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.*

PART I.

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

SECTION FIRST.

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 *phlogiſtication*, 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-

giſticated 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, *à 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 phlogiſtication, 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

water

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

of

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

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 œconomical 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 œconomical, 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° to 200° 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 reginæ*.

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 the

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 phlogiſticated, 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 phlogiſtication 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 phlogiſticated 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 platina; 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.

PART II.

On the precipitation of ſilver from nitrous acid by iron.

SECTION I.

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

* Diſſert. 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 "phænomenon appears to me deducible from a circumſtance firſt obſerved by "SCHEELE, 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-diſſoved, 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 phænomena, 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 phænomena 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

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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.

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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 decompounded 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 decompounded by martial vitriol; conſequently there is no operation of a double affinity. Nevertheleſs, this luna cornea may be decompounded 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 phænomena will be attempted in the ſubſequent Papers which I propoſe to preſent on this ſubject to the Society.