XXXIII.—*On the Action of the Dry Gases on Organic Colouring Matters, and its relation to the Theory of Bleaching.* By GEORGE WILSON, M.D., Lecturer on Chemistry, Edinburgh.

(Read, April 17, 1848.)

I. *Preliminary Remarks.*

The remarkable power which chlorine possesses, of destroying all colours of organic origin, has long been an object alike of speculative and practical interest. The theory of bleaching, however, has hitherto remained imperfect, in consequence chiefly of the observation of Sir H. DAVY, that chlorine loses the power of decolorising when deprived of water. So striking is the difference, in this respect, between wet and dry chlorine, that it led the distinguished chemist mentioned, to deny to this gas the character of being essentially, or *per se*, a bleacher. He regarded as the true decolorising agent the oxygen of the water, which must be associated with chlorine before the latter can bleach. The late Dr TURNER has stated DAVY's view so shortly and clearly, that I quote his abstract in preference to any statement of my own. "DAVY," says he, "proved that chlorine cannot bleach, unless water is present. Thus dry litmus suffers no change in dry chlorine; when water is admitted the colour speedily disappears. It is well known also, that hydrochloric acid is always generated when chlorine bleaches. From these facts, it is inferred that water is decomposed during the process; that its hydrogen unites with the chlorine, and that decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of binoxide of hydrogen, and of chromic and permanganic acids, of which oxygen is certainly the decolorising principle, leaves little doubt of the accuracy of the foregoing explanation."*

The opinions of chemists on this point have now entirely changed. Chlorine is reinstated in the place it formerly held as the possessor of positive and intrinsic bleaching powers, and is looked upon as exerting these even when water is present. I quote Sir ROBERT KANE's views on this subject, as more fully expressed than the statements of most of our chemical authorities, and because he has demonstrated experimentally the falsity of DAVY's conclusion. "The theory," says he, in allusion to bleaching, "of this action of chlorine, which had been formerly thought to depend upon a mere oxidation of the colouring matter, water being decomposed, has been shewn by my results with orceine, and confirmed by those of ERDMAN on indigo, to consist in the formation of new substances con-

* Elements of Chemistry, 7th edit., p. 275.

taining chlorine. The chlorine in some cases replaces hydrogen ; in others, it combines directly with the colouring matter ; in others, again, water is decomposed, and the product, besides containing chlorine, is also more highly oxidised.”*

Beautiful, however, and satisfactory as the investigations of KANE, ERDMAN, DUMAS, LAURENT, and others are, they leave unconsidered the question, why has chlorine, which so rapidly and permanently destroys the colour of organic compounds when moist, no action on them when dry ?

The object of the researches I am about to detail, is to supply, in part at least, this defect in the theory of bleaching, by endeavouring to shew how the removal of water from chlorine arrests or suspends its decolorising power. Before entering at length into this question, however, I would observe, that DAVY’s conclusion, that oxygen is the efficacious bleaching constituent of moist chlorine, cannot be regarded as marked by the felicity which generally characterised that great chemist’s interpretations of obscure or complicated phenomena.

1. His view assumed, against all probability, that the acknowledged great affinity of chlorine for hydrogen would be exerted solely towards the hydrogen of water, but not towards that present in a colouring matter ; or at all events, that the affinity in question would be efficacious only in relation to the elements of water. We certainly must set aside, as entirely arbitrary, the notion, if that were implied in DAVY’s statement, that chlorine in the presence of two bodies—water and a colouring matter—each containing hydrogen, would be indifferent to that element, as a constituent of the one, but eager to unite with it as present in the other. Although free chlorine, however, must be regarded as equally ready to unite with the hydrogen of every compound which comes within the sphere of its affinity, it does not follow that it will obtain that element with equal ease from every substance containing it. On the other hand, we may be certain, that those more unstable compounds which part most readily with their elements, will be the first to have the hydrogen removed from them by chlorine, whilst less easily decomposed substances may resist its action altogether. DAVY’s view, however, gains nothing from this acknowledgment ; for it represents water, an enduring compound of but single equivalents of two elements, as compelled to abandon its hydrogen to chlorine, whilst the proverbially fading colouring principle of a flower or an insect—a frail combination of many equivalents of three or more elements—is assumed to be able to retain its hydrogen unaffected by chlorine. In the justice of such a conclusion, no chemist could concur.

2. Again, DAVY’s argument proved too much, and was in truth, self-destructive ; for if chlorine be denied the character of a positive bleaching agent, because it does not bleach when dry, then oxygen, judged by the same rule, must

* Elements of Chemistry, p. 1054.

be refused that character also, for when the latter gas is deprived of moisture, it is more indifferent to colouring matter than even chlorine. DAVY'S reasoning, then, if pushed to its logical consequences, conducts us to the strange conclusion that since, when moist chlorine bleaches, the chlorine and oxygen are not the active agents, and the only other body present except the colouring matter is hydrogen, which certainly does not decolorise when dry, bleaching must be regarded as an inexplicable phenomenon, an effect without a cause.

It would not be difficult to point out other objections to the consistency of DAVY'S opinion; but those given may suffice to prove that, before the analysis of the products of chlorine-bleaching shewed the erroneousness of his conclusion, its inherent untenableness admitted of easy illustration.

II. *Influence of Sunlight on the Bleaching Action of Dry Chlorine.*

The chief object of the experiments which this paper details was, to ascertain the cause of the indifference of chlorine when free from moisture to anhydrous organic colouring matters. But before entering on this inquiry, it occurred to me to doubt, whether DAVY'S original proposition, that dry chlorine does not bleach dry colours (which seems to have been universally assented to by his successors), could be admitted without limitation.

A repetition of his experiments appears, at first sight, to justify unconditionally his conclusion. Among the specimens which accompany this communication are two sealed tubes, containing blue and red litmus-paper shut up in an atmosphere of chlorine. The paper was first dried in a current of air previously passed through chloride of calcium. A stream of carefully desiccated chlorine was then sent over the paper for five minutes, and the tube, whilst full of gas, sealed at the blow-pipe. The coloured papers were thus exposed, in the first place, to the bleaching action of some sixty cubic inches of chlorine; and have, in addition, remained in contact with that gas since the 28th of July 1847, a period of more than eight months, yet they still retain their original tints, though somewhat faded. Had water been present in these experiments, the colours would have been irrecoverably destroyed in a few seconds, or minutes at the farthest.

Striking as these results are in supplying confirmation of DAVY'S views, they are curiously contradicted, or rather qualified, by other experiments, differing from those just mentioned, as to mode of trial, only in one particular.

The affinity of chlorine for hydrogen, when both gases are free, is greatly modified by the action of sunlight, so that whilst in perfect darkness they may be kept mingled without combining, they unite with explosion if exposed to the direct rays of the sun, and more or less rapidly in diffuse daylight, according to its intensity. So faithfully, indeed, do free chlorine and hydrogen obey what natural

philosophers and chemists have agreed to call the actinic influence of the sun-beam, that the mixed gases contained in a graduated tube over water are found to form a delicate actinometer, the intensity of the actinism being measured by the rapidity with which the water rises in the tube, as it dissolves the hydrochloric acid produced by the union of the gases.* This actinic exaltation of affinity, so striking when both gases are free, continues to manifest itself, though less powerfully, when chlorine is in contact with substances containing hydrogen, although the latter is in a state of combination.

Chlorine water remains unchanged in the dark, but is rapidly converted by sunlight into hydrochloric acid, and free oxygen. Dutch liquid, chloroform, and chloric ether, besides various other bodies, are known to give up their hydrogen to chlorine much more swiftly when exposed to the direct rays of the sun than if shaded from them. It seemed in the highest degree probable that the hydrogen of organic colouring matters would, in like manner, resist the action of dry chlorine for a much shorter period in sunlight than in diffuse daylight, or in darkness. To determine this point, the following experiment was tried. A wide glass-tube, open at both ends, was constricted in the middle so as to present a narrow central canal, like that of an hour-glass. Pieces of blue and of red litmus-paper were then placed on either side of the constricted portion, and the open ends of the tube drawn out at the blow-pipe, so as to admit of their being put in communication, by means of caoutchouc connectors, with an arrangement for drying the paper, and furnishing chlorine. After the paper had been exposed to a current of dried air at the temperature of 220° Fahr. for three hours, washed chlorine, transmitted through Nordhausen sulphuric acid, and a tube three feet long containing fused chloride of calcium, was sent along the double tube containing the papers, for five minutes. The ends of the tube were then sealed whilst it remained full of gas, and the constricted middle portion closed and divided at the blow-pipe, so that the double tube was converted into two single hermetically sealed ones, each containing dried litmus-paper in an atmosphere of chlorine. In this way two tubes were procured, each containing portions of the same coloured paper, which had been dried in the same current of air, and exposed in exactly similar circumstances to the same stream and the same amount of dry chlorine.

The one of these twin tubes was hung up inside a window, with a western exposure, on or about the 31st of July 1847. The other was laid aside in a cupboard, out of reach of the direct rays of the sun, but not protected from the influence of dull daylight. It was frequently brought out, moreover, to be examined, and was at no time during the day in absolute darkness. I shew the Society this tube after remaining in the circumstances described for more than eight

* Lond. and Edin. Phil. Mag., 1844, vol. xxv., pp. 2-3.

months. The inclosed papers still retain their original colours little altered; and in perfect darkness would, in all probability, have retained them still better. Side by side with this tube I have placed its twin, which was exposed to full sunshine, and the papers in which are bleached to the purest white. In how short a time his change occurred I cannot precisely say, as absence from town between the 1st of August and the 16th of September 1847 prevented me from watching the progress of the actinic bleaching. But, on the last-mentioned date, I found the paper completely decolorised, so that six weeks of sunshine sufficed totally to bleach paper in dry chlorine, whilst that gas excluded from direct sunlight has failed to produce the same effect in eight months and a half.* In another quite similar experiment, the results were much less striking. A tube with dry chlorine and litmus-paper has hung since 1st August 1847 in a western exposure, yet, at the date of my writing, (April 13, 1848), the litmus-paper, though much faded, as appears when it is contrasted with the contents of the twin tube which was kept out of sunshine, is far from being entirely bleached. This difference in result leads to the suspicion, that in the experiment first recorded, the chlorine or the paper may not have been so dry as both were in the second trial. Great precautions (the same in both cases) were taken to secure absence of moisture from the gas and the paper, but I know of no test of perfect dryness applicable to gases, and I cannot affirm that, in either case, the chlorine or the colouring matter was absolutely anhydrous. Nor does it admit of doubt that the presence of even a trace of water would sensibly quicken bleaching under sunlight, which rapidly decomposes chlorine-water. Yet every chemist will acknowledge that chlorine, which could be retained over litmus without bleaching it for nearly nine months, must have made a close approximation to perfect dryness. We are as yet, moreover, too ignorant of the laws and conditions of actinic action, to know well how to dispose of apparent discrepancies in its effects.

I could not try more than the two experiments recorded, last summer, and I did not think it desirable to attempt a repetition of them during the clouded season of the year. Meanwhile, different as is the testimony these experiments afford, as to the rapidity of actinic chlorine-bleaching, they agree in proving that darkness, as well as dryness, is essential to the preservation of organic colours from destruction by chlorine, and that this gas, at least when assisted by sunlight, is a positive bleacher. DAVY's original proposition must be accepted with this qualification.

I close my remarks on this subject, with the observation, that in bleaching on the large scale it should make a sensible difference on the rapidity of the process, whether it be carried on in open sunlight, or in exclusion from it. Our present bleaching process is as rapid as could well be wished, so that it is not in the direc-

* The papers shut up with chlorine, and kept in darkness, have not become bleached by two months' longer retention in the gas June 19, 1848

tion of quickening his methods, that the practical bleacher probably desires improvement. One may expect, however, that the same amount of chlorine, especially if moist, should be more efficacious in bleaching, if assisted by sunlight, than if debarred from it; or what comes to the same thing, that a small amount of chlorine should, in practice on the great scale, bleach as powerfully in sunshine, as a larger one in darkness. It might be possible, accordingly, to economise chlorine, or chloride of lime, in this country, in the brighter seasons of the year, and at all times in sunny climates, if the bleaching operations were carried on in the open air.

III. *Influence of Water over the Bleaching Action of Oxygen, Sulphurous Acid, and Sulphuretted Hydrogen.*

The fact that actinised chlorine bleaches, though dry, supplies no explanation of the function which water performs, when it invests that gas with decolorising power. With a view to solve this problem, I made two series of experiments; 1st, The object of the one was to observe to what extent other bleaching gases resemble chlorine in being dependent for bleaching power on the presence of water, and likewise to ascertain whether the acid gases and the volatile alkali, when made anhydrous, lose that power of changing the tints of dry organic colouring matters, which characterises them when moist. These experiments promised to shew whether the action of dry chlorine on colours is exceptional and anomalous, so as to demand a special explanation, such as DAVY gave, or but a particular case of a general law, to which all elastic fluids are obedient.

2d, The object of the other set of trials was to determine, whether bleaching power can be conferred upon dry chlorine, by dissolving it and anhydrous colouring matters in liquids containing no oxygen. I begin with the experiments first referred to.

Five gases besides chlorine have marked bleaching powers when in the condition of perfect elastic fluidity, and not anhydrous, viz., chlorous acid, hypochlorous acid, sulphurous acid, sulphuretted hydrogen, and oxygen.* To these may be added provisionally, the curious body *ozone*, which BERZELIUS regards as an allotropic form of oxygen, and SCHOENBEIN as a volatile peroxide of hydrogen. I have made no experiments with this substance, because, in the present state of our knowledge concerning it, it could not supply crucial results. Chlorous acid is too explosive to admit of satisfactory researches being made with it. The same remark applies with limitation to hypochlorous acid, a substance so interesting, from its high bleaching power, and its containing, like chlorous acid, the two most important bleaching agents, chlorine and oxygen. I have made no experiments with this substance, but PELOUZE has quite recently supplied us with a new and much

* I omit from this list hydrogen, because, although it bleaches powerfully in the nascent state, it has no sensible bleaching action, whether moist or dry, after it has attained the condition of perfect gasity.

more manageable process for preparing it, by means of which we may hope to make researches as to its action on colours.* My experiments have been limited to sulphurous acid, sulphuretted hydrogen, and oxygen. I begin with the last as the chief rival in bleaching power of chlorine.

Oxygen.

I have not thought it necessary to make many experiments with oxygen, as to its relative bleaching power when moist and dry. Test papers can be preserved for years, without sensibly changing tint in air, *i. e.*, diluted oxygen, only moderately dry, especially if free exposure to light be avoided. The general experience of mankind has led to the same conclusion, in reference to the comparative permanence of tint, of dyed tissues kept in the shade. I have exposed coloured papers for four and five hours to a current of dry air, without permanently altering their hue. The paper in such trials always exhibits a duller tint at the end than at the beginning of the experiment; but that this is the result merely of its loss of water, is evident from the fact that, on moistening the paper, the original brightness of tint is restored. No one, probably, will dispute the conclusion, that dry oxygen does not, at least in darkness, bleach more than dry chlorine.

The effect, on the other hand, of the addition of water to oxygen in increasing its decolorising power, is so strikingly demonstrated by the practical experience of the domestic bleacher, that experiments on the small scale did not seem necessary to prove the fact. No point is more attended to, in the familiar practice of bleaching cloth by free exposure to rain, wind, and sun, than the constant keeping of the tissue wet. I am far from affirming that other important agencies, such as the actinic, concerned in the bleaching, are not affected by the presence of water; yet I think no one will doubt, that one important function it serves, is the increasing (I do not at present say how) the bleaching action of the oxygen of the atmosphere.

The unquestionable decolorising power of peroxide of hydrogen, chromic, and permanganic acids, to which Dr TURNER refers as confirming DAVY'S view regarding the bleaching action of moist chlorine, only demonstrates that *nascent* oxygen bleaches, and is of no service in proving that that gas, when in its state of perfect elastic fluidity, possesses bleaching powers. The nascent hydrogen of decomposing water bleaches readily; so that, if Dr TURNER'S view were accepted as valid in relation to oxygen, a theory of chlorine-bleaching might, with some plausibility, be defended, in which hydrogen, instead of, or as well as, oxygen, should be represented as the positive bleaching agent in chlorine-water.

* It would be peculiarly interesting to observe the effect of drying this gas in modifying its action on colouring matters. Should it lose its bleaching power when dry, it would be curious to watch the effect of exploding it in the presence of an anhydrous colouring matter. The result would shew whether *nascent* oxygen and chlorine bleach as powerfully when *dry* as moist.

Sulphurous Acid.

The bleaching power of moist sulphurous acid is so well known, and has so long been turned to account in the arts, that I need enter into no details in proof of the gas possessing this property. With a view to determine whether it loses its bleaching power when made anhydrous, I passed washed sulphurous acid, obtained by the action of mercury on oil of vitriol, through strong sulphuric acid, and over chloride of calcium, so as to deprive it of moisture. The gas was then made to stream for five minutes through a tube containing blue litmus-paper, carefully dried, and the tube hermetically sealed while full of the gas. This experiment was made on March 31, 1848. The paper was not altered in tint during the passage of the gas, and at the present date (April 17) it remains unchanged.* I made a similar experiment on the 10th of July 1847, only the sulphurous acid, being obtained by the action of charcoal on oil of vitriol, was mingled with carbonic acid. The mixed gases were passed dry over blue litmus-paper for seven minutes, but did not change its tint in the slightest; the tube was then sealed, and is included among the specimens laid before the Society. After the lapse of nearly nine months, the paper continues not appreciably altered. Gaseous sulphurous acid, then, is no better bleacher when dry than chlorine.

Sulphuretted Hydrogen.

The other remarkable properties of sulphuretted hydrogen have prevented its bleaching power from attracting very much attention; nevertheless, it has long been recognised. Nascent sulphuretted hydrogen bleaches powerfully. An acidulated infusion of litmus has its colour rapidly destroyed by the addition to it of a metallic sulphuret, such as that of calcium, barium, or iron. The free gas bleaches much less distinctly, yet its action is tolerably rapid. In proof of this, I have sent with this communication a tube, which, after the blue litmus-paper contained in it had been dried, was opened for a few seconds to the atmosphere, in consequence of a derangement of the apparatus. The paper was thus exposed for a very short period to the amount of vapour which is diffused through air at the temperature of about 60° F. Immediately after this accident, carefully-dried sulphuretted hydrogen was passed over the litmus for five minutes, and the tube sealed. The paper was distinctly, though faintly, reddened during the passage of the gas, and after the lapse of about twenty hours the colour was found almost completely gone. In contrast with this result obtained with slightly moist sulphuretted hydrogen, I shew the Society a tube containing dry blue litmus-paper, and brown-red rhubarb paper, which were exposed to the action of equally dry sulphuretted hydrogen for six minutes. The papers were not altered in tint.

* The colours are still unaltered; a remark which applies also to the experiment next recorded, June 19, 1848.

They have remained sealed up in the tube, in an atmosphere of the gas in question, since July 9, 1847, when the experiment was made. No decided change was observed in the tints of the papers up to July 30, when I ceased to make notes of their appearance. The rhubarb paper is now little altered, but the blue has, here and there, a few small red spots, some with white borders upon them. Both tints, however, are still, after so many months' exposure to the gas, very slightly affected.* I shew the Society also tubes containing blue paper, which were exposed for five minutes to dry sulphuretted hydrogen on the 25th March 1848, and have since remained shut up in the gas. They exhibit, at the present date (April 17), no sensible change in tint.† Sulphuretted hydrogen, then, has its bleaching power arrested by depriving it of water.

IV. *Action of the Acid Gases and of Ammonia on Organic Colours.*

I pass now to the acid gases and ammonia, which so characteristically alter the tints of organic colouring matters, when water is present. The gases I tried were, sulphurous acid, carbonic acid, sulphuretted hydrogen, and hydrochloric acid, in addition to the volatile alkali.

Sulphurous Acid.

I need not say anything further concerning sulphurous acid, as it is implied in what was stated as to its negative action on vegetable blues, that its reddening action is as much arrested as its bleaching one by depriving it of water. Dry sulphurous acid, I also find, does not change alkalised turmeric or rhubarb paper to yellow.

Carbonic Acid.

I have already referred to the retention of its full blue tint, by dry litmus-paper, exposed for many months to a mixture of anhydrous carbonic and sul-

* The papers have not sensibly altered after the lapse of two additional months; nor is there any change in the litmus-paper referred to in the next experiment, June 19, 1848.

† One of the arguments in favour of the "Binary Theory of Salts" is the fact, that the so-called oxygen acids do not affect vegetable colours unless associated with water, which they are assumed to decompose, so as to become by appropriation of its elements hydracids of new radicals. The experiments recorded in the text, however, shew that one hydracid, at least, has its action on colouring matter as much negatived by the withdrawal of water as any oxyacid. It does not follow that the rationale of the change is the same in both cases; but the fact that anhydrous gaseous hydrosulphuric acid does not redden vegetable blues, lessens the value of the argument alluded to. In the great majority of cases, the rendering of an oxyacid anhydrous implies its alteration from the liquid state to the solid or gaseous one. This change in condition is of itself sufficient to alter most materially the influence of a reagent. It appears, however, to have been altogether overlooked in explaining the indifference of a dry oxyacid to organic colours. The phenomena recorded further on, as observed with gaseous hydrochloric acid and liquefied sulphurous acid, bear upon this point, but it cannot be discussed at length here.

phurous acid gases. Pure carbonic acid is equally negative in its action on vegetable blues and browns.

Sulphuretted Hydrogen.

Sulphuretted hydrogen, even when moist, does not change organic colours to so great an extent as the stronger acids do. Solutions of litmus, *ex. gr.*, become, under its action, only of a purple-red tint, like that which carbonic and boracic acids give them, whilst the more powerful acids destroy all shade of blue. If I may judge from the few experiments I have made on this subject, the reddening power of sulphuretted hydrogen is more dependent than its bleaching action on the presence of water. At all events, it is equally dependent on moisture, for blue litmus has been reddened very slightly by eight months' exposure to the dry gas, neither has brown rhubarb paper become yellow, or appreciably grown paler.

Hydrochloric Acid.

No acid excels hydrochloric in full and rapid action on organic colours; nor is any one, according to the prevailing opinions of chemists, less likely to be indebted to association with water for its characteristic properties. It is the simplest type of a perfect acid, and as such, might be expected to exhibit, even when gaseous and anhydrous, the same relation to organic colours which it does when moist. I looked upon hydrochloric acid, therefore, as the most interesting of the acid gases with which experiments could be made.

I have not hitherto referred particularly to the method followed for drying the gases, because none of those I have yet mentioned present great difficulties in the way of rendering them,—I will not say certainly anhydrous,—but at least sufficiently dry not to affect colours. It is otherwise with hydrochloric acid. I have failed more frequently than I have succeeded, in rendering this gas, by drying, indifferent to colours; nor have I been able to preserve blue litmus for any length of time unchanged in an atmosphere of the dry gas. It is necessary, therefore, to be more particular in describing the process for drying, which was followed with hydrochloric acid; although it differed in no respect from that pursued with the majority of the other gases.

The general arrangement, especially in the later and more perfect trials, was the following:—The thinnest India letter-paper was stained with an infusion or tincture of the colouring matter intended to be used, and afterwards dried at the temperature of the air. Slips of the paper were introduced into a tube, varying in different cases from half an inch to one inch in diameter, and from six to eighteen inches in length. The tube was then hermetically sealed at one extremity, and drawn out at the other into a narrow canal, which was left open. A

smaller open tube was afterwards attached to each side of the larger one, near to its shut end, so as to communicate with its cavity. These lateral tubes projected for a short distance at right angles to the long axis of the larger tube, and then ran parallel to it, with their open mouths pointing in the opposite direction from that of the single canal at the other end of the tube. To prevent confusion, I shall call the lateral appendages which I have described, the horns of the tube.

When the latter was arranged for an experiment, the narrowed termination at one end was placed in communication with a short tube filled with chloride of calcium, by means of a caoutchouc connector. The free extremity of this tube was bent at right angles, and dipped into oil, so as to cut off communication with the outer air. To each of the open horns, also, a chloride of calcium tube, three feet in length, was attached. The one of these tubes was intended to convey, and render anhydrous, a current of air, which should dry the paper. The other, in like manner, was to carry and dry the gas, which should be brought in contact with the paper, when the latter was deprived of moisture. At the beginning of an experiment, the tube through which the gas subsequently passed, after being connected with one of the horns, was sealed at the end furthest from the paper. Its presence from the first was essential, because otherwise the dried paper must have been put in communication with the moist outer air, when a fresh chloride of calcium tube to carry the gas was substituted for that which previously conveyed the air: for if the same tube in whole, or in part, had been employed, first to dry the air, and then the gas, the freedom of the latter from moisture could not have been counted upon.

I found, after trying various devices, a pair of common bellows the most convenient instrument for furnishing a current of air. The air was first passed through a bulbed tube, immersed in a freezing mixture, and then through the chloride of calcium tube into the one containing the paper; from which it escaped through the smaller drying tube that dipped into oil, as already mentioned. The paper was maintained by gas lights at a temperature of about 220° Fahr., and the air was kept passing over it, for at least two, generally for three, hours.

When the paper appeared perfectly free from moisture, the lateral horn, by which the air reached it, was sealed at the blow-pipe, and the drying apparatus detached. The shut end of the other long chloride of calcium tube was then opened, and connected with an apparatus for furnishing the gas to be used in the experiment.

The woodcut on the following page will make the description more intelligible. Only the more essential parts of the arrangement are represented in the diagram; the bellows and connecting flexible tube on the one hand, and the retort in which the gas was generated on the other, as well as the washing bottles, &c., being omitted.

A, Tube in which coloured paper was placed.

a, Narrow canal, communicating by a caoutchouc collar, with small tube containing chloride of calcium.

b and c, Lateral appendages or horns, communicating with long drying tubes, C and D.

B, Small drying tube, dipping into oil, through which the elastic fluids, after passing over the paper, escaped into the air.

C, Long drying tube, which was sealed at e, at the commencement of an experiment, but opened when the paper had been dried, and employed to convey the gas which was to act on it.

D, Second long drying tube employed to carry air, to render the paper in A anhydrous. When the paper was dried, the horn c was sealed at the blow-pipe, and D detached. Gas was then transmitted through C.

The arrangement I have described was followed with all the gases except ammonia. Chlorine and sulphurous acid were sent through oil of vitriol before reaching the chloride of calcium tube. The other gases were generally passed simply through a bulb immersed in a freezing mixture, before being transmitted through the drying tube. I found it essential to success in the experiments recorded to dispense with corks, asbestos, and cotton, in connecting or loosely stopping the tubes, as these bodies retained moisture with the greatest obstinacy. Caoutchouc collars were used in every case to unite the detached portions of the apparatus. The special devices followed in particular cases are mentioned under the gases which called for them.

I procured hydrochloric acid gas by the action of Nordhausen sulphuric acid on common salt previously fused. Theoretically, the gas should carry with it a mere trace of moisture, yet in spite of the apparently effectual drying apparatus made use of, the acid, in the majority of trials, changed the tint of blue litmus as soon as it came in contact with it, giving it a dark lilac or deep wine-red colour. Nevertheless, on three occasions I was able to pass a current of dried hydrochloric acid for five minutes over blue litmus-paper, without sensibly altering its tint, according to the judgment of four persons besides myself, who were witnesses of the experiments. These positive results outweigh the negative ones already referred to. The majority of the latter, moreover, were only partial failures, and went the length, at least, of proving that the removal of moisture from hydrochloric acid gas delays, if it does not prevent, its characteristic action on organic colours. In the successful experiments mentioned above, the negative action of the acid was only transient; for when the tubes containing the gas and paper were sealed and set aside, the colour invariably passed from its original blue tint to a more or less decided red. In several trials, however, the ultimate effect of the hydrochloric acid fell far short of the full reddening which

even the slightly moist gas produces. I shew the Society a tube, containing litmus-paper, which withstood, without change, a current of hydrochloric acid passed over it for five minutes. The experiment was made on 23d February 1848; and the paper is at this date not a bright red, but only a dark lilac.

Three explanations suggest themselves as to the ultimate though imperfect reddening of the blue litmus. 1. The gas may not have been quite dry. 2. Hydrogen acids, though perfectly dry, may, unlike the so-called oxygen acids, be able to modify the tints of colours. 3. Hydrochloric acid, which has a great affinity for water, can compel its elements to unite to form it, so that the gas may combine with the liquid. Hydrogen and oxygen are present, both in the colouring matter and in the paper. In the paper, indeed, they are present in the proportion to form water. This solvent, therefore, may be slowly generated within the sealed tube, and be the cause of the gradual reddening of the blue paper.

As to the first of these views, I can neither disprove nor confirm it. It is probably as difficult to render a gas absolutely anhydrous, as it is to produce a perfect vacuum. Moreover, as I have stated already, we have no test of absolute dryness, applicable to a gas. It would interrupt the argument, however, to consider this question at length here; I have devoted, accordingly, the section which succeeds this to its discussion.

Of the second explanation, I would say much the same as I have said of the first. It is highly probable that a powerful hydracid like the hydrochloric should retain, more or less, as a gas, its characteristic action on organic colours.

I would speak most positively of the third view. The power of bodies which have a great affinity for water, to compel its formation and separation, is so great, that I ventured to predict, that it would be impossible to preserve, for any length of time, blue litmus unchanged in tint in the driest hydrochloric acid. I do not dwell at length, however, on the cause of the ultimate reddening, as the fact that the paper was only slowly and imperfectly reddened, is sufficient for my present purpose. At lowest, the experiments I have detailed demonstrate that the removal of water from hydrochloric acid gas delays its action on colours.

Ammonia.

The last of the gases I tried was ammonia. According to KANE,* when dry it has no action on organic colours, although no body, when moist, affects these substances more powerfully. I might content myself with adducing this distinguished chemist's statement as to the negative action of dry ammonia, and add it to the list of gases which have their action on colouring matter arrested by the removal of moisture. My own experiments, however, have been so much less decisive than KANE's statement led me to expect they would be, that I cannot, without comment, avail myself of his evidence. The difference between his results and

* Elements of Chemistry, p. 852.

mine is probably sufficiently accounted for by the supposition, that I did not thoroughly dry the ammonia. This gas is more difficult to render anhydrous than even hydrochloric acid ; not so much, perhaps, because it has a greater affinity for water, but because our most powerful desiccating agents, such as the deliquescent chlorides and oil of vitriol, cannot be employed to dry it. We are restricted, accordingly, to substances much less hygrometric, such as unslaked lime, hydrate of potass, and its fused carbonate.

It would serve no purpose to record a series of unsuccessful experiments : I merely mention, therefore, that I have never been able to obtain ammonia in a condition in which it did not change the tint of reddened litmus and of yellow turmeric paper as soon as it came in contact with them. I have found its action on colouring matter, however, sensibly reduced by passing it over the hygrometrics last referred to. Reddened litmus, for example, became only purple when it first encountered dried ammonia, and did not acquire a bright-blue tint, when left in the gas, till after the lapse of some hours.* For the reasons mentioned above, I do not, in the meanwhile, feel myself at liberty to say more than that the presence of water greatly quickens the action of ammonia on colours.

It would appear, then, from the results I have detailed, that there is little, if anything, anomalous or exceptional in the negative bleaching of dry chlorine. Oxygen, sulphurous acid, and sulphuretted hydrogen, are equally powerless as bleachers, when deprived of moisture, as that gas. Sulphurous and carbonic acids are probably more indebted than chlorine to water for their power of modifying colouring matters, both as regards changing and destroying their tints. Hydrochloric acid and ammonia have their influence on colours at least temporarily arrested by the absence of water ; and, after all, it is a question with the whole of the gases referred to, only of degree. It is not likely that even in absolute darkness chlorine has no action on anhydrous colouring matter. If this be conceded, the whole of the gases referred to may be included in one category, as having their modifying action on organic colours accelerated by the presence and retarded by the absence of water. I trust to supply an additional datum towards the settlement of this question, by observing the difference which exposure to sunlight makes, in relation to the action of all the gases with which experiments were tried.

* In the experiment which yielded the most successful result, the ammonia was first passed through a bulb immersed in a freezing mixture, and afterwards through long tubes containing lime, caustic potass, and its fused carbonate. The gas was then allowed to flow through a tube for some minutes till it had expelled the air, and the tube was sealed. The one end of this tube had been previously expanded into a large ball, which was filled with fragments of the hygrometrics just mentioned : in the other end of the tube a small sealed bulb was placed, containing a piece of carefully dried red litmus-paper. The ammonia was left in contact with the drying agents for a week, when the tube was shaken till the bulb broke, and allowed the gas and the paper to meet. The latter, as mentioned in the text, immediately became purple, and after some hours bright blue.

Before proceeding to detail the second series of researches, I have thought it desirable to offer some observations on the processes employed for drying gases.

V. *On the Methods applicable to the Drying of Gases.*

The methods at present in use for drying gases cannot be considered as yielding more than an approximation to absolute dryness in the case of any elastic fluid. The processes employed are inherently defective, both mechanically and chemically. When chloride of calcium and pumice-stone, steeped in oil of vitriol, are employed as the desiccating agents, they cannot be made use of except in fragments of considerable size, otherwise the containing tubes become choked, and the gas does not pass. Interstices, accordingly, comparatively speaking large, occur between the separate fragments of the drying agent; and the gas, in moving along, has a certain portion of its mass not in physical contact with the hygrometrics, or directly exposed to their desiccating action. In like manner, when a gas is sent through a column of oil of vitriol, only the surface of each bubble is in contact with the liquid, and the gas-bells rise very rapidly through so dense a fluid, so that they can be dried only imperfectly during their ascent.

Those defects admit only of partial remedy, by extending the surface of chloride of calcium or pumice-stone, or by multiplying the columns of oil of vitriol through which the gas shall pass. A practical limit is set to such devices by the obstruction which they offer to the passage of elastic fluids. This can be overcome only by increasing the pressure at which the gas is delivered, and it is not easy to regulate this, so that the gas shall not flow in too swift a current, and so neutralise, by the rapidity of its passage, the benefit which would otherwise result from its coming in contact with an extended hygrometric surface.

The imperfections just alluded to are not, perhaps, beyond the reach of suitable mechanical contrivances; but even if they were all remedied, the important question still remains, will the protracted and complete contact of a gas containing water-vapour with the most powerful hygrometrics, suffice entirely to deprive the gas of moisture? With a view to determine this point, I shut up muriatic acid gas, previously passed through a freezing mixture, and over chloride calcium, within a glass tube containing fragments of the same salt. It was left for a week in contact with the chloride, and then allowed to meet carefully dried blue litmus-paper, enclosed along with it at the commencement of the experiment, in a small sealed bulb of thin glass, which was readily broken by shaking the tube. The paper began to change tint as soon as it met the gas; and if this alteration in colour be accepted as an evidence of moisture being present in the muriatic acid, then the latter was not dry. A similar experiment, with a like result, has already been related in reference to ammonia.

These results, however, are not decisive of the point whether the gas was anhydrous or not, for the change in tint of the litmus may possibly be accounted

for otherwise than by assuming the presence of water; and the fault, moreover, even if water were present, may have lain with the coloured paper, not with the gas. The same objection does not apply to the following observation. If air at the temperature of 60° F. be sent through a long tube filled with fused chloride of calcium, it parts with moisture, which the chloride absorbs and combines with. If this dried air be thereafter transmitted over moist chloride of calcium, the latter becomes, to appearance, speedily dry. Here we have the apparently contradictory results of chloride of calcium drying air, and air drying chloride of calcium. The inference seems unavoidable, that there must be a neutral point where the chloride of calcium and air will be mutually indifferent, so that neither shall be able to deprive the other of moisture. This point will vary in reference to, 1. the relative quantities of the hygrometric salt and air acting on each other; 2. the relative dryness of the gas and solid; and, 3. the temperature at which the trial is conducted. Experiments on gases are generally made in apartments having an average temperature of or about 60° F., at which the tension of water-vapour is probably great enough to resist, so far as complete condensation is concerned, the absorbing power, and affinity for it, of all hygrometrics. This remark leads directly to the observation, that reduction of temperature is probably the most effectual of all processes for drying a gas. It has been employed with great success by FARADAY, in his later researches on the liquefaction of the gases;* and I was induced, in consequence, to make use of it in my experiments. The value of the method admits of easy demonstration. The great obstacle to rendering a gas anhydrous, is the tension which heat confers on the water-vapour diffused through it. We generally endeavour to overcome this tension by opposing to it the condensing force of porous hygrometrics, and the chemical affinity of substances which combine readily with water; yet it is not at all certain that these forces have the maximum condensing power attributed to them. On the other hand, it is certain, that the tension of water-vapour is exceedingly small at zero, and rapidly decreases as we descend the thermometric scale.

FARADAY'S discovery, moreover, of the existence of a limit to vaporisation, teaches that there must be a temperature at which ice abruptly ceases to give off vapour. If this point be within reach of our frigorific appliances, and were ascertained, we should possess, in the reduction of gases to this temperature of no vapour, a theoretically perfect process for rendering gases anhydrous. It would be applicable, however, only to the less condensible elastic fluids, for the more easily liquefied ones would become liquid before the temperature of no-water vapour had been attained. It is further to be noticed, and the remark is important, that all volatile bodies have their vaporising point lowered in the presence of bodies more volatile than they are. The fact is familiar to every chemist. The

* Phil. Trans., 1845. Part I., p. 155.

essential oils, *ex. gr.*, whose boiling points are much above that of water, are entirely dissipated in vapour if mingled with water raised only to the temperature of 212° F. Even bodies ranked, when anhydrous, among fixed substances, such as common salt, nitre, and boracic acid, rise with the vapour of water below its boiling point. It cannot be doubted that, in like manner, a temperature sufficiently low to hinder ice from volatilising *in vacuo*, or in still air, would not prevent it yielding a continuous stream of vapour in a current of gas. This power, indeed, of gases, as the more volatile bodies, to solicit and compel water-vapour to accompany them, is, at all temperatures, but especially at high ones, a formidable obstacle to rendering elastic fluids anhydrous. On the other hand, this diffusive power greatly increases the desiccating effect of gases, even not absolutely dry, when sent in currents over moist solids.

How near an approximation may be made to perfect dryness in the case of gases, cannot be determined till we have a test of the anhydrous state applicable to elastic fluids. A criterion of some value would be the passage of a considerable volume of the gas (ammonia excepted), through a weighed tube containing chloride of calcium, which should not increase in weight if the gas were anhydrous; but, if the preceding observations are well founded, this test would cease to act before the gas was quite dry.

I have tried whether the change of tint which the so-called sympathetic inks (solutions of the salts of cobalt and nickel) undergo when deprived of water, would serve as an indication of dryness on the part of gases; but I find that it is a test of no delicacy.

Indifference to colouring matter will certainly be found a negative indication of some value. Chlorine, *ex. gr.*, which immediately bleaches, and sulphurous or carbonic acid, which reddens litmus, cannot be dry. This test, of necessity, is limited to the gases which affect organic colours, and would be useless in the case of oxygen, nitrogen, hydrogen, the carburetted hydrogens, &c. &c.

A convenient way of examining the dryness of gases by means of colouring matters is to prepare, by blowing at short distances along a thin glass-tube, a series of small bulbs, in each of which a piece of litmus-paper may be placed. The papers are then to be dried in a current of air, passed through oil of vitriol and over chloride of calcium, and each bulb sealed off separately. In this way, a large number of bulbs can be prepared at the same time, and kept ready for use when required. One of these is to be placed in a tube forming part of the arrangement employed in the particular experiment, so that it shall be enveloped in the gas whose dryness is to be tested. By a sharp tap on the tube, the enclosed bulb is easily broken, and the gas and paper allowed to meet. There is no difficulty in making the bulbs thick enough to bear handling, and yet sufficiently thin to give way when required.

In the preceding remarks, I have chiefly referred to the difficulty experienced

in drying gases. But organic solids, such as litmus and colouring matter, though probably more readily dried than gases, are certainly with difficulty rendered anhydrous. The difficulty is too familiar to every chemist who has made organic analyses, to call for any illustration or proof. Reference has already been made to the desiccating power of currents of air, and to the likelihood of a solid being more effectually dried by a gas than a gas by a solid. If, however, it is impossible to supply a current of perfectly dry air, it may be doubted whether it is possible to render a solid anhydrous by passing air over it. It is difficult to imagine that air, containing *ex hypothesi* some moisture, should make a solid absolutely dry, drier than the air itself is; yet it is not impossible that it should. The tension which heat gives to water-vapour; its great dilatation when present in small quantity; and its diffusion through a large volume of gas, may more than balance any power on the part of the solid to attract or condense it. There may be a limit to condensation, as well as to vaporisation.

Notwithstanding all that has been urged in this section, in reference to the difficulty of rendering gases *absolutely* dry, it will not, I think, be questioned, that in the experiments I have recorded, a close approximation to actual dryness was attained in many of the trials. And, conceding that traces of moisture may have been present, I may, nevertheless, with some justice, argue, that if the removal of a certain amount of water from gases arrests for months their action on colours, *a fortiori*, the total abstraction of moisture would still more decisively negative that action.

VI. *On the Action on Dry Organic Colouring Matters of the liquefied Anhydrous Gases, and of Chlorine dissolved in liquids containing no Oxygen.*

The second series of experiments, as I have already mentioned, was made with the view of ascertaining in what way water acts, when it accelerates the action on colouring matter of the gases referred to, but particularly of chlorine. According to the prevailing theories of chemists, when water meets dry carbonic and sulphurous acid, or dry ammonia, it does not merely dissolve them, but allows its elements to be appropriated by each of these gases, which become, in consequence, compounds possessed of new relations to bases, acids, colouring matters, and the like. I shall therefore set these gases aside, as not admitting of direct comparison with chlorine, which chiefly concerns us. There is no reason, on the other hand, for supposing that water does more than merely dissolve oxygen, sulphuretted hydrogen, and hydrochloric acid, so that that liquid may be supposed to change their relation to colours in the same way as it does that of chlorine.

The older chemists held by the axiom, “*Corpora non agunt nisi soluta,*” and by means of it could fully have accounted for the difference in action on colours

of the dry and moist gases. In our own day, however, the problem takes a somewhat different shape, for we have learned to liquefy the gases without the intervention of a solvent. Three of the four gases last referred to, which simply dissolve in water, viz., chlorine, sulphurous acid, and sulphuretted hydrogen, admit of liquefaction, although quite anhydrous. It has been held, accordingly, that the liquefaction of a gas changes its properties, in the same way as dissolving it in water would.

With a view, so far at least, to examine this point, I exposed carefully dried blue litmus-paper to the action of liquid bromine (which is equivalent to a liquefied gas), repeatedly rectified from chloride of calcium, and supposed to be anhydrous. Ultimately the paper was quite bleached; but the decolorising action was slow, certainly much slower than that of hydrated bromine. Specimens accompany this paper. The dark colour, however, of that element makes it an unsatisfactory substance to work with, in relation to changes of tint in the bodies upon which it acts. From experiments such as I have described, as well as from theoretical observations, it has been inferred that the function of water in relation to the gases I have been considering is simply to effect their mediate liquefaction, and thereby to bring them into closer physical contact with the colouring matters than their elastic condition permits. So general a conclusion, however, as this, which would imply that a liquefied gas has the same properties as a dissolved one, is certainly in the meanwhile without proof, and is probably untenable. So far as they have been examined, the liquefied gases present properties very different from those exhibited by the same bodies when in aqueous solution, although their action on colouring matters has been less inquired into than might have been expected.

There is, moreover, this manifest distinction between the action on a colouring matter of a liquefied gas, and of an aqueously dissolved one, that in the former case the gas only is in the liquid form, the colouring matter remaining solid, whilst in the latter the water dissolves alike the colouring principle and the gas, and brings both into a condition far more favourable to chemical action than where the one only is liquid.

It is further certain that much must depend on the force of the adhesive attraction of the liquidised gas for the dry colour. A liquid which cannot wet a solid will exert little, perhaps no chemical action upon it, although it may produce a marked effect when both are dissolved in water.

Again, if the liquidised gas can dissolve the colouring matter, we may be certain that, sooner or later, it will affect it; but if it cannot dissolve it, the latter may be totally unaltered by its presence. The slow action of dry bromine is probably related, either to incapacity of quickly wetting, or of dissolving litmus; perhaps to both.

In connection with this subject, I tried an experiment with liquefied anhydrous

sulphurous acid, which yielded a result so interesting, that I mention it particularly. A piece of blue litmus-paper was exposed for three hours to a current of dry air, and then sealed up in the narrow tube in which it had been dried. The sealed bulb, containing the paper, was placed in a tube immersed in a mixture of pounded ice and salt, and carefully dried sulphurous acid transmitted through the arrangement. As soon as a sufficient quantity of the gas had assumed the liquid form, at the low temperature to which it was exposed, the open ends of the tube were sealed, and it was shaken till the bulb within broke, and allowed the paper and the liquefied gas to come in contact with each other. The paper was instantaneously soaked through, and completely wetted, but its blue colour remained totally unaltered, whilst an aqueous solution of sulphurous acid would have instantly reddened it. The liquidised gas acquired no colour itself, even after a fortnight's contact with the litmus-paper. It appeared to wet it without dissolving anything from it.

The retention of the blue tint on the part of the paper was, however, only temporary. In an hour and a quarter it had become dark purple, and the blue slowly faded, till, in twenty hours, the paper was bright red. No indication of bleaching action appeared.

I attribute the final reddening to the production of water, generated out of its elements in the litmus or paper, or both, by the influence of the sulphurous acid. For, if anhydrous liquid sulphurous acid possessed the power, *per se*, of reddening vegetable blues, there seems no reason why its action should be so long delayed, when it wetted the coloured paper so readily. And it could not owe its reddening power to water present in it, ready formed from the first, otherwise it would have reddened instantaneously.

I set aside, therefore, as at least unproven, and, further, as not probable, the dogma, that the mere passage of an elastic fluid, such as chlorine, from the state of gaseity to that of liquidity, is the whole cause of its accelerated action on colours, when dissolved in water. It seemed to me, indeed, that the acceleration of action was as much owing to the water liquefying the colouring matter as to its liquefying the gas, and that one might venture, in the spirit of the elder chemists' motto already quoted, to infer, that any liquid which dissolves alike the gas and the colouring matter, would be as efficacious as water in determining the destruction or modification of the colour. But, I have learned by experiment, that this also is too general a conclusion, and that it is quite possible for a liquid to dissolve simultaneously a colouring matter and a gas, and yet not exhibit the results which it would present if water were the solvent of both.

So far as this branch of the inquiry is concerned, I have been compelled, by want of leisure and opportunity, to limit myself almost entirely to chlorine. This gas is dissolved by chloroform, by bisulphuret of carbon, and by the volatile oils of the type of spirit of turpentine ($C^5 H^4$). None of these liquids, when pure, contain

oxygen, and all of them dissolve several colouring matters. Yet, not only dry, but moist chlorine may be passed through solutions of the colouring principle of false alkanet root (*anchusa tinctoria*), in the solvents mentioned, without bleaching occurring.

On the other hand, solutions of blue litmus, in chloroform and bisulphuret of carbon, are bleached instantaneously by dry chlorine. I took the greatest precautions in these trials to exclude moisture. Paper was dispensed with. A solution of blue litmus was dried up in a glass tube, and desiccated in a current of air. The chloroform, or sulphuret of carbon, was repeatedly rectified over chloride of calcium, and finally distilled into a bulb communicating with the outer air, through a narrow tube filled with the same hygrometric salt. The bulb was then sealed, and placed within the tube containing the litmus at the commencement of the experiment. Chlorine was ultimately passed over the colouring matter for some minutes, in order to make certain that the gas was too dry to act unaided on the colour. The tube was then sealed, full of chlorine, and shaken till the bulb broke. The blue colour immediately disappeared, and the liquid became of a pale yellow tint.

The tincture of alkanet in chloroform or sulphuret of carbon retained its bright red colour, if kept in darkness; but less than an hour's exposure in the open air, though the sky was clouded, sufficed to turn the scale in favour of bleaching, and the colour disappeared.

From these results it appears that, contrary to DAVY'S view, chlorine can bleach though oxygen be absent, for chloroform contains none; and that neither of the elements of water is essential to its bleaching action, for sulphuret of carbon is devoid of both. The further conclusion seems unavoidable, that neither water nor any other liquid is essential to the decolorising action of chlorine, otherwise than as enabling the gas and the colour to come within the sphere of chemical action, by dissolving both. This function, water probably performs better than any other liquid, in virtue of its solvent power for most substances exceeding that of almost all other fluids.

A similar conclusion, *mutatis mutandis*, may be extended to oxygen, sulphurous, hydrosulphuric, and hydrochloric acids, but with this qualification, that specific differences may be expected to occur with all the gases named, as to their action on any one colouring matter, and with different colouring matters, as to their deportment with any one of the gases.