XVI. *Observations on Naphthaline, a peculiar substance resembling a concrete essential oil, which is apparently produced during the decomposition of coal tar, by exposure to a red heat.* *By* J. KIDD, *M. D. Professor of Chemistry, Oxford. Communicated by* W. H. WOLLASTON, *M. D. F. R. S.*

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ALTHOUGH the existence, and many of the properties of the substance above-mentioned, have been already noticed in two of the Philosophical Journals of this country,* there has not yet appeared, as far as I can discover, any systematic description of the mode by which it may be obtained, or of its relation to the substance from which it is produced; on which account I have been induced to offer to the Royal Society the following observations respecting these points of its history.

In the experiments which led, in the present instance, to the detection of the substance in question, it was proposed to effect the decomposition of coal tar by passing its vapour through an ignited iron tube; and, in order to increase to the utmost the extent of the ignited surface, that portion of the tube which was constantly kept up to a red heat, was filled, in the first instance, with a series of hollow iron cylinders open at both extremities, and successively decreasing in diameter, so as to be included one within another. In

* THOMSON's Annals of Philosophy, January, 1820, page 74; and Mr. BRANDE's Quarterly Journal, January, 1820, page 287.

other instances these cylinders were removed, and their place supplied by sand, or by pieces of well burnt coke, or by pieces of brick; but it was found that the interstices between the cylinders, or between the particles of sand, &c. were so soon choaked up with carbon from the decomposition of the tar, as to be rendered absolutely impervious to the gas produced during the decomposition; so that it became necessary to pass the vapour of the tar simply through the tube *itself.*

Connected with the tube in which the tar was decomposed was a vessel, in which any undecomposed vapour of the tar, or any products resulting from its decomposition, might be condensed; and at the end of every experiment this condensing vessel was found to contain an aqueous fluid having an ammoniacal odour, and a dark coloured liquid, resembling tar in appearance.

This dark coloured liquid is characterized by the following properties:

Its colour, in the mass, is black; but when spread in a thin stratum on paper or glass, it is of a clear deep reddish brown colour.

It is a much thinner liquid than the coal tar from which it was produced; and has a peculiar and slightly aromatic odour, together with the smell of ammonia; about three-fourths of a given quantity of it pass through unsized paper; and that which remains on the paper resembles common tar. Sp. gr. 1050; the sp. gr. of the tar from which it was produced being 1109.

Readily and entirely soluble in ether.

Soluble, but not entirely, in alcohol; the solution becoming

milky upon the addition of water, and this milky mixture passing unaltered through the pores of the closest filtering paper.

Not miscible with water; but readily communicating to it a light brown colour, and a taste at first sweet, but followed by an aromatic pungency. The water acquires alkaline properties, and holds ammonia in solution. When poured out on a flat surface, it catches fire almost immediately on the application of flame, and burns for a time exactly in the same manner as a thin stratum of alcohol, the flame being blue and lambent, and without smoke; but after a few seconds the flame becomes white, and the liquid begins to burn with much black smoke, and with a crackling noise.

A pint of this dark coloured liquid was submitted to very slow distillation in a large glass retort connected with a large glass receiver, from the interior of which all communication with the external air was excluded by means of a common safety valve. The heat was supplied from the flame of an Argand gas burner, and was so slight as scarcely to inconvenience the naked hand, when held over it immediately under the bottom of the retort.

The same degree of heat was applied constantly during forty hours; at the end of which time there had distilled into the receiver rather more than half a pint of a liquid, which consisted of two perfectly distinct portions, which, however, had uniformly passed over together from the very commencement of the distillation.

The uppermost of these portions, in appearance, resembled pale olive oil, and amounted to not quite a quarter of a pint. The lowermost portion resembled water, but was not

perfectly transparent, and amounted to rather more than a quarter of a pint: but there is ground for believing, from the results of subsequent distillations, that the proportion of the aqueous product is variable; and that it is greater when the distillation is carried on slowly, than when it is carried on rapidly.

After the above-mentioned products had passed over, a concrete substance as white as snow began to collect in dispersed crystalline flocculi, in the upper part of the body and neck of the retort, so as in a short time almost wholly to obstruct the passage; the oily fluid and the water continuing to pass over at the same time, but much more slowly than before.

At the end of sixty hours the original quantity of the dark coloured liquid was reduced to about a quarter of a pint; and what remained was much thickened in consistence: the heat was therefore increased: and now there began to pass over a darker coloured and thicker oil, which, as it advanced farther from the source of heat, congealed into a substance of the consistence of butter. The heat being still more increased, this oil became darker coloured and more dense; and when at the last there remained in the retort not above one-eighth of the quantity originally poured into it, and the heat of the gas burner had been increased to the utmost, there arose a heavy yellow vapour, which was condensed in the neck of the retort in the form of a farina of a bright yellow colour.

When it appeared that the heat no longer separated any thing from the black matter in the retort, which still however retained a degree of fluidity, the apparatus was suffered to

cool; during which time the residuum became fixed, and to the eye resembled pitch.

The several products of the distillation above described being carefully separated from each other, the more remarkable of them were submitted to examination; but as leisure was wanting for a full investigation of their characters, the Society is requested to accept, with some indulgence, the following description of such of their properties as were ascertained.

Properties of the aqueous product.

Taste, saline and alkaline; with an ammoniacal and slightly aromatic odour.

Sp. gr. 1023.

Became faintly blue by the addition of a solution of prussiate of potash.

Grs. 700 of this aqueous fluid were evaporated under an exhausted receiver inclosing a quantity of dry muriate of lime: the residuum of the 700 grains weighed not more than half a grain, and consisted partly of a brown oil and partly of a sparingly soluble saline matter, which by the proper tests was found to contain sulphuric acid and muriatic acid; the former apparently in greater quantity than the latter.

Properties of the oily fluid.

Taste, pungent, bituminous, and aromatic; with an odour similar to the taste, and slightly ammoniacal.

Sp. gr. 0.9204.

Boils at about 210° of Fahrenheit: remains perfectly fluid at 32°.

Evaporated at a medium atmospheric temperature, it leaves

about one-sixth of its weight of the peculiar concrete substance, which will be described in the next section: by the assistance of heat, dissolves about one-third its own weight of that substance.

Readily catches fire upon the application of flame, and emits a very great quantity of smoke while burning.

By agitation mixes temporarily with water at the common temperature; from which however it soon separates like oil.

Slightly soluble in boiling water; but in cooling is deposited so as to give a milky appearance to the water, which remains perfectly transparent while at or near the boiling point.

Unites readily with alcohol and with ether at all temperatures.

By agitation with an aqueous solution of potash, or of ammonia, it communicates a slight wheyishness to those fluids; but soon separates from and floats on the top of them.

Absorbs several times its volume of ammoniacal gas, without any sensible change.

Absorbs also several times its volume of muriatic acid gas; becoming, in consequence, opaque and thick.

Forms a uniform white soapy curd with a solution of acetate of lead, by the intervention of an aqueous solution of potash or of ammonia; but, if simply mixed with the metallic solution, it soon separates without any sensible change.

Properties of the white concrete substance.

Taste, pungent and aromatic.

It is particularly characterized by its odour, which is faintly aromatic, and not unlike that of the narcissus and some other fragrant flowers. This odour is readily diffused through the surrounding atmosphere to the distance of several feet, and obstinately adheres for a long time to any substance to which it has been communicated.

When in its purest state, and reduced to powder, it is exceedingly smooth and slightly unctuous to the touch; is perfectly white, and of a silvery lustre.

Sp. gr. rather greater than that of water.

It does not very readily evaporate at the common atmospherical temperature: for, a comparison being made between this substance and camphor, in the quantity of half a grain of each in a very minute state of division, it was found that the camphor had entirely disappeared at the end of 18 hours, while the substance in question had not disappeared entirely at the end of 4 days.

A quantity of it being exposed to heat, in a glass vessel, soon melted; but did not begin to boil till the temperature had reached 410° of FAHRENHEIT: the heat being then withdrawn, it remained liquid till cooled down to 180; at which point the lowest portion was seen suddenly to congeal: the remaining portion congealed gradually; and when the whole had become solid, its temperature was 170°. The structure of the congealed mass was distinctly crystalline, and the crystalline laminæ were slightly flexible.

It is not very readily inflamed; but when inflamed it burns rapidly, and emits an unusually copious and dense smoke, which soon breaks into distinct particles that fall down in every direction.

Does not affect the colour either of litmus or of turmeric.

Insoluble in cold water; and very sparingly soluble in boiling water, from which it separates, in cooling, in such a manner as to render the water milky, which was before transparent: a portion however still remains dissolved, for the water, when filtered, possesses in a slight degree the taste and odour of the substance, and after a few hours deposits it in minute crystals.

Readily soluble in alcohol, and still more so in ether, at any temperature; the solubility, in either instance, greatly increased by increase of temperature.

A solution of this substance in four times its weight of boiling alcohol becomes, in cooling, a solid crystalline mass. It is precipitated from its solution in alcohol by water, without acquiring any additional weight.

It is soluble in olive oil, and in oil of turpentine.

It does not combine either with an aqueous solution of potash or ammonia; nor is it sensibly affected by contact with ammoniacal gas.

Soluble in acetic and in oxalic acid, to each of which it communicates a clear pink colour. A saturated hot acetic solution becomes a solid crystalline mass in cooling.

It blackens sulphuric acid when boiled in it; the addition of water to the mixture having no other effect than to dilute the colour: neither does any precipitation take place upon saturating the acid with ammonia.

Sparingly soluble in hot muriatic acid, to which it communicates a purplish pink colour.

When boiled in nitric acid, it both decomposes the acid, and is itself altered in its composition; and, in cooling, is

abundantly deposited in short acicular crystals aggregated in stelliform groups. These crystals pressed between folds of unsized paper, in order to separate the adhering acid, and then exposed to heat, are readily melted: in cooling, the melted mass shows evident traces of acicular crystallization, and the crystals are of a yellow colour. This yellow substance is readily inflamed, burns with a bright flame, emits much smoke, and leaves a considerable residuum of carbon.

Of all the characters of the white concrete substance described in this section, its ready disposition to crystallize is perhaps the most remarkable.

If thrown into a red hot crucible, a dense white vapour arises from it; which being received into a bell glass placed over the crucible, is condensed round the lower part of the glass in the form of a white powder; but in the upper and cooler part of the glass distinctly crystalline plates are formed, of a beautiful silvery lustre.

A similar and equally beautiful crystallization may be obtained by boiling this substance in water, in a glass matrass having a long neck; in the upper part of which crystals will be formed and deposited during the boiling.

If exposed to a degree of heat not more than sufficient to melt it under a bell glass, the vapour that rises from it crystallizes before it reaches the surface of the glass, and flies about the interior with exactly the appearance of a shower of minute particles of snow.

If a piece of cotton twine be coiled up like the wick of a candle, and after having been dipped in this substance while melted, be set on fire for a second or two, and then blown

out, the vapour will soon begin to crystallize round the wick in very distinct thin transparent laminæ.

This experiment affords one mark of distinction between this substance and benzoic acid, and also between it and camphor: for under similar circumstances, benzoic acid crystallizes in acicular crystals, which are often grouped in a stelliform manner; and camphor crystallizes, or is rather congealed, in globular particles having a stalagmitic appearance.

The most usual crystalline form of this substance is a rhombic plate, of which the greater angle appears to be from 100° to 105°: crystals at least of that form I have repeatedly obtained from its solutions in water, in alcohol, in acetic acid, in the yellow oil described in the last section; and lastly, by melting and very slowly cooling the substance itself. Sometimes several of these plates are variously grouped together; sometimes a single plate intersects another plate at nearly right angles, so that in some points of view the compound crystal appears simply cruciform. The only distinct modifications which I have observed of the common form are a rhomboidal plate, which is very nearly rectangular; and an hexagonal plate: the latter variety may be easily traced from the rhombic plate by the incomplete developement of the smaller angles of the usual rhomb.

The following process has been found most successful in illustrating the crystallization of this substance.

If 25 grains of it be dissolved by the assistance of heat in half a fluid ounce of alcohol, and the solution be cooled slowly in a glass matrass, it will begin to crystallize when

nearly cool; and the matrass being placed between the eye and a tolerably strong light, numerous transparent rhombic crystals will be visible; some of them reflecting from their whole surface a green colour; others, a blue; or a red; or some other of the prismatic colours.

With respect to the elementary constitution of this substance I am not enabled to give any satisfactory information; but it is evident that it contains a very great proportion of carbon. A small quantity of it was passed in the state of vapour through peroxide of copper heated to redness, and the only gaseous product was carbonic acid: whether any water were formed, I could not ascertain.

It cannot be irrelevant to the object of this paper to state, that the white concrete substance which I have been describing, has twice been observed by me in the form of minute crystals, which beautifully reflected the prismatic colours, in the neck of an earthen retort, in which animal matter had been submitted to destructive distillation.

Properties of the yellow farina.

From the minute quantity of this substance which I was capable of obtaining, I could only ascertain one or two of its properties. It is soluble in alcohol, and forms a solution of a bright yellow colour; and it is precipitable from the solution, by the addition of water, in the form of a yellow powder, which remains permanently suspended in the mixture.

When heated, it melts into a substance of the consistence of a soft tough gum of a deep reddish brown colour.

Of the four several substances which result from the distillation of the black liquid described in the former part of this paper, it is probable that the water and the yellow farina are the only real products, and that the others are mere educts of that distillation: for, with respect to the water, its proportion is variable according to the greater or less degree of rapidity with which the distillation is conducted; and if it were present as water in the black liquid, there is reason to believe it would be found supernatant on its surface, after having remained still for some time. The essential liquid oil, and the white concrete substance, which pass over during the distillation, are probably contained originally in that thin portion of the black liquid which may be filtered through unsized paper; for the odour of this filtered portion closely resembles that of the oil; and the oil, by exposure to light, frequently becomes of a darker and darker shade, so as at last to be nearly of a deep brown colour; and, with respect to the white concrete substance, this was not only found crystallized in that part of the original apparatus where the black liquid was condensed, but has been obtained from that liquid by simple evaporation of it at the common temperature of the atmosphere.

The yellow farina is probably produced from the tar which is contained in the proportion of about one-fourth in the black liquid; for it does not make its appearance till towards the end of the distillation; when the more volatile substances have ceased to pass over, and the heat has been increased to the utmost: and if common coal tar be exposed to a low red heat, it will be found, that when the tar has

been nearly evaporated, this yellow farina will begin to pass off.

It remains for me to propose a name for the white concrete substance which has been described in this paper: and, unless a more appropriate term should be suggested by others, I would propose to call it naphthaline.