

XIV. On the determination of chemical affinity in terms of electromotive force.—Part IX

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which I pointed out in 1880 is in any fair sense a refutation of my theory. Fresnel's theory of reflection cannot be fairly said to be refuted because it leaves unexplained the gradual change of phase of the components near the polarizing angle. All that is required in order to make my theory more complete is a little fearlessness as to complicated mathematics, which I regret to say either my laziness or my busyness prevents me from displaying, as it has till now prevented my noticing Prof. Kundt's paper.

I have roughly compared my formula with Prof. Kundt's results, and find that the calculated rotations are of the same order of magnitude as he has observed. As he does not give experiments on the rotations produced by reflection and transmission under exactly similar conditions, any comparison must of necessity be rough.

Yours obediently,

GEORGE FRANCIS FITZGERALD.

XIV. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part IX. By C. R. ALDER WRIGHT, D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics, and C. THOMPSON, F.C.S., Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

[Continued from p. 29.]

B. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Chlorides.*

I. Cadmium.

180. A number of cells were set up with amalgamated-zinc and electro-cadmium plates, and solutions of equal molecular strength, m MCl_2 100 H_2O , on each side, and examined precisely as before. The following average values were obtained, the probable error in each case being from $\pm \cdot 001$ to $\pm \cdot 002$ volt. The values of E_H annexed are calculated from the heat-valuations of Julius Thomsen, viz. Zn, Cl_2 aq. = 112840, and Cd, Cl_2 aq. = 96250, for molecular strength $\cdot 25$ MCl_2 100 H_2O ; so that the heat of displacement of cadmium by zinc from chloride solution m CdCl_2 100 H_2O is

$$112840 - h_1 - (96250 - h_2) = 16590 - (h_1 - h_2),$$

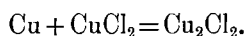
where h_1 and h_2 are the heats of dilution of zinc- and cadmium-chloride solutions respectively from the strength m MCl_2 100 H_2O to $\cdot 25$ MCl_2 100 H_2O : the values of h_1 and h_2 are derived from the table given in § 160, Part VIII.

Value of m .	E .	$16590 - (h_1 - h_2)$.	E .	$E - E_H$.
·25	·330	16590	·366	—·036
·5	·329	16190	·357	—·028
1·0	·324	15340	·338	—·014
2·0	·315	13890	·306	+·009
4·0	·307	12290	·271	+·036
6·0	·296	11390	·251	+·045
8·0	·262	10890	·240	+·022

It is here evident that whilst the voltaic constant for cadmium-zinc-chloride cells continually diminishes as the solution-strength increases, the value of E_H diminishes still more rapidly; so that the thermovoltaic constant is negative for weaker solutions and positive for stronger ones, the actual values of this constant being somewhat larger than those observed with zinc-cadmium-sulphate cells (§ 172), but still always under 5 centivolts. With the sulphate cells the values of the constant were opposite in sign, viz. positive for weaker, and negative for stronger solutions.

II. Copper.

181. On immersing a plate of clean metallic copper in a strong solution of cupric chloride, the plate speedily becomes visibly coated with a film of sparingly soluble cuprous chloride formed in virtue of the reaction



With weaker solution the actual deposition of cuprous chlorides in the solid state is not always noticeable, although its formation and presence are readily detected analytically. It is hence evident that any cell containing as one half a solution of cupric chloride and a copper plate must really contain as the electrolyte on this side a mixture of cuprous chloride with more or less cupric chloride, the film of fluid in immediate contact with the copper plate containing but little if any of the latter salt in solution. In point of fact, on examining a number of similar cells set up with electro-copper plates immersed in ·25 CuCl_2 100 H_2O on the one side and amalgamated-zinc plates immersed in ·25 ZnCl_2 100 H_2O on the other, values were obtained fluctuating between 1·083 and 1·106 volt; whilst another series of analogous values fluctuating between almost exactly the same limits, and averaging practically the same value, was obtained with a corresponding set of cells in which the copper plate was immersed, not in cupric-chloride solution alone to begin with, but in a magma

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of cuprous-chloride crystals suspended in $\cdot 25 \text{ CuCl}_2$ $100 \text{ H}_2\text{O}^*$.
The values of the two series of observations combined were as
follows :—

Maximum E.M.F.	1·106
Minimum „	1·083
Average „	1·0985
Probable error of average value . . .	$\pm \cdot 0018$

It is noticeable in this connection that precisely analogous results were obtained with other sets of cells, containing, on the one hand, cupric chloride alone, and on the other a magma of cuprous-chloride crystals and cupric chloride, when opposed to cadmium; whilst similarly various mercury cells gave substantially the same values whether pure metallic mercury and corrosive-sublimate solution were used, or mercury and a magma of calomel and corrosive-sublimate solution (§ 183).

It results from the above average value that the voltaic constant for electro-copper immersed in $\cdot 25 \text{ CuCl}_2$ $100 \text{ H}_2\text{O}$ (or, what is the same thing, a magma of this solution and crystals of cuprous chloride) is $+1\cdot 0985$, when referred to amalgamated zinc immersed in $\cdot 25 \text{ ZnCl}_2$ $100 \text{ H}_2\text{O}$ as zero. Sensibly the same value results as the sum of the E.M.F.'s of zinc-cadmium and cadmium-copper cells in solutions of strength $\cdot 25 \text{ MCl}_2$ $100 \text{ H}_2\text{O}$ throughout. With the latter cells the following numbers were obtained :—

Maximum	·778
Minimum	·756
Average	·769
Probable error	$\pm \cdot 0018$

Voltaic constant from Zinc-copper cells = $1\cdot 0985$

Do. from Zinc-cadmium + Cadmium-
copper cells } $\cdot 330 + \cdot 769 = 1\cdot 099$

Mean = $1\cdot 099$

The heat of displacement of copper from cuprous chloride by zinc with formation of $\cdot 25 \text{ ZnCl}_2$ $100 \text{ H}_2\text{O}$ results from Thomsen's values, thus :—

Zn, Cl_2 , aq.	112840
Cu $_2$, Cl_2	65750
	<hr/>
	47090 = $1\cdot 038$ volt.

* The cuprous chloride was prepared by boiling together copper-sulphate solution with common salt and spongy copper, filtering hot, and allowing cuprous chloride to crystallize out on cooling.

Whence the thermovoltaic constant for electro-copper in contact with cuprous chloride suspended in cupric-chloride solution of strength $\cdot 25 \text{ CuCl}_2 \text{ } 100 \text{ H}_2\text{O}$ is $1\cdot099 - 1\cdot038 = +\cdot061$.

The experiments detailed in § 174 indicated that when lead-sulphate was suspended in cadmium-sulphate solution a higher E.M.F. was observed, *cæteris paribus*, with zinc-lead-sulphate cells than when zinc-sulphate solution was employed; from which it would seem probable that, if cuprous chloride be suspended in zinc-, cadmium-, and copper-chloride solutions in three zinc-copper-chloride cells otherwise alike, the E.M.F. will be smallest in the first case and greatest in the last. This is in fact the case. The following values were obtained in a number of experiments on the point, indicating that the use of cadmium-chloride solution gives values intermediate between those obtained with zinc- and copper-chloride solutions respectively. The solutions were in all cases of strength $\cdot 25 \text{ MCl}_2 \text{ } 100 \text{ H}_2\text{O}$.

	Cu_2Cl_2 suspended in zinc chloride.	Cu_2Cl_2 suspended in cadmium chloride.
Maximum E.M.F. ...	$\cdot 993$	$1\cdot011$
Minimum „ ...	$\cdot 980$	$\cdot 993$
Average „ ...	$\cdot 988$	$1\cdot001$
Probable error	$\pm \cdot 0028$	$\pm \cdot 0035$

Hence the thermovoltaic constants for electro-copper in contact with cuprous chloride suspended in zinc- or cadmium-chloride solutions of strength $\cdot 25 \text{ MCl}_2 \text{ } 100 \text{ H}_2\text{O}$ are *negative* in sign, viz.:—

Suspended in zinc-chloride solution . $\cdot 988 - 1\cdot038 = -\cdot050$
 „ cadmium „ „ . $1\cdot001 - 1\cdot038 = -\cdot037$

It should hence result that cells set up with electro-cadmium immersed in $\cdot 25 \text{ CdCl}_2 \text{ } 100 \text{ H}_2\text{O}$ on the one side, and on the other side electro-copper immersed in a magma of cuprous chloride suspended in zinc-chloride solution of the same strength, will have an E.M.F. of $\cdot 672 - \cdot 050 - (-\cdot 036) = \cdot 658$; and, similarly, that analogous cells set up with cuprous chloride suspended in cadmium-chloride solution will have an E.M.F. of $\cdot 672 - \cdot 037 - (-\cdot 036) = \cdot 671$ ($\cdot 672$ being the E.M.F. corresponding with the heat of displacement of copper

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from cuprous chloride by cadmium = $96250 - 65750 = 30500$).
On setting up a number of such cells the following values
were obtained, the averages being sensibly identical with
those thus calculated :—

	Cu_2Cl_2 suspended in zinc chloride.	Cu_2Cl_2 suspended in cadmium chloride.
Maximum E.M.F.....	·667	·674
Minimum „	·654	·666
Average „	·659	·671
Probable error	± 0027	± 0016

It is noticeable in connection with these values, that whereas zinc-cadmium, cadmium-copper, and zinc-copper cells set up with sulphate solutions of various strengths possess E.M.F.'s. in no case differing by more than ± 010 volt from the values calculated from the difference between the heats of formation of the two electrolytes, the divergence between the two values is usually much greater when corresponding cells are set up with chloride solutions. Thus, for example :—

	Calculated.	Observed.	Difference.
Zinc-Cadmium ($\cdot 25 \text{MCl}_2$ $100 \text{H}_2\text{O}$) ...	·366	·330	— ·036
Do. (60MCl_2 $100 \text{H}_2\text{O}$)	·251	·296	+ ·045
Zinc-Copper (Cu_2Cl_2 in ZnCl_2)	1·038	·988	— ·050
Do. (Cu_2Cl_2 in CdCl_2)	1·038	1·001	— ·037
Do. (Cu_2Cl_2 in CuCl_2)	1·038	1·099	+ ·061
Cadmium-Copper (Cu_2Cl_2 in ZnCl_2)...	·672	·659	— ·013
Do. (Cu_2Cl_2 in CdCl_2) ...	·672	·671	— ·001
Do. (Cu_2Cl_2 in CuCl_2) ...	·672	·769	+ ·097

III. Silver.

182. A number of cells were set up with amalgamated-zinc and zinc-chloride solution on one side, and on the other side electro-silver immersed in a magma of freshly precipitated, well-washed silver chloride, suspended in zinc-chloride solution. The following values were finally obtained for cells where the zinc-chloride solution is of the same strength, $m \text{ZnCl}_2$ $100 \text{H}_2\text{O}$,

on each side. The probable error is in all cases below $\pm \cdot 003$.

The thermovoltaic constants for electro-silver thus immersed are calculated from the heat of displacement of silver from silver chloride by zinc forming $m\text{ZnCl}_2$ 100 H_2O , viz.:—

$$112840 - 58760 - h = 54080 - h;$$

where

$$112840 = \text{Zn, Cl}_2, \text{ aq. } (m = \cdot 25),$$

$$58760 = \text{Ag}_2, \text{ Cl}_2,$$

$$h = \text{heat of dilution of } m\text{ZnCl}_2 \text{ 100 H}_2\text{O to } \cdot 25 \text{ ZnCl}_2 \text{ 100 H}_2\text{O } (\S \text{ 160}).$$

m .	h .	$54080 - h$.	E_{H} .	E .	$E - E_{\text{H}}$.
$\cdot 25$	0	54080	1.192	1.080	$-\cdot 112$
$\cdot 5$	400	53680	1.184	1.068	$-\cdot 116$
1.0	1250	52830	1.165	1.049	$-\cdot 116$
3.0	3800	50280	1.109	1.026	$-\cdot 083$
6.0	5300	48780	1.076	1.014	$-\cdot 062$

Hence it results that both the voltaic and thermovoltaic constants diminish in value as the solutions become stronger; and that whilst the thermovoltaic value of silver in contact with silver chloride (suspended in zinc-chloride solution) is negative in sign as with the sulphate, its numerical value is considerably less than in that instance.

Some cells were next examined, containing on the one side electro-silver plates immersed in a magma of silver chloride suspended in zinc-chloride solution, and on the other side electro-copper or electro-cadmium in their respective chloride solutions, the solution-strength being $\cdot 25\text{MCl}_2$ 100 H_2O throughout. The following values were obtained, sensibly agreeing with the value $-\cdot 112$ for the thermovoltaic constant above obtained with zinc-silver-chloride cells for this molecular strength. It is to be noticed that the values of E_{H} with these two kinds of cells respectively are $\cdot 827$ and $\cdot 154$, corresponding with the heat-evolutions $96250 - 58760 = 37490$, and $65750 - 58760 = 6990$. In the former case $E_{\text{H}} + (k_1 - k_2)$ is positive in sign, in the latter case negative; so that the copper-silver cells are analogous to the zinc-cadmium-sulphate and

cadmium-iron-sulphate cells above described, in that the metal actually acquiring the higher potential is not the one predicable from the formation-heats of the electrolytes, but the other one—a result indicated by the — sign prefixed to the values of E.

	Cadmium-Silver.	Copper-Silver.
Maximum E.M.F. observed.....	·758	— ·017
Minimum „ „	·743	— ·025
Average „ „	·751	— ·020
Probable error	± ·0017	± ·0015
Value of thermovoltaic constant deduced from average observed E.M.F.	+ ·751	— ·020
	+ ·330	+ 1·099
	—	—
	+ 1·081	+ 1·079
	— 1·192	— 1·192
	— — — — — ·111	— — — — — ·113

The general average of the three values —·112, —·111, and —·113 thus obtained with zinc-silver, cadmium-silver, and copper-silver cells respectively is —·112, representing the thermovoltaic constant for electro-silver in contact with precipitated silver chloride suspended in zinc-chloride solution of strength ·25 ZnCl₂, 100 H₂O.

In precisely similar fashion six other kinds of cells were examined, containing respectively zinc in zinc-chloride, cadmium in cadmium-chloride, and copper in cupric-chloride solutions, opposed in one series to silver immersed in silver chloride suspended in cadmium-chloride solution, and in the other to silver immersed in silver chloride suspended in cupric-chloride solution, the solution-strength being ·25 MCl₂, 100 H₂O throughout. In the copper-silver cells, where the silver chloride was suspended in cadmium-chloride solution, the same peculiarity is observable as when suspended in zinc-chloride solution, viz. that the copper, and not the silver, acquires the higher potential; but where the silver chloride is suspended in cupric-chloride solution this is not the case, the silver here acquiring the higher potential, and the current flowing in the direction predicable from the heats of formation of the electrolytes, and not in the opposite direction. The following values were obtained :—

Silver Chloride suspended in Cadmium-Chloride Solution.			
	Zinc-Silver.	Cadmium-Silver.	Copper-Silver.
Maximum	1·091	·766	—·009
Minimum	1·082	·757	—·014
Average	1·088	·761	—·010
Probable error	± ·0010	± ·0010	± ·0012
Silver Chloride suspended in Cupric-Chloride Solution.			
Maximum	1·139	·809	+·038
Minimum	1·128	·806	+·031
Average	1·136	·807	+·035
Probable error	± ·0017	± ·0006	± ·0015

From these figures the following concordant values result for the thermovoltaic constants of electro-silver immersed in silver chloride suspended in cadmium and copper chlorides respectively :—

Silver Chloride suspended in Cadmium-Chloride Solution.			
	E.	E _H .	E—E _H .
Zinc-Silver cells.....	1·088	1·192	—·104
Cadmium-Silver+Zinc-Cadmium {	+ ·761	1·091	—·101
	+ ·330	1·192	—·101
Copper-Silver+Zinc-Copper ... {	+ 1·099	1·089	—·103
	— ·010	1·192	—·103
	Average 1·089		—·103
Silver Chloride suspended in Cupric-Chloride Solution.			
Zinc-Silver cells.....	1·139	1·192	—·053
Cadmium-Silver+Zinc-Cadmium {	+ ·807	1·137	—·055
	+ ·330	1·192	—·055
Copper-Silver+Zinc-Copper..... {	+ 1·099	1·134	—·058
	+ ·035	1·192	—·058
	Average 1·137		—·055

It is noticeable that suspending silver chloride in zinc-, cadmium-, or copper-chloride solution affects the E.M.F. of a cell in the same way as the use of the same fluids for the suspension of cuprous chloride (§ 181), viz. that the E.M.F. is lowest with zinc and highest with copper-chloride solution.

Since the E.M.F. of a zinc-silver-chloride cell continually diminishes as the solution-strength rises, just as with a Clark's cell (§ 179), it is evident that De-la-Rue and Müller's cell must possess an E.M.F. variable with the strength and nature of the solution used. A number of rods of pure silver chloride fused round strips of pure silver were obtained from Messrs. Johnson and Matthey, and set up opposed to zinc and cadmium in various solutions of their chlorides respectively. Variations of 4 to 5 centivolts were observed in the E.M.F. of such cells with different silver-chloride rods, everything else being the same, and the observations being made with the electrometer to avoid possible diminution in E.M.F. The average values found were slightly lower than those found with the same solution-strengths and precipitated silver chloride, as might perhaps be expected, inasmuch as the silver strips inside the fused rods were not electro-coated but were of bright metal, which has been found in the case of sulphate-cells to give lower values than electro-coated metal (§ 125).

	Zinc-Silver.		Cadmium-Silver.	
	$\cdot 25 \text{ Zn Cl}_2$ 100 H_2O .	$2 \cdot 0 \text{ Zn Cl}_2$ 100 H_2O .	$\cdot 25 \text{ Cd Cl}_2$ 100 H_2O .	$2 \cdot 0 \text{ Cd Cl}_2$ 100 H_2O .
Maximum	1·097	1·048	·776	·740
Minimum	1·058	·995	·726	·714
Average	1·075	1·020	·750	·730
Value with precipitated silver chloride	1·080	1·037	·761	...

IV. Mercury.

183. When metallic mercury and corrosive-sublimate solution are brought into contact, calomel is formed; so that by agitating the two together almost the whole of the metal and chlorine are removed from solution. Hence it is to be expected that the same peculiarity would apply to these cells as to copper cells (§ 181), viz. that much the same E.M.F. will be given whether mercury be in contact with corrosive-sublimate solution, or with a magma of calomel and corrosive-sublimate solution. In point of fact this is the case; cells set

up in the two ways with the mercury opposed to cadmium (or zinc) giving values as nearly identical as the considerably wide range of fluctuation in E.M.F. observed with different cells would permit to be deduced. In each case the values ranged between .89 and .95 volt (cadmium), and between 1.21 and 1.28 (zinc). Combining the two sets of cells, the following values were obtained, the solution being .25 MCl₂, 100 H₂O throughout.

	Zinc-Mercury.	Cadmium-Mercury.
Maximum	1.282	.948
Minimum	1.207	.892
Average	1.256	.929
Probable error ...	± .0056	± .0053

From these two values nearly the same voltaic constant is deduced for mercury in contact with mercuric-chloride solution (or with a magma of mercuric chloride suspended in mercuric-chloride solution) of strength .25 HgCl₂ 100 H₂O.

Zinc-mercury 1.256

Cadmium-mercury + Zinc-cadmium . $\left\{ \begin{array}{l} .929 \\ .330 \end{array} \right\} = 1.259$

Mean 1.257

Since Hg₂Cl₂=82550, the value of E_H corresponds with 112840—82550=30290 gramme-degrees for zinc-mercury-chloride cells, and with 96250—82550=13700 for cadmium-mercury-chloride cells, or .668 and .302 volt respectively; whence evidently both classes of cells resemble lead-copper-sulphate cells (§ 174) in actually giving rise to an E.M.F. greatly superior to that corresponding with the net chemical change. The thermovoltaic constant deduced from the above mean voltaic constant is 1.257—·668=+.589; so that mercury in this class of cells resembles iron, aluminium, and magnesium in their sulphate cells, possessing a large positive thermovoltaic constant.

Some observations were next made with cells containing calomel suspended in zinc-chloride solution in contact with mercury on one side, and amalgamated zinc immersed in the same zinc-chloride solution on the other side. Like the analogous zinc-silver-chloride, zinc-lead-sulphate, and zinc-mercury-sulphate cells above described, the E.M.F. of this combination was found to decrease as the solution-strength

rises. Thus the following numbers were obtained with solution-strengths $m\text{ZnCl}_2$ $100\text{H}_2\text{O}$, the probable error being from ± 0.002 to ± 0.003 in each case.

$m = .25$	1.123
$= 1.0$	1.093
$= 5.0$	1.043
$= 9.5$.988

From these values the following thermovoltaic constants result, the values of E_H being calculated from the heat-values $112840 - 82550 - h = 30290 - h$, where h is heat of dilution of $m\text{ZnCl}_2$ $100\text{H}_2\text{O}$ to $.25\text{ZnCl}_2$ $100\text{H}_2\text{O}$.

m .	h .	$30290 - h$.	E_H .	E .	$E - E_H$.
.25	0	30290	.668	1.123	+.455
1.0	1250	29040	.640	1.093	+.453
5.0	4800	25490	.562	1.043	+.481
9.5	6000	24290	.536	.988	+.452

Observations with cells containing electro-cadmium immersed in $.25\text{CdCl}_2$ $100\text{H}_2\text{O}$ opposed to mercury in contact with calomel suspended in zinc-chloride solution of the same strength led to nearly the same value for the thermovoltaic constant when $m = .25$:—

Maximum E.M.F. observed806
Minimum " "	.791
Average " "	.799
Probable error	$\pm .0030$

	Voltaic constant.	$E - E_H$.
Zinc-cadmium + Cadmium-mercury... $\left\{ \begin{smallmatrix} .799 \\ .330 \end{smallmatrix} \right\}$	$= 1.129$	+.461
Zinc-mercury cells.....	$= 1.123$	+.455
Mean	1.126	+.458

Substituting cadmium-chloride solution for zinc-chloride solution as the menstruum in which the calomel is suspended raises the value of E , as might be anticipated from various analogous results above described. Thus the following values were obtained with zinc-mercurous-chloride and cadmium-mercurous-chloride cells so set up, the amalgamated-zinc plates being surrounded by zinc-chloride, and the electro-cadmium plates employed with cadmium-chloride solution, the solution-strength being uniformly $.25\text{MCl}_2$ $100\text{H}_2\text{O}$.

	Zinc-Mercury.	Cadmium-Mercury.
Maximum E.M.F. observed.....	1·144	·815
Minimum „ „	1·137	·808
Average „ „	1·140	·812
Probable error	± ·0013	± ·0014

From these figures the following values result as the thermovoltic constant for mercury in contact with calomel suspended in ·25 CdCl₂ 100 H O₂ :—

	E.	E _H .	E—E _H .
Zinc-mercury	1·140	·668	+·472
Cadmium-mercury . { ·812 } .	1·142	·668	+·474
{ ·330 }			
Mean	1·141		+·473

From the values of the heats of formation of silver chloride and mercurous chloride respectively, it might, *à priori*, be expected that an E.M.F. of +·525 should result (corresponding with 82550—58760=23790 gramme-degrees) in silver-mercury-chloride cells, silver acquiring the higher potential. On the other hand, whether the silver chloride be suspended in zinc or cadmium-chloride solutions, and whether the mercurous chloride be similarly suspended, in all four cases the value of $k_1 - k_2$ is not only negative, but is numerically greater than $E_H = \cdot 525$; so that, in fine, the current flows in the opposite direction to that *à priori* predicable, the mercury acquiring the higher potential. Then the E.M.F. of the four kinds of silver-mercury-chloride cells are as follows :—

Calculated from formula $E = E_H + k_1 - k_2$.			Observed.		
AgCl suspended	Hg ₂ Cl ₂ suspended		Maximum.	Minimum.	Average.
in ZnCl ₂ ...	in ZnCl ₂ ...	·525 + (—·112) —·458 = —·045	—·040	—·051	—·046
Ditto ...	in CdCl ₂ ...	·525 + (—·112) —·473 = —·060	—·055	—·062	—·058
in CdCl ₂ ...	in ZnCl ₂ ...	·525 + (—·103) —·458 = —·036	—·034	—·041	—·038
Ditto ...	in CdCl ₂ ...	·525 + (—·103) —·473 = —·051	—·047	—·053	—·050

Considerably larger negative values were obtained with analogous cells in which mercurous chloride was suspended in mercuric-chloride solution instead of zinc or cadmium-chloride solution, as would naturally be inferred from the larger values of the thermovoltic constant in this case. The

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observed values ranged between $-.134$ and $-.187$, averaging
 $-.167$, that deduced as the above being $-.176$.

V. Lead.

184. A number of cells were examined, set up with electro-lead plates immersed in saturated lead-chloride solution, opposed (a) to amalgamated zinc in zinc-chloride solution; (b) to electro-cadmium in cadmium-chloride solution; (c) to electro-silver immersed in silver chloride suspended in zinc-chloride solution; the solution-strength being $.05 \text{ MCl}_2$, $100 \text{ H}_2\text{O}$ throughout. The following values were obtained:—

	Zinc-Lead.	Cadmium-Lead.	Lead-Silver.
Maximum	$.596$	$.268$	$.504$
Minimum	$.586$	$.248$	$.484$
Average	$.591$	$.260$	$.489$
Probable error ...	$\pm .0017$	$\pm .0023$	$\pm .0024$

These numbers give the following valuations for the voltaic constant of electro-lead in the lead-chloride solution:—

$$\begin{aligned}
 \text{Zinc-lead} & \dots\dots\dots = .591 \\
 * \text{Zinc-cadmium} + \text{Cadmium-lead} & .260 + .330 = .590 \\
 * \text{Zinc-silver} - \text{Silver-lead} & .1080 - .489 = .591 \\
 \text{Mean} & \dots\dots = .591
 \end{aligned}$$

Since $\text{Pb}, \text{Cl}_2 \text{ aq.} = 75970$, the value of E_H is $.813$ (corresponding with $112840 - 75970 = 36870$ gramme-degrees); whence the thermovoltaic constant for electro-lead in saturated lead-chloride solution is $.591 - .813 = -.222$.

It is noteworthy that whilst $k_1 - k_2$ is negative for both zinc-lead and cadmium-lead cells, so that their electromotive forces are notably below the values corresponding with the heat-evolution during the net chemical change, the reverse is the case for lead-silver cells: here the heat-evolution is $75970 - 58760 = 17210$ gramme-degrees, corresponding with $.379$ volt; whilst the actual E.M.F. is $.379 + (-.112) - (-.222) = .489$ volt (observed average = $.489$ volt). So that whilst lead-silver-sulphate cells give rise to electromotive

* The zinc-cadmium and zinc-silver values are assumed to be the same for the solution-strength used as those above found for somewhat stronger solutions $.25 \text{ MCl}_2$, $100 \text{ H}_2\text{O}$; the error thus introduced is but small, if not inappreciable.

forces considerably *below* the value of E_H pertaining to that class of cell, lead-silver-chloride cells possess electromotive forces considerably *above* the corresponding value of E_H .

On substituting lead-chloride solution for zinc-chloride solution as the medium in which silver chloride is suspended, but little change is produced in the E.M.F. Thus a number of lead-silver-chloride cells containing solution of strength $\cdot 25 \text{ PbCl}_2$, $100 \text{ H}_2\text{O}$ throughout gave values ranging from $\cdot 453$ to $\cdot 522$ volt, and averaging near to $\cdot 480$.

Some lead-copper-chloride cells were examined; but for some unknown reason they failed to give concordant results, the observed E.M.F. always falling short of that deduced from the voltaic constants for lead and copper in chloride-solution (viz. $1\cdot 099 - \cdot 591 = \cdot 508$). In some cases the falling off was small; in others it exceeded $\cdot 050$: these cells, moreover, exhibited no constancy even for half an hour after setting up, the E.M.F. rapidly falling as time elapsed. In all cases, however, higher electromotive forces were observed than correspond with the difference between $\text{Pb, Cl}_2 \text{ aq.} = 75970$ and $\text{Cu}_2, \text{Cl}_2 = 65750$, viz. 10220 gramme-degree $= \cdot 225$ volt.

On the other hand, numbers closely agreeing with those calculated from the above-described thermovoltaic constants were obtained with cells set up with electro-lead immersed in lead-chloride opposed to mercury in contact with mercurous chloride suspended in zinc- or cadmium-chloride solution, the strength being $\cdot 25 \text{ MCl}_2$, $100 \text{ H}_2\text{O}$ throughout. The value of E_H in these cells is $+ \cdot 145$ volt, corresponding with $82550 - 75970 = 6580$ gramme-degrees, the metal giving the smaller heat-value, and consequently acquiring the higher potential in consequence of the chemical action, being lead. Since, however, the thermovoltaic constant for lead is $-\cdot 222$, and that for mercury in contact with mercurous chloride suspended in zinc-chloride solution $+ \cdot 458$, and when suspended in cadmium-chloride solution $+ \cdot 473$, the value of $k_1 - k_2$ is in each case largely negative, and considerably greater numerically than E_H . Hence the calculated electromotive forces for the two cells are respectively $\cdot 145 + (-\cdot 222) - \cdot 458 = -\cdot 535$, and $\cdot 145 + (-\cdot 222) - \cdot 473 = -\cdot 550$ volt. The observed values were $-\cdot 539$ and $-\cdot 549$ respectively, *i. e.* electromotive forces of $\cdot 539$ and $\cdot 550$ volt were observed, the mercury, and not the lead, acquiring the higher potential. These cells are remarkable not only for the large negative values of $k_1 - k_2$, but also for the high negative values of $E_H + k_1 - k_2$, exceeding in this respect all other cells examined with the exception of zinc-aluminium-sulphate cells (§ 178), which gave the numerical value $\cdot 537$.

VI. *Magnesium.*

185. A series of cells was set up containing bright magnesium (wire) opposed to amalgamated zinc and electro-cadmium in their respective chloride-solutions, the strength being uniformly $\cdot 25 \text{ MCl}_2$ $100 \text{ H}_2 \text{ O}$. The values exhibited much greater fluctuations as time elapsed than were observed with most of the other cells examined; whilst the mean readings during the first half-hour after setting up also showed much less concordance, as the following figures show. As with the sulphate-cells (§ 177), magnesium acquired the lower potential when opposed to zinc, and *à fortiori* when opposed to cadmium.

	Magnesium-Zinc.	Magnesium-Cadmium.
Maximum	·771	1·101
Minimum	·636	·966
Average	·702	1·030
Probable error ...	$\pm \cdot 012$	$\pm \cdot 012$

Hence the following valuations of the voltaic constant result, these values necessarily being negative, as with the sulphate-cells:—

Zinc-magnesium cell $-\cdot 702$

Cadmium-magnesium—Zinc-cadmium $\left\{ \begin{array}{l} -1\cdot 030 \\ + \cdot 330 \end{array} \right\} -\cdot 700$

Mean . . . $-\cdot 701$

Julius Thomsen finds $\text{Mg, Cl, aq.} = 186930$ for solution of strength $\cdot 25 \text{ MgCl}_2$ $100 \text{ H}_2 \text{ O}$; whence $E_H = -1\cdot 634$. Consequently the thermovoltic constant for bright magnesium in contact with chloride solution of this strength is

$$-\cdot 701 - (-1\cdot 634) = +\cdot 933,$$

or, approximately, the same large positive quantity as that found with sulphate solutions.

VII. *Aluminium.*

186. In precisely the same way were two series of observations made with cells containing plates of bright aluminium opposed to amalgamated zinc and electro-cadmium immersed in solutions of their chlorides respectively, the solution-strength being $\cdot 25 \text{ Al}_3 \text{ Cl}_2$ $100 \text{ H}_2 \text{ O}^*$, and equivalent amounts

* The aluminium-chloride solution was prepared by saturating dilute hydrochloric acid with recently precipitated well-washed aluminium hydroxide.

throughout. As with the magnesium cells, the values fluctuated considerably, so that the final averages had much larger probable errors than usual.

	Zinc-Aluminium.	Aluminium-Cadmium.
Maximum	-.239	+.091
Minimum	-.352	-.022
Average	-.280	+.050
Probable error	±.011	±.011

Each of these averages leads to the same value, +.280, for this voltaic constant.

$$\begin{array}{rcl}
 \text{Zinc-aluminium} & . & +.280 \\
 \text{Zinc-cadmium} - \text{Aluminium-cadmium} & \left\{ \begin{array}{l} +.330 \\ -.050 \end{array} \right\} & +.280 \\
 \text{Mean} & . & +.280
 \end{array}$$

This constant being of + sign, since aluminium was found to acquire the higher and zinc the lower potential (as with the sulphate-cells, § 178); whilst, on the other hand, the readings observed with the zinc-aluminium cells are marked - above because this cell is another example of the case where $E_H + k_1 - k_2$ has a negative value, the current actually set up passing in the direction opposite to that predicable from the heats of formation of the electrolytes.

Julius Thomsen finds $\text{Al}_3, \text{Cl}_2 \text{ aq.} = 158550$, whence $E_H = -1.008$; consequently

$$E - E_H = +.280 - (-1.008) = +1.288;$$

i. e. the thermovoltaic constant for bright aluminium in contact with its chloride solution is a large positive quantity, as with the sulphate.

VIII. Iron.

187. Cells were set up containing plates of nearly pure sheet-iron (bright) opposed to amalgamated zinc and electro-cadmium in solution of constant strength .25 MCl_2 100 H_2O ; also to electro-silver immersed in a magma of precipitated silver-chloride suspended in zinc-chloride solution of this same strength. The following numbers were obtained as the average readings during the first half-hour after setting up.

	Zinc-Iron.	Cadmium-Iron.	Silver-Iron.
Maximum	·497	—·154	·597
Minimum	·483	—·167	·583
Average	·490	—·157	·592
Probable error ...	±·0030	±·0027	±·0033

Hence the following three valuations for the voltaic constant result; the values with the cadmium-iron cell being marked —, since in this case (as with the corresponding sulphate cells, § 175) iron, and not cadmium, actually acquires the higher potential.

Zinc-iron ·490

Zinc-cadmium—Cadmium-iron $\cdot \left\{ \begin{array}{l} \cdot 330 \\ + \cdot 157 \end{array} \right\} = \cdot 487$

Zinc-silver—Iron-silver $\cdot \left\{ \begin{array}{l} 1\cdot 080 \\ - \cdot 592 \end{array} \right\} = \cdot 488$

Mean . . . ·488

Julius Thomsen finds $\text{Fe}, \text{Cl}_2 \text{ aq.} = 99950$ for $\cdot 25 \text{FeCl}_2$, $100\text{H}_2\text{O}$; whence $E_H = \cdot 284$. Hence the thermovoltic constant for bright metallic iron in ferrous-chloride solution of this strength is

$$E - E_H = \cdot 488 - \cdot 284 = + \cdot 204;$$

i. e. it is a considerable *positive* quantity, as in the case of the sulphate-cells.

It is noticeable that whilst with silver-iron cells the value of $k_1 - k_2$ is negative, so that E is considerably less than E_H , the opposite holds with zinc-iron cells, the $E.M.F.$ actually set up being not much below double that corresponding with the net heat-development in the cell.

C. Voltaic and Thermovoltic Constants of Metals immersed in Solutions of their Nitrates.

I. Copper.

188. A number of cells were set up with amalgamated-zinc and electro-copper plates, and solutions of the nitrates of the respective metals prepared by dissolving pure metals in nitric acid, and saturating any excess of acid by means of the metallic carbonate freshly precipitated from a portion of the respective solution, and well washed. The following values were obtained as the mean readings during the first twenty

minutes after setting up. The readings during this period did not always exhibit constancy, especially with the weaker solutions; but the extreme alteration usually only amounted to a few millivolts, concurrently with a visible alteration in the surfaces of the plates. Strength of solutions, $mM(NO_3)_2$ 100 H_2O .

	$m=.25$.	$m=1.0$.	$m=2.0$.	$m=8.0$.
Maximum	1.087	1.104	1.112	1.095
Minimum	1.053	1.073	1.108	1.087
Average	1.066	1.089	1.109	1.091
Probable error ...	$\pm .0035$	$\pm .0034$	$\pm .0005$	$\pm .0009$

These figures correspond with the following thermovoltaic constants, the values of E_H being deduced from the experiments of Julius Thomsen, including his valuations of the heats of dilution of zinc- and copper-nitrate solutions. The difference between the heats of formation of $mM(NO_3)_2$ 100 H_2O are given by the formula

$$102510 - h_1 - (52410 - h_2) = 50100 - (h_1 - h_2),$$

where Zn, O, N_2O_5 aq. = 102510, and Cu, O, N_2O_5 aq. = 52410 for solution-strengths $.25 M(NO_3)_2$, 100 H_2O ; whilst h_1 and h_2 are the heats of dilution of solutions of zinc and copper nitrate respectively from the strength $mM(NO_3)_2$ 100 H_2O to $.25 M(NO_3)_2$ 100 H_2O .

m .	h_1 .	h_2 .	$50100 - (h_1 - h_2)$.	E_H .	E .	$E - E_H$.
.25	0	0	50100	1.105	1.066	-.039
1.0	- 40	- 47	50093	1.105	1.089	-.016
2.0	- 132	- 175	50057	1.104	1.109	+.005
8.0	+ 439	+ 214	49875	1.100	1.091	-.009

It is here noticeable that the thermovoltaic constant for electro-copper in nitrate solution has in no case any large value; whilst of negative sign for low-solution strengths, it becomes positive for stronger fluids, and again negative with highly concentrated solutions, following the variations in the voltaic constant, which has a maximum value for fluids of medium strength.

II. Cadmium.

189. Cells were set up with electro-cadmium plates immersed in cadmium-nitrate solution, opposed on the one hand to electro-copper, and on the other to amalgamated zinc immersed in solutions of their nitrates respectively, the constant solution-strength being $\cdot 25 \text{ M}(\text{NO}_3)_2$ 100 H_2O . The following values were obtained :—

	Zinc-Cadmium.	Cadmium-Copper.
Maximum	$\cdot 359$	$\cdot 722$
Minimum	$\cdot 344$	$\cdot 707$
Average	$\cdot 351$	$\cdot 713$
Probable error ...	$\pm \cdot 0026$	$\pm \cdot 0024$

From these figures the following valuations result for the voltaic constant of cadmium in nitrate solution $\cdot 25 \text{ Cd}(\text{NO}_3)_2$ 100 H_2O :—

Zinc-cadmium	$\cdot 351$
Zinc-copper—Cadmium-copper	$1\cdot 066 - \cdot 713 = \cdot 353$
Mean	$= \cdot 352$

Julius Thomsen finds Cd , O , N_2O_5 aq. = 86300 (for $\cdot 25 \text{ Cd}(\text{NO}_3)_2$ 100 H_2O), whence $E_{\text{H}} = \cdot 357$. Hence the thermovoltic constant for electro-cadmium in nitrate solution of this strength is

$$E - E_{\text{H}} = \cdot 352 - \cdot 357 = -\cdot 005.$$

It is here noticeable that the value of the thermovoltic constant is negative, as in the case of chloride solution of corresponding strength, whereas it is positive in the case of sulphate solution of the same strength; but in no case is the numerical value of the constant large.

III. Lead.

190. Cells containing electro-lead opposed to amalgamated zinc and electro-copper in nitrate solution of strength $m\text{M}(\text{NO}_3)_2$ 100 H_2O gave the following average values, the probable error in no case exceeding $\pm \cdot 004$, and being usually considerably less :—

	$m = \cdot 25$.	$m = 1\cdot 0$.	$m = 2\cdot 0$.
Zinc-Lead	$\cdot 580$	$\cdot 588$	$\cdot 591$
Lead-Copper ...	$\cdot 486$	$\cdot 501$	$\cdot 519$

These two sets of figures lead to practically identical valuations of the voltaic constant:—

	$m = \cdot 25$.	$m = 1\cdot 0$.	$m = 2\cdot 0$.
Zinc-Lead	·580	·588	·591
Zinc-Copper—Copper-Lead	$\left\{ \begin{array}{l} 1\cdot 066 \\ \cdot 486 \end{array} \right\}$ ·580	$\left\{ \begin{array}{l} 1\cdot 089 \\ \cdot 501 \end{array} \right\}$ ·588	$\left\{ \begin{array}{l} 1\cdot 109 \\ \cdot 590 \end{array} \right\}$ ·590
Mean	·580	·588	·591

Taking the valuations of Julius Thomsen, including his determinations of the heats of dilution of zinc- and lead-nitrate solution, h_1 and h_2 respectively, the following values result for E_H , the value of Pb, O, N_2O_5 aq. being 68070 for $\cdot 25$ Pb(NO_3)₂ 100 H₂O:—

m .	h_1 .	h_2 .	H.	E_H .	E.	$E - E_H$.
·25	0	0	34440	·759	·580	—·179
1·0	— 40	—1274	33206	·732	·588	—·144
2·0	—132	—2092	32462	·716	·591	—·125

Hence the thermovoltaic constant for electro-lead in nitrate solution is always negative (as with sulphate and chloride); the numerical value, however, decreases with increasing solution-strength, whilst the opposite is the case with lead sulphate, whether suspended in zinc- or in cadmium-sulphate solution.

Lead-copper-nitrate cells resemble lead-copper-sulphate cells in that they give an E.M.F. notably above that calculable from the net heat-evolution taking place in the cell due to the chemical change. Similarly zinc-lead-nitrate cells resemble zinc-lead-sulphate cells in giving values below those thus calculable.

IV. Silver.

191. The following mean values were obtained with cells set up with electro-silver plates opposed to amalgamated zinc, electro-copper, and electro-lead in nitrate solutions of strength $mM(NO_3)_2$, 100 H₂O (the probable error ranged from $\pm \cdot 002$ to $\pm \cdot 004$ throughout):—

m .	Zinc-Silver.	Copper-Silver.	Lead-Silver.
·25	1·495	·429	·914
1·0	1·540	·450	·951
2·0	1·556	·446	·965

From these figures sensibly identical values result for the voltaic constant of electro-silver in nitrate solution:—

	$m=.25$.	$m=1.0$.	$m=2.0$.
Zinc-silver	1.495	1.540	1.556
Zinc-Copper + Copper-Silver	$\left\{ \begin{array}{l} 1.066 \\ .429 \end{array} \right.$ 1.495	$\left\{ \begin{array}{l} 1.089 \\ .450 \end{array} \right.$ 1.539	$\left\{ \begin{array}{l} 1.109 \\ .446 \end{array} \right.$ 1.555
Zinc-Lead + Lead-Silver	$\left\{ \begin{array}{l} .580 \\ .914 \end{array} \right.$ 1.494	$\left\{ \begin{array}{l} .588 \\ .951 \end{array} \right.$ 1.539	$\left\{ \begin{array}{l} .591 \\ .965 \end{array} \right.$ 1.556
Mean ...	1.495	1.539	1.556

The heats of dilution of silver-nitrate solutions being as yet undetermined, the value of E_H can only be exactly calculated for the strength $.25 \text{ Ag}_2(\text{NO}_3)_2$ 100 H_2O . The subjoined values for the higher strengths are calculated on the supposition that the heat of dilution of silver- and zinc-nitrate solutions is the same; so that E_H remains the same for all solution-strengths Ag_2 , O , N_2O_5 aq. = 16780.

m .	E .	E_H .	$E - E_H$.
.25	1.495	1.890	-.395
1.0	1.539	1.890	-.351
2.0	1.556	1.890	-.334

Hence the thermovoltaic constant for silver in nitrate solution is not widely different from that in sulphate solution, being in each case far greater than that for silver in contact with silver chloride, whether suspended in zinc cadmium or cupric-chloride solution. With all three kinds of silver salt, however, under all circumstances, the value is negative in sign.

V. Mercury.

192. Mercuric-nitrate solution, like mercuric chloride, becomes rapidly and completely converted into mercurous salt by agitation with mercury. In order to prepare mercurous nitrate with but little excess of acid, mercury was dissolved in nitric acid, and the crystallized mass washed on the filter-pump with a little water, and then well agitated with water and mercury. The solution thus obtained was free from

mercuric nitrate, and contained free nitric acid to an amount representing almost exactly one eighth of that present as mercurous nitrate, and was finally made of strength $\cdot 25 \text{ Hg}_2(\text{NO}_3)_2$, $\cdot 03 \text{ H}_2(\text{NO}_3)_2$ $100 \text{ H}_2\text{O}$. On setting up cells with pure mercury and this fluid, opposed to amalgamated zinc, electro-copper, electro-lead, and electro-silver respectively in contact with solutions of their nitrates of constant strength $\cdot 25 \text{ M}(\text{NO}_3)_2$ $100 \text{ H}_2\text{O}$, the following values were obtained. It is noticeable that with the last cell the current sometimes passed from mercury to silver and sometimes in the opposite direction, the average E.M.F. being negative,—*i. e.* mercury, and not silver, acquiring the higher potential, contrary to the result predicable from the relative heats of formation of mercurous and silver nitrates (*viz.* 47990 and 16780 respectively—Julius Thomsen), which corresponds with an E.M.F. of $\cdot 688$ volt, silver acquiring the higher potential. The probable error amounted to $\pm \cdot 003$ to $\pm \cdot 004$ in each instance.

	Maximum.	Minimum.	Average.
Zinc-Mercury	1·535	1·476	1·500
Copper-Mercury	·470	·410	·433
Lead-Mercury	·944	·896	·917
Silver-Mercury	−·041	+·019	−·004

Practically identical values for the voltaic constant for mercury in contact with mercurous-nitrate solution result in all four cases:—

$$\begin{array}{lcl}
 \text{Zinc-mercury} & . & 1\cdot500 \\
 \text{Zinc-copper + Copper-mercury} & \left\{ \begin{array}{l} 1\cdot066 \\ \cdot433 \end{array} \right\} & = 1\cdot499 \\
 \text{Zinc-lead + Lead-mercury} & \left\{ \begin{array}{l} \cdot917 \\ \cdot580 \end{array} \right\} & = 1\cdot497 \\
 \text{Zinc-silver — Mercury-silver} & \left\{ \begin{array}{l} 1\cdot495 \\ +\cdot004 \end{array} \right\} & = 1\cdot499 \\
 \text{Mean} & . & = 1\cdot499
 \end{array}$$

The average value is thus but slightly below that found for mercury in contact with mercurous sulphate suspended in weak zinc sulphate, *viz.* 1·514 (§ 179).

Since E_H represents a distinctly less amount (1·202 volt), it results that $E - E_H = 1\cdot499 - 1\cdot202 = +\cdot297$; *i. e.* the thermovoltaic constant for mercury in contact with mercurous-

nitrate solutions is a considerable + number, as found in the chloride-cells.

It hence follows that the E.M.F. actually set up in zinc-mercury, copper-mercury, and lead-mercury nitrate-cells is in excess of that corresponding with the difference between the heats of formation of the electrolytes in each case respectively, the excess amounts being $+ \cdot 297$, $+ \cdot 297 - (- \cdot 039) = + \cdot 336$, and $+ \cdot 298 - (- \cdot 179) = + \cdot 477$ respectively.

VI. *Magnesium.*

193. Two sets of cells were examined containing bright magnesium (wire), opposed to amalgamated zinc and electro-cadmium respectively, in solutions of constant strength $\cdot 25 \text{ M}(\text{NO}_3)_2$ $100 \text{ H}_2\text{O}$. The following values were obtained, the readings exhibiting the same kinds of fluctuations as those previously found with magnesium sulphate and chloride cells.

	Magnesium-Zinc.	Magnesium-Copper.
Maximum	$\cdot 570$	$1 \cdot 636$
Minimum	$\cdot 503$	$1 \cdot 569$
Average	$\cdot 531$	$1 \cdot 595$
Probable error	$\pm \cdot 011$	$\pm \cdot 011$

These two sets of readings lead to sensibly the same values for the voltaic constant, which is negative (as with the sulphate and chloride cells), since zinc now acquires the higher potential.

Zinc-magnesium $- \cdot 531$

Copper-magnesium $\left\{ \begin{array}{l} -1 \cdot 595 \\ +1 \cdot 066 \end{array} \right\} - \cdot 529$

Mean $- \cdot 530$

From Julius Thomsen's figures, the heat of formation of magnesium-nitrate solution, $\cdot 25 \text{ Mg}(\text{NO}_3)_2$ $100 \text{ H}_2\text{O}$, is 176480 , whence $E_H = -1 \cdot 631$. Hence the thermovoltaic constant is

$$- \cdot 530 - (-1 \cdot 630) = +1 \cdot 101,$$

or positive to a great extent, as with the other magnesium-cells.

[To be continued.]