CONCENTRATION CELL WITH TERNARY ELECTROLYTE.

By Kosaku MASAKI

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Since the electromotive force of the concentration cell with ternary electrolyte had been studied by H. M. Goodwin⁽¹⁾ in 1894, it was studied by many investigators.⁽²⁾ But there is no information on the theoretical determination of the electromotive force of the cell except the work by J. E. Geissler.⁽³⁾

He assumed the following two reversible reactions in the next cell.

$$\mathrm{Hg} \mid \mathrm{Hg_2Cl_2},\ \mathrm{MgCl_2}\,(c_1) \mid \mathrm{MgCl_2}\,(c_2),\ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg} \qquad \text{(A)}$$

$$\begin{array}{ccccc} \mathrm{AB} & \rightleftarrows & \mathrm{AB^+} & + & \mathrm{B^-} \\ d,\ o & & c,\ \gamma & & b,\ \beta \end{array} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

$$\begin{array}{ccccc} \mathrm{AB^+} & \rightleftarrows & \mathrm{A^{++}} & + & \mathrm{B^-} \\ c,\ \gamma & & a,\ \alpha & & b,\ \beta \end{array} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

where a, b, c, d are the ionic concentrations and α, β, γ are the transport number of each ions and also he showed that when the mentioned two reversible reactions take place in the cell A, the electromotive force of the cell is

$$e = -\frac{RT}{F}\left[\left(m+\frac{\beta-\gamma}{\beta+\gamma}\right)\ln\frac{a_2}{a_1}+\left(m-\frac{\alpha-\gamma}{2\alpha-\gamma}\right)\ln\frac{b_2}{b_1}+\left(-m+\frac{\alpha-\beta}{2\alpha+\beta}\right)\ln\frac{c_2}{c_1}\right.$$

$$\left.+\left(-\frac{\beta-\gamma}{\beta+\gamma}+\frac{\alpha-\gamma}{2\alpha-\gamma}-\frac{\alpha-\beta}{2\alpha+\beta}\right)\ln\frac{x_1}{x_2}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ (3)$$

where x_1, x_2 are the specific conductance of c_1 and c_2 and the value of m is

$$m = \frac{(2\alpha+\beta)(-8\alpha-\beta+3\gamma)}{(2\alpha+\gamma)(\beta+\gamma)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

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(1) *Z. physik. Chem.*, **13** (1894), 577.

(2) W. Consad, Dissert. V. Gottingen 1903; E. Biron, *J. Russ. physik. Chem.*, **39** (1908), 1506; **40** (1908), 79; E. Biron and Afranasjer, *J. Russ. physik. Chem.*, **41** (1909), 1175; J. N. Pearce and R. W. Gelbach, *J. physik. Chem.*, **29** (1925), 1023.

(3) *Z. Elektrochem.*, **18** (1912), 135.

Measurements of the electromotive force had been studied to confirm of the existence of AB^+ ion in the mentioned electrolyte, and also he calculated the electromotive force of the cell A by assuming the value of γ, for example, $\gamma = 20$ or $\gamma = 10$.

In this investigation the electromotive force of the following cells were studied in the very dilute solution and also the theoretical value of the electromotive force was calculated.

$$Hg \mid Hg_2Cl_2,\ MeCl_2\,(c)_1 \mid MeCl_2\,(c_2),\ Hg_2Cl_2 \mid Hg \qquad (B)$$

$$Ag \mid AgCl,\ MeCl_2\,(c_1) \mid MeCl_2\,(c_2),\ AgCl \mid Ag \qquad (C)$$

$$\text{Me-Amalgam} \mid MeCl_2\,(c_1) \mid MeCl_2\,(c_2) \mid \text{Amalgam-Me} \qquad (D)$$

where Me are magnesium, calcium, strontium, barium and zinc.

Experimental.

Chlorides of magnesium, calcium, strontium, barium and zinc used were of Kahlbaum and purified by recrystallization, and also calomel were of Kahlbaum and purified by washing with conductivity water.

Silver chloride was prepared from the dilute solution of corresponding potassium chloride (Kahlbaum) by precipitating with purified silver nitrate at the dark room. Silver electrode was prepared by electrolysing a one percent solution of pure potassium silver cyanide with pure silver wire as a cathode. Mercury used was of purified by vacuum distillation from the commercial mercury. The amalgams were made by electrolysing a 10 % solution of pure chlorides of zinc, barium, strontium and calcium with mercury as a cathode in the hydrogen atmosphere.

The cells were of ordinary form. All the electromotive force measurements were carried out after the cells was kept for about one hour in a thermostat at a constant temperature, the variation of which was regulated within 0.05°C. For the measurements a potentiometer and a D.L. type mirror galvanometer were used. Constants necessary for the calculation are given in the following tables.

The values of mobility at 18°C. were taken from the results of Noyes and Falk⁽¹⁾ and also were calculated from the values of Λ_∞ for the salts. The values at 30°C. were calculated from the following equations.

$$C = \frac{(l_{t_2} - l_{t_1})}{(t_2 - t_1)l} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (5)$$

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(1) *J. Am. Chem. Soc.*, **34** (1912), 454.

$$l = (l_{t_2}+l_{t_1})2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where l_{t_2}, l_{t_1}, are mobilities at t_2, t_1.

Table 1.

Mobilities of the Various Ions.

Ion	Mobility		Temperature coefficient $C \times 10^4$
	18°C	30°C	
$\frac{1}{2}Zn^{++}$	47.0	63.9	254
$\frac{1}{2}Sr^{++}$	51.9	70.2	247
$\frac{1}{2}Ca^{++}$	51.9	70.2	247
$\frac{1}{2}Ba^{++}$	55.4	80.2	239
$\frac{1}{2}Mg^{++}$	45.9	55.6	256
Cl^-	65.5	85.0	216

Table 2.

Activity Coefficients of Chlorine Ion at Various Concentrations.

Molarity	0.1	0.05	0.02	0.01	0.005	0.004	0.003	0.0025	0.002	0.00125	0.001	0.0005	0.00025
Activity coefficient	0.79	0.84	0.89	0.92	0.95	0.955	0.965	0.967	0.97	0.975	0.98	0.985	0.99

Table 3.

Activity Coefficients of Ions of Zinc, Strontium, Calcium and Barium at Various Concentrations.

Molarity	0.05	0.025	0.02	0.01	0.005	0.0025	0.00125	0.000625
Activity coefficient	0.34	0.43	0.46	0.53	0.60	0.66	0.73	0.775

These values in Tables 2 and 3 were calculated from the Table 8 of "Thermodynamics" by Lewis and Randall, and the values of ion concentration were calculated from the general formula:

$$\mu = \frac{Z_a^2(a)+Z_b^2(b)+Z_c^2(c)}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where Z_a, Z_b, Z_c, are the valencies of ions and a, b, c are the ion concentrations.

Calculation of the Electromotive Force. At the mentioned concentration cell with ternary electrolyte, in the very dilute solution, if the concentration $c = o$, from the equation (4) we will obtain as follows.

$$a = \frac{b}{2} \qquad \text{and} \qquad m = \frac{\alpha-\beta}{2\alpha+\beta}$$

Therefore,

$$\frac{a_2}{a_1} = \frac{b_2}{b_1} = \frac{x_2}{x_1}$$

So, the next equation derived from the equation (3)

$$e = -\frac{RT}{F}\frac{\alpha-\beta}{2\alpha+\beta}\ln\frac{b_2}{b_1} = -\frac{RT}{F}\frac{\alpha-\beta}{2\alpha+\beta}\ln\frac{a_2}{a_1} \quad \dots\dots\dots \quad (8)$$

If it is the concentration cell with regard to anion reversible, we have

$$e = -\frac{RT}{F}\frac{3\alpha}{2\alpha+\beta}\ln\frac{b_2}{b_1} \quad \dots\dots\dots\dots\dots\dots\dots \quad (9)$$

and also, if it is the concentration cell with regard to cation reversible, we have

$$e = \frac{RT}{F}\frac{3\beta}{2(2\alpha+\beta)}\ln\frac{a_2}{a_1} \quad \dots\dots\dots\dots\dots\dots\dots \quad (10)$$

If l_k, l_a are the mobilities of the two ions, the next equation may be obtained from the Kohlraush's theory.

$$\frac{l_k}{l_a} = \frac{\beta}{\alpha} \qquad \text{or} \qquad \frac{l_k}{\beta} = \frac{l_a}{\alpha} \quad \dots\dots\dots\dots\dots\dots \quad (11)$$

Hence, if we put the equation (11) equal to $\frac{1}{K}$ (K: constant)

$$\frac{l_k}{\beta} = \frac{l_a}{\alpha} = \frac{1}{K}$$

so,

$$\alpha = Kl_a \qquad \text{or} \qquad \beta = Kl_k \quad \dots\dots\dots\dots\dots\dots \quad (12)$$

by substituting these values to the equation (9), we get

$$e = -\frac{RT}{F}\frac{3Kl_a}{2Kl_a+Kl_k}\ln\frac{b_2}{b_1}$$

by simplification,

$$e = -\frac{RT}{F}\frac{3l_a}{2l_a+l_k}\ln\frac{b_2}{b_1} \quad \dots\dots\dots\dots\dots\dots\dots (13)$$

Therefore, we obtained the following formula from the equation (13)

$$e = -\frac{RT}{F}\frac{3l_a}{2l_a+l_k}\ln\frac{f_2b_2}{f_1b_1} \quad \dots\dots\dots\dots\dots\dots\dots (14)$$

where f_1, f_2 are activity coefficients of chlorine ion at the various concentrations, and also we obtained the next equation by substituting the values of (12) to the equation (10)

$$e = \frac{RT}{F}\frac{3l_k}{2(2l_a+l_k)}\ln\frac{f_4a_2}{f_3a_1} \quad \dots\dots\dots\dots\dots\dots\dots (15)$$

where f_3, f_4 are activity coefficients of Me^{++} ion at the various concentrations.

Electromotive Force of Anion Reversible cell with Mercury Electrode. The combination of the cell was as follows.

$$Hg \mid Hg_2Cl_2,\ MeCl_2\,(c_1) \mid MeCl_2\,(c_2),\ Hg_2Cl_2 \mid Hg$$

A series of measurements were carried out on the cells of the solutions of the different concentrations. Each experiment was done after keeping the cell at 30°C. for about an hour. All equations in the following tables obtained from the equation (14).

Table 4.

E. M. F. of Cell: $Hg \mid Hg_2Cl_2,\ ZnCl_2\,(c_1) \mid ZnCl_2\,(c_2),\ Hg_2Cl_2 \mid Hg$

$$e = -0.065524 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $ZnCl_2$ (c_2)	Concentration of $ZnCl_2$ (c_1)	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	−0.01790	−0.01873
0.005	0.0025	−0.01835	−0.01879
0.0025	0.00125	−0.01882	−0.01919
0.00125	0.001	−0.00579	−0.00625

Table 5.

E. M. F. of Cell: $Hg \mid Hg_2Cl_2,\ SrCl_2(c_1) \mid SrCl_2(c_2),\ Hg_2Cl_2 \mid Hg$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $SrCl_2\,(c_2)$	Concentration of $SrCl_2\,(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	—	−0.01821
0.005	0.0025	—	−0.01828
0.0025	0.00125	−0.01850	−0.01863
0.0025	0.002	−0.00589	−0.00601
0.002	0.001	−0.01853	−0.01861

Table 6.

E. M. F. of Cell: $Hg \mid Hg_2Cl_2,\ BaCl_2(c_1) \mid BaCl_2(c_2),\ Hg_2Cl_2 \mid Hg$

$$e = -0.061244 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $BaCl_2\,(c_2)$	Concentration of $BaCl_2\,(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	−0.01619	−0.01751
0.005	0.0025	−0.01723	−0.01757
0.0025	0.00125	−0.01753	−0.01794
0.0025	0.001	−0.02380	−0.02382
0.002	0.001	−0.01785	−0.01788

Table 7.

E. M. F. of Cell: $Hg \mid Hg_2Cl_2,\ CaCl_2(c_1) \mid CaCl_2(c_2),\ Hg_2Cl_2 \mid Hg$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $CaCl_2\,(c_2)$	Concentration of $CaCl_2\,(c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	—	−0.01821
0.005	0.0025	−0.01799	−0.01828
0.0025	0.002	−0.00593	−0.00601
0.0025	0.00125	−0.01875	−0.01863
0.002	0.001	−0.01853	−0.01861

From the data given in Tables 4, 5, 6 and 7, it will be found that the differences between the measured electromotive forces and calculated ones are 0.00043, 0.00011, 0.00017 and 0.00014 volt on 0.005 molal or more dilute solutions.

Electromotive Force of Anion Reversible cell with Silver Electrode. The combination of the cell was as follows.

$$\mathrm{Ag} \mid \mathrm{AgCl},\ \mathrm{MeCl_2}\,(c_1) \mid \mathrm{MeCl_2}\,(c_2),\ \mathrm{AgCl} \mid \mathrm{Ag}$$

Silver chloride used was purified by washing several times with the electrolyte at a dark room to avoid the disturbing effect by sun beams. The measurements of the electromotive force of the cell were carried out at 30°C. and also in the dark. The results are summarized in the following tables.

Table 8.

E. M. F. of Cell: $\mathrm{Ag} \mid \mathrm{AgCl},\ \mathrm{ZnCl_2}\,(c_1) \mid \mathrm{ZnCl_2}\,(c_2),\ \mathrm{AgCl} \mid \mathrm{Ag}$

$$e = -0.065524 \log \frac{f_2 b_2}{f_1 b_1} .$$

Concentration of $\mathrm{ZnCl_2}$ (c_2)	Concentration of $\mathrm{ZnCl_2}$ (c_1)	E. M. F. in volt	
		Measured	Calculated
0.005	0.0025	−0.01866	−0.01879
0.0025	0.00125	−0.01895	−0.01919
0.01	0.005	−0.01877	−0.01883

Table 9.

E. M. F. of Cell: $\mathrm{Ag} \mid \mathrm{AgCl},\ \mathrm{CaCl_2}\,(c_1) \mid \mathrm{CaCl_2}\,(c_2),\ \mathrm{AgCl} \mid \mathrm{Ag}$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1} .$$

Concentration of $\mathrm{CaCl_2}$ (c_2)	Concentration of $\mathrm{CaCl_2}$ (c_1)	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	−0.01834	−0.01821
0.005	0.0025	−0.01812	−0.01828
0.0025	0.00125	−0.01855	−0.01863

Table 10.

E. M. F. of Cell: $Ag \mid AgCl,\ SrCl_2(c_1) \mid SrCl_2(c_2),\ AgCl \mid Ag$

$$e = -0.063769 \log \frac{f_2 b_2}{f_1 b_1}.$$

Concentration of $SrCl_2$ (c_2)	Concentration of $SrCl_2$ (c_1)	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	−0.01811	−0.01821
0.005	0.0025	−0.01825	−0.01828
0.0025	0.00125	−0.01857	−0.01863

Table 11.

E. M. F. of Cell: $Ag \mid AgCl,\ MgCl_2(c_1) \mid MgCl_2(c_2),\ AgCl \mid Ag$

$$e = -0.06791 \log \frac{f_2 b_2}{f_1 b_1}$$

Concentration of $MgCl_2$ (c_2)	Concentration of $MgCl_2$ (c_1)	E. M. F. in volt	
		Measured	Calculated
0.005	0.0025	−0.01899	−0.01948
0.0025	0.00125	−0.01983	−0.01989
0.00125	0.0006	—	−0.02016

From Tables 8, 9, 10 and 11, the differences between the measured E. M. F. and calculated ones are found 0.00018, 0.00012, 0.00004 and 0.00027 volt at lower molal solutions than 0.005 respectively. A larger value of difference than above will be found by using the more concentrated solution. In this investigation, it is very important to contact silver chloride with silver electrode.

E. M. F. of Cation Reversible cell with Amalgam Electrode. The cell used were of following type.

$$Me\text{-}Hg \mid MeCl_2(c_1) \mid MeCl_2(c_2) \mid Hg\text{-}Me$$

Preparation of amalgam was already mentioned. Prepared amalgam was carried into the acetone solution and shakened, then the amalgam was introduced into the cell which contained the electrolyte. Every measurement of the electromotive force of the cell was carried out after keeping it at 30°C. for about one hour. All equations in the following tables were obtained from the equation (15). The results are as follows.

Table 12.

E. M. F. of Cell: Zn-Hg | $ZnCl_2 (c_1)$ | $ZnCl_2 (c_2)$ | Hg-Zn

$$e = 0.02458 \log \frac{f_4 a_2}{f_3 a_1} .$$

Concentration of $ZnCl_2 (c_2)$	Concentration of $ZnCl_2 (c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	0.00600	0.00588
0.005	0.0025	0.00615	0.00607
0.0025	0.00125	0.00655	0.00638
0.00125	0.000625	0.00638	0.00632

Table 13.

E. M. F. of Cell: Ba-Hg | $BaCl_2 (c_1)$ | $BaCl_2 (c_2)$ | Hg-Ba

$$e = 0.028897 \log \frac{f_4 a_2}{f_3 a_1} .$$

Concentration of $BaCl_2 (c_2)$	Concentration of $BaCl_2 (c_1)$	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	0.00700	0.00691
0.005	0.0025	0.00725	0.00713
0.0025	0.00125	0.00731	0.00750
0.00125	0.000625	0.00728	0.00743

Table 14.

E. M. F. of Cell: $\text{Ca-Hg} \mid \text{CaCl}_2\,(c_1) \mid \text{CaCl}_2\,(c_2) \mid \text{Hg-Ca}$

$$e = 0.026343 \log \frac{f_4 a_2}{f_3 a_1}.$$

Concentration of $CaCl_2$ (c_2)	Concentration of $CaCl_2$ (c_1)	E. M. F. in volt	
		Measured	Calculated
0.01	0.005	0.00615	0.00630
0.005	0.0025	0.00639	0.00651
0.0025	0.00125	0.00675	0.00683
0.00125	0.000625	0.00664	0.00677

In these experiments, from Tables 12, 13 and 14, the differences between measured electromotive forces and calculated ones are found 0.00010, 0.00015 and 0.00011 volt at lower molal solutions than 0.005 molal respectively. It was found that amalgams have the disturbing effect in the presence of air. Therefore in these experiments, amalgam was introduced into the solution with keeping off from air.

Summary.

(1) The electromotive forces of the concentration cells with ternary electrolytes were studied by the three methods.

(a) At anion reversible cell with mercury electrode.
(b) At anion reversible cell with silver electrode.
(c) At the cation reversible cell with amalgam electrode.

(2) Several equations were theoretically obtained to calculate the electromotive forces of the cells above mentioned.

(3) Mobilities at 30°C. and activity coefficients of chlorine, zinc, calcium, barium, strontium and magnesium ions were calculated.

(4) We had a very good agreement between measured electromotive forces and calculated ones in the very dilute solutions.

Yokohama Higher Technical School.