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## INFLUENCE OF THE SOLVENT ON THE ELECTROMOTIVE FORCE OF SILVER-SILVER HALIDE CELLS

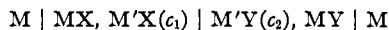
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### Introduction

Many investigations in recent years have given ample justification for the extension of Nernst's osmotic theory and the ordinary laws of thermodynamics to non-aqueous solutions. On this basis A. E. Brodsky<sup>1</sup> has given a formula for the change in electromotive force (e. m. f.) with solvent for the cell



in two solvents (M, metal; MX and MY, slightly soluble salts (depolarizers) of the metal; M'X and M'Y, very soluble salts;  $c_1 = c_2$ , equal concentrations of the salts). Brodsky's formula is

$$E - E' = \frac{RT}{nF} \ln \frac{L_1\nu_1 \times L_2\nu_2'}{L_1'\nu_1' \times L_2\nu_2'} \quad (1)$$

in which  $E$  and  $E'$  represent the e. m. f.'s of the cell in Solvents I and II, and  $L$  and  $\nu$  are the solubilities and activity coefficients of the salts M'X and M'Y in saturated solutions in Solvents I and II. In saturated solutions in the different solvents the relationships  $\nu_{M'X} = \nu_{M'X}'$  and  $\nu_{M'Y} = \nu_{M'Y}'$  are approximately true. This has been demonstrated for  $\alpha$  in the classic theory by Walden and van Laar,<sup>2</sup> and then

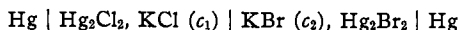
$$E - E' = \frac{RT}{nF} \ln \frac{L_1 \times L_2'}{L_1' \times L_2} \quad (2)$$

This formula is a consequence of the general formula given by Brodsky,<sup>1</sup> and has been deduced thermodynamically through a series of two cycles relating the free energy of reaction both in solution and without solvent, the initial activities and the activities of salts in saturated solutions. The

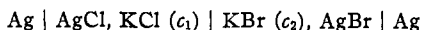
<sup>1</sup> Brodsky, *Z. physik. Chem.*, 121, 126 (1926); *Z. Elektrochem.*, 32, 5 (1926); "Scientific Magazine of the Chemical Cathedral of Katerinoslaw," 1926, Vol. I; *Physik. Z.*, 35, 665 (1929).

<sup>2</sup> Walden, *Z. physik. Chem.*, 55, 683 (1906); van Laar, *ibid.*, 58, 571 (1907).

equilibrium in solution may be calculated from thermal data by means of these cycles. Formula 2 may be applied only in dilute solutions. Professor Brodsky has demonstrated the correctness of this formula, using the cell



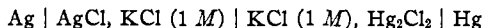
and suggested to the writer the problem of applying the formula to the cell



in ethyl alcohol-water and methyl alcohol-water mixtures, using various concentrations of potassium chloride and bromide.

### Experimental

The potentials of the Ag-AgCl and Ag-AgBr electrodes vary considerably depending on the methods of preparation, as has been shown by numerous investigators during the last thirty-five years. For example, the e. m. f. of the cell



in water at 25° has been measured by a number of workers since 1917, and has given values of  $E$  varying from +0.0422 to +0.0467.<sup>3</sup> Further data have been presented by Brönsted<sup>4</sup> and by Abegg and Cox.<sup>5</sup> The theoretical value given by Lewis and Randall<sup>6</sup> is  $E = 0.0466$  v. These differences may be ascribed to the lack of a uniform method of electrode preparation. The variable manipulatory and thermal conditions under which silver and its halides are prepared have a marked effect on the characteristics of the surfaces of the products and, as a result, the silver has different solution tensions ("elektrolytische Lösungstension" of Nernst) and the halides differ in solubility. These points have been discussed in detail by Lewis, Randall, and others.<sup>7</sup>

In the early part of this work, electrolytically coated silver-silver halide electrodes were used, prepared according to the directions of Goodwin, Jahn and Halla.<sup>8</sup> A pure white silver layer was prepared by electrolysis on a carefully cleaned platinum wire. The electrolysis lasted for five to six days and

<sup>3</sup> Noyes and Ellis, *THIS JOURNAL*, 39, 2532 (1917), give  $E = 0.0438$  v.; R. Gerke, *ibid.*, 44, 1684 (1922),  $E = 0.0458$  v.; Scatchard, *ibid.*, 47, 648, 696 (1925),  $E = 0.0466$  v.; Nonhebel and Hartley, *Phil. Mag.*, [6] 50, 729 (1925),  $E = 0.0467$  v.; Randall and Young, *THIS JOURNAL*, 50, 989 (1928),  $E = 0.455$  v.; Mazee, *Trans. Am. Electrochem. Soc.*, (1929), using different methods of preparation,  $E = 0.0422, 0.0442, 0.0444, 0.0466$  v.

<sup>4</sup> Brönsted, *Z. physik. Chem.*, 50, 481 (1905).

<sup>5</sup> Abegg and Cox, *ibid.*, 46, 1 (1903).

<sup>6</sup> Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 335, 407.

<sup>7</sup> Lewis, *THIS JOURNAL*, 28, 158 (1906); MacInnes and Parker, *ibid.*, 37, 1447 (1915); Güntelberg, *Z. physik. Chem.*, 123, 198 (1926); Randall and Young, Ref. 3; Mazee, Ref. 3; Carmody, *THIS JOURNAL*, 51, 2901 (1929).

<sup>8</sup> Goodwin, *Z. physik. Chem.*, 13, 577 (1894); Jahn, *ibid.*, 33, 545 (1900); Halla, *Z. Elektrochem.*, 17, 179 (1911).

was carried out in a  $KAg(CN)_2$  solution containing an excess of KCN, using a current density of 0.9 milliampere per sq. cm., with 15-20 electrodes in each set. The electrolyte was prepared as directed by Ullmann.<sup>9</sup> The electrodes were not protected from diffused daylight. After completion of the electrolysis, they were soaked in distilled water for one or two days, then immersed in a dilute silver nitrate solution and short-circuited to eliminate occasional differences in potential. The electrodes were then coated with a layer of silver halide by electrolysis as anodes in 0.75 *M* hydrochloric or hydrobromic acid, with a current density of 0.2 milliampere per sq. cm. The electrolysis was carried out in complete darkness and lasted for five to six hours. After completion the electrodes were placed in dilute potassium chloride or bromide solution, short-circuited and kept in the dark.

Despite the careful preparation, these electrodes were reproducible only to within 0.1-0.2 mv., whereas other investigators have prepared electrodes of this type reproducible to within 0.01-0.5 mv.<sup>10</sup> It seems that the reproducibility of electrodes of this type depends upon many factors which are either accidental or imperceptible. Carmody<sup>10</sup> has noted the influence of the absorption of cyanide ion and of exposure to daylight, both of which may be possible explanatory factors. Since the reproducibility of this type of electrode was unsatisfactory, they were used only in the early part of the work (water and ethyl alcohol-water solutions).

Subsequent work was carried out with electrodes of the type recommended by Noyes and Ellis<sup>3</sup> and by Lewis.<sup>7</sup> This type differs from that of Goodwin and Jahn in that the electrolytic layer is replaced by a silver sponge produced by thermal decomposition of silver oxide on the silvered platinum. The method of halogenizing was the same as before. The electrodes as prepared differed by about 0.01 mv. both in water and alcohol solution. Other workers<sup>11</sup> have obtained a reproducibility of 0.00-0.25 mv.

<sup>9</sup> Ullmann, "Enzyklopädie der technischen Chemie," "Starke Versilberung."

<sup>10</sup> Goodwin, Ref. 8, 0.1-0.2 mv.; Jahn, Ref. 8, several tenths of a mv.; Sackur, *Z. physik. Chem.*, **38**, 128 (1901), 0.01-0.02 mv.; Brønsted, Ref. 4, 0.1-0.5 mv.; Byron, *J. Russ. Phys.-Chem. Soc.*, **39**, 1506 (1907), 0.00-0.02 mv.; Byron and Boris Afanasiev, *ibid.*, **40**, 70 (1908); **41**, 1175 (1909), 0.03 mv.; Drucker, *Z. Elektrochem.*, **18**, 562 (1912), 0.5 mv.; MacInnes and Parker, Ref. 7, several tenths of a mv.; MacInnes and Beattie, *THIS JOURNAL*, **42**, 1117 (1920), 0.03-0.05 mv., but from divers series 0.1-0.2 mv.; Nonhebel and Hartley, Ref. 3, 0.02 mv.; Güntelberg, Ref. 7, several tenths of a mv.; Carmody, Ref. 7, 0.02 in one series. Other work with this type of electrode has been reported by Thiel, *Z. anorg. Chem.*, **24**, 1 (1900); Abegg and Cox, Ref. 5; Pearce and Hart, *THIS JOURNAL*, **43**, 2483 (1921); Sheppard and Elliot, *Science*, **56**, 578 (1922); Randall and Young, Ref. 3; Horsch, *THIS JOURNAL*, **41**, 1787 (1919); Mazee, Ref. 3.

<sup>11</sup> Güntelberg, Ref. 7, 0.02-0.2 mv.; Noyes and Ellis, Ref. 3, 0.05 mv.; Mazee, Ref. 3, 0.00 mv. Other workers with this type of electrode have been Harned and Fleysher, *THIS JOURNAL*, **47**, 82 (1925); Harned and Douglas, *ibid.*, **48**, 3095 (1926); Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922); Harned and Robinson, *ibid.*, **50**, 3157 (1928); Lucasse, *ibid.*, **47**, 743 (1925); *ibid.*, **51**, 2598, 2605 (1929); Randall and Young, Ref. 3.

with this type of electrode. The writer also replaced the electrolytically silvered platinum spiral with unsilvered spirals of pure silver, but the potential was not changed.<sup>12</sup>

The type of electrode recommended by Noyes and Ellis is definitely to be preferred. The third type, similar to the Hg-Hg<sub>2</sub>Cl<sub>2</sub> electrode is of no particular interest. The electrodes were protected from actinic light during and after halogenizing, and the measurements were carried out by the light of a dark yellow incandescent lamp. Each type of electrode was used exclusively in half of the work, the Goodwin-Jahn type in the first half and the Noyes-Ellis type in the last half; this necessitated great care in washing the electrodes whenever the solutions were changed. The apparatus was as usual: wire bridge, Weston normal cell, galvanometer (sensitive to 10<sup>-9</sup> ampere). The apparatus was not thermostated, since the temperature variation was not over 0.1–0.2° during a series of measurements, corresponding to a difference in measured e. m. f. of less than the experimental error (about 0.03 mv.). The precision of the e. m. f. measurements was about 0.1–0.2 mv. All materials and reagents were chemically pure and many times crystallized (the potassium chloride, for example, was 99.85% pure). The solvents were prepared from Kahlbaum's "Methanol zur Analyse" and from c. p. ethyl alcohol. The electrodes were prepared in the same way both in water and alcohol, and the compositions are given in "gewicht prozent."

### Results

The e. m. f. values given are the average of three measurements on three different pairs of electrodes, the separate values differing from one another by not more than 0.1–0.3 mv. The temperature coefficients were measured approximately at 15–30°.

TABLE I  
TEMPERATURE COEFFICIENT DATA

| Solvent   | Water    | Ethyl alcohol |          | Methyl alcohol |          |
|-----------|----------|---------------|----------|----------------|----------|
|           |          | 24.67%        | 50.60%   | 26.32%         | 45.03%   |
| dE/dT, v. | -0.00018 | -0.00017      | -0.00012 | -0.00017       | -0.00014 |

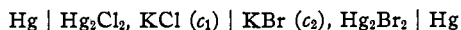
No correction was made for diffusion potential since the mobilities of Cl<sup>-</sup> and Br<sup>-</sup> are practically the same in equal concentrations of potassium chloride or bromide, and they are unknown for water-alcohol mixtures. No activity correction is necessary, since the activities of Cl<sup>-</sup> and Br<sup>-</sup> are almost identical in equal concentrations of the potassium salts.<sup>13</sup>

One point which should be noted is the systematic decrease of e. m. f. as the concentration is diminished, notwithstanding that  $c_{\text{KCl}}$  remains equal to  $c_{\text{KBr}}$ . This same effect was observed by A. E. Brodsky<sup>14</sup> on the cell

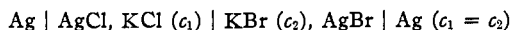
<sup>12</sup> See also Randall and Young, Ref. 3.

<sup>13</sup> Harned, *THIS JOURNAL*, 51, 416 (1929).

<sup>14</sup> Brodsky, *Z. Elektrochem.*, 32, 5 (1926), and Ref. 1.



The writer has made the same observation on the same cell at concentrations of 0.1 to 0.0001 *M*. The value found for the e. m. f. may be compared with Goodwin's results. Goodwin measured the e. m. f. of the cell



and found in water an e. m. f. of 0.148 mv. at 25° (*c* = 0.1 *M*), 0.149 v. (*c* = 0.05 *M*). Must be 0.150 v. at 15° (*c* = 0.1 *M*), 0.151 v. (*c* = 0.05 *M*). The writer's measurements at 15° give an e. m. f. of 0.1533 v. at *c* = 0.1 *M* and 0.1528 v. (interpolated) at *c* = 0.05 *M*. The discrepancy is explainable on the basis of insufficient precision in Goodwin's measurements made in 1894, since his individual observations at the same concentration and temperature differed by 4–6 mv. The observed increase of e. m. f. with diminishing concentration is easily accounted for on this basis.

TABLE II  
RESULTS

| Solvent                | Concentration |           | <i>t</i> , °C. | <i>E</i> at this <i>t</i> ,<br>volt | <i>E</i> corrected<br>at 15°,<br>volt |
|------------------------|---------------|-----------|----------------|-------------------------------------|---------------------------------------|
|                        | KCl           | KBr       |                |                                     |                                       |
| Water                  | 0.10010       | 0.10008   | 18.7           | 0.1528                              | 0.1533                                |
| Water                  | .01006        | .01006    | 18.6           | .1514                               | .1519                                 |
| Water                  | .00100067     | .00100064 | 10.5           | .1515                               | .1507                                 |
| Ethyl alcohol, 24.67%  | .10011        | .10011    | 15.1           | .1469                               | .1469                                 |
|                        | .01006        | .01006    | 15.2           | .1447                               | .1447                                 |
|                        | .001013       | .001081   | 15.9           | .1419                               | .1421                                 |
| 50.6%                  | .10012        | .10007    | 16.8           | .1392                               | .1394                                 |
|                        | .01006        | .01006    | 16.5           | .1371                               | .1374                                 |
|                        | .001011       | .001011   | 16.6           | .1344                               | .1346                                 |
| 75.06%                 | .050053       | .050055   | 15.0           | ...                                 | .1307                                 |
|                        | .0050305      | .0050307  | 15.0           | ...                                 | .1294                                 |
| Methyl alcohol, 26.32% | .100062       | .100069   | 9.9            | .1463                               | .1455                                 |
|                        | .010058       | .010059   | 10.2           | .1455                               | .1446                                 |
| 45.03%                 | .100059       | .100025   | 14.2           | .1400                               | .1399                                 |
|                        | .010056       | .010053   | 14.5           | .1387                               | .1386                                 |
| 74.72%                 | .100015       | .100011   | 16.5           | .1313                               | .1315                                 |
|                        | .010049       | .010049   | 16.6           | .1307                               | .1309                                 |
| 99.69%                 | .010007       | .010008   | 15.7           | .1245                               | .1247                                 |

**Verification of the Theory.**—The e. m. f. values obtained were used in verifying Formula 2. Solubility data were taken from the work of S. Zeitlin.<sup>15</sup> Table III gives the observed e. m. f. values and those calculated with the aid of Formula 2. Column 1 lists the first solvent, for which the e. m. f. (*E*) is known, and Column 2 gives the second solvent, for which the e. m. f. (*E'*) has been measured and calculated from *E* and the solubilities. *E* and *E'* correspond to the same concentrations; *t* is 15°; the e. m. f. values are rounded to millivolts and the solvent compositions are given to even

<sup>15</sup> S. Zeitlin, *Z. physik. Chem.*, 121, 39 (1926).

percentages. Values in parentheses are interpolated from closely adjacent concentrations.

TABLE III  
RESULTS

| Solvent I | Solvent II | 0.1 M                |                  |                 | 0.05 M       |                  |                 |              |
|-----------|------------|----------------------|------------------|-----------------|--------------|------------------|-----------------|--------------|
|           |            | $E - E'$ ,<br>calcd. | $E'$ ,<br>calcd. | $E'$ ,<br>meas. | $\Delta$ , % | $E'$ ,<br>calcd. | $E'$ ,<br>meas. | $\Delta$ , % |
| Water     | EtOH, 25%  | 0.0054               | 0.148            | 0.147           | 1            | (0.147)          | (0.146)         | 1            |
| Water     | EtOH, 50%  | .0118                | .141             | .139            | 1.5          | (.141)           | (.139)          | 1.5          |
| Water     | EtOH, 75%  | .0184                | ..               | ..              | ...          | (.134)           | .131            | 2            |
| EtOH, 25% | EtOH, 50%  | .0064                | .140             | .139            | 1            | (.140)           | (.139)          | 1            |
| EtOH, 25% | EtOH, 75%  | .0129                | ..               | ..              | ...          | (.133)           | .131            | 2            |
| EtOH, 50% | EtOH, 75%  | .0065                | ..               | ..              | ...          | (.132)           | .131            | 1.5          |
| Water     | MeOH, 26%  | .0041                | .149             | .145            | 3            | (.149)           | (.145)          | 2.5          |
| Water     | MeOH, 45%  | .0098                | .143             | .140            | 3            | (.143)           | (.140)          | 2.5          |
| Water     | MeOH, 75%  | .0153                | .138             | .131            | 5            | (.137)           | .131            | 4.5          |
| Water     | MeOH, 100% | .0204                | ..               | ..              | ...          | ..               | ..              | ...          |
| MeOH, 25% | MeOH, 45%  | .0057                | .140             | .140            | 0            | (.139)           | (.139)          | 0            |
| MeOH, 25% | MeOH, 75%  | .0111                | .135             | .131            | 2            | (.134)           | .131            | 2            |
| MeOH, 25% | MeOH, 100% | .0163                | ..               | ..              | ...          | ..               | ..              | ...          |
| MeOH, 45% | MeOH, 75%  | .0055                | .135             | .131            | 2            | (.134)           | .131            | 2            |
| MeOH, 45% | MeOH, 100% | .0174                | ..               | ..              | ...          | ..               | ..              | ...          |
| MeOH, 75% | MeOH, 100% | .0051                | ..               | ..              | ...          | ..               | ..              | ...          |

| 0.01 M           |                 |              | 0.005 M         |                |              | 0.001 M         |                |              |
|------------------|-----------------|--------------|-----------------|----------------|--------------|-----------------|----------------|--------------|
| $E'$ ,<br>calcd. | $E'$ ,<br>meas. | $\Delta$ , % | $E$ ,<br>calcd. | $E$ ,<br>meas. | $\Delta$ , % | $E$ ,<br>calcd. | $E$ ,<br>meas. | $\Delta$ , % |
| 0.147            | 0.147           | 0            | (0.146)         | (0.144)        | 1.5          | 0.145           | 0.142          | 2            |
| .140             | .137            | 2            | (.140)          | (.137)         | 2            | .139            | .135           | 3            |
| .133             | .130            | 2.5          | (.133)          | .129           | 2.5          | ..              | ..             | .            |
| .138             | .137            | 0.5          | (.138)          | (.137)         | 1            | .136            | .135           | 1            |
| .132             | .130            | 0.5          | (.131)          | .129           | 1            | ..              | ..             | .            |
| .131             | .130            | 1            | (.130)          | .129           | 0.5          | ..              | ..             | .            |
| .148             | .145            | 2            | ..              | ..             | ...          | ..              | ..             | .            |
| .142             | .139            | 2.5          | ..              | ..             | ...          | ..              | ..             | .            |
| .137             | .131            | 4            | ..              | ..             | ...          | ..              | ..             | .            |
| .131             | .125            | 5            | ..              | ..             | ...          | ..              | ..             | .            |
| .139             | .139            | 0            | ..              | ..             | ...          | ..              | ..             | .            |
| .133             | .131            | 1            | ..              | ..             | ...          | ..              | ..             | .            |
| .128             | .125            | 3            | ..              | ..             | ...          | ..              | ..             | .            |
| .133             | .131            | 1            | ..              | ..             | ...          | ..              | ..             | .            |
| .121             | .125            | -2.5         | ..              | ..             | ...          | ..              | ..             | .            |
| .126             | .125            | 1            | ..              | ..             | ...          | ..              | ..             | .            |

The average deviation between  $E'_{\text{meas.}}$  and  $E'_{\text{calcd.}}$  is about 1.8%. These differences may be due to the somewhat uncertain values for the solubilities in the concentrated alcohols (the absolute values are not very large). The observed data demonstrate the validity of Formula 2 and its premises. A comparison of these results with recent data obtained in this Laboratory<sup>16</sup> indicates the correctness of the premises and shows that Nernst's osmotic

<sup>16</sup> Brodsky and Trachtenberg, *Z. physik. Chem.*, **143A**, 287 (1929); Brodsky and Boruhovich, *J. chim. phys.*, **26**, 542 (1929).

theory is applicable to the usual electrodes as well as to oxidation-reduction electrodes.

The writer wishes to express his thanks to Professor A. E. Brodsky both for suggesting the problem and for help in carrying it out. Part of the material presented appeared in *Z. Elektrochem.*, **39**, 220 (1929). Slight corrections are necessary to part of the published data; the corrections have been applied in this report.

### Summary

1. The methods of preparation of silver-silver chloride and silver-silver bromide electrodes have been studied, and it has been found that the procedure recommended by Noyes and Ellis is to be preferred.

2. Measurements have been made of the e. m. f. of the cell  $\text{Ag} \mid \text{AgCl}, \text{KCl} (c_1) \mid \text{KBr} (c_2) (c_1 = c_2), \text{AgBr} \mid \text{Ag}$  in water and in ethyl and methyl alcohol-water mixtures of various concentrations.

3. The results obtained justify the application of Nernst's osmotic theory to non-aqueous solutions, as has been carried out by Professor A. E. Brodsky.

DNIEPROPETROVSK, EKATERINOSLAW, U. S. S. R.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE, ENGLAND,  
AND THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## THE PROPERTIES OF SELENIUM TETRACHLORIDE<sup>1</sup>

By J. H. SIMONS

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The tetrahalogen compounds of the electronegative elements in group number six of the periodic table are of considerable interest from the point of view of molecular structure. On the Lewis theory the central atom should be represented with a shell of ten electrons, four pair of which are shared with the halogen atoms and one pair which is not shared. Henley and Sugden<sup>2</sup> propose a shell of eight electrons with two of the halogen atoms held by single electron bonds.

Of these compounds the following are known:  $\text{SCl}_4$ ,  $\text{SF}_4$ ,  $\text{SeBr}_4$ ,  $\text{SeCl}_4$ ,  $\text{SeF}_4$ ,  $\text{TeI}_4$ ,  $\text{TeBr}_4$  and  $\text{TeCl}_4$ . The formulas of most of these have, however, been assigned from only an analysis of the crystalline compound. The molecular weights and therefore the number of atoms in the molecule have not been determined. In fact, a number of these compounds are very unstable crystalline substances, the crystal structures of which are not known. The stability of these compounds increases in the expected man-

<sup>1</sup> Part of this work was done while the author was a National Research Fellow at Cambridge University.

<sup>2</sup> Henley and Sugden, *J. Chem. Soc.*, 1058 (1929).