

By regularly increasing the strength of the solution, the electromotive force at first increased very rapidly, then with decreasing rapidity, and finally remained uniform. The total increase was 0.38 volt. The smallest proportion of bromine required to upset the balance lay between 1 in 77,500,000 and 84,545,000 parts of water.

With each of these substances, and with all others which I have examined, a gradual and regular increase of strength of the solution from the weakest up to a saturated one, was attended by a more or less irregular change of electromotive force.

By plotting the quantities of dissolved substance as ordinates to the electromotive forces as abscissæ, each substance or mixture of substances in every case yielded a different curve of variation of electromotive force by uniformly changing the strength of its solution. With a given voltaic couple at a given temperature, the curve was constant and characteristic of the substance. As the least addition of a soluble foreign substance greatly changed the "minimum-point," and altered the curve of variation of potential, both the curve and the minimum proportion of a substance required to upset the voltaic balance may probably be used as tests of the chemical composition of the substance, and as means of examining its state of combination when dissolved. By varying the strength of the solution at each of the metals separately, a curve of change of potential was obtained for each positive metal, but not for every negative one.

III. "Influence of the Chemical Energy of Electrolytes upon the 'Minimum Point' and Change of Potential of a Voltaic Couple in Water." By G. GORE, F.R.S. Received June 7, 1888.

In a communication to the Royal Society, May 3rd, 1888, on "The Effect of Chlorine upon the Electromotive Force of a Voltaic Couple," and in a subsequent one on "The Minimum Point of Change of Potential of a Voltaic Couple," I have shown that by opposing to each other two currents of equal electromotive force from two perfectly similar couples of magnesium-platinum or zinc-platinum in distilled water, and gradually adding to one of the cells sufficiently minute quantities of a suitable substance, such as chlorine, hydrochloric acid, or a soluble salt, &c., the voltaic balance is not disturbed until a certain definite proportion of the substance has been added, and that the proportion required to be added is excessively small (about 1 in 17,000 millions) in the case of chlorine

with a magnesium-platinum couple, and extremely different with unlike substances.

In the present paper my object is to describe a few similar experiments, made to examine the influence of liquids of different chemical composition, upon this phenomenon and upon the degrees of electromotive force produced by further additions of the substances. All the solutions were made with distilled water, and the substances employed were of considerable degree of purity. The voltaic cell consisted in each case of zinc and platinum in distilled water, and its electromotive force was balanced by that of a suitable thermo-electric pile (see 'Proceedings of the Birmingham Philosophical Society,' vol. 4, p. 130), and the measurements made under that condition.

The electromotive force of a zinc-platinum couple in ordinary distilled water at 16° C. is about 1·088 volt; provided the zinc is free from oxide, and the platinum contains no absorbed hydrogen. The presence of hydrogen (not removable by rubbing but removable by heating to redness) may reduce the electromotive force to 0·91 volt, and a film of oxide upon the zinc may reduce it 1 or 2 per cent., whilst carbonic acid absorbed by the water from the air, &c., may increase it about 2 per cent. In all cases, therefore, where very exact measurements of electromotive force are necessary, these circumstances have to be considered. In the present case the measurements are sufficiently accurate for the purposes intended.

A series of measurements were made with a zinc-platinum couple in water, adding uniform quantities of hydrochloric acid up to 0·15 grain per 465 grains of water, and heating the platinum to redness previous to each measurement. The variations of electromotive force obtained were nearly the same as when the platinum was not heated, the only material difference being that the electromotive force throughout was about 0·10 volt higher.

The following are the results of the experiments made upon the influence of the chemical energy of the liquid. The numbers are corrected for the influence of hydrogen absorbed by the platinum.

Table I.—KIO₃ in 465 grains of Water at 15° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|---------|---------|--------|---------|--------|
| 37·05 | 1·40586 | 22·05 | 1·26 | 7·05 | 1·1456 |
| 34·05 | 1·36296 | 19·05 | 1·2428 | 4·05 | 1·1313 |
| 31·05 | 1·3172 | 16·05 | 1·2085 | 1·05 | 1·1370 |
| 28·05 | 1·2829 | 13·05 | 1·2028 | 0·94 | 1·0884 |
| 25·05 | 1·2743 | 10·05 | 1·14 | water | „ |

The strongest solution employed was a saturated one. Four different solutions, each weaker than 0·94 grain, gave the same

electromotive force as water. The least proportion of the iodate necessary to upset the balance lay between 1 part in 443 and 494 parts of water. The increase of electromotive force by increased strength of the solution was nearly regular, as may be seen by plotting the quantities of substance as ordinates to the electromotive forces as abscissæ. In order to remove any trace of free iodine, the iodate was previously kept at 100° C. during one hour; it was then perfectly white and free from odour.

Table II.—KBrO₃ in 465 grains of Water at 14° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 19·5 | 1·2886 | 12 | 1·260 | 4·5 | 1·3344 |
| 18·0 | 1·2743 | 10·5 | " | 3·0 | 1·3000 |
| 16·5 | " | 9 | 1·3344 | 1·5 | 1·2600 |
| 15 | 1·2772 | 7·5 | " | .. | .. |
| 13·5 | 1·2972 | 6 | " | .. | .. |

The strongest solution was a saturated one.

Table III.—Ditto at 15° C.

| Grains. | Volts. |
|---------|--------|
| 1·5 | 1·260 |
| 1·35 | 1·117 |
| 1·2066 | 1·0884 |
| water | " |

Eight other solutions, all of different strengths below 1·2006, gave the same electromotive force as water. The smallest proportion of bromate required to upset the balance lay between 1 in 344 and 387 parts of water. The increase of electromotive force by increase of strength of the solution was extremely irregular.

The effects obtained with solutions of potassic chlorate have already been given in the paper on "The Change of Potential of a Voltaic Couple by Variation of Strength of its Liquid." The smallest proportion of the salt required to disturb the voltaic balance lay between 1 in 221 and 258 parts of water. Three solutions, each weaker than 1·8 grain in 465 grains of water, viz., 0·09, 0·009, and 0·0009 grain, gave the same electromotive force as water.

The following table shows the results obtained with this group of salts:—

Table IV.

Iodate, minimum point of change lay between 1 in 443 and 494.

Bromate, " " " 1 ,, 344 ,, 384.

Chlorate, " " " 1 ,, 221 ,, 258.

The minimum points of change of these three salts constitute a series indicating a gradation of degree of chemical union of the negative constituent of the salt with its base, feeblest in the iodate, intermediate with the bromate, and strongest in the chlorate. The more feebly united the negative constituent, the smaller was the proportion of the salt required to disturb the voltaic balance.

Table V.—KI in 465 grains of Water at 15° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 762 | 1·0584 | 727 | 1·1252 | 692 | 1·1728 |
| 755 | 1·0727 | 720 | 1·1442 | 685 | " |
| 748 | 1·0784 | 713 | 1·1585 | 678 | " |
| 741 | 1·0899 | 706 | 1·1728 | .. | .. |
| 734 | 1·2071 | 699 | " | .. | .. |

The strongest solution was a saturated one.

Table VI.—Ditto at 13° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 678 | 1·1728 | 426 | 1·1556 | 174 | 1·1556 |
| 594 | 1·1899 | 342 | " | 90 | " |
| 510 | 1·1556 | 258 | " | 6 | " |

Table VII.—Ditto at 14° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 6·00 | 1·1556 | 4·89 | 1·0584 | 3·69 | 1·0584 |
| 5·49 | 1·1442 | 4·29 | " | 3·09 | " |

Table VIII.—Ditto at 19° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 3·0 | 1·0497 | 1·68 | 1·0669 | 0·36 | 1·0697 |
| 2·67 | 1·0583 | 1·35 | 1·0583 | 0·03 | 1·0716 |
| 2·34 | 1·0697 | 1·02 | 1·0697 | 0·027 | 1·0812 |
| 2·01 | 1·0726 | 0·69 | „ | water | „ |

The great solubility of the salt rendered several groups of measurements necessary in order to include the entire range of solution. The salt was odourless and colourless, but slightly alkaline. The smallest proportion of the iodide necessary to change the balance lay between 1 in 15,500 and 17,222 parts of water. The variation of electromotive force with strength of solution was very irregular. The greatest electromotive force was with a solution containing from 680 to 700 grains of the salt.

Table IX.—KBr in 465 grains of Water at 12·5° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 273 | 1·1442 | 153 | 1·2457 | 33 | 1·230 |
| 243 | 1·1771 | 123 | 1·2314 | 3 | 1·2357 |
| 213 | 1·2314 | 93 | 1·1485 | .. | .. |
| 183 | 1·2171 | 63 | 1·230 | .. | .. |

• The salt was well crystallised, dry, odourless, and neutral to test-paper. The strongest solution of it was a saturated one.

Table X.—Ditto at 9° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 0·03 | 1·2872 | 0·01668 | 1·2443 | 0·00336 | 1·087 |
| 0·02667 | 1·2729 | 0·01335 | 1·3015 | water | „ |
| 0·02334 | 1·2529 | 0·01001 | 1·2872 | .. | .. |
| 0·02001 | 1·2443 | 0·00669 | 1·1871 | .. | .. |

Six different strengths of solution, each weaker than 0·0036, gave the same electromotive force as water. The smallest proportion of the salt which upset the balance lay between 1 part in 66,428 and 67,391 parts of water.

Table XI.—KCl in 465 grains of Water at 12° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|---------|---------|---------|---------|---------|
| 147 | 1·30436 | 93 | 1·30436 | 39 | 1·30436 |
| 129 | " | 75 | " | 21 | " |
| 111 | " | 57 | " | 3 | " |

The strongest solution was a saturated one. Four other solutions between those of 129 and 147 grains were tried, but they all gave 1·30436 volt. The abscissæ of the electromotive forces in this table formed a straight line.

Table XII.—Ditto at 8° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|----------|--------|----------|--------|----------|--------|
| 0·003 | 1·3056 | 0·001335 | 1·2014 | 0·000224 | 1·087 |
| 0·002667 | 1·2671 | 0·001001 | 1·1728 | 0·000112 | " |
| 0·002334 | 1·2043 | 0·000669 | 1·1442 | water | " |
| 0·002001 | 1·2443 | 0·000660 | 1·087 | .. | .. |
| 0·001668 | 1·230 | 0·000336 | " | .. | .. |

The smallest proportion of the salt necessary to disturb the voltaic balance lay between 1 in 695,067 and 704,540 parts of water. The variation of electromotive force in these solutions was not uniform.

The following table shows the proportions of these three salts required to upset the balance:—

Table XIII.

| | | | |
|----------|--------------|------------|------------------------|
| Iodide, | between 1 in | 15,500 and | 17,222 parts of water. |
| Bromide | " | 1 " | 66,428 " 67,391 " " |
| Chloride | " | 1 " | 695,067 " 704,540 " " |

By comparing these numbers with those in Table IV, it will be perceived that each of the haloid salts acted much more powerfully than either of the oxygen ones, and that the order of degrees of activity in the two series was reverse.

(Suspecting a decomposition of the chloride solution by the couple, I divided a solution of 8 grains of the salt per ounce of water into two equal portions in two glass vessels, then immersed a piece of zinc wire in one portion, and a second piece of the same wire in contact with a piece of platinum in the other, and set the vessels aside. In about 24 hours the liquid containing the couple was distinctly alkaline,

whilst the other remained neutral. I have examined this phenomenon further.)

The three halogens of the salts were now employed separately. A saturated solution of iodine was prepared by digesting a weighed amount of that substance in a known volume of hot distilled water in a stoppered glass flask with continual agitation; it contained 1 part of dissolved iodine in 3516 parts of water.

Table XIV.—Iodine in 465 grains of Water at 13·5° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|----------|--------|
| 0·1320 | 1·374 | 0·0546 | 1·374 | 0·00015 | 1·0894 |
| 0·1191 | „ | 0·0417 | „ | 0·000132 | 1·088 |
| 0·1062 | „ | 0·0288 | „ | 0·000075 | „ |
| 0·0933 | „ | 0·0159 | „ | water | „ |
| 0·0804 | „ | 0·003 | 1·2659 | .. | .. |
| 0·0675 | „ | 0·0003 | 1·1372 | .. | .. |

Four other solutions, weaker than 0·000075 grain, gave each 1·088 volt. The minimum proportion of iodine required to upset the balance lay between 1 part in 3,100,000 and 3,521,970 parts of water. Except in very weak solutions, variations of strength of the liquid had no effect upon the electromotive force.

The effects obtained with bromine have already been given in the paper on “The Change of Potential of a Voltaic Couple by Variations of Strength of its Liquid.” The smallest proportion of that substance required to disturb the balance lay between 1 part in 77,500,000 and 84,545,000 parts of water. By dissolving bromine in the proportions of 0·000075, 0·00015, 0·000165, and 0·00018 grain respectively in 13,950 grains of distilled water at 12°C., the three first of these solutions gave the same potential with zinc-platinum as that given by water, whilst the fourth gave 0·0064 volt greater.

Table XV.—Chlorine in 465 grains of Water at 11° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|---------|--------|
| 1·0695 | 2·312 | 0·6537 | 2·3349 | 0·2379 | 2·3405 |
| 1·0002 | 2·3206 | 0·5844 | 2·332 | 0·1686 | 2·2862 |
| 0·9309 | 2·3349 | 0·5151 | „ | 0·0993 | 2·2805 |
| 0·8616 | „ | 0·4458 | 2·3092 | 0·0300 | 2·226 |
| 0·7923 | „ | 0·3765 | 2·3891 | .. | .. |
| 0·723 | 2·2692 | 0·3072 | 2·2577 | .. | .. |

The strongest solution was about three-fourths saturated.

Table XVI.—Ditto at 13° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|---------|--------|---------|--------|-----------|--------|
| 0·03 | 2·2261 | 0·018 | 1·8457 | 0·006 | 1·7748 |
| 0·027 | 2·1317 | 0·015 | 1·84 | 0·003 | „ |
| 0·024 | 2·0459 | 0·012 | 1·817 | 0·0000003 | 1·18 |
| 0·021 | 1·9716 | 0·009 | 1·7748 | water | 1·088 |

Table XVII.—Ditto at 13° C.

| Grains. | Volts. | Grains. | Volts. | Grains. | Volts. |
|-----------|--------|------------|--------|-------------|--------|
| 0·003 | 1·7748 | 0·0000937 | 1·4173 | 0·00000293 | 1·26 |
| 0·0015 | 1·6604 | 0·0000468 | 1·403 | 0·000001464 | 1·2457 |
| 0·00075 | 1·6318 | 0·0000234 | 1·3887 | 0·000000732 | 1·1799 |
| 0·000375 | 1·5346 | 0·00001172 | 1·3744 | water | 1·0884 |
| 0·0001875 | 1·4316 | 0·00000585 | 1·3605 | .. | .. |

Table XVIII.—Ditto in 13,950 grains of Water at 11° C.

| Grains. | Volts. | Grains. | Volts. |
|------------|--------|-------------|--------|
| 0·00001247 | 1·1313 | 0·00000713 | 1·0884 |
| 0·00001104 | 1·0998 | 0·000003565 | „ |
| 0·00001069 | 1·0884 | water | „ |
| 0·0000089 | „ | .. | .. |

The mode by which the chlorine-water was prepared and its strength ascertained has been already described ('Roy. Soc. Proc.' vol. 44, 1888, p. 151, 'Nature,' vol. 38, p. 117). The minimum proportion of chlorine necessary to upset the balance was found more nearly by adding very small quantities of an exceedingly dilute solution of it to the water until the required strength was attained, thus avoiding the risk of error attending more numerous dilutions. The proportion lay between 1 in 1264 million and 1300 million parts of water. The variation of electromotive force by uniform increase of the strength of the solution was irregular.

The following are the minimum proportions of iodine, bromine, and chlorine, arranged for comparison :—

Table XIX.—Minimum Proportions.

| | | |
|---------------------------|----------------|--------------|
| Iodine, between 1 part in | 3,100,000 and | 3,521,970 |
| Bromine „ 1 „ | 77,500,000 „ | 84,545,000 |
| Chlorine „ 1 „ | 1264,000,000 „ | 1300,000,000 |

This series of numbers suggests a quantitative relation of the “minimum proportions” to the atomic and molecular weights of the substances.

On comparing these numbers with those of the two previous groups of bodies, we find that the proportion of substance required to upset the voltaic balance was largest with the oxygen salts, intermediate with the haloid ones, and least with the free elementary bodies. It was smaller the greater the degree of chemical energy of the substance; thus it was about 400 times less with chlorine than with iodine. And it was smaller the greater the degree of freedom to exert that energy; thus it was about 5,416,000 times smaller with free chlorine than with potassic chlorate, or 1,570,000 times less than with the combined chlorine of the chlorate; and about 185 times smaller than with potassic chloride, or 88 times less than with the combined chlorine of that salt.

At the lowest potentials, the rate of increase of electromotive force per grain of substance is usually larger the smaller the proportion of substance necessary to disturb the potential. Iodine is an exception to this, but probably only an apparent one, because on substituting magnesium for the zinc, the addition of iodine caused an increase of potential as usual.

The curve of variation of potential was different with the solution of each substance, and was apparently characteristic of the body in each case; and a great number of such representative curves might be obtained by change of strength of solution, in nearly all electrolytes, with a zinc-platinum or other voltaic couple.

IV. “The Electric Organ of the Skate. The Electric Organ of *Raia radiata*.” By J. C. EWART, M.D., Regius Professor of Natural History, University of Edinburgh. Communicated by Professor J. BURDON SANDERSON, F.R.S. Received June 6, 1888.

(Abstract.)

The first part of this paper is chiefly devoted to a comparison of the electric organs of *Raia radiata*, *R. batis*, and *R. circularis*. It is shown that the organ in the species *radiata* differs in many respects from the organ in the two other species, and that an exhaustive