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# XLI. On the theory of voltaic action

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piece of rag at the bottom of the pendulum, set fire to the rag, and blow out the flame, still allowing the rag to smoke; then put the pendulum in motion, and the smoke will be seen passing along in the direction of the pendulum's motion, even before it can be observed that it has begun to descend.

Had Captain Kater been aware of this fact, he would have been at no loss to account for his pendulum losing its adjustment, when by the hygrometer he observed a great and sudden change in the air from moisture to dryness. This observation shows the accuracy with which his experiments were conducted; it also indicates that dry air is more dense than moist, as the current generated in the latter state offered more resistance to the return of the pendulum than in the former.

For, in his experiments, at the time when the smaller weight of the pendulum was down, the vibrations would be slower than when the greater weight was down; the smaller weight presenting a larger surface to the resisting medium, in proportion to its weight, than the greater weight, the current then generated would oppose its descent more than the current generated by the greater weight.

[To be continued.]

XLI. On the Theory of Voltaic Action. By Mr. JOHN PRIDEAUX.

[Concluded from p. 220.]

Sect. IV. Of the Conducting Property of the Liquid.

25. **T**HE conducting power of the liquid is a main point in voltaic phaenomena; and acid liquids are understood, generally, to be the best conductors (liquid metals of course left out of the question); alkaline liquids the worst, of aqueous solutions; and alcohol, oils, and the like, as non-conductors. Thus, from whatever kind of coincidence, the conducting and electro-negative properties seem to bear some mutual relation.

26. Whether this conduction in the voltaic battery be from particle to particle, or, like that of caloric in liquids, connected with transference of the particles themselves, becomes the next inquiry. Of such transference we have abundant evidence; but in what degree it is *essential* to the conducting process, it may be difficult to ascertain by direct experiment.

27. Separate glasses, filled with acid and alkaline solutions, and connected by a siphon filled with water, separated cells, similarly filled, and divided by bladder, each having a copper plate plunged in the alkali, a zinc plate in the acid, and con-

nected through a wire,—have their contents gradually altered by transference of the acid into the alkali, and *vice versâ*, until either neutralization has taken place, or the activity of the circuit is so far lowered as to have no longer power to communicate the requisite impetus. Oxygen goes to the zinc, and hydrogen to the copper, in most cases; and we have seen (22) that not only this took place, but that the alkali continued to rise, and the acid to descend, in opposition to their specific gravity.

28. It is seen (23) that addition to the quantity of copper augments the effect; but I do not find this happen unless the additional copper be in *immediate* liquid communication with the zinc.

a) A 3-inch zinc plate was set in a water-tight copper case (open at top), with due precautions against contact: the case was nearly filled with diluted nitric acid (1·60), and placed in a vessel of the same liquid, which just reached its upper edge. The case and zinc being both furnished with conducting wires, were put in communication with the magnetest;

Deflection . . . . 40°

b) An additional copper case, open at both ends, was then placed about the first, clear of contact, and also made to communicate with the same mercury box as the first case.

No increase of deflection.

c) A little more of the same acid was then poured on, to overflow the whole, and establish immediate liquid communication between the zinc and the external copper. As soon as it ran over the edges,

Deflection . . . . 42°

The conducting medium is the same in (b) as in (c); but the transference of particles from the zinc to the external copper is intercepted in (b), and no other evident difference appears. The communication in (c) being only over the edge of the inner case, the increase is proportionally small; 40° to 42°, or 38 to 43 current.

Thus we may imagine the copper exalting, by contact or by metallic communication, the positive character of the zinc; the zinc thus exalted decomposing the water with peculiar vivacity, attracting the negative oxygen, *charging* and repelling the positive hydrogen; the latter being at the same time attracted, and oxygen charged and repelled by the copper:—oxygen thus continually travelling from copper to zinc; hydrogen from zinc to copper; and each discharging its *excess* of electricity as it arrives. This attraction and repulsion being of course stronger, and the motion of the charged particles consequently quicker, the less the interval between the plates;

and we know how greatly approximation increases the activity of voltaic plates.

29. If this transference be the real conducting agency, it should follow, that when the poles are disconnected, as the electricity accumulates, and counterbalances those attractions and repulsions between the plates, the action between them should become gradually weaker, and at last cease, but be renewed on restoring the connexion. And such we know to be the fact.

Also, when the plates, and consequently the intermediate imperfectly conducting strata of liquid, are multiplied, resistance to the passage of electricity is increased. It must therefore accumulate, in degree, on each pair of plates; and the atom of hydrogen from the zinc of pair A should be unable to discharge itself into the copper of pair B, unless its charge be high enough to overcome the resistance forward, and *vice versa*. Hence the electricity at the poles of a numerous voltaic battery, though greater in tension, should be less in quantity of current than at those of a battery equal in surface, but in fewer divisions.

And this also may be seen to be true by the following experiment.

30. For comparisons of this kind I employ a trough of wood, twenty-four inches long, seven wide, and four deep, divided by transverse partitions into six cells, and well lined with cement. Each of these cells contains a small calorimotor, nearly on Dr. Hare's plan, composed of 10 zinc and 11 copper plates, each three inches square, the zinc and copper working into separate mercury boxes (3, &c.) on the top of each calorimotor.

By passing connecting wires along 13, 23, 33, 43, &c., and 1 c, 2 c, 3 c, 4 c, &c., the whole six sets become a single pair; but connecting them 13, 2 c; 23, 3 c; 33, 4 c, &c., they become as many pairs as there are sets. And it is easy to understand how, by arranging the connexions, they become two or three pairs. It is this convenient divisibility which led to the preference of the number 6.

The following Table shows the deflections, in proportion to the manner in which the calorimotors were divided.

Connexion	Experiments				Mean.	Curr.
	1	2	3	4		
into 1 pair.....	60°	58°	58°	59°	59°	75?
2 pair.....	49	48	48	49	48·5	62
3 pair.....	42	42	42	43	42	43·4
6 pair.....	30	30	30	30	30	22·6

The number 75 is an estimate, and I think considerably below the truth. Becquerel's table does not go so high.

These facts do not appear so easy of explanation upon any other hypothesis of liquid conduction, as on that by transference of particles.

31. As, however, we are unacquainted with any standard of the *actual* quantity of electricity circulating in any given voltaic action, and as it would be difficult to measure even the relative quantity that a given portion of positive and negative liquid matter can convey by transference of particles, under a given tension,—we cannot ascertain by calculation, any more than by direct experiment, whether this transference is likely to be the chief, or even a partial agent, in conveying the electricity through the liquid. The discharge of a Leyden jar through a water-tube, though with great diminution of its impetus, yet exhibits a rapidity of conduction inconsistent with our notions of the transference of particles; and a discrepancy is occasionally found between the transmitting or conducting power, and the facility of decomposition, as in the case of dilute sulphuric and nitric acids.

Still such a notion materially assists our understanding the opposite electrical accumulations at the poles of the pile, and some of the phænomena accompanying them; and the high tension of a charged jar *may* enable the electricity to pass through liquids in a manner which could not be produced by the actions between the plates of a voltaic pile.

#### Sect. V. *Of the Loss of Power by continued Voltaic Circulation.*

32. However uncertain be the degree in which molecular transference in the liquid acts as an auxiliary, no doubt exists of the tendency of the negative particles toward the positive plate, and *vice versâ*: and if the leading principle of this paper be true (20), they should, when thus arranged in the order of electrical attraction, *after discharging* their acquired electricity, oppose, and gradually tend to neutralize, the electromotive action of the plates on each other.

33. Thus, whilst a voltaic pair, kept, the zinc in alkali, the copper in acid, retains its electricity unimpaired for a long time, we find them, when charged with solution of a neutral salt, become gradually weaker in action, until, after a short period, they hardly affect the multiplier. If we now take the plates out of the liquid, leave them exposed to the air, and replace them, the action is renewed with a vigour and permanence proportionate (to a certain extent) to the length of time the plates have been withdrawn from the liquid.

34. During this time of separation, the liquid particles at-

tached to the plates will gradually drain off, and those remaining in the liquid may reassume the arrangement due to their natural affinities. Thus the energy of action should be renewed on replacing the plates in the liquid; and this renovation should have more or less permanence, according as the re-establishment of the natural order of affinities were more or less complete, and freed from remaining electrical influence. And this, in an imperfectly conducting liquid, subject to the effects of combination and decomposition before noticed (28), may be an operation not quite instantaneous.

35. If such an electrical arrangement of molecules be the chief cause of decay of power in a battery (when the neutralization of acid or alkaline charges is not concerned), then washing the plates instantly, on their removal from the liquid (although kept beneath the surface of the water all the time they are out of the charge), should make them as effective, on being plunged into a fresh solution, as hanging for any length of time in the air. And keeping them in the second solution until the force be again much reduced, should give the first charge time to recover its natural state, by which the plates on being removed from the second, washed, and returned to the first, should have all their original energy. And thus the action should be renewable by washing and alternation, until the formation of a coat of suboxide on the plates should impede their contact with the liquid, and therefore require friction or an acid to cleanse them.

36. The apparatus described (30), in which the cells are nearly filled by the little calorimotors, and the whole liquid charge consequently subjected to their action, gave results corresponding so accurately with these anticipations, that doubts might have been excited of their fairness, particularly as the structure of the instrument is a little complicated, which would make the experiments troublesome to repeat; and as each calorimotor is bound by a wooden frame, which might be supposed to retain a portion of the water or acid employed in washing, the following simple arrangement was therefore substituted.

A pair of zinc and copper plates, 3 inches square, each provided with a conducting wire, were fixed together at the interval of  $\frac{1}{4}$  inch, by short cylinders of sealing-wax at the four corners, with the aid of heat. The backs of the plates were then varnished; so that the polished faces, opposed to each other at an invariable distance, were the only parts capable of action. The liquid charge was 4 ounces sulphate of zinc, dissolved in a quart of water, and it was contained in two glasses, G and H.

The plates being dipped in water, to remove any foreign material, or fugitive impression at the first contact with moisture, the ends of the wires were connected with a multiplier, and the plates plunged into H,—Deflection . . . 40°

Left in H until the needle had receded to . . . 25°,

Then taken out and plunged into G,—Deflection . . . 40°.

As the plates occupied only the middle of the glass, and the backs were varnished, it was probable that but little of the charge, perhaps only the part immediately between the faces of the plates, had suffered electrical change. The needle was therefore allowed to recede to 28°, when the plates were lifted out and replaced in the same liquid,—Deflection . . . 38°, but unsteady. After receding to . . . 30°, removed to H,—Deflection again . . . 40°.

After receding to 20°, taken out and replaced,—Deflection . . . 40°, but receded quickly.

Washed and placed in G,—Deflection . . . 42°.

Taken out, washed, and left all night in the air. In the morning plunged into H,—Deflection . . . 42°: So that washing produced the same deflection as hanging all night in the air.

Receded in 15 minutes to . . . 20°.

37. It then became a question whether the mere discontinuance of electromotion, without moving the plates, might not allow the reaction of the natural affinities, and thus restore the action.

The needle having fallen back, as above stated, to . . . 20°, the connexion through the multiplier was severed. Re-connected after 10 minutes . . . 42°, but fell back, in 10 minutes connexion, to . . . 18°.

Disconnected 5 minutes; on re-connexion . . . 30°.

Again disconnected 10 minutes; on re-connexion . . . 30°. The face of the copper covered with small bubbles; doubtless hydrogen gas. Detached 2 minutes to wipe away the bubbles with a feather,—Re-connected . . . 35°.

The plates had now continued two hours and a half in the solution, and the zinc was black with suboxide; yet simply washed and placed in H,—the Deflection was . . . 37°.

It is unnecessary to occupy more space with the further variations of this experiment, all which give the same result.

38. But one circumstance must not be passed over. Hanging in the air two or three hours gave a deflection of 45°, which fell back to 35° so rapidly as to allow only time for turning to the desk and writing the figures; whilst remaining

for twenty-four hours in the air gave only 35°, but steady. Hence some accumulation seems to take place in the air during the drying of the plates, perhaps communicated by the vapour.

39. These experiments go in confirmation of the supposition (35), that the electric attraction, arranging the negative particles of the liquid against the face of the positive metal, and *vice versa*, and thus tending to saturate itself, should gradually extinguish its own action.

And from previous observations (14, 15, 19, 22,) it might be inferred, that the destruction of zinc by acid charges is waste.

Entire extinction of the electromotion by saturation is, however, prevented by the unsteadiness of liquid particles; and by the imperfection of liquid conducting power, whatever its mode of action, obstructing the effects on the particles not in immediate contact with the metals; which are sufficient to keep some action alive for a good while, where only neutral charges are employed. But when free acids are used, which dissolve the zinc, a more powerful compensating force comes into play.

#### Sect. VI. *Of the Effects of Chemical Action.*

40. It has long been shown by Becquerel\*, that when a metal is acted on by an acid, and forms with it an oxide or a salt, the metal becomes negatively, the liquid positively, electric; and accordingly it is familiar to Voltaists, that when, into an acid liquid, two plates of zinc are plunged, the one new and bright, the other corroded, connexion being made through a multiplier, the corroded plate is positive (in the liquor) to the bright one.

41. It has also been shown by Sturgeon, and had been shown before him by Davy, that if two plates of iron with bright surfaces be plunged into dilute muriatic acid, and after a time one of them be withdrawn, and kept for some seconds out of the acid, on being replaced it acts as copper; and so alternately *either* plate withdrawn for a few seconds, acts as copper on reentering the liquor. And the case is the same with zinc, as any one possessing a couple of zinc plates may prove in a minute.

42. These two experiments (40, 41), and Becquerel's general principle (40) explain each other. When bright and corroded zinc are brought into contact with an acid, the latter yields most readily to its action, and gives off electricity to the liquid, which returns through the bright plate and the wire.

\* *Ann. de Chim. et de Phys.* May 1829.



When of two similar plates, one is withdrawn from the action of the acid, the other remaining subject to it, the latter will give off positive electricity to the liquor, which the former, on reentering, must take up and convey back through the wire, as copper does.

So in a voltaic pair, when acid is brought by electrical attraction or otherwise into contact with zinc, the metal is attacked; the acid or water being decomposed on the one hand, and the zinc dissolved on the other. The positive electricity passes from the zinc into the liquid (40) in the direction of the galvanic current (and assuming the theory of two electricities, the negative passes from the acid to the zinc, also in the direction of the current). Thus the chemical action compensates, or surpasses, the neutralizing effect of the negative liquid particles on the zinc, in proportion to its facility of decomposition, and to the electrical character of its residual ingredients; whilst the copper is negatively excited by the acid to the highest degree (23).

43. Sulphuric acid decomposes the water, as does probably the muriatic; hydrogen gas being given off in both cases, and carrying with it\* some of the positive electricity generated. But nitric acid gives rise to no gas (in moderate charges); and there being no waste of electricity, its action should be the greater, as is known to be the fact.

44. These three acids, employed in atomic proportions, in equal quantities of water, placed in three cells of the trough (30); one of the calorimotors being moved from one to the other and back again alternately, so as to give all the acids equal opportunity for action, gave the following deflections.

Acids.	Experiments				Mean.	Curr.
	1	2	3	4		
Sulphuric.....	26°	20°	14°	10°	17·5	9·7
Muriatic .....	30	23	†	13	22·	13·3
Nitric .....	42	34	21	17	28·5	20·5

Why the muriatic acted so much more powerfully than the sulphuric acid is not evident, as the acids were pure. Possibly the muriatic acid may be itself decomposed, and the chlorine combine directly with the metal. No evidence occurred to me, when employing atomic proportions, of the less durability of nitric acid, as stated by Singer; but my experience is not to be set in competition with his.

45. An experiment quoted by Berzelius‡, and which I do

\* Pouillet, *Ann. de Chim. et de Phys.* September 1827.

† This figure was not recorded, through oversight.

‡ *Tr. de Chim.* tom. i. p. 152.

not recollect to have encountered elsewhere, is in point here, and compares well with the stimulative action of the electric state of the liquid (20).

If a large and a small plate of zinc connected through a multiplier be plunged into a weakly acid liquor, the larger acts as copper; but increase the acidity, or warm the liquid, the larger acts as zinc.

Here when the acid is too weak to attack the zinc, the larger surface giving the greater field for the influence of the negative liquor, positive electricity sets away from it (20) through the wire, to the smaller plate, as happens with copper. But when the metal is acted on, either by increasing the acidity, or warming the liquor, the larger surface gives off the more positive electricity to the liquor, which then sets through the wire in the other direction, as in the case of zinc; thus not only compensating, but surpassing (42), the *negative* stimulation of the acid first demonstrated.

It must here be confessed, that my results in repeating this experiment have not been constant, though generally confirmatory. The authority of Berzelius is, nevertheless, abundantly sufficient; and proofs of the efficacy of chemical action, in augmenting the voltaic current, are too familiar to the experimentalist to need further exemplification here.

#### Conclusion.

The theory here advocated may be thus generally stated.

When zinc and copper come into contact, positive electricity passes from the copper into the zinc, until their mutual relation to that fluid be *in equilibrio*: this is initial electro-motion; which may be continued, in the condition of circulation, through a conducting liquid (12). But if an electro-positive liquid be placed in contact with the negative metal, and *vice versâ*, and the circulation kept up, the disposition of the liquids being in *counteraction* to that of the metals, the electro-motive action is obstructed (19). On the contrary, when the positive and negative liquids are in contact with the homo-electric metals, the tendency of the whole is in the same direction, and the electro-motive action is expedited (19).

When the electricity thus passes into the zinc, and on into the positive element of the liquid, the so *charged* liquid particle is repelled, and attracted by the copper, in proportion to the approximation of the plates; and having free motion, proceeds in that direction with proportionate velocity. The converse takes place between the copper and the electro-negative liquid particle; and the particles discharging themselves on their arrival, thus maintain the circulation.

When discharged of their *acquired* electricity, they remain attached to the anti-electric plates, and thus assume the counteracting character above mentioned, obstructing the current in proportion to the quantity collected on the surface of the plates (32). But when there is free acid, it no sooner comes in contact with the zinc, than it begins to act upon it, and the zinc, in the act of dissolution, gives out positive electricity to the liquid; *i. e.* in the direction of the current (40), thus balancing, or more commonly overcoming, the neutralizing influence of the negative liquid particles (42), whilst they act with their full effect in exalting the copper: and hence the superiority of acid charges (23).

The reader will perceive that the theory of two fluids is most conformable to these views. It has not been insisted on, because not fully received in this country, nor quite free from ambiguity in its application.

**XLII.** *Abstract of Meteorological Observations made at St. Petersburg, in 1830, at the Astronomical Observatory. By MM. Wisniewsky and Tarkhanof; and calculated by Professor M. A. KUPFFER\*.*

**I**N the following observations the thermometer is divided according to Reaumur, and the barometer into French inches. The barometric heights have been reduced to the temperature of 14° of Reaumur, and the months are reckoned according to the New Style.

**TABLE I.** *Containing the Mean of the Thermometric Observations for every Month of 1830.*

Months.	7 <sup>h</sup> A.M.	2 <sup>h</sup> P.M.	9 <sup>h</sup> P.M.	Means.
January.. ...	— 9·46	— 8·03	— 8·44	— 8·64
February ...	8·54	6·55	7·24	7·45
March.....	— 4·59	— 1·13	— 3·25	— 2·99
April.....	+ 0·83	+ 4·30	+ 1·18	+ 2·10
May .. ..	4·46	7·76	3·86	5·36
June .....	11·59	14·67	10·89	12·38
July .....	13·11	15·73	12·66	13·83
August.....	13·16	16·65	12·65	14·15
September...	6·08	10·77	7·33	8·06
October .....	+ 3·17	5·68	3·86	4·24
November ...	— 0·36	+ 0·72	+ 0·28	+ 0·21
December....	— 4·76	— 3·64	— 4·11	— 4·17
Means.....	+ 2·6	+ 4·74	+ 2·47	+ 3·09

According to the tables communicated by Dr. Brewster†, we

\* Communicated by Professor Kupffer.

† Edinb. Journal of Science, for June 1826.