

## Electrical Conductivities of Binary and Ternary Melts between $\text{MgCl}_2$ , $\text{CaCl}_2$ , $\text{NaCl}$ , and $\text{KCl}$

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Specific conductivities have been measured for the binary systems  $\text{MgCl}_2$ - $\text{CaCl}_2$ ,  $\text{MgCl}_2$ - $\text{NaCl}$ ,  $\text{MgCl}_2$ - $\text{KCl}$ ,  $\text{CaCl}_2$ - $\text{NaCl}$ ,  $\text{CaCl}_2$ - $\text{KCl}$  and the ternary systems  $\text{MgCl}_2$ - $\text{CaCl}_2$ - $\text{NaCl}$ ,  $\text{MgCl}_2$ - $\text{CaCl}_2$ - $\text{KCl}$  by an AC conduction bridge. Binary excess functions were calculated from a three parameter equation using orthonormal functions. The ternary excess functions were compared with calculated excess functions from binary excess terms and good agreement was obtained.

Investigation of the electrical conductivity of the  $\text{MgCl}_2$ - $\text{CaCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  system is important both from a technical and a theoretical point of view. This system is the basis of the so-called I.G. Farbenindustrie process for producing magnesium electrolytically. Electrical conductivity is directly related to the energy and current efficiency of the technical processes. The electrolyte used today is a mixture of about 35 wt. %  $\text{CaCl}_2$ , 30 wt. %  $\text{NaCl}$ , 20 wt. %  $\text{KCl}$  and 15 wt. %  $\text{MgCl}_2$ . A further insight into this system, outside the concentration range normally employed, is necessary for further optimization of the technical conditions.

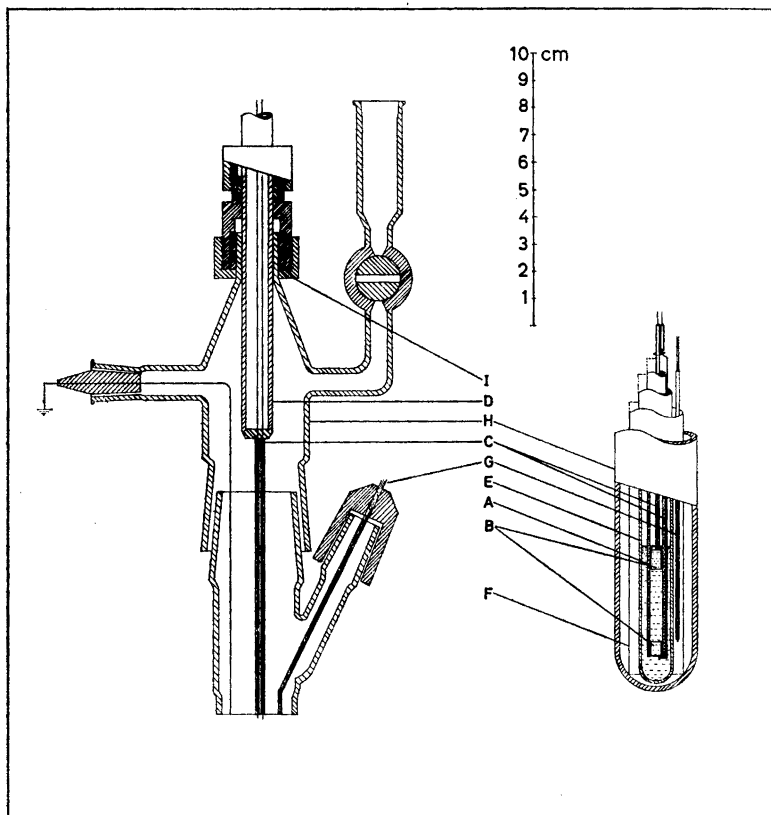
Furthermore, the system is interesting as an example of a mixture of cations with different charge and size but with each having a common anion. The small and bivalent  $\text{Mg}^{2+}$  will, for example, form stronger bonds than the monovalent  $\text{Na}^+$  or  $\text{K}^+$ . One of the properties by which the electrostatic interaction can be depicted is based on the ionic potential defined as the ratio between the charge and the ionic radius. Though the difference in ionic potential between  $\text{Na}^+$  and  $\text{K}^+$  is quite small, the difference between alkali metals and alkaline earth metals is large enough to make these systems theoretically interesting.

In spite of its technical importance, the electrical conductivity in these systems has not been extensively investigated. A few publications deal with

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the electrical conductivity of alkali and alkaline earth halides and their binary mixtures.<sup>1-5</sup> Only two papers,<sup>6,7</sup> on the conductivity of the  $\text{MgCl}_2$ - $\text{CaCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  system, have been published, but both works were concerned with constant concentration of  $\text{MgCl}_2$  being 10 weight % and 9.1 and 20 weight %, respectively.

In the present work the electrical conductivity in the ternary systems  $\text{NaCl}$ - $\text{CaCl}_2$ - $\text{MgCl}_2$  and  $\text{KCl}$ - $\text{CaCl}_2$ - $\text{MgCl}_2$  was investigated over the whole concentration range of all the components, at temperatures between 700 and 900°C.



*Fig. 1.* The conductivity cell. A:  $\text{Al}_2\text{O}_3$  tube. B: Platinum electrodes. C: Platinum wire leads. D: Pyrex glass piston. E: Quartz tube container. F: Platinum shield. G: Pt-Pt 10 % Rh thermocouple. H: Outer quartz tube. I: O-ring seals.

#### EXPERIMENTAL

*Apparatus.* The details of the apparatus are shown in Fig. 1. The conductivity cell was made from an  $\text{Al}_2\text{O}_3$  tube (A), 4 mm inside diameter and 13 cm length. Cylindrical platinum electrodes (B) with a surface area  $0.5 \text{ cm}^2$  were placed in the cell with one

electrode at the lower end of the  $\text{Al}_2\text{O}_3$  tube with the connecting leads outside the tube. The other electrode was on the inside of the tube and 6 cm below the top. Platinum wire leads (C) connected to the electrode were embedded in "Araldite" in a pyrex glass piston (D), so that the distance between the electrodes was constant (6.5 cm). The cell constant was about  $50 \text{ cm}^{-1}$ . The salt mixture was contained in a quartz tube (E). A platinum cylinder (F), at earth potential, eliminated interference from electromagnetic fields due to A. C. in the furnace resistor. The temperature was measured with a Pt—Pt 10 % Rh thermocouple (G) which was placed between the crucible and the platinum cylinder at a level corresponding approximately to the middle of the cell.

The apparatus was placed inside an outer quartz glass tube (H). This was connected by a ground joint to a pyrex cap. The cap contained O-ring seals (I) in which the glass piston (D) could be moved, together with an outlet for the grounding of the shield and a stopcock with a ground joint which could be connected to a vacuum line. The arrangement was vacuum tight to the extent that a pressure of  $10^{-5}$  torr could be attained in the vacuum line when the conductivity apparatus was coupled to it.

The furnace used in this study was a "general purpose laboratory furnace" as used in the authors' laboratory.<sup>8</sup> Adjustments of the power supply gave a temperature regulation of  $\pm 0.6^\circ\text{C}$  in the region of the furnace where the conductivity cell was placed.

Resistance measurements were made using a Tinsley A. C. bridge, type 4725. An external audio oscillator, Hewlett-Packard, model 201C, supplied an alternating current with frequencies up to 20 kHz and peak to peak voltage = 0.6 V when loaded. A Wheatstone bridge, with Wagner earth grounding to eliminate leak currents, was utilized for the conductivity measurements. Special care was taken when grounding the different leads in order to reduce the noise to a minimum as this would otherwise affect the balancing of the bridge. The balancing of the bridge was accomplished with a Hewlett-Packard, 130C oscilloscope by simultaneously balancing resistance and capacitance on the Wagner earth along the  $x$ -axis and the bridge along the  $y$ -axis.

*Chemicals and handling of samples.* All the salts used were of analytical grade quality.

Because of the shrinking of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  under dehydration anhydrous  $\text{MgCl}_2$  was prepared in two stages.

500 g  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was dried at a temperature of  $50$ – $70^\circ\text{C}$  under a vacuum of  $10^{-1}$  torr for a minimum of two days. Dry HCl gas was then passed through the salt at a flow rate of 4 l/min, the temperature was slowly raised to  $400^\circ\text{C}$  over a 1 day period. A temperature of  $400^\circ\text{C}$  was maintained for 4–5 h with a flow of HCl of about 6 l/min. The heat was then switched off and the nearly anhydrous  $\text{MgCl}_2$  was cooled in a dry argon flow.

In a dry-box the  $\text{MgCl}_2$  was transferred to another vessel with a quartz frit in the bottom. The  $\text{MgCl}_2$  was heated to the melting point ( $714^\circ\text{C}$ ) over a 6–7 h period with an HCl flow of 4 l/min through the frit. When the salt had melted the gas flow was reduced to 0.5 l/min in order to avoid splashing of the melt. This gas flow was large enough to keep the molten salt above the frit, and the melt was further heated to  $800^\circ\text{C}$  and kept at this temperature for 2 h with HCl bubbling through. The melt was then flushed with dry argon for about 2 h. The gas flow was stopped, the vessel under the frit evacuated and the melt filtered down through the frit. The  $\text{MgCl}_2$  was then sealed off in the vessel and stored till use.

Titration with HCl showed the oxide content of the  $\text{MgCl}_2$  to be = 0.01 weight % MgO. The melt was also tested by a DC polarogram according to Laitinen *et al.*<sup>9</sup> and water was not detected.

Anhydrous  $\text{CaCl}_2$  was prepared in the same way starting with  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . Since  $\text{CaCl}_2$  is less hygroscopic than  $\text{MgCl}_2$ , the whole drying process was carried out within 2 days.

NaCl and KCl were used after drying at  $300^\circ\text{C}$  and melting under vacuum. The salts were then crystallized slowly and only clear crystals were used. KCl for the standard conductivity solution was recrystallized in water.

Samples for conductivity measurements were prepared in a "dry-box" with a water content < 50 ppm by weighing appropriate amounts of the anhydrous salts. The mixture was then melted under vacuum and filtered down into a quartz tube which was used as a crucible. Considerable care was taken to keep the samples anhydrous. The apparatus was evacuated to  $10^{-4}$  –  $10^{-5}$  torr, filled with dry nitrogen at 0.5 atm and placed in the furnace. By heating of the cell the pressure reached about 1 atm.

The salt mixture was then melted while the piston containing the conductivity cell and leads was kept above the salt. When the salt had melted, the conductivity cell was lowered into the melt, the level of melt was then 8 mm above the upper electrode.

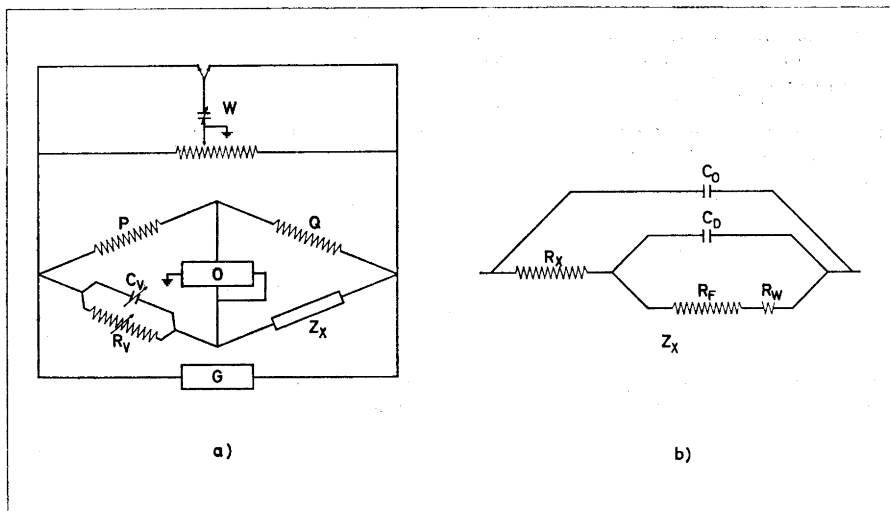
**Bridge measurements.** The conductivities were measured in a Wheatstone-bridge arrangement. The cell was calibrated before each measurement with 1 M KCl solution at 20.0°C. The cell constant was also checked several times with saturated NaCl solution at 20°C and was found to be the same within 0.5%. Correction was made for the change in the cell constant due to thermal expansion of the Pt leads and the  $\text{Al}_2\text{O}_3$  tube, after heating from 20°C to the operating temperature of 700–900° ( $\kappa(\text{corr})/\kappa(\text{exp})=0.993$ ).

Measurements of the resistance of the melt were carried out at various temperatures between 700 and 900°C, both after raising and after lowering the temperature and no significant difference was observed in the results.

For each measurement the resistance was measured as a function of frequency,  $\omega$  between 2 and 20 kHz and was found to be a linear function of  $1/\sqrt{\omega}$  (see later). The resistance was extrapolated to infinite frequency. The change in the resistance when the frequency was changed from 2000–20 000 cycles was about 8% for molten salts and about 3% for 1 M KCl solution. The value of the resistance at infinite frequency was 20–40  $\Omega$  in the melts and about 450  $\Omega$  in 1 M KCl.

The measurements were carried out with bright platinum electrodes. Platinization of the electrodes reduced the frequency dependence of the resistance but this effect changed with time thus complicating any extrapolation procedure.

Values of the resistance were corrected to take into account the resistance in the leads. The latter was measured in a separate experiment by means of a standard resistance. Correction for the change of resistance with temperature for the part of the leads in the furnace was also made. The total correction was 1–2%.



**Fig. 2.** a) Simplified circuit diagram for the bridge. G: Audio oscillator.  $R_v$ : Variable resistance in bridge.  $C_v$ : Variable capacitance in bridge.  $Z_x$ : Impedance of cell arm. P, Q: Ratio arm in bridge, pure resistances. O: Oscilloscope for zero detection. W: Wagner earth grounding.

b) Equivalent circuit according to Feates *et al.*<sup>11</sup>  $R_x$ : Ohmic resistance of cell.  $R_f$ : Frequency-independent Faradaic resistance.  $R_w$ : Warburg impedance.  $C_D$ : Double layer capacity.  $C_0$ : Outer capacity between cell leads.

## CIRCUIT SYSTEM

The circuit diagram is given in Fig. 2a. With a resistance ratio in the bridge  $P/Q=10$  for all measurements, the cell was balanced with the variable resistance  $R_V$  and capacitance  $C_V$  as well as balancing the Wagner earth grounding (Fig. 2a).

The impedance model for water solutions and molten salts is shown on Fig. 2b.<sup>10-12</sup>  $C_O$  denotes a possible outer capacitance while  $R_F$  is the Faradaic resistance and  $C_D$  a double layer capacity. Both  $C_O$ ,  $R_F$ , and  $C_D$  are assumed to be frequency independent.  $R_W$  denotes a Warburg impedance consisting of a capacitance and resistance in series both being frequency dependent:

$$R_W = n/\sqrt{\omega} \quad C_W = 1/n\sqrt{\omega} \quad R_W C_W \omega = 1 \quad (1)$$

Fig. 3 gives resistance as a function of frequency for a typical molten salt

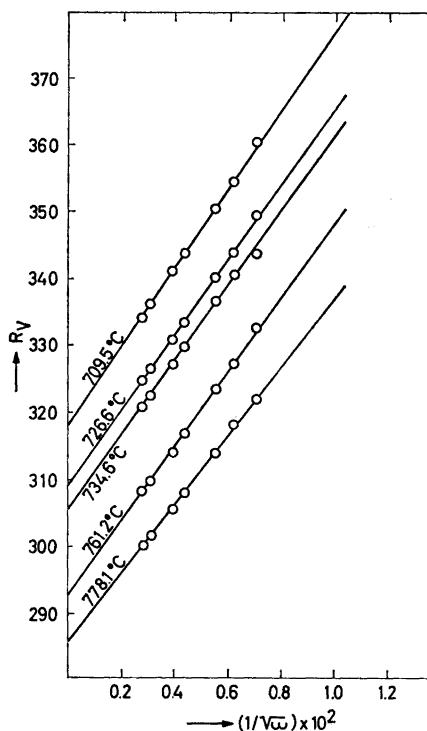


Fig. 3. Resistance as a function of frequency for a melt containing 60 mole %  $MgCl_2$ , 20 mole %  $CaCl_2$ , 20 mole %  $NaCl$  at various temperatures.

mixture (60 mole %  $MgCl_2$ , 20 mole %  $CaCl_2$ , and 20 mole %  $NaCl$ ) at various temperatures. A straight line was obtained between 3 and 20 kHz when plotting the resistance against  $1/\sqrt{\omega}$ . At lower frequencies than 3 kHz the resistance curved off upwards and these measurements were therefore not used for

extrapolation to infinite frequencies. A similar behaviour was observed for 1 M KCl solutions.

To test the appropriate circuit model for the molten salt systems corresponding values of resistance and capacitance for one of the experiments given in Fig. 3 were tabulated (Table 1).

Table 1. Measured resistance and capacitance for 60 mole % MgCl<sub>2</sub>, 20 mole % CaCl<sub>2</sub>, 20 mole % NaCl at 709.5°C compared with the contribution from a pure Warburg capacitance.

Frequency (kHz)	$R_V$ ( $\Omega$ )	$C_V$ (nF)	$\frac{P}{Q} \frac{580}{R_V^2} \omega^{-3/2}$ (nF)
3	360.2	15.68	17.35
4	354.4	10.49	11.60
5	350.5	7.74	8.55
8	343.6	4.30	4.37
10	340.9	2.90	3.17
16	336.2	1.60	1.61
20	334.2	1.17	1.17

With bright platinum electrodes usually  $R_w \gg R_f$  and assuming in addition  $C_D$  but not necessarily  $C_O$  to be negligible:

$$R_V = \frac{P}{Q} (R_x + R_w) \left( 1 + \frac{1}{\omega^2 C_w^2 (R_x + R_w)^2} \right)$$

$$\simeq \frac{P}{Q} R_x (1 + n/R_x \sqrt{\omega}) (1 + (n/R_x \sqrt{\omega})^2) \quad (2)$$

$$\simeq \frac{P}{Q} R_x (1 + n/R_x \sqrt{\omega}) \quad (3)$$

for  $R_x \gg R_w$

The cell resistance is then obtained by extrapolation to infinite frequency according to eqn. 3.

As seen from Fig. 3 this model (eqns. 2 and 3) does explain well the measured resistance and also explaining the upward curving found at lower frequencies when  $R_x$  is no longer made much larger than  $R_w$ ;  $R_x/R_w \simeq 10$  only.

From eqn. 3 we calculated  $n = 580 \Omega \text{ sec}^{-1/2}$ . If this model is correct we should find that according to eqn. 1:

$$C_w = 1/580 \sqrt{\omega}$$

Using the same assumption (neglecting  $R_f$  and  $C_D$ ):

$$C_V = \frac{Q}{P} \left( C_O + \frac{C_w}{1 + \omega^2 C_w^2 (R_x + R_w)^2} \right) \quad (4)$$

Neglecting 2. order terms in  $R_w/R_x$  setting:

$$R_v = \frac{P}{Q} (R_x + R_w)$$

gives

$$C_v = \frac{Q}{P} C_o + \frac{P}{Q} \frac{580}{R_v^2} \omega^{-3/2} \quad (5)$$

A possible outer capacity  $C_o$  will give a constant contribution to  $C_v$  while the contribution from the Warburg impedance will decrease with increasing frequency. The last column of Table 1 gives the calculated contribution from the Warburg impedance which can be compared with the experimental value for  $C_v$  (column 3).

Assuming  $C_o$  to be zero Table 1 shows good agreement with experimentally determined capacitance as compared with capacitance calculated from the variation of resistance. The agreement is surprisingly close at the highest frequencies while the calculated  $C_v$  becomes somewhat higher at lower frequencies. The discrepancy at lower frequencies cannot be explained on the basis of a double layer capacitance  $C_D$  which would give  $C_v$  equal to:

$$C_v = \left( \frac{P}{Q} \frac{n}{R_v^2} \omega^{-3/2} \right) / \left( 1 + \frac{2n^2 \omega C_D^2}{1 + 2n\sqrt{\omega} C_D} \right) \quad (6)$$

when  $C_o$  and  $R_F$  and 2. order terms are neglected. The denominator will decrease with decreasing  $\omega$ , which is opposite to the effect observed.

When it is realized that the capacitance changes by a factor of 14, and that the capacitance measurements are carried out near the lower limit of our instrument, we do not consider these discrepancies serious. It will in any case not affect the extrapolation of resistance to infinite frequency.

We would hence conclude that the impedance, in addition to the resistance of the electrolyte, is well represented as a Warburg impedance:

$$R_w = n/\sqrt{\omega} \text{ and } C_w = 1/n\sqrt{\omega}$$

A possible contribution from  $R_F$  cannot be excluded, but this resistance is usually smaller than the Warburg impedance.<sup>10</sup>

## RESULTS

The specific conductivities for  $MgCl_2$ - $CaCl_2$ - $NaCl$  and  $MgCl_2$ - $CaCl_2$ - $KCl$  were measured over a temperature range of at least 60°C usually between 700 and 800°C, or up to 100°C above the melting point for high-melting compositions. The results are given in Table 2. In order to get the picture of the ternary system as clear as possible with a minimum of measurements, a measuring program was set up for the binary and ternary melts in which compositions having mole percent with a multiple of 20 were determined.

The obtained data were fitted to the following two equations:

$$\text{Specific conductivity: } \kappa = A + BT$$

$$\text{Equivalent conductance: } A = C \exp(-D/RT)$$

Table 2. Specific conductivities of MgCl<sub>2</sub>-CaCl<sub>2</sub>-NaCl and MgCl<sub>2</sub>-CaCl<sub>2</sub>-KCl.

Mole % MgCl <sub>2</sub>	Mole % CaCl <sub>2</sub>	Mole % NaCl	Mole % KCl	Temp. (°C)	$\kappa$ ( $\Omega^{-1}\text{cm}^{-1}$ )
100				746.8	1.073
100				765.3	1.117
100				809.2	1.222
80	20			723.7	1.497
80	20			743.5	1.540
80	20			762.6	1.590
80	20			765.0	1.597
80	20			783.3	1.642
80		20		706.5	1.475
80		20		721.5	1.506
80		20		745.0	1.556
80		20		770.6	1.629
80		20		784.2	1.656
80			20	718.3	1.216
80			20	741.0	1.258
80			20	760.0	1.296
80			20	766.8	1.312
80			20	780.6	1.334
60	40			703.9	1.663
60	40			721.4	1.730
60	40			738.7	1.786
60	40			756.2	1.841
60	40			773.3	1.892
60	20	20		703.3	1.572
60	20	20		709.5	1.589
60	20	20		722.8	1.625
60	20	20		726.3	1.638
60	20	20		734.5	1.661
60	20	20		742.8	1.683
60	20	20		754.4	1.725
60	20	20		761.2	1.732
60	20	20		762.8	1.745
60	20	20		778.0	1.772
60	20	20		780.0	1.789
60	20		20	713.4	1.389
60	20		20	732.4	1.434
60	20		20	752.7	1.481
60	20		20	766.4	1.514
60		40		683.2	1.740
60		40		699.7	1.791
60		40		716.7	1.853
60		40		740.7	1.914
60			40	713.6	1.279
60			40	732.5	1.315
60			40	756.6	1.353
60			40	763.1	1.364
60			40	772.4	1.382



Table 2. Continued.

Mole % MgCl <sub>2</sub>	Mole % CaCl <sub>2</sub>	Mole % NaCl	Mole % KCl	Temp. (°C)	$\kappa$ ( $\Omega^{-1}\text{cm}^{-1}$ )
40	60			718.6	1.780
40	60			734.0	1.828
40	60			760.7	1.915
40	60			771.9	1.956
40	60			786.2	2.014
40	40	20		697.5	1.646
40	40	20		737.4	1.787
40	40	20		748.0	1.821
40	40	20		758.0	1.850
40	40	20		782.3	1.927
40	40		20	714.5	1.339
40	40		20	720.6	1.367
40	40		20	739.0	1.414
40	40		20	759.0	1.464
40	20	40		694.7	1.738
40	20	40		704.0	1.768
40	20	40		712.0	1.786
40	20	40		728.7	1.832
40	20	40		756.7	1.910
40	20	40		789.2	1.994
40	20		40	717.3	1.236
40	20		40	734.5	1.279
40	20		40	754.8	1.328
40	20		40	768.0	1.350
40	20		40	787.8	1.407
40		60		707.0	2.110
40		60		733.5	2.171
40		60		756.8	2.227
40		60		774.4	2.253
40		60		799.4	2.303
40		60		820.2	2.342
40			60	712.9	1.270
40			60	730.4	1.301
40			60	749.3	1.325
40			60	763.4	1.346
40			60	773.4	1.367
20	80			772.0	2.014
20	80			792.5	2.104
20	80			807.5	2.192
20	80			821.8	2.261
20	60	20		718.5	1.756
20	60	20		740.2	1.846
20	60	20		754.2	1.901
20	60	20		767.4	1.938
20	60	20		774.0	1.970
20	60	20		791.5	2.029

Table 2. Continued.

Mole % MgCl <sub>2</sub>	Mole % CaCl <sub>2</sub>	Mole % NaCl	Mole % KCl	Temp. (°C)	$\kappa$ ( $\Omega^{-1}\text{cm}^{-1}$ )
20	60		20	722.1	1.385
20	60		20	739.7	1.441
20	60		20	761.7	1.500
20	60		20	779.8	1.546
20	40	40		723.4	1.864
20	40	40		742.1	1.930
20	40	40		758.1	1.990
20	40	40		787.6	2.096
20	40		40	730.0	1.254
20	40		40	749.3	1.298
20	40		40	762.1	1.315
20	40		40	770.7	1.342
20	20	60		715.0	2.131
20	20	60		728.9	2.182
20	20	60		745.7	2.233
20	20	60		767.5	2.291
20	20		60	716.6	1.235
20	20		60	732.6	1.277
20	20		60	752.6	1.332
20		80		743.3	2.867
20		80		762.4	2.917
20		80		781.1	2.962
20		80		795.3	2.992
20			80	716.6	1.482
20			80	737.6	1.526
20			80	757.2	1.554
20			80	776.0	1.584
	100			820.5	2.173
	100			838.5	2.233
	100			852.4	2.279
	100			863.3	2.326
	100			900.3	2.465
	80		20	781.7	1.572
	80		20	799.1	1.636
	80		20	815.0	1.689
	80		20	831.4	1.742
	60	40		799.1	2.224
	60	40		847.3	2.400
	60	40		916.0	2.621
	60		40	733.1	1.237
	60		40	744.2	1.274
	60		40	757.1	1.307
	60		40	765.6	1.343
	60		40	771.8	1.357
	60		40	784.6	1.398

Table 2. Continued.

Mole % MgCl <sub>2</sub>	Mole % CaCl <sub>2</sub>	Mole % NaCl	Mole % KCl	Temp. (°C)	$\kappa$ ( $\Omega^{-1}\text{cm}^{-1}$ )
	40	60		800.2	2.510
	40	60		827.8	2.588
	40	60		858.5	2.712
	40	60		901.1	2.834
	40		60	800.4	1.449
	40		60	809.8	1.468
	40		60	822.6	1.504
	40		60	837.4	1.548
	20	80		804.1	3.003
	20	80		821.9	3.060
	20	80		860.4	3.147
	20	80		902.6	3.222
	20		80	723.4	1.438
	20		80	742.2	1.489
	20		80	761.1	1.556
	20		80	768.2	1.579
	20		80	781.0	1.616
		100		822.2	3.675
		100		832.4	3.699
		100		843.7	3.727
		100		853.2	3.752
		100		862.4	3.774
			100	802.8	2.234
			100	821.7	2.286
			100	850.4	2.347
			100	876.8	2.420

The results of this calculation are given in Table 3. The densities for calculating  $\Delta$  are taken from the recent work of Grjotheim *et al.*<sup>13</sup>

In Figs. 4 and 5 the specific conductivities at 800°C are given together with the temperature coefficient B.

The specific conductivities for the pure salts at 800°C are found to be in  $\Omega^{-1}\text{cm}^{-1}$ : MgCl<sub>2</sub>: 1.200, CaCl<sub>2</sub>: 2.093, NaCl: 3.619 (extrapolated), KCl: 2.228. The deviation from recent values given by National Bureau of Standards<sup>14</sup> are MgCl<sub>2</sub>: +1.6 %, CaCl<sub>2</sub>: -1.1 %, NaCl: +1.3 %, KCl: -0.4 %. From the scattering and uncertainties in the determination of the cell constant the standard deviation of our data is estimated to be within 1.5 %.

Table 3. Two parameter description of conductance data, for equivalent conductance and specific conductivity with deviation from additivity for specific conductance.

Composition			Equivalent conductance: $A = C \exp(-D/RT)$			Specific conductivity: $\kappa = A + BT$		Specific conductivity at 800°C		
MgCl <sub>2</sub>	CaCl <sub>2</sub>	KCl	C	D	A <sub>1073</sub>	A	B × 10 <sup>3</sup>	$\kappa(\text{exp})$	$\kappa(\text{add})$	$\kappa^E = \kappa(\text{exp}) - \kappa(\text{add})$
Mole %			$\Omega^{-1}\text{cm}^2\text{val}^{-1}$	kcal	$\Omega^{-1}\text{cm}^2\text{val}^{-1}$	$\Omega^{-1}\text{cm}^{-1}$	$\Omega^{-1}\text{cm}^{-1}\text{deg.}^{-1}$	$\Omega^{-1}\text{cm}^{-1}$	$\Omega^{-1}\text{cm}^{-1}$	$\Omega^{-1}\text{cm}^{-1}$
100	—	—	351.3	4.951	34.4 <sub>5</sub>	-1.363	2.388	1.20 <sub>0</sub>	—	—
80	20	—	263.8	3.692	46.6 <sub>6</sub>	-0.953	2.455	1.68 <sub>2</sub>	1.37 <sub>8</sub>	+0.30 <sub>4</sub>
80	—	20	275.3	3.663	49.3 <sub>6</sub>	-0.861	2.380	1.69 <sub>4</sub>	1.68 <sub>4</sub>	+0.01 <sub>0</sub>
80	40	—	240.6	3.716	42.0 <sub>6</sub>	-0.694	1.925	1.37 <sub>3</sub>	1.40 <sub>6</sub>	-0.03 <sub>3</sub>
60	40	—	390.8	4.222	53.9 <sub>0</sub>	-1.534	3.278	1.98 <sub>3</sub>	1.55 <sub>7</sub>	+0.42 <sub>6</sub>
60	20	20	318.5	8.840	52.5 <sub>4</sub>	-1.156	2.794	1.84 <sub>3</sub>	1.86 <sub>2</sub>	-0.01 <sub>9</sub>
60	20	20	243.4	3.642	44.0 <sub>6</sub>	-0.931	2.351	1.59 <sub>3</sub>	1.58 <sub>4</sub>	+0.00 <sub>9</sub>
60	—	40	381.7	3.813	63.7 <sub>6</sub>	-1.186	3.062	2.10 <sub>6</sub>	2.16 <sub>8</sub>	-0.06 <sub>8</sub>
60	—	40	231.6	3.325	48.6 <sub>6</sub>	-0.414	1.716	1.42 <sub>3</sub>	1.61 <sub>1</sub>	-0.18 <sub>3</sub>
40	60	—	395.0	4.195	55.1 <sub>8</sub>	-1.620	3.425	2.05 <sub>5</sub>	1.73 <sub>6</sub>	+0.31 <sub>9</sub>
40	40	20	414.6	4.270	55.9 <sub>2</sub>	-1.569	3.316	1.99 <sub>0</sub>	2.04 <sub>1</sub>	-0.05 <sub>1</sub>
40	40	20	385.4	4.484	47.0 <sub>1</sub>	-1.345	2.724	1.57 <sub>8</sub>	1.76 <sub>3</sub>	-0.18 <sub>5</sub>
40	20	40	282.4	3.291	60.2 <sub>1</sub>	-0.746	2.569	2.01 <sub>1</sub>	2.34 <sub>6</sub>	-0.33 <sub>5</sub>
40	20	40	344.2	4.302	45.7 <sub>3</sub>	-1.114	2.373	1.43 <sub>3</sub>	1.79 <sub>6</sub>	-0.35 <sub>7</sub>
40	—	60	249.6	2.571	74.6 <sub>6</sub>	0.126	2.030	2.30 <sub>5</sub>	2.65 <sub>1</sub>	-0.34 <sub>4</sub>
40	—	60	234.3	3.121	54.1 <sub>7</sub>	-0.251	1.543	1.40 <sub>6</sub>	1.81 <sub>7</sub>	-0.41 <sub>3</sub>
20	80	—	895.9	5.852	57.5 <sub>1</sub>	-3.240	5.023	2.15 <sub>1</sub>	1.91 <sub>4</sub>	+0.23 <sub>7</sub>
20	60	20	482.0	4.569	57.6 <sub>6</sub>	-1.918	3.710	2.06 <sub>4</sub>	2.22 <sub>0</sub>	-0.15 <sub>6</sub>
20	60	20	424.9	4.501	51.4 <sub>3</sub>	-1.374	2.775	1.60 <sub>5</sub>	1.94 <sub>1</sub>	-0.33 <sub>6</sub>
20	40	40	498.7	4.393	63.4 <sub>5</sub>	-1.748	3.624	2.14 <sub>1</sub>	2.52 <sub>5</sub>	-0.38 <sub>4</sub>
20	40	40	302.1	3.905	48.3 <sub>6</sub>	-0.824	2.071	1.40 <sub>0</sub>	1.96 <sub>8</sub>	-0.56 <sub>8</sub>
20	20	60	292.7	2.909	74.7 <sub>5</sub>	-0.280	2.446	2.34 <sub>6</sub>	2.83 <sub>0</sub>	-0.48 <sub>4</sub>
20	20	60	552.6	4.926	54.7 <sub>6</sub>	-1.434	2.696	1.45 <sub>9</sub>	1.99 <sub>5</sub>	-0.53 <sub>6</sub>
20	—	80	318.3	2.382	104.0 <sub>6</sub>	0.418	2.410	3.00 <sub>5</sub>	3.13 <sub>5</sub>	-0.12 <sub>9</sub>
20	—	80	291.5	3.017	70.7 <sub>7</sub>	-0.189	1.691	1.62 <sub>6</sub>	2.02 <sub>2</sub>	-0.39 <sub>6</sub>
—	100	—	474.3	4.553	56.0 <sub>6</sub>	-1.862	3.685	2.09 <sub>3</sub>	—	—
—	80	20	597.3	5.355	48.4 <sub>0</sub>	-2.027	3.413	1.63 <sub>7</sub>	2.12 <sub>0</sub>	-0.48 <sub>3</sub>
—	60	40	459.1	4.133	66.0 <sub>3</sub>	-1.399	3.383	2.23 <sub>2</sub>	2.70 <sub>3</sub>	-0.47 <sub>1</sub>
—	60	40	667.5	5.636	47.4 <sub>1</sub>	-1.925	3.142	1.44 <sub>7</sub>	2.14 <sub>7</sub>	-0.70 <sub>0</sub>
—	40	60	447.4	3.686	79.3 <sub>6</sub>	-1.010	3.277	2.50 <sub>7</sub>	3.00 <sub>9</sub>	-0.50 <sub>2</sub>
—	40	60	571.4	5.064	53.0 <sub>7</sub>	-1.462	3.708	1.44 <sub>5</sub>	2.17 <sub>4</sub>	-0.72 <sub>9</sub>
—	20	80	329.1	2.464	103.5 <sub>7</sub>	0.655	2.189	3.00 <sub>5</sub>	3.31 <sub>4</sub>	-0.30 <sub>9</sub>
—	20	80	754.1	5.058	70.2 <sub>5</sub>	-1.709	3.155	1.67 <sub>7</sub>	2.20 <sub>1</sub>	-0.52 <sub>4</sub>
—	20	100	436.5	2.494	135.4 <sub>3</sub>	0.944	2.492	3.61 <sub>9</sub>	—	—
—	—	—	591.1	3.592	109.5 <sub>6</sub>	-0.416	2.464	2.22 <sub>9</sub>	—	—

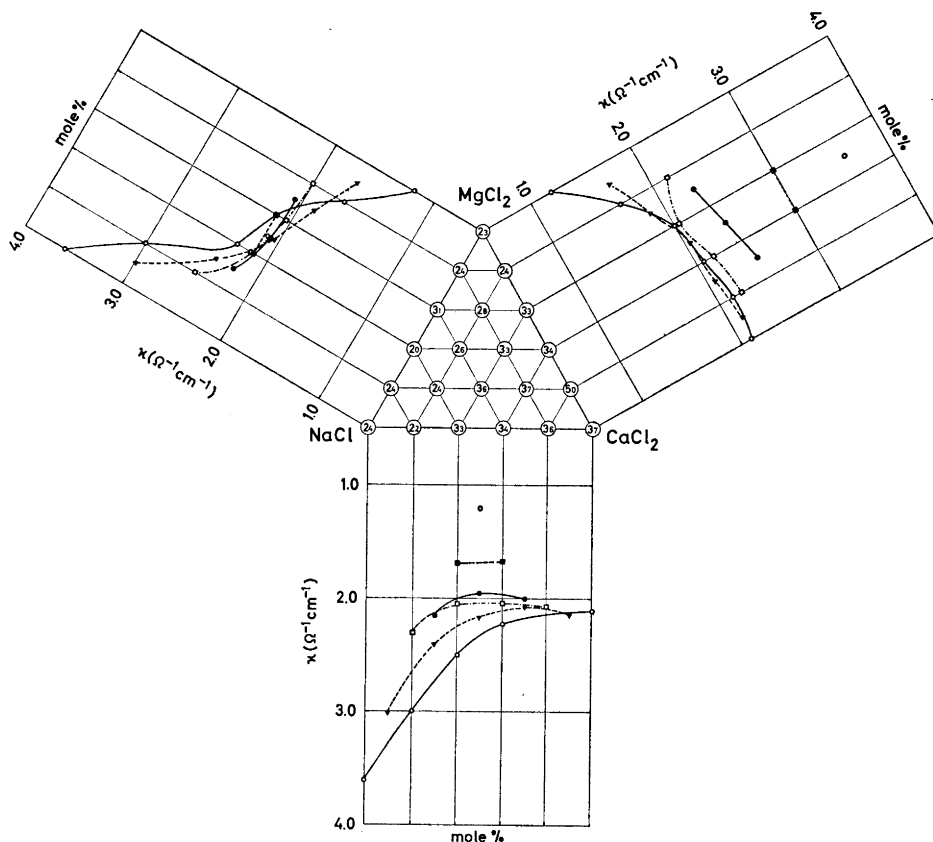


Fig. 4. Specific conductivities of the ternary system  $MgCl_2$ - $CaCl_2$ - $NaCl$  at  $800^\circ C$ . Conductivities corresponding to the lines in the composition diagram are projected in the three rectangular diagrams.

○, ———: Binary system.  $\Delta$ , — — —: Mole % of component with constant composition: 20.  $\square$ , — · — ·: Mole % of component with constant composition: 40.  $\bullet$ , ———: Mole % of component with constant composition: 60.  $\blacksquare$ , — — —: Mole % of component with constant composition: 80.  $\circ$ : Pure components.

Given in circles: Temperature coefficient  $B \times 10^4$  for the corresponding composition.

### DISCUSSION

*Pure molten salts:* The two different two-parameter descriptions (Table 3):

$$\kappa = A + BT \quad \text{or} \quad A = C \exp(-D/RT)$$

do describe the data equally well, both with a standard deviation of 0.25 %. The parameter  $D$  then corresponds to the heat of activation for conductance. It is worth noting that  $NaCl$  has a considerably lesser heat of activation than the other salts and that  $CaCl_2$  has a larger temperature coefficient of specific conductance:  $3.6 \times 10^{-3}$ , as compared with the value of about  $25 \times 10^{-3}$  found for the others.

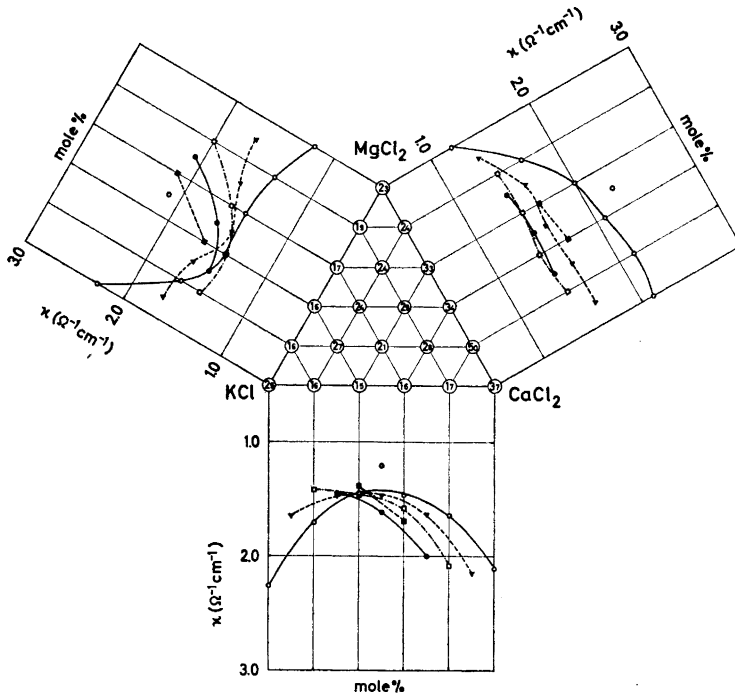


Fig. 5. Specific conductivities of the ternary system  $\text{MgCl}_2\text{-CaCl}_2\text{-KCl}$  at  $800^\circ\text{C}$ . Conductivities corresponding to the lines in the composition diagram are projected in the three rectangular diagrams.

○, —: Binary system. △, ---: Mole % of component with constant composition: 20. □, -.-: Mole % of component with constant composition: 40. ●, —: Mole % of component with constant composition: 60. ■, ---: Mole % of component with constant composition: 80. ○: Pure components.

Given in circles: Temperature coefficient  $B \times 10^4$  for the corresponding composition.

Figs. 4 and 5 show the variation of conductivity with composition. We see that specific conductances do vary in a fairly complex way as a function of composition.

Before discussing this behaviour it is useful to discuss the conductance of the pure fused salts. A relationship that demonstrates the difference of these pure salts is the so-called Waldens rule. For infinite, diluted, charged spheres moving in a continuum and equating the electrical force to the viscous drag according to Stokes law one gets:

$$\Delta\eta = (\Lambda_+ + \Lambda_-)\eta = \frac{eF}{6\pi} \left( \frac{z_+}{r_+} + \frac{z_-}{r_-} \right) \quad (7a)$$

or

$$\frac{6\pi\Delta\eta}{eF(z_+/r_+ + z_-/r_-)} = 1 \quad (7b)$$

where

$\Lambda = \Lambda_+ + \Lambda_-$ : equivalent conductance

$\eta$ : viscosity

$e$ : charge of the electron

$F$ : Faraday constant

$z_+, z_-$ : charge numbers

$r_+, r_-$ : ionic radii

Table 4. Test of Waldens rule for  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}$  and  $\text{KCl}$  at  $800^\circ\text{C}$ . Viscosity for  $\text{MgCl}_2$ ,  $\text{NaCl}$ ,  $\text{KCl}$  from Ref. 15 and for  $\text{CaCl}_2$  from Ref. 14.

	$\Lambda$ $\text{cm}^2\Omega^{-1}\text{val}^{-1}$	$\eta$ cP	$\frac{6\pi\Lambda\eta}{eF(z_+/r_+ + z_-/r_-)}$
$\text{MgCl}_2$	34.4	1.80	0.20
$\text{CaCl}_2$	56.0	3.11	0.83
$\text{NaCl}$	135.4	0.97	0.99
$\text{KCl}$	109.5	0.98	1.01

Table 4 shows to what degree eqn. (7b) does describe the behaviour of the pure molten salts  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and  $\text{KCl}$  at  $800^\circ\text{C}$ .  $\Lambda$  is taken from this investigation,  $\eta$  from Dumas *et al.*<sup>15</sup> and for the ionic sizes the Pauling radii are chosen:

$$\begin{aligned}
 r_{\text{Mg}^{2+}} &= 0.65 & r_{\text{Ca}^{2+}} &= 0.99 & r_{\text{Na}^+} &= 0.95 \\
 r_{\text{K}^+} &= 1.33 & r_{\text{Cl}^-} &= 1.81
 \end{aligned}$$

Using our viscosity data Waldens rule is obeyed remarkably well for  $\text{NaCl}$  and  $\text{KCl}$ . This is in spite of the close packing of ions in molten salts making the movements of anions and cations cooperative.

The viscosity is about the same for  $\text{NaCl}$  and  $\text{KCl}$  with the specific and equivalent conductivity increasing from  $\text{KCl}$  to  $\text{NaCl}$  (Table 4). This is in qualitative agreement with a Stokes law behaviour where the velocity will be proportional to the inverse of the radii for the same field gradient. For  $\text{MgCl}_2$  we do observe great deviations from Waldens rule. This disagreement does also show up from measurements of transport numbers:

$$\frac{t_+}{t_-} = \frac{\Lambda_+}{\Lambda_-} \quad (8a)$$

and according to eqn. (7a)

$$\frac{t_+}{t_-} = \frac{z_+ r_-}{r_+ z_-} = 5.6 \quad (8b)$$

The experimentally observed ratio  $t_+/t_- \simeq 1$ ,<sup>16</sup> *i.e.* the current is carried about equally by cations and anions.

The deviation from Waldens rule and the transport numbers not being inversely proportional to the ionic radii do indicate a basically different transport mechanism in  $\text{MgCl}_2$  as compared to  $\text{NaCl}$  and  $\text{KCl}$ . It points to a greater influence of bond strength in  $\text{MgCl}_2$  than effects due to Stokes law behaviour, the small  $\text{Mg}^{2+}$  ion creating strong partly covalent bonds with  $\text{Cl}^-$  which reduces the electrical conductivity. The covalency will, however, not be reflected in an increase of viscosity since this property characterizes more the movements of neutral ion groups rather than charged particles. A similar but weaker mechanism might be attributed to the ratio for  $\text{CaCl}_2$  in eqn. 7b.

*Binary mixtures.* As will be discussed below Waldens rule is not at all obeyed for binary mixtures containing  $\text{MgCl}_2$ .

There is no ideal model for conductivity of salt mixtures. Because of the co-operative effect of movements there is for instance no reason to assume the rule of additivity. However, conductivities of simple salt mixtures like  $\text{NaCl-KCl}$  show a closely linear dependence on composition in spite of the specific conductivity of  $\text{NaCl}$  being 60 % higher than that of  $\text{KCl}$ . We will also see that deviation from additivity provides a useful method for rationalizing the present data.

For a theoretical description of the salt mixture we will choose to describe the specific conductivity of the binary systems as an additive term and with the excess conductivity defined by:

$$\kappa_{12}^{\text{E}}(\text{"exp"}) = \kappa_{12} - (X_1\kappa_1 + X_2\kappa_2) \quad (9)$$

Mathematically we will describe  $\kappa_{12}^{\text{E}}$  as:

$$\kappa_{12}^{\text{E}}(\text{calc}) = a_{12}^i \psi_{12}^i + a_{12}^j \psi_{12}^j + a_{12}^k \psi_{12}^k \quad (10a)$$

$$\psi_{12}^i = \sqrt{30} X_1 X_2$$

$$\psi_{12}^j = \sqrt{210} X_1 X_2 (X_1 - X_2) \quad (10b)$$

$$\psi_{12}^k = \sqrt{17640} X_1 X_2 (X_1 - (\frac{1}{2} - 1/\sqrt{28}))(X_2 - (\frac{1}{2} - 1/\sqrt{28}))$$

Eqns. (10a, b) are simply polynoms in  $X_1$  of the form

$$y = a + bX_1 + cX_1^2 + dX_1^3 + eX_1^4 \quad (10c)$$

but with the additional condition that  $\kappa_{12}^{\text{E}} = 0$  for pure components attained by the common factor  $X_1 X_2$  and requiring  $\psi_1, \psi_2, \psi_3$  to be orthonormal:

$$\int \psi_{12}^i \times \psi_{12}^j dX_1 = \delta^{ij} \begin{cases} \delta^{ij} = 0 \text{ for } i \neq j \\ \delta^{ij} = 1 \text{ for } i = j \end{cases} \quad (11)$$

This latter condition makes the coefficients independent of each other:

$$a_{12}^i = \int_0^1 \kappa_{12}^{\text{E}}(\text{exp}) \psi_{12}^i dX_1 \quad (12)$$

and the magnitude of the coefficient is a direct expression of the weight of the corresponding  $\psi$  function in describing the experimental data.

The  $a^i$  is analogous to what in thermochemistry is called the interaction parameter,<sup>17,18</sup> and the  $a^j$  is an orthonormal asymmetry parameter:



$$a_{12}^j = \frac{1}{2\sqrt{210}} \left( \lim_{X_2 \rightarrow 0} \frac{\kappa_{12}^E}{X_1 X_2} - \lim_{X_1 \rightarrow 0} \frac{\kappa_{12}^E}{X_1 X_2} \right)$$

$a^k$  is best described as a second order interaction parameter since:

$$a_{12}^k = \frac{2}{\sqrt{17640}} \left( 2 \frac{\kappa_{12}^E}{X_1 X_2} - \left( \lim_{X_1 = X_2} \frac{\kappa_{12}^E}{X_1 X_2} + \lim_{X_1 \rightarrow 0} \frac{\kappa_{12}^E}{X_1 X_2} + \lim_{X_2 \rightarrow 0} \frac{\kappa_{12}^E}{X_1 X_2} \right) \right)$$

We choose to describe the specific conductance  $\kappa$  rather than the equivalent conductance  $\Lambda$  since the former is more directly measured and exhibits less variation *versus* composition than  $\Lambda$ . The calculated coefficients are given in Table 5.

Table 5. Least square values of the parameters in eqn. 9.

	$a^i$	$a^j$	$a^k$	Stand. dev. in $\kappa$
MgCl <sub>2</sub> -CaCl <sub>2</sub>	0.292	0.035	-0.013	0.03
MgCl <sub>2</sub> -NaCl	-0.132	0.074	-0.040	0.08
MgCl <sub>2</sub> -KCl	-0.232	0.137	0.010	0.02
CaCl <sub>2</sub> -NaCl	-0.353	0.022	-0.027	—
CaCl <sub>2</sub> -KCl	-0.554	0.016	0.016	0.00
NaCl - KCl	-0.211	0.009	0.002	0.00

Except for the system MgCl<sub>2</sub>-NaCl all data are well represented by a two-parameter description, the interaction parameter  $a^i$  and the asymmetry parameter  $a^j$ . The parameter  $a^k$  is unimportant and does not improve the description significantly even for the system MgCl<sub>2</sub>-NaCl where the largest standard deviation is observed. Positive  $a^i$  means positive excess functions. Positive  $a^j$  means a tendency to positive deviation for component 1 (containing the cation with highest ionic potential) and negative deviation for component 2.

We see some clear correlations in Table 5. All  $a^j$  are positive when the ion with highest ionic potential is chosen as component 1. The  $a^i$  is negative for all mixtures except MgCl<sub>2</sub>-CaCl<sub>2</sub>. For alkaline earth chloride — alkali chloride mixtures  $a^i$  increases from NaCl to KCl and from MgCl<sub>2</sub> to CaCl<sub>2</sub>.

The excess conductivities are given on Fig. 6 in which the excess conductivity for NaCl-KCl from the data of van Artsdalen and Yaffe<sup>5</sup> is added for completeness.

By a visual inspection of the excess functions of the binary systems between alkaline-earth and alkali chlorides for the enthalpy of mixing,<sup>17-19</sup> the volume of mixing<sup>13</sup> and the conductivity, a striking similarity is observed. This is in spite of that the excess functions in some of the cases contain a significant asymmetric term. The enthalpy of mixing and conductivity have the same signs while excess volume has the opposite sign.

It is, however, impossible to explain the conductivity data purely from a transport theory ignoring changes in the forces between the ions because of the fact that excess volume and excess conductivity have opposite signs. On the alkali chloride side of the systems  $\text{MgCl}_2\text{-NaCl}$  and  $\text{MgCl}_2\text{-KCl}$  excess conductivity and excess viscosity<sup>16</sup> are both negative which also is contrary to the Walden rule behaviour based on Stokes law and viscous drag.

The data can, however, be correlated by considering the bond strength as the primary force and the other properties as density, conductivity and viscosity reflecting the accompanying structural and thermodynamic change.

Following the arguments of Førland<sup>20</sup> and Kleppa *et al.*<sup>17,18</sup>  $\text{MgCl}_2$  can in the melt be depicted as having a layer structure with a covalent nature. The addition of  $\text{CaCl}_2$  will tend to partially destroy this structure and thus give rise to an endothermic heat of mixing and a volume contraction as a

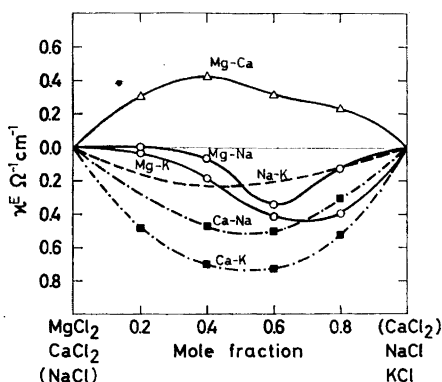


Fig. 6.  $\kappa_{12}^E(\text{“exp”}) = \kappa_{12} - (X_1\kappa_1 + X_2\kappa_2)$  for binary systems between  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}$  and  $\text{KCl}$ . The data for  $\text{NaCl-KCl}$  are taken from van Artsdalen and Yaffe.<sup>5</sup>

result of better balanced packing. The positive excess conductivity will then be due partly to the increased ionization but also to the weakening of the bonds. A similar effect arises from an increase in the excess conductivity on the  $\text{CaCl}_2$  side. The small hump seen on Fig. 6 for  $X_{\text{MgCl}_2} \approx 0.4$  is believed to be significant. The hump becomes more pronounced for the quasibinary system  $\text{MgCl}_2\text{-CaCl}_2$  with a constant amount of  $\text{KCl}$  equal to 20 and 40 mole %, respectively (Fig. 5). The hump may be due to partial cluster formation similar to what is observed for  $\text{MgCl}_2\text{-NaCl}$  and  $\text{MgCl}_2\text{-KCl}$ .

With addition of  $\text{NaCl}$  and  $\text{KCl}$  to  $\text{MgCl}_2$  the same tendency is observed but on a weaker scale. This effect decreases with decreasing ionic potential of the cation. Here the enthalpy of mixing is negative but asymmetric<sup>18</sup> and volume contraction<sup>13</sup> is found. The tendency to positive excess conductivity may mainly be due to the increased ionization of the melt.

On adding  $\text{MgCl}_2$  to  $\text{NaCl}$  and  $\text{KCl}$  a quite different phenomenon is observed. Here a large negative enthalpy of mixing is observed<sup>17</sup> giving an asymmetric enthalpy curve, the minimum being on the alkali chloride side. A corresponding positive excess volume<sup>13</sup> and negative excess conductivity is found. This is mainly caused by the formation of strong clusters of  $\text{Cl}^-$  with a low coordination number around  $\text{Mg}^{2+}$ ,  $(\text{MgCl}_4^{2-})$ , which will then make the liquid expand and

give a decreasing conductivity due to the reduction in the number of effective current carriers. For instance, for the composition  $K_2MgCl_4$  there will be 2 equivalents of current carriers per  $Cl^-$  ion, if one assumes complete dissociation of the complex ions and only 1 equivalent per  $Cl^-$  ion if a complete formation of  $MgCl_4^{2-}$  can be assumed.

For the systems  $CaCl_2$ -NaCl,  $CaCl_2$ -KCl and NaCl-KCl an exothermic enthalpy of mixing is observed<sup>17,18</sup> with some asymmetry in the  $CaCl_2$  system weakly resembling the corresponding  $MgCl_2$  systems. Correspondingly the excess volumes are positive and the excess conductivities negative.

*Ternary mixtures.* One purpose of this investigation was to obtain data of the ternary systems for use in connection with industrial electrolysis of magnesium. For this purpose the rectangular diagrams on Figs. 4 and 5 are more useful than equations from a practical point of view. Variations in conductivity when the amount of one component is held constant can be seen from the different diagrams. Conductivities for specific compositions not listed in Table 2 are most easily found by linear interpolation in the diagrams where the conductivities show the most regular behaviour.

Table 6. Excess specific conductivity for the ternary compositions compared with excess specific conductivities calculated from binary excess data.

Composition				$\kappa_{123}^E(\text{"exp"})$	$\kappa_{123}^E(\text{calc})$			
					Eqn. (14a)		Eqn. (15)	
MgCl <sub>2</sub>	CaCl <sub>2</sub>	NaCl	KCl		A	B	A	B
Mole %				$\Omega^{-1}cm^{-1}$	$\Omega^{-1}cm^{-1}$	$\Omega^{-1}cm^{-1}$	$\Omega^{-1}cm^{-1}$	$\Omega^{-1}cm^{-1}$
60	20	20	—	-0.01 <sub>9</sub>	+0.10 <sub>2</sub>	+0.14 <sub>0</sub>	+0.02 <sub>5</sub>	+0.07 <sub>2</sub>
40	40	20	—	-0.05 <sub>1</sub>	+0.03 <sub>7</sub>	+0.06 <sub>5</sub>	-0.04 <sub>0</sub>	+0.00 <sub>6</sub>
40	20	40	—	-0.33 <sub>5</sub>	-0.18 <sub>1</sub>	-0.17 <sub>1</sub>	-0.24 <sub>0</sub>	-0.22 <sub>4</sub>
20	60	20	—	-0.15 <sub>6</sub>	-0.08 <sub>3</sub>	-0.07 <sub>1</sub>	-0.15 <sub>0</sub>	-0.13 <sub>4</sub>
20	40	40	—	-0.38 <sub>1</sub>	-0.29 <sub>9</sub>	-0.30 <sub>6</sub>	-0.36 <sub>2</sub>	-0.37 <sub>3</sub>
20	20	60	—	-0.48 <sub>4</sub>	-0.31 <sub>9</sub>	-0.31 <sub>2</sub>	-0.32 <sub>2</sub>	-0.31 <sub>3</sub>
60	20	—	20	+0.00 <sub>9</sub>	+0.04 <sub>1</sub>	+0.07 <sub>1</sub>	-0.09 <sub>7</sub>	-0.05 <sub>3</sub>
40	40	—	20	-0.18 <sub>5</sub>	-0.05 <sub>8</sub>	-0.03 <sub>7</sub>	-0.19 <sub>6</sub>	-0.16 <sub>4</sub>
40	20	—	40	-0.35 <sub>7</sub>	-0.30 <sub>5</sub>	-0.30 <sub>3</sub>	-0.42 <sub>7</sub>	-0.42 <sub>3</sub>
20	60	—	20	-0.33 <sub>6</sub>	-0.23 <sub>5</sub>	-0.23 <sub>9</sub>	-0.35 <sub>4</sub>	-0.36 <sub>0</sub>
20	40	—	40	-0.56 <sub>8</sub>	-0.48 <sub>3</sub>	-0.51 <sub>4</sub>	-0.61 <sub>6</sub>	-0.65 <sub>9</sub>
20	20	—	60	-0.53 <sub>6</sub>	-0.56 <sub>3</sub>	-0.59 <sub>9</sub>	-0.62 <sub>7</sub>	-0.67 <sub>2</sub>
Standard deviation					0.101	0.113	0.074	0.087

In Table 6, column 5, the ternary excess conductivities have been calculated as the deviation from additivity of the pure salts:

$$\kappa_{123}^E(\text{"exp"}) = \kappa_{123} - (N_1\kappa_1 + N_2\kappa_2 + N_3\kappa_3) \quad (13)$$

where  $N$  is the mole fraction in the ternary melt.

There are no well founded theories for predicting the functional conductivities of ternary melts. Because of the formal resemblance of the binary excess conductivities with those of the corresponding enthalpies and volumes it is however, tempting to choose a model for the excess conductivity resembling the regular solution models for enthalpies and volumes of ternary mixtures.<sup>21</sup>

We define:

$$\kappa_{123}^{\text{E(calc)}} = N_1 N_2 \frac{\kappa_{12}^{\text{E(calc)}}}{X_1 X_2} + N_1 N_3 \frac{\kappa_{13}^{\text{E(calc)}}}{X_1 X_3} + N_2 N_3 \frac{\kappa_{23}^{\text{E(calc)}}}{X_2 X_3} \quad (14a)$$

where  $N$  denotes the mole fraction in the ternary system and  $X$  in the binary system.  $\kappa_{ij}^{\text{E(calc)}}$  are then from eqn. 10a. Contrary to the regular solution model  $\kappa_{ij}^{\text{E}}/X_1 X_2$  will be a function of composition.

As binary excess functions one can make two different choices:

A). Binaries corresponding to drawing perpendiculars from the composition point in the ternary composition diagram to the sides of the diagrams.

B). Binaries corresponding to drawing lines through the corners and the ternary composition point down to the sides of the diagram.

In case B the binary compositions are characterized by having the same composition ratios as the ternary mixtures. The two different models are given in Table 6, column 6 and 7.

For case B we have:

$$\frac{N_i N_j}{X_i X_j} = \frac{N_i N_j}{\frac{N_i}{N_i + N_j} \frac{N_j}{N_i + N_j}} = (N_i + N_j)^2$$

and the alternate expression for  $\kappa_{123}^{\text{E(calc)}}$

$$\kappa'_{123}{}^{\text{E(calc)}} = (N_1 + N_2)^2 \kappa_{12}^{\text{E(calc)}} + (N_1 + N_3)^2 \kappa_{13}^{\text{E(calc)}} + (N_2 + N_3)^2 \kappa_{23}^{\text{E(calc)}} \quad (14b)$$

In Table 6 we also have calculated the ternary excess conductivity as

$$\kappa''_{123}{}^{\text{E(calc)}} = (N_1 + N_2) \kappa_{12}^{\text{E(calc)}} + (N_1 + N_3) \kappa_{13}^{\text{E(calc)}} + (N_2 + N_3) \kappa_{23}^{\text{E(calc)}} \quad (15)$$

There is no real theoretical foundation for this equation but it fulfills the requirement that the amount of each binary is proportional to the amount of the components. Eqn. (15) as well and eqns. (14) also fulfills the necessary requirement that

$$\kappa_{ijk}^{\text{E(calc)}} = \kappa_{ij}^{\text{E(calc)}} \text{ for } N_k = 0$$

The excess functions are here also calculated according to model A (perpendiculars) and B (corners) and are given in the last two columns of Table 6. We see that the found models describe the data with a standard deviation between 0.113 and 0.074  $\Omega^{-1} \text{ cm}^{-1}$ . The model according to eqn. (15) is better than the "regular solution model" and choosing perpendiculars instead of lines through corners gives slightly smaller standard deviations.

The average specific conductivity of the four salts  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}$  and  $\text{KCl}$  is  $2.29 \Omega^{-1} \text{cm}^{-1}$  and the best model, eqn. (15) A, describe the ternary data with a standard deviation of 3.2 % relative to this average conductivity. We will hence conclude that the ternary melts are satisfactory described by this model and we do not consider it justified at the present stage to introduce an additional ternary excess term.

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