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placement of the iron lines in the spectrum of the metal would result. There would be both a displacement toward the less refrangible end caused by the recession of the atom, and one toward the more refrangible end of the spectrum caused by the approach of the atom. The great amount of dispersion afforded by a concave grating of 20,000 lines to the inch enabled me to easily detect a movement equivalent to a tenth-metre. I accordingly took a photograph of the iron lines with the terminals in the position I have described, and on the same plate immediately above this photograph a comparison photograph was taken with the terminals paral-
lel to the slit. In this case the iron atoms did not make their supposed excursions away and toward the slit, and therefore no displacement of the spectrum-lines was to be expected.

The photographic plate was exposed in the neighbourhood of the great H-lines. A movable shutter enabled me to expose different portions of the same plate without changing any adjustments of the apparatus. The resulting photographs showed no displacement of the iron-lines. The iron-lines in the two photographs met exactly (continued in an unbroken line across the double photograph), and were of the same breadth throughout their extent (see figure).

The conclusion seems to be a strong one that the electrical oscillations do not carry the atoms of metals with them—in spark-discharges. The atom is merely shaken up and caused to emit the vibrations or subsidiary ripples which appeal to our senses as light and heat, while the electrical waves pass on without conveying the atoms.

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LV. *The Greater Influence of First Quantities of Electrolytes on Volta-Electromotive Force.* By Dr. G. GORE, F.R.S.*

IN thermochemical research, Favre and others observed that, on adding equal quantities of water in succession to a fixed amount, either of nitric or sulphuric acid, the quantity of heat evolved was greater with the first than with any succeeding dilution (Watts's 'Dictionary of Chemistry,' vol.iii. p. 310); and similar effects were noticed by J. Thomsen on diluting concentrated hydrochloric, hydrobromic, and hydriodic acids. Nicol has observed that the total contraction of volume of a saline solution increases with the proportion of dissolved salt, and that each successive equivalent weight of the salt produces less contraction. Kohlrausch and others

* Communicated by the Author.

have also shown that very minute proportions of dissolved acids, salts, &c. exercise a relatively great influence upon the electric conduction-resistance of pure water; and I have found "that a much greater increase of electromotive force is usually caused by the first amount of substance added to the water than by the subsequent amounts" ("On a New Method and Department of Chemical Research," *Phil. Mag.* May 1890, p. 421), and have given a number of instances. According to the researches of M. Lindeck also (*Ann. Phys. Chem.* [2] vol. xxxv. pp. 311-331), whilst the first portion of zinc added to mercury increases its electromotive force in electrolytes, further additions have scarcely any effect.

In the present research I have extended the inquiry, and have not only examined the effect of adding equal quantities in succession of acids and salts to a fixed amount of water, but of water to fixed amounts of acids and salts, and of bases to acids, upon the electromotive force of a simple voltaic couple immersed in the water at ordinary atmospheric temperatures. The electromotive force was measured by the method of balance, with the aid of a suitable thermoelectric pile of iron and German silver (see *Proc. Birm. Phil. Soc.* vol. iv. p. 130; 'The Electrician,' 1884, vol. xii. p. 414), and a differential astatic galvanometer having 50 ohms' resistance in each coil.

In consequence of the following circumstances very little error or inconvenience was caused by polarization:—(1) all the measurements were made at the null-point, when no perceptible current was passing; (2) by experience in working, the null-point could be almost instantly attained; (3) the metals were only immersed during a very short period of time; (4) the positive metal was cleaned each time before immersion; (5) the platinum was washed each time, and heated to redness occasionally; and (6) to test whether the energy of the couple remained unchanged, it was occasionally balanced in distilled water by a similar freshly prepared one in distilled water.

The relatively great increase of electromotive force with a zinc-platinum couple, on adding the first unit quantity of chlorine, bromine, iodine, hydrochloric, hydrobromic, hydriodic, nitric, and sulphuric acid, and the chlorides, bromides, iodides, and sulphates of potassium and sodium, and certain other salts, to a fixed amount of water, have already been shown in the paper referred to (*Phil. Mag.* May 1890, p. 421).

The similar range effects upon a cadmium-platinum couple in the reverse process of adding the first unit quantity of water to a fixed amount of hydrochloric, sulphuric, and nitric acid are shown by the following curves. The electromotive force

of the couple in distilled water at 20° C. was .85 volt. The constant difference or unit quantity of water added to each acid was 89.1 grains. In order to obtain more reliable results, and to make the conditions more alike, and to obtain curves more comparable with each other, each acid was so far diluted previous to adding the first unit quantity of water as to contain one equivalent weight proportion, in 100ths of a grain of absolute acid, in 18 grains of water; for instance, the starting-point solution of hydrochloric acid contained .365 grain of HCl in that amount of water.

The electromotive force of the couple in pure concentrated hydrochloric acid containing 5.81 grains of HCl per cubic centimetre at 15° 6 was 1.235 volt; in pure concentrated sulphuric acid it was 1.278; and in pure concentrated nitric acid it was 1.477 volt, each at 20° 5 C. These electromotive forces, especially that of nitric acid, are much less accurate than those obtained with the same acids when diluted as above.

Fig. 1.

Fig. 2.

Fig. 3.
 HNO_3 .63 grain, with CdPt at 21°C .

On examining these curves, the greater effect of the first unit quantity of water added to the acid than the succeeding ones is distinctly visible in each case. On comparing them with those obtained by adding unit quantities of the same acids to water (Phil. Mag. May 1890, p. 421), we find that the greater effects of the first added unit quantities of acid were much more conspicuous than those of the first added unit quantities of water; and that whilst the first quantities of acids added to water increased the electromotive force, the first quantities of water added to acids decreased it. The less conspicuous effects produced by adding water to acids than by acids to water, were probably due to the circumstance that the acids had each been already largely diluted, about 30 to 50 times their weight, before adding the first units of water to them. In confirmation of this statement, I have found by experimental measurements that both with hydrochloric and with sulphuric acid the greater influence of the first added unit of water was more conspicuous when the acids were less diluted beforehand.

The results obtained with these three acids indicate that the greater influence of the first added unit quantity of water is not limited to water added to absolute acid, but extends to that added to acid already considerably diluted, and therefore the property under consideration is a more general one.

I have similarly examined the effect of adding successive unit quantities of water to a saturated aqueous solution of potassium chloride, containing 25.0 grains of the salt in 77.5 grains of water, upon the electromotive force of a zinc-platinum couple. The annexed curve shows the results:—

Fig. 4.—KCl 25 grains, with ZnPt at 21° C.

The greater effect of the first added unit quantity is in this case also clearly manifested.

With the object of arriving at some idea of the relative amounts of effect of the first and last unit portions of potassium chloride added to water, and to obtain a complete curve of electromotive force of that salt in water, the degrees of electromotive force with a zinc-platinum couple were measured, using five series of aqueous solutions of the salt, comprising the entire range from water to a saturated solution. In order also to show the manifest effect of an extremely minute quantity in the first addition, and not to extend the entire curve to an extraordinary length, it was found necessary to divide the entire range into five sections, and to increase the magnitude of the unit quantity to ten times its amount in each successive section; the unit quantities added, therefore, are 10,000 times larger in the last section than in the first one.

Fig. 5.—Potassium Chloride, with ZnPt at 24° C. Unit quantity = 1.

Fig. 6.—Potassium Chloride, at 23° 5 C. Unit quantity = 10.

Fig. 7.

Potassium Chloride, at 15° C. Unit quantity=100.

Fig. 8.

Potassium Chloride, at 21° 5 C. Unit quantity=1000.

Fig. 9.

Potassium Chloride, at 27° C. Unit quantity = 10,000.

These curves and numbers show that increasing the unit quantity of salt added from .0005 grain in the first section to 5 grains or 10,000 times the amount, in the last one, only produced about 5.27 times the amount of average difference of electromotive force, and therefore the addition of the same weight (*i. e.* .0005 grain) had only about one 1897th part of the average effect upon the electromotive force in the series of strong solutions that it had in the weak ones.

In all these cases the phenomenon was produced, either by increasing the degree of dilution or that of concentration of the liquid, and not by strong chemical union. In order

therefore to ascertain whether the same effect occurred when two electrolytic substances united chemically together I made two experiments, in each of which the combined influences of dilution and strong chemical union cooperated together. I took in each experiment the same fixed quantity of the same mixture of .365 grain of hydrochloric acid and 18 grains of water as before, and added to this diluted acid four unit quantities in succession of a mixture of .088 grain of $\text{Na}_2\text{C}_2\text{O}_3$ and 89.1 grains of water in one experiment, and .115 grain of K_2CO_3 and 89.1 grains of water in the other. The total quantity of alkali added in each experiment was just sufficient to neutralize two thirds of the acid. The following curves show the results :—

Fig. 10.
 $\text{HCl} + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$,
with CdPt at 19°C .

Fig. 11.
 $\text{HCl} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$,
with CdPt at 19°C .

These curves show distinctly, 1st, the greater degree of influence of the first unit quantity of substance added than that of the succeeding one, and prove the existence of the same phenomenon in cases of strong chemical union; and, 2nd, that strong chemical union *increased* the magnitude of the phenomenon.

To determine the influence upon the phenomenon of strong chemical action alone, apart from that of dilution, I made a precisely similar experiment to the last one, but employing anhydrous carbonate of sodium and omitting the unit quantities of water. The following curve represents the results :—

Fig. 12.
 $\text{HCl} + \text{Na}_2\text{CO}_3$, with CdPt at 22°C .

The greater effect of the first unit quantity of the anhydrous alkali is quite conspicuous, and is about equal in magnitude to that of mixed soda and water in the immediately previous experiment. The amount of such effect, however, obtained with the first unit quantity of mixed soda and water was not equal to the united amounts of first effect of dry soda and that of water alone (see curve, fig. 1).

I have found the same effect with dilute hydrochloric acid and the anhydrous carbonates of lithium, sodium, potassium, rubidium, barium, strontium, calcium, magnesium, zinc, and cadmium; with dilute sulphuric acid and the carbonates of rubidium, potassium, sodium, magnesium, zinc, and cadmium; with dilute nitric acid and the carbonates of sodium and potassium; with dilute hydrochloric, hydrobromic, and hydriodic acids, and carbonate of sodium; ditto with the carbonates of calcium and cadmium. In no case has an exception been observed.

The curves of electromotive force obtained in this research and in the one referred to (Philosophical Magazine, May 1890, p. 421) support in greater or less degree the general conclusion, that *when successive equal quantities of one electrolyte are added to a fixed and much larger quantity of another, the first added quantity has usually a much greater effect than any of the immediately succeeding ones in altering the amount of electromotive force of a voltaic couple, and consequently also in altering that of all other properties inseparably related to it.*

This conclusion is further supported by the facts already mentioned, viz., 1st, that on adding equal quantities of water

in succession to a fixed amount of either nitric, sulphuric, hydrochloric, hydrobromic, or hydriodic acid, the largest amount of heat is evolved by the first quantity added ; 2nd, by the diminishing amount of contraction which usually occurs on adding successive equal portions of a salt to water ; and, 3rd, by the circumstance that on adding equal quantities in succession, either of an acid or a salt, to water, the electric conduction-resistance is much more largely diminished by the first quantity added than by any of the succeeding ones.

It is evident from these considerations that the property in question, which I may term "*the greater influence of first quantities*," is a very general one of electrolytes, and that the four several phenomena mentioned are instances of it, and are probably results of one common cause. The method of examining this property by means of variations of electromotive force is very convenient, and the curves thus obtained implicitly contain more detail of information than those obtained by thermal measurements, because they represent more perfectly integrated effects.

The relatively greater increase of electric conductivity by addition of the first unit quantity of acid or salt than by any succeeding one, has been explained by the theory of dissociation ; but it is also consistent with the simple mechanical view that the molecules of the first added unit of the dissolved substance have greater freedom and velocity of motion ; the relatively greater electromotive force under those conditions is also consistent with this idea. The increase of electromotive force by addition of acid to water, and its decrease by addition of water to acid, admit of a very simple explanation. The degree of electromotive force depends partly upon the average velocity of the molecules of the liquid. Strong acids possess greater molecular velocity and excite greater electromotive force than water. By admixture of the acid and water heat is evolved and the average molecular velocity of each uniting substance is diminished. When we add a little water to a large amount of acid, the average molecular velocity of the mixture is less than that of the acid, first, because water has less molecular velocity than the acid, and, second, because heat is set free and molecular motion is lost. But when we add a little acid to a large quantity of water, the average molecular velocity of the mixture is greater than that of water, because the molecular velocity of the acid is so much greater than that of water that it more than compensates for the loss of motion which occurs in the form of heat during the act of mixing.