LXXVIII. Experiments in Voltaic electricity

Andrew Crosse Esq.

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Metallic salts are also subject to similar changes. We see then, that salts in general, alkaline, earthy, and metallic, partake with barytes of the property of being precipitated under similar circumstances by their respective acids;—and generally, according to the greater or less solubility of salts in water, they are precipitated by their acids more or less concentrated.

Had the facts here contained been generally known, the authors of chemical rudiments must necessarily incur great censure, for plunging deeper into mystery, that which is already intricate; it must have involved many novices in the science into the greatest difficulties; for their first attempts are generally to form the salts, and in performing which, if instead of solution they obtain a precipitate, they conclude that the experiment by some unknown accident has failed,—they refer to the instructions and repeat the experiments in vain; and this they are subject to, not only in the formation of alkaline and earthy salts, for metallic salts, as we have seen, are included in the common error. What can be a greater discouragement?—But long after, when least expected, they by some fortunate accident obtain by means of a dilute acid the earnestly sought-for solution; this event steals on them, not as a discovery, for they charge it to their own ignorance rather than the instructor's neglect. Water then, when required to the effect, should be expressed, as it cannot be supposed that one who is ignorant of its properties can understand that it should in this case be present, when in many experiments its absence to a certain degree is absolutely necessary.

Rudiments should be such, that the inexperienced learner should obtain by them a competent knowledge of those laws by which the more abstruse parts of a science should become less difficult, as he has been more arduous in imbibing the means of success.

Under these circumstances, I cannot forbear to advise the authors of chemical rudiments, to explain more clearly that it is the acid which unites with the base, and the water alone which dissolves this combination.

Your obedient servant,

Nov. 15, 1815.

H.


To Mr. Tillock.

Sir,—Having seen a statement in your Magazine for August, that M. Dobereiner of Jena subjected mercury in contact with water
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water to the Voltaic action, and obtained at the negative pole, where the mercury was placed, an amalgam of that metal and hydrogen, which was not given off in the form of gas; I thought it worth while to repeat the experiment, which I have varied in every possible way, and of which the following is an accurate account,—if you think it worth while to make room for it among the more important communications you are in the habit of receiving. Having let fall a globule of pure mercury of about twice the size of a pea into a watch-glass of common spring water, I plunged two platina wires, proceeding from each end of a Voltaic trough, into the water, neither of them touching the globule, but removed to the opposite extremities of the glass.—Oxygen and hydrogen were given out by each as usual, the mercury remaining unaltered; the wires being brought nearer, the mercury lost its globular form, extending itself in an oval shape, much flattened, appearing equally attracted by each wire. The wires being both made to touch the globule and drawn back again, the mercury adhered to the negative. In this situation, the positive wire not touching the metal, no hydrogen gas was given out by the negative, or so small a quantity that it required very minute inspection to detect it: the mercury appeared of less specific gravity, more fluid and brilliant than before; whilst the positive wire separated a copious stream of oxygen. In two or three minutes some bubbles of hydrogen began to arise, but in small quantity.

If the positive wire is brought within a small distance of the mercury when connected with the negative, a great portion of the oxygen passes over the surface of the globule and of the water in a rapid current towards the negative wire; and on bringing it almost in contact, the mercury is attracted by it, touches it, and immediately shrinks from it, assuming the form of a cone, and again expanding so as to touch the wire a second time, continuing this motion or rather pulsation for some time. When the trough is first charged, this motion is inconceivably rapid, and has continued with a single two-inch trough of 30 plates for two hours or more. The negative wire will be found coated with mercury on being removed. If the positive wire is plunged into the globule (the negative not touching it), and even drawn out of it immediately, it becomes fixed in a moment, losing its brilliancy and fluidity, depositing a black oxide at first, and after some hours a beautiful lemon-coloured oxide; but it does not become less fluid after remaining in this situation a week than it does after a few seconds. No oxygen is given out by the positive wire at first; but after some seconds, when the globule appears a good deal oxidized, a few bubbles begin to appear, while the negative wire gives out a copious
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copious stream of hydrogen. Examined by the microscope, a metallic crystallization appears to shoot over the surface of the metal accompanied with prismatic colour. Heat tends to make the globule less fluid, by evaporating the mercury and leaving the oxide. Having evaporated the water from a globule exposed to the Voltaic action for 16 hours, the glass being much heated, a series of small explosions accompanied with coruscations of fire appeared to take place from the residuum surrounding the mercury; but as I have failed in reproducing this effect by the same means, it is not impossible to have been an ocular deception. On touching with the negative wire the globule after it has been oxidized by the positive, the oxide falls off in scales, and the metal quickly reappears in its pristine brilliancy and fluidity, a portion of oxide passing to the negative pole, and no hydrogen gas given off, being absorbed by the globule—so that it is easy to fix or make fluid the metal, which is best done by separate watch-glasses connected with each other by a conducting substance—the positive globule will be fixed, the negative fluid, and by reversing the glasses, both will be changed. If the mercury has remained in contact with the negative wire some time, and the positive is withdrawn so as to break the connexion with the poles, the metal contracts and expands for some seconds, as if to get rid of the hydrogen gas. The mercury cannot be set in motion after having been connected with the negative for several minutes, until, having been first touched by the positive, it is put in contact with the negative. These effects take place when the globule is subjected to the action of a small trough charged with common water, but in a much less degree. If the globule is very small, gas is given out by the wire in contact with it, as well as by the other. If the water is warmed by a lamp during the action of the wires on the mercury, gas is more copiously liberated from both, and the oxide instead of being dark is of a lemon colour; but when the water boils, the oxide is dissolved, the mercury is rendered clear, and cannot be fixed; nor has the negative any attraction for it, nor can it be coated with metal. In vacuo gas is given out by both wires at the same time, and in a much greater quantity; when the air is admitted, the wires cease to give out more than before it was exhausted. The watch-glass with its globule under common water being subjected to a stream of common electricity, passing from one platina wire to the other, and not intercepted; precisely the same effects took place as with the Voltaic trough, but it required longer time. An intercepted stream put the globule in most violent motion between the wires. No gas was visible from either wire when the current of electricity was un-
interrupted; but when broken by Lane's electrometer, gas was
given out by both wires, accompanied with a torrent of small
sparks, and a cloud of oxide rising between the positive wire and
the globule. This current of electricity, when not intercepted,
had power to tinge litmus paper red and turmeric paper brown
at the respective positive and negative wires—a few turns of the
winch made this visible. The above-mentioned effects took
place when the globule was subjected to the Voltaic action un-
der double distilled rain-water, but in a much less degree, as the
pure water was with difficulty decomposable with a hundred
four-inch plates highly charged. This appeared to arise from
its being so imperfect a conductor in consequence of being freed
from acid; indeed, a successive minute stream of sparks attended
with an electrical snapping, took place from one wire to the
other, and not much gas was discernible from either; but the
moment a drop of acid was let fall into the water, the snapping
ceased, and gas was most copiously disengaged from both wires.
No motion could be given to the mercury, until the water was
slightly acidified. If the sulphuric, nitric, or solution of citric
acid are added to the distilled water in any quantity, the gas is
abundantly increased; but the mercury is not easily fixed nor set
in motion as with common water, and the surface when in con-
tact with the negative wire is covered with bubbles of hydrogen
rising from every part of the globule. Under water impregnated
with carbonic acid gas or acetic acid much the same effects take
place as under common water, except that more gas is liberated;
but with the acetic acid less gas is liberated than with the car-
bonic acid, and the globule is not so easily fixable. When the
pure water was acidified with either the muriatic or oxalic acids,
a most singular effect took place on connecting the globule with
the positive wire—it lost all fluidity in a moment, and could be
drawn out in very long fibres as small as the finest hair—with
the muriatic acid the mercury in contact with the positive be-
came partially coated with a very beautiful deep-blue coat, oc-
casionally mixed with a fine orange-coloured oxide; when
touched by the negative the coloured scales fell off in a moment,
and the metal appeared perfectly brilliant—the oxalic acid pro-
duced no colour. This is a beautiful experiment. Under so-
lution of boric acid in alcohol, the mercury was not so friable
nor capable of being set in motion as under water. A singular
smell was emitted when the trough was highly charged. With
all these acids gas was liberated by both wires, whether in con-
tact with the globule of mercury or not. When the platina
wires are plunged in liquid ammonia, and held even an inch
asunder, the most violent motion is communicated to the glo-
bule,
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bule, and a great quantity of gas arises from both wires—in contact with the positive, it is fixed and oxidized in a moment—in contact with the negative the metal first resumes its former brilliancy and fluidity, then appears more fluid and brilliant; lastly, it begins to swell and become dull, gradually increasing in size till it becomes more than ten times its original bulk. In this state it appears like a spongy light metallic mass, covered with protuberances, of very irregular shape, being a complete amalgam of mercury and ammonia. When the connexion is broken by removing the positive wire from the ammonia, a vast quantity of hydrogen gas is liberated by the amalgam, and the mercury gradually returns to its former state. When solution of pure soda or potash is made use of, nearly the same appearances occur as with the ammonia, excepting the swelling of the mercury. Under lime-water it is fixed and oxidized slowly, when in contact with the positive, but appeared evidently inclined to form an amalgam; when touching the negative, a quantity of gas arose from both wires.

Under alcohol or ether the same appearances were visible as under distilled water; the quantity of gas was increased if the spirit was heated or fired; no change takes place in the globule under naphtha unless the mercury is ignited by the Voltaic stream, in which case a great deposit of charcoal is visible on the negative side. Under ether holding phosphorus in solution, the positive wire in contact with the mercury causes it to lose its fluidity and be oxidized rapidly; and it is so much flattened that it covers four times the surface it occupied before, extending itself in a singular manner in every direction from the positive wire, till it ceases to touch it, leaving around it a circular space; gas is given out by the wire not touching the metal as under water. No effect takes place under phosphorized olive oil, and very little under olive oil holding sulphur in solution, the mercury being slowly fixed by the positive wire, but no perceptible gas given out by either wire.

From the foregoing experiments I venture to draw the following conclusions: That the change in the mercury from a fluid to a more solid substance when in contact with the positive pole is simply occasioned by the metal being oxidized, which oxygen unites with the hydrogen from the negative wire when touching it, and restores it to its fluidity. That this is proved by its being difficult or impossible to fix the mercury under a fluid which has power rapidly to dissolve the oxide formed. That phosphorus and sulphur are still simple substances, and have no metallic base; that carbon has never been metallized, as in that case it would in all probability form an amalgam with the mercury under naphtha, instead of being deposited in its state.
state of powder. That consequently ammonia, the fixed alkalies and lime, are the only substances mentioned in this course of experiments which contain a metallic base.

I am, sir,
Your obedient humble servant,
Broomfield, near Taunton,
Nov. 25, 1815.

ANDREW CROSE.

LXXIX. On the Action of Acids on the Salts usually called Hyperoxymuriates, and on the Gases produced from them.

By Sir Humphry Davy, LL.D. F.R.S. *

The effects produced when concentrated hydro-sulphuric acid (oil of vitriol) is poured upon hyperoxymuriate of potassa, have been often objects of chemical discussion; the acid and the salt, it is well known, become deep orange, and if any moisture is present, or if heat is applied to the mixture, a detonation occurs. In a paper read before the Royal Society, I have ventured to suppose that these phenomena depend upon the development and sudden decomposition of the compound of chlorine and oxygen, which I have named euchlorine.

A statement, which I understand has been made by M. Gay Lussae, namely, that a peculiar acid, which he has called chloric acid, may be procured from the hyperoxymuriate of baryta by sulphuric acid, led me to examine the action of acids on the hyperoxymuriates under new circumstances, and I have made some observations which appear to me not unworthy of being communicated to the Royal Society.

If 30 or 40 parts of sulphuric acid be poured upon one part of dry hyperoxymuriate of potassa in a wine-glass, and the salt be agitated in the acid, there is a very slight effervescence only, the acid becomes of a deep orange tint, and white fumes, mixed with orange fumes, fill the upper part of the glass, which have a very peculiar and not a disagreeable smell.

The slight effervescence taking place in this process, induced me to suppose that the substance which coloured the acid must contain a larger proportion of oxygen than euchlorine; for I have shown, in a work published in 1812, that hyperoxymuriate of potassa contains six proportions of oxygen; and by its decomposition 2.5 volumes of oxygen ought to be evolved for every volume of chlorine; and euchlorine procured from the hyperoxynmuriate of potassa by solution of muriatic acid, yields only one volume of oxygen, and two volumes of chlorine.

* From the Philosophical Transactions for 1815, part ii.
† Elem. of Chem. Phil.