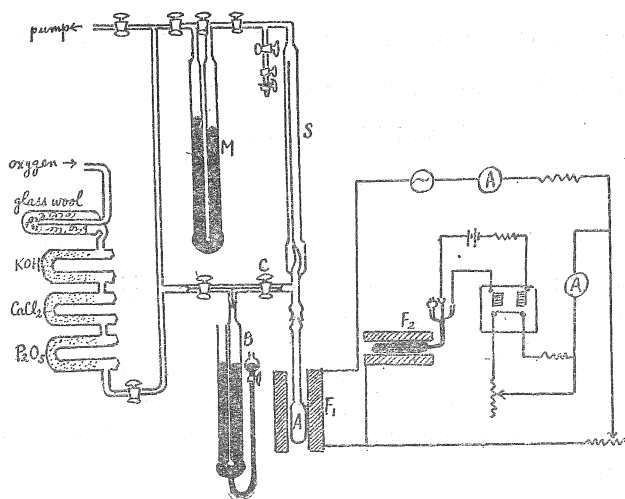
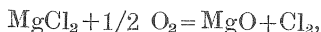


Fig. 1

When the initial pressure in this system is expressed as p_0 and the equilibrium pressure in it as p_e , the equilibrium constant K_p in the reaction,



is given as follows :

$$K_p = \frac{p_{\text{Cl}_2}}{\sqrt{p_{\text{O}_2}}} = \frac{2(p_e - p_0)}{\sqrt{2(p_0 - p_e)}}, \quad (1)$$

where p_{Cl_2} is the partial pressure of chlorine and p_{O_2} is that of oxygen. In all cases the pressures were read in units of atmosphere.

The initial pressure was estimated in such a manner as described below.

The certain volume of air measured by gas buret was sent into the reaction tube A without sample and the pressures in it at various temperatures were read. Then the relation between its pressure and temperature was calculated by method of least squares. In other several volumes of air the same estimations as above were performed. From these formulas the pressures of air in each volumes were obtained at the several temperatures in the present experiment and according to the application of method of least squares to them the relation between the volume of air and its pressure at each temperatures was computed. Then the correction against the initial pressure was done by using the volume of the reaction tube previously measured and that of the sample in order to obtain the real initial pressure when the sample was inserted, where the volume of sample was calculated.

by using the next formulas :

$$\text{density of MgCl}_2 = 1.660 - 0.00027(t - 800)$$

$$\text{KCl} = 1.535 - 0.00056(t - 768)$$

$$\text{NaCl} = 1.500 - 0.00054(t - 900)$$

and the additional density was considered to be close to the density in the mixed electrolyte.

The equilibrium constant K_p was calculated by substituting the initial pressure obtained as described above and the equilibrium pressure into the formula (1).

II. Experimental Results.

1-1.8 g. of new sample and 8-14 c. c. of oxygen were used, being exactly measured at every determination. From the equilibrium pressure read the vapor pressure on magnesium chloride was subtracted in case of the liquid state.

The experimental results were listed in Table 1 in connection with the solid anhydrous magnesium chloride and in Table 2 in connection with the liquid one.

Table 1.

Temp.(°C)	Initial Pressure (mmHg)	Equilibrium Pressure (mmHg)	Equilibrium Constant K_p	$1/T \times 10^4$	$\log K_p$	$\log K_p(\text{calc.})$
550	183.4	326.6	1.64	12.15	0.215	0.218
600	188.8	347.0	2.07	11.46	0.316	0.309
650	332.1	600.5	2.44	10.83	0.387	0.390
700	307.1	570.6	2.89	10.28	0.461	0.463

Table 2.

Temp.(°C)	Initial Pressure (mmHg)	Equilibrium Pressure (mmHg)	Equilibrium Constant K_p	$1/T \times 10^4$	$\log K_p$	$\log K_p(\text{calc.})$
740	341.1	627.1	2.80	9.87	0.447	0.451
760	456.7	817.4	2.67	9.68	0.427	0.430
780	374.5	677.0	2.59	9.50	0.413	0.410
800	522.5	916.5	2.52	9.32	0.401	0.392
820	390.1	693.2	2.36	9.15	0.373	0.374
840	371.8	658.7	2.26	8.99	0.354	0.356
860	382.5	672.7	2.19	8.83	0.340	0.339
880	376.6	657.8	2.09	8.67	0.320	0.323

III. Discussion.

1. Relation between the Equilibrium Constant and Temperature.

A plot of the reciprocal temperature versus the logarithm of the pressure in connec-

tion with the solid magnesium chloride measured by author and other investigators is given in Fig. 2. These lines are practically linear respectively. Fig. 3 is another one in connection with the solid and liquid chlorides published in this paper for the first time. The relation formulas between them are obtained by the method of least squares as shown in (2) and (3).

$$\text{MgCl}_2 (\text{s}) : \log K_p = -\frac{1308.9}{T} + 1.8079 \quad (2)$$

$$\text{MgCl}_2 (\text{l}) : \log K_p = \frac{1064.0}{T} - 0.59995 \quad (3)$$

It is found that the calculated values of $\log K_p$ on the seventh column in Table 1 and 2 are in relative agreement with the observed ones on the sixth column in them.

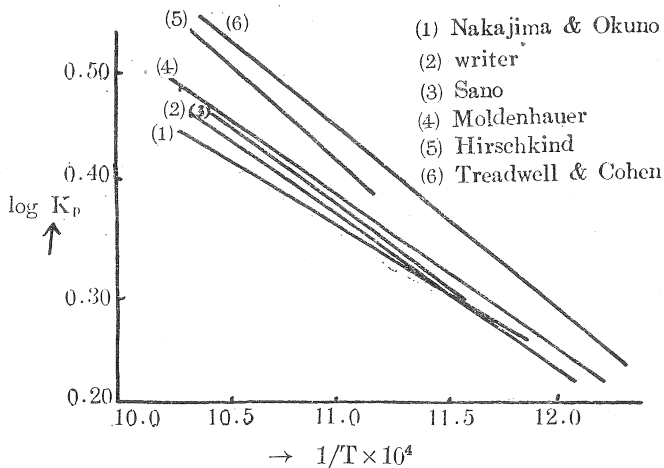


Fig. 2

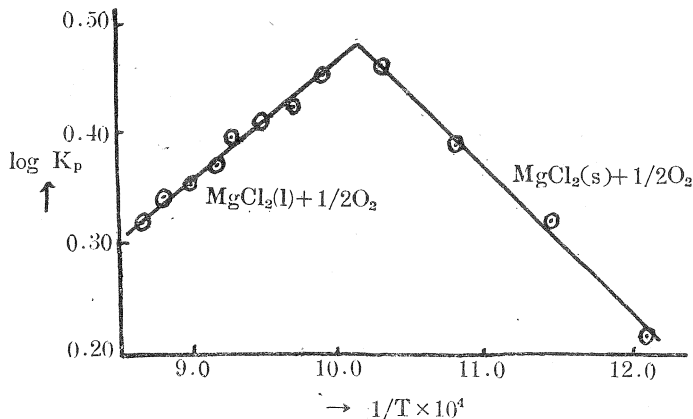
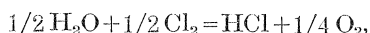


Fig. 3

2. Oxidation Equilibrium of Anhydrous Magnesium Chloride by Water Vapor.

According to the combination of the above formulas, (2) and (3), with those of Deacon process, the oxidation equilibrium of solid and liquid magnesium chloride by water vapor can be obtained. As for Deacon process, the investigations are known by Lewis,⁷⁾ von Falkenstein,⁸⁾ Marmier,⁹⁾ Neumann,¹⁰⁾ Korvezee,¹¹⁾ Lewis and Landall¹²⁾, and Sano.¹³⁾ Since their results are almost cooperated, the calculation by using Sano's formula has been tried as described below.

While the equilibrium constant in Deacon process,



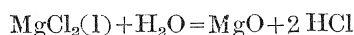
is written as

$$K_p = \frac{p_{\text{HCl}} \cdot p_{\text{O}_2}^{1/4}}{p_{\text{H}_2\text{O}}^{1/2} \cdot p_{\text{Cl}_2}^{1/2}},$$

its logarithm is given by Sano as

$$\log K_p = -\frac{1397.42}{T} + 1.613.$$

Then when the latter formula is doubled and it is added to (2) and (3) respectively, as the relation between the equilibrium constants $K_p = p_{\text{HCl}}^2/p_{\text{H}_2\text{O}}$ in the reactions



and the temperature, the next formulas are obtained, which are plotted in Fig. 4.

$$\text{MgCl}_2(\text{s}) : \log K_p = -\frac{4103.74}{T} + 5.0339$$

$$\text{MgCl}_2(\text{l}) : \log K_p = -\frac{1730.84}{T} + 2.62605$$

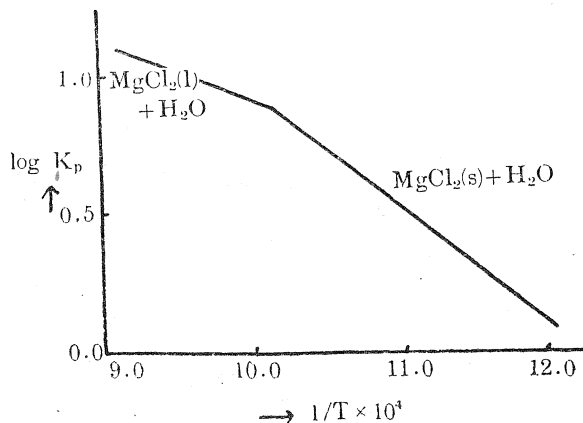


Fig. 4

3. Heat of Reaction and Change of Free Energy.

In order to find the heat of reaction and the change of free energy in the reaction

of solid and liquid magnesium chloride with oxygen the next values in the literatures are used as the molecular heat of each substances.

$$\text{MgCl}_2 (\text{s}) \quad C_p = 17.3 + 0.00377 T$$

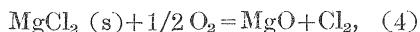
$$\text{MgCl}_2 (\text{l}) \quad C_p = 24.24$$

$$\text{MgO} (\text{s}) \quad C_p = 7.93 + 0.00497 T$$

$$\text{O}_2 \quad C_p = 6.5 + 0.001 T$$

$$\text{Cl}_2 \quad C_p = 7.4 + 0.001 T$$

In case of the reaction



the change of the molecular heat can be written by applying the above data to each substances as

$$\Delta C_p = -5.22 + 0.0017 T.$$

By integrating it,

$$\Delta H = H_0 - 5.22 T + 0.00085 T^2$$

is obtained as the heat of reaction. Then the change of free energy is

$$\Delta F^\circ = H_0 + 5.22 T \ln T - 0.00085 T^2 + I T.$$

In this formula

$$-R \ln K_p - 5.22 \ln T + 0.00085 T = H_0/T + I = \Sigma,$$

by substituting the experimental data into K_p at various temperatures T and applying the method of least squares to these equations obtained above, H_0 and I are decided. Then the heat of reaction and the change of free energy are given as the following formulas.

$$\Delta H = 9704 - 5.22 T + 0.00085 T^2$$

$$\Delta F^\circ = 9704 + 5.22 T \ln T - 0.00085 T^2 - 47.16 T$$

The change of entropy is obtained by using the formula

$$\Delta S^\circ = \frac{\Delta H - \Delta F^\circ}{T}.$$

In case of the reaction



by the similar calculation as before the change of the molecular heat, the heat of reaction and the change of free energy are also

obtained; that is to say,

$$\Delta C_p = -12.16 + 0.00547 T$$

$$\Delta H = 4870 - 12.16 T + 0.002735 T^2 \quad (6)$$

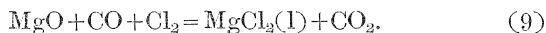
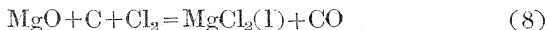
$$\Delta F^\circ = 4870 + 12.16 T \ln T - 0.002735 T^2 - 88.27 \quad (7)$$

The heat of reaction, the change of free energy and that of entropy in the reactions (4) and (5) at 25°C are summarized in Table 3.

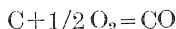
Table 3.

	ΔH_{293} (cal.)	ΔF_{298}° (cal.)	ΔS_{298}° (cal./deg.)
MgCl ₂ (s)(write:)	8224	4438	12.71
∕(Moldenhauer)	9620	4130	11.17
∕(Sano)	8103	4353	12.58
∕(Nakajima) Okuno)	8117	4330	12.39
MgCl ₂ (l)(writer)	1489	-1029	8.44

4. Calculation of the Thermodynamic Values in the Two Reactions,

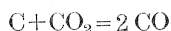


Since the heat of formation of carbon monoxide and the change of free energy in the next two reactions are given by J. Chipmann¹⁴⁾ as follows :



$$\Delta H = -27070 + 2.05 T - 0.00225 T^2 + 0.0000004 T^3 \quad (10)$$

$$\Delta F^\circ = -27070 - 2.05 T \ln T + 0.0025 T^2 - 0.0000002 T^3 - 7.92 T \quad (11)$$



$$\Delta H = 40070 + 4.40 T - 0.0048 T^2 + 0.00000090 T^3 \quad (12)$$

$$\Delta F^\circ = 40070 - 4.40 T \ln T + 0.0048 T^2 - 0.00000045 T^3 - 14.90 T \quad (13)$$

so the heat of reaction and the change of free energy in (8), are obtained by the combination of (10) and (11) with (6) and (7) such as;

$$\Delta H = -31940 + 14.21 T - 0.004985 T^2 + 0.0000004 T^2$$

$$\Delta F^\circ = -31940 - 14.21 T \ln T + 0.004985 T^2 - 0.0000002 T^3 + 80.35 T$$

$$\Delta H_{298} = 28137 \text{ cal.}$$

$$\Delta F_{298}^\circ = 31687 \text{ cal.},$$

and those in (9) are obtained by the combination of (12) and (13) with (6) and (7) such as;

$$\Delta H = -72010 + 9.81 T - 0.000185 T^2 - 0.00000050 T^3$$

$$\Delta F^\circ = -72010 - 9.81 T \ln T + 0.000185 T^2 + 0.00000025 T^3 + 95.25 T$$

$$\Delta H_{298} = 69117 \text{ cal.}$$

$$\Delta F_{298}^\circ = 60261 \text{ cal.}$$

5. Melting Point of Anhydrous Magnesium Chloride.

When the formulas (2) and (3) are made equal, the melting point of anhydrous magnesium chloride, which is shown as the intersecting point of two lines in Fig. 3, is obtained as 712°C (T=985°K). It is found that this value is satisfactory, because it is not far from those which have been reported such as 718°C (E. Korreng), 711°C (O. Menge; K. Scholich), 712-713°C (W. Biltz; W. Klemm), 720°C (G. A. Abramov) 712°C (C. Sandonini; K. K. Kelley) and 716°C (A. E. Aushbekowitch).

6. Heat of Fusion.

If 712°C presented by author is appointed as the melting point of magnesium chloride, the next two values are obtained as the heat absorbed in the reaction of solid magnesium chloride with oxygen and that emitted in the reaction of liquid one, that is,

$$\Delta H_{985} = 5387 \text{ cal.} \quad \Delta H_{985} = -4453 \text{ cal.}$$

Then from the difference in the above two values,

$$\Delta H = 9840 \text{ cal.},$$

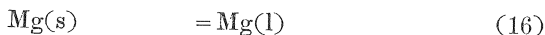
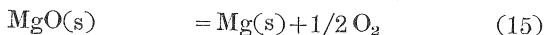
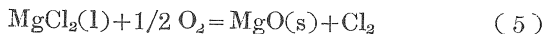
is calculated as the heat of fusion of anhydrous magnesium chloride. It may be written for reference that 9790 cal. (W. S. Ljaschenko), 10770 cal. (A. E. Aushbekowitch) and 8100 cal. (K. K. Kelley) are reported as the heat of fusion.

7. Decomposition Voltage of Magnesium Chloride.

The decomposition voltage of magnesium chloride in the reaction,



is calculated by means of the combination of the thermodynamic values in the three reactions,



as described below.

In order to obtain the change of free energy in the reaction (15), using the molecular heat in the literature, i. e.,

$$\text{Mg}(s) : C_p = 5.223 + 0.00263 T$$

$$\text{MgO}(s) : C_p = 7.93 + 0.00497 T$$

$$\text{O}_2 : C_p = 6.5 + 0.001 T,$$

the change of molecular heat in it,

$$\Delta C_p = -0.543 + 0.00184 T,$$

is computed, being conducted to

$$\Delta H = H_0 - 0.543 T + 0.00092 T^2$$

$$\Delta F^\circ = H_0 + 0.543 T \ln T - 0.00092 T^2 + I T.$$

In the latter formula by adopting $\Delta H_{298} = -144100$ cal. and $\Delta F_{298}^\circ = -136440$ cal. presented by Sano, H_0 and I are decided, being obtained,

$$\Delta F^\circ = -144020 + 0.543 T \ln T - 0.00092 T^2 + 22.62 T \quad (17)$$

In the reaction (16), using the molecular heat,

$$\text{Mg}(s) : C_p = 5.223 + 0.00263 T$$

$$\text{Mg}(l) : C_p = 7.4$$

the next formulas are obtained in the same manner as before.

$$\Delta C_p = 2.177 - 0.00263 T$$

$$\Delta H = H_0 + 2.177 T - 0.001315 T^2$$

$$\Delta F^\circ = H_0 - 2.177 T \ln T + 0.001315 T^2 + I T$$

By adopting 650°C as the melting point of magnesium and 1160 cal. as the heat of fusion given by K. K. Kelley, i. e.,

$$\Delta H_{923} = 1160 \text{ cal.},$$

and by taking into account also,

$$\Delta F_{923}^\circ = 0,$$

the change of free energy is calculated as,

$$\Delta F^\circ = 271 - 2.177 T \ln T + 0.001315 T^2 + 13.36 T \quad (18)$$

Therefore, the change of free energy in the reaction (14), adding the equation (7) in the reaction (5) to those, (17) and (18), is represented in the next formula.

$$\Delta F^\circ = 149161 + 9.44 T \ln T - 0.0005 T^2 - 97.53 T.$$

While there is the relation,

$$\Delta F^\circ = 2 E F,$$

where E expresses the decomposition voltage of magnesium chloride and F, Faraday's constant, the decomposition voltage of magnesium chloride is given as,

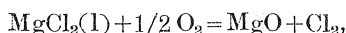
$$E = 3.2322 + 2.0456 \times 10^{-4} T \ln T - 1.0835 \times 10^{-8} T^2 - 2.1135 \times 10^{-8} T.$$

Those values calculated from the above formula at 700°C, 750°C, 800°C and 850°C are shown as 2.535, 2.509, 2.480 and 2.459 volts respectively. In the literature the value of 2.5 volts is found at 750°C.

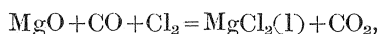
IV. Summary.

The oxidation equilibrium of liquid anhydrous magnesium chloride by oxygen was investigated by the statical method. From the result the thermodynamic functions were brought out and the consideration for them was deduced as follows :

1. The relation between the equilibrium constant and the temperature was obtained.
2. The oxidation equilibrium of liquid anhydrous magnesium chloride by water vapor was computed.
3. The heat of reaction and the change of free energy in the reaction,



were calculated, and by using them, the thermodynamic values in the reactions,



were also done.

4. The melting point and heat of fusion of anhydrous magnesium chloride was found.
5. The decomposition voltage of magnesium chloride was calculated from the change of free energy concerning to magnesium chloride.

In conclusion the writer wishes to express his best thanks to Prof. F. Ishikawa of Tohoku University for his kind guidance and to Mr. S. Urano of Kanto-denka Co. for his appreciative supports throughout this work.

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