

XX. *Experiments and Observations on the Dissolution of Metals in Acids, and their Precipitations; with an Account of a new compound acid Menstruum, useful in some technical Operations of parting Metals.* By James Keir, Esq. F. R. S.

Read May 20, 1790.

IN the following Paper, I intend to relate two sets of experiments; one, shewing the effects of *compounding the vitriolic and nitrous acids in dissolving metals*; and the other, describing some curious *appearances which occur in the precipitation of silver from its solution in nitrous acid by iron, and by some other substances*. In a subsequent Paper I hope to continue the subject of metallic dissolution\* and precipitation, first, by adding some *experiments on the quantities and kinds of gas produced by dissolving different metals in different acids, under various circumstances*; secondly, by submitting certain *general propositions*,

\* The English word *solution* has two significations in chemistry; one, expressive of the act of dissolving, as when we say, that “solution is a chemical operation;” and the other, denoting the substance dissolved in its solvent, as “a solution of silver in nitrous acid.” The French language is equally equivocal, as the word “dissolution” is used in both the above-mentioned senses. In treating on this subject, in which both meanings were very frequently required, sometimes in the same sentence, I could not but be sensible of confusion in the style, and I have therefore confined the word *solution* to express the substance dissolved together with its solvent, and the word *dissolution* to denote the act of dissolving,

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which seem deducible from the facts related; and, lastly, by concluding with some *reflexions* relative to the *theory of metallic dissolution and precipitation*.

## P A R T I.

*On the effects of compounding the vitriolic and nitrous acids, under various circumstances, upon the dissolution of metals.*

### S E C T I O N F I R S T.

*On the mixture of oil of vitriol and nitre.*

1. The properties of the several acids, in their separate states, have been investigated with considerable industry and success; and those of one compound, *aqua regis*, are well known on account of its frequent use in dissolving gold: yet not only various other combinations of different acids remain to be examined; but also the changes of properties to which these mixed acids are subject, from the difference of circumstances, especially those of *concentration, temperature*, and of that quality which is called, properly or improperly, *phlogistication*, are subjects still open for enquiry.

2. As I shall have frequent occasion to speak of the *phlogistication* and *dephlogistication* of acids, I wish to premise, that by these terms I mean only certain *states* or *qualities* of those bodies, but without any *theoretical* reference. Thus vitriolic acid may be said to be phlogisticated by addition of sulphur or other inflammable matter, by which it is converted into sulphureous acid, without determining whether this change be

caused by the addition of the supposed principle *phlogiston*, as one set of philosophers believe, or by the action of the added inflammable substance in drawing from the acid a portion of its aërial principle, by which the sulphur, its other element, is made to predominate, as others have lately maintained. It were much to be wished, that we had words totally unconnected with theory; that chemists, who differ from each other in some speculative points, may yet speak the same language, and may relate their facts and observations, without having our attention continually drawn aside from these to the different modes of explanation which have been imagined. But at present we have only the choice of terms between words derived from the ancient theory, and those which have been lately proposed by the opposers of that theory. In this dilemma I have preferred the use of the former, not that I wish to shew any predilection to either theory, but because that system, having long been generally adopted, is understood by all parties; and principally because, by using the words of the old theory, I am at liberty to define them, and to give significations expressive merely of facts, and of the actual state of bodies; whereas the language and theory of the antiphlogistic chemists being interwoven and adapted to each other, the former cannot be divested of its theoretical reference, and therefore seems inapplicable to the mere exposition of facts, but ought to be reserved solely for the explanation of the doctrines from which this language is derived. Thus by the definition which I have mentioned of *phlogification*, this word expresses not the presence or existence of an hypothetical principle of inflammability; but a certain well-known quality of acids and of other bodies, communicated to them by the addition of many actual inflammable substances. Thus nitrous acid acquires a phlo-

gified quality by addition of a little spirit of wine, or by distillation with any inflammable substance.

3. No two substances are more frequently in the hands of chemists and artists than *vitriolic acid* and *nitre*, yet I have found, that a mere mixture of these, when much concentrated, possesses properties which neither the vitriolic acid nor the nitrous, of the same degree of concentration, have singly, and which could not easily be deduced, *a priori*, by reasoning from our present knowledge of the theory of chemistry.

4. Having found by some previous trials that a mixture composed of nitre dissolved in oil of vitriol was capable of dissolving silver easily and copiously, while it did not affect copper, iron, lead, regulus of cobalt, gold, and platina, I conceived, that it might be useful in some cases of the parting of silver from copper and the other metals above mentioned; and having also observed, that the dissolving powers of the mixture of vitriolic and nitrous acids varied greatly in different degrees of concentration and phlogification, I thought that an investigation of these effects might be a subject fit for philosophical chemistry, and might tend to illustrate the theory of the dissolution of metals in acids. With these views I made the following experiments.

5. I put into a long-necked retort, the contents of which, including the neck, were 1400 grain measures, 100 grain measures of oil of vitriol of the usual density at which it is prepared in England, that is, whose specific gravity is to that of water as 1,844 to 1, and 100 grains of pure and clean nitre, which was then dissolved in the acid by the heat of a water-bath. To this mixture 100 grains of standard silver were added; the retort was set in a water bath, in which the

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water was made to boil, and a pneumatic apparatus was applied to catch any air or gas which might be extricated.

The silver began to dissolve, and the solution became of a purple or violet colour. No air was thrown into the inverted jar, excepting a little of the common air of the retort, by means of the expansion which it suffered from the heat of the water-bath, and from some nitrous fumes which appeared in the retort, and which having afterwards condensed, occasioned the water to rise along the neck of the retort, and mix with the solution. The remaining silver was then separated and weighed, and it was found that 39 grains had been dissolved; but probably more would have been dissolved if the operation had not been interrupted by the water rushing into the retort.

6. In the same apparatus 200 grains of standard silver were added to a mixture of 100 grains of nitre previously dissolved in 200 grain-measures of oil of vitriol; and in this solvent 92 grains of the silver were dissolved, without any production of air or gas. The solution, which was of a violet colour, having been poured out of the retort while warm (for with so large a proportion of nitre, such mixtures, especially after having dissolved silver, are apt to congeal with small degrees of cold), in order to separate the undissolved silver from it, and having been returned into the retort without this silver, I poured 200 grains of water into the retort, upon which a strong effervescence took place between the solution and the water, and 3100 grain-measures of nitrous gas were thrown into the inverted jar. Upon pouring 200 grains more of water into the retort, 600 grain-measures of the same gas were expelled. Further additions of water yielded no more gas; neither did the silver, when afterwards added to this diluted solution, give

any sensible effervescence, or suffer a greater loss of weight than two grains.

7. In the same apparatus 100 grains of standard silver were exposed to a mixture of 30 grains of nitre dissolved in 200 grain-measures of oil of vitriol; and in this operation, 80 grains of silver were dissolved, while at the same time 4500 grain-measures of nitrous gas were thrown into the inverted jar. When the undissolved silver was removed, 200 grains of water were added to the solution, which was of a violet colour, and upon the mixture of the two fluids an effervescence happened; but only a few bubbles of nitrous gas were then expelled.

8. In the same apparatus 100 grains of standard silver were exposed to a mixture of 200 grain-measures of oil of vitriol, 200 grains of nitre, and 200 grains of water; and in this operation 20 grains of the silver were dissolved without any sensible emission of air or gas.

9. In these experiments, the copper contained in the standard silver gave a reddish colour to the saline mass which was formed in the solution, and seemed to be a calx of copper interspersed through the salt of silver. I perceived no other difference between the effects of pure and standard silver dissolved in this acid.

10. I then exposed *tin* to the same mixture of oil of vitriol and nitre, in the same apparatus, and in the same circumstances, taking care always to add more metal than could be dissolved, that, by weighing the remainder, the quantity capable of being dissolved might be found, as I had done with the experiments on silver: and the results were as follow.

11. No tin was dissolved nor calcined by the mixtures in the proportion of 200 grain-measures of oil of vitriol to 200 grains  
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of nitre; nor by another mixture in the proportion of 200 grain-measures of oil of vitriol to 150 grains of nitre, and consequently no gas was produced in either instance.

12. With a mixture in the proportion of 200 grain-measures of oil of vitriol and 100 grains of nitre, the tin began soon to be acted on, and to be diffused through the liquor; but no extrication of gas appeared until the digestion had been continued two hours in boiling water; and then it took place, and gave a frothy appearance to the mixture, which was of an opaque white colour, from the powder of tin diffused among it. In this experiment the quantity of tin thus calcined was 73 grains, and the quantity of nitrous gas extricated during this action on the tin was 8500 grain-measures. Then, upon pouring 200 grains of water into the retort, a fresh effervescence took place between the water and the white opaque mass, and 4600 grain-measures of nitrous gas were thrown into the inverted receiver.

13. With a mixture in the proportion of 100 grain-measures of oil of vitriol to 30 grains of nitre, 30 grains of tin were dissolved or calcined, and the nitrous gas, which began to be extricated much sooner than in the last mentioned experiment with a larger proportion of nitre, amounted to 6300 grain-measures. Water, added to this solution of tin, did not produce any effervescence.

14. With a mixture in the proportion of 200 grain-measures of oil of vitriol, 200 grains of nitre, and 200 grains of water, 133 grains of tin were acted on with an effervescence, which took place violently, and produced 6500 grain-measures of nitrous gas.

15. The several mixtures above mentioned, in different proportions of nitre and oil of vitriol, did, by the help of the heat

heat of the water-bath, calcine *mercury* into a white or greyish powder. *Nickel* was also partly calcined and partly dissolved by these mixtures. I did not perceive that any other metal was affected by them, excepting that the surfaces of some of them were tarnished.

16. These mixtures of oil of vitriol and nitre were apt to congeal by cold, those especially which had a large proportion of nitre. Thus, a mixture of 1000 grain-measures of oil of vitriol and 480 grains of nitre, after having kept fluid several days, in a phial not so accurately stopped as to prevent altogether the escape of some white fumes, congealed at the temperature of 55° of FAHRENHEIT's thermometer; whereas some of the same liquid, having been mixed with equal parts of oil of vitriol, did not congeal with a less cold than 45°. The congelation is promoted by exposure to air, by which white fumes rise, and moisture may be absorbed, or by any other mode of slight dilution with water.

17. Dilution of this compound acid, with more or less water, alters considerably its properties, with regard to its action on metals. Thus it has been observed, that in its concentrated state it does not act on *iron*; but, by adding water, it acquires a power of acting on that metal, and with different effect, according to the proportion of the water added. Thus, by adding to two measures of the compound acid one measure of water, the liquor is rendered capable of calcining iron, and forming with it a white powder, but without effervescence. With an equal measure of water effervescence was produced. With a larger proportion of water the iron gave also a brown colour to the liquor, such as phlogisticated nitrous acid acquires from iron, or communicates to a solution of martial vitriol in water.

18. Dilution with water renders this compound acid capable of dissolving *copper* and *zinc*, and probably those other metals which are subject to the action of the dilute vitriolic or nitrous acids.

## SECTION SECOND.

*An account of a new process for separating silver from copper.*

19. The properties of this liquor, in dissolving silver easily without acting on copper, have rendered it capable of a very useful application in the arts. Among the manufactures at Birmingham, that of making vessels of silver plated on copper is a very considerable one. In cutting out the rolled plated metal into pieces of the required forms and sizes, there are many shreds, or *scraps* as they are called, unfit for any purpose but the recovery of the metals by separating them from each other. The easiest and most economical method of parting these two metals, so as not to lose either of them, is an object of some consequence to the manufacturers. For this purpose two modes were practised; one, by melting the whole of the mixed metals with lead, and separating them by eliquation and testing; and the second, by dissolving both metals in oil of vitriol, with the help of heat, and by separating the vitriol of copper, by dissolving it in water, from the vitriol of silver, which is afterwards to be reduced and purified. In the first of these methods, there is a considerable waste of lead and copper; and in the second, the quantity of vitriolic acid employed is very great, as much more is dissipated in the form of volatile vitriolic, or sulphureous acid, than remains in the composition of the two vitriols.

Some years ago, I communicated to an artist the method of effecting the separation of silver and copper by means of the above-mentioned compound of vitriolic acid and nitre; and, as I am informed, that it is now commonly practised by the manufacturers in Birmingham, I have no doubt but it is much more oeconomic, and it is certainly much more easily executed than any of the other methods: for nothing more is required than to put the pieces of plated metal into an earthen glazed pan; to pour upon them some of the acid liquor, which may be in the proportion of eight or ten pounds of oil of vitriol to one pound of nitre; to stir them about, that the surfaces may be frequently exposed to fresh liquor, and to assist the action by a gentle heat from  $100^{\circ}$  to  $200^{\circ}$  of FAHRENHEIT's scale. When the liquor is nearly saturated, the silver is to be precipitated from it by common salt, which forms a luna cornea, easily reducible by melting it in a crucible with a sufficient quantity of pot-ash; and, lastly, by refining the melted silver, if necessary, with a little nitre thrown upon it. In this manner the silver will be obtained sufficiently pure, and the copper will remain unchanged. Otherwise, the silver may be precipitated in its metallic state, by adding to the solution of silver a few of the pieces of copper, and a sufficient quantity of water to enable the liquor to act upon the copper.

The property which this acid mixture possesses of dissolving silver with great facility, and in considerable quantity, will probably render it an useful menstruum in the separation of silver from other metals; and as the alchemists have distinguished the peculiar solvent of gold under the title of *aqua regis*, a name sufficiently distinctive, though founded on a fanciful allusion; so, if they had been acquainted with the properties

properties of this compound, they would probably have bestowed on it the appellation of *aqua reginae*.

SECTION THIRD.

*The change of properties communicated to the mixture of vitriolic and nitrous acids by phlogistication.*

20. The above-described compound acid may be phlogisticated in different methods, of which I shall mention three.

1st, By digesting the compound acid with sulphur by means of the heat of a water-bath, the liquor dissolves the sulphur with effervescence, loses its property of yielding white fumes; and if the quantity of sulphur be sufficient, and if the heat applied be long enough continued, it exhibits red nitrous vapours, and assumes a violet colour.

2dly, If, instead of dissolving nitre in concentrated vitriolic acid, this acid be impregnated with nitrous gas, or with nitrous vapour, by making this gas or vapour pass into the acid, this compound will be phlogisticated, as it contains not the entire nitrous acid, but only its phlogisticated part, or element, the nitrous gas, without the proportion of pure air necessary to constitute an acid. This impregnation of oil of vitriol with nitrous gas or nitrous vapour was first described, and some of the properties of the impregnated liquor noticed, by Dr. PRIESTLEY. See Experiments and Observations on Air, Vol. III. p. 129 and 217.

3dly, By substituting nitrous ammoniac instead of nitre in the mixture with oil of vitriol.

21. The compound prepared by any of these methods, but especially by the first and second, differs considerably in its

properties with regard to its action on metals from the acid described in the first section. It has been observed, that the latter compound has little action on any metals but silver, tin, mercury, and nickel. On the other hand, the phlogisticated compound not only acts on these, but also on several others. It forms with *iron* a beautiful rose-coloured solution, without application of any artificial heat; and in time a rose-coloured saline precipitate is deposited, which is soluble in water with considerable effervescence. It dissolves *copper*, and acquires from this metal, and also from regulus of *cobalt*, *zinc*, and *lead*, pretty deep violet tinges. *Bismuth* and *regulus of antimony* were also attacked by this phlogisticated acid.

To ascertain more exactly the effects of this phlogisticated acid on some metals, I made the following experiments, with a liquor prepared by making nitrous gas pass through oil of vitriol during a considerable time.

22. To 200 grain-measures of the oil of vitriol impregnated with nitrous gas, put into a retort with a long neck, the capacity of which, including the neck, was 1150 grain-measures, I added 144 grains of standard silver, and immersed the mouth of the retort in water, under an inverted jar filled with water, to catch the gas which might be extricated.

The acid began to dissolve the silver with effervescence by application of heat; the solution became of a violet colour, and the quantity of nitrous gas received in the inverted jar was 14700 grain-measures. Upon weighing the silver remaining, the quantity which had been dissolved was found to be 70 grains. When water was added to the solution, an effervescence appeared, but only a very small quantity of gas was extricated. By means of the water, a white saline powder of silver, soluble in a larger quantity of water, was precipitated from

from the solution. The solution of silver, when saturated and undiluted, congeals readily in cool temperatures, and, when diluted to a certain degree with water, gives foliated crystals.

23. In the same apparatus, and in the same manner, 100 grain-measures of this impregnated oil of vitriol were applied to *iron*. An effervescence appeared without application of heat, the surface of the iron acquired a beautiful rose colour or redness mixed with purple: and this colour gradually pervaded the whole liquor, but disappeared on keeping the retort some time in hot water. Notwithstanding a considerable apparent effervescence, the quantity of air expelled into the inverted jar was only 400 grain-measures, of which  $\frac{1}{4}$  was nitrous, and the rest phlogisticated. The solution was then poured out of the retort, and the iron was found to have lost only two grains in weight. The solution was returned into the retort, without the iron, and 200 grains of water were added to it; upon which a white powder was immediately precipitated, which re-dissolved with great effervescence. When 2000 grain-measures of nitrous gas had been expelled into the inverted jar, without application of heat, the retort was placed in the water-bath, the heat of which rendered the effervescence so strong, that the liquor boiled over the neck of the retort, so that the quantity of gas extricated could not be ascertained.

24. In the same manner 11 grains of *copper* were dissolved in 100 grain-measures of impregnated oil of vitriol. The solution was of a deep violet colour, and at last was turbid. The quantity of nitrous gas expelled into the inverted jar during the operation was 4700 grain-measures. When the copper was removed, and 200 grains of water were added to the solution, an effervescence took place, 1700 grain-measures of

nitrous gas were expelled, and the solution then acquired a blue colour.

25. In the same apparatus and manner, 100 grain-measures of the impregnated oil of vitriol were applied to *tin*, which was thereby diminished in weight 16 grains, while the liquor acquired a violet colour, became turbid by the suspension of the calx of tin, and a quantity of nitrous gas was thrown into the inverted receiver equal to 4100 grain-measures, without application of heat, and another quantity equal to 4900 grain-measures, after the retort was put into the water-bath.

26. *Mercury* added to the impregnated oil of vitriol formed a thick white turbid liquor, which was rendered clear by addition of unimpregnated oil of vitriol. In a little time this mixture continuing to act on the remaining mercury acquired a purple colour. The mercury acted upon sunk to the bottom of the glass in the form of a white powder, and the purple liquor, when mixed with a solution of common salt in water, gave no appearance of its containing any mercury in a dissolved state.

27. The nitrous gas with which the oil of vitriol is impregnated shews no disposition to quit the acid by exposure to air; but, on adding water to the impregnated acid, the gas is expelled suddenly with great effervescence, and with red fumes, in consequence of its mixture with the atmospherical air.

Upon adding 240 grains of water to 60 grain-measures of impregnated oil of vitriol, 2300 grains of nitrous gas were thrown into the receiver; but as the action of the two liquors is instantaneous, the quantity of gas expelled from the retort before its neck could be immersed in water, and placed under the receiver, must have been considerable. The whole of the gas, however, was not extricated by means of the water, for  
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the remaining liquor dissolved 5 grains of copper, while 800 measures of nitrous gas were thrown into the retort.

28. The following facts principally are established by the preceding experiments.

1. That a mixture of the vitriolic and nitrous acids in a concentrated state has a peculiar faculty of dissolving silver copiously.

2. That it acts upon, and principally calcines, tin, mercury, and nickel; the latter of which, however, it dissolves in small quantity, and that it has little or no action on other metals.

3. That the quantity of gas produced while the metal is dissolving is greater, relatively to the quantity of metal dissolved, when the proportion of nitre to the vitriolic acid is small than when it is large; and that when the metals are dissolved by mixtures containing much nitre, and with a small production of gas, the solution itself, or the metallic salt formed in it, yields abundance of gas when mixed with water.

4. That dilution with water renders the concentrated mixture less capable of dissolving silver, but more capable of acting on other metals.

5. That this mixture of highly concentrated vitriolic and nitrous acids acquires a purple or violet colour when phlogistified, either by addition of inflammable substances as sulphur, or by its action on metals, or by very strong impregnation of oil of vitriol with nitrous gas\*.

\* Dr. PRIESTLEY has noticed this colour communicated to oil of vitriol by impregnation with nitrous gas or vapour, and also the effervescence produced by adding water to this impregnated liquor. See Experiments and Observations, Vol. III. p. 129 and 217.

6. That this phlogification was found to communicate to the mixture the power of dissolving, though in small quantities, copper, iron, zinc, and regulus of cobalt.

7. That water expels from a highly phlogified mixture of concentrated vitriolic and nitrous acids, or of oil of vitriol impregnated with nitrous gas, a great part of its contained gas; and that therefore this gas is not capable of being retained in such quantity by dilute as by concentrated acids. Water unites with the mixture of oil of vitriol and nitre, without any considerable effervescence.

29. To these observations I shall subjoin one other fact, namely, that, when to the mixture of oil of vitriol with nitre a saturated solution of common salt in water is added, a powerful aqua regis is produced, capable of dissolving gold and platinum; and this aqua regis, though composed of liquors perfectly colourless and free from all metallic matter, acquires at once a bright and deep yellow colour. The addition of dry common salt to the concentrated mixtures of vitriolic and nitrous acids produces an effervescence, but not the yellow colour; for the production of which therefore a certain proportion of water seems to be necessary.

## P A R T II.

### *On the precipitation of silver from nitrous acid by iron.*

#### S E C T I O N I.

I. BERGMAN relates, that upon adding iron to a solution of silver in the nitrous acid no precipitation ensued\*; although

\* Differt. de Phlog. quantitate in Metallis.

the affinity of iron to acids in general is known to be much stronger than that of silver; and although, even with regard to the nitrous acid, other experiments evince the superior affinity of iron: for as iron precipitates copper from this acid, and as copper precipitates silver, we must infer the greater affinity of iron than of silver. In the course of his experiments, however, some instances of precipitation occurred, which he attributed to the peculiar quality of the irons which he then employed \*. I was desirous of discovering the circumstances,

\* BERGMAN tried many different kinds of iron, and he thought he found two which were capable of precipitating silver. But as he did not discover the circumstances according to which this precipitation sometimes does, and at other times does not happen, he may have been mistaken with regard to the peculiar quality of these two kinds of iron. At least the several kinds which I have tried always precipitated silver in certain circumstances, and always failed to precipitate in certain other circumstances. I do not know any other author who has mentioned this subject, excepting Mr. KIRWAN; who, in the conclusion of his valuable Papers on *the Attractive Powers of Mineral Acids*, says, "I have always found silver to be easily precipitated from its solution in the nitrous acid by iron. The sum of the quiescent affinities being 625, and that of the divellent 746. Yet Mr. BERGMAN observed, that a very saturated solution of silver was very difficultly precipitated, and only by some sorts of iron, even though the solution was diluted, and an excess of acid added to it. The reason of this curious phenomenon appears to me deducible from a circumstance first observed by SCHEELÉ, in dissolving mercury, namely, that the nitrous acid when saturated with it will take up more of it in its metallic form. The same thing happens in dissolving silver in the nitrous acid in a strong heat; for, as I before remarked, the last portions of silver thrown in afford no air, and consequently are not dephlogisticated. Now this compound of calx of silver, and silver in its metallic form, may well be unprecipitable by iron, the silver in its metallic form preventing the calx from coming into contact with the iron, and extracting phlogiston from it." In this Paper I shall not enter into the explanation of these appearances; but I thought it necessary to premise what so eminent a chemist as Mr. KIRWAN has suggested on the subject, that the reader may see at once the present state of the question. I shall only remark, that the above explanation,

stances, and of investigating the cause, if I should be able, of this irregularity and exception to the generally received laws of affinity.

2. I digested a piece of fine silver in pure and pale nitrous acid, and while the dissolution was going on, and before the saturation was completed, I poured a portion of the solution upon pieces of clean and newly-scraped iron wire into a wine glass, and observed a sudden and copious precipitation of silver. The precipitate was at first black, then it assumed the appearance of silver, and was five or six times larger in diameter than the piece of iron wire which it enveloped. The action of the acid on the iron continued some little time, and then it ceased; the silver re-dissolved, the liquor became clear, and the iron remained bright and undisturbed in the solution at the bottom of the wine glass, where it continued during several weeks, without suffering any change, or effecting any precipitation of the silver.

3. When the solution of silver was completely saturated, it was no longer affected by iron, according to BERGMAN'S observation.

4. Having found that the solution acted on the iron, and was thereby precipitated, before it had been saturated, and not afterwards, I was desirous of knowing, whether the *saturation* was the circumstance which prevented the action and precipitation. For this purpose, I added to a portion of the saturated solution some of the same nitrous acid, of which a part had been employed to dissolve the silver; and into this mixture,

tion, not being founded on any peculiarity in the nature of iron, seems to suppose, that the silver is also incapable of being precipitated, from such solutions as iron cannot act upon, by any other metal. But this is not the case: copper and zinc readily precipitate silver from these solutions.

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abounding with a superfluous acid, I threw a piece of iron, but no precipitation occurred. It was thence evident, that the saturation of the acid was not the only circumstance which prevented the precipitation.

5. To another portion of the saturated solution of silver I added some red smoking nitrous acid; and I found, upon trial, that iron precipitated the silver from this mixture, and that the same appearances were exhibited as had been observed with the solution previously to its saturation.

6. The same effects were produced when vitriolic acid was added to the saturated solution of silver, and iron afterwards applied.

7. To some of the same nitrous acid, of which a part had been employed to dissolve the silver, I added a piece of iron; and, while the iron was dissolving, I poured into the liquor some of the saturated solution of silver; upon which a precipitation of silver took place instantly; although, when the same acid had been previously mixed with the solution of silver, and the iron was then added to the mixture, no precipitation had ensued.

8. The quantity of vitriolic acid, or of the red fuming nitrous acid, necessary to communicate to the saturated solution of silver the property of being acted on by iron, varies according to the concentration, and to the degree of phlogistication of the acids added; so that a less quantity than is sufficient does not produce any apparent effect. Nevertheless, when the solution of silver is by addition of these acids brought nearly to a precipitable state, the addition of spirit of wine will, in a little time, render it capable of acting on iron.

9. It appears then, that a solution of silver is not precipitated by iron in cold, unless it have a superabundance of phlogisticated acid\*.

10. Heat affects the action of a solution of silver on iron: for if iron be digested with heat, in a perfectly saturated solution of silver, such as a solution of crystals of nitre of silver in water, the silver will be deposited in its bright metallic state on different parts of the iron, and the iron which has been acted on by the solution appears in form of a yellow ochre.

11. BERGMAN relates, that he has sometimes observed beautiful crystallizations or vegetations of metallic silver formed on pieces of iron immersed long in a solution of silver.

I have found that no time is able to effect this deposition, unless the solution be in a state *nearly* sufficiently phlogisticated to admit of a precipitation by iron, but not completely phlogisticated enough to effect that purpose immediately.

12. Dilution with a great deal of water seemed to dispose the solutions of silver to be precipitated by iron more easily.

\* It was said, at § 4. that the addition of dephlogisticated nitrous acid to a saturated solution of silver did not render this solution precipitable by iron. Nevertheless, as this acid dissolves iron, such a quantity may be added, as to overcome the counteracting quality of the solution of silver, so that the acid shall be able to act on the iron; and while this metal is dissolving, it phlogisticates the mixture, which then becomes capable of being precipitated, and is in fact reduced to the same circumstances as are described at § 7. The limits of the quantities which produce changes cannot be ascertained, because they depend on the degrees of concentration and phlogistication of the substances employed; and therefore, whenever a change is said to be produced by a certain substance, it means that it may be produced by *some* proportion, but does not imply by *every* proportion, of that substance. Without attending to these considerations, persons trying to repeat the experiments mentioned in this Paper will be liable to be deceived.

A solution of silver, which did not act on iron, upon being very much diluted, and having a piece of iron immersed in it, during several hours, gave a precipitate of silver in the form of a black powder.

SECTION II.

*On the alterations which iron or its surface undergoes by the action of a solution of silver in nitrous acid, or of a pure concentrated nitrous acid.*

13. It has been said, that when iron is exposed to the action of a phlogisticated solution of silver, it instantly precipitates the silver, is itself acted upon or dissolved by the acid solution during a certain time, longer or shorter, according to the degree of phlogistication, quantity of superabundant acid, and other circumstances, and that at length the solution of the iron ceases; the silver precipitate is re-dissolved, if there is superfluous acid; the liquor becomes clear again, but only rendered a little browner by its having dissolved some iron; while the piece of iron remains bright and undisturbed at the bottom of the liquor, where it is no longer able to affect the solution of silver.

14. I poured a part of the phlogisticated solution of silver which had passed through these changes, and which had ceased to act upon the piece of iron, into another glass, and dropped another piece of fresh iron wire into the liquor; upon which I observed a precipitation of silver, a solution of part of the iron, a redissolution of the precipitated silver, and a cessation of all these phenomena, with the iron remaining bright and quiet at the bottom of the liquor, as before. It appeared

then, that the liquor had not lost its power of acting on *fresh* iron, although it ceased to act on that piece which had been exposed to it.

15. To one of the pieces of iron which had been employed in the precipitation of a solution of silver, and from which the solution, no longer capable of acting upon it, had been poured off, I added some phlogisticated solution of silver which had never been exposed to the action of iron, but no precipitation happened. It appeared then, that the iron itself, by having been once employed to precipitate a solution of silver, was rendered incapable of any further action on any solution of silver. And it is to be observed, that this alteration was produced without the least diminution of its metallic splendour, or change of colour. The alteration, however, was only superficial, as may be supposed; for by scraping off its altered coat, it was again rendered capable of acting on a solution of silver. To avoid circumlocution, I shall call iron thus affected, *altered* iron; and iron which is clean, and has not been altered, *fresh* iron.

16. To a phlogisticated solution of silver, in which a piece of bright altered iron lay, without action, I added a piece of fresh iron, which was instantly enveloped with a mass of precipitated silver, and acted on as usual; but what is very remarkable, in about a quarter of a minute, or less, the altered iron suddenly was covered with another coat of precipitated silver, and was now acted on by the acid solution like the fresh piece. In a little time the silver precipitate was re-dissolved, as usual, and the two pieces of iron were reduced to an altered state. When a fresh piece of iron was then held in the liquor, so as not to touch the two pieces of altered iron, they were nevertheless soon acted upon by the acid solution,

and suddenly covered with silver precipitate as before; and these phenomena may be repeated with the same solution of silver, until the superfluous acid of the solution becomes saturated by the iron, and then the re-dissolution of the precipitated silver must cease.

17. I poured some dephlogisticated nitrous acid on a piece of altered iron, without any action ensuing, although this acid readily acted on fresh iron, and when to the dephlogisticated nitrous acid, with a piece of altered iron lying immersed in it, I added a piece of fresh iron, this immediately began to dissolve, and soon afterwards the altered iron was acted on also by the acid.

18. I poured upon a piece of altered iron a solution of copper in nitrous acid; but the copper was not precipitated by the iron; neither did this iron precipitate copper from a solution of blue vitriol.

19. Altered iron was acted on by a dilute phlogisticated nitrous acid; but not by a red concentrated acid, which is known to be highly phlogisticated.

20. I put some pieces of clean fresh iron wire into a concentrated and red fuming nitrous acid. No apparent action ensued; but the iron was found to be altered in the same manner as it is by a solution of silver; that is, it was rendered incapable of being attacked either by a phlogisticated solution of silver, or by dephlogisticated nitrous acid.

21. Iron was also altered by being immersed some little time in a saturated solution of silver, which did not shew any visible action on it.

22. The alteration thus produced on the iron is very superficial. The least rubbing exposes some of the fresh iron beneath

neath the surface, and thus subjects it to the action of the acid.

It is therefore with difficulty that these pieces of altered iron can be dried, without losing their peculiar property. For this reason, I generally transferred them out of the solution of silver or concentrated nitrous acid into any other liquor, the effects of which I wanted to examine. Or they may be transferred first into a glass of water, and thence into the liquor to be examined. But it is to be observed, that if they are allowed to remain long in the water, they lose their peculiar property or alteration. They may be preserved in their altered state by being kept in spirit of sal ammoniac.

23. To a saturated solution of copper in nitrous acid (which was capable of being readily precipitated by fresh iron) I added some saturated solution of silver. From this mixture a piece of fresh iron neither precipitated silver nor copper: nor did the addition of some dephlogisticated nitrous acid effect this precipitation.

24. A solution of copper, formed by precipitating silver from nitrous acid by means of copper, was very reluctantly and slowly precipitated by a piece of fresh iron; and the iron thus acted on by the acid was changed to an ochre.

25. A saturated solution of silver having been *partly* precipitated by copper, acquired the property of acting upon fresh iron, and of being thereby precipitated.

26. Fresh iron immersed some time in solutions of nitre of lead, or of nitre of mercury in water, did not occasion any precipitation of the dissolved metals; but acquired an *altered* quality. These metals then in this respect resemble silver.

27. It is well known, that a solution of martial vitriol, added to a solution of gold in aqua regis, precipitates the gold

in its metallic state. I do not recollect, that the precipitation of a solution of silver by the same martial vitriol has been observed. However, upon pouring a solution of martial vitriol into a solution of silver in the nitrous acid, a precipitate will be thrown down, which acquires in a few minutes more and more of a metallic appearance, and is indeed perfect silver. When the two solutions are pretty concentrated, a bright argentine film swims on the surface of the mixture, or silvers the sides of the glass in which the experiment is made. When a phlogisticated solution of silver is used, the mixture is blackened, as happens generally to a solution of martial vitriol, when a phlogisticated nitrous acid is added to it.

I added about equal parts of water to a mixture of a phlogisticated solution of silver and a solution of martial vitriol, in which *all* the silver had been precipitated, and digested the diluted mixture with heat, by which means most of the precipitated silver was re-dissolved. BERGMAN has observed a similar re-dissolution of gold precipitated by martial vitriol upon boiling the mixture; but he attributes the re-dissolution to the concentration of the aqua regis by the evaporation. As this explanation did not accord with my notions, I diluted the mixture with water, and found that the same re-dissolution occurred both with the solution of silver and with that of gold. But with neither of the metals did I find that the re-dissolution ever took place, unless there had been a superabundant acid in the solutions of gold and silver employed.

28. Mercury is also precipitated in its metallic state from its solution in nitrous acid by a solution of martial vitriol. When the liquor is poured off from the precipitate, this may be changed into running mercury by being dried near the fire.

29. I found also, that silver may be precipitated in its metallic state, from its solution in vitriolic acid, by addition of a solution of martial vitriol. A vitriol of mercury may also be decomposed by a solution of martial vitriol, and the mercurial precipitate, which is a black powder, forms globules, when dried and warmed.

30. Luna cornea is not decomposed by martial vitriol; consequently there is no operation of a double affinity. Nevertheless, this luna cornea may be decomposed by the elements of martial vitriol, while they are in the act of dissolution; that is, the silver may be precipitated in its metallic state, by digesting luna cornea with a dilute vitriolic acid, to which some pieces of iron are added. And it is to be observed, that this reduction of the silver and precipitation take place, while the acid is yet unsaturated. Marine acid and iron applied to luna cornea effect the same reduction of the silver to a metallic state, even when there is more acid than is sufficient for both metals.

The explanation of these phenomena will be attempted in the subsequent Papers which I propose to present on this subject to the Society.

