XIX. *On the Action of Rays of high Refrangibility upon Gaseous Matter.*

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§ I.

Introduction.

WITHIN the last ten years I have had the honour of submitting to the Royal Society a series of investigations the principal aim of which was to render the less refrangible rays of the spectrum interpreters and expositors of the molecular condition of matter.

Unlike the beautiful researches of MELLONI and KNOBLAUCH, these inquiries made radiant heat a means to an end. My thoughts were fixed on it in relation to the matter through which it passed. Placing before my mind such images of molecules and their constituents as modern science justifies or renders probable, such images of the luminiferous ether and its motions as the undulatory theory enables us to form, I endeavoured to fashion and execute experiments founded upon these conceptions which should give us a surer hold upon molecular constitution.

Thus, definite physical ideas have accompanied and guided the whole course of these researches. That matter is constituted of atoms and molecules has been accepted as a verity throughout. The phenomena under examination rendered it impossible for me to halt at the law of multiple proportions, which so many chemists of the present day appear inclined to make their intellectual bourne. In following up a train of ether waves, in idea, to their source, I could not place at that source a multiple proportion; the waves could not be connected physically with such a multiple; I was forced to put there a bit of matter, in other words, a *molecule*, which bore the same relation to the ether as a vibrating string does to the air which accepts its motions and transmits them as waves of sound.

One result among many others which these researches established will, I think, play an important part in the chemistry of the future. I refer to the proved change of relation between the luminiferous ether and ordinary matter which accompanies the act of chemical combination. Here, without any alteration in the quantity, or in the ultimate quality of the medium traversed by the ethereal waves, vast changes may occur in the amount of wave-motion intercepted. Let pure nitrogen and ordinary oxygen be mixed mechanically together in the proportion by weight of 14 : 8. Radiant heat, it is now known, will pass through the mixture as through a vacuum. No doubt a certain amount of heat is intercepted; but it is so small an amount as to be practically insensible. At all events it is multiplied by hundreds, if not by thousands, the moment the oxygen and nitrogen combine to form nitrous oxide. Or let nitrogen and hydrogen be mixed me-

chanically together in the proportion of 14 : 3; the amount of radiant heat which they then absorb is augmented more than a thousandfold* the moment they build themselves together into molecules of ammonia. Neither the quantity nor the ultimate quality of the matter is here changed; the act of chemical union is the sole cause of the enormous alteration in the amount of heat intercepted. The converse of these statements is of course also true; dissolve the chemical bond, either of the nitrous oxide or of the ammonia, and you instantly destroy the absorption. As a proof that our atmosphere is a mixture, and not a compound, no experiment with which I am acquainted matches in point of conclusiveness that which demonstrates the deportment of dry air to radiant heat.

But the molecules which can thus intercept the waves of ether must be shaken by those waves, possibly shaken asunder. That ordinary thermometric heat provokes chemical actions is one of the commonest facts of observation. These actions, considered from a physical point of view, are changes of molecular position and arrangement consequent on the acceptance of motion from the source of heat. Radiant heat also, if sufficiently intense and if absorbed with sufficient avidity, could produce all the effects of ordinary thermometric heat. The dark rays, for example, which can make platinum white-hot, could also, if absorbed, produce the chemical effects of white-hot platinum. They could decompose water, as now in a moment they can boil water. But the decomposition in this case would be effected by the virtual conversion of the radiant heat into thermometric heat. There would be nothing in the act characteristic of *radiation*, or demanding it as an essential element in the decomposition.

The dark calorific rays are powerfully absorbed by various bodies, but, as a general rule, they do not appear competent to set up that particular motion among the constituents of a molecule which breaks the tie of chemical affinity. All the rays of the spectrum exercise no doubt chemical powers. We should have scant vegetation upon the earth's surface if the red and ultra-red rays of the sun were abolished. But the chemical actions in which the *radiant form* comes into play, are mainly produced by the least energetic rays of the spectrum. The photographer has his heat focus in advance of the chemical focus; which latter, though potent for his special purposes, possesses almost infinitely less mechanical energy than its neighbour. Some special relation must, therefore, as a general rule, subsist between chemical molecules and the more refrangible rays; we arrive at the conclusion that chemical decomposition by *rays*, to keep to the ordinary term, is less a matter of *amplitude* on the part of the vibrating ether particles than of *time of vibration*.

The decomposition of a molecule must result from the internal strain of its parts; to them, therefore, and not to the molecule as a whole, the vibrations which produce chemical change must be imparted. The question remains an outstanding one in molecular physics, why it is that the longer and more powerful ether waves are generally incompetent to set up the motion which results in decomposition. The influence of

* It may be a millionfold; for we do not yet know how small the absorption of the absolutely pure mixture really is.

synchronism here suggests itself. These shorter waves are effectual because their motion is *stored up*. Their infinitesimal impulses, because imparted at the proper intervals, *accumulate* and finally become intense enough to jerk asunder the atoms with whose periods they are in accordance.

§ II.

The investigation which I have now the honour to offer to the Royal Society is in a certain sense complementary to those referred to at the outset of this paper. It deals with the relations of gaseous matter to the most refrangible rays of the spectrum. It treats of the chemical energies of such rays as exerted upon such matter. If we except the combination of chlorine and hydrogen by light, and the decomposition of carbonic acid by the solar rays in the leaves of plants, which latter, however, may not be the decomposition of *a gas*, no fact I believe has hitherto been known to exist in which light, or heat in the radiant form, acts chemically upon a gas or vapour*. By this inquiry the range of radiant energy as a chemical agent is considerably extended; the phenomena resulting from that energy are exhibited in a new and exceedingly impressive form, and they prompt reflections regarding the possible influence of solar radiation on the gases, vapours, and effluvia of our atmosphere which could not previously be entertained.

The inquiry was started thus:—It is known to the Society that the experiments on radiant heat already referred to, were for the most part performed in tubes of brass or glass, called for the sake of distinction "experimental tubes." It is also known to the physical members of the Society that a difference† exists between my eminent friend Professor MAGNUS‡ and myself with regard to the deportment of aqueous vapour towards radiant heat. Last autumn, and in reference to the reasons assigned by him for this difference, I scrutinized the appearance of my experimental tubes during the entrance into them of various gases and vapours. The vapours were carried into the tubes by dry air which had been permitted to bubble through their liquids. I watched carefully, and with the aid of magnifying-lenses, for any signs of the precipitation of moisture either upon the surface of the experimental tube itself or upon the plates of rock-salt employed to close it, keeping at the same time my eyes open to any other action which the intensely concentrated beam employed in the inquiry might reveal.

On the 9th of October, 1868, while thus engaged upon the vapour of the nitrite of amyl, I observed a curious cloudiness in the experimental tube when the beam was sent through the vapour. For a moment this appearance troubled me; for it required a little reflection to assure me that in my previous publications I had not sometimes ascribed to pure cloudless vapour actions which were really due to such nebulous matter as was then before me. The appearance, however, immediately declared itself to my mind as a product of chemical action then and there exerted on the vapour.

* Professor STOKES reminds me that Phosgen gas derives its name from its formation under the influence of light.—[J. T., July 1870.]

† To be still cleared up.

‡ Unhappily lost to science since these words were written.—[J. T., July 1870.]

The nitrite vapour was then intentionally subjected to the action of the light. The beam employed was convergent. As the vapour reached the point of greatest concentration of the beam cloudy matter was there precipitated, which was afterwards whirled by the moving air into the more distant parts of the tube. The cloud thus carried away was incessantly renewed, and after the mixed air and vapour had ceased to enter, precipitation occurred all along the cone of rays in front of the focus.

The lamp was then extinguished, and the mixture of air and nitrite vapour permitted to enter the tube in the dark. When the tube was full the condensed beam was sent through it. For a moment the light seemed to pass through air only; but after a moment's pause a white cloud fell suddenly upon the conical portion of the beam, causing it to flash forth almost like an illuminated solid.

When the beam, previous to allowing it to enter the vapour, was caused to pass through a red or yellow glass, the action though visible was feeble; it was much more energetic when the beam passed through a blue glass. I sent a convergent beam through a red glass and observed the feeble effect. A blue glass was then added, and by the concert of both the light was completely cut off. On withdrawing the red glass, a very beautiful blue cloud came down upon the conical beam. The experiment proved that in this case, as in so many others, the blue rays are the "chemical rays."

Solar light, as might be expected, produces all the effects of the electric light, and in regions more favoured than London may be employed in continuous researches of this nature. When the parallel beams of the sun are duly concentrated, the precipitation which they invoke in passing through nitrite-of-amyl vapour is copious and immediate.

§ III.

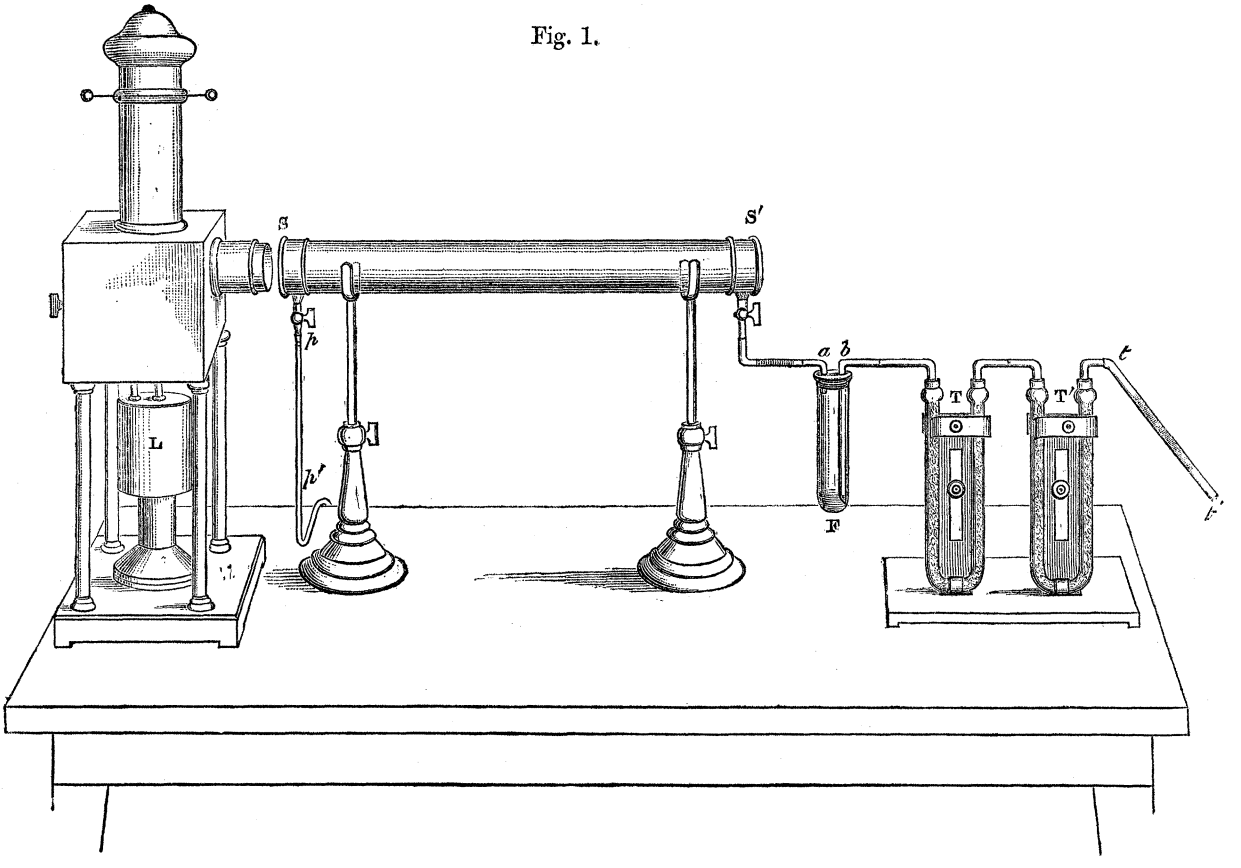
The simple apparatus employed in these experiments will be at once understood by reference to fig. 1. S S′ is the glass experimental tube which has varied in length from 1 to 5 feet, and which may be from 2 to 3 inches in diameter. From the end S the pipe $p p'$ passes to an air-pump. Connected with the other end we have the flask F, containing the liquid whose vapour is to be examined; then follows a U-tube, T, filled with fragments of clean glass wetted with sulphuric acid; then a second U-tube, T′, containing fragments of marble wetted with caustic potash; and finally a narrow straight tube $t t'$, containing a tolerably tightly fitting plug of cotton-wool. To save the air-pump gauge from the attack of such vapours as act on mercury, as also to facilitate observation, a separate barometer tube was employed.

Through the cork which stops the flask F two glass tubes, a and b, pass air-tight. The tube a ends immediately under the cork; the tube b, on the contrary, descends to the bottom of the flask and dips into the liquid. The end of the tube b is drawn out so as to render very small the orifice through which the air escapes into the liquid.

The experimental tube S S′ being exhausted, a cock at the end S′ is carefully turned on. The air passes slowly through the cotton-wool, the caustic potash, and the sulphuric

acid in succession. Thus purified it enters the flask F and bubbles through the liquid. Charged with vapour it finally passes into the experimental tube, where it is submitted

Fig. 1.



to examination. The electric lamp L placed at the end of the experimental tube furnished the necessary beam.

§ IV.

The floating Matter of the Air.

Prior to the discovery of the foregoing action, and also during the experiments just referred to, the nature of my work compelled me to aim at obtaining experimental tubes absolutely clean upon the surface, and absolutely empty within. Neither condition is, however, easily attained.

For however well the tubes might be washed and polished, and however bright and pure they might appear in ordinary daylight, the electric beam infallibly revealed signs and tokens of dirt. The air was always present, and it was sure to deposit some impurity. All chemical processes, not conducted in a vacuum, are open to this disturbance. When the experimental tube was exhausted it exhibited no trace of floating matter, but on admitting the air through the U-tubes containing caustic potash and sulphuric acid, a *dust-cone* more or less distinct was always revealed by the powerfully condensed electric beam.

The floating motes resembled minute particles of liquid which had been carried me-

chanically into the experimental tube. Precautions were therefore taken to prevent any such transfer. They produced little or no mitigation. I did not imagine at the time that the dust of the external air could find such free passage through the caustic potash and the sulphuric-acid tubes. But the motes really came from without. They also passed with freedom through a variety of ethers and alcohols placed in the flask F. In fact, it requires long-continued action on the part of an acid first to *wet* the motes and afterwards to destroy them. By carefully passing the air through the flame of a spirit-lamp or through a platinum tube heated to bright redness, the floating matter was sensibly destroyed. It was therefore combustible, in other words, *organic* matter*. I tried to intercept it by a large respirator of cotton-wool tied round the end of the tube $t\,t'$. Close pressure was necessary to render the wool effective. A plug of the wool rammed pretty tightly into the tube $t\,t'$ was finally found competent to hold back the motes. They appeared from time to time afterwards and gave me much trouble; but they were invariably traced in the end to some defect in the purifying-apparatus,—to some crack or flaw in the sealing-wax used to render the tubes air-tight. Without due care, moreover, liquid particles may also be carried mechanically over. To prevent the entrance of such into the experimental tube, the narrow conduit which connects it with the flask F is plugged with clean asbestos. Thus through proper care, but not without a great deal of searching out of disturbances, the experimental tube, even when filled with pure air or vapour, contains nothing competent to scatter the light. The space within it has the aspect of an absolute vacuum.

An experimental tube in this condition I call *optically empty*.

Here follows one of the numerous experiments executed in relation to this subject. A platinum tube 9 inches long, 0·4 of an inch wide, and having within it a roll of platinum gauze, was placed in a gas-furnace where it could be intensely heated. One end of this tube was connected with the entry stopcock of the experimental tube S S′, fig. 1, the other end was open to the air of the laboratory. The air was sent first through the platinum tube cold, then through the same tube heated to various degrees of redness, into the experimental tube, where it was subjected to the scrutiny of the concentrated electric beam. Here are the results.

Quantity of air.	State of platinum tube.	State of experimental tube.
15 in. of mercury.	Cold.	Full of floating particles.
15 „	Red-hot.	Optically empty.
15 „	Cold.	Full of floating particles.
15 „	Red-hot.	Optically empty.
15 „	Intensely heated.	An exceedingly fine cloud, which discharged perfectly polarized blue light in a direction at right angles to the illuminating beam.

* Mr. Dancer has recently examined microscopically the dust of Manchester, and found it to consist almost wholly of organic particles.

Here the character of the floating matter is very clearly shown. The non-combustible or inorganic part of it was too minute to be revealed by the concentrated beam. The tube after its combustion appeared "optically empty."

The "blue cloud" just referred to was due to the too rapid passage of the air through the intensely heated tube, which prevented the perfect combustion of the floating matter. It was to all intents and purposes the *smoke* of the particles*. The subject is further illustrated by the following series of experiments:—

Quantity of air.	State of platinum tube.	State of experimental tube.
15 inches.	Cold.	Full of particles.
15 „	Dull red.	Optically empty.
15 „	Intensely heated.	Optically empty.
30 „	Intensely heated.	Optically empty.
15 „ (admitted quickly).	„	A perfectly polarized blue cloud.
15 „ (quickly).	Barely visible redness.	Particles.
15 „ (quickly).	Intensely heated.	Blue cloud.
15 „ (slower).	„	A very fine blue cloud.
15 „ (very slow).	„	Optically empty.
15 „	Cold.	Full of particles.
15 „ (quickly).	Red-hot.	Blue cloud.

The polarization of light by such clouds as the blue ones here mentioned will receive due attention subsequently.

A remarkably fine experiment may be thus made:—Placing a spirit-lamp underneath the cylindrical beam of the electric lamp as it marks its track upon the illuminated dust of the atmosphere, torrents of what would be infallibly mistaken for black smoke rise from the flame into the beam. A Bunsen's flame produces the same effect. But the action of a red-hot poker placed underneath the beam is precisely similar; the action of a hydrogen flame, moreover, where smoke is out of the question, is not to be distinguished from that of the spirit-lamp flame. The apparent smoke rises even when the flame or the poker is placed at a good distance below the beam. The action is really due to the destruction of the floating matter by contact with the heated body. It sends upwards streams of air from which every thing competent to scatter the light has been removed. This air, in passing through the beam, jostles aside the illuminated particles, the space it occupies being *black* in contrast with the adjacent luminosity. The experiment is capable of various instructive modifications, and may of course be executed with sunlight.

It is needless to dwell upon the possible influence of the floating organic matter of the air upon health. Its quantity, when illuminated by a powerful and strongly concentrated beam, appears sometimes to be enormous. One recoils from the idea of placing the mouth at the intensely illuminated focus and inhaling the swimming dirt revealed there. Nor

* In subsequent experiments I found that this "smoke" arose in great part from the action of the heated air upon the india-rubber joint which connected the platinum tube with the experimental tube.

is the disgust removed by the reflection that at a distance from the focus, though we do not see the dirt, we are breathing precisely the same air. The difficulty of wetting it before referred to, may render this suspended matter comparatively harmless to the lungs, but where these are fragile its mere mechanical irritation must go for something. Perhaps a respirator of cotton-wool might in some cases be found useful*.

§ V.

I now return to the nitrite of amyl. The action of light upon the vapour of this substance is exceedingly prompt and energetic. It may be illustrated by simply blowing the vapour into a concentrated sunbeam. Or the experiment may be made to take the following form:—Connecting the tube *b* of the flask F with the pipe of a bellows, after inflating the latter a sharp tap upon its board sends a puff of vapour through the tube *a* into the air. In a moderately lighted space nothing is seen; but when the puff is projected into a concentrated sunbeam, or into the beam from the electric lamp, on crossing the limiting boundary of light and shade it is instantly precipitated as a *white ring*. The ring has of course the same mechanical course as the smoke-rings puffed from the mouth of a cannon, but it is *latent* until revealed by actinic precipitation†.

In every one of the numerous experiments made with the nitrite of amyl, the chemical energy appeared to exhaust itself in the frontal portion of the experimental tube. A dense white cloud would fall for a distance of 12 or 15 inches upon the beam, while beyond this distance the tube would appear almost empty. This absence of action might naturally be ascribed to the diffusion of the beam beyond the focus; but when the light was so converged as to bring the focus near the distant end of the tube the effect was the same. When, moreover, a concave mirror received a parallel beam which had traversed the tube, and returned it into the vapour in a high state of luminous concentration, the light was ineffectual. The passage of the beam through a comparatively small depth of the vapour appeared to extract from it those constituents which produced decomposition. That the vapour was present at the distant end of the tube, was proved by the fact that both with the sun and with the electric light the reversal of the tube instantly brought down a heavy cloud. As regards the chemical rays nitrite of amyl is the *blackest* substance that I have yet encountered. It rapidly extinguishes them, leaving behind a beam of sensibly undiminished photometric intensity, but powerless as a chemical agent as far as the nitrite is concerned.

In these experiments air was employed as the vehicle of the nitrite-of-amyl vapour. By varying the quantity sent into the experimental tube, it was possible to vary in a remarkable manner the character of the resulting decomposition. The most splendid diffraction colours could be thus produced, and the finest texture could be imparted to the clouds. When pure oxygen or pure nitrogen was used, the effect was almost the same

* Since this paper was forwarded to the Royal Society these experiments have been greatly extended. See Proceedings of the Royal Institution, January 1870.—[J. T., July 1870].

† By a special arrangement it is easy to obtain such rings 2 inches and more in diameter.

as with air. With hydrogen the clouds appeared more delicate and lustrous; and they sometimes fell immediately after their formation in nebulous festoons to the bottom of the tube. This doubtless is to be ascribed to the attenuation of the atmosphere in which they floated. In many cases, however, the particles remained suspended, and some of them continued to float even after the tube had been so far exhausted as to produce a tolerably good air-pump vacuum.

An additional effect of considerable beauty and interest is obtained in the following way. Permitting the convergent beam to play for a time upon the mixture of air and nitrite-of-amyl vapour, or, better still, upon mixture of hydrogen and vapour, a coarse cloud is formed. Suspending the action of the lamp for a minute or so, a new distribution of the vapour appears to occur; for, on reigniting the lamp, along its convergent beam, and *within* the old cloud, a new cloud is precipitated. The tint of this new cloud is a delicate bluish white, and its texture is of exquisite fineness. This precipitation of one cloud within another may be obtained a dozen times in succession. Or, permitting a parallel beam to pass for a time through the coarser cloud, on pushing out the lens so as to concentrate the light, the fine cloud comes suddenly down upon the beam about its place of greatest concentration. This effect also may be obtained several times with the same charge of vapour.

No phenomena of the kind thus far described have, I believe, been hitherto observed. The necessary conditions for their production are, first, that the light should decompose the vapour, and secondly, that one or more of the products of decomposition should either be a solid, or should possess a boiling-point so high as to ensure its precipitation when set free.

For though chemical action might occur, and be even energetic, if the products of decomposition be vaporous and colourless they will remain unseen. In the case just considered, the *nitrate* of amyl is in all probability a product of the decomposition of the *nitrite*. The boiling-point of the latter is estimated at from 91° to 96° C., that of the former being 149° C. The nitrite, therefore, can maintain itself as true vapour in a space where the nitrate, at the moment of its liberation, must fall as a cloud.

§ VI.

An exceedingly fine example of actinic action is furnished by the vapour of the iodide of allyl. The effect of light upon this substance was observed on the 7th of October, 1868, but I did not then know the meaning of the "thin cloud like a kind of smoke" which showed itself in the experimental tube. On satisfying myself regarding the deportment of nitrite of amyl, the iodide of allyl occurred to me, and on it experiments were immediately made.

The decomposition of this vapour was slower than that of the nitrite of amyl. The slowness, moreover, augmented rapidly as the quantity of vapour was diminished. When only a few inches of the mixed air and vapour were in the experimental tube the action was very slow. The clouds were formed both in oxygen and in air. After the

action had been continued for some time, the fine purple colour of iodine exhibited itself at the end of the tube most distant from the source of light. When hydrogen was the vehicle, the clouds were particularly lustrous and beautiful. Here and there also, amid the white and coarser sections of a cloud, spaces of delicate blue would reveal themselves, reminding one of the colour of a pure sky. The words "wonderful," "beautiful," "lustrous," and others of a similar nature, occur frequently and naturally in my notes of this period; for in those earlier experiments the cloud-forms obtained were so amazing, and their colours and textures so fine, as to rivet attention upon them alone.

With long-continued action the colour due to the discharge of iodine became very intense. It was strong enough to empurple the beam which passed through the air of the laboratory after its transmission through the experimental tube, and to colour deeply a white screen on which the beam was permitted to fall. In what condition was this iodine? It could be liberated by a beam deprived almost wholly of its calorific rays. The temperature of the experimental tube was indeed so moderate that a quantity of iodine placed within it and permitted to saturate the space with its vapour, produced a barely perceptible flush on a piece of white paper placed there expressly to detect it. The far more deeply coloured iodine revealed by the beam in the actinic cloud must, I think, have been for the most part liquid, and not vaporous iodine. I say liquid, because the substance was probably dissolved by the particles of the cloud with which it was so intimately mixed. Di-allyl, for example, is a powerful solvent of iodine, and it was probably one of the products of decomposition.

The iodide of isopropyl also capitally illustrates the action of light upon vapours. It is more slowly acted upon than either the nitrite of amyl or the iodide of allyl; nevertheless, in sufficient quantity, its decomposition is very brisk and energetic. Purified air which had bubbled through the liquid iodide was conducted into the experimental tube. When the pressure was 1 inch of mercury, the light playing upon the vapour for five minutes produced no action; but when it was 10 inches a blue cloud made its appearance in two minutes, and in ten minutes it had almost filled the tube. When the pressure was 20 inches, the action commenced more quickly, and the cloud generated was more dense. The whirling motions of this cloud appeared to be more brisk than that of the others examined. With 30 inches of the mixed air and iodide the action began in a quarter of a minute, and in five minutes a dense cloud was formed throughout the tube. The purple of the discharged iodine was also very plain in this cloud.

§ VII.

In the preliminary notice of these experiments laid before the Royal Society in June 1868, considerable stress is laid upon the fact that the same rays are absorbed by the nitrite of amyl in the liquid and in the vaporous state. A layer of the liquid not more than one-eighth of an inch in thickness was found competent to withdraw from a powerful beam all the constituents which could effect the decomposition of its vapour. The action of the nitrite resembles in this respect that of the sulphate of quinine on the rays which

cause it to fluoresce. Both substances quench the effectual rays close to the surface at which they enter.

I endeavoured at the time to apply this fact to the solution of the question whether the absorption of chemical energy was the act of the molecule as a whole, or of its constituent atoms. I tried to show that on the first of these assumptions it is impossible for the self-same rays to be absorbed by a liquid and its vapour. For absorption depends upon the rate of molecular vibration, and reaches its maximum when this rate synchronizes perfectly with the rate of succession of the ethereal waves. Now as the rate of molecular vibration depends upon the elastic forces exerted between the molecules, and as it could hardly be imagined that these forces would remain undisturbed during the passage of a vapour to the liquid condition, the fact of the liquid nitrite of amyl and its vapour absorbing the same rays indicated that the absorption was not molecular. We were thus driven to conclude that it was atomic*; and this conclusion was fortified by the consideration already adverted to,—that were the absorption the act of the molecule as a whole, no mechanical ground could be assigned for the falling asunder of its atoms. Thus actinic action itself pointed out the seat of the absorption.

A wide, if not entire generality was anticipated for the proposition that the same rays are absorbed by a liquid and its vapour. I have now no reason to retract this anticipation; but when it was expressed I believed that liquids in general would be found so destructive of the effectual rays as to render transmission through moderate depths of them sufficient to rob a beam of all power to act upon their vapours. This idea, entertained though not expressed, has not been verified, and the deportment of iodide of allyl may be taken as representative of a class of facts which contradict it.

Glass cells were employed varying from one-eighth of an inch to an inch in width. Filled with the transparent iodide, these cells were placed between the electric lamp and the experimental tube charged with the iodide vapour. The rays after traversing an inch of the liquid produced copious decomposition in the tube. A marked distinction was thus proved to exist between the liquid iodide of allyl and the liquid nitrite of amyl.

But the same distinction extends to their vapours. The exceeding absorbent avidity of the nitrite-of-amyl vapour, and the rapidity with which it deprives a powerful beam of its effective constituents, have been already noticed. It is quite different with the iodide of allyl. A tube 5 feet long was charged with the iodide vapour, and after it, in the same line, was placed another tube 3 feet long charged with the same vapour. On sending a beam through both tubes in succession, the 5-foot tube, through which the light first passed, was filled immediately with an actinic cloud; but a similar cloud was at the same time falling in the second tube. A transmission through 5 feet did not seem to

* When I use the word "atomic" in contrast with "molecular," I by no means pledge myself to an absolute limit of divisibility. The molecule may resemble a house, the atoms the hard bricks composing that house. But while it is both convenient and correct to regard the house as constituted of bricks definitely bounded, it is by no means essential to regard the bricks themselves as absolutely indivisible. The divisibility or non-divisibility of the atoms does not in the least affect the atomic theory as a *working conception*.

diminish very materially the power of the beam. A passage through 1 foot of the nitrite of amyl would have been far more destructive.

As these actions are representative and, I believe, important, I will here sum up some recent confirmatory experiments executed with the two substances now under consideration.

1°. The vaporous nitrite of amyl absorbs with such avidity the rays competent to decompose it, that a very small depth of the vapour quenches the efficient rays of a powerful beam of solar or electric light.

2°. The vaporous iodide of allyl, on the contrary, permits a beam to traverse it for long distances without very materially diminishing the chemical power of the beam.

3°. The liquid nitrite of amyl, in a stratum one quarter of an inch thick, quenches all the rays which could act chemically upon its vapour.

4°. The liquid iodide of allyl, on the contrary, in a stratum of four times the thickness just mentioned, does not materially diminish the power of the beam to act upon its vapour.

5°. A very marked difference exists between the deportment of the nitrite of amyl alone, and its deportment when mixed with hydrochloric acid. The *chemical penetrability* of the mixture is far greater than that of the pure vapour. The actinic cloud, which with the vapour alone is confined to the anterior portion of the experimental tube, extends in the case of the mixture through the entire tube.

6°. A beam, moreover, which has been transmitted through a quarter of an inch of the liquid nitrite is also competent to act chemically upon the mixture, and to produce in it dense actinic clouds.

The action in this last case, though not stopped by the liquid nitrite, is retarded. Employing first the liquid screen, it was interesting to observe the sudden development of a fine-grained luminous cloud, and its violent tumbling about by the decomposing beam the moment the liquid was withdrawn. The action of a solution of the yellow chromate of potash is substantially the same as that of the liquid nitrite. By the successive introduction and removal of a cell containing either substance, successive flashes of actinic energy may be produced a dozen times and more in the same vapour.

The molecular relationship of a liquid and its vapour receives new illustration from these experiments. Whatever alters the action of the one appears to change in a proportionate degree the action of the other.

§ VIII.

Carbonic acid is decomposed by the solar beams in the leaves of plants; but here it is in presence of a substance, chlorophyll, ready, as it were, to take advantage of the loosening of the atoms by the solar rays. The present investigation has furnished numerous cases of a similar mode of action. All the vapours examined may be more or less powerfully affected in their actinic relations by the presence of a second body with which they can interact. The presence, for example, of nitric acid, or of hydrochloric

acid, may either greatly intensify or greatly diminish the visible action of the light on many vapours decomposable alone or when mixed with air; while the presence of the one or the other of the same acids may provoke energetic actions in substances which are wholly inactive when left to themselves.

We need not go beyond the nitrite of amyl for an example of this kind. For, prompt and copious as the decomposition of this substance is when mixed with air, the energy and brilliancy of the action are materially augmented by the presence of hydrochloric acid. Let a quantity of the nitrite vapour mixed with air be sent into the experimental tube till the mercury column sinks, say, 8 inches. Then let the flask containing the nitrite be removed and one containing strong hydrochloric acid be put in its place. Let purified air which has bubbled through the acid be carried into the experimental tube until a further depression of 8 inches is obtained. On allowing the convergent beam to play upon this mixture a cloud of extraordinary density and brilliance is precipitated. The beam appears to pierce like a shining sword the nebulous mass of its own creation, tossing the precipitated particles in heaps right and left of it. This experiment is very easily made, and nothing could more finely or forcibly illustrate the phenomena here under consideration.

By varying the proportions of the vapour to the acid we vary the effects. For example, the proportion of 1 inch of the nitrite vapour to 15 inches of the hydrochloric acid did not produce so brilliant an effect as the proportion 8 : 8. The same is true of the proportion 15 inches of nitrite vapour to 1 inch of hydrochloric acid. But in this latter case, though the general action was less intense than in the case of 8 : 8, the iridescences due to diffraction were much finer. No doubt for each particular substance a determinable proportion exists which corresponds to the maximum of actinic action*.

The nitrite of butyl affords another striking example of the influence of a second body in the experimental tube. With air, or alone, it was not visibly affected by the light; there was no cloud formed by its exposure. It was also mixed with nitric acid in various proportions, but no visible effect was produced by the beam.

It was then tried with air which had been permitted to bubble through pure hydrochloric acid in the following proportions:—

1. 1 inch of air and vapour to 15 inches of air and acid.
2. 8 inches „ „ 8 „ „
3. 15 inches „ „ 1 inch „ „

In the first case a dense and brilliant cloud was immediately precipitated. In the second case the precipitation of the fine white cloud was confined to the convergent luminous cone, coarser particles being scattered through the rest of the tube. In the third case the cloud was very coarse and very scanty. The experiment indicates that the best effect is obtained when a small quantity of the vapour is mixed with a considerable quantity of the acid.

Benzol is also a good example of a substance which, when alone, defies the power of

* This might form the subject of an interesting inquiry.

the light, but which in the presence of other substances is readily decomposed. During the earlier stages of this inquiry a vast number of experiments were made with benzol and *commercial* hydrochloric acid. The results well illustrate actinic action, but they are not to be accepted as indicative of the action of *pure* hydrochloric acid. Indeed with the pure acid and benzol vapour there is no visible action.

On the 16th of November, 1868, 2 inches of air and benzol vapour were sent into the experimental tube, and afterwards the tube was filled with air which had bubbled through the commercial acid. My notes, written at the time, describe the action of light upon the mixture as producing a cloud of an exquisite sky-blue colour, only more luminous and ethereal than the sky. The figure of the cloud was also very wonderful.

This cloud was permitted to remain for fifteen hours in the experimental tube uninfluenced by light. After this interval it was found still floating, being composed of curiously shaped granular sections joined together by others of more delicate hue and texture. The renewed light set the cloud immediately in motion, the granular parts disappeared, and the whole for a length of 18 inches resumed its primitive delicate hue and texture. In some portions it became white or whitish grey, but at others it was a pure firmamental blue. It became very dense as the light continued to act, and finally developed itself into a form of astonishing complexity and beauty.

The experimental tube had then a current of dry air swept through it, and it was afterwards exhausted. 2 inches of the benzol vapour were admitted as before, and dry air was added until the tube was full. It required five minutes' action of the light to develope the faintest visible cloud; even after ten minutes' action the cloud was very faint*. The tube was again cleansed and exhausted, 2 inches of the benzol vapour were admitted, followed by air and hydrochloric acid until the tube was full. On starting the light chemical action began almost immediately, and ended by the formation of a cloud throughout the tube. The influence of the commercial hydrochloric acid is here demonstrated. The interaction of nitric acid and benzol will be immediately referred to.

Bisulphide of carbon is also an illustration in point. Alone or mixed with air it resists the action of the light; in the presence of hydrochloric or of nitric acid it is responsive to that action. On the 17th of November, 1868, for example, the pure vapour was admitted into the experimental tube until a depression of 2 inches of the mercury column was observed. A powerful light was permitted to act for twelve minutes upon the vapour, but no action was observed. A quantity of air which had passed through aqueous hydrochloric acid was then admitted into the tube. Six minutes subsequent action of the light developed a cloud of considerable density. Toluol and other substances might here be mentioned in further illustration of this mode of decomposition. But I pass over hundreds of these earlier experiments which were made chiefly to instruct myself and to secure me from error. Some definite results will be given further on.

* It was certainly due to a residue of the previous charge.

§ IX.

I have now to introduce, though only for partial treatment, a subject which might with advantage be kept isolated, but which is so mixed up with my notes of 1868 as to be inseparable from the descriptions of chemical action which they contain. I refer to the blue colour always exhibited at the birth of clouds obtained from small quantities of vapour in the case of active substances, and often from large quantities in the case of substances of slow decomposition. The first distinct record of this appearance occurs in my notes for the 10th of October, 1868. On the 9th I had been engaged upon the iodide of allyl with reference to its interaction with hydrochloric acid. Small quantities only of the vapour had been employed; and it was found that when the acid was fresh and strong the action was vigorous, that it declined in energy as successive charges of dry air were sent through the acid, becoming vanishingly feeble on the fifth filling of the experimental tube.

On the morning of the 10th the tube used on the preceding day was washed with distilled water, and swept out by a current of dry air. A mixture of air and hydrochloric acid was then sent into it, no vapour of any kind being employed. When the light first passed through it, and for some time afterwards, the experimental tube appeared perfectly empty. Slowly and gradually, however, upon the condensed beam a cloud was formed which passed in colour from the deepest violet, through blue, to whiteness. To this record of my note-book the remark is added, "connect this blue with the colour of the sky."

In fact it was impossible to avoid seeing the relationship of both. Previous to this entry the blue had attracted my attention. It was unfailing it its appearance when the action was slow. The blue colour was in all cases the herald of the denser actinic cloud. I took a pleasure in developing it in connexion with general actinic action, and in determining whether in all its bearings and phenomena the blue light was not identical with the light of the sky. This to the most minute detail appears to be the case. The incipient actinic clouds are to all intents and purposes pieces of artificial sky, and they furnish an experimental demonstration of the constitution of the real one.

Reserving the fuller discussion of the subject for a subsequent paper, it may be stated in a general way that all the phenomena of polarization observed in the case of skylight are manifested by these blue actinic clouds; and that they exhibit additional phenomena which it would be neither convenient to pursue, nor perhaps possible to detect, upon the actual firmament. They enable us, for example, to follow the growth and modification of the phenomena of polarization from their first appearance in the barely visible blue, to their final extinction when the cloud has become so coarsely granular as no longer to scatter polarized light.

These changes, as far as it is now necessary to refer to them, may be thus described.

1°. The incipient cloud, as long as it continues blue, discharges polarized light in all directions, but the direction of *maximum* polarization is at right angles to the direction of the illuminating beam.

2°. As long as the colour of the cloud remains distinctly blue, the light discharged from it normally is *perfectly polarized*; this light may be utterly quenched by a Nicol's prism, the cloud from which it issues being caused to disappear. Any deviation of the line of vision from the normal enables a portion of the light to reach the eye in all positions of the prism.

3°. The plane of polarization of the perfectly polarized light is parallel to the direction of the illuminating beam. Hence a plate of tourmaline with its axis parallel to the beam stops the light, and with its axis perpendicular to the beam transmits it.

4°. A plate of selenite placed between the Nicol and the cloud shows the colours of polarized light, and as long as the cloud continues blue these colours are most vivid in the direction of the normal.

5°. The particles of the incipient cloud are immeasurably small, but they gradually grow in size, and at a certain period of their growth cease to discharge perfectly polarized light. For some time afterwards the light that reaches the eye, when the Nicol is in its position of minimum transmission, is of a magnificent blue colour. It is called in the following pages the *residual blue*.

6°. Thus the waves *that first feel the influence of size*, both at the minor and major polarizing limits of the growing particles, are the smallest waves of the spectrum. These waves are the first to accept polarization and the first to escape from it.

7°. As the actinic cloud grows coarser in texture the direction of maximum polarization changes from the normal, enclosing an angle more or less acute with the axis of the illuminating beam.

8°. In passing from section to section of the same cloud the plane of polarization often undergoes a rotation of 90°. In the following pages this is designated as a change from positive to negative polarization, or the reverse.

§ X.

The experiments on benzol vapour and hydrochloric acid now to be described are of interest on optical rather than on chemical grounds. They were preceded by other experiments in which the vapour was mixed with nitric acid, and a minute residue of the latter lingering in the experimental tube may have influenced the results. The hydrochloric acid employed, moreover, was the commercial acid, and could not be regarded as pure. Thus though the decomposition of *a* vapour was certain, that it was not the pure vapour of benzol mixed with pure hydrochloric acid gas may be taken for granted. Indeed other experiments executed with the pure acid reduced the action to nil.

Dry air charged with the benzol vapour was permitted to enter the tube till a depression of *one inch* of the mercurial column was obtained; half an atmosphere of air charged with hydrochloric acid was then added. The action of light on this mixture was very powerful. The tube was for a moment optically empty, but its transparent contents were immediately shaken into a dense and luminous cloud. The normal polarization was here feeble, the oblique strong; the selenite colours in the former case were weak,

in the latter brilliant. When the line of vision was transverse, the colours seemed mainly limited to red and green.

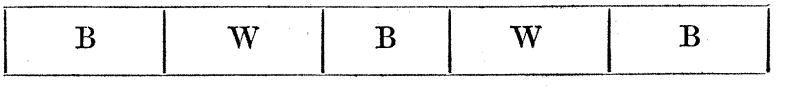
The tube was swept with dry air and exhausted. *Half an inch* of air and benzol vapour was admitted, and after it half an atmosphere of air and hydrochloric acid. A fine blue colour soon appeared, and as long as it continued the direction of maximum polarization was along the normal. But a luminous white cloud was rapidly generated, the normal polarization becoming feeble and the oblique strong. The distant end of the cloud, however, continued blue, and in passing from it to the white cloud the plane of polarization changed 90°.

The tube was again exhausted, and *a quarter of an inch* of air and benzol vapour was permitted to enter it, followed by a quarter of an atmosphere of air and hydrochloric acid. The incipient cloud showed an exceedingly fine blue, the polarization along the normal being a maximum. The cloud gradually thickened at the centre, and finally the polarization there disappeared. As before, when the normal polarization became feeble the oblique became strong.

The tube was once more cleansed and *one-tenth of an inch* of air and vapour was admitted, followed by one-tenth of an atmosphere of hydrochloric acid and air. The blue of the incipient cloud was here superb, and it lasted longer than in the last case. The selenite tints produced by the normally polarized light were exceedingly brilliant; but they faded gradually as the cloud passed from blue to whitish blue. At the centre of the cloud the normal polarization first fell to nil and then reappeared, having changed, however, from positive to negative, the two ends remaining as before. The influence of attenuation on the production of the blue colour is here strikingly exemplified.

The tube containing the benzol vapour was again cleansed and exhausted, and the last experiment was repeated. That is to say, one-tenth of an atmosphere of the air and vapour was mixed with one-tenth of an atmosphere of hydrochloric acid. After ten minutes' action the actinic cloud was found divided into five segments, alternately blue and white. Every two adjacent segments of the cloud were oppositely polarized, being divided from each other by a section of no polarization. The rectangle (fig. 2) represents the several divisions of the cloud; the letters B and W denoting the blue and white segments respectively. The transverse lines represent the neutral sections.

Fig. 2.



On the 9th of December, 1868, some experiments were made with the nitrite of butyl which merit a passing notice.

Atmospheric air was permitted to bubble through the nitrite until the experimental tube was quite filled with the mixture. Fifteen minutes' exposure produced a very slight action, an exceedingly scanty and coarse precipitate being formed. When due care is taken the action entirely disappears.

1 inch of the mixed air and vapour was now admitted into the experimental tube, and after it half an atmosphere of air which had bubbled through aqueous hydrochloric acid. The instant the beam passed through the experimental tube an intensely white cloud was precipitated.

The tube being cleansed, one-tenth of an inch of the nitrite and air, followed by one-tenth of an atmosphere of air and hydrochloric acid, was sent into it. The blue of the incipient cloud was in this instance perfectly superb. The polarization at right angles to the beam was perfect, and the selenite colours exceedingly vivid. As the cloud thickened the polarization along the normal disappeared, but it became strong obliquely. Two neutral points were observed *by oblique vision* in the case of this cloud. This effect is not uncommon.

The tube was withdrawn from the light for six minutes; on reexamination the cloud was found to have lost its beauty of form; and now the cloud-centre, by normal vision, polarized the light in a plane opposite to that of the two ends.

Twelve bubbles of the air and nitrite vapour were then sent into the exhausted experimental tube, and after them thirty-six bubbles of air and hydrochloric acid; several minutes' exposure produced no action. 3 inches of hydrochloric acid were then added, and the same superb blue as that noticed in the last experiment soon made itself manifest. It faded gradually as the cloud became more dense, and finally merged into whiteness.

The mixture of nitrite of amyl and hydrochloric acid was also examined in small quantities; but though the blue was fine, it had not the splendid depth and purity of the colour obtained with the nitrite of butyl.

§ XI.

The whole of the autumn of 1868 was devoted to the investigation from which I have taken the foregoing brief extracts. During this period 100 different substances must, I think, have been subjected to examination, and in the case of many of them the experimental tube must have been exhausted and refilled from 50 to 100 times. In some instances, indeed, the largest of these numbers falls considerably short of the truth. For a time I had no notion of the delicacy of the inquiry, nor of the caution required to prevent the action of infinitesimal residues and impurities from being mistaken for the decomposition of substances really inert. The necessity of thoroughly cleansing, or renewing, every tube and every stopcock, on passing from one substance to another, became gradually apparent. Water, alcohol, caustic potash, and acids were successively employed to cleanse the experimental tubes; but the method found most convenient, and that finally adopted, consists in the thorough lathering and sponging out of the tubes with soft soap and hot water, and the flooding of them with pure water afterwards. They are then dried with clean towels, and finally polished by the passing to and fro within them, by means of a ramrod, of a clean silk handkerchief. The stopcocks are cleansed by suitable brushes; fresh cocks, a fresh tube, and a fresh plug of asbestos being employed for each fresh substance.

From the draft of the present memoir, written last February, I take a few notes indicative of the difficulties caused by small impurities. Wishing to set my mind at rest with regard to nitric acid and hydrochloric acid, I operated for a time upon these substances unmixed with any vapour. 15 inches of air which had been permitted to bubble through aqueous nitric acid were sent into the experimental tube. The decomposing beam was first sent through a stratum of the liquid acid an inch in thickness. It screened the vapour effectually; no visible decomposition was produced. In this case, at the beginning of the experiment, there were a few scattered particles in the tube.

The cell containing the liquid acid was removed, and a minute afterwards a delicate blue colour began to shed itself among the floating particles. It augmented in intensity for five minutes, but during that time it could be entirely quenched by the Nicol, the particles floating in the blue being left intact.

These floating particles (mechanically carried in) extended only about 6 inches down the experimental tube. Beyond them was a streak of fine actinic blue perfectly polarized, and beyond this again a dusky grey cloud, which showed no trace of polarization.

After ten minutes' action the cloud had assumed a fair density, but it suggested doubts whether it was due purely to the nitric acid or to the interaction of the acid and some accidental impurity. The experiment was repeated four times with substantially the same result. In all cases the beam when passed through the liquid acid proved powerless; but always on the removal of this screen, or on displacing it by a cell of water, an action was manifested. To all appearance the nitric acid alone generated an actinic cloud.

The experiments, however, did not quite set my mind at rest. The tube was cleansed and the stopcocks heated to redness. When subsequently exposed the nitric acid required a much longer time to develope a cloud. After five minutes' exposure with no cell interposed the faintest blue cloud was visible. After ten minutes' exposure the cloud, at first seen with difficulty, was evident for some distance down the tube. By the complete removal of residues and by strict attention to the cerate employed to make the tubes air-tight, the action thus lessened was caused finally to disappear. In each of the experiments with nitric acid recorded in the following pages the acid itself was first tried, and not until its perfect visible inertness had been proved was it permitted to mix with the vapour.

I also wished to set my mind at rest regarding the action of hydrochloric acid. Several experimental tubes were sponged with soap and hot water, washed with alcohol, and finally flooded with hot water. They were then thoroughly dried and mounted. On a first trial most of them showed a feeble actinic action, which on a second trial usually disappeared. In one case the light generated a fine blue cloud which stretched throughout the entire length of an experimental tube 3 feet long. One whitish spot only of the cloud discharged imperfectly polarized light. The cloud could be utterly quenched by the Nicol, with the exception of a small patch of residual blue about 2 inches long, which was left curiously suspended in the general darkness of the tube.

On thoroughly cleansing with dry air the tube containing the cloud, and trying the

acid a second time, an exposure of twenty minutes was found to produce no action. This and many other similar experiments demonstrate the inertness of pure hydrochloric acid. The inert acid of the foregoing experiment was permitted to remain in the experimental tube all night. Next morning, when the beam was permitted to play upon it, a blue streak became visible in less than a minute. In ten minutes the tube was filled with a delicate cloud. This was an almost every-day occurrence at the time here referred to. There must have been something in this tube in the morning which was not there on the preceding night. An infinitesimal residue had crept out of the stopcocks, or the hydrochloric acid had acted on the cerate employed to render the tube air-tight.

And here I would allude in passing to an effect which at a future stage of this inquiry will be found suggestive of the mechanism by which the complex cloud-forms are produced. I touched the top and bottom of the experimental tube for a moment with my two fingers; the cloud, which was of exceeding lightness, immediately showed responsive convection. It was wonderfully sensitive to the slightest local change of temperature. Once started in this simple way the motions of the cloud went on, and ended in the development of a splendid cloud-figure.

The influence of a minute residue is also strikingly illustrated by the following fact. 15 inches of mixed hydrochloric acid and air, exposed for fifteen minutes to a powerful beam, showed not the slightest trace of action. A small pellet of bibulous paper, not half the size of a pea, was moistened with the iodide of allyl. I held the pellet between my fingers till it became almost dry, then inserted it into a connecting piece, and sent a little air over it into the experimental tube. On stopping the flow of air a blue cloud began to form immediately, and in five minutes the rich colour had extended quite through the experimental tube. This cloud was 3 feet long and discharged a good body of light, but for some minutes it could be completely quenched by the Nicol. At the end of fifteen minutes a white massive cloud filled the experimental tube. Considering the amount of matter concerned in the production of this nebula, it seemed like the development of a cloud-world out of nothing.

But this is not all. The pellet of bibulous paper was removed, and the experimental tube was cleansed by allowing a current of dry air to sweep through it. *The current passed through the connecting piece in which the pellet of bibulous paper had rested.* The supply of air was at length cut off and the experimental tube exhausted. 15 inches of hydrochloric acid were sent into the tube through the same connecting piece. It is here to be noted, 1°, that the whole quantity of iodide of allyl absorbed by the pellet was exceedingly small; 2°, that I had allowed almost the whole of this small quantity to evaporate; 3°, that the pellet had been cast away and the tube in which it had rested had been rendered the conduit of a strong current of pure air. It was such a residue as could linger after all this in the connecting piece that was carried by the hydrochloric acid into the tube, and there acted on by the light.

A minute after the ignition of the lamp chemical action declared itself by the forma-

tion of a faint cloud. It appeared first at the focus. In a couple of minutes more a faint blue, perfectly polarized along the normal, filled the anterior portion of the tube. The blue also extended from the place of most vigorous action down the tube. An amorphous cylinder of cloud soon filled the first 10 inches of the tube, and pushed gradually down it. It was followed by a complicated cloud-figure, and it again by a vase-shaped nebula fainter than either. At the end of fifteen minutes a body of light, which, considering the amount of matter involved, was simply astonishing, was discharged from the cloud. In one position of the Nicol this cloud was a salmon-colour, in the other a blue-green. When a plate of tourmaline, with its axis parallel to the beam, was passed along in front of the cloud, at some places it showed a particularly vivid blue-green. When placed perpendicular at these places, the field of the crystal was a yellow-green.

I doubt whether spectrum analysis itself is competent to deal with more minute traces of matter than those revealed by actinic decomposition. I think it probable that if the weight of the cloud formed in this experiment were multiplied by trillions it would not amount to a single grain. Bodies placed behind it were seen undimmed through the cloud. The flame of a candle suffered no sensible diminution of its light. It was easy to read through the cloud a page which the cloud itself illuminated. In fact the cloud was a comet's tail on a small scale. It proved that matter of almost infinite tenuity is competent to shed forth light of similar quality, and in far greater quantity than that discharged by the tails of comets*.

These facts render the statement intelligible that even when all reasonable precautions appear to have been taken it is not easy to escape every trace of chemical action on first charging the experimental tube even with an inert substance. In my earlier experiments, when distilled water only was employed to cleanse the tube, the first experiment with air alone was sure to develope an actinic cloud of a beautiful fern-leaf pattern. And even now, after the most careful employment of the soft soap and hot water, the first charge of pure nitric, or of pure hydrochloric acid often developes a blue and exceedingly delicate actinic cloud. As regards the optical question, these irregular clouds exhibit some of the finest effects. One additional fact will illustrate a class of disturbances already touched upon. Pure nitric acid had been proved over and over again to exhibit no visible action; but after having demonstrated its inertness, a case occurred where it produced rather dense actinic clouds five times in succession. Indeed there seemed to be no end to their possible development. The only thing to which this change from inertness to activity could be ascribed, was a change in the cerate used to render the ends of the tube air-tight. On examination it was found that the infinitesimal effluvia yielded by the new cerate to the nitric acid was the sole cause of the anomaly. Nitric acid, then, produces no actinic cloud; hydrochloric acid produces no actinic cloud; air passed throughout potash and sulphuric acid produces no actinic cloud, no matter how powerful or how long-continued the action of the light may be.

* The action here referred to has been since developed into a formal hypothesis of cometary phenomena. I shall return to the subject.

I hoped during the present year to be able to go over again a vast amount of ground rendered debateable by the discovery of such irregular actions as those here recorded. An accident in the Alps has unfortunately disqualified me from doing this. But as I find that ardent workers have already entered this new field of inquiry, I think it right to lay before the Society this first part of my researches. I omit not only descriptions of the deportment but even the names of the vast majority of the substances with which I have experimented; confining myself to eight or ten closely examined and well-established cases of actinic decomposition, and putting aside for reconsideration all such matters as might vainly occupy the attention of the Society.

§ XII.

The vapours of the substances mentioned in this section were sent into the tube in the manner described in § III. They were mixed, in the proportions stated, with air which had been permitted to bubble through aqueous nitric acid, and the effect produced by exposure to the condensed beam of the electric lamp is in each case described.

Toluol ($C_7 H_8$):—A transparent colourless liquid.

Contents of experimental tube.

I. Air with toluol vapour . . . 1 inch; then
Air with aqueous nitric acid . 15 inches.

On igniting the lamp the experimental tube was optically empty.

After thirty seconds the track of the beam through the experimental tube became blue; the blue was about as pure as that of an ordinary cloudless sky in England. After two minutes the colour began to change to a whitish blue.

The light discharged normally by the blue cloud continued to be perfectly polarized for four minutes after the first appearance of the cloud. A rich residual blue was afterwards observed when the Nicol was in its position of minimum transmission.

At the end of ten minutes the residual colour was no longer blue, but bluish white. Hence the light which first exhibited perfect polarization, and which first escaped from perfect polarization, was blue.

At the end of fifteen minutes a very beautiful cloud-figure was developed. The denser portions of the cloud were very luminous.

II. Air and toluol vapour . . . 8 inches; then
Air and aqueous nitric acid . . 8 inches.

The experimental tube was optically empty for a moment at starting, but the action was so rapid that in two or three seconds the tube was filled with a heavy cloud. At the beginning the colour of the cloud was blue. The incipient cloud which whirled round the beam discharged for two or three seconds perfectly polarized light; but the perfection of the polarization ceased almost immediately.

The cloud for a time was divided from beginning to end into two longitudinal lobes, separated from each other by an apparently empty space about a quarter of an inch wide. When the cloud was looked at *obliquely* in a vertical plane, one of these lobes was found to polarize the light positively, the other negatively. In passing from the one to the other the selenite tints were reversed.

The quantity of light scattered by this cloud was very considerable; it brightly illuminated the walls and ceiling of the laboratory. As the cloud became denser, the central empty space, which at first divided it into two lobes, gradually disappeared.

Looked at *normally* the polarization of the one half of this cloud was positive, and that of the other negative. Between the two a neutral point existed. The oblique polarization of the dense cloud was strong.

III. Air and aqueous nitric acid . . 1 inch; then
Air and toluol vapour . . . . . 15 inches.

The action here was not so prompt as in the last case, nor was the cloud generated so dense. The cloud-particles, moreover, were coarser, and showed iridescent colours. Still the chemical action of the light was distinct and copious.

Looked at normally, a portion of this light was salmon-coloured. The selenite bands appeared to be of this colour, and its complementary greenish tint.

Bisulphide of Carbon (CS_2):—A transparent colourless liquid.

Contents of experimental tube.

I. Air and bisulphide-of-carbon vapour . 1 inch; then
Air and aqueous nitric acid . . . . 15 inches.

On starting the experimental tube was optically empty; but in a minute afterwards the track of the beam became blue, which was particularly deep and rich in the middle portion of the beam.

The blue light discharged normally was perfectly polarized, but the least deviation of the line of vision from the normal caused a portion of the light to pass through the Nicol.

The growth of this cloud and the gradual brightening and subsequent whitening of the blue were very instructive.

The light discharged normally remained perfectly polarized for seven minutes after the first appearance of the blue colour. A faint but rich residual blue was seen for some time afterwards.

The selenite colours were exceedingly vivid with this cloud. When, moreover, a plate of tourmaline was placed with the crystallographic axes parallel to the beam it was black; placed at right angles to the beam, a large portion of the light of the cloud was transmitted.

After ten minutes' exposure the cloud itself still showed a distinct trace of blue. The residual blue was then particularly rich and pure. After fifteen minutes the selenite colours were still vivid, though the cloud had then become greyish white.

II. Air and bisulphide-of-carbon vapour . . . . 8 inches; then
Air and aqueous nitric acid . . . . . 8 inches.

When the lamp was ignited the experimental tube was found optically empty; but the chemical action commenced three-quarters of a minute afterwards, the convergent beam assuming the appearance of a fine blue spear. The action was more energetic than in the last case, though the battery was sensibly sinking in power.

The light discharged normally remained perfectly polarized for two minutes after its first appearance. The selenite colours were rich and vivid, and the tourmaline in its two characteristic positions showed the same striking contrast observed in the last experiment.

In five or six minutes the entire tube was filled with cloud, the residual blue being then perfectly gorgeous.

III. Air and aqueous nitric acid . . . . 1 inch; then
Air and bisulphide-of-carbon vapour . 15 inches.

The tube was optically empty when the lamp was ignited. The chemical action soon commenced, a series of layers of blue cloud stretching through the entire tube. The action was less energetic than in the former cases, this being due in part to the sinking of the battery. The light discharged normally remained perfectly polarized for ten minutes.

Cyanide of Ethyl ($C_2 H_5 Cn$):—A transparent colourless liquid.

Contents of experimental tube.

I. Air and cyanide-of-ethyl vapour . . . . 1 inch; then
Air and aqueous nitric acid . . . . . 15 inches.

The tube was optically empty when the lamp was ignited. In a minute and a half the track of the beam became distinctly blue. The blue light was at first perfectly polarized.

The beam was crossed by a series of disks, which were denser and more whitish than the general mass of the cloud. The extinction of these disks by the Nicol was curious and interesting.

The growth of the particles in this case was so slow that the light emitted normally continued perfectly polarized for thirteen minutes after the first appearance of the cloud. A faint residual blue was afterwards developed.

II. Air and cyanide-of-ethyl vapour . . 8 inches; then
Air and aqueous nitric acid . . . 8 inches.

The experimental tube was optically empty for two seconds after the starting of the lamp; a fine blue colour was then observed upon the upper boundary of the convergent beam. The light emitted normally did not remain perfectly polarized for more than half a minute. In two minutes the tube was filled with cloud, the anterior portion being

white, and the posterior portion bluish. The posterior portion could be utterly extinguished by the Nicol long after the anterior portion had began to show a residual blue. Passing with the Nicol from the densest to the least dense portion of the cloud, the residual colour changed from a bright blue through a gorgeous Alpine skyblue to absolute extinction.

Looked at obliquely in a vertical plane, the two semicylinders into which the cloud was longitudinally divided were found in opposite states of polarization.

This was a truly splendid action. The chemical effect was exceedingly vigorous, and the cloud-form fine.

III. Air and aqueous nitric acid . . . . . 1 inch; then
Air and cyanide-of-ethyl vapour . . . . 15 inches.

On starting the light the experimental tube was found optically empty. In a quarter of a minute, however, the track of the beam, which previously had been invisible, was coloured blue. The chemical action appeared to exert itself with almost the same intensity throughout the entire length of the experimental tube.

For a brief interval the whole of the light emitted normally was polarized. Then for a time about three-fourths of the length of the cloud could be quenched by the Nicol, the remainder showing a fine residual blue. This sank from a brilliant azure at the densest portion of the cloud through deep rich blue to entire extinction.

The selenite bands were exceedingly vivid long after this cloud had ceased to be blue. An immense quantity of polarized light was discharged normally, even after the cloud had become white. Placed between the cloud and the eye, a plate of tourmaline with its axis parallel to the beam was practically black, while when placed across the beam a bright green light was copiously transmitted.

In one position of the Nicol this cloud was yellow, in the rectangular position it was blue. Here also the chemical action was very vigorous, and the cloud-form very fine.

Benzol ($C_6 H_6$):—A transparent colourless liquid.

Contents of experimental tube.

I. Air and benzol vapour . . . . . 1 inch; then
Air and aqueous nitric acid . . . 15 inches.

Nitric acid is known to form with benzol nitro-benzol, a liquid possessing a high boiling-point. But though the mixed vapours were allowed to remain together for ten minutes before starting the lamp, when the beam passed through the experimental tube it was optically empty.

Chemical action commenced a quarter of a minute after the ignition of the lamp; a very delicate blue light was then discharged from the beam, the centre of which was particularly bright and transparent. The light emitted normally remained perfectly polarized for one minute.

I looked through the Nicol towards the cloud. For a minute it was absolutely extinguished. Continuing to look in the same direction the residual colour appeared, and passed from a rich deep violet to a hard whitish blue. It was exceedingly interesting to watch the growth and change of the residual colour. At a certain period of its existence it rivalled the richest blue of the spectrum.

In two or three minutes the anterior portion of the tube was filled by a thick cloud generated by the beam. The cloud rapidly diminished in density as the more distant end of the tube was approached. It was composed of two longitudinal lobes, which, looked at obliquely in a vertical plane, discharged light polarized in planes at right angles to each other.

When the cloud was looked at normally, the line of vision being horizontal, on one side of the centre the polarization was positive, on the other side negative. Moved to and fro across the neutral section, the sudden expansion and contraction of the selenite bands was very curious.

After twenty minutes' action the neutral section was abolished, and the normal polarization (now feeble) became the same throughout the entire length of the cloud.

II. Air and benzol vapour . . . . . 8 inches; then
Air and aqueous nitric acid . . . 8 inches.

On starting the light the tube was not optically empty, but crowded with particles. Through them the beam appeared to force its way like a spear, bringing down upon itself a finer cloud, which soon swathed and masked the coarser spherules.

This experiment was many times repeated, but it was found impossible to bring the benzol and nitric acid together in the quantities here employed without the formation of a crowd (cloud would hardly be the word) of coarse particles. Chemical action had manifestly set in without the intervention of the light.

The chemical action without light appearing to depend on the quantity of benzol vapour and nitric acid present, I varied that quantity. When 2 inches of each were admitted into the experimental tube, no particles were seen when the lamp was ignited. A quarter of a minute after the starting of the lamp the track of the beam became blue. This light remained perfectly polarized for a minute. In three minutes a dense cloud had filled the tube. In the two rectangular positions of the Nicol the cloud exhibited a salmon-colour and a hard bluish greenish white.

When the quantities of the two vapours were 4 inches each, there were no particles in the tube when the lamp was ignited. No doubt the substances were ready to attack each other, and in less than a quarter of a minute the beam precipitated the attack. The action was exceedingly vigorous. For a moment, and only for a moment, the polarization was perfect. In less than a minute the rapid thickening of the cloud and the quick growth of its particles abolished almost all traces of polarization.

When the quantities were 5 inches to 5, particles were found in the experimental tube on starting; and the same occurred with all greater quantities. When, for example, the

quantities were 6 inches to 6, 10 inches to 10, or 15 inches to 15, there were invariably particles. In some of the experiments it seemed as if the chemical attractions were satisfied before the light started, the subsequent action being very feeble. In other instances this did not seem to be the case; for though the particles existed, the spaces between them became immediately filled by a fine dense cloud when the beam passed among them. In some instances the precipitation was exceedingly sudden and copious. Mr. COTTRELL, who has assisted me with zealous intelligence in these experiments, thus describes one result. "Some coarse particles were in the tube on commencing, and these, when the light was started, remained perfectly tranquil for a moment; but after an instant's pause the beam appeared to pierce like a ploughshare the cloud it had formed, throwing right and left of it heaps of precipitated particles. This cloud filled the tube almost instantaneously."

To give the benzol and nitric acid more time to act upon each other, on Tuesday evening, the 16th of February, 2 inches of each were admitted into the experimental tube, and allowed to remain there through the night. Sixteen hours subsequently the beam was permitted to act upon the mixture. The tube which contained it was to all appearance absolutely empty; no particles whatever had formed during the night. In a quarter of a minute after starting the lamp chemical action began, and in five minutes the beam had filled the tube with a dense cloud.

The deportment of benzol may be thus summed up:—

Benzol.	Nitric acid.	
2 inches.	2 inches.	No particles; strong actinic action.
4 „	4 „	No particles; very strong actinic action.
5 „	5 „	Particles; dense actinic cloud precipitated among them.
6 „	6 „	„ sometimes „ „
10 „	10 „	„ sometimes „ „
15 „	15 „	„ sometimes „ „
1 „	15 „	No particles; strong actinic action.
15 „	1 „	Particles.

IODIDE OF ALLYL ($C_3 H_5 I$):—A transparent yellowish liquid.

Contents of experimental tube.

I. Air and iodide-of-allyl vapour . . . 1 inch; then
Air and nitric acid . . . . . 15 inches.

The beam traversed the tube for an instant as if the space within it were a vacuum, but in the fraction of a second a brilliant shower of particles fell upon the beam. The cloud became coarse immediately. The action occurred in the anterior part of the tube, the most distant part being apparently free from action. This is quite different from the deportment of iodide of allyl and hydrochloric acid. On reversing the tube another cloud, of finer texture than the first, was precipitated. The cloud assumed

beautiful and curious forms. The inner portions of its two longitudinal lobes were shaped like screws; they moreover rotated like screws, moving as if they were pushed mechanically into the mass of cloud in front of them. The whole effect was very fine, and the action extremely vigorous. As might be expected from the density of the cloud, the normal polarization was almost *nil*.

II. Air and iodide-of-allyl vapour . . 8 inches; then
Air and nitric acid . . . . . 8 inches.

The tube was optically empty at first, but the action, though not so brilliant as in the last case, was very prompt and energetic. A very coarse cloud was rapidly formed throughout the entire tube, upon the bottom of which the particles appeared to fall in showers.

The cloud having apparently ceased to thicken, the lamp was suspended. On its accidental reignition a fine cloud, dense and luminous, was suddenly precipitated among the coarser particles. On suspending the lamp the finer cloud vanished, but the coarser particles remained. On reignition the fine white cloud was precipitated as before, entirely masking the coarser one by its superior density and closeness of texture. This action was repeated several times in succession.

Allowing the *parallel* beam from the lamp to act for a time upon the cloud, on changing it to a convergent one the superior intensity of the light immediately caused a fine, dense, and luminous precipitation. By rendering the beam alternately parallel and convergent, this action could be reproduced several times in succession.

III. Air and nitric acid . . . . . 1 inch; then
Air and iodide-of-allyl vapour . . 15 inches.

Immediately after the starting of the lamp the action commenced, and spread through the entire tube in less than two minutes. The falling of the particles in vertical showers occurred here also.

After it had acted for a time the lamp was extinguished, and the tube was permitted to remain quiescent for an hour. On reigniting the lamp the tube appeared to be quite empty. The cloud that had previously filled it had entirely disappeared. Half a minute's action of the beam brought down upon it copious precipitation, a revival of the action occurring afterwards throughout the entire tube.

Iodide of Isopropyl ($CH(CH_3)_2I$).

Contents of experimental tube.

I. Air and iodide-of-isopropyl vapour . . 1 inch; then
Air and nitric acid . . . . . 15 inches.

After a moment of apparent emptiness a very splendid action set in. A cloud of exceeding brightness suddenly filled the space occupied by the convergent beam. The

light scattered by this anterior cloud was very powerful. At the distant end of the tube the action was feeble. I reversed the tube; but the precipitation here was by no means so prompt and copious as at the other end, into which the vapour had been evidently swept by the air and nitric acid.

The lamp was suspended for about five minutes; on reigniting it a coarse cloud was found within the tube; but instantly through this coarseness a finer cloud of exquisite colour, luminousness, and texture was shed. A violent whirling motion was set up at the same time. The longitudinal lobes in this case were very curiously found.

II. Air and iodide-of-isopropyl vapour . . . 8 inches; then
Air and nitric acid . . . . . 8 inches.

Tube optically empty, but in the fraction of a minute a shower of very coarse particles had fallen upon the beam. They augmented up to a certain point and then appeared to diminish. The reversal of the tube caused fresh precipitation. The rendering of the beam more convergent also caused augmented precipitation, but nothing so fine as in the last experiment. The action, indeed, was altogether inferior to the last in point both of beauty and of energy.

I suspended the lamp for a few minutes; on restarting it the tube appeared empty, but in a moment a cloud much finer than that at first obtained was precipitated on the beam. Curious masses of particles gushed at irregular intervals upon the beam. On reversing the tube the action was decidedly finer than at first.

Thus, suspending the lamp after it has been acting for a time, the vapour during the period of suspension undergoes a change which enables it to fall as a finer and more visibly copious cloud than at the beginning of the action.

III. Air and nitric acid . . . . . 1 inch; then
Air and iodide-of-isopropyl vapour . . . 15 inches.

Action commenced immediately, and in less than a minute the beam had filled the tube with an unbroken cloud. The beam was rendered parallel, and the action continued for eight minutes. The end nearest the light became rapidly empty, while in the distant half of the tube the particles fell in heavy showers. The whole tube subsequently became almost empty; the disappearance of the dense cloud first generated was very striking. It would appear as if after the first sudden precipitation evaporation had set in and restored the particles to the gaseous condition.

Nitrite of Amyl ($C_5 H_{11} ONO$):—A transparent yellowish liquid.

Contents of experimental tube.

I. Air and nitrite-of-amyl vapour . . . . . 1 inch; then
Air and nitric acid . . . . . 15 inches.

The tube was optically empty at starting; action commenced in half a minute, the

cloud particles formed being very coarse. In four minutes the anterior two-thirds of the tube were filled with a very coarse cloud, the remaining third with a finer one. The whole rotated round a longitudinal axis, and the finer portion was rolled into a curious spiral form, and was tinged throughout with iridescent colours. The normal polarization was almost *nil*, except in the finer part of the cloud, which was slightly blue.

II. Air and nitrite-of-amyl vapour . . . . 8 inches; then
Air and nitric acid . . . . . 8 inches.

The tube was optically empty for an instant only, a dense precipitation occurring immediately upon the concentrated beam. The distant part of the tube, however, was but scantily filled, showing the sifting action of the nitrite vapour. On reversing the tube copious precipitation occurred. After ten minutes' exposure the particles tended to settle at the bottom of the tube.

III. Air and nitric acid . . . . . 1 inch; then
Air and nitrite-of-amyl vapour . . . . 15 inches.

The tube was optically empty only for an instant; as in the last experiment, a dense cloud was immediately precipitated on the cone of rays. Here also the distant end of the tube was protected by the vapour in front.

In all these cases the action was distinctly less energetic than when the nitrite vapour mixed with air alone was exposed to the light; and very much less energetic than when hydrochloric acid was mixed with the vapour.

Nitrite of Butyl ($C_4 H_9 ONO$):—A transparent yellowish liquid.

This substance gives no sensible action with nitric acid; but with hydrochloric, as already mentioned, the action is vigorous and brilliant. Here are a few of the results.

Contents of experimental tube.

I. Air and nitrite-of-butyl vapour . . . . . 1 inch; then
Air and hydrochloric acid . . . . . 15 inches.

The action began a quarter of a minute after starting, a very white and brilliant cloud forming upon the concentrated beam and quickly spreading throughout the tube.

II. Air and nitrite-of-butyl vapour . . . . . 8 inches; then
Air and hydrochloric acid . . . . . 8 inches.

The action began about half a minute after starting, a cloud of comparatively fine particles being precipitated in the cone of rays, while the distant part of the tube was filled with coarse particles. The cloud was coarser, and the action less energetic than in the last experiment.

III. Air and hydrochloric acid. . . . . 1 inch; then
Air and nitrite-of-butyl vapour . . . . 15 inches.

After four minutes' action a number of coarse particles had formed in the tube together with a faint scroll of cloud. The action was very feeble. For vigorous action with the nitrite of butyl the proportion of the acid to the vapour must be large.

The hydrochloric acid here employed was that ordinarily used by chemists in quantitative analysis. The same series of experiments was executed with *commercial* hydrochloric acid; the action in this case was distinctly more energetic than when the pure acid was employed.

HYDRIDE OF CAPROYL ($C_6 H_{11} O$, H):—A transparent colourless liquid.

Contents of experimental tube.

Air and hydride of caproyl	8 inches.
Air and nitric acid	8 inches.

The tube was optically empty at starting. In three quarters of a minute a blue cloud had formed throughout the tube. It remained perfectly polarized for three minutes; then became gradually white, discharging imperfectly polarized light. At the end of ten minutes a dense white cloud filled the tube.

§ XIII.

I thought it worth while, for the sake of bringing out the influence of vibrating period, to contrast the action of powerful foci of dark rays with the feeble foci produced by the convergence of the more refrangible rays of the spectrum. It is known that the dark calorific rays pass freely through a solution of iodine in bisulphide of carbon; such a solution was employed to hold back the luminous part of the electric beam. A cell containing ammonia sulphate of copper was employed to hold back the rays of low refrangibility and allow those of high refrangibility transmission. The destructive action of the ammonia sulphate in the calorific rays is well known. Its depth in the present case was such as to quench completely the red, orange, and yellow of the spectrum, but it allowed transmission to the violet and blue, and a small portion of the green. The vapours employed were mixed with the various acids mentioned.

Nitrite of amyl	8 inches.
Pure hydrochloric acid . .	8 inches.

The convergent beam of the lamp was sent through the cell containing the solution of iodine, and was permitted to act upon the mixed acid and vapour for ten minutes. The ammonia-sulphate cell was then introduced and the opaque solution removed. For an instant afterwards the tube was optically empty. Then a dense cloud was precipitated, which advanced like a moving share towards the most distant end of the tube. Within half a minute after the withdrawal of the opaque solution the tube was filled with cloud, which augmented in density for five minutes, when the experiment ceased. A repetition of the experiment yielded the same result.

Iodide of allyl . . . . . 8 inches.
Nitric acid . . . . . 8 inches.

Looked at for an instant after the vapour and acid had entered, with the white light of the electric lamp, the experimental tube was seen to be optically empty. The opaque solution was immediately introduced, and the vapour was subjected to the action of the dark rays for ten minutes.

The opaque solution was then removed for an instant, and the tube was seen to be optically empty. The strong calorific rays had produced no action.

The cell containing the blue liquid was then introduced; in less than half a minute the action became visible, and augmented rapidly. In three minutes a cloud stretched quite through the tube from end to end. The scattering of the blue light by the coarse particles of this cloud produced a very pretty effect.

Benzol . . . . . 4 inches.
Nitric acid . . . . . 4 inches.

Looked at for an instant after the admission of the vapour and acid the tube was optically empty. The opaque solution was introduced, and the invisible rays permitted to act for ten minutes. The solution was then removed, and the tube was examined for a moment with white light. It was optically empty. The blue liquid being interposed, visible action commenced $2\frac{1}{2}$ minutes afterwards*, and in ten minutes a cloud was formed throughout the tube. A repetition of this experiment confirmed the inaction of the calorific rays, and showed the action of the blue rays to be visible a minute after the introduction of the ammonia-sulphate cell.

Toluol . . . . . 8 inches.
Nitric acid . . . . . 8 inches.

Looked at for an instant after the admission of the vapour and acid, the tube was found optically empty. Ten minutes' action of the calorific rays produced no effect. The blue liquid was then interposed, and in two minutes a cloud was visible upon the feeble blue beam. At the end of ten minutes this cloud stretched throughout the tube.

Iodide of β propyl . . . 8 inches.
Nitric acid . . . . . 8 inches.

The tube was optically empty at the commencement. At the end of ten minutes' exposure to the calorific rays the tube was also empty. The blue cell was introduced, but in two minutes after its introduction, no cloud appearing, the cell was removed for an instant. The action had begun, though the coarse particles of the actinic cloud were too sparsely distributed to be seen by the weak blue light. The experiment was repeated. As before, ten minutes' action of the calorific rays proved quite ineffectual. In one minute after the introduction of the blue liquid, no cloud being visible in the tube, the cell was removed. A crowd of particles were then seen upon the cone of light.

* No doubt it had previously commenced, but it was invisible in the feeble light.

The cell was again introduced, and after three minutes again withdrawn. The particles had increased considerably. Seven minutes' action rendered them sufficiently numerous to be visible in the blue light. After ten minutes the coarse cloud was very plainly seen. The action was continued with white light after the removal of the blue liquid; it was scarcely more energetic than that produced by the blue rays.

Nitrite of butyl	1 inch.
Hydrochloric acid	15 inches.

Examined for a moment by white light the tube was optically empty. After ten minutes' exposure to the dark rays the tube was again examined by the white beam; it was still optically empty. The blue liquid was then introduced, and in a $\frac{1}{4}$ of a minute a long streak of cloud had formed. In $2\frac{1}{2}$ minutes a dense cloud had formed throughout the entire tube. An exceedingly delicate blue light, and at some parts a deep violet, was scattered by this cloud. After five minutes' exposure to the blue rays an intensely white cloud had formed, which completely filled the tube. The action here was very fine.

Bisulphide of carbon. . .	8 inches.
Nitric acid	8 inches.

The tube was optically empty when the opaque solution was introduced; but after ten minutes' exposure to the calorific rays a faint blue tinge was observed, when the opaque solution was removed*. The experiment was abandoned, and the mixed vapour and acid were again introduced. At the beginning the tube was optically empty; after ten minutes' exposure to the calorific rays it was also empty. In two minutes after the introduction of the blue cell, a cloud became visible; it quickly increased, and after four minutes extended throughout the tube. After ten minutes' action a dense whitish-blue cloud filled the entire tube. The experiment was repeated twice with the bisulphide, with substantially the same result.

These experiments are quite conclusive as to the inability of the calorific rays to produce actinic clouds; they are the product of the more refrangible rays of the spectrum.

* It is sometimes difficult to get the bisulphide into the tube without this blue tinge. It is certainly due to some impurity. With care it can be caused to disappear wholly.