



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

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XXII. *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*.

[Concluded from p. 124.]

D. *Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Acetates.*

I. *Copper.*

194. A NUMBER of cells were set up with amalgamated-zinc and electro-copper plates immersed in solutions of their respective acetates, the constant molecular strength being $\cdot 25 \text{ M}(\text{C}_2\text{H}_3\text{O}_2)_2 \text{ H}_2\text{O}$ *. The following values were obtained :—

Maximum	1·104
Minimum	1·073
Average	1·091
Probable error	·0029

Julius Thomsen's thermochemical data lead to the values $\text{Zn, O, } 2\text{C}_2\text{H}_4\text{O}_2\text{aq.} = 100710$, and $\text{Cu, O, } 2\text{C}_2\text{H}_4\text{O}_2\text{aq.} = 50340$; whence $E_{\text{H}} = 1\cdot111$, corresponding with 50370 grammes-degrees. Hence $E - E_{\text{H}} = -\cdot020$ for electro-copper in contact with copper-acetate solution of strength $\cdot 25 \text{ Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ 100 H_2O .

II. *Lead.*

195. Two series of cells set up with electro-lead opposed to amalgamated zinc and electro copper respectively, with acetate solutions uniformly of strength $\cdot 25 \text{ M}(\text{C}_2\text{H}_3\text{O}_2)_2$ 100 H_2O , gave the following results ; the differences observed between the values obtained for different cells set up in the same way being notably greater than with most of the other combinations examined :—

	Zinc-Lead.	Lead-Copper.
Maximum	·616	·503
Minimum	·587	·471
Average	·608	·485
Probable error	$\pm \cdot 0048$	$\pm \cdot 0044$

* The acetate solutions employed were prepared by dissolving the freshly-precipitated, well-washed carbonates of the metals in boiling dilute acetic acid somewhat stronger than that required, filtering after cooling, and diluting to the proper extent.

From these average values the following valuations result for the voltaic constant for lead in acetate solution of strength $\cdot 25 \text{ Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ 100 H_2O :—

Zinc-lead	$\cdot 608$
Zinc-copper—Copper-lead	$\left\{ \begin{array}{l} 1\cdot 091 \\ -\cdot 485 \end{array} \right\} = \cdot 606$
Mean	$\cdot 607$

Hence, since Thomsen finds that Pb , O , $2\text{C}_2\text{H}_3\text{O}_2 \text{ aq.} = 65770$, the value of E_{H} is $\cdot 770$, corresponding with 34940 gramme-degrees, whence

$$E - E_{\text{H}} = -\cdot 163 ;$$

i. e. the thermovoltaic constant for lead in acetate solution is negative, and of nearly the same magnitude as in nitrate solution, or in contact with lead sulphate suspended in zinc or cadmium-sulphate solution of corresponding strength, $\cdot 25 \text{ PbX}$ 100 H_2O . In consequence the actual E.M.F. of a lead-copper-acetate cell *exceeds* that due to the net chemical change taking place therein, just as in lead-copper-sulphate and lead-copper-nitrate cells.

Some observations were made on the rate of depreciation in E.M.F. with increasing current-density in zinc-lead-acetate cells, with the result of showing that the average rate of fall is indicated by a curve lying between the analogous curves obtained with zinc-silver-sulphate and iron-copper-sulphate cells (§§ 130 and 176), being below the former and above the latter, which, as already shown, overlie the analogous curves obtained with zinc-copper-sulphate and zinc-cadmium-sulphate cells. It is remarkable, in this connection, that the thermovoltaic constants for the metals silver, lead, iron, copper, and cadmium in these solutions respectively follow in the same order as regards numerical magnitude, though not as regards sign:—

Silver (in sulphate solution) . . .	$\div \cdot 351$
Lead (in acetate solution) . . .	$-\cdot 163$
Iron (in sulphate solution) . . .	$+\cdot 113$ to $+\cdot 148$
Copper (in sulphate solution) . . .	$+\cdot 009$
Cadmium (in sulphate solution) . . .	$+\cdot 005$ to $-\cdot 010$

III. Silver.

196. The following values were obtained with cells containing electro-silver immersed in saturated silver-acetate solution opposed to amalgamated zinc and electro-copper immersed in their respective acetate solutions, the constant strength being $\cdot 057 \text{ M}(\text{C}_2\text{H}_3\text{O}_2)_2$ 100 H_2O :—

trace out whether the different halogen salts exhibit analogy with these oxygen-acid salts, or whether they differ materially amongst themselves, a number of cells were examined containing various metals immersed in solutions of their respective bromides of constant strength $\cdot 25 \text{MBr}_2$ 100 H_2O , or in magmas of their bromides immersed in zinc-bromide solution of this strength (saving in the case of lead bromide, where the sparing solubility necessitated the use of weaker solutions).

I. Cadmium.

The following values were obtained with zinc-cadmium-bromide cells:—

Maximum	$\cdot 319$
Minimum	$\cdot 311$
Average	$\cdot 315$
Probable error	$\pm \cdot 0014$

Julius Thomsen finds the values $\text{Zn}, \text{Br}_2 \text{ aq.} = 90960$, and $\text{Cd}, \text{Br}_2 \text{ aq.} = 75640$; whence $E_{\text{H}} = \cdot 338$, corresponding with 15320 gramme-degrees. Hence

$$E - E_{\text{H}} = -\cdot 023 ;$$

that is, the thermovoltaic constant for electro-cadmium in bromide solution of strength $\cdot 25 \text{CdBr}_2$ 100 H_2O is a small negative quantity, not quite so large numerically as that for the corresponding chloride solution (viz. $-\cdot 036$).

II. Silver.

198. The following values were obtained with cells set up with amalgamated zinc opposed to electro-silver immersed in a magma of freshly precipitated well-washed silver bromide suspended in zinc-bromide solution, the solution-strength throughout being $\cdot 25 \text{ZnBr}_2$ 100 H_2O .

Maximum	$\cdot 909$
Minimum	$\cdot 901$
Average	$\cdot 906$
Probable error	$\pm \cdot 0012$

Julius Thomsen finds $\text{Ag}_2, \text{Br}_2 = 45400$; whence $E_{\text{H}} = 1\cdot 005$, corresponding with 45560 gramme-degrees. Hence

$$E - E_{\text{H}} = -\cdot 099 ;$$

that is, the thermovoltaic constant for silver in contact with silver bromide suspended in zinc-bromide solution is a notable negative quantity, slightly less numerically than the corresponding value for silver chloride suspended in equally strong zinc-chloride solution (viz. -112).

silver in contact with a magma of silver bromide suspended in zinc-bromide solution, the solution-strength being $\cdot 25 \text{ ZnBr}_2$ 100 H_2O throughout. The following values were obtained, the current passing, in the latter case, in the direction opposite to that predicable from the relative heats of formation of mercurous and silver bromides :—

	Zinc-Mercury.	Mercury-Silver.
Maximum	·974	—·062
Minimum	·969	—·073
Average	·972	—·066
Probable error	$\pm \cdot 0006$	$\pm \cdot 0019$

These figures lead to the following valuations for the voltaic constant of mercury in contact with mercurous bromide suspended in $\cdot 25 \text{ ZnBr}_2$ 100 H_2O :—

Zinc-mercury ·972

Zinc-silver—Mercury-silver . . $\left\{ \begin{array}{l} \cdot 906 \\ + \cdot 066 \end{array} \right\} = \cdot 972$

Mean $\overline{\cdot 972}$

Julius Thomsen finds $\text{Hg}_2, \text{Br}_2 = 68290$; whence $E_{\text{H}} = 500$ volt, corresponding with 22670 gramme-degrees. Hence

$$E - E_{\text{H}} = + \cdot 472 ;$$

that is, the thermovoltaic constant for mercury in contact with this bromide magma is a large positive quantity, somewhat greater than that observed with the corresponding chloride magma, viz. $+ \cdot 458$.

It is noticeable that the heat of formation of mercurous bromide exceeds that of lead-bromide solution ($\text{Hg}_2, \text{Br}_2 = 68290$, $\text{Pb}, \text{Br}_2 \text{ aq.} = 54410$, difference 13880, corresponding with $\cdot 306$ volt); whilst the value of $k_1 - k_2$ for lead-mercury-bromide cells is

$$- \cdot 235 - (+ \cdot 472) = - \cdot 707 ;$$

so that $E_{\text{H}} + k_1 - k_2$ is negative relatively to E_{H} , being $= - \cdot 401$. On examining various such cells (solution-strength $= \cdot 037 \text{ MBr}_2$ 100 H_2O), the E.M.F. was found to be actually of negative sign, the average observed value being $- \cdot 402$.

V. Iron.

201. A series of cells was examined containing plates of nearly pure sheet iron (bright) opposed to amalgamated zinc

	Zinc-Iron.	Iron-Cadmium.
Maximum	·441	—·086
Minimum	·401	—·126
Average	·417	—·103
Probable error	±·005	±·005

These numbers lead to the following valuations for the voltaic constant for bright iron in solution of strength $\cdot 25 \text{ FeBr}_2$ 100 H_2O :—

Julius Thomsen finds $\text{Fe, Br}_2 \text{ aq.} = 78070$; whence $E_H = .284$ volt, corresponding with 12890 gramme-degrees. Hence

i. e. the thermovoltaic constant is a notable positive quantity, less, however, in magnitude than the corresponding value for ferrous-chloride solution of the same strength, viz. +.204.

202. A number of cells were set up with bright aluminium plates opposed to amalgamated zinc and electro-cadmium, immersed in their respective bromide solutions of strength $\cdot 25 \text{ MBr}_2 \cdot 100 \text{ H}_2\text{O}$. The readings exhibited the same fluctuations as were observed with the sulphate and chloride cells previously examined (§ 178 and § 186). The following readings were obtained, the current passing in the opposite direction to that calculable from the relative heats of forma-

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tion of zinc- and aluminium-bromide solutions in the first
case, but in the normal direction in the second case :—

	Zinc-Aluminium.	Cadmium-Aluminium.
Maximum	—·323	+·037
Minimum	—·278	+·013
Average	—·296	+·022
Probable error	±·007	±·005

These numbers lead to the following valuations for the
voltaic constant for bright aluminium in bromide solution
·25 Al₃Br₂ 100 H₂O :—

$$\begin{array}{rcl} \text{Zinc-aluminium} & . & +\cdot296 \\ \text{Zinc-cadmium} - \text{Aluminium-cadmium} & \left\{ \begin{array}{l} \cdot315 \\ -\cdot022 \end{array} \right\} & = +\cdot293 \\ \text{Mean} & . & +\cdot295 \end{array}$$

the constant being of + sign, since aluminium actually
acquires the higher potential, although it might *a priori* be
expected to acquire the lower potential.

Julius Thomsen's thermochemical data lead to the value
Al₃, Br₂ aq. = 136680 ; whence E_H = —1·008 volt, corre-
sponding with 45720 gramme-degrees. Consequently

$$E - E_H = +\cdot295 - (-1\cdot008) = +1\cdot303 ;$$

i. e. the thermovoltaic constant for bright aluminium in
bromide solution ·25 Al₃Br₂ 100 H₂O is a large positive
quantity, slightly greater than that found with the corre-
sponding chloride solution, viz. +1·288.

F. Voltaic and Thermovoltaic Constants of Metals immersed in Solutions of their Iodides.

I. Cadmium.

203. The following values were obtained with a number of
cells set up with amalgamated zinc and electro-cadmium
immersed in solutions of their iodides of strength ·25 MI₂
100 H₂O :—

Maximum	·326
Minimum	·320
Average	·322
Probable error	±·0008

III. *Mercury.*

205. Cells were set up with mercury in contact with freshly precipitated mercurous iodide suspended in zinc-iodide solution, and opposed, firstly, to amalgamated zinc in zinc-iodide solution, and, secondly, to electro-silver immersed in a magma of freshly precipitated silver-iodide and zinc-iodide solution, the solution-strength being uniformly $\cdot 25 \text{ ZnI}_2$ 100 H_2O . The following values were obtained :—

	Zinc-Mercury.	Mercury-Silver.
Maximum	·806	—·092
Minimum	·797	—·101
Average	·800	—·096
Probable error	±·0013	±·0014

the current passing in the latter case in the direction opposite to that predicable from the relative heats of formation of silver and mercurous iodides. From these values the following valuations result for the voltaic constant of mercury in contact with mercurous iodide suspended in .25 ZnI₂, 100 H₂O :—

Zinc-mercury	·800
Zinc-silver — Mercury-silver $\left\{ \begin{array}{l} \cdot706 \\ + \cdot096 \end{array} \right\}$	·802
Mean	·801

Julius Thomsen finds that $Hg_2, I_2=48440$; whence $E_H = \cdot 267$ volt, corresponding with 12100 gramme-degrees. Hence $E - E_H = +\cdot 534$; *i. e.* the thermovoltaic constant for mercury in contact with a magma of mercurous iodide suspended in $\cdot 25 ZnI_2, 100 H_2O$ is a large positive quantity, as similarly found for mercury in contact with mercurous-bromide and zinc-bromide solution and with mercurous-chloride and zinc-chloride solution of the same solution-strength, these latter two values being respectively $+\cdot 472$ and $+\cdot 458$. So that the bromide value is intermediate between the values for chloride and iodide; whilst the direction of variation with the three halogens is the same as that observed both with cadmium and with silver, viz. that the iodide value is algebraically the greatest.

IV. *Lead.*

206. The very sparing solubility of lead iodide rendered it impracticable to obtain good readings with cells set up with

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value is algebraically the greatest, as was found with cadmium-silver and mercury.

It is hence evident that whilst the thermovoltaic constants of metals in contact with their oxy salts (sulphates, nitrates, and acetates) do not vary widely, the same remark is not true for their halogen salts (chlorides, bromides, iodides). In general the thermovoltaic constant is decreased (algebraically) by substitution of bromide for iodide or of chloride for bromide; although this rule is not without exception, *e. g.* in the case of iron, where the values for $\cdot 25 \text{ FeX}_2$, $100 \text{ H}_2\text{O}$ are $+ \cdot 204$ and $+ \cdot 134$, where X represents chlorine and bromine respectively, the substitution of chlorine for bromine thus causing a notable *increase*.

Summary of Results.

207. The experiments above described lead to the general conclusion that electromotors, consisting of voltaic cells in which two different metals are surrounded by solutions of corresponding salts respectively, are capable of generating electromotive forces which (when not depreciated sensibly below their maximum value by giving rise to currents of densities greater than certain small limiting values) usually *stand in no simple relationship to the chemical action taking place in the cell* during the passage of the current, or to the heat-evolution taking place during that passage, or to the heats of formation of the two solutions electrolyzed. The values of the maximum E.M.F.'s thus generated may, however, be deduced within very close limits of accuracy by taking the algebraic difference between certain numerical values or *voltaic constants* assigned to each metal in contact with each given solution, these values varying slightly according to the surface-nature of the immersed metal, and being also dependent on the nature and strength of the solution of metallic salt in contact with the metal, and probably also varying with the temperature, but being otherwise actually constant.

Further, these maximum E.M.F. values may be connected with the difference in heat of formation between the two solutions electrolyzed by supposing that *the total difference of potential set up is due to two superposed causes*:—one, the heat-evolution due to the difference in heat of formation of the two solutions, which tends to make the metal immersed in the electrolyte of lesser formation-heat acquire the higher potential (like the copper plate of a Daniell cell); the other, a *thermo-voltaic* action akin to the *modus operandi* of an ordinary

thermovoltaic couple, in virtue of which a difference of potential is set up expressible by the algebraic difference between two numerical values, or *thermovoltaic constants*, assignable to each metal respectively, the which values vary *pari passu* with the variations in the corresponding voltaic constants. This thermovoltaic action being expressible by $k_1 - k_2$, and the first source of potential-difference being indicated by E_H , the total difference of potential set up is

$$E = E_H + k_1 - k_2,$$

where, if $k_1 - k_2$ be materially different from zero (which is most frequently the case), the value of E will differ materially from that of E_H , exceeding or falling short of it according as $k_1 - k_2$ is positive or negative in sign with respect to E_H . In the latter case, if $k_1 - k_2$ be numerically greater than E_H , the direction of the current actually generated is the reverse of that predictable from the relative heats of formation of the electrolytes.

208. The following Table furnishes a brief epitome of the mean values of the voltaic and thermovoltaic constants deduced above for various metals and fluids at a temperature within a very few degrees above or below 18°C. ; the solutions surrounding both plates being of equal strength (m zinc-salt molecules per 100 water molecules), the plate-surfaces being freshly amalgamated ones for zinc (standard), bright fused metal for iron, magnesium, and aluminium, and freshly electro-coated plates in all other cases.

Metal.	Surrounding Fluid.	m .	Voltaic constant.	E_H .	Thermovoltaic constant.
COPPER	Sulphate	·1 to 2·25	{ 1·114 invariable.	{ 1·105 invariable.	+·009
	Nitrate	·25 to 8·0	1·066 to 1·109	1·105 to 1·100	—·039 to +·005
	Acetate	·25	1·091	1·111	—·020
	Chloride: Cu_2Cl_2 suspended in CuCl_2 solution; or CuCl_2 solution alone	·25	1·099	} 1·038 {	+·061
	Chloride: Cu_2Cl_2 suspended in CdCl_2 solution.	·25	1·001		—·037
	Chloride: Cu_2Cl_2 suspended in ZnCl_2 solution.	·25	·988		—·050
CADMIUM ...	Sulphate	·1 to 5·0	·362 to ·357	·357 to ·367	+·005 to —·010
	Nitrate	·25	·352	·357	—·005
	Chloride.....	·25 to 8·0	·330 to ·262	·366 to ·240	—·036 to +·045
	Bromide.....	·25	·315	·338	—·023
	Iodide	·25	·322	·279	+·043

Table (continued).

Metal.	Surrounding Fluid.	<i>m</i> .	Voltaic constant.	E_H .	Thermovoltaiic constant.
SILVER	Sulphate	·042	1·539	1·890	—·351
	Nitrate	·25 to 2·0	1·495 to 1·556	1·890	—·395 to —·334
	Acetate	·057	1·489	?	{ Probably near to —·40
	Chloride: AgCl suspended in ZnCl ₂ solution.	·25 to 6·0	1·080 to 1·014	1·192 to 1·076	
	Chloride: AgCl suspended in CdCl ₂ solution.	·25	1·089	{ 1·192	—·103
	Chloride: AgCl suspended in CuCl ₂ solution.	·25	1·137		—·055
	Bromide: AgBr suspended in ZnBr ₂ solution.	·25	·906	1·005	—·099
	Iodide: AgI suspended in ZnI ₂ solution.....	·25	·706	·726	—·020
LEAD	Sulphate: PbSO ₄ suspended in ZnSO ₄ solution.	·1 to 5·0	·536 to ·487	{ ·712 to ·704	—·176 to —·217
	Sulphate: PbSO ₄ suspended in CdSO ₄ solution.	·1 to 5·0	·550 to ·505		—·162 to —·189
	Nitrate	·25 to 2·0	·580 to ·591	·759 to ·716	—·179 to —·125
	Acetate	·25	·607	·770	—·163
	Chloride.....	·05	·591	·813	—·222
	Bromide.....	·037	·571	·806	—·235
	Iodide: PbI ₂ suspended in ZnI ₂ solution.....	·25	·455	·457	—·002
IRON	Sulphate.....	0·1 to 1·0	·432 to ·398	·284	+·148 to +·114
	Chloride.....	·25	·488	·284	+·204
	Bromide.....	·25	·418	·284	+·134
MERCURY ...	Sulphate: Hg ₂ SO ₄ suspended in ZnSO ₄ solution.	·1 to 5·75	1·457 to 1·514	?	{ Probably near +·25 to +·30
	Nitrate (mercurous)	·25	1·499	1·202	
	Chloride: Hg ₂ Cl ₂ suspended in HgCl ₂ solution.	·25	1·257	{ ·668	+·589
	Chloride: Hg ₂ Cl ₂ suspended in CdCl ₂ solution.	·25	1·141		+·473
	Chloride: Hg ₂ Cl ₂ suspended in ZnCl ₂ solution.	·25 to 9·5	1·123 to ·988	·668 to ·536	+·455 to +·481
	Bromide: Hg ₂ Br ₂ suspended in ZnBr ₂ solution	·25	·972	·500	+·472
	Iodide: Hg ₂ I ₂ suspended in ZnI ₂ solution.....	·25	·801	·267	+·534
MAGNESIUM.	Sulphate.....	1·0	—·725	—1·634	+·909
	Nitrate	·25	—·530	—1·631	+1·101
	Chloride.....	·25	—·701	—1·634	+·933
ALUMINIUM...	Sulphate.....	·5	+·537	—·982	+1·519
	Chloride.....	·25	+·280	—1·008	+1·288
	Bromide.....	·25	+·295	—1·008	+1·303

209. The following is a list of the cells examined, in which the value of $k_1 - k_2$ is opposite in sign to, and numerically greater than, E_H ; so that the current actually generated flows in the direction opposite to that predicable from the relative heats of formation of the electrolytes :—

Combination.	m .	E .	E_H .	$E - E_H = k_1 - k_2$.
Iron-cadmium-sulphate ...	0.1 to 1.0	-.073 to -.035	+ .075	-.110 to -.148
Iron-cadmium-chloride25	-.157	+ .082	- .239
Iron-cadmium-bromide25	-.103	+ .054	- .157
Zinc-aluminium-sulphate5	+ .537	- .982	+1.519
Zinc-aluminium-chloride25	+ .280	-1.008	+1.288
Zinc-aluminium-bromide25	+ .296	-1.008	+1.304
Copper-silver-chloride. AgCl suspended in ZnCl ₂ solution25	-.020	+ .154	{ - .174 - .164
Copper-silver-chloride. AgCl suspended in CdCl ₂ solution25	-.010		
Mercury-silver-nitrate25	-.004	+ .688	- .692
Mercury-silver-chloride. Both suspended in ZnCl ₂ }	.25	-.046	+ .525	- .571
Mercury-silver-bromide. Both suspended in ZnBr ₂ }	.25	-.066	+ .505	- .571
Mercury-silver-iodide. Both suspended in ZnI ₂ }	.25	-.096	+ .460	- .556
Mercury-silver-chloride. AgCl suspended in ZnCl ₂ Hg ₂ Cl ₂ " CdCl ₂ }	.25	-.058	+ .525	{ - .583 - .563 - .575 - .692
Mercury-silver-chloride. AgCl suspended in CdCl ₂ Hg ₂ Cl ₂ " ZnCl ₂ }	.25	-.038		
Mercury-silver-chloride. Both suspended in CdCl ₂ }	.25	-.050		
Mercury-silver-chloride. AgCl suspended in ZnCl ₂ Hg ₂ Cl ₂ " HgCl ₂ }	.25	-.167		
Lead-mercury-chloride. Hg ₂ Cl ₂ suspended in CdCl ₂05	-.549	+ .145	- .694 - .684
Lead-mercury-chloride. Hg ₂ Cl ₂ suspended in ZnCl ₂05	-.539		
Lead-mercury-bromide. Hg ₂ Br ₂ suspended in ZnBr ₂037	-.402	+ .306	- .708
Lead-mercury-iodide. Both suspended in ZnI ₂ }	.025	-.347	+ .190	- .537

210. The following is a list of the cells examined in which the value of $k_1 - k_2$ is of the same sign as E_H ; so that the E.M.F. actually set up *exceeds* in numerical value that predicable from the relative heats of formation of the electrolytes; only those cells are named where the excess is somewhat considerable, *i. e.* 0.1 volt or upwards.

Combination.	<i>m</i> .	<i>E</i> .	<i>E_H</i> .	Excess.
Lead-copper-sulphate. PbSO ₄ suspended in ZnSO ₄ solution	0.1 to 2.0	.577 to .611	.393 to .394	{ +.184 to +.217 +.171 to +.202
Lead-copper-sulphate. PbSO ₄ suspended in CdSO ₄ solution.....	0.1 to 2.0	.564 to .596		
Lead-copper-nitrate25 to 2.0	.486 to .519	.345 to .388	+ .141 to + .128
Lead-copper-acetate25	.485	.341	+ .144
Lead-copper-chloride05	{ Irregular, about .475	.225	About +.25
Zinc-iron-sulphate	0.1 to 1.0	.445 to .399	.284	+ .161 to + .115
Zinc-iron chloride25	.490	.284	+ .206
Zinc-iron-bromide25	.417	.284	+ .133
Zinc-mercury-sulphate.....	.1 to 5.75	1.514 to 1.457	?	{ Probably about +.3
Zinc-mercury-nitrate25	1.500	1.202	+ .298
Zinc-mercury-chloride. Hg ₂ Cl ₂ suspended in HgCl ₂ solution25	1.256	.668	{ +.588 +.572
Zinc-mercury-chloride. Hg ₂ Cl ₂ suspended in CdCl ₂ solution.....	.25	1.140		
Zinc-mercury-chloride. Hg ₂ Cl ₂ suspended in ZnCl ₂ solution25 to 9.5	1.123 to .988	.668 to .536	+ .452 to + .481
Zinc-mercury-bromide. Hg ₂ Br ₂ suspended in ZnBr ₂ solution25	.972	.500	+ .472
Zinc-mercury-iodide. Hg ₂ I ₂ suspended in ZnI ₂ solution.....	.25	.800	.287	+ .533
Cadmium-mercury-chloride. Hg ₂ Cl ₂ suspended in HgCl ₂ solution25	.929	.302	{ +.627 +.510 +.497
Cadmium-mercury-chloride. Hg ₂ Cl ₂ suspended in CdCl ₂ solution25	.812		
Cadmium-mercury-chloride. Hg ₂ Cl ₂ suspended in ZnCl ₂ solution25	.799		
Copper-mercury-nitrate25	.433	.097	+ .336
Lead-mercury-nitrate25	.917	.443	+ .474
Lead-silver-chloride. AgCl suspended in ZnCl ₂ solution05	.489	.379	{ +.110 +.101
Lead-silver-chloride. AgCl suspended in PbCl ₂ solution05	.480		

211. The following is a list of the cells examined in which the value of $k_1 - k_2$ is of the opposite sign to, but not greater in magnitude than, E_H ; so that the E.M.F. actually set up is less in numerical value than that predicable from the relative heats of formation of the electrolytes; only those cells are

named where the deficiency is somewhat considerable, viz.
0·1 volt and upwards.

Combination.	m.	E.	E _H .	Deficiency.
Zinc-silver-sulphate	·042	1·536	1·890	·354
Zinc-silver-nitrate	25 to 2·0	1·495 to 1·556	1·890	·395 to ·364
Zinc-silver-acetate	·057	1·490	?	Probably near ·40
Zinc-silver-chloride. AgCl suspended in ZnCl ₂ solution	25 to 6·0	1·080 to 1·014	1·192 to 1·076	·116 to ·062
Zinc-silver-chloride. AgCl suspended in CdCl ₂ solution	·25	1·088	1·192	·104
Copper-silver-sulphate	·042	·4235	·785	·3615
Copper-silver-nitrate	25 to 2·0	·429 to ·446	·785 to ·786	·356 to ·340
Copper-silver-acetate	·057	·397	?	Probably about ·39
Copper-silver-chloride. AgCl suspended in CuCl ₂ solution	·25	·035	·154	·119
Cadmium-silver-sulphate	·042	1·1805	1·533	·3525
Zinc-lead-sulphate. PbSO ₄ suspended in ZnSO ₄ solution	1 to 5·0	·537 to ·487	·712 to ·704	·175 to ·217
Zinc-lead-sulphate. PbSO ₄ suspended in CdSO ₄ solution	1 to 5·0	·550 to ·505		
Zinc-lead-nitrate	25 to 2·0	·580 to ·591	·759 to ·716	·179 to ·125
Zinc-lead-acetate	·25	·608	·770	·162
Zinc-lead-chloride	·05	·591	·813	·222
Zinc-lead-bromide	·037	·571	·806	·235
Cadmium-lead-sulphate	1 to 3·0	·173 to ·133	·355 to ·345	·182 to ·212
Cadmium-lead-chloride	·05	·260	·447	·187
Cadmium-lead-bromide	·037	·256	·468	·212
Lead-silver-sulphate. PbSO ₄ in ZnSO ₄ solution...	·042	1·003	1·1775	·1745
Lead-silver-nitrate	25 to 2·0	·914 to ·965	1·131 to 1·174	·217 to ·207
Lead-silver-acetate	·037	{ Irregular, about 0·8	?	Probably about ·3
Iron-lead-sulphate. PbSO ₄ suspended in ZnSO ₄ solution	1 to 1·0	·120 to ·112	·428	·308 to ·316
Iron-copper-sulphate	1 to 1·0	·685 to ·715	·821	·136 to ·106
Iron-silver-sulphate	·042	1·103	1·605	·502
Iron-silver-chloride. AgCl in ZnCl ₂ solution	·25	·592	·908	·316
Zinc-magnesium-sulphate	1·0	·724	1·634	·910
Zinc-magnesium-nitrate	·25	·531	1·631	1·100
Zinc-magnesium-chloride	·25	·702	1·634	·932
Copper-magnesium-sulphate	1·0	1·840	2·739	·899
Copper-magnesium-nitrate	·25	1·595	2·736	1·141
Cadmium-magnesium-chloride	·25	1·030	2·000	·970
Aluminium-copper-sulphate	·5	·578	2·087	1·509
Aluminium-cadmium-chloride	·25	·050	1·374	1·324
Aluminium-cadmium-bromide	·25	·022	1·346	1·324

212. The following is a list of the cells examined in which the value of $k_1 - k_2$ is not numerically greater than E_H , and lies within the limits ± 0.1 volt. It is evident that the number of cells coming into this category is only a fraction of the total number of combinations examined.

Combination.	m .	E .	E_H .	Differences.
Zinc-copper-sulphate	·25 to 2·25	$\left\{ \begin{array}{l} 1.114 \\ \text{invariable} \end{array} \right.$	$\left\{ \begin{array}{l} 1.105 \\ \text{invariable} \end{array} \right.$	$\left\{ \begin{array}{l} +.009 \end{array} \right.$
Zinc-copper-nitrate	·25 to 8·0	1.066 to 1.091	1.105 to 1.100	+·005 to -·039
Zinc-copper-acetate	·25	1.091	1.111	-·020
Zinc-copper-chloride. Cu_2Cl_2 suspended in CuCl_2 sol., or CuCl sol. alone...	·25	1.0985	1.038	+·061
Zinc-copper-chloride. Cu_2Cl_2 suspended in CdCl_2 solution	·25	1.001		-·037
Zinc-copper-chloride. Cu_2Cl_2 suspended in ZnCl_2 solution	·25	.988		-·050
Zinc-cadmium-sulphate	·1 to 5·0	.362 to .357	.357 to .367	+·005 to -·010
Zinc-cadmium-nitrate	·25	.351	.357	-·006
Zinc-cadmium-chloride	·25 to 8·0	.330 to .262	.366 to .240	-·036 to +·045
Zinc-cadmium-bromide	·25	.315	.338	-·023
Zinc-cadmium-iodide	·25	.322	.279	+·043
Copper-cadmium-sulphate	·1 to 2·0	.752 to .755	.743 to .748	+·009 to +·007
Copper-cadmium-nitrate	·25	.713	.748	-·035
Copper-cadmium-chloride. Cu_2Cl_2 in CuCl_2 sol., or CuCl_2 sol. alone	·25	.769	.672	+·097
Copper-cadmium-chloride. Cu_2Cl_2 in CdCl_2 solution ..	·25	.671		-·001
Copper-cadmium-chloride. Cu_2Cl_2 in ZnCl_2 solution ..	·25	.659		-·013
Zinc-silver-chloride. AgCl in CuCl_2 solution ...	·25	1.136	1.192	-·056
Zinc-silver-bromide. AgBr in ZnBr_2 solution...	·25	.906	1.005	-·099
Zinc-silver-iodide. AgI in ZnI_2 solution	·25	.7055	.726	-·0205
Cadmium-silver-chloride. AgCl in CuCl_2 sol.	·25	.807	.826	-·019
Cadmium-silver-chloride. AgCl in CdCl_2 solution ...	·25	.761		-·065
Cadmium-silver-chloride. AgCl in ZnCl_2 solution ...	·25	.751		-·075
Cadmium-silver iodide. AgI in ZnI_2 solution	·25	.384	.447	-·063
Zinc-lead-iodide. PbI_2 in ZnI_2 solution.....	·25	.455	.457	-·002