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III. Microscopic Observations on the so-called Vesicular Vapours of Water, as existing in the Vapours of Steam, and in Clouds, &c. By A. WALLER, Esq., M.D. Communicated by P. M. ROGET, M.D., Sec. R.S.

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IN a paper published in the Philosophical Magazine, February 1846, respecting some molecular actions of crystalline particles, I endeavoured to explain the fixation of particles of mercury, and the consequent formation of images in the Daguerreotype process. My experiments led me at that time to the conclusion, that the vapours, or rather fumes of condensed steam, consist of minute globules or spherules of water, and not of small vesicles according to the theory universally received at present, and expressed by the term of vesicular vapour.

My opinion on this point was founded on the results obtained by microscopic inspection of the condensed vapours of mercury and of other bodies, at the same time I stated that I was unable in the case of water to confirm it by direct observation. Subsequently, however, I have succeeded in doing so, and propose to show from the following observations that the opinions entertained respecting vesicular particles of water are completely erroneous. But before I describe my own experiments, I think it proper to state some of the ideas of our predecessors in science on vapours of water, and likewise the grounds on which they supported them.

Sir ISAAC NEWTON, on various occasions in his Optics, mentions the particles composing clouds, fogs and mists, &c., so as to leave no doubt that he considered them to be composed of minute globules or spherules, as may be seen in the following passages :---- "Between the parts of opaque and coloured bodies, are many spaces either empty or replenished with mediums of other densities; as water between the tinging corpuscles wherewith any liquor is impregnated, air between the aqueous globules that constitute clouds and mists."-Prop. III. Book 2nd. "But when in order to compose drops of rain they begin to coalesce and constitute globules of all intermediate sizes, these globules, when they become of a convenient size to reflect some colours and transmit others, may constitute clouds of various colours according to their sizes. And I see not what can be rationally conceived in so transparent a substance as water for the production of these colours, besides the various sizes of its fluid and globular particles."-Prop. V. In noticing the coloured areola surrounding the sun and moon in certain circumstances, he does not fail, when giving the measurement of their diameters, to mention the way in which they may be applied in obtaining a knowledge of the relative diameters of the globules of water which give rise to them. M. KAEMTZ has obtained several interesting results in making use of this mode of observation, which has so long been neglected by meteorologists; by means of these rings he has ascertained that the average sizes of these particles vary in the different months of the year, and that in summer they are much smaller than in winter; the mean size he assigns to them is about  $0.0224^{\text{mm}}$ .

The opinion now entertained respecting these particles of water, consists in regarding them as composed of small bladders or vesicles, similar in all respects, but their size, to the common soap-bubble. This theory is generally ascribed to HALLEY. Neither NEWTON nor HALLEY appears to have taken any steps to submit their hypotheses to direct observation. This was first attempted by KRATZENSTEIN, whose experiments on this subject, dating from 1743, evince great ingenuity. The original work is very scarce in France, and not to be obtained in this country. But DE SAUSSURE, in his 'Traité sur l'Hygrométrie,' has cited them textually, from whence I extract the following. "M. KRATZENSTEIN qui s'est beaucoup occupé de ces vésicules et qui a même prétendu réduire à elle seules tous les genres de vapeurs, a tenté de les mésurer et les a comparés avec un cheveu, et il a même cru pouvoir assurer que leur diamètre était douze fois plus petit. Le cheveu avait suivant M. K.  $\frac{1}{300}$  de pouce et par conséquent ces vésicules une 3600 de la même mesure\*."

KRATZENSTEIN, after measuring the diameter of these supposed vesicular globules, attempted to determine the thickness of the pellicle which he believed to exist around them, and thus states his experiment in § 4 of his dissertation :---" J'ai pris un globe de verre qui avait cinq pouces de diamètre ; à son orifice était adapté un robinet. En soufflant dans le globe j'ai comprimé l'air qui y était contenu, puis ayant fermé le robinet j'ai exposé le globe aux rayons du soleil dans la chambre obscure; mais je n'ai pu appercevoir aucune des vapeurs que j'avais fait entrer en y soufflant. Ayant ouvert le robinet pour faire sortir l'air comprimé, j'ai vu d'abord une grande quantité de vapeurs qui tombaient ; mais elles ont encore disparu lorsque j'ai comprimé de nouveau l'air qui était dans le globe. Regardant de manière que mon œil fit avec le rayon du soleil un angle entre 5 et 10 degrés, j'ai apperçu avec un grand plaisir une suite de très belles couleurs qui se changaient peu à peu en d'autres à mesure que l'air comprimé sortait de la boule. Voici la suite de couleurs telle que je l'ai remarquée, rouge, verd, bleuâtre, rouge, verd. Ayant mis mon œil entre le soleil et les vapeurs et les avant regardé sous les mêmes angles que je viens de dire, j'ai apperçu les mêmes couleurs que donnaient la réflexion, mais elles étaient dans un ordre inverse." KRATZENSTEIN supposes that these colours arose from the expansion of the vesicles which caused their parietes to become thinner, and to assume colours in the same way as the soap-bubble; he calculated their thicknesses accordingly, which on an average he found to be about 0.06mm. DE SAUSSURE, in quoting this experiment, states that it never succeeded in his hands, for the colours were simul-

<sup>\*</sup> Théorie de l'élevation des vapeurs et des exhalaisons démontré mathématiquement, par M. GOTTLIEB KRATZENSTEIN. Bordeaux, 1743.

taneous and not successive, as is required. These appearances are easily explained in the present state of science, which could not be done in the time of KRATZENSTEIN. The condensation of the vapours of water is caused by the sudden demand for caloric by the rarefied air in the glass globe, and the same takes place in the receiver of the pneumatic machine when there is a commencement of a vacuum. As the gas within recovers its caloric from surrounding bodies, the globular vapours and the moisture deposited on the inner surface of the glass recover their elastic condition. With regard to the colours observed, they are owing to the *diffraction of light* by the particles in suspension, and more particularly by those parts condensed on the sides of the glass, as in some of FRAUNHOFER'S experiments. Therefore it is in no manner possible to connect these colours either with the thickness of the vesicles, or with the vesicular theory.

I have related these experiments thus fully, because I find that even at the present day, they still pass current with observers of a deservedly high reputation. Thus they are reproduced in KAEMTZ'S Treatise on Meteorology, perhaps the most profound work on the science, and now rendered popular in this country by Mr. WALKER'S translation of his Manual.

DE SAUSSURE, on examining with a lens of an inch focus the steam of water floating over a dark surface, in speaking of the vesicles, says, "La légéreté de ces petites sphères, leur blancheur, leur apparence absolument différente de celles des globules solides, leur parfaite ressemblance avec les bulles volumineuses que l'on voit nager à la surface du liquide ne laissent aucun doute sur leur nature ; il suffit de les voir pour être convaincu que ce sont des sphères creuses, semblable à la grosseur près à celles que l'on forme avec l'eau de savon." He further states that he confirmed these ideas by the examination of fogs or clouds on high mountains, when he was enabled to perceive in the same way minute vesicles, sometimes accompanied with drops or globules of water. He estimates the smallest at  $\frac{1}{4500}$ th of an inch, and the largest at  $\frac{1}{2780}$ th. When these vesicles came in contact, they burst and formed a small drop of water. These experiments have been adopted and reproduced by most modern authors, among whom may be mentioned BERZELIUS, FRESNEL, MITSCHER-LICH, &c.

As I have already stated in the Philosophical Magazine, I had an opportunity of repeating DE SAUSSURE's observations on the clouds, at the Monastery of St. Bernard. I will quote the passage: "Globules of various sizes are frequently discerned by the naked eye floating in all directions. I have endeavoured to ascertain their vesicular structure, but have been unable to do so from direct observations. It is frequently a most difficult point in microscopic investigation to decide upon the existence of a thin transparent membrane. It is still more so to pronounce upon the vesicular or spherular structure of globules in constant agitation; and I believe that if minute spherules and vesicles could be mixed together, we do not possess any means at present of distinguishing them. I have never been able to detect that appearance

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of bursting of the globules mentioned by DE SAUSSURE, but sometimes when the agitation of the air is slight, two of the larger globules may be seen floating towards each other, and afterwards disappear suddenly, which may be explained, if we admit that it is caused by the union of the two spherules into one, which is too heavy to remain any longer in suspension, and whose rapid deposition conceals it from the sight." From the commencement of my experiments, I found that the greatest obstacle to a perfect investigation of these globules arose from their excessive mobility. Even to the naked eye this is very great, and is the cause of several optical delusions; but by the use of magnifying instruments, this mobility must necessarily be increased in proportion to their power. With the simple microscope of DE SAUS-SURE, a globule might occasionally be perceived, and its diameter estimated to a certain extent; but with the compound achromatic microscope I employ, their angular displacement is too rapid to form any correct sensation on the retina. For this reason I was led to adopt the plan of fixing the condensed vapours arising from the breath or other sources, in some liquid which, like oil, possesses no affinity for water. The liquids with which I thus mixed the vapours of water were very numerous; and as the appearances thus presented under the microscope were not the same in all cases, I will only mention some of the most interesting.

Canada balsam is, perhaps, of all other vehicles, the most adapted for these observations. A slip of glass covered with a thin layer of it is to be used. By breathing on it with a little force, the vapours of the breath will not only be condensed on its surface, but will penetrate below, where they may be easily recognized in opake streaks of a white colour. By reason of the viscousness of the balsam, they will remain almost stationary for more than an hour, and for a much longer period if covered with another thin piece of glass or talc. Under the microscope these streaks are decomposed into minute globules perfectly spherular like shot, or the globules of mercurv. See Plate II. fig. 1.bb. Their sizes vary within certain limits, between which they occur, of all intermediate sizes. They agglomerate together in various ways, forming lines composed of several rows of them touching each other, but without any signs of coalescing, unless attentively examined for some time, when two smaller ones may be perceived to disappear, and in their place is seen another of larger size resulting from their fusion. A certain degree of attraction exists between them, as they are generally packed together as closely as possible, and any hiatus caused by any of them coalescing is quickly filled by others. Thus a group will sometimes have its form modified and reduced by their pressing inwards to supply any hiatus left after one or two have coalesced. Another proof of their mutual attraction is offered in the movement en masse of a single file of globules without their separating from each In favourable circumstances, I have found some of them still in "statu quo" other. after a lapse of twenty-four hours or more. Their diameters vary generally from 0.001<sup>mm</sup> to 0.003<sup>mm</sup>. They disappear at length by adhering to and wetting the surface of the glass above or below them, where they may easily escape notice, as from



their flattened surfaces they possess but little power to deviate the light from its regular course. Their shape is very irregular, generally of an angular, and frequently of an hexagonal form. See fig. 1. *aa*. That part condensed on the surface of the balsam presents exceedingly minute globules of the same nature.

Instead of condensing the breath as above, I have placed the slip of glass covered with balsam in the open air, on grass covered with hoar-frost, and after it had become slightly turbid on its surface from the moisture deposited, I submitted it to the microscope. It was then seen to be covered with lines of single globules like strung beads, following the most tortuous courses; and wherever the balsam had been disturbed by the passage of any body through it even for a long time previous to the exposure, the direction of these lines showed the manner in which it had been disturbed. The diameters of some of these globules appeared as mere points under the strongest magnifying power, and were probably less than  $0.0001^{\text{mm}}$ . As the glass became warm the globules coalesced at intermediate points into a single one, which soon vanished in its turn. When steam from boiling water in a glass tube was condensed in Canada balsam, the globules which are represented in fig. 2 are much more voluminous, varying from  $0.01^{\text{mm}}$  to  $0.015^{\text{mm}}$ , though in other respects they were exactly the same. The globules arising from water at  $60^{\circ}$  REAUMUR are the same size as those of the breath.

No doubt can possibly be entertained, after having inspected these globules attentively, of their being perfect spherules of liquid without any central part whatever, for containing a gasiform fluid, which could not escape detection when they coalesce and adhere to the glass. Globules of gas, of whatever nature, cannot possibly be confounded with one of these liquid globules, from their being much darker, and the smallest of them considerably larger than those of water, independently of their remaining permanent when inclosed between two surfaces of glass. In Canada balsam they present, on a very minute scale, the exact representation of external objects which surround the microscope, which, however, is seen on liquid globules when they are sufficiently large. Thus, in looking through the microscope, I have seen at the lower part of one of these air-globules portions of my own face or body; and in the same way an extensive view of trees, houses, &c. may be traced with all its details on one of these microscopic globules not larger than 0.01mm or 0.02mm. Fig. 3 represents the image of part of the hand, as seen in a globule of air, drawn under the camera lucida. I mention this fact, as I believe that the telescopic action of the microscope, by means of these hollow prisms, may be capable of several interesting applications.

By breathing gently on the surface of Canada balsam, it will become covered with a film of moisture, reflecting various colours in proportion to the quantity deposited. Any bright object viewed through it will appear surrounded by a halo of brilliant colours, such as those seen sometimes encircling the sun or moon. These coloured films, under the microscope, are decomposed into colourless particles of water, which are all of the same form, although an irregular one, not completely circular. If a surface of balsam be placed aside for a short time and afterwards examined, we find that these particles, which before were disposed in a regular manner, appear to have altered their position, and that they have grouped themselves in radiating lines towards a variety of points. See fig. 4.

Particles of water may be examined in a solid and crystalline state. A slip of glass or a small glass tray, coated with Canada balsam on its under surface, and a freezing mixture at the upper, will gradually condense the moisture from the air, and the balsam will become covered with the well-known spongy deposit of frozen par-The manner in which the crystallization takes place is remarkable. At first ticles. the moisture condensed is liquid and globular in form, but as the refrigeration continues a sudden molecular change occurs, and the globules are found to assume various crystalline shapes. When they are small and numerous, on consolidating, they form a kind of areolar net-work, the appearance of which is caused by the reflexion of numerous crystalline facets (see fig. 7); at other places may be seen small pyramidal crystals covering a solid globular nucleus like the head of a mace; sometimes they assume the form of small aciculæ, of hexagonal prisms with various secondary facets, of octohedrons, &c. At the moment when this molecular action takes place, I have sometimes perceived with the microscope a kind of flitting movement, as the globules are assuming their various shapes, like that which occurs in the crystallization of particles from a state of solution\*.

The globules which compose mists or fogs may be condensed by exposing a slip of glass coated with balsam in the open air, but as the deposition takes place very slowly, it is preferable to employ the rotatory bellows, so placed as to throw the current of air at an angle of about  $60^{\circ}$  on the plate. Steam or other volatile substances may be condensed in the same manner. When the current is created by the common bellows, I have found it much more difficult to fix the globules. Those obtained by this process are exactly similar to those of steam. In my experiments they were between  $0.02^{\text{mm}}$  and  $0.03^{\text{mm}}$  in size.

Essence of turpentine may be used in the same manner as Canada balsam. The globules condensed in this manifest much greater mobility, as might be expected from the nature of the liquid, frequently rebounding from each other as they come in contact. They disappear very rapidly, either by adhering to the glass, or by coalescing together. I have observed them moving in vortices around several central points where they rapidly collapsed. Their diameters vary between the

<sup>\*</sup> The most favourable season for performing these experiments is the winter. In summer, when the air is warm and loaded with moisture, the particles on condensing, form liquid or solid globules, or very confused crystals, and whenever the freezing mixture is moved aside, so as to expose a portion of the under surface to microscopic inspection, a very few moments suffice for the particles to liquefy. Solid globules may be distinguished from liquid ones by their borders being much darker, and from their frequently containing smaller globules, as in fig. 8.

0.001<sup>mm</sup> and the 0.003<sup>mm</sup>. Essence of turpentine is still better adapted than the balsam for retaining the globules suspended in the air, as in fogs, &c. When, after having been cooled below the common temperature, it is breathed upon, a whitish precipitate of a streaky appearance is formed like an insoluble salt, which slowly descends to the bottom of the vessel, where it coalesces into larger globules\*. This is also the case with water-globules condensed in this way from the air, which form a cloudy precipitate intercepting the passage of light. On being preserved in a bottle this cloud will still remain after the lapse of a couple of days, when the water will be found at the bottom of the vessel in a globular shape like metallic mercury, without adhering to the sides of the glass. By means of this permanent cloud, we might be enabled to perform a series of experiments of great interest to meteorology. In this way we might determine the influence of water-globules of various sizes in the passage of luminous, thermic, and chemical rays.

Copaiva balsam, upon being breathed upon, becomes coated with a milky film, which, to the naked eye, assumes a reticulated appearance after a few moments, which is caused by the disappearance of the film sooner at some points than at others. Under the microscope the uniform film is decomposed into minute globules, which occupy the space of mere points under the strongest magnifying power. They disappear very rapidly by agglomerating and forming larger globules. This process of agglomeration commences simultaneously on the surface of the liquid at a variety of different points. From these it proceeds to form circular areas, which continue to extend until their line of demarcation consists of merely a single row of globules, which also in their turn contract and coalesce into small groups of about a dozen separate spherules. At this time the process of fusion ceases, and the globules are seen suddenly to fly apart in virtue of some molecular repulsion, and then gradually disappear. With boiling water the like phenomena are produced, except that the globules are all much larger. In fig. 5 are seen these actions in all their different stages.

Oil of peppermint condenses moisture which presents phenomena very similar to those of copaiva balsam. If the breath be passed through a narrow tube, a system of rays is produced, composed of separate globules, which remind one of the form of some of the species of Asterias which radiate from a centre, and are likewise composed of a multitude of separate globular pieces. The irisated colours formed on this oil are very brilliant, but soon disappear unless the current of air is constantly kept up. The particles of water which give rise to these colours, disappear by immersion into the oil, as well as with all the other oils which are susceptible of presenting them. The oils of anethum, carraway and cajeput, also present very similar appearances.

\* A bottle containing condensed water-globules and essence of turpentine, exposed night and day in a northern aspect, became coated at its inner surface on the north side with condensed moisture, and around this with transparent acicular crystals arranged in zones around the moisture. The crystals were not obtained in sufficient quantity to admit of their being analysed. Creosote condenses the breath, which agglomerates into globules apparent to the naked eye and long remains unaltered.

Olive oil.—The globules are very minute and agglomerate slowly. The surface assumes a lacerated appearance, and the molecular dispersion appears simultaneously over the entire field of vision. Croton oil condenses a film reflecting the various spectral colours.

Castor oil.—The condensed particles of water present the same appearance to the naked eye, or when assisted by the microscope, as the two preceding. If, before the globules have disappeared, they are covered over with another slip of glass having a film of oil previously placed on it, they are retained for a much longer period than if the surface of the glass had been perfectly dry. Almost all of them are adherent together, as in fig. 6, but without agglomerating into one. In some instances a larger globule, like a central nucleus, is seen covered with others adhering to it. Their appearance reminds one strongly of the manner in which the condensed vapours of sulphur are found adhering together.

Another means of subjecting particles of water to microscopic observation, consists in fixing them upon minute filaments, such as those of the spider's web. I have found it most convenient to employ the filaments which contain the ova of the spider, or those of the cocoon of the silk-worm. Thin bundles of either of these exposed to steam from boiling water, were found after a few moments to have very minute globules condensed upon them, mostly imperceptible to the naked eye, about the same size as those obtained in Canada balsam from boiling water. These particles of water were all liquid globules without any signs of vesicular structure. In foggy weather the filaments of the spider's web generally become covered with small globules of water, which in some cases are so minute as to give the filament a grey whitish aspect, like globules floating in the air, or in spirit of turpentine. These filaments, fixed between two small frames pressed close together, may be examined under the microscope. They are then seen covered with globules of water, and with others of an organic nature secreted by the spider. The former may readily be distinguished, by their quick evaporation, from the others which are permanent. The globules of water were about 0.02<sup>mm</sup>.

We may therefore conclude from the foregoing observations, that the term vesicular structure of globules, which was first proposed at a time when the knowledge of gaseous bodies was still in its infancy, has been adopted without sufficient foundation; that the experiments on which it was grounded were unsatisfactory and imperfect; and that whenever we are enabled to inspect the minutest particles of water arising from condensed steam or vapour, they consist of minute liquid globules without any appearance of internal cavity.

Kensington, April 12th, 1846.