

XXII. *Experiments and Observations on the Matter of Cancer, and on the ærial Fluids extricated from animal Substances by Distillation and Putrefaction; together with some Remarks on sulphureous hepatic Air.* By Adair Crawford, M. D. F. R. S.

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THERE are several varieties in the colour and consistence of the matter discharged by cancerous ulcers. It is in some cases of a pale ash colour; in others, it has a reddish cast; and in many instances it has more or less of a brown tinge, sometimes approaching nearly to black. Its consistence is for the most part thin; but in the cancerous, as well as in other malignant ulcers, we frequently meet with a white fordes, which closely adheres to the surface of the sore, and which appears to be scarcely miscible with water. In the same patient the appearance of the discharge is frequently varied by internal remedies, or by external applications; but if we except the temporary variations produced by accidental circumstances, the cancerous ulcer is, in its advanced stage, very generally accompanied with a peculiar odour more highly fetid and offensive than that which is emitted by other malignant ulcers.

It is well known, that the cancerous matter occasions by its absorption schirrous tumors of the lymphatic glands contiguous to the parts affected; and that it gradually corrodes the  
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branches of the larger blood-vessels, which have a peculiar power of resisting the action of other purulent discharges.

Apprehending that some light might possibly be thrown upon the nature of cancerous diseases, by enquiring into the properties of this substance, I procured a portion of it from a patient who had for several years been afflicted with a cancer in the breast. Having diffused it through pure water, I divided it into three parts, which were put into small glass vessels. To one of these I added a solution of vegetable fixed alkali; to the second, a little concentrated vitriolic acid; and to the third, syrup of violets. By the vegetable fixed alkali no sensible change was produced: upon the addition of the vitriolic acid, the liquor in the second glass acquired a deep brown colour, a brisk effervescence took place, and at the same time the peculiar odour of the cancerous matter was greatly increased, and diffused itself to a considerable distance through the surrounding air. The syrup of violets communicated to the liquor in the third glass a faint green colour.

The cancerous matter used in these experiments had a brownish cast. It had been imbibed by cotton, and kept for some days before the trials were made.

Mr. GEBER has shewn, that animal substances upon their first putrefaction do not effervesce with acids; that, after the process has continued for some time, a manifest effervescence takes place; and that this effect again disappears before the putrefaction has ceased.

Suspecting that the effervescence in the preceding experiment might have arisen from a change which the matter underwent, in consequence of its having been kept some days before the trial was made, I repeated the experiment with a portion of reddish matter recently obtained from a cancerous penis. Upon

the addition of the acid, the liquor, as before, acquired a brown colour, its feter was much increased, and a manifest effervescence took place, although it was not so considerable as in the former instance. A portion of the same matter diffused through distilled water communicated a blue tinge to tincture of litmus, and a greenish cast to syrup of violets.

It is proper to observe, that when syrup of violets was mixed with portions of cancerous matter from a variety of different subjects, the change produced was in some cases scarcely perceptible; but in every instance the presence of an alkali was detected by dipping into the matter a slip of paper that had been previously tinged blue by tincture of litmus, and afterwards slightly reddened by acetous acid. The red colour was invariably in the course of a few minutes abolished, and the blue restored.

The cancerous matter, as has been already remarked, acquired, upon the addition of the vitriolic acid, a brown hue. It is well known, that this acid, when it is highly concentrated, communicates a brown or black colour to all animal and vegetable substances. Being desirous of learning whether the change which took place upon the addition of the acid to the cancerous matter in this experiment, was different from that which would be produced by the same acid in other animal substances, and particularly in recent healthy pus; I took equal quantities of the latter, and of ash-coloured cancerous matter, and having diffused each of them through thrice its weight of distilled water, I added to them equal quantities of concentrated vitriolic acid; the weight of the acid being nearly the same with that of the matter used in the experiment. The mixture containing the pus acquired from the acid a faint brown colour; but that which contained the cancerous matter, was

suddenly changed to a deep brown, approaching to black. When these mixtures were diluted with about twice their weight of distilled water, the brown tinge of the former entirely disappeared; but the latter still retained its brown colour, although it was somewhat fainter than it had been upon the first addition of the acid.

The ærial fluid which was disengaged in the foregoing trials from the matter of cancer, by the vitriolic acid, appeared from its odour to have a nearer resemblance to hepatic than to any other species of air. As it seemed, from its sensible qualities, to be a very active, and probably a deleterious principle, I endeavoured more particularly to enquire into its nature, and to compare it with common hepatic air. But before I relate the trials which were made with that view, it may not be improper briefly to mention the characters by which common hepatic air is distinguished.

It has a smell resembling that of rotten eggs; it is inflammable, and during its combustion in the open air, sulphur is deposited; it communicates a black colour to silver and copper, and a brownish tinge to lead and iron; it is soluble in water, and when a solution of nitrated silver is dropped into water impregnated with it, the mixture becomes turbid, and a dark-coloured precipitate falls to the bottom; by the addition of the nitrated silver, the odour of the hepatic air is rendered much fainter; and it is entirely destroyed by concentrated nitrous, or by dephlogisticated marine acid.

To determine whether the ærial fluid contained in the cancerous matter possessed these properties, a portion of this substance was diffused through distilled water. The mixture being filtered, a small quantity of nitrated silver was dropped into it. In a little time, an ash-coloured cloud was produced,  
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which soon afterwards acquired a brownish purple hue, and at the end of two hours the colour of the mixture was changed to a deep brown. The fetid smell was now rendered much fainter than that of a similar mixture of cancerous matter, and of distilled water, to which nitrated silver had not been added. When a little concentrated nitrous acid was dropped into the mixture which had been thus altered by the addition of nitrated silver, a slight effervescence took place, the brown hue was instantly changed to an orange colour, and the fetid smell was abolished. The fetor was likewise entirely destroyed, when dephlogisticated marine acid was added either to cancerous matter in its separate state, or to a portion of that substance which had been previously mixed with nitrated silver.

By the foregoing properties the cancerous virus is distinguished from common pus: for when dilute vitriolic acid is added to common pus, no effervescence is produced; and when a solution of nitrated silver is dropped into this substance previously diffused through distilled water, the mixture does not acquire a brown colour; nor does any sensible precipitation take place for several hours. It appeared, however, that when the last experiment was repeated with matter obtained from a venereal bubo, the mixture upon the addition of the nitrated silver became slightly turbid, and, at the end of two hours, it acquired a brownish cast. The same effects were perceived when the trial was made with matter obtained from a carious bone. But in these instances the precipitation was much less considerable than that which was produced by the cancerous matter.

I next endeavoured to procure, in its separate state, a portion of the air which is extricated from the matter of cancer by the vitriolic acid. With this intention a quantity of reddish cancerous matter was mixed in a small proof, with about

thrice its weight of distilled water. To this mixture a little vitriolic acid was added; upon which an effervescence took place, and the air that was disengaged was received in a phial over mercury. When one half of the mercury was expelled from the phial, the latter was inverted over distilled water, and the portion of the mercury that remained in it being suffered to descend, and the water to rise into its place, the phial was closely corked. The air and water were then briskly agitated together, and the phial being a second time inverted over distilled water, the cork was removed; when it appeared by the height to which the water rose, that a part of the air had been absorbed. The water contained in the phial was now found to be strongly impregnated with the odour of the cancerous matter, and a little nitrated silver being dropped into it, a purplish cloud, inclining to red, was produced. It is proper to observe, that the change of colour upon the addition of the nitrated silver, in this experiment, was at first scarcely perceptible; but in the course of a few minutes it became very distinct. As it might perhaps be doubtful, whether this alteration would not be produced in the nitrated silver by exposure to the air alone, the colour of the mixture was compared with that of a similar mixture of nitrated silver and of pure distilled water, which had remained exposed to the open air for an equal length of time. Although a slight change of colour was produced in the latter instance, yet it was much less considerable than that which took place in the former.

In the above recited experiment, the air came over mixed with the common air that was contained in the proof. The quantity of aerial fluid that can be thus extricated by the addition of the acid without the assistance of heat, is not very considerable.

If heat be applied, a larger portion of fetid air, having the odour of cancerous matter, may be disengaged; but in that case it will be found to be mixed with vitriolic acid air.

With a view to obtain the former of these fluids in as pure a state as possible, the experiment was repeated in the following manner. A portion of the cancerous virus, diffused through distilled water, was introduced into a small proof; a little vitriolic acid was added; the vessel was filled with distilled water, and a crooked tube, also filled with that fluid, was fixed to its neck. The extremity of the tube being then introduced into the mouth of an inverted bottle containing water, and the flame of a candle being applied to the bottom of the proof, a quantity of air was expelled, which was received in the bottle. This air, when it was first disengaged, rose in the form of white bubbles; it had a very fetid smell, similar to that of the cancerous matter; and the water which was impregnated with it occasioned a dark-brown precipitate in a solution of nitrated silver. The crooked tube being separated from the proof, a very offensive white vapour, resembling in its odour the air extricated during the experiment, arose from the mixture, and continued to ascend for nearly half an hour. When to a portion of this smoking liquor, previously filtered, a little concentrated nitrous acid was added, the fetid smell was entirely destroyed, a slight effervescence took place, and a flaky substance that floated through the mixture was disengaged.

The foregoing experiments prove, in general, that the fetid odour of the matter of cancer is increased by the vitriolic, but entirely destroyed by the concentrated nitrous and dephlogisticated marine acids; that the aerial fluid, which is disengaged by the vitriolic acid, is soluble in water; and that the solution

tion deposits a reddish brown precipitate upon the addition of nitrated silver. Whence it follows, that the cancerous matter contains a principle which has many of the properties of hepatic air, and which may perhaps not improperly be termed animal hepatic air.

It has moreover been shewn, that the matter of cancer is impregnated with an alkali which is in such a state as to change the colour of vegetable tinctures. I had very little doubt that this was the volatile alkali: for it is well known, that putrid animal substances frequently abound with that salt; but have never, I believe, been found to contain a fixed alkali in a disengaged state. With a view, however, more decisively to determine this point, I tried the following experiment. A quantity of cancerous matter, diffused through distilled water, was introduced into a glass retort to which a receiver was adapted. The mixture was slowly distilled by means of a sand heat; and a small quantity of the liquor which came over into the receiver being poured into an infusion of Brazil wood, instantly imparted to it a deep red colour.

Hence it clearly appears, that the alkali contained in the cancerous matter was the volatile, because it was separated by distillation with a heat which did not exceed that of boiling water.

It seemed extremely probable, that the above-mentioned alkali was united to the aerial fluid with which the matter of cancer is impregnated. Of the truth of this fact I was persuaded by observing, that the smell of the cancerous matter was greatly increased by the addition of the vitriolic acid: for I could scarcely avoid concluding, that this phenomenon arose from an union between the acid and alkali, in consequence of which the odoriferous principle was extricated by a superior attraction.



attraction. This conclusion will be confirmed by experiments to be recited in the sequel, which prove, that the volatile alkali is capable of entering into a chemical combination with the aerial fluid contained in the matter of cancer.

*Of the air extricated from cancerous matter, and from other animal substances, by distillation.*

A portion of matter from a cancerous breast was diffused through distilled water, and introduced into a small coated glass retort, which was gradually exposed to heat in a sand bath till the bottom of the retort became red-hot. The neck of the latter was introduced below an inverted jar filled with water, and a quantity of air was received in the jar, which was found to consist of the common air contained in the retort. Two measures of it, mixed with one of nitrous air, occupied the space of a little less than two measures. This portion of air was strongly impregnated with the peculiar smell of the cancerous matter.

The heat continuing to increase, the water began to boil, and a large quantity of aqueous vapour arose; which, as soon as it came into contact with the common air, produced a white smoke. The smell that was now perceived was remarked by those who were present to be similar to that of fresh animal substances when they are boiled. The aqueous vapour in this part of the process was not mixed with any permanently elastic fluid.

When the greater part of the water was evaporated, the jar containing the first portion of air was removed, and the neck of the retort was introduced beneath an inverted vessel filled with mercury. Soon after this, a considerable quantity of air, having a fetid smell similar to that of burned bones, was extri-

cated. This aërial fluid was mixed with a yellow empyreumatic oil. A portion of it being agitated with water was found to be partly imbibed by that fluid; and nitrated silver, dropped into the water thus impregnated, produced a reddish precipitate.

One measure of the air, obtained in the foregoing experiment, being mixed over mercury with an equal bulk of alkaline air, the volume of the mixture was found gradually to decrease; and, at the end of three hours, the air in the tube occupied the space of only one measure and two tenths. An oily deposit was now made upon the inner surface of the tube. At the expiration of eight days, the interior surface of the tube was covered with slender films, which had a yellowish cast, and which were irregularly spread upon it. The upper surface of the mercury within the tube was corroded; in some places it had a reddish burnished appearance; in others, it was changed into an ash-coloured powder, interspersed with brown spots. The tube was now removed from the mercury, and the air that remained in it had a strong fetid smell, resembling that of burned bones.

It has been already observed, that before the water was entirely evaporated, the vapour had lost the odour of the cancerous matter, and had acquired that of animal substances recently boiled. Hence it appears, that the matter upon which the peculiar smell of cancerous ulcers depends, is a very volatile substance, for it escaped at the beginning of the process. It also appears, that this volatile substance, which is probably the active principle in the matter of cancer, is not changed, by simple exposure to heat, into a permanently elastic fluid; for the air that escaped at the beginning of the process, although it smelled strongly of the cancerous matter, was found by Dr.

PRIESTLEY's test to be as pure as common air; and it was evident, that the aqueous vapour which came over in the middle of the process was not mixed with any permanently elastic fluid; because, when this vapour was received in an inverted bottle filled with mercury, it was condensed into water, without any admixture of air. Indeed, if the odoriferous principle in the matter of cancer consist of volatile alkali combined with animal hepatic air, it could not be expected that it should acquire a permanently elastic form by simple exposure to heat; because when alkaline and animal hepatic air unite together, they form a non-elastic substance that condenses upon the inner surface of the vessel in which they are mixed.

To discover whether other animal substances yield an aerial fluid, similar to that which was extricated in the foregoing experiment from the matter of cancer by means of heat, a portion of the flesh of the neck of a chicken was introduced into a small coated glass retort, which was gradually exposed to heat in a sand bath till it became red-hot. A thin phlegm, of a yellowish colour, first came over: this was soon succeeded by a yellow empyreumatic oil, and at the same time a permanently elastic fluid, having an odour resembling that of burned feathers, began to be disengaged. A slip of paper, tinged with litmus and reddened by acetic acid, being held over this fluid, became blue. The neck of the retort was now introduced below an inverted jar filled with mercury, and a considerable quantity of air, together with a fetid empyreumatic oil, were received in the jar. This air was highly inflammable: it had a very fetid odour. When a bottle, containing a portion of it, was agitated with distilled water, nearly one-half of it was absorbed. The residue was inflammable, and burned first with a slight explosion, and afterwards with a blue lambent flame. A little nitrated silver being dropped into the

water with which the air had been agitated, the mixture instantly acquired a reddish brown colour; after some time it became turbid, and a brown precipitate fell to the bottom. When two measures of the air, extricated in this experiment, were mixed with one of alkaline air, they occupied the space of a little more than one measure and an half. A second measure of alkaline air being added, and the airs being suffered to remain together for three days, at the end of that time the residue occupied the space of two measures and one-eighth. Soon after they were mixed, an oily fluid, of a pale colour, was deposited on the internal surface of the jar. At the end of the third day this substance had acquired a light olive colour. It was collected in globules, irregularly distributed over the interior surface of the jar. These globules were nearly of a solid consistence. When the jar was removed from the mercury, the air contained in it at first smelled strongly of volatile alkali. After a little time the smell of the alkali disappeared, and the odour of empyreumatic oil was distinctly perceived. A small quantity of distilled water, which was now agitated in the jar, acquired a brown colour, but did not entirely dissolve the viscid substance that adhered to its surface. The water, thus coloured, was divided into two portions. To one of these was added a little strong vitriolic acid, by which the smell was exalted, and a slight effervescence was produced. Concentrated nitrous acid being added to the other portion, the smell and colour were destroyed, and a brisk effervescence took place.

When a portion of the solid substance that adhered to the interior surface of the jar was separated, it felt viscid and adhesive between the fingers, and smelled strongly of empyreumatic oil. A little spirit of wine being introduced into the

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jar, this viscid substance was dissolved; the spirit acquired a yellow colour and empyreumatic smell, and upon adding to it distilled water the mixture became whitish and slightly turbid.

I next examined the air extricated from putrid veal by distillation. A portion of the latter substance being introduced into a coated glass retort was exposed to a red heat, and the air disengaged was received in a jar over mercury. This aerial fluid was found to possess nearly the same properties with that which was obtained in the preceding experiments. It was very inflammable; about one-half of it was soluble in distilled water. The water, thus impregnated, became turbid upon the addition of nitrated silver, and a brown precipitate fell to the bottom. To another portion of distilled water saturated with this fluid, dephlogisticated marine acid being added, the fetid smell was destroyed, a brisk effervescence took place, and a whitish gelatinous substance was separated. This substance being evaporated to dryness, became black upon the addition of concentrated vitriolic acid. When a quantity of the air obtained in the experiment was agitated with distilled water until no more was absorbed, the residue took fire upon the application of an ignited body, and burned with a lambent flame. It is proper to observe, that the air extricated from the putrid veal had less of the empyreumatic smell than that which was disengaged from fresh animal substances. Its odour indeed was nearly similar to that of animal substances in a state of putrefaction.

We learn from these experiments that the aerial fluids, which are extricated from fresh as well as from putrid animal substances by distillation, have nearly the same properties with that which is disengaged, by a similar process, from the matter of cancer. Each of them appears to consist of two distinct fluids; one of which is soluble, and the other insoluble, in

water. The portion that is insoluble burns with a lambent flame, and has all the characters of heavy inflammable air; whereas the soluble part resembles the fluid which is extricated from cancerous matter by the vitriolic acid: it has a fetid odour, it decomposes nitrated silver, combines with caustic volatile alkali, and possesses many of the properties of common hepatic air.

There are several particulars, however, in which the animal and common hepatic air materially differ from each other. Although they are both fetid, yet their odours are not exactly similar. When common hepatic air is decomposed by the concentrated nitrous or dephlogisticated marine acid, sulphur is separated; but when animal hepatic air is decomposed by these acids, a white flaky matter is disengaged which is evidently an animal substance, because it becomes black by the addition of concentrated vitriolic acid. Sulphur is moreover separated during the combustion of common hepatic with atmospherical air; but when the air from animal substances is burned with atmospherical air, no precipitation of sulphur takes place. Indeed, that animal hepatic air does not contain sulphur will be apparent from the following experiment.

Equal parts of pure air and of air extricated from fresh beef by distillation, were fired by the electric shock in a strong glass tube over mercury. A little distilled water was then introduced through the mercury into the tube, and was agitated with the air which it contained. A portion of this water being filtered, and a small quantity of muriated barytes being dropped into it, the mixture remained perfectly transparent. Hence it appears, that the air extricated from fresh beef by distillation does not contain sulphur; for, if it had contained that substance, the sulphur, by its combustion with the pure air, would have been

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changed into the vitriolic acid, and the muriated barytes would have been decomposed.

I frequently repeated the preceding experiment with the air extricated, by distillation, from the putrid as well as from the fresh muscular fibres of animals; but I could not, in any instance, discover the least vestige of the vitriolic acid.

The following experiments were made with a view more accurately to analyse the airs which are disengaged from animal substances by heat, and to determine the products resulting from the union of these fluids with pure air.

About an ounce of the lean of fresh mutton was introduced into a small coated glass retort, and exposed to a red heat. The air that was extricated towards the end of the distillation was received over mercury; and soon after its production, being agitated with water, very nearly one half of it was absorbed. A similar experiment being made with the air disengaged towards the middle of the distillation, the part of it which was soluble in water was found to be to the part not soluble in that fluid as 2 to 3. Having suffered a separate portion of the air disengaged towards the end of the distillation to remain over mercury for seven hours, it was found gradually to diminish in bulk, and a fluid, which had the colour and the odour of a thin empyreumatic oil, was collected at the bottom of the jar\*. The air being now agitated with water, only one-eighth of it was absorbed. Hence it appears, that a portion of the air, extricated from animal substances by heat, resembles a species of hepatic air which was first discovered by Mr. KIRWAN, and which exists in an intermediate state between the aerial and the vaporous; this fluid not being permanently elastic like

\* The above-mentioned appearance is not constant. The air when placed over mercury sometimes diminishes, and at other times it retains its original bulk. I have not as yet discovered the cause of this difference.

air, nor immediately condensed by cold like vapour, but gradually assuming the non-elastic form, in consequence probably of the tendency of its several parts to unite with each other.

The air produced in the foregoing experiment rendered lime-water turbid; it therefore contained a quantity of fixed air; and towards the end of the distillation a little volatile alkaline air came over, agreeably to the observation of M. BERTHOLLET: for, when a portion of the air received during this part of the process was mixed with an equal quantity of marine acid air, a white vapour was produced, and a diminution of about one twenty-fifth of the whole took place.

I endeavoured, by the following experiment, to ascertain the proportion of fixed air contained in the ærial fluid which is disengaged from the lean of animal substances by heat.

A quantity of air, extricated from the lean of fresh mutton, was received over mercury in a large phial which had a narrow neck. When the phial was a little more than half filled, the remaining portion of the mercury was displaced by introducing water that had been previously boiled. The phial being then closely corked, the air and water were briskly agitated together; and the liquor, thus impregnated with the soluble part of the animal air, was put into a proof, to the bottom of which heat was applied. By this means a portion of the air was again disengaged, which was received in a tube inverted over mercury. The process was continued till the liquor in the proof no longer rendered lime-water turbid. As the air received in the tube contained the fixed air that had been extricated from the liquor, together with a quantity of common air expelled from the proof, it was a second time agitated with water; and the exact measure of the fixed air was known by the portion which the water imbibed. The fixed air, thus ascertained, being compared with the entire quantity of air that had been originally absorbed, it appeared, that



that the former was to the latter in bulk as 1 to 4. One-fourth therefore of the volume of the soluble part of animal air consists of fixed air, and the remaining three-fourths of hepatic, mixed with a very small proportion of alkaline air\*.

It appeared from the experiment, that animal hepatic air, when it was absorbed by water, was not capable of being again disengaged by a heat which raised the water to the boiling temperature; for, after the fixed air was expelled, the liquor in the proof was made to boil nearly half an hour, but no permanently elastic fluid could be disengaged. The portion of the liquor which now remained had a faint yellow colour; it smelled strongly of animal hepatic air, and deposited a brown precipitate upon the addition of nitrated silver.

It appears, therefore, that the soluble part of the air which is disengaged from the lean of animal substances by heat, consists of three distinct fluids; of alkaline air, fixed air, and animal hepatic air. It seemed extremely probable, that these three aerial fluids, slowly combining together, formed the oily empyreumatic substance which was collected at the bottom of the jar, while the air was undergoing the diminution described above. In this conclusion I was confirmed by trials that were made with the empyreumatic oil that came over during the latter part of the distillation: for when it was examined by chemical tests, soon after it was obtained, it was found to contain fixed air, volatile alkali, and animal hepatic air.

\* It is proper to remark, that, in some experiments, the relative quantity of animal hepatic air was found to be less than that which has been stated above. I do not as yet know, with certainty, the causes to which this difference is to be attributed; but I believe it principally depends upon the period of the distillation, in which the air is received, the degree of heat applied to the bottom of the retort, and the nature of the animal substance employed in the experiment.

I next endeavoured to determine the products which result from the combustion of pure air, with animal air, or with the compound aërial fluid extricated from the lean of animal substances by heat. With this intention I exposed the lean of fresh mutton, in a small coated glass retort, to a red heat. The air which was received over mercury towards the end of the distillation was divided into two separate portions; one of which was agitated with water till the soluble part was absorbed; the other was not agitated with that fluid. One measure of the former was introduced, over mercury, into a strong glass tube adapted for the purpose of firing aërial fluids by the electric shock. This was mixed with one measure and an half of pure air. The portion of the tube occupied by the mixture was one inch and two-tenths. A small shock being made to pass through it, a violent explosion took place, and the space occupied by the residue was nine-tenths of an inch. The height of the mercury in the tube, previously to the combustion, was 4.8 inches. After the airs were fired, its height was 5.1 inches. Allowance being made for the difference of expansion produced by this cause, it appeared, that the volumes of the airs, previously to the combustion, and subsequent to it, were as 100 to 75 nearly. The residue being agitated with water, six-tenths were absorbed; and the portion which was thus absorbed was found, by the precipitation which it produced in lime water, to be fixed air. Of the insoluble remainder, five parts being mixed with five of nitrous air, a diminution of three parts took place; whence it follows, that one-fifth of the insoluble residue was pure air.

The pure air which was used in this experiment had been previously agitated with water, to free it entirely from fixed air, and the inflammable air had undergone a similar agitation.

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It is therefore manifest, that, by the combustion of the pure and inflammable air in the foregoing trial, fixed air was produced; the phlogisticated air, found in the residue, being that which was contained in the pure air before the inflammation took place.

I next examined the products resulting from the combustion of pure air with that portion of the animal air which had not been previously agitated with water. One measure of this fluid, at the expiration of three-fourths of an hour after it had been obtained, was mixed over mercury with one measure and an half of pure air, and fired by the electric shock. The portion of the tube occupied by the mixture, previously to the deflagration, was one inch and  $\frac{1.5}{10.8}$ ; after the deflagration, it occupied the space of one inch and one-tenth. Being agitated with lime-water, very nearly one-third was absorbed. A portion of the insoluble residue was exposed to a lighted taper, and burned with a faint blue flame\*.

The dephlogisticated air used in this experiment had been previously agitated with water, to free it entirely from fixed air. It was the purest dephlogisticated air I had ever seen: for when one measure of it was mixed with one measure and nine-tenths of nitrous air, the residue occupied the space of only one-fortieth of a measure. From the foregoing trial it was evident, that  $1\frac{1}{2}$  parts of pure air were insufficient to saturate one of the animal air that had not been previously agitated with water. The experiment was therefore repeated as follows. Two

\* When I first made the above experiment, the residue did not appear to be inflammable. It had been tried by applying an inflamed slip of paper to the mouth of a phial which was filled with it; but, upon repeating the experiment, when the phial containing the residuary air was carried into a dark room, and an ignited wax taper was applied to its mouth, an evident inflammation took place.

parts of pure air being mixed with one of animal air, occupied .8 of an inch. The mixture being fired by the electrical shock, the residue stood at a little less than .5. When this residue was agitated with lime-water, it was almost wholly absorbed. By a subsequent trial it was found, that nearly one-half of the animal air used in this experiment was soluble in water.

Hence it appears, that the quantity of pure air required to saturate the insoluble part of the animal air is somewhat less than that required to saturate the compound fluid which had not been previously agitated with water. But the latter fluid has been shewn to consist almost entirely of heavy inflammable, animal hepatic, and fixed air; and as the last of these is already saturated with pure air, it is manifest, that the above-mentioned difference must depend upon the animal hepatic air. Whence it follows, that the latter contains a large portion of the inflammable principle. From the quantity of fixed air produced in the last of the preceding experiments, there is, moreover, the utmost reason to believe, that the basis of heavy inflammable forms one of the constituent parts of animal hepatic air.

When equal parts of pure and animal air were burned together, a considerable increase of bulk almost invariably took place; and when the proportion of the animal was to that of pure air as 21 to 15, the bulk of the mixture was increased one half. The air that remained after the combustion in the last mentioned experiments was inflammable: for a portion of it being introduced into a small phial, and exposed to a lighted candle, it first exploded, and then burned with a blue lambent flame.

Being desirous of learning the cause of the increase of bulk in the foregoing experiments, the following trials were made.

Three measures of animal were mixed with two of pure air, and several strong electrical shocks were made to pass through the mixture, but it would not take fire. Half a measure of pure air was then added, and the mixture being fired, its bulk was increased from .9 of an inch to 1 inch and .3.

Three measures of this residuary air were then mixed with three of pure air, and fired by the electric shock. The bulk of the mixture was reduced from 1 inch to .56. This being agitated with lime-water, two-thirds were absorbed, and the remainder consisted almost wholly of pure air. From these facts it seems probable, that animal hepatic air consists of a combination of heavy and light inflammable air; and that when it is fired with a quantity of pure air not sufficient to saturate it, a portion of the animal air is resolved into its elementary principles, in consequence of which its bulk is increased.

It was before observed, that three parts of animal mixed with two of pure air would not take fire. In some experiments it was found, that when the animal air was mixed with a still smaller proportion of pure air, an increase of bulk was produced by the electric shock, although no deflagration took place; but when the electric shock was repeatedly taken through animal air *alone*, it did not in any instance, as far as I could perceive, produce the smallest increase of size.

I was next desirous of learning whether an increase of size would be produced by making the electric shock pass through a mixture of pure and alkaline air. Having first accidentally taken two or three small shocks through a little alkaline air, and not observing a sensible augmentation of bulk, I then mixed it with an equal volume of pure air; and, as I supposed that no decomposition had taken place, I was not apprehensive

of an explosion. Contrary, however, to my expectation, the airs, when the electric shock was made to pass through them, entered rapidly into an union with each other. The jar which I held loosely in my hand, as it was inverted over the mercury, was carried obliquely upwards with great violence. Having broken the stand of the prime conductor in its passage, it forced its way through the cylinder of the electrical machine, which it shivered to a thousand pieces.

I afterwards repeated this experiment with a very strong apparatus, the jar being pressed down by a plate of iron, for the purpose of retaining it in its place.

It appeared, that when the alkaline and pure air were immediately mixed together, and a small shock was made to pass through them, they would not take fire; but when three or four shocks were previously taken through the alkaline air, and the latter was afterwards mixed with an equal bulk of pure air, they exploded with great violence. The residue, having cooled to the temperature of the surrounding air, was reduced to half the original bulk of the mixture. Of this residue one-sixth was undecomposed alkaline air. The remainder was phlogisticated air.

*Of the products which result from the combustion of sulphureous hepatic with pure air.*

The hepatic air employed in the following experiments was procured, agreeably to the method which Mr. KIRWAN has recommended, by adding marine acid to an artificial combination of sulphur and iron. Three measures of the air thus obtained were mixed in a strong glass tube over mercury, with four of pure air, and fired by the electric shock.

The pure air was previously agitated with lime-water to free it from fixed air, and a portion of the hepatic air, having been likewise agitated with lime-water, was found not to occasion any precipitation in that fluid. The airs were reduced by the explosion to one-fourth of their original bulk. The residue was then transferred over mercury into a slender graduated tube, and distilled water being admitted, eight-tenths were absorbed. To a portion of this water, when filtered, vitriolated silver was added, which instantly occasioned a copious precipitate. To a second portion was added muriated barytes, which occasioned a slight white precipitate not re-dissolvable in a large quantity of water; lime-water being added to a third portion, did not produce any sensible precipitation. From the last fact it does not follow, that no fixed air existed in the residue, because the marine acid, which it evidently contained, would dissolve the calcareous earth of the lime-water. As a great diminution, however, resulted from the combustion; and as it appeared, from chemical tests, that the residue was mostly composed of marine and vitriolic acid airs, it is manifest, that, if any fixed air was produced, its quantity must have been very inconsiderable.

It has been already observed, that a slight precipitation took place upon the addition of the muriated barytes. The precipitate was much more considerable when, upon repeating the experiment, the residue after the explosion was not transferred into a graduated tube previously to the admission of the distilled water; but the latter was immediately introduced into the vessel in which the airs were fired. The reason of this difference is evident. The slight precipitate by the muriated barytes, in the first instance, depended upon the existence of a small quantity of vitriolic acid in an aerial form, or in the  
state

state of volatile vitriolic acid, which was transferred together with the phlogificated and marine acid air into the second tube; but the greater part of the vitriolic acid produced by the combustion adhered, in a fixed state, to the surface of the tube in which the airs were fired; and therefore, when the distilled water was immediately introduced into this tube, a copious precipitate was deposited upon the addition of muriated barytes.

Hence it appears, that when pure air and sulphureous hepatic air, obtained from artificial pyrites by the marine acid, are fired together in the above proportions, the products are fixed vitriolic acid, together with a small quantity of the volatile vitriolic, and marine acids, in an ærial form. The residue, which the distilled water did not absorb, was the phlogificated air that existed in the pure air previously to the combustion.

From subsequent trials it appeared, that, when hepatic and pure air were fired in equal bulks, the residue had a strong odour of volatile vitriolic acid, and moreover contained a small proportion of undecomposed hepatic air. These facts seem to prove, that the conversion of sulphur into volatile or fixed vitriolic acid depends upon the quantity of pure air with which it is supplied.

The marine acid air, found in this experiment, did not appear to form one of the constituent principles of the hepatic air, but to be merely diffused through it; for it was almost wholly separated, by means of distilled water, from a different portion of the same air, which was placed in a tube inverted over mercury; the water having a stronger attraction to the marine acid than to the hepatic air.

By the following experiment I endeavoured to determine  
whether



whether vitriolic acid be produced by the combustion of hepatic with atmospherical air. One measure of hepatic air, obtained from artificial pyrites, was mixed over mercury with about six measures of atmospherical air, and fired by the electric shock. A copious precipitation of sulphur took place, the remaining air was then agitated with distilled water, the latter was filtered, and muriated barytes was added, which produced a white precipitate not dissoluble in a large quantity of water.

From this, and the foregoing experiment, it appears, that when sulphureous hepatic is burned with atmospherical air, a part of the sulphur is changed into vitriolic acid, and the rest is precipitated; but when it is burned with a sufficient quantity of pure air, the sulphur is wholly converted into vitriolic acid. Agreeably to this conclusion, I have found that the odour of the volatile vitriolic acid constantly accompanies the combustion of hepatic with common air in open vessels; and that when concentrated nitrous acid is added to water impregnated with hepatic air, the filtered liquor becomes turbid upon the addition of muriated barytes.

The quantity of pure air required to saturate sulphureous hepatic air, does not appear to correspond with the supposition that the last of these fluids consists of sulphur dissolved in light inflammable air: for sulphur, in order to its complete saturation, requires only 1.43 times its weight of pure air; but light inflammable air requires for its saturation at least six times its weight of that fluid. The specific gravity of hepatic air, as determined by Mr. KIRWAN, is nearly equal to that of pure air. If, therefore, one-sixth of the weight of hepatic consisted of light inflammable air, that fluid would require for its saturation 2.26 times its bulk of pure air: for the portion

of it which consisted of light inflammable air would require a quantity of pure air equal in bulk to the hepatic; and the remaining portion, consisting of sulphur, would require a quantity equal to 1.26 of the hepatic. The entire quantity of pure air would therefore be to that of the hepatic as 2.26 to 1. If the hepatic contained one-twelfth of its weight of light inflammable air, it would require for its saturation 1.64 of its bulk of pure air. But from the foregoing experiments it appears, that the quantity of pure air, necessary to saturate one measure of hepatic air, is only 1.33 measures. Hence it is probable, that this fluid does not consist of sulphur dissolved in light inflammable air.

If we make allowance for the marine acid which was diffused through the hepatic air, it will be found, that the quantity of pure air required to saturate it is nearly the same with that which would be required to change an equal weight of sulphur into vitriolic acid. Whence it may be inferred, agreeably to the opinion of Mr. KIRWAN, that hepatic air is sulphur which has acquired an aerial form by the application of heat. This conclusion is, I think, confirmed by the following experiment.

A little pure sulphur was introduced into an inverted tube, which had been previously filled with mercury, and the flame of a candle was applied to the extremity of the tube. In a short time a permanently elastic fluid was produced, which was found to have all the characters of hepatic air. It is probable, however, that some degree of moisture is necessary to the success of this experiment, because the quantity of hepatic air which was thus obtained was not very considerable.

It has been already shewn, that an oily matter was produced by the union between fixed air, volatile alkali, and animal  
hepatic

hepatic air. The following experiment proves, that a substance, which has very much the appearance of oil, is formed by the combination of *fulphureous* hepatic air with fixed air and volatile alkali.

A quantity of impure hepatic air was obtained by adding vitriolic acid to common liver of sulphur. When this fluid was agitated with lime-water, it produced a copious precipitation. It therefore contained a considerable proportion of fixed air. One measure of it was now introduced into a slender graduated tube, inverted over mercury, and was mixed with an equal bulk of alkaline air. As soon as the airs came into contact with each other, a white cloud was produced, the mercury began gradually to rise in the tube, and at the end of six hours the air that remained occupied the space of only one measure and one-third. The surface of the mercury within the tube first became black, and a part of it afterwards acquired a red colour resembling cinnabar. In the course of the experiment, a yellowish oleaginous substance was deposited upon the interior surface of the tube. This substance, in some parts of the surface, formed itself into globules; in others, it was extended into ramifications, having the resemblance of trees in miniature, and it gradually assumed a deeper colour, till at length it acquired a greenish cast. The substance, thus obtained, had a very fetid odour: it appeared to have a near resemblance to an animal oil which had become green by putrefaction. It was, however, soluble in water, and the odour of the solution was increased by the vitriolic, and destroyed by the concentrated nitrous and dephlogisticated marine acids.

Mr. CRUIKSHANK, who assisted me in most of the foregoing experiments, and on whose accuracy I could place the greatest reliance, examined, in my absence, the red and black

powders which were formed by the action of the hepatic air upon the surface of the mercury, and found them to be æthiops mineral, and cinnabar.

*Of the air extricated from animal substances by putrefaction.*

In the beginning of July, 1789, about two ounces of veal, slightly putrid, was introduced into a large phial, which was filled with distilled water, and inverted over a quantity of the same fluid. At the end of three days a few bubbles of air had appeared at the bottom of the phial; the water had acquired a light brown colour, and emitted a fetid smell. At the expiration of seven days we could perceive that the quantity of air at the bottom of the phial was manifestly increased, although its progress was very slow. The water, by the dissolution of a part of the veal, had now acquired the consistence of a thin mucus, its brown colour was somewhat deepened, and it emitted a highly fetid smell. A little nitrated silver being dropped into a portion of this water, previously filtered, a dark brown precipitate was immediately produced. Lime-water, mixed with another portion of it, occasioned an ash-coloured precipitate; and when concentrated nitrous acid was added to a third portion, the fetid smell was destroyed, a slight effervescence took place, and a yellow flaky matter was disengaged. At the end of seven weeks, a quantity of air, amounting to two and one-sixth dram measures was collected in the phial. This air had a fetid odour. Being agitated with water, six-tenths of it was absorbed. The residue extinguished flame.

I next examined the air extricated from veal which was suffered to putrefy over mercury.

On the 28th of July, 1789, two drams and twenty-four grains of the lean of fresh veal was introduced into a narrow jar, which was filled with mercury, and inverted over that fluid. At the end of eight days the air, which was slowly extricated, had communicated a brown colour to the surface of the mercury. On the 13th of September, the quantity of air disengaged was a little more than two ounce measures. This fluid had a very fetid smell. Two separate portions of distilled water being saturated with it, the first, upon the addition of nitrated silver, deposited a brown precipitate; and the last, when it was mixed with lime-water, produced a brownish ash-coloured cloud. A third portion of the air being strongly agitated with distilled water, was reduced to one-sixteenth of its original bulk. The residue extinguished flame.

The veal which had remained so long in contact with the mercury had not lost its firm texture. Its smell was putrid, but not very offensive.

The quantity of elastic fluid collected in this experiment was much greater than in the preceding one; because in the preceding experiment, although the putrefaction advanced more rapidly, yet the fixed and hepatic air were absorbed by the water nearly as fast as they were disengaged from the putrid substance.

Hence it appears, that the ærial fluids, which are extricated from the muscular fibres of animals by putrefaction, consist of fixed and animal hepatic, mixed with a very small proportion of phlogisticated air\*.

\* It may be proper to remark, that I have obtained, by distillation from the green leaves of a cabbage, an ærial fluid, which, in most of its properties, resembles animal hepatic air.

*Of the effects produced by exposing fresh animal substances to atmospherical, hepatic, and pure air.*

Two tubes, of nearly the same size, were inverted over mercury. Into one of these was introduced common air, and into the other an equal bulk of hepatic air, obtained from liver of sulphur by the vitriolic acid. Equal quantities of fresh veal, consisting of a mixture of muscular fibres and of fat, and weighing each one dram, were then exposed to these airs. At the end of three days the piece that was in contact with the common air had not altered its colour or consistence, but smelled a little putrid. The colour of the fatty parts of the piece that was exposed to the hepatic air was changed to a dark green, the muscular fibres were cracked and shrivelled on the surface as if they had been seared with a hot iron, and the whole had acquired a soft consistence.

Similar trials were made with two pieces of fresh veal, one of which was exposed over mercury to common air, and the other to air extricated from putrid veal by distillation. The former in three days had not changed its appearance; the latter had become green round the edges, and was interspersed with green spots. The surface of the mercury in the jar which contained the last had acquired a brown colour; whereas that of the mercury in the jar which contained the common air was clear and bright. The pieces of veal were suffered to remain in this situation for six weeks. After a few days had expired, *that* which was exposed to the animal air did not appear to suffer any farther change. Its colour, which in the course of a week had become brown, continued unaltered, and no dissolution took place. The air at the last was very fetid; it occasioned

fioned a copious precipitate in lime-water; it was highly inflammable, and burned with a blue lambent flame.

The piece, on the contrary, which was exposed to the common air, did not, as has been already observed, so soon lose its fibrous texture, nor so speedily acquire a dark colour, as that which was in contact with the animal air. But the progress of its putrefaction did not appear to stop at the end of a few days, as in the latter instance. It advanced slowly, and at the expiration of six weeks a considerable part of the muscular fibres had run down to a brown liquid. The air in which it was placed now occasioned a copious precipitation in lime-water, and the brown liquid was found to be impregnated with animal hepatic and fixed air; the existence of the latter being known by means of lime-water, and that of the former by its occasioning a dark precipitate in a solution of nitrated silver, as well as by its fetid odour, which was increased by the vitriolic, and destroyed by the concentrated nitrous and dephlogisticated marine acids.

The following experiment was made with a view to determine whether pure air accelerates the progress of putrefaction in animal substances.

In the month of December, 1789, equal portions of pure and of common air were introduced into two equal jars over mercury, in each of which was placed about two drams of fresh beef. At the end of a week, the beef which was exposed to the pure air had become highly putrid; but very little change was produced in that which was exposed to the common air.

The facts which have been ascertained by the preceding experiments, appear to lead to the following conclusions respecting the process of putrefaction in the lean of animal substances.

The muscular fibres of animals contain fixed and phlogisticated air, the inflammable principle in the state of heavy and of light inflammable air, and a substance which, by means of heat or of putrefaction, is capable of being converted into animal hepatic air\*. When the muscular fibre, after the death of the animal, is exposed to the pure air of the atmosphere; the latter, by a superior attraction, combining with the heavy inflammable air, produces fixed air, and at the same time furnishes the quantity of heat necessary to the formation of animal hepatic air. The cohesion of the fibre being thus destroyed, the fixed, as well as the light inflammable and phlogisticated air, which enter into its composition, are disengaged, and the two latter fluids uniting with each other produce the volatile alkali.

The alterations which take place in putrefaction are in most respects similar to those which arise from destructive distillation. By exposure to heat the fixed air of the animal fibre is extricated, hepatic air and volatile alkali are produced, and the inflammable principle not coming into contact with the pure air of the atmosphere, is raised in the form of heavy inflammable air.

I have found, that the fetid odour of animal hepatic air is destroyed by mixing it with pure air, and suffering it to remain in contact with that fluid for several weeks. When it was placed in this situation, it acquired an odour which was not exactly similar to any that I had ever before perceived, but which bore some resemblance to that of inflammable air obtained by dissolving iron in spirit of vitriol.

\* It is scarcely necessary to observe, that the existence of fixed, inflammable, and phlogisticated air in animal substances, and the composition of volatile alkali, were discovered before I began to give particular attention to this subject.



The peculiar smell of animal hepatic air is likewise destroyed by agitating it with vinegar, or with the concentrated vitriolic acid. But the fluids which most speedily produce this effect, are the concentrated nitrous and dephlogisticated marine acids; and these fluids are known to abound with pure air. It is therefore extremely probable, that this alteration depends upon an union between the pure air of the latter substances and the animal hepatic air, or some of its constituent parts.

It appears from the experiments which have been recited above, that in cancerous and other malignant ulcers, the animal fibres undergo nearly the same changes which are produced in them by putrefaction, or by destructive distillation. The purulent matter prepared for the purpose of healing the ulcer is, in such cases, mixed with animal hepatic air and volatile alkali. The compound formed by the union of these substances, which may perhaps not improperly be termed hepatised ammonia, decomposes metallic salts, and acts upon metals: for we have seen, that when it was placed in a jar over mercury for several days, the surface of the mercury acquired a black colour; and that it instantly occasioned a dark precipitate in a solution of nitrated silver. These facts seem to afford an explanation of the changes produced in metallic salts, when they are applied to malignant ulcers. The volatile alkali combines with the acid of the metallic salt, and the animal hepatic air revives the metal, either by imparting to it the inflammable principle, or by uniting with the pure air which the calx is supposed to contain. The metal, thus revived, is probably in some cases again corroded by the hepatised ammonia, which communicates to it a black colour. Thus we may account for the dark incrustation frequently formed upon the  
tongue

tongue and internal fauces, when venereal ulcers of the throat are washed with a solution of corrosive sublimate. And hence also the dark tinge which is frequently communicated by ill-conditioned ulcers to poultices made with a solution of sugar of lead. The action of the hepatised ammonia likewise explains the reason why the probes are frequently corroded when they are introduced into sinuous ulcers, or applied to the surfaces of carious bones. To the same cause it is probably owing, that polished metallic vessels are quickly tarnished, when they are exposed to the effluvia of putrid animal substances.

From the foregoing experiments it moreover appears, that animal hepatic air imparts to the fat of animals recently killed a green colour; that it renders the muscular fibres soft and flaccid, and increases the tendency to putrefaction. It is therefore a septic principle; and hence it is extremely probable, that the compound of this fluid with volatile alkali, which is found in the matter discharged by the open cancer, produces deleterious effects: for although the mischief in cancerous ulcers seems principally to depend upon a morbid action of the vessels, whence the unhealthy state of the matter discharged by such ulcers is supposed to derive its origin, yet from the corrosion of the coats of the larger blood-vessels, and the obstructions in the contiguous glands, there can be little doubt that this matter aggravates the disease. The experiments recited above appear to prove, that the hepatised ammonia is the ingredient which communicates to the cancerous matter its putrid smell, its greater thinness, and, in a word, all the peculiar properties by which it differs from healthy pus.

From these considerations it was inferred, that a medicine which would decompose the hepatised ammonia, and destroy the fetor of the animal hepatic air, without at the same time increasing

increasing the morbid action of the vessels, would be productive of salutary effects. The nitrous acid does not destroy the fœtor of hepatic air, unless it be highly concentrated; and in this state it is well known that it speedily corrodes animal substances. But the fœtor of hepatic air quickly disappears when it is mixed with the dephlogisticated marine acid, even though the latter be so much diluted with water as to render it a very mild application. I have found that this acid, diluted with thrice its weight of water, gives but little pain when it is applied to ulcers that are not very irritable; and in several cases of cancer it appeared to correct the fœtor, and to produce a thicker and more healthy pus. It is proper, however, to remark, that other cases occurred in which it did not seem to be attended with the same salutary effects. Indeed, some cancerous ulcers are so extremely irritable, that applications which are at all of a stimulating nature cannot be ventured upon with safety. And hence if the observations, which I have made on the efficacy of this acid as an external application, should be confirmed by future experience, it must be left to the judgment of the surgeon to determine both the degree of its dilution, and the cases in which it may be employed with advantage.

The dephlogisticated marine acid, as is generally known, has the power of destroying the colour, the smell, and perhaps the taste, of the greater part of animal and vegetable substances. We have seen that it corrects the fœtor of putrid flesh. And I have found, that, when it is poured in sufficient quantity upon hemlock and opium, these narcotics speedily lose their sensible qualities. As it appears, therefore, to possess the power of correcting the vegetable, and probably many of the animal poisons, it seemed not unlikely, that it might be useful as an internal medicine. Conceiving that its exhibition

would be perfectly safe, I once took twenty drops of it diluted with water. I soon afterwards, however, felt an obtuse pain, with a sense of constriction, in my stomach and bowels. This uneasiness, notwithstanding the use of emetics and laxatives, lasted for several days, and was at length removed by drinking water impregnated with sulphureous hepatic air. I afterwards found, that the manganese, which had been used in the distillation of the acid, contained a small portion of lead.

Dr. INGEN-HOUZ informed me, that a Dutchman of his acquaintance, some time ago, drank a considerable quantity of the dephlogisticated marine acid: the effects which it produced were so extremely violent, that he narrowly escaped with his life. If therefore this acid should hereafter be employed as an internal medicine, it would be necessary to prepare it by means of manganese that has been previously separated, by a chemical process, from the lead and the other metals with which that substance is usually contaminated.

