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XXIV. *Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c. of Electrolytes.* By Dr. G. GORE, F.R.S.\*

IN a research "On Changes of Voltaic Energy of Alloys during Fusion" (Phil. Mag. *ante*, p. 27) I have shown that when an alloy of bismuth, lead, tin, and cadmium, and one of bismuth, lead, and tin, changed from the solid to the liquid state by gradual and uniform application of heat whilst immersed in a suitable electrolyte, it suddenly increased in electropositive state, showing that whilst absorbing latent heat it acquired greater electromotive force, and that when these alloys solidified, reverse effects occurred. M. J. Regnault had previously shown (*Comptes Rendus Acad. Sci.* June 10, 1878; *Chemical News*, vol. xxxviii. p. 33) that liquid gallium was electropositive to solid gallium in a neutral solution of gallous sulphate.

In order to ascertain whether, in cases where the mere act of mixing or diluting electrolytes is known to be attended by absorption of heat, a similar increase of the power of exciting electromotive force occurs, I took the separate ingredients of a chilling-mixture, each in a liquid state and at the same atmospheric temperature, measured the electromotive force of a simple couple of cadmium and platinum† in each liquid separately by the null method of balance, with the aid of a suitable thermoelectric pile (see *Proc. Birm. Phil. Soc.* vol. iv. p. 130; *The Electrician*, 1884, vol. xii. p. 414), and a galvanometer, then mixed the liquids, immediately took the temperature of the mixture, and, after having allowed the liquid to acquire the atmospheric temperature, measured the electromotive force of the couple in it. As the changes of energy depend upon *each* of the ingredients of the mixture, it was necessary in each case to consider the alterations of the *mean* amount of electromotive force.

Distilled water was used in making all the solutions. The proportions of substances employed were in nearly all cases simple multiples of their equivalent weights. The thermometer employed in the first four experiments was graduated to .2 of a Fahr. degree, and that used in all the other ones was capable of being read to .01 of a Centigrade degree. The following are the particulars of the experiments:—

\* Communicated by the Author.

† In experiments "Nos. 7 and 15" a zinc-platinum couple was used.

*Experiment 1.*

Saturated solution of Sulphate of Sodium + Dilute Sulphuric Acid.

4 oz. by vol. of sat. sol. of $\text{Na}_2\text{SO}_4$	{	Temp. before mixing	Fahr. 55·6
" " 1 vol. $\text{H}_2\text{SO}_4$ + 19 vols. $\text{H}_2\text{O}$		" after "	54·4
Decrease			1·2 F. deg.

E.M.F. with Cd + Pt at 55°·6 Fahr.

Sat. sol. of $\text{Na}_2\text{SO}_4$	Volts. = ·993	{	Calc. mean E.M.F. by vol. = 1·1388
Dilute $\text{H}_2\text{SO}_4$	..... = 1·28473		
The mixture	.....	= 1·1789	
Increase			p.cent. ·0401 = 3·51

The mean electromotive force had therefore increased whilst heat was being absorbed and rendered latent.

In all the remaining experiments the influence of dilution with water alone was examined.

*Experiment 2.*

823·5 grains of liquefied "glacial Acetic Acid"  
( $\text{C}_2\text{H}_4\text{O}_2$ ) + Water.

50 c.c. of glacial acid	{	Temperature before mixing	.....	Fahr. 57·8
21 " water		" after "	.....	56·2
Decrease				1·6 F. deg.

E.M.F. with Cd + Pt at 17° C.

The glacial acid	Volts. = 1·1074	{	Mean E.M.F. by weight = 1·0344
Water	..... = ·850		
The diluted acid	.....	= 1·1074	
Increase			p.cent. ·073 = 7·06

*Experiment 3.*

430 grains of Tartaric Acid in 310 grains of Water + Water.

30 c.c. of the strong acid solution	{	Temp. before mixing	..	Fahr. 53·5
20 " water		" after "	..	53·2
Decrease				·3 F. deg.

E.M.F. with Cd + Pt at 61° Fahr.

The concent. acid sol.	Volts. = 1·1417	{	Mean E.M.F. by weight = ·9151
Water	..... = ·850		
The diluted acid	.....	= 1·1074	
Increase			p.cent. ·1923 = 21·0

The mean electromotive force had increased 21 per cent., notwithstanding that the amount of heat absorbed was relatively small, and that the water had nearly 24 per cent. less power of exciting electromotive force than the concentrated acid solution.

*Experiment 4.*

575 grains of Nitrate of Ammonium in 662 grains of Water + Water.

44 centim. of sat. sol. of $\text{AmNO}_3$	{	Temp. before mixing	Fahr.
34    „    water .....			60.0
		„ after    „	52.0
			Decrease 8.0 F. deg.

E.M.F. with Cd + Pt at 60° Fahr.

	Volts.		Volts.
Saturated sol. of $\text{AmNO}_3$	= .993	{	Mean E.M.F. by weight = .9530
Water .....	= .850		
The diluted solution .....			
			= .9930
			———— p.cent.
			Increase .0400 = 4.18

When two similar couples of cadmium platinum, one being in the concentrated and the other in the diluted solution, were opposed to each other with the galvanometer in the circuit, the one in the diluted liquid showed slightly the greater electromotive force; this was a much more delicate test. It is evident that notwithstanding the water had about fourteen per cent. less power than the saturated solution of exciting electromotive force, its addition to that liquid did not reduce the mean amount of that property.

In the remainder of the experiments a more sensitive thermometer capable of measuring .01 of a Centigrade degree was employed.

*Experiment 5.*

Saturated solution of Nitrate of Sodium + Water.

500 grains $\text{NaNO}_3$ in 43 c.c. of water	{	Temp. before mixing	C.
298 c.c. of water .....			15.40
		„ after    „	13.98
			Decrease 1.42 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volts		Volts
The saturated solution	= 1.0073	{	Mean E.M.F. by weight = .8816
Water .....	= .850		
The diluted solution .....			
			= 1.0044
			———— p.cent.
			Increase .1228 = 13.9

*Experiment 6.*

Saturated solution of Nitrate of Strontium + Water.

600 grains $\text{Sr}2\text{NO}_3$ in 63 c.c. of water	{ Temp. before mixing	C. 15.52
164.5 c.c. of water.....		„ after „ 14.44
	Decrease	1.08 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The saturated solution	= .9930	{ Mean E.M.F. by weight	= .9046
Water .....	= .850		
The diluted solution .....			= .9787
			p.cent. Increase .0741 = 8.19

*Experiment 7.*Solution of 40 grains of Chloride of Sodium in 40 c.c.  
of Water + 40 c.c. of Water.

I did not ascertain the change of temperature produced by dilution in this case. J. Thomsen and others had already shown by experiment that the dilution of an aqueous solution of chloride of sodium is attended by absorption of heat.

E.M.F. with Zn + Pt at 22° C.

	Volts.		Volts.
The strong solution	= 1.2471	{ Mean E.M.F. by weight	= 1.1889
Water .....	= 1.1270		
The diluted solution .....			= 1.2557
			p.cent. Increase .0668 = 5.61

*Experiment 8.*

Strong solution of Sulphate of Sodium + Water.

142 grains $\text{Na}_2\text{SO}_4$ in 75.4 c.c. of water	{ Temp. before mixing	C. 15.22
40.6 c.c. of water ... ..		„ after „ 15.08
	Decrease	.14 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The strong solution	= .993	{ Mean E.M.F. by weight	= .9513
Water .....	= .850		
The diluted solution .....			= .9872
			p.cent. Increase .0359 = 3.77

Experiment 9.

Strong solution of Sulphate of Ammonium + Water.

264 grns. $\text{Am}_2\text{SO}_4$ in 69.8 c.c. of water	{ Temp. before mixing	C.
46 c.c. of water .....		14.98
	{ „ after „	14.84
	Decrease	0.14 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The strong solution =	.9815	{ Mean E.M.F. by weight =	.9356
Water .....	.850		
The diluted solution .....			.9758
			p.cent.
		Increase	.0402 = 4.30

Experiment 10.

Strong solution of Carbonate of Sodium + Water.

106 grns. $\text{Na}_2\text{CO}_3$ in 58 c.c. of water	{ Temp. before mixing =	C.
58 c.c. of water .....		12.70
	{ „ after „	12.42
	Decrease	0.28 C. deg.

E.M.F. with Cd + Pt at 16° C.

	Volt.		Volt.
The strong solution =	.7499	{ Mean E.M.F. by weight =	.7972
Water .....	.850		
The diluted solution .....			.7527
			p.cent.
		Decrease	.0445 = 5.58

Experiment 11.

Strong solution of Nitrate of Potassium + Water.

200 grains of $\text{KNO}_3$ in 58 c.c. of water	{ Temp. before mixing	C.
58 c.c. of water .....		15.24
	{ „ after „	14.70
	Decrease	0.54 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volts.		Volts.
The strong solution =	1.0216	{ Mean E.M.F. by weight =	.9443
Water .....	.850		
The diluted solution .....			1.01588
			p.cent.
		Increase	.07158 = 7.57

Experiment 12.

Strong solution of Chloride of Ammonium + Water.

400 grains $\text{AmCl}$ in 86.5 c.c. of water	{ Temp. before mixing	C.
129.6 c.c. of water .....		14.80
	{ „ after „	14.61
	Decrease	0.19 C. deg.

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## E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The strong solution =	·9358	{ Mean E.M.F. by weight =	·8898
Water .....	= ·850		
The diluted solution .....			·92436
		Increase	·0345 = 3·87 p.cent.

As in each of the foregoing twelve instances there was absorption of heat during the act of dilution, I now examined some cases in which dilution is known to be attended by evolution of heat. Care was taken to select those in which chemical action as usually understood did not operate.

*Experiment 13.*

272 grains of Hydrated Acetate of Sodium in  
Water + Water.

		C.
164 grains of the anhydrous salt in	{ Temp. before mixing	16·30
39·5 c.c. of water .....		16·44
155 c.c. of water .....		
	Increase	·14 C. deg.

## E.M.F. with Cd + Pt at 20° C.

	Volt.		Volt.
The concentrated soln. =	·9157	{ Mean E.M.F. by weight =	·8712
Water .....	= ·850		
The diluted solution .....			·9072
		Increase	·036 = 4·13 p.cent.

*Experiment 14.*

Strong solution of Sulphate of Magnesium  
in Water + Water.

		C.
240 grains of anhydrous MgSO <sub>4</sub> in	{ Temp. before mixing	15·68
46 c.c. of water .....		15·90
115 c.c. of water .....		
	Increase	·22 C. deg.

## E.M.F. with Cd + Pt at 20°.

	Volt.		Volt.
The strong solution =	·993	{ Mean E.M.F. by weight =	·900
Water .....	= ·850		
The diluted solution .....			·9787
		Increase	·0787 = 8·74 p.cent.

*Experiment 15.*

Concentrated solution of Chloride of Potassium + Water.

This case was selected from the curve of electromotive

force given in "Fig. 8" on page 489 of the Philosophical Magazine, Dec. 1890, as showing an increase of electromotive force on dilution.

20 grains of KCl in 20 c.c. of water	{	Temp. before mixing	C. 14.50
180 c.c. of water.....	}	" after "	14.54
Increase			.04 C. deg.

E.M.F. with Zn + Pt at 21.5° C.

	Volts.		Volts.	
The strong solution =	1.1850	{ Mean E.M.F. by weight =	1.1331	
Water .....	= 1.1270			
The diluted solution .....			= 1.2550	
Increase			.1219	= 10.75 p. cent.

The mean electromotive force had increased 10.75 per cent. notwithstanding that there was not only no absorption, but even a slight evolution and loss of heat during the act of dilution.

*Experiment 16.*

Saturated solution of Caustic Soda + Water.

			C.
600 grains of 90 per cent. Soda in	{	Temp. before mixing	15.74
37 c.c. of water.....		" after "	23.85
384.4 c.c. of water .....			
Increase			8.14 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.	
The saturated solution =	.9072	{ Mean E.M.F. by weight =	.8602	
Water .....	= .850			
The diluted solution .....			= .89004	
Increase			.0298	= 3.46 p. cent.

*Experiment 17.*

50 c.c. of Concentrated Aqueous Hydrochloric Acid + Water.

			C.
655 grains of absolute HCl in 250	{	Temp. before mixing	14.12
grains of H <sub>2</sub> O .....		" after "	16.52
381.5 c.c. of water .....			
Increase			2.40 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volts.		Volts.	
The concentrated acid =	1.3362	{ Mean E.M.F. by weight =	.9148	
Water .....	= .850			
The diluted acid .....			= 1.20.	
Increase			.2869	= 31.39 p. cent.



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Notwithstanding the loss of heat during dilution, the mean electromotive force had greatly increased. The electromotive force was quite variable in the acid solutions owing to their great degrees of strength and the evolution of gas.

*Experiment 18.*

Partly diluted Sulphuric Acid + Water.

The acid was sufficiently diluted to prevent the formation of a definite hydrate by chemical union.

30 c.c. of $H_2SO_4$ in 20 c.c. of water	{ Temp. before mixing	C.
20 c.c. of water .....		13.0
	„ after „	24.0
	Increase	11.0 C. deg.

E.M.F. with Cd + Pt at 15° C.

	Volts.		Volts.
The strong acid soln.	= 1.2504	{ Mean E.M.F. by weight =	.9585
Water .....	= .850		
The diluted solution .....			= 1.1960
			———— p. cent.
		Increase	= .2375 = 24.68

Notwithstanding the great loss of heat, there was a large increase of the mean amount of electromotive force.

*Experiment 19.*

Concentrated solution of Caustic Potash + Water.

377 grns. of KHO in 233 c.c. of water	{ Temp. before mixing	C.
155.7 c.c. of water .....		11.74
	„ after „	11.76
	Increase	.02 C. deg.

E.M.F. with Cd + Pt at 17° C.

	Volt.		Volt.
The concentrated soln.	= .8951	{ Mean E.M.F. by weight =	.8779
Water .....	.850		
The diluted solution .....			= .8929
			———— p. cent.
		Increase	.0150 = 1.7

*Experiment 20.*

Diluted solution of Caustic Ammonia + Water.

94.7 grains AmHO in 97.9 c.c. of water	{ Temp. before mixing	C.
62.8 c.c. of water .....		13.46
	„ after „	13.56
	Decrease	.10 C. deg.

E.M.F. with Cd + Pt at 18° C.

	Volt.		Volt.
The less diluted solution =	·89004	{ Mean E.M.F. by weight =	·8746
Water .....	= ·850		
The more diluted solution .....			= ·8786
			— p.cent.
		Increase	·004 = ·45

The amounts of electromotive force in this case were variable.

The following table contains the chief results of the experiments:—

TABLE I.

Mixture.	Temperature.	Mean E.M.F.
	Degrees.	
Solution of $\text{Na}_2\text{SO}_4$ + dilute $\text{H}_2\text{SO}_4$ ...	Decrease 1·2 Fahr.	Increase ·0401
Liquid Acetic Acid + Water .....	" 1·6 "	" ·073
Solution of Tartaric Acid + Water ...	" ·3 "	" ·1923
" $\text{AmNO}_3$ + Water .....	" 8·0 "	" ·040
" $\text{NaNO}_3$ + " .....	" 1·42 C.	" ·1223
" $\text{Sr}_2\text{NO}_3$ + " .....	" 1·08 "	" ·0741
" $\text{NaCl}$ + " .....	" ? "	" *·0668
" $\text{Na}_2\text{SO}_4$ + " .....	" ·14 "	" ·0359
" $\text{Am}_2\text{SO}_4$ + " .....	" ·14 "	" ·0402
" $\text{Na}_2\text{CO}_3$ + " .....	" ·28 "	Decrease ·0445
" $\text{KNO}_3$ + " .....	" ·54 "	Increase ·0715
" $\text{AmCl}$ + " .....	" ·19 "	" ·0345
" $\text{NaAcetate}$ + " .....	Increase ·14 "	" ·0360
" $\text{MgSO}_4$ + " .....	" ·22 "	" ·0787
" $\text{KCl}$ + " .....	" ·04 "	" *·1219
" $\text{NaHO}$ + " .....	" 7·14 "	" ·0298
" $\text{HCl}$ + " .....	" 2·38 "	" ·2872
" $\text{H}_2\text{SO}_4$ + " .....	" 11·00 "	" ·2375
" $\text{KHO}$ + " .....	" ·02 "	" ·0150
" $\text{H}_4\text{N}$ + " .....	" ·10 "	" ·004

The various cases of absorption and evolution of heat given in this table agree with those given by J. Thomsen in his thermochemical researches (see P. Muir's 'Elements of Thermal Chemistry,' Appendix v.).

An inspection of the results thus obtained shows, 1st, that in 19 cases out of 20 *diluting an electrolyte or mixing it with another increased the mean amount of electromotive force of the two liquids*; and 2nd, that in 12 instances out of the 20 there was a lowering of temperature and an absorption of heat, and in the remainder an evolution and loss of latent heat, during the act of mixing.

As in the whole of the 8 cases in which there was evolution and loss of heat there was an increase of mean amount of

\* In these two cases a positive plate of zinc was used.

electromotive force, it was evident that this increase could not be due to absorption of energy in the form of heat. I therefore examined the phenomena in another manner, to ascertain whether they were related to changes of total volume and of mean specific gravity of the two liquids during the act of mixing.

Different investigators have shown that when a concentrated aqueous solution of an acid, a salt, or an alkali, is diluted with water, a contraction of the total volume of the two liquids and an increase of the mean amount of their specific gravities occur in nearly every case (see Watts's 'Dictionary of Chemistry,' 2nd Supp. pp. 596-604). Marignac, however, found an exception with a mixture of a solution of neutral sulphate of sodium and sulphuric acid: in this case "expansion always occurs" (*ibid.* p. 604); he further observed that contraction takes place on diluting solutions of hydrochloric acid, sulphuric acid, chloride of sodium, and sulphate of sodium (*ibid.* pp. 603, 604). J. Thomsen and others have also shown that when a solution of caustic soda, and of various other substances, is diluted, the total volume of the two liquids becomes less (*ibid.* pp. 597-600). And Nicol has obtained similar results by separately diluting aqueous solutions of potassium chloride, potassium nitrate, sodium chloride, and sodium nitrate (Phil. Mag. vol. xv. 1883, p. 97; Journ. Chem. Soc. 1883, vol. xliii.; Trans. p. 136).

In order to ascertain whether contraction occurred in the whole of the remainder of the cases in which I had found an increased mean amount of electromotive force developed during the mixing, the following arrangement (see figure) was employed:—A is a glass tube about 12 inches high and  $\frac{1}{2}$  an inch in diameter, with a perfectly fitting stopcock in the middle. The lower end of this tube was closed by a vulcanized rubber bung, and the upper end was fitted with a perforated bung surmounted by a tall glass tube of narrow bore open at both ends, and provided with a scale or index capable of sliding up or down. The stopcock and bungs were coated with grease, and the apparatus was proved to be perfectly water-tight. The entire portion of the apparatus below the index-scale was immersed side by side with a sensitive thermometer in a large vessel of water at about 16° C., in order to keep the apparatus at a sufficiently uniform



temperature during the short period of an experiment. The thermometer was capable of measuring to  $\cdot 01$  of a Centigrade degree.

The lower compartment of the large tube and the bore of the stopcock were perfectly filled with the lightest of the two liquids at exactly the proper temperature; if this lower space was not sufficiently large a glass bulb was previously fixed water-tight on the lower end of the tube. The upper compartment and a part of the narrow tube was now filled with the heavier liquid, and the apparatus immersed in the bath. When the whole had acquired the same temperature, the tap was slightly opened for an instant and closed again, the index adjusted to the level of the meniscus, the tap then fully opened, the apparatus occasionally inverted, the liquids allowed to mix, and the changes of total volume of the liquids and the temperatures noted at stated intervals of time until all change of volume ceased. The apparatus and method are suitable for making accurate measurements. The following are the results obtained:—

TABLE II.  
Change of Volume of Electrolytes by Dilution.

Substance.	Solution.	Water.	Change of Volume.
Acetic acid...	11.0 c.c. of concentrd. Acid.	c.c. 10.5	Contraction 1.66 per cent.
KHO .....	11.0 " satd. solution.	10.5	" .93 "
Am <sub>2</sub> SO <sub>4</sub> .....	11.0 " " "	10.5	" .61 "
Sr2NO <sub>3</sub> .....	11.0 " " "	10.5	" .58 "
MgSO <sub>4</sub> .....	11.0 " " "	10.5	" .293 "
Na Acetate...	11.0 " " "	10.5	" .187 "
AmCl .....	11.0 " " "	36.0	" .12 "
AmHO .....	10.5 " $\frac{1}{8}$ " "	11.0	" extremely small.
" .....	10.5 " $\frac{1}{2}$ " "	11.0	Expansion .0587 per cent.

With the solution of aqueous ammonia, if sufficiently dilute, contraction occurred, but when strong, expansion took place; probably similar results would be obtained with dilute hydrocyanic acid. Some practical mechanical application of liquid expansion by mixture might perhaps be made to produce hydrostatic pressure.

The above results, together with those previously obtained by other investigators (see references already given), show that in 18 out of the 20 mixtures of liquids employed in this research, contraction of total volume of the two electrolytes occurred during the act of mixing. This large proportion of cases of contraction indicates the existence of a great number of instances of the same kind, and that probably nearly all

electrolytes increase in mean amount of their specific gravities during mixture or dilution; these statements agree with the usual views entertained on the subject.

By comparison of these results with those in Table I., and those of Table I. with one another, it appears, 1st, that increase of mean specific gravity of the two liquids during dilution or mixing occurs not only in cases in which heat is evolved and lost, but also in those in which heat is absorbed and becomes latent; 2nd, that increase of mean electromotive force of the two liquids also occurs not only in those cases in which heat is absorbed and becomes latent, but also in those in which it is set free. And 3rd, that in 17 cases out of 20 an increase of mean specific gravity of the two liquids was attended by an increase of the mean amount of their electromotive force. We may therefore conclude that *in cases of mere physical mixture, the changes of mean specific gravity and of mean electromotive force of electrolytes are probably related to each other as concomitant effects of the same cause, change of molecular motion.* From the known general relation of increase of specific gravity to decrease of specific heat, it further suggests the inference that in cases of simple dilution the mean electromotive force of electrolytes is related to their mean specific heat.

As in all such cases, each phenomenon, whether it be physical mixture, dilution, specific gravity, specific heat, latent heat, or electromotive force, involves the mutual action of two substances, it is essentially necessary in every case to ascertain the *mean* amount of change occurring in the two substances.

In a separate and more extensive research, not yet published, I have measured the losses and gains of electromotive force by means of different positive metals in different classes of mixtures of electrolytes, including cases of chemical union as well as of mere physical mixture.

## XXV. *The Study of Transformers.*

By Prof. JOHN PERRY, *F.R.S., D.Sc.\**

[The following paper was written in February last, at a time when I had been compelled to listen to many discussions on the Transformer. It has been nearly forgotten till now; but I see that it ought to be published now, so that it may precede my paper read four days ago before the Physical Society on 'Mr. Blakesley's method of Measuring Power in Transformers.'—26th May, 1891.]

I HAVE been engaged on quite other matters during the last few years, and thought a few weeks ago that I must be hopelessly in arrear concerning the subject of

\* Communicated by the Author.