# THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF SILVER CHLORIDE AND SODIUM CHLORIDE

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Extremely little complete thermodynamic information is available concerning solid salts and their solid solutions. Where so many of these crystals have been examined by the methods of x-ray analysis and their lattice arrangements in many cases satisfactorily established, the possibility of correlating the space lattice data with the thermodynamic properties, especially of solid solutions, is a very attractive one.

The galvanic cell has been employed to furnish a great mass of valuable data which permit the calculation of important thermodynamic quantities for aqueous solutions of salts. Little attention has been paid to the possibility of constructing such cells with the pure crystalline salt or its solid solutions as electrolyte. Haber and Tolloczko,[2] Katayama,[3] and Reinhold[4] have shown that this type of cell can be constructed for certain simple systems, and that their electromotive force can be determined by the usual varieties of electrical equipment. Unfortunately, the presence of unknown potentials between electrolytes in many of their cells prevents precise thermodynamic calculations.

In considering the properties of any material which is to be employed as the electrolyte in a reversible galvanic cell, in addition to the chemical considerations concerning the cell reaction, it is necessary to be certain that the conduction processes through the material are entirely ionic, that Faraday's law of electrolysis is obeyed, and that the diffusion of ions is sufficiently rapid to avoid the uncertainties of cumulative polarization effects produced by the passage of small currents in the experimental determination of the electromotive force. Aqueous solutions of salts, if not too dilute, as well as fused salts, completely fulfil these requirements. However, for non-aqueous salt solutions and for solid salts these considerations become important factors in the choice of materials. We have satisfactory proof of a transfer of charges by the transfer of matter according to Faraday's law. Tubandt and his co-workers[5] quantitatively checked Faraday's law on silver chloride, silver bromide, silver

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[2] Haber and Tolloczko, Z. anorg. Chem., 41, 407 (1904).

[3] Katayama, Z. physik. Chem., 61, 566 (1908).

[4] Reinhold, Z. anorg. allgem. Chem., 171, 181 (1928).

[5] Tubandt and co-workers, Z. physik. Chem., 87, 513, 543 (1914); Z. anorg. allgem. Chem., 110, 196 (1920); 115, 105 (1921); 117, 1, 48 (1921); 160, 222, 297 (1927); 165, 195 (1927).

iodide, lead chloride, lead fluoride, silver sulfide and cuprous sulfide. A transfer of matter by the current was found for a large number of different solid halides, nitrates, sulfates and even for lithium hydride.[6] There is no doubt that in all of these substances we have to do with an ionic conductivity following the Faraday law for electrolytes. Bruni,[7] Fraenkel and Houben,[8] and Vegard[9] have shown that diffusion processes in crystalline solids may be very rapid even at temperatures well below the melting point.

This research is a part of an extensive program now in progress involving the experimental determination of the procedure and technique necessary for the construction and manipulation of reversible cells containing solid electrolytes.

## Experimental Considerations

The cell studied in this research can be represented by Pb/PbCl$_2$/-AgCl, NaCl, Ag, where all the materials are solid, and sodium chloride is present in solid solution with silver chloride. The cell reaction is

$$Pb(s) + 2AgCl_{(solution)} = PbCl_2(s) + 2Ag(s)$$
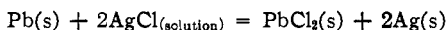
The mechanism whereby this reaction may take place is entirely analogous to that for the aqueous cell Pb/PbCl$_2$(aq.)/AgCl(s), Ag, the silver–silver chloride electrode playing a similar role in both. To avoid the uncertainties of a transference potential across the interface AgCl/PbCl$_2$, it is necessary to place the silver electrode in contact with both the silver chloride and the lead chloride. When a small negative current passes through the cell from right to left, silver ions which are present in the lead chloride in small concentrations and in equilibrium with the solid solution are discharged at the silver electrode. Chloride ions traverse the lead chloride to form more lead chloride with the lead ions which are produced at the lead electrode. A reversal of the current reverses this process.

Cells must be free from vitiating factors such as side reactions at the electrodes due to the reaction of the electrode with the electrolyte or to the cell reaction taking place at the electrodes themselves. For example, in the cell studied in this research, silver must not react with lead chloride or sodium chloride, and lead must not reduce lead chloride. In addition, silver and sodium chlorides must not react with or be soluble in lead chloride. The melting points of all the salts should fall within an experimentally convenient range. For this system all of these conditions are fulfilled. Silver chloride forms a complete series of solid solutions with

[6] Peters, *Z. anorg. allgem. Chem.*, **131,** 140 (1923).

[7] Bruni, *Chem. Reviews*, 1, 345 (1925).

[8] Fraenkel and Houben, *Z. anorg. allgem. Chem.*, 116, 1 (1921).

[9] Vegard, *Z. Physik*, **5,** 393 (1921).

sodium chloride.[10]  Lead chloride gives a simple eutectic with silver chloride[11] and sodium chloride,[12] at temperatures of 310 and 410°, respectively.

In order to prepare a homogeneous solid solution the fused salt mixture must be cooled rapidly and then annealed for a long time just below its melting point.  Crystalline materials may exhibit slight differences of thermodynamic behavior due to strains.  The higher the temperature and the softer the substance the less the magnitude of these effects.[13]

**Materials and Apparatus.**—The silver wire and lead used in this research were of the highest purity obtainable from commercial sources.  These substances were used without further purification.  Lead chloride was freed from moisture and hydrolysis products by fusing and bubbling dry hydrogen chloride through the melt for an hour.  The hydrogen chloride was generated by dropping concentrated sulfuric acid on pure concentrated hydrochloric acid, and was dried by bubbling through a glass-bead tower containing concentrated sulfuric acid.  Silver chloride was prepared by precipitation from a solution of silver nitrate by hydrochloric acid.  It was washed repeatedly by decantation with dilute hydrochloric acid solution until freed from nitric acid, and then dried and fused in the absence of light.  Small sticks were prepared by pouring the fused silver chloride into graphite molds. Sodium chloride of the highest purity from commercial sources was freed from moisture by drying in an electric oven at 300° for two hours.

The cell containers were made of Pyrex glass tubing in a simple U-tube form, 1 cm. in diameter and 20 cm. long, as shown in Fig. 1.  C, in the figure, represents two copper wires, one of which is soldered by means of german silver to a tungsten wire, D, and the other to a silver wire, A.  B is a solid solution of silver and sodium chlorides; F is solid lead chloride; and E is solid lead.

The hand-regulated, high temperature thermostat consisted of a well insulated three-liter beaker filled with a good grade of heavy motor oil which was electrically heated and efficiently stirred.



Fig. 1.—Cell container.

The thermometers employed in measuring the temperature of the bath were compared with primary standards which had been certified by the Bureau of Standards and which were used for standardization purposes only. The accuracy was about 0.1°.

An electrical, hand-regulated crucible furnace with a chamber 7 × 15 cm. was employed for annealing purposes.  Its temperature was measured by a chromel-alumel thermocouple connected to a potentiometer indicator.

All electromotive force measurements of the cells were made on a Leeds and North-
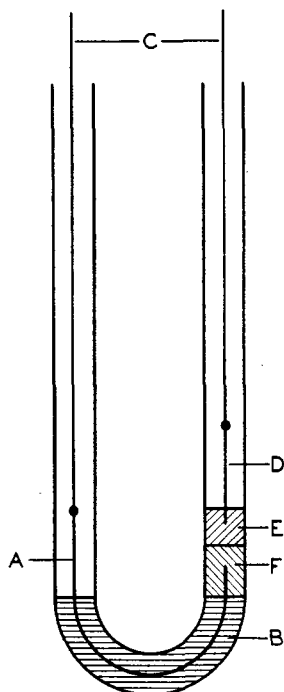
[10] Zhemchuzhnui, Z. anorg. allgem. Chem., 153, 47 (1926).

[11] Tubandt and Eggert, ibid., 110, 196 (1920).

[12] Treis, Neues Jahr. Mineral. Geol., Beilage Band, 37, 766 (1914).

[13] Lewis and von Ende, THIS JOURNAL, 32, 732 (1910).

rup type K potentiometer in conjunction with a high resistance galvanometer with a sensitivity of 2075 megs. Special care was taken to insulate all lead wires and mercury cups were used wherever possible to make electrical contact. Since the resistance of the cells in the thermostat varied from about 50,000 to 100,000 ohms, it was easily possible to read their e. m. f. to 0.1 mv.

**Experimental Procedure.**—The silver electrode was inserted around the bend in the empty glass cell. Weighed quantities of silver and sodium chlorides were then dropped into the other arm, fused in the blast lamp and permitted to solidify. Care must be taken to have the tip of the silver wire project about 1 cm. out of the melt. The cell was then placed in the annealing furnace, where it was kept at a temperature just below the melting point of the solid solution for about twenty-four hours. During the last few hours of this period the temperature was slowly lowered until room temperature was reached. Lead chloride was fused and poured into the open arm of the cell, covering the projecting tip of the silver wire. Lead was then melted into the cell, covering the solid lead chloride, and the tungsten–copper wire inserted. The cell was immediately put into the oil-bath. Both the silver and tungsten wires were kept below the surface of the bath to avoid any possible thermocouple potentials. Equilibrium was established within twenty-four hours at 200°. The composition of the solid solutions was varied from mole fraction 1 to 0.160 of silver chloride. The temperature of the bath covered the range 200 to 300° for the cells containing pure silver chloride and 150 to 230° for those containing the solid solutions. It was never permitted to change at a rate greater than about 5° an hour, so that a simultaneous reading of the e. m. f. and temperature proved quite satisfactory. Readings were taken over a period of one or two weeks, all of the cells being constant to within 0.5 mv.

The high temperatures at which the cells were kept, the care taken to avoid rapid fluctuations of temperature, the rapidity with which the cells responded to changes of temperature, the reproducibility of the results with different cells ascending and descending the temperature scale, as well as the constancy of any cell after several weeks in the high temperature bath, indicate a well-defined, reversible reaction reasonably free from disturbing factors.

Several cells were constructed of the form $Pb/PbCl_2/AgCl/Ag$, where the silver wire was not in contact with the lead chloride. With none of these cells could reproducible results be obtained. Obviously, we are dealing here with a variable potential across the interface between silver chloride and lead chloride.

## Experimental Results

The results of the e. m. f. measurements are given in Table I and plotted for two compositions in Fig. 2. The values for pure silver chloride represent four different cells, indicated in the figure by points of different styles. The agreement, it is observed, is quite good. The average deviation of the points from the straight line of the plot is less than 0.5 mv. The e. m. f. of the cell containing pure silver chloride extrapolated to 25° is 0.4879 v. as compared with 0.4883 v. from the "International Critical Tables,"[14] a difference of only 0.4 mv.

Since the variation of e. m. f. with composition is of greatest interest to us, a large-scale plot of Fig. 2 was made and the values of the e. m. f. for the different compositions read off at 150 and 200°. This is given in Fig. 3. Using the relation $\Delta_F = -23{,}074 \, \mathbf{NE}$, where $\mathbf{N}$ is the number

[14] "International Critical Tables," 1930, Vol. VII, pp. 248, 265.

TABLE I

E. M. F. IN VOLTS OF CELLS CONTAINING SILVER CHLORIDE OF VARIOUS MOLE FRACTIONS, $N_1$, DILUTED WITH SODIUM CHLORIDE

| $t$, °C. | E. m. f. | $t$, °C. | E. m. f. | $t$, °C. | E. m. f. | $t$, °C. | E. m. f. |
|---|---|---|---|---|---|---|---|
| $N_1 = 1.000$ | | $N_1 = 0.805$ | | 192.1 | 0.4519 | 210.0 | 0.4476 |
| 201.5 | 0.4568 | 171.3 | 0.4571 | 200.4 | .4497 | $N_1 = 0.296$ | |
| 203.7 | .4564 | 172.6 | .4568 | 204.8 | .4489 | | |
| 208.5 | .4549 | 174.3 | .4565 | 212.3 | .4471 | 152.7 | .4610 |
| 210.5 | .4548 | 176.3 | .4560 | 216.0 | .4462 | 155.5 | .4603 |
| 213.6 | .4539 | 182.2 | .4548 | 223.7 | .4444 | 158.2 | .4597 |
| 218.0 | .4526 | 192.3 | .4527 | | | 164.2 | .4589 |
| 223.0 | .4512 | 214.0 | .4482 | $N_1 = 0.596$ | | 166.8 | .4578 |
| 225.3 | .4512 | | | 172.4 | .4561 | 174.7 | .4562 |
| 232.3 | .4487 | $N_1 = 0.719$ | | 179.6 | .4543 | 178.2 | .4555 |
| 234.1 | .4486 | 150.4 | .4619 | 183.6 | .4532 | 183.6 | .4539 |
| 238.9 | .4474 | 153.0 | .4611 | 188.7 | .4523 | 188.7 | .4534 |
| 243.2 | .4468 | 156.0 | .4604 | 192.1 | .4513 | 192.1 | .4524 |
| 245.9 | .4462 | 159.8 | .4596 | 199.5 | .4494 | 198.2 | .4508 |
| 250.4 | .4454 | 167.2 | .4580 | 200.6 | .4492 | 202.0 | .4500 |
| 253.7 | .4446 | 172.2 | .4568 | 204.9 | .4486 | 204.9 | .4495 |
| 261.6 | .4424 | 175.2 | .4564 | 212.3 | .4468 | 208.0 | .4489 |
| 269.9 | .4408 | 178.8 | .4556 | 216.1 | .4461 | 212.3 | .4478 |
| 272.6 | .4400 | 187.7 | .4535 | 223.7 | .4446 | 216.1 | .4469 |
| 279.5 | .4383 | 190.5 | .4530 | $N_1 = 0.440$ | | 224.6 | .4452 |
| 284.6 | .4373 | 196.5 | .4518 | 168.3 | .4566 | $N_1 = 0.193$ | |
| 287.7 | .4366 | 206.5 | .4499 | 172.4 | .4558 | | |
| 289.3 | .4357 | 208.8 | .4494 | 179.0 | .4542 | 149.5 | .4612 |
| 295.4 | .4350 | 211.7 | .4487 | 192.0 | .4519 | 152.6 | .4606 |
| 298.5 | .4341 | 221.3 | .4467 | 192.5 | .4510 | 155.9 | .4596 |
| | | $N_1 = 0.636$ | | 199.2 | .4490 | 189.1 | .4520 |
| $N_1 = 0.870$ | | 165.4 | .4571 | 200.4 | .4503 | 189.7 | .4513 |
| 149.7 | .4618 | 168.5 | .4559 | 204.3 | .4481 | 218.2 | .4440 |
| 155.8 | .4605 | 175.7 | .4543 | 209.9 | .4472 | $N_1 = 0.160$ | |
| 159.8 | .4593 | 177.5 | .4542 | 210.7 | .4465 | | |
| 174.5 | .4561 | 180.3 | .4533 | 212.7 | .4464 | 170.8 | .4555 |
| 189.2 | .4535 | 181.1 | .4529 | 215.3 | .4460 | 184.4 | .4519 |
| 191.3 | .4530 | 196.5 | .4498 | $N_1 = 0.368$ | | 187.7 | .4512 |
| 195.2 | .4519 | 203.8 | .4483 | 177.1 | .4552 | 190.7 | .4504 |
| 196.2 | .4523 | $N_1 = 0.601$ | | 180.1 | .4546 | 196.4 | .4490 |
| 206.4 | .4502 | 172.4 | .4561 | 187.7 | .4527 | 197.6 | .4486 |
| 208.9 | .4496 | 178.7 | .4554 | 193.5 | .4515 | 200.7 | .4478 |
| 211.7 | .4490 | 183.6 | .4538 | 195.4 | .4509 | 206.3 | .4463 |
| 217.8 | .4470 | 188.7 | .4526 | 196.6 | .4506 | 209.0 | .4456 |
| 221.3 | .4469 | | | 199.9 | .4498 | 211.7 | .4449 |
| | | | | | | 221.4 | .4427 |

of equivalents per mole, and **E** is the e. m. f. in volts, we calculate $\Delta_F$, the free energy of the cell reaction. This varies with the mole fraction of silver chloride, $N_1$, and we will use $\Delta_F^\circ$ to denote pure silver chloride. The partial molal free energy of silver chloride in solution, $\bar{F}_1$, is then $\bar{F}_1 = \Delta_F^\circ - \Delta_F$. The entropy change for the cell reaction, $\Delta_S$, is given

in calories per mole per degree by $\Delta s = 23,074$ **N** $d\mathbf{E}/dT$, and the partial molal entropy $\bar{s}_1 = \Delta s° - \Delta s$. The change in heat content is $\Delta H = \Delta F - T\Delta s$ and the partial molal heat $\bar{H}_1 = \Delta H° - \Delta H$. The activity of silver chloride in its solutions, $a_1$, taking pure silver chloride as the standard state, is calculated by the relation $\bar{F}_1 = RT \ln a_1$. The activity of the sodium chloride, $a_2$, is obtained by means of the Duhem equation in the integrated form

$$\log \frac{a_2}{N_2} = \int_1^{N_2} \frac{N_1}{N_2} \, d \log \frac{a_1}{N_1}$$

performing a graphical integration and taking pure sodium chloride as the standard state. The thermodynamic values so calculated are given in Table II and the activity at 150° is plotted in Fig. 4. The straight diagonal lines represent Raoult's law.

### Discussion of Results

In most liquid systems it is possible to produce a slight degree of supersaturation. In no case has an investigation been made of a system going through a complete course of supersaturation wherein it passes continuously from the composition stable at the normal breakdown temperature to another composition also stable at that temperature. The smaller the mobilities of the solute molecules the greater the degree of supersaturatio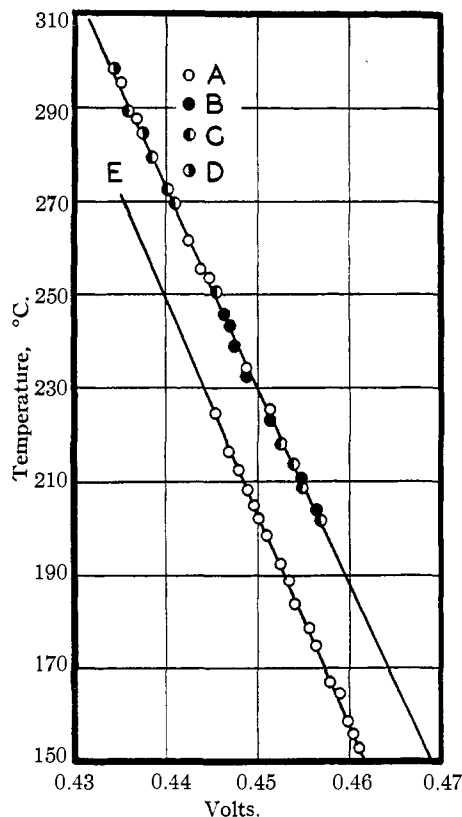n it is possible to attain. It is entirely conceivable that in solid solutions, where the ions possess relatively small mobilities, an unstable, supersaturated condition might persist indefinitely. Inspection of the activity curves in Fig. 4 shows that we are dealing here with a unique system in which, over a range of compositions, the activity of either constituent decreases while its mole fraction increases. A continuous, complete curve of supersaturation is experimentally obtained.

Fig. 2.—Temperature variation of e. m. f. of cells containing two different mole fractions of silver chloride–sodium chloride solutions. Mole fraction of silver chloride in A, B, C and D is 1.000, and in E is 0.296.

TABLE II

THERMODYNAMIC PROPERTIES OF SILVER CHLORIDE DILUTED WITH SODIUM CHLORIDE

| $N_1$ | $dE/dT.$ m$\overline{v}$./deg. | $-\Delta s,$ cal./deg. | $\overline{s}_1,$ cal./deg. | $-\Delta H,$ cal. | $-\overline{H}_1,$ cal. |
|---|---|---|---|---|---|
| 1.000 | 2.32 | 10.71 | 0 | 26150 | 0 |
| 0.900 | 2.14 | 9.88 | −0.83 | 25560 | 590 |
| .800 | 2.12 | 9.78 | − .93 | 25440 | 710 |
| .700 | 2.16 | 9.97 | − .74 | 25490 | 660 |
| .600 | 2.22 | 10.25 | − .46 | 25580 | 570 |
| .500 | 2.24 | 10.34 | − .37 | 25620 | 530 |
| .400 | 2.26 | 10.43 | − .27 | 25690 | 460 |
| .300 | 2.24 | 10.34 | − .37 | 25680 | 470 |
| .200 | 2.40 | 11.08 | + .37 | 25980 | 170 |
| .100 | 2.70 | 12.46 | +1.75 | 26400 | −250 |

150°

| $N_1$ | E. volts | $-\Delta F,$ cal. | $-\overline{F}_1,$ cal. | $a_1$ | $a_2$ |
|---|---|---|---|---|---|
| 1.000 | 0.4685 | 21620 | 0 | 1 | 0 |
| 0.900 | .4632 | 21380 | 240 | 0.748 | 0.155 |
| .800 | .4615 | 21300 | 320 | .681 | .354 |
| 700 | .4608 | 21270 | 350 | .655 | .711 |
| .600 | .4605 | 21250 | 370 | .645 | .962 |
| .500 | .4605 | 21250 | 370 | .645 | .955 |
| .400 | .4610 | 21280 | 340 | .663 | .930 |
| .300 | .4617 | 21310 | 310 | .689 | .908 |
| .200 | .4613 | 21290 | 330 | .674 | .910 |
| .100 | .4578 | 21130 | 490 | .556 | .935 |

200°

| 1.000 | .4569 | 21090 | 0 | 1 | |
|---|---|---|---|---|---|
| 0.900 | .4525 | 20880 | 210 | 0.806 | |
| .800 | .4509 | 20810 | 280 | .745 | |
| .700 | .4500 | 20770 | 320 | .713 | |
| .600 | .4494 | 20740 | 350 | .692 | |
| .500 | .4493 | 20730 | 360 | .689 | |
| .400 | .4497 | 20750 | 340 | .702 | |
| .300 | .4505 | 20790 | 300 | .731 | |
| .200 | .4493 | 20730 | 360 | .689 | |
| .100 | .4443 | 20510 | 580 | .539 | |

Tammann and his co-workers,[15] investigating the chemical properties of a large number of solid solutions, have discovered striking discontinuities in the variations of the intensity of action with the concentration of the solid solution. This phenomenon he has labeled "limits of resistance." For silver chloride–sodium chloride solid solutions which were extracted with water it was found that crystals with less than five-eighths mole of silver chloride yield all their sodium chloride, while those with more than six-eighths mole lose none of it. In the range of five-eighths to six-eighths,

[15] Tammann, *Z. anorg. allgem. Chem.*, **107**, 1 (1919); Schmidt, Dissertation, Göttingen, 1917.

rapidly increasing amounts were extracted. On the basis of numerous such experiments and because the resistance limits for cubic crystals
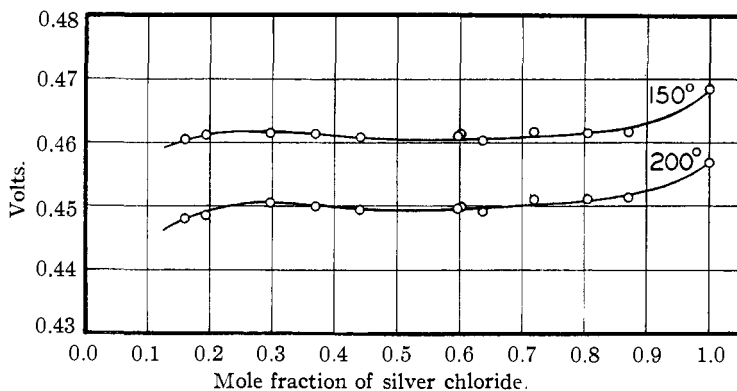


Fig. 3.—Variation of e. m. f. of cells with composition.

can be expressed as multiples of one-eighth mole of one of the two constituents, Tammann draws his fundamental conclusion that the arrange-
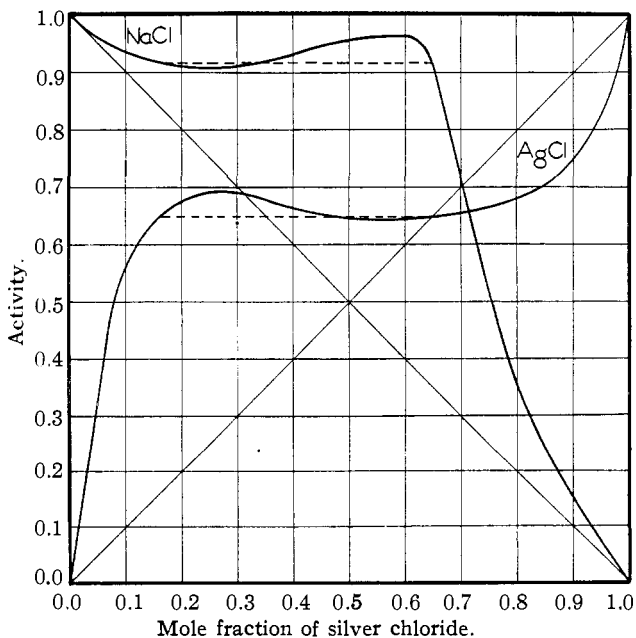


Fig. 4.—Activity curves for silver chloride–sodium chloride solid solutions at 150°.

ment of foreign atoms in solid solutions is regular. A regular arrangement in the silver chloride–sodium chloride solid solutions would consist

of the substitution of eight sodium ions for the silver ions at the corners of the silver chloride unit cell. This, in effect, can be regarded as a loose compound.

The opposing view is taken by Vegard,[16] who, from many x-ray investigations of the changes in lattice constant of solid solutions with composition, concludes that substitution is perfectly random, because a regularity in substitution would give rise to new interference maxima and none have ever been observed.[17] At best, however, these new lines would be very weak.

Experimental determinations of the deviations from Raoult's law for each component of a binary solution furnish a sensitive means of determining the nature of the solution. Increasing positive deviations[18] indicate an increasing tendency toward unmixing and the formation of two phases. Increasing negative deviations indicate the possibility of compound formation, since such a factor would reduce the activities of both components and would tend to annul the effect of any factor which produces abnormally large activities. An examination of Fig. 4 yields the information, then, that as sodium chloride is added to silver chloride, there is, at first, a tendency toward formation of a partly dissociated compound. As the proportion of sodium chloride increases, a very strong tendency toward unmixing manifests itself. However, the solution does not break down into two phases. The supersaturated condition persists through a minimum point of inflection and a maximum of the activity curve until the stable, homogeneous phase rich in sodium chloride is reached. A considerable portion of the sodium chloride activity curve lies above the value 0.9, indicating an extremely large escaping tendency from solution. Abruptly, at mole fraction 0.625 of silver chloride, this curve drops extremely rapidly, compound formation enormously reducing the escaping tendency of the sodium chloride. This completely confirms the extraction results of Tammann. However, the indications are that the "normal" distribution is not the only factor operating in this system to produce "limits of resistance," but that a very strong tendency toward separation into two phases intensifies this phenomenon.

Broomé[17] found that an x-ray analysis of a solid solution containing four-eighths mole of silver chloride showed two patterns indicating unmixing at room temperature. LeBlanc and Quenstadt,[19] however, found no unmixing after keeping the crystals for six weeks at room temperature.

The broken lines in Fig. 4 were obtained graphically by drawing two

[16] Vegard, *Z. Physik*, **5**, 17 (1921).

[17] Broomé, *Z. anorg. allgem. Chem.*, **143**, 60 (1925).

[18] *Cf.* Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, pp. 55, 72.

[19] LeBlanc and Quenstadt, *Z. physik. Chem.*, [Abt. A] **150**, 321 (1930).

horizontal lines so that each one would intersect the stable portion of its respective activity curve at the same mole fraction. The values of the mole fraction, $N_1$, thus obtained are 0.835 and 0.352. These values represent the compositions at which unmixing should occur. Inspection of these curves shows that only one pair of horizontal lines will satisfy the above conditions.

Experiments are now in progress applying these methods to other solid solutions. It is hoped that extending the temperature range, especially in the direction of lower temperatures, will yield a more thorough knowledge of the nature of these solutions. Certainly, we would expect to find that any tendency toward the formation of compounds would become intensified with a decrease in temperature.

## Summary

1. The technique of making precise potential measurements of galvanic cells containing solid electrolytes has been described.

2. The energy changes of solid silver chloride upon a dilution with sodium chloride have been determined at mole fractions of silver chloride varying from 1 to 0.160, between the temperatures of 150 and 230°.

3. The course of an activity curve for a supersaturated condition has been followed experimentally over its complete range of composition.

4. It is pointed out that Tammann's "limits of resistance" can be explained on the basis of this type of activity function.

5. The existence of a regular arrangement of sodium ions in the silver chloride–sodium chloride lattice is verified.

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# AQUEOUS SOLUBILITY OF SALTS AT HIGH TEMPERATURES. I. SOLUBILITY OF SODIUM CARBONATE FROM 50 TO 348°[1]

By WILLIAM F. WALDECK, GEORGE LYNN AND ARTHUR E. HILL

This investigation was carried out for the purpose of developing a satisfactory method for the determination of solubilities at high temperatures and pressures, and with its aid determining the solubility of sodium carbonate up to the critical temperature of water. From the solubility curve it was intended to ascertain the temperature of the transition of the monohydrate to the anhydrous form in contact with the solution under its own vapor pressure.

**Previous High-Temperature High-Pressure Solubility Methods.**—The

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[1] Presented by W. F. Waldeck as thesis for the degree of Master of Science at New York University.