THE MECHANISM OF THE MOVEMENT OF IONS AND ELECTRONS IN SOLIDS AND THE INTERPRETATION OF REACTIONS BETWEEN SOLIDS.

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Received 4*th February*, 1938.

1. The Movement of Ions.

In many solid ionic compounds electrical conductivity is caused by the movement of ions.[1] The first model was given by Frenkel,[2] and the theory was further developed by Wagner and Schottky,[3] and by Jost.[4] There are two general possibilities:

(1) Some ions exist interstitially within the normal lattice. Motion (*i.e.* electrical conductivity) is possible by jumps of ions from one interstitial position to the neighbouring one (*cf.* Fig. 1). Another possibility is given in Fig. 1, where an interstitial ion takes the place of a neighbouring lattice ion and the latter jumps to the nearest interstitial place.

(2) Some positions of the normal lattice are vacant. Movement of ions is possible by jumping of ions from an adjacent lattice place to a vacant position (Fig. 1).

At higher temperatures (about 100° or 200° below the melting-point) there is, in general, a thermodynamical equilibrium of the interstitial ions and the vacant places with the whole lattice and therefore we have a definite electrical conductivity.

At lower temperatures the effect of impurities is very important. Moreover, conductivity depends upon the mechanical and thermal history of the specimen. Deviations from the strict lattice order which are not in thermodynamical equilibrium may give a remarkable contribution to electrical conductivity ("irreversible *Gitterauflockerung*," according to von Hevesy;[5] "*Lockerstellen*" according to Smekal;[6] *e.g.* movement of ions on internal surfaces). Such instabilities are not discussed in this paper. It seems useful to investigate first the states in thermodynamical equilibrium at higher temperatures.

Schottky, Hägg[7] and Strock[8] have surveyed the different types of disorder in ionic lattices. Koch and Wagner[9] have indicated general

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[1] See C. Tubandt, *Handb. Experimentalphysik*, **12**, Part I, Leipzig 1932; W. Seith, *Z. Elektrochem.*, 1936, **40**, 635.

[2] *Z. Physik*, 1926, **35**, 652.

[3] C. Wagner and W. Schottky, *Z. physikal. Chem.*, *B*, 1930, **11**, 163; C. Wagner, *ibid.*, 1931, Bodenstein-Festband, 177; *Physikal. Z.*, 1935, **36**, 721; W. Schottky, *Z. physikal. Chem.*, *B*, 1935, **29**, 335.

[4] W. Jost, *J. chem. physics*, 1933, **1**, 466; *Z. physikal. Chem.*, *A*, 1934, **169**, 129; W. Jost and G. Nehlep, *ibid.*, *B*, 1936, **32**, 1.

[5] *Handbuch d. Physik*, **13**, 286, Berlin 1928.

[6] *Z. techn. Physik*, 1927, **8**, 570; *Handbuch Physik*, **24**, Part II, 2nd edition, Berlin, 1934.

[7] *Z. Kristallogr.*, *A*, 1935, **91**, 114.

[8] *Ibid.*, 1936, **93**, 285.

[9] *Z. physikal. Chem.*, *B*, 1937, **28**, 295.

methods for experimental work. Some special cases may be described in detail:—

(1) **Silver Chloride.**—According to Tubandt and Eggert,[10] the electrical conductivity of silver chloride is caused only by the movement of cations (Ag^+). Therefore it is only the cations which are in disorder; some have left the normal positions and are at interstitial positions, their original positions being vacant (Fig. 1).

The consequences of this supposition were shown to be correct by Koch and Wagner.[9] If the model is correct, the electrical conductivity should increase on increasing the concentration of vacant positions, *e.g.* by addition of cadmium chloride giving a solid solution in silver chloride (up to 10 mol. per cent. between 210° and 350° C.). In $CdCl_2$ the ratio of cation number to anion number is 1 to 2 instead of 2 to 2 for AgCl; there is therefore one cation too few for every Cd^{++} ion, corresponding to one vacant position in the cation lattice of the solid solution of $CdCl_2$ in AgCl (Fig. 2), if the anion lattice is the same as in pure silver chloride.

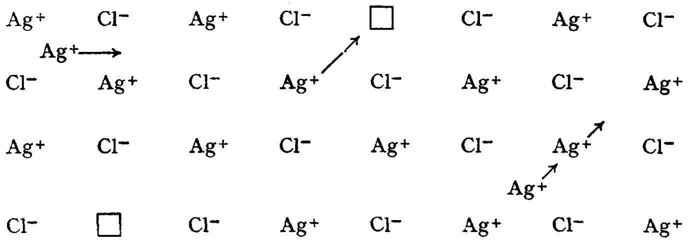

FIG. 1.—Disorder in silver chloride according to J. Frenkel.

The electrical conductivity of solid solutions of $CdCl_2$ in AgCl (with not too small $CdCl_2$ concentration) is in the main determined by the product of the concentration and of the mobility of vacant positions, whereas the contribution of the interstitial ions may be neglected. As the concentration of the vacant positions is equal to the $CdCl_2$ concentration, the mobility of vacant positions can be calculated from electrical conductivity and $CdCl_2$ concentration. The same result was obtained from measurements on solid solutions of $PbCl_2$ in AgCl. By exact mathematical analysis of the increase of electrical conductivity with small $CdCl_2$ concentrations Koch and Wagner have further estimated, that the mobility of an interstitial Ag^+ ion in AgCl is nearly the same as the mobility of a vacant position in the cation lattice.

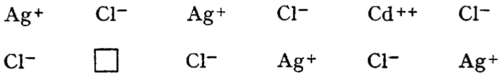

FIG. 2.—Solid solution of $CdCl_2$ in AgCl.

Thus the concentration of vacant positions in pure silver chloride (equal to the concentration of interstitial ions) can be calculated from the electrical conductivity of pure silver chloride and the mobilities determined before. The results for AgCl and AgBr, too, are given in Table I.

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[10] *Z. anorgan. Chem.*, 1920, **110**, 196; C. Tubandt, *ibid.*, 1921, **115**, 105.

TABLE I.—CONCENTRATIONS AND MOBILITIES OF INTERSTITIAL IONS AND VACANT POSITIONS IN SILVER HALIDES.

Compound.	Temp.	Electrical Conductivity (ohm^{-1} . cm.$^{-1}$).	Mobility of the Vacant Positions in the Ag$^+$ Lattice = Velocity (cm./sec.) for 1 Volt/cm.	Fraction of the Ag$^+$ Ions on Interstitial Places = Fraction of Vacant Positions in the Ag$^+$ Lattice.
1.	2.	3.	4.	5.
AgCl	350	7·57 . 10^{-3}	6·6 . 10^{-4}	1·5 . 10^{-3}
,,	300	1·84 . 10^{-3}	4·2 . 10^{-4}	5·5 . 10^{-4}
,,	250	3·82 . 10^{-4}	2·3 . 10^{-4}	2·2 . 10^{-4}
,,	210	8·96 . 10^{-4}	1·5 . 10^{-4}	8·1 . 10^{-5}
AgBr	300	2·01 . 10^{-2}	7·6 . 10^{-4}	4·0 . 10^{-3}
,,	250	4·13 . 10^{-3}	3·4 . 10^{-4}	1·8 . 10^{-3}
,,	210	1·01 . 10^{-3}	2·0 . 10^{-4}	7·6 . 10^{-4}

(2) **Silver Iodide.**—Extreme disorder occurs in αAgI, αAg_2S, and similar compounds. According to the X-ray investigations of Strock[11] and Rahlfs[12] there is a perfect anion lattice within which the cations are distributed in almost complete disorder. Thus the ionic conductivities of solid and molten AgI are nearly[13] the same ($\sim$ 1 Ohm^{-1} . cm.$^{-1}$).

(3) **Potassium Chloride.**—Cations and anions give a measurable contribution to the electrical conductivity[14] of KCl. A certain degree of disorder must exist in both the cation and anion lattices. As the cations and anions are approximately of the same size, the interstitial space is small and the repulsive force is somewhat large; interstitial ions are therefore unlikely; Schottky has suggested that there are equal numbers of empty places in the cation and anion lattice (Fig. 3). The higher the temperature, the more cations and anions leave their normal positions, moving onto the surface, in order to build there new layers of the normal lattice. This model is now being examined by Wagner and co-workers.

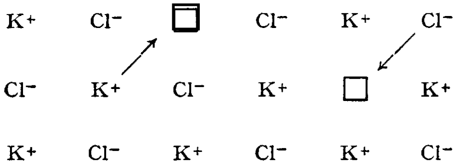

FIG. 3.—Disorder in potassium chloride according to W. Schottky.

2. The Movement of Electrons.

The movement of electrons in metals and in compounds similar to metals (*e.g.* Fe_3O_4, PbS) is not discussed here. In this paper we treat only ionic compounds, the electronic conductivity of which is much smaller than that of metals and falls, like ionic conductivity, with decreasing temperature.

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[11] *Z. physikal. Chem.*, *B*, 1934, **25**, 441; 1935, **31**, 132.

[12] P. Rahlfs, *ibid.*, 1935, **31**, 157.

[13] C. Tubandt and E. Lorenz, *Z. physikal. Chem.*, 1914, **87**, 513.

[14] C. Tubandt, H. Reinhold and G. Liebold, *Z. anorgan. Chem.*, 1931, **197**, 225.

In a few oxides (*e.g.* CuO at 1000° C.) there is observed a definite electronic conductivity which is characteristic for the compound; the surrounding gas atmosphere has no influence.[15] Some electrons have left their Cu^{++} ions and become attached to other Cu^{++} ions with formation of Cu^{+} and Cu^{+++} ions (electrons in excess and deficient, as in the model for cation disorder in AgCl). Conductivity is possible by electron exchange with adjacent Cu^{++} ions (see below). This interpretation is only valid for higher temperatures, whereas for 600° C. and lower temperatures complications are found.[16]

In most oxides electronic conductivity is primarily caused by small deviations from the strict stoichiometric composition (excess of metal or of oxygen). The behaviour of sulphides and halides is analogous. Bädecker[17] showed that the electronic conductivity of cuprous iodide increases on adding excess iodine. Many observations of this kind were made by Skaupy, Gudden, von Auwers, Schottky, Waibel, Tubandt, Reinhold, Le Blanc, Sachse, Wagner, Kröger, Friedrich, Meyer, Podszus, Pohl, Hilsch, Mollwo, Stasiw and others.[18] Two cases are described here.

(1) **Oxide with Metal Excess.**—At a temperature of nearly 600° C. zinc oxide[19] has already lost some oxygen to the surrounding gas atmosphere; an excess of metal remains in solid solution, at least partially, in the form of cations and quasi-free electrons. Thus the higher the oxygen pressure of the gas, the less excess zinc there is in the oxide phase, the fewer free electrons and the smaller the electronic conductivity. The cation excess appears to be on interstitial positions.

(2) **Oxide with Oxygen Excess:**[20] Cu_2O.—Additional oxygen atoms take up electrons in order to form negative ions. The electrons are taken from the shells of the Cu^{+} ions, leaving them as Cu^{++} ions. Electronic conductivity is possible by exchange of electrons between Cu^{+} and Cu^{++} ions. Thus the higher the oxygen pressure, the more oxygen excess there is in the oxide ($\sim$0·1 per cent. at 1000° C. under 30 mm. Hg oxygen pressure), the more Cu^{++} ions and the greater the electronic conductivity by electron exchange between Cu^{+} and Cu^{++}. Complications at lower temperatures out of thermodynamic equilibrium are not discussed here. Oxygen ions in excess on interstitial positions are

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[15] H. Dünwald, H. H. von Baumbach and C. Wagner, *Z. physikal. Chem., B*, 1933, **22**, 226.

[16] M. Le Blanc, H. Sachse and H. Schöpel, *Ann. Physik*, 1933 (5), **17**, 334; G. Kapp and M. Treu, *Sitzungsber. physik. med. Soz., Erlangen*, 1934, **65**, 215; J. Gundermann and C. Wagner, *Z. physikal. Chem.*, 1937, *B*, **37**, 157.

[17] K. Bädecker, *Ann. Physik*, 1907 (4), **22**, 749; 1909, **29**, 566; *Physikal. Z.*, 1908, **9**, 431; 1912, **13**, 1080.

[18] *Cf.* B. Gudden, *Ergebnisse der exakten Naturwiss.*, 1934, **13**, 223; C. Wagner, *Physikal. Z.*, 1935, **36**, 721; A. Smekal, *Die Physik in regelmässigen Berichten*, 1936, **4**, 173.

[19] F. Skaupy, *Z. Physik*, 1920, **1**, 259; H. H. von Baumbach and C. Wagner, *Z. physikal. Chem., B*, 1933, **22**, 199; M. Kröger, *Grenzflächenkatalyse*, 1933; O. Fritsch, *Ann. Physik*, 1935 (5), **22**, 375.

[20] B. Gudden, *Sitzungsber. physik. med. Soz., Erlangen*, 1930, **62**, 289; B. Gudden and G. Mönch, *Naturwiss.*, 1931, **19**, 361; W. Vogt, *Ann. Physik*, 1930 (5), **7**, 183; E. Engelhard, *Ann. Physik*, 1933 (5), **17**, 501; O. von Auwers, *Naturwiss.*, 1931, **19**, 133; F. Waibel, *Wiss. Veroff. Siemens-Konzern*, 1931, **10**, **4**, 65; 1936, **15**, **3**, 75; W. Schottky and F. Waibel, *Physikal. Z.*, 1933, **34**, 858; 1935, **36**, 912; M. Le Blanc and H. Sachse, *Ann. Physik*, 1931 (5), **11**, 727; M. Le Blanc, H. Sachse and H. Schöpel, *Ann. Physik*, 1933, (5), **17**, 334; W. P. Jusé and B. W. Kurtschatow, *Physik. Z. Sowjet-Union*, 1932, **2**, 453; H. Dünwald and C. Wagner, *Z. physikal. Chem., B*, 1932, **17**, 467; 1933, **22**, 212; J. Gundermann, K. Hauffe and C. Wagner, *ibid.*, 1937, **37**, 148; J. Gundermann and C. Wagner, *ibid.*, 1937, **37**, 155.

unlikely, as the ionic radius is somewhat large ($O^{=}$: 1·32 A ; C^{+} : 0·96 A) ; on the other hand, vacant positions appear in the cation lattice (Fig. 4). Indeed, the cations contribute but slightly to the electrical conductivity (0·05 per cent. at 1000° C.). In analogous cases (FeO, FeS, FeSe) the existence of empty cation positions was proved by X-ray investigations.[21]

Cu^{++} Cu^{+} □ Cu^{+} Cu^{+} Cu^{+}

O^{-} O^{-} O^{-} O^{-} O^{-}

Cu^{+} Cu^{++} Cu^{+} Cu^{+} □ Cu^{+}

FIG. 4.—Disorder in cuprous oxide with oxygen excess.

Analogous observations are made for alkali halides by Pohl and co-workers ; [22] *e.g.* in pure potassium iodide only a slight ionic conductivity is found, but it is increased by excess either of metal or of iodine, due to electronic transfer.

The description given in this paper is in agreement with conclusions based upon wave mechanics.[23]

3. The Oxidation of Metals.

When a metal is heated in oxygen, oxide is formed on the surface. If the volume of the metallic oxide is greater than the volume of the metal (*e.g.* Cu, Fe, Ni), the oxide layer is generally not porous, so that further reaction is only possible by diffusion of metal or oxygen within the solid oxide. If the diffusion is fairly slow, the rate is controlled only by this process. According to Tammann,[24] Pilling and Bedworth [25] and others, the rate is inversely proportional to the thickness of the oxide layer. In some cases the rate is controlled by reactions on the phase boundaries.[26] Other complications (*e.g.* irreversible changes of the metallic oxide layer) [27] are found at lower temperatures on rather thin layers. According to Tammann and Köster [28] an exponential formula may be valid under such conditions.

Wagner [29] has suggested that it is not neutral atoms, but ions and electrons which diffuse. Therefore the rate can be calculated from the affinity of the reaction, electrical conductivity and transfer numbers

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[21] E. R. Jette and F. Foote, *J. Chem. Physics*, 1933, **1**, 29; G. Hägg and J. Sucksdorff, *Z. physikal. Chem., B*, 1933, **22**, 444 ; G. Hägg and A. L. Klingström, *ibid.*, 1933, **22**, 453.

[22] R. W. Pohl, *Physikal Z.*, 1934, **35**, 107 ; *Z. techn. Physik*, 1935, **16**, 338 ; O. Stasiw, *Nachrichten Gesellsch. d. Wissenschaft Göttingen, Mathemat. Physik. Kl.*, 1932, 261 ; 1933, 387, *N.F.* ; 1935, **1**, 147 ; A. Smakula, *ibid.*, *N.F.*, 1934, **1**, 55 ; E. Mollwo, *ibid.*, *N.F.*, 1935, **1**, 215 ; *Z. techn. Physik*, 1935, **16**, 346 ; *Ann. Physik*, 1935 (5), **29**, 394.

[23] A. H. Wilson, *Proc. Roy. Soc., A*, 1931, **133**, 485 ; **134**, 277 ; F. Bloch, *Physikal. Z.*, 1931, **32**, 881 ; R. Peierls, *Ergebnisse der exakten Naturwissenschaften*, 1932, **11**, 264 ; B. Gudden and W. Schottky, *Physikal. Z.*, 1936, **36**, 717 ; F. Hund, *Physikal. Z.*, 1935, **36**, 725 ; R. H. Fowler, *Proc. Roy. Soc., A*, 1933, **140**, 505.

[24] *Z. anorgan. Chem.*, 1920, **111**, 78.

[25] *J. Inst. Metals*, 1923, **29**, 529.

[26] K. Fischbeck, L. Neundeubel and F. Salzer, *Z. Elektrochem.*, 1934, **40**, 517 ; H. Reinhold and H. Seidel, *ibid.*, 1935, **41**, 499.

[27] V. Kohlschütter and E. Krähenbühl, *ibid.*, 1923, **29**, 570 ; G. I. Finch and A. G. Quarrell, *Nature*, 1933, **131** 877 ; *Proc. Roy. Soc., A*, 1933, **141**, 398 ; *Proc. physic. Soc.*, 1934, **46**, 148 ; A. Steinheil, *Ann. Physik*, 1934 (5), **19**, 465.

[28] *Z. anorgan. Chem.*, 1923, **123**, 196.

[29] *Z. physikal. Chem., B*, 1933, **21**, 25.

of ions and electrons in the oxide layer, if the rate is controlled only by diffusion. The calculated values are confirmed by experiments.[30] Frequently the smaller cations and the electrons diffuse from the metallic phase towards the oxygen phase, as was first proved by Pfeil[31] for the oxidation of iron. The reactions between metal and halogen or sulphur occur in a quite analogous manner (Fig. 5).

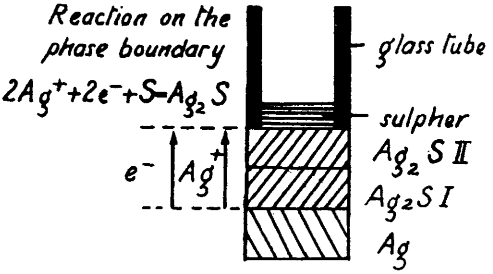

FIG. 5.—Reaction, $2\ Ag + S = \alpha - Ag_2S$. Temperature, 220° C. Depth of the Ag_2S cylinders I + II, 0·65 cm.; diameter, 0·5 cm. Change of weight after 1 hour:

Ag, −108 mg.;
Ag_2S I, +2 mg.;
Ag_2S, +126 mg.

Silver is moving from the metal phase through the Ag_2S phase to the sulphur phase. Ag_2S cylinder I receives nearly the same mass from the metal phase as loses to the Ag_2S cylinder II. On the upper boundary of the Ag_2S cylinder II new silver sulphide is formed; the Ag_2S phase is growing into the glass tube.

The diffusion in oxide layers, etc., is caused by slight deviations from the strict stoichiometrical composition. The cuprous oxide in contact with metallic copper has very nearly the ratio $Cu : O = 2 : 1$, whereas on the boundary Cu_2O/gas there is a slight deficit of metal ($\sim$ 0·1 per cent. at 1000° C. under 30 mm. Hg oxygen pressure). For the oxidation of iron the concentration difference within the ferrous oxide phase is considerably greater (between 5 and 10 per cent. iron deficit).[32] For this reason iron tarnishes more rapidly than other metals.[33]

4. The Formation of Double Salts, Spinels and Silicates.

If there is a reaction of the type: Solid A + Solid B = Solid AB, the reaction product is formed between the phases of the initial state. Thus further reaction is only possible by diffusion in the solid phase of the reaction product. Wagner[34] has suggested that there is diffusion of those ions which are moving in an electrical field. This supposition was proved for the reaction: $2AgI + HgI_2 = Ag_2HgI_4$. Ketelaar[35] has shewn that within the αAg_2HgI_4 phase both Ag^+ ions and Hg^{++} ions contribute measurably to electrical conductivity (94 and 6 per cent. at 65° C.), as the anion lattice is in perfect order, whereas the cations (Ag^+ and Hg^{++}) are scattered in disorderly fashion and some cation positions are empty. According to this structure the αAg_2HgI_4 phase takes up AgI or HgI_2 excess in solid solution. Thus there is a somewhat

[30] C. Wagner, *loc cit.*, and *Z. physikal. Chem.*, *B*, 1936, **32,** 447; K. Nagel and C. Wagner, *ibid.*, 1934, **25,** 71; H. Reinhold and H. Seidel, *Z. elektrochem.*, 1935, **41,** 499; H. Reinhold and H. Möhring, *Z. physikal. Chem.*, *B*, 1935, **28,** 178.

[31] *J. Iron Steel Inst.*, 1929, **119,** 501.

[32] L. B. Pfeil, *ibid.*, 1931, **123,** 237; E. R. Jette and F. Foote, *Am. Inst. Min. Met. Eng.* (*Iron and Steel Division*), 1933, **105,** 276.

[33] *Cf. e.g.*, N. B. Pilling and R. E. Bedworth [25].

[34] *Z. physikal. Chem.*, *B*, 1936, **34,** 309.

[35] J. A. A. Ketelaar, *ibid.*, 1934, **26,** 327; 1935, **30,** 53; *Z. Kristallogr.*, *A*, 1934, **87,** 436.

considerable difference of the Ag^+ and Hg^{++} concentrations within the Ag_2HgI_4 phase in contact with AgI and HgI_2 respectively.[36]

Koch and Wagner[37] have piled four cylinders (each 1 mm. high) one upon the other, as in Fig. 6. After a run of 66 days at 65° C. nearly equivalent quantities of Ag^+ and Hg^{++} ions are exchanged between the cylinder pairs $1 + 2$ and $3 + 4$ in conformity with the supposed mechanism. Only slight transport of HgI_2 through the gas phase had occurred. In the same manner as for the oxidation of metals the rate of this reaction can be calculated from the affinity, the electrical conductivity of the reaction product and the transfer numbers of the different ions. Quite good agreement with experiment was found.

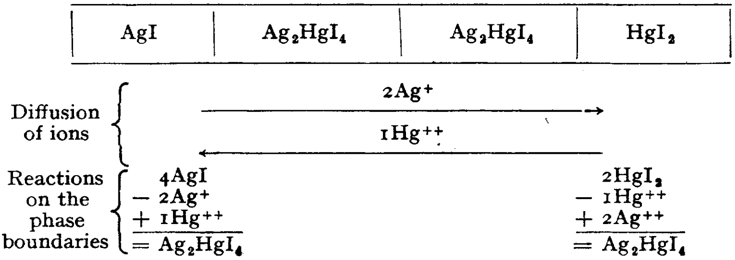

FIG. 6.—Reaction : $2AgI + HgI_2 = Ag_2HgI_4$.

Analogous interpretation is possible for the formation of spinel $MgO . Al_2O_3$ from MgO and Al_2O_3 and for silicate reactions;[38] but experiment is lacking.

Different conditions are supposed for reactions of the type CaO (solid) + CO_2 (gas) = $CaCO_3$ (solid). A measurable rate of this reaction seems only possible, if within the $CaCO_3$ phase formed between CaO and gas there are some pores for diffusion of CO_2 molecules, perhaps in an adsorbed state on internal surfaces. An analogous mechanism is supposed by Frankenburger[39] for the reaction

$$6Li \text{ (solid)} + N_2 \text{ (gas)} = 2Li_3N \text{ (solid)}.$$

5. The Reaction Cu + AgCl = Ag + CuCl.

There are a great many reactions of the type

$$\text{Solid A} + \text{Solid B} = \text{Solid C} + \text{Solid D},$$

mostly investigated in powder mixtures.[40] Wagner[41] has examined the reaction Cu + AgCl = Ag + CuCl with compact pieces of copper and silver chloride. The reaction products are formed between the phases of the initial state; a disorderly conglomeration of the phases Ag and CuCl is found. Chemical change is only possible by diffusion in this conglomeration. Ions and electrons move as short electrical currents in the galvanic cell: Ag | AgCl | CuCl | Cu (Fig. 7); its E.M.F.[42] is about 0·5 v. This current corresponds to the current of local elements on the

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[36] A. Steger, *Z. physikal. Chem.*, 1903, **43**, 595.

[37] *Z. physikal. Chem.*, *B*, 1936, **34**, 317.

[38] C. Wagner, *loc. cit.*

[39] *Z. Elektrochem.*, 1926, **32**, 481.

[40] G. Tammann, *Z. angew. Chem.*, 1926, **39**, 869; W. Jander, *ibid.*, 1928, **41**, 73; J. A. Hedvall, *Z. Elektrochem.*, 1930, **36**, 853; *Z. angew. Chem.*, 1931, **44**, 781; 1936, **49**, 875; *Reaktionsfähigkeit fester Stoffe*, Leipzig, 1938.

[41] *Z. anorgan. Chem.*, 1938, **236**, 320.

[42] F. Haber and St. Tolloczko, *Z. anorgan. Chem.*, 1904, **41**, 407.

phase boundary metal/aqueous solution. With some approximation the rate of chemical change can be calculated from the current.

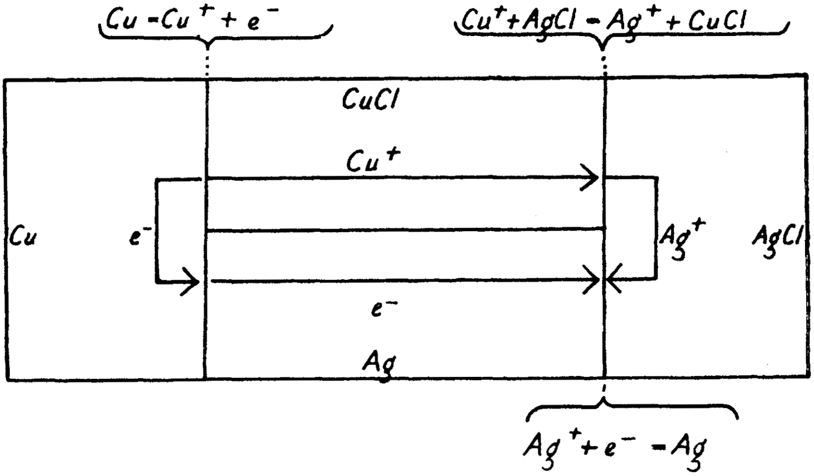

FIG. 7.—Reaction, $Cu + AgCl = Ag + CuCl$.

This interpretation can be extended to other reactions of ionic compounds in the absence of metallic phases, *e.g.*:

$$AgCl + NaI = AgI + NaCl. \quad (\text{Fig. } 8).$$

Experiments still fail.

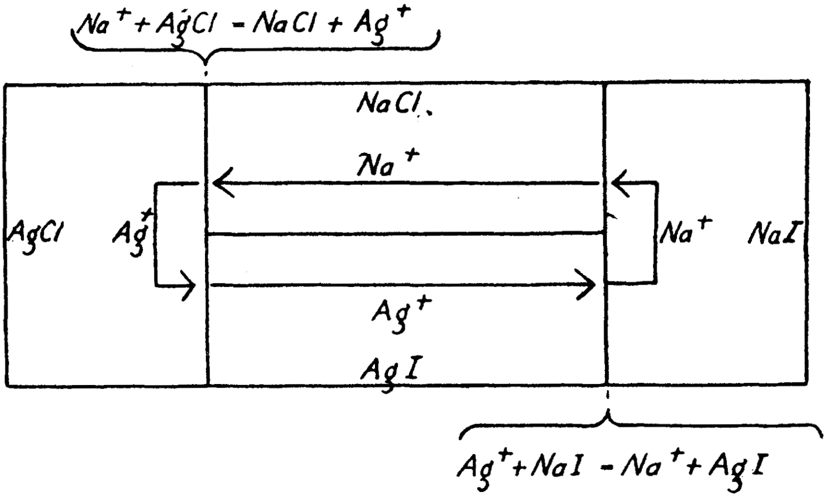

FIG. 8.—Reaction, $AgCl + NaI = AgI + NaCl$.

Summary.

(1) In solid ionic compounds movement of ions and electrons is possible, if there are deviations from the strict order of an ideal lattice. Some typical cases are described qualitatively.

(2) The degree of disorder in AgCl can be calculated from the electrical conductivities of pure AgCl and of solutions containing $CdCl_2$ or $PbCl_2$ in AgCl. Dates are communicated for AgCl and AgBr too.

(3) Reactions between solids require diffusion processes in the layers of the reaction products. This diffusion frequently can be interpreted as the moving of ions and electrons. The mobilities of these particles may be calculated from electrical measurements (electrical conductivity and transfer numbers). Thus, in simple cases, the rate of chemical change, too, may be calculated from electrical data. Some typical cases are described qualitatively.

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