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Condensation of Water Vapour in the Presence of Dust-Free Air and Other Gases

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XI. *Condensation of Water Vapour in the Presence of Dust-free Air and other Gases.*

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THE behaviour of air saturated with aqueous vapour and allowed to expand suddenly, has been investigated by COULIER,[*] AITKEN,[†] KIESSLING,[‡] and R. v. HELMHOLTZ.[§] As is well known, if the moist air has been previously freed from "dust," no condensation takes place except on the walls of the vessel, even if the expansion be sufficient to produce considerable supersaturation. For convenience, the term "dust" is here used to include all nuclei which can be removed either by filtering or by repeatedly forming a cloud by expansion and allowing it to settle.

What is the limit, if such exists, to the degree of supersaturation which can be attained without condensation taking place throughout the moist air, is a question of considerable meteorological as well as purely physical interest. It was primarily with the object of finding an answer to this question that the experiments to be described were undertaken, such experimental evidence as already existed on the subject being of a very incomplete and contradictory character.

AITKEN[||] observed condensation when a large quantity of steam was passed into a receiver containing air which had been filtered through cotton wool. KIESSLING[¶] also produced a rainlike condensation in the same way. The latter observer also states that if saturated filtered air be even slightly expanded, scattered drops are formed visible only in direct sunlight. Again, AITKEN[**] mentions that in his dust-counting experiments, in which sudden expansion of the saturated air was produced by means of an air-pump, a very quick stroke of the pump was found to produce a

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[*] 'Journal de Pharmacie et de Chimie," vol. 22, pp. 165 and 254, 1875.

[†] 'Trans. Roy. Soc.,' Edin., vol. 30, p. 337, 1880–81, and vol. 35, p. 1, 1890; 'Proc. Roy. Soc.,' Lond., vol. 51, p. 408, 1892.

[‡] 'Hamburger Abhandl. der Naturwissenschaften,' vol. 8, 1884; 'Götting. Nachr.,' p. 122, 1884, and p. 226, 1884.

[§] 'Wied. Ann.,' vol. 27, p. 509, 1886.

[||] 'Trans. Roy. Soc.,' Edin., vol. 30, p. 337.

[¶] 'Götting. Nachr.,' p. 226, 1884.

[**] 'Trans. Roy. Soc.,' Edin., vol. 35, p. 1, 1890.

shower of drops even in filtered air, while a slow steady one had no such effect. The increase of volume was always the same, and amounted to one-third of the initial volume. He attributes the difference to the shock which results from a rapid stroke of the pump.

R. v. HELMHOLTZ,[*] on the other hand, was unable to observe any trace of condensation in saturated filtered air, even with a fall of pressure of half an atmosphere. Whether, however, the pressure was reduced from one atmosphere to one-half, or from one-and-a-half atmospheres to one, is not clear; from his description of the method one would naturally take the latter interpretation. He deduces, however, a theoretical lowering of 50° C., and a ten-fold supersaturation which correspond to the former alternative.

BARUS,[†] who made an extensive series of observations on the colour phenomena of a steam jet under varying conditions as to boiler-pressure and the temperature and dust contents of the surrounding air, concluded that with sufficient supersaturation, condensation takes place independently of dust. He does not appear, however, to have been able to deduce from his measurements the degree of supersaturation which is required to bring about this condensation.

None of the experiments referred to above are entirely free from objection.

When steam is blown into filtered air, as was done by AITKEN and KIESSLING, it is likely to carry over with it small drops of spray from the boiler. Even if these drops be made to evaporate by superheating the steam, each will leave behind a nucleus consisting of the solid matter which it contained in solution or suspension.

The condensation noticed by KIESSLING with very slight expansion may have been due to a similar cause, for he appears to have brought the air in his apparatus into a saturated state by allowing it to bubble through water after it had been filtered. That such treatment does actually introduce nuclei requiring only a slight expansion of the saturated air to cause condensation upon them is proved by certain experiments described below. AITKEN[‡] noticed, too, that if the water in his dust-counting apparatus was allowed to splash about, such nuclei were produced.

In none of the experiments mentioned above was the expansion very rapid, the apparatus in no case having been specially designed for the purpose of investigating this particular question. HELMHOLTZ's failure to obtain condensation may easily be explained by the expansion not being sufficiently rapid to produce anything like the theoretical lowering of temperature as, indeed, he himself admits.

The interpretation of steam-jet experiments, such as those of BARUS, is very difficult, especially as the phenomena depend largely on the roughness or smoothness of the bore of the nozzle from which the steam escapes. They cannot be taken as

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[*] HELMHOLTZ, *loc. cit.*

[†] "Report on the Condensation of Atmospheric Moisture;" U.S. Department of Agriculture, Weather Bureau, 1895; also 'Phil. Mag.,' vol. 38, p. 19, 1894.

[‡] 'Edin. Trans.,' vol. 35, p. 17, 1890.

proving beyond doubt that condensation may be made to take place by increasing the supersaturation alone, as so many of the conditions besides the degree of supersaturation must vary as the initial pressure of the steam, and consequently the velocity with which it escapes from the nozzle are increased.

Conditions to be satisfied by the Expansion Apparatus.

To obtain unequivocal proof of the production of condensation in moist air, free from all extraneous nuclei, it is necessary that we should not be dependent upon any process of filtering, for it might always be objected that the filtering apparatus only removed those particles which exceeded a certain size.

If, however, we expand repeatedly the same sample of moist air, while protecting it from all chance of contamination, we are able to test whether all nuclei of a permanent kind have been removed. For by making an expansion rather greater than is sufficient to cause condensation, and allowing the drops formed to settle, we remove in this way a certain proportion at least, and if the drops be few and large, almost the whole of the nuclei which are able to cause condensation with this degree of supersaturation.

If this process can be repeated indefinitely without any diminution in the number of drops formed, we are justified in concluding that the nuclei are being replaced by others as fast as they are removed, and are thus an essential part of the structure of the moist gas.

It is desirable also that the expansion should admit of accurate measurement and be exceedingly rapid, so that the lowest temperature and maximum supersaturation reached may be calculated with as small an error as possible due to the influx of heat during the expansion.

In a note* read before the Cambridge Philosophical Society, I gave an account of some preliminary results obtained with a form of apparatus which I believed to satisfy these conditions. It was there stated that condensation results from the sudden expansion of saturated dust-free air when v_2/v_1 exceeds a value not differing much from 1·258, where v_1, v_2 are the volumes of the air before and after expansion.

No description of the apparatus was published, as it was then in quite a rudimentary condition.

The first series of experiments to be described here was carried out with an improved apparatus of the same type.

Apparatus used in the first series of Experiments.

This is represented in vertical section in fig. 1.

The air to be expanded is contained in the inverted cylindrical glass vessel A,

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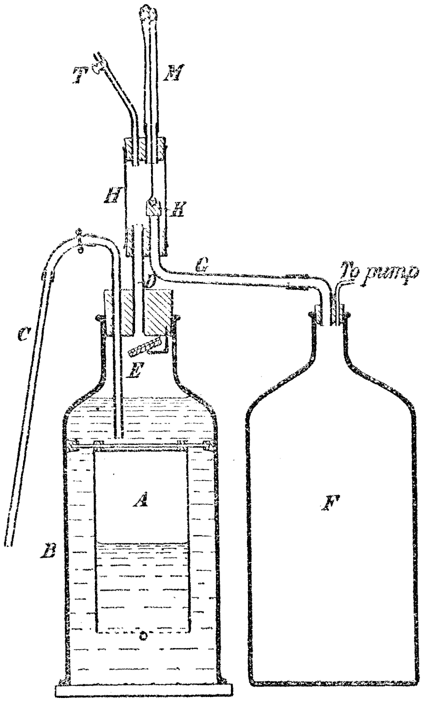
* 'Proc. Camb. Phil. Soc.,' vol. 8, p. 306, 1895.

fixed like a diving-bell below the surface of the water, which nearly fills the outer vessel B.

The latter is a bell-jar of the form shown in the figure, resting on a ground-glass plate, to which it is wired down, and having a wide neck, closed by an indiarubber cork through which pass two glass tubes, the one, C, serving to regulate the quantity of water in B, and provided with a pinch-cock; through the other, D, the air occupying the upper part of B can be suddenly removed by opening communication with a large exhausted stoneware bottle F.

The water is prevented from following the air by means of the valve E.

Fig. 1.



The result is a sudden expansion of the air in A. The increase in volume is equal to the volume of the space in the upper part of B occupied by air before the expansion, and can therefore be made more or less by running a little water out, or drawing some more in through the tube C.

By opening the tap T, which communicates with the atmosphere, air is admitted through the tube D, and the air in A contracts to its original volume.

To bring about very sudden communication with the exhausted vessel F, the arrangement shown in the upper part of the figure was used. A short glass tube, H, is closed at both ends by indiarubber corks, each bored to receive two glass tubes. Of these, D and T have already been referred to. The tube G, which leads to the vacuum vessel F, has its upper end ground smooth, and upon this rests the flat surface of an indiarubber cork K. This closes the opening of the tube in a perfectly air-tight manner, when the air above it is at atmospheric pressure, and the pressure in F is a small fraction of this, as it always was maintained during a series of experiments.

K can be pulled up by means of the vertical wire shown in the diagram, thus rapidly making free communication between D and G and causing the expansion. The tap T must of course previously be closed. In order that one may be able to work the arrangement from the outside without admitting air, the wire passes up through a thin-walled indiarubber tube, M, closed at its upper end by a cork in which the end of the wire is fixed. A cord attached to this cork and passing over a smooth peg fixed vertically above it, enables the observer to make the expansion, while watching the behaviour of the air in the cloud chamber A.

The tubes D and G had an internal diameter of about 8 millims., so that the fall of pressure in the air-space in the upper part of B must be very rapid. The valve E, which prevented the water in the bell-jar B from following the air into the tube D, was made by cutting a thin slice from the end of an indiarubber cork and supporting it with the smooth surface uppermost on a piece of cork just thick enough to float it. It was fixed by means of a wire hinge to the lower surface of the indiarubber cork of the bell-jar, in such a position that when raised by the water reaching it, it covered the hole bored for the tube D. The latter did not quite reach the lower surface of the indiarubber cork, so that when the valve closed the contact was between two indiarubber surfaces.

This valve was found to work perfectly when the excess of pressure below was sufficient, and smooth indiarubber surfaces were used.

The bell-jar had a diameter of about 14 centims. and was about 30 centims. high. The inner vessel had a diameter of about 9 centims. A vertical glass scale, divided into millimetres, fixed by means of sealing-wax to the outside of the inner vessel, enables the observer to note with the aid of a telescope the level of the water before and after expansion. From a subsequent calibration the initial and final volumes are obtained.

To make visible any condensation in the form of fog or rain, the light from a luminous gas-flame is brought by means of a convex lens to a focus at the centre of the cloud chamber A. Any condensation which may result is most distinctly seen when the eye is placed just out of reach of the directly transmitted light. This method of illumination was used both by AITKEN and R. v. HELMHOLTZ. The experiments were performed in a dark room. When an expansion was made the only source of light was that mentioned above. After the result had been noted, light was admitted by raising a shutter in order that the readings of volume might be made.

The inside of the inner vessel, A, was cleaned before use, first with caustic potash and then with nitric acid, and well washed with distilled water. After this treatment the water forms a uniform film over the surface of the glass, instead of collecting into drops and preventing a satisfactory view of the interior.

This apparatus appeared to fulfil very well the purpose for which it was designed. Nothing can gain access to the air imprisoned in the inner vessel except by solution in and diffusion through the surrounding water.

The water surface which forms the lower boundary to the space occupied by the air under observation, drops suddenly to a new position, where it comes to a sudden stop, without any splashing, and remains stationary as long as may be desired. The whole movement is certainly over in a small fraction of a second, as the expansion appears to the eye to be instantaneous. That it should be rapid is what one would expect, as the initial driving pressure is nearly one atmosphere, and the distance travelled rarely amounted to more than two centimetres.

There is this further advantage in such a method of expanding the air, that the rate of expansion is most rapid just before it is completed, because the driving pressure still remains considerable, and the water is therefore moving with constantly increasing velocity until it brings itself to a sudden stop by closing the valve E.

Thus the final stage of the expansion, when the temperature is lowest, and therefore the influx of heat most rapid, is that which is most quickly passed through.

The motion of the water cannot, of course, be stopped instantaneously ; in practice it was always found that some small air bubbles were left imprisoned around the valve E. These, being compressed by the impact, probably served to diminish considerably the strain on the apparatus.

With a thin float the volume of these bubbles was quite a negligible fraction of that of the air which escaped before the valve closed. If any considerable fraction of the air were left behind when the valve closed, an error would be introduced by its momentary compression, the actual maximum value reached being really greater than what is afterwards measured by an amount equal to the momentary diminution in the total volume of the air bubble.

Method of Conducting the Experiments.

To charge the apparatus with air reasonably free from laboratory gases, the bell-jar, with the inner vessel fixed inside it, was removed from the ground-glass plate on which it rested, and allowed to remain at an open window for some time. It was then placed on the glass plate, and bound tightly down with wire.

Distilled water, which had been boiled for some time to remove the greater part of the dissolved gases, was then poured in till it nearly filled the bell-jar. By inclining the whole, air was allowed to escape from the inner vessel till only a convenient volume remained. The bell-jar was then again nearly filled up with water, and the apparatus then connected up as already described and shown in fig. 1.

The glass-plate was levelled by means of levelling screws supporting the tripod on which the plate was fixed. The reading telescope was then fixed some distance off, on a level with the surface of the water in the inner vessel.

Some water was now allowed to escape through the tube C, and the level of the water read on the glass scale by means of the telescope. The tap T was then closed, expansion made by pulling the cord which opens communication with the vacuum vessel F, and the effect on the contents of the expansion chamber A noted. The new level of the water in the inner vessel was again read by the telescope, and the air made to contract to its former volume by opening the tap T. The same expansion could be repeated as often as was wished, or the air could be expanded to a greater extent by first running out a little water through C. If it was desired to try the effect of a smaller expansion the tap T was only slightly opened, and was closed before the water in B had quite returned to its original level. Then the pinch-cock on the tube C was opened for a moment while the end of the tube was dipped into a beaker of water.

To find the volumes corresponding to the various readings, the bell-jar, with its inner vessel, was removed from the glass plate after every series of observations, and fixed in an inverted position so that the water could be poured into the inner vessel. The whole arrangement was then adjusted so that the ground surface of the rim of the bell-jar was level. The weight of water which had to be poured in to fill the inner vessel up to the various readings on the scale was then determined, the telescope being fixed in exactly the same relative position as in the expansion experiments.

General Account of the Phenomena Observed.

The air was generally admitted into the apparatus in the way already described, and, therefore, without any attempt to remove dust by filtering. Repeated expansion of saturated air, as AITKEN has shown, removes all "dust" particles, and this method was generally employed in these experiments.

The first expansion made, whether large or small in amount, unless the air had been allowed to stand for many hours in the apparatus, always produced a fog. This was allowed to settle as completely as possible before allowing the air to contract to its original volume. In this way a considerable proportion of the dust was removed, the particles being carried down by the drops which condensed upon them into the water below.

When this process was several times repeated, the resulting fog became by degrees coarser-grained, the drops being both fewer and larger, and therefore, falling more quickly. The fog passed at length into a fine rain. When this stage was reached one more expansion was generally sufficient to remove the remainder of the dust particles, and any further expansion, unless it exceeded the limit spoken of below, was without visible effect.

AITKEN[*] was able to remove all the dust particles from saturated air by repeatedly increasing its volume by $\frac{1}{50}$ of its initial amount. An even smaller expansion was found in these experiments to be sufficient for that purpose, but the time taken for the removal of the dust was naturally much shorter when larger expansions were used, on account of the larger size and more rapid fall of the drops in the latter case.

If, after the dust has been removed in this way the successive expansions be made greater and greater, no visible effect is produced till v_2/v_1, the ratio of the final to the initial volume, is equal to about 1·252. When v_2/v_1 exceeds this value a shower of drops is invariably produced. The drops are not very numerous, even with considerably greater expansions, yet, however often we expand the air, no diminution in the number of the drops can be detected.

Now, when, owing to the presence of dust particles, a shower of similar density is produced with a smaller expansion, all the dust particles appear to be carried down with the water drops, and the next expansion produces no condensation.

Thus, the nuclei which enables condensation to take place when the expansion exceeds the limit mentioned, are only present in small numbers at any given time, but as fast as they are removed they are replaced by others of the same kind.

Expansion required to produce Rain-like Condensation in Dust-free Saturated Air.

A large number of observations must generally be made in order to obtain within narrow limits a single determination of the ratio of v_2 to v_1 when condensation just takes place.

When expansions of comparatively small amount had ceased to cause condensation, each increase in volume was made considerably greater than the preceding, till a shower of drops was observed. Then an observation was made with the apparatus adjusted to give a rather smaller final volume (the initial volume remaining practically constant), and perhaps no condensation seen. By making in this way a series of alternately greater and smaller expansions of gradually diminishing difference, a stage was at length reached when the smallest measurable difference in the final volume was sufficient to determine whether condensation should result or not.

A large number of experiments were made during the summer of 1895. Only the results of the last series of measurements then made are given in the table which follows. The apparatus has been improved from time to time and the later experiments were carried out exactly as described above.

The mean of the results previously obtained for the critical value of v_2/v_1, however, is practically identical with that given below, and all the determinations of this ratio have results lying between 1·24 and 1·26.

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[*] 'Edin. Trans.,' 35, p. 1.

In the following table, v_1 is the initial volume and v_2 the final volume when the expansion is just sufficient to cause rain-like condensation.

	Date.	t° C.	v_1	v_2	v_2/v_1
1.	September 4	22·0	292·9	367·3	1·254
2.	,, 4	22·4	293·4	367·8	1·253
3.	,, 5	28·8	313·1	392·5	1·253
4.	,, 5	27·2	308·5	385·8	1·250
5.	,, 6	27·8	312·5	390·8	1·250
6.	,, 6	26·0	309·8	386·7	1·248
7.	,, 7	24·5	302·0	378·3	1·252
				Mean	1·252

The same air was used on September 7 as on the previous day; otherwise the experiments were made on a different sample of air each day.

It will be noted that the expansion required is sensibly the same at all temperatures between 22° and 28° C. Accurate measurements of the initial temperature are therefore unnecessary in these experiments.

The results given in the table show no greater variation than are to be expected from the degree of accuracy of the volume measurements. The level of the water could be read by means of the telescope to the nearest tenth of a millimetre, corresponding to an error of half a cubic centimetre in the volume measurements. There may be an error of this amount in the measurement of both v_1 and v_2, and hence an error of 4 units in the fourth figure in the ratio, when the initial volume amounts to about 300 cub. centims.

Other Experiments made with the same Apparatus.

1. When sunlight was used to illuminate the drops, exactly the same expansion was required to bring about visible condensation.

The result, therefore, does not depend on the kind of illumination used.

2. Experiments were made to see if the nuclei which cause the rain-like condensation could be removed by repeated filtering. For this purpose a hole was bored through the glass plate on which the apparatus rested. A glass tube reaching to the roof of the inner vessel was passed through a cork which closed this hole. Through it the air could be drawn out into an inverted WOLFF's bottle, arranged to act as an aspirator, and could be driven from the one vessel to the other as often as was desired.

A tightly-packed cotton-wool filter was inserted between the expansion apparatus and the WOLFF's bottle. Passing the air repeatedly backwards and forwards through the filter was found to be without effect upon the appearance of the rain-like condensation, or the expansion required to produce it.

3. When no cotton-wool filter was present the air could be passed from the one vessel to the other and back without any effect, so long as it was not allowed to bubble through the distilled water in either vessel. If, however, the air had to bubble through water on being driven back, quite a small expansion was sufficient to cause a shower even some minutes later.

4. As already stated, the air may be allowed to expand considerably more than is necessary to produce condensation without the drops becoming very numerous.

With very great expansions, however, if, for example, the increase in volume be made twice as great as is necessary for condensation to result, a dense fog showing colours and settling slowly is produced.

Second Form of Apparatus.

The apparatus already described was not suitable for experiments upon pure gases, on account of the large volume of water present.

To remove all the dissolved gases from so large a quantity of water would have been very difficult.

Another reason for changing the form of the apparatus was that I wished to investigate in what way the number of drops produced depended upon the degree of supersaturation reached. It appeared, from the experiments already made, that the drops remained comparatively few with expansions considerably greater than that required to cause condensation to begin, and over a considerable range there was no appreciable increase in the number with increasing expansion. Yet, with very large expansions, the number was very great, and the drops sufficiently small to produce a coloured fog which settled very slowly.

The first apparatus was not convenient for making measurements with very large expansions, so no attempt was made to investigate with it whether there was a sudden transition from the one form of condensation to the other. It was thought that another form of apparatus would be more suitable for the purpose.

A very rapid expansion is evidently required for this investigation. For, let us consider one cubic centimetre of saturated air which is expanded rapidly. If we suppose the effect of the walls to be negligible, the ordinary equation for the cooling of a gas by adiabatic expansion may be applied to find the lowering of temperature and the resulting supersaturation till the volume amounts to 1·252 centims. At this stage, as we have seen, condensation begins upon a comparatively small number of scattered nuclei. There must at once result from the initial condensation a simultaneous loss of vapour and rise of temperature in the region immediately surrounding each incipient drop. The subsequent growth of the drop must be more or less gradual, being the result of the comparatively slow processes of diffusion and heat conduction.

If the expansion be slow, the supersaturation can nowhere greatly exceed that required for the formation of the first drops.

With very sudden expansions, however, even if they be much greater than that required to produce rain-like condensation, the drops which are the first to begin to form will not have time to grow sensibly before the expansion is completed, and their influence on the temperature and vapour contents of the air will be confined to a very small region round each. In that case the lowest temperature and maximum supersaturation reached throughout the greater part of the moist air will be the same as that calculated on the assumption that no condensation takes place.

The more numerous the drops, the shorter must the time taken in expansion be made, in order that there should be no sensible error due to the formation of the drops commencing before the expansion is completed.

Now the time of expansion can be made shorter in a small machine. The new expansion apparatus was therefore made upon quite a small scale, the effect of the reduced dimensions in increasing the error due to the walls being counterbalanced by the great reduction in the time of expansion.

The expansion ought evidently to be made most rapid just before it is completed, since it is just in the later stages of the expansion that drops are being formed, and we wish to reduce, as far as possible, their chance of growing appreciably before the expansion is completed. This end was kept in view in designing the apparatus.

The expansion apparatus (fig. 2), is made wholly of glass, to reduce the risk of contamination of the gas under investigation. This is contained in the space A under a pressure of from 20 to 40 centims. of mercury above that of the atmosphere. This expansion chamber A, is bounded below by the hollow-glass piston P, which is ground down so that it just slides freely in the outer tube.

There is, as indicated in the figure, an annular constriction on the latter. Into this the lower end of the piston has been ground with fine emery, so that, with no other lubricant than water, it prevents the gas in A escaping, even when the excess of pressure above is half an atmosphere or more.

The lower end of the tube is conical, with a circular aperture about 1 centim. in diameter, closed by a glass plug G. The grinding here, too, has to be sufficiently thorough to enable a pressure of two atmospheres to be maintained above it for several minutes without leakage, with only one or two drops of water to serve as lubricant.

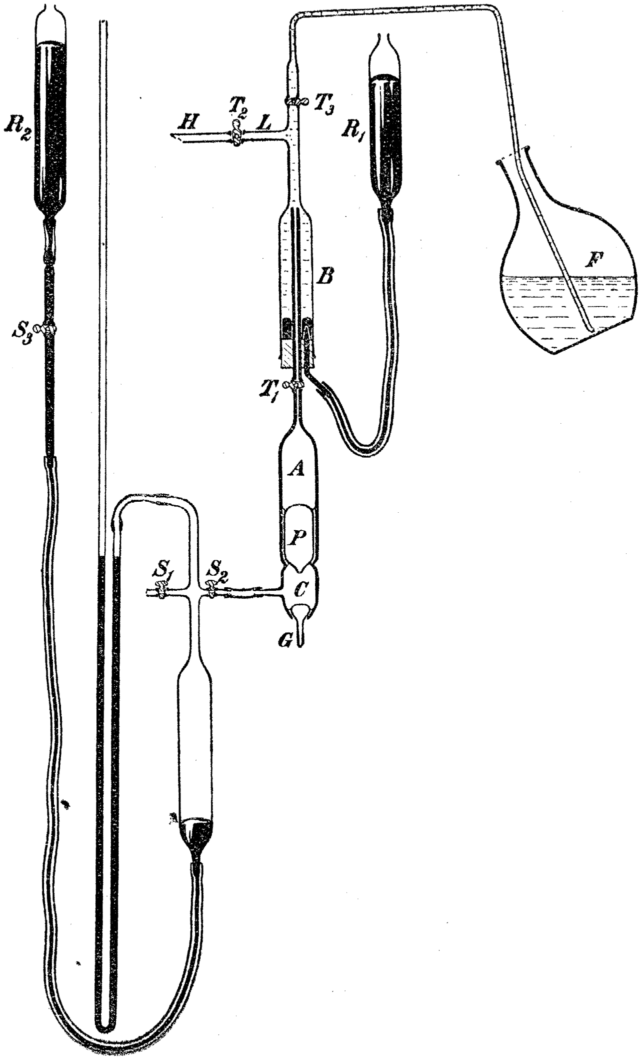
The upper end of the tube is drawn out and joined to a narrow-bore tube provided with a stopcock T_1, serving for the introduction of the gas and water.

When the apparatus is in use, the inner surface of A is covered with a film of water, which also fills the narrow space left between the piston and the walls of the tube.

By pumping air by means of the mercury pump on the left, into the space C below the piston, we can drive up the latter and so compress the gas in A to any extent we please. Then, on pushing up the plug G, we suddenly reduce the pressure in the small space C to that of the atmosphere, and the piston flies back to its original position, producing a sudden expansion of the gas in A.

After each expansion a small quantity of water is driven in through T_1. This serves to keep the walls of A covered with a film of water and to lubricate the piston. The greater part of it runs down and collects above the latter. When the piston is driven up again so that it is suspended freely in the tube, it gradually floats up through this water till it comes to rest with the water scarcely reaching above the straight part of its sides. In this way the water which lubricates the piston is continually being renewed, and the gradual contamination of the gas which would otherwise result by solution and diffusion of the air from below through the water is almost indefinitely retarded.

Fig. 2.



The machine used in nearly all the experiments described below was made from moderately thick-walled tubing, having an internal diameter of 2 centims. The expansion chamber A was between 4 and 5 centims. long, and had a capacity, when the piston was in its lowest position, of about 15 cub. centims. The cylindrical part of the piston was about 3 centims. in length.

The time required for the expansion to be completed must be very short. For the distance travelled by the piston was never so great as 2 centims., even with the greatest expansions used. To support the weight of the piston alone, required an excess of pressure below of 1 millim. of mercury. Now the driving pressure, even when the expansion was almost completed, was probably never less than 100 times as great as this. With the largest expansions used, when the piston had still to travel less than 2 centims., the initial driving pressure was more than an atmosphere, that is, about 760 times that required to balance the weight of the piston. This is on the assumption of an exceedingly rapid fall of pressure in the space below the piston when the plug G is driven up. If we make this assumption, the force driving the piston is always some hundreds of times its weight, and its initial acceleration some hundreds of time "*g*." Even an average acceleration of $100g$ would enable the 2 centims. to be travelled in about $\frac{1}{150}$ of a second.

Although the time taken may actually be considerably greater than this, these considerations are sufficient to show that it is likely to be exceedingly short.

Further, the piston must be moving with constantly increasing velocity till brought to a sudden stop at the constriction into which it fits.

The fact that contact takes place simultaneously over a considerable area, probably saves the tube from being broken by the blow it receives from the piston. The film of water which covers both surfaces, doubtless helps to break the shock. On two occasions, a machine was made only slightly larger than the one whose dimensions are given above, but in each case it was shivered by the impact almost the first time the piston was allowed to fly. More than one machine was useless, owing to the piston being driven so tightly home when the expansion was made, that all efforts failed to release it. To avoid this latter defect, it was found necessary to make the constriction a very sudden one. Great care has also to be taken to make it perfectly symmetrical; otherwise there is almost certain to be a space left between the piston and some part of the wall of the tube just above the constriction. In this, air-bubbles are apt to be entangled when the piston flies into the constriction. These may work their way up into A, and in addition they cause a splashing of the water by their momentary compression and subsequent expansion.

A supply of water for the lubrication of the piston is stored in the vessel B. The space over the mercury is completely filled with water up to the stopcocks T_2 and T_3, which remain closed throughout any series of experiments. By fixing the mercury reservoir R_1 at a sufficient height, the water in B is kept at a pressure high enough to drive it into A when the tap T_1 is opened. In this way the water is preserved from contamination with air, and only comes in contact with glass and mercury. It has been obtained free from dissolved gases by boiling distilled water rapidly down to about one-sixth of its bulk in the flask shown on the right. While it is boiling down, R_1 is repeatedly raised and lowered, to wash out any imprisoned air or unboiled water from B and the tube leading to the flask.

While the water is still boiling, B is filled by lowering R_1, a depth of about 1 centim. of mercury being, however, always left in B to prevent the water from coming in contact with the indiarubber stopper which closes the lower end of the tube. The tap T_3 is then closed and R fixed high enough to give the requisite pressure.

Introduction of the Gas.

The apparatus used in the preparation of the various gases was, in all cases, made entirely of glass, all joints being made with the blow-pipe. It was fused on to the end of the tube H (fig. 2). The methods of preparing the various gases are described later. The whole gas generating apparatus must first be filled with the pure gas up to the tap T_2, which is now kept closed.

Before introducing the gas into the expansion apparatus, A and B must first be filled with air-free water. This is done in the following way.

The piston P is drawn up to the top of A by opening the tap T_1 and lowering the mercury reservoir R_1, the other taps being closed. The gas which has collected in B is then driven out through T_3 by raising R_1 after closing T_1. Water is then drawn from the flask F, which is kept boiling the whole time, into B, and T_3 is closed. Again, T_1 is opened and water is introduced into A, driving the piston before it. A now contains water with a bubble of air at the top; this is driven into B by lowering R_1. The tap T_1 is closed, while the greater part of the water still remains in A, from which it slowly escapes by the floating up of the piston.

The small quantity of water which remains above the piston has, of course, been contaminated by contact with the air or other gas which originally occupied A. To replace it by pure water, B is first filled with air-free water as described in the last section. A small quantity of this is then passed into A while still hot, so that it floats above the cold water already there. It is, therefore, mainly the latter which flows away as the piston gradually rises. More water is run in from B before the piston quite reaches the top of A. This process is repeated two or three times, and finally the piston is driven right down to the bottom of A, which is thus completely filled with water. The tap T_1 is left open and R_1 raised to a considerable height, and the piston thus pressed down into the constriction so that the water does not escape.

When the apparatus has cooled, the piston is drawn up by lowering R_1, but is not allowed to rise quite to the top of A. There is very little risk of contamination by air at this stage, because the piston is slowly floating upwards, and the water filling the narrow space round the piston has therefore a comparatively great downward velocity. Diffusion of the air upwards through this water is thus prevented.

Then T_1 is closed, and some of the gas to be investigated drawn into B by lowering R_1 and opening T_2. It is then driven into A by opening T_1 and raising R_1, T_2 being closed. This pumping process is repeated till the pressure in A is rather in excess of what is required.

The gas which remains in B is driven out through T_3, which is then closed, and T_1 opened for a moment, so that the narrow-bore tube and stop-cock are filled with water. It is necessary, of course, for this purpose that R_1 should be raised high enough to overcome the pressure in A; it is, in fact, now kept permanently fixed at such a level throughout all subsequent operations.

The excess of water always remaining above the piston in A at this stage is now allowed to escape by applying sufficient pressure below to drive the piston up a little. The pressure is applied by pumping air into C, by means of the mercury compressing pump shown at the extreme left of the diagram. The plug G is then pushed up and the piston thus allowed to fly back into the constriction.

To prevent contamination of the gas, the glass taps T_1 T_2 T_3 are lubricated with water only. The only one which requires to be used after the above operations are completed is T_1. Since this is filled with water under considerable pressure, there is no danger of air gaining access through it.

Method of producing expansion of any desired amount.

With this apparatus, direct volume measurements were not made, but the relative volume change was deduced from measurements of the initial pressure, and the pressure exerted by the saturated gas at the same temperature when occupying the increased volume. The final volume v_2, being that of A when the piston is at the bottom, is always the same; and the corresponding pressure p_2 at the temperature of the room shows only comparatively small changes resulting from variations temperature, and from the solution of the gas by the small quantity of water which is run through the apparatus.

This final pressure p_2 was measured in the following way. A mark was made in the wall of A approximately on a level with the top of the piston, when this was in its lowest position.

A telescope was then fixed in a clamp about one metre off, and its height adjusted till the mark appeared to coincide with the top of the piston. By means of the compressing pump air was driven into C till the pressure was sufficient to drive up the piston a little. Then S_2 being left open and S_1 closed, the tap S_3, regulating the flow of mercury in the pump, was closed and the reservoir R_2 lowered and fixed in such a position that S_3 could be worked by the observer while looking through the telescope.

S_3 was then opened very slightly so that the mercury flowed very slowly through it into R_2 thus lowering the pressure in C. The slow descent of the piston was watched and S_3 closed just as the piston reached its zero position. The pressure in C as indicated by the open mercury pressure gauge was then read to the nearest millimetre.

To obtain the actual pressure in A we have to add to the pressure indicated by the gauge the barometer reading and to subtract the pressure required to support the weight of the piston. This last term enters as a constant correction which was determined combined with any constant error of the manometer, by noticing the pressure required to support the piston, when there was free communication between the inside of A and the atmosphere. At the same time the freedom of the apparatus from errors in the pressure-readings due to friction between the piston and the walls of the tube was tested by taking readings first while the piston was being raised and then while it was allowed to sink slowly down. No difference was detected.

To obtain any desired initial pressure in A, S_3 is opened, while R_2 is in its lower position in order to draw in air through S_1 which is then closed and S_2 opened, R_2 is then hung on a support fixed as high as can be conveniently reached, and S_3 is closed just as the pressure, as indicated by the manometer, reaches the desired amount. To make the expansion S_2 is closed and the plug G suddenly pressed up. The manometer is again read after expansion.

In the case of the more insoluble gases, when the temperature was steady, the measurement of the final pressure did not require to be determined after each expansion. Several expansions could under such conditions be made without any sensible change in the pressure measured when the piston was at the bottom of the tube.

In order that the rain-like condensation might be visible, the experiments were done in a dark room, and the same method of illumination was employed as in the case of the larger apparatus.

The glass, too, was kept clear inside by periodically removing the expansion apparatus and washing the inside with caustic potash and nitric acid and rinsing well with distilled water.

Temperature was measured by a mercury thermometer hung beside the expansion apparatus. This method is sufficiently accurate for the purpose, as the result of an expansion of a given amount was sensibly constant throughout the ordinary range of room temperature. It is necessary, however, that the temperature should be known sufficiently accurately to enable the vapour pressure to be found within the nearest millimetre of mercury. An error of half a degree in the temperature reading does not make a difference of much more than half a millimetre in the vapour pressure.

Calculation of v_2/v_1 from the Observations of Pressure.

To obtain the ratio of the final to the initial volume we have, when the gas present obeys BOYLE's law,

$$v_2/v_1 = P_1/P_2,$$

where P_1 is the pressure exerted by the gas alone before expansion, and P_2 is its pressure after expansion, when the temperature has risen to its former value.

Now

$$P_1 = p_1 + B - \pi - w,$$

and

$$P_2 = p_2 + B - \pi - w,$$

where p_1, p_2 are the pressures measured by the mercury gauge, before and after expansion, as already described, B is the atmospheric pressure, π is the maximum vapour pressure at the temperature of experiment, and w is the pressure required to balance the weight of the piston.

Results obtained with Air in the small Apparatus.

The same phenomena are observed as in the larger apparatus, as well as others to be described later.

After the removal of "dust" by repeated expansion, no condensation takes place within the moist air, unless v_2/v_1 exceeds a certain limit. With greater expansions rain-like condensation results. As will be seen from the following table, measurements of this critical value of v_2/v_1 made with the two machines give identical results, although the larger one contained twenty times as great a volume of air as the smaller. The expansion, therefore, appears to be sufficiently rapid to prevent the walls having any sensible effect.

EXPANSION required for Rain-like Condensation in Air.

Pressures all given in millims. of mercury. Correction for piston weight $w = 1$ millim.

	Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
1	February 13 . .	775	18·5	16	651	1409	372	1130	1·247
2	,, 14 . .	775	17·5	15	685	1444	386	1145	1·261
3	,, 17 . .	776	15·5	13	685	1447	392	1154	1·254
4	,, 22 . .	764	16·5	14	602	1351	330	1079	1·252
5	,, 22 . .	764	16·5	14	506	1255	254	1003	1·251
6	March 2 . . .	750	18·5	16	654	1387	377	1110	1·250
								Mean	1·252

The apparatus was charged with a fresh supply of air each day.

The results of all the measurements made with the small apparatus on the rain-like condensation are given in the table.

The expansion can be measured with quite as great accuracy as in the larger apparatus, but the whole number of drops when condensation first begins is inconveniently small in the small apparatus. This makes the measurements of the critical value of v_2/v_1 more troublesome.

Each determination of this requires a large number of observations to be made, p_1 being always made less or greater according as the previous expansion had brought down a shower or not. In this way it was possible, finally, to obtain the least value of p_1, necessary in order that a shower should result within about 2 millims.

It will again be noticed that the result obtained is with the limits of experimental error independent of the temperature between 15·5° and 18·5° C.

We may summarise the results of the measurements made with both machines upon the expansion required for rain-like condensation in the following statement.

When saturated air free from all extraneous nuclei is suddenly expanded, rain-like condensation takes place if the ratio of the final to the initial volume exceeds 1·252. This is true if the initial temperature is between 15° and 28° C.

It will be noticed that this expansion is less than that used by AITKEN in the experiments already referred to. The difference between the result of making the stroke of his pump slow or quick was therefore evidently due to the expansion not being quick enough to give the theoretical lowering of temperature.

Phenomena observed with Expansions greater than that required to produce Rain-like Condensation.

If a series of expansions be made of constantly increasing amount, the following phenomena are observed.

The drops are, if the expansion be only slightly greater than is sufficient to produce condensation, only few in number. More of them are seen if the expansion be somewhat greater, but even when v_2/v_1 is as great as 1·37, the condensation still takes the form of a shower of drops, which settle within a few seconds. To the eye there is no marked difference in the density of the shower over quite a wide range of expansions.

If, however, v_2/v_1 be increased from 1·37 to 1·38, the increase in the number of drops is so great that there is no longer any resemblance to a shower of rain, but a fog results, taking a minute or more to settle.*

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* [*Note added July 22nd*, 1897.—When expansion results in a fog, it is of course necessary to get rid of all traces of it before proceeding to a fresh observation. This was done by repeated expansions of moderate amount, as in the removal of the original dust particles.]

With expansions greater than this, the density of the fog appears to go on increasing with great rapidity as the expansion is increased. It is now convenient to remove the condensing lens and examine the fog by looking directly through it at the gas-flame. Coloured diffraction rings make their appearance when v_2/v_1 is about 1·38 and they increase rapidly in brilliancy and size as the expansion is made greater and greater.

Before v_2/v_1 reaches 1·40, the region within the first ring, which is whitish with smaller expansions, becomes brightly coloured. With greater expansions, the rings rapidly become so large that the colour corresponding to the central part of the field fills the whole tube.

The colour phenomena beyond this stage are surprisingly definite. They are best observed by looking through the cloud chamber slighly to one side of the source of light, which ought now to be made as bright as possible, and have a black background.

If v_2/v_1 be between 1·41 and 1·42, brilliant greens and blue-greens are seen. At about 1·42 there is a very rapid change from blue to red through violet. The violet appears only for a very small range of expansion, a change of one or two millimetres in the initial pressure being sufficient to complete the change from blue to red.

As the expansion is further increased, the colour passes from red through yellow to white. With expansions greater than about 1·44, the fog is always white with a greenish or bluish tinge.

The whole of these colour phenomena, it will be seen, are confined to quite a narrow range of expansions. Below 1·38 the drops are too large and few; and above 1·44 they appear to be too small to produce the colours.

Colours of exactly the same kind were obtained by KIESSLING* and by AITKEN† by expanding ordinary moist unfiltered air; but in the reverse order, pale yellow being the first to appear, followed with increasing expansions by a reddish colour, then by blue, and then green.

The explanation of the difference plainly, is that in their experiments the number of the drops was determined by the number of "dust" particles present, and increased expansion caused a larger quantity of water to condense on each particle.

Increasing the expansion thus increased the size of the drops. Now in the experiments here described, the greater the expansion, the smaller appear to be the resulting drops, which indicates that as the supersaturation is increased, a larger number of nuclei come into play, so that each receives a smaller share of the water which condenses.

Similar phenomena are exhibited by light transmitted through a steam-jet under

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* GÖTTING., 'Nachr.,' 1884, p. 226.

† 'Proc. Roy Soc.,' vol. 51, p. 422, 1892.

certain conditions. They have been investigated by R. V. HELMHOLTZ,[*] AITKEN[†] and, in a more elaborate way, by BARUS.[‡]

Measurements of the Expansion required to produce Cloud-like Condensation.

The transition from rain-like to cloud-like condensation is sudden enough to enable one to measure, with considerable accuracy, the value of the ratio v_2/v_1 when cloud-like condensation just begins. There is, in fact, a second condensation point, below which the drops are few, and the number shows only a slight increase with increasing expansion; while above it the number increases at an excessively rapid rate with increasing expansion.

EXPANSION required for Cloud-like Condensation in Saturated Air.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.	Result.
February 14. .	775	17·5	15	706	1465	308	1067	1·373	Rain
„ 14. .	775	17·5	15	712	1471	308	1067	1·378	Fog
„ 15. .	775	18·5	16	791	1549	369	1127	1·375	Rain
„ 15. .	775	18·5	16	795	1553	369	1127	1·378	Fog
„ 18. .	769	15·0	13	803	1558	381	1136	1·372	Rain
„ 18. .	769	15·0	13	813	1568	381	1136	1·380	Fog

The transition from rain to fog takes place when v_2/v_1 is between 1·37 and 1·38.

The above results were obtained using the same method of illumination as in the experiments on rain-like condensation. Observations were also made with the condensing lens removed.

FIRST Appearance of Diffraction Rings.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
February 24	776	15	13	676	1438	279	1041	1·381
„ 25	772	13	11	667	1427	277	1037	1·376
March 2	750	18	15	807	1541	380	1114	1·383
„ 2	750	18·5	16	715	1448	318	1051	1·378
							Mean .	1·379

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[*] 'Wied. Ann.,' 32, p. 1, 1887.

[†] 'Proc. Roy. Soc.,' vol. 51, p. 422, 1892.

[‡] BARUS, *loc. cit.*, also 'Phil. Mag.,' vol 35, p. 315, 1893.

Observations were also made of the time taken by the drops to settle, as v_2/v_1 was gradually increased. This was of course very short when the condensation took the rain-like form. It showed a very sudden increase when the rain was replaced by fog. For example, such measurements were made in connection with the last observation given in the preceding table.

v_2/v_1.	
1·378	Colours scarcely visible, drops settled in a few seconds.
1·381	Rings faint, drops took about one minute to settle.
1·385	Rings brilliant, took several minutes to settle.

All these methods of making evident the change from rain to fog agree in showing that this takes place when v_2/v_1 lies between 1·37 and 1·38.

Colour Observations.

The colour phenomena change so rapidly as v_2/v_1 is increased from 1·38 to 1·40 that consistent measurements were not possible. In the tables which follow the observations therefore begin where the brilliant greens previously referred to first appear. The colours are those seen on looking through the tube, almost, but not quite in the direction of the source of light.

February 25. $t = 13°$ C.		March 3. $t = 18°$ to $19°$ C.	
v_2/v_1.	Colour.	v_2/v_1.	Colour.
1·408	Brilliant green	1·410	Green
1·408	" "	1·410	"
1·412	" "	1·413	"
1·414	" "	1·416	Blue-green
1·414	" "	1·418	Brilliant blue
1·419	Blue-green	1·419	Violet
1·419	Purple	1·420	"
1·422	"	1·420	Reddish-purple
1·424	Brilliant red	1·426	Red
1·426	Red	1·429	Reddish-yellow
1·428	"	1·436	Yellowish-white
1·429	"	1·448	White
1·434	Reddish	1·469	Greenish-white
1·437	Reddish-white		
1·453	Greenish-white		
1·458	" "		

When the greenish-white fog appeared, the colour was the same from whatever point the tube was viewed, out of the direct line of the incident light. The particles are then evidently small enough to scatter the red light less than the blue.

Meteorological Applications.

The question of the degree of supersaturation reached in these experiments is postponed till the results obtained with other gases have been given. In considering the meteorological applications we are directly concerned with the expansion required to cause condensation in air originally saturated. For adiabatic expansion to result in condensation in saturated air free from all foreign nuclei, we have seen that the final volume must exceed 1·252 times the initial volume.

To obtain the corresponding ratio between the final and initial pressures we have

$$p_1 v_1{}^\gamma = p_2 v_2{}^\gamma,$$

or

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^\gamma.$$

where γ is the ratio of the specific heat of air at constant pressure to that at constant volume. The difference in γ for dry and moist air is small, and may here be neglected, γ being therefore taken as equal to 1·41.

Now

$$\frac{v_1}{v_2} = \frac{1}{1{\cdot}252}, \quad \text{therefore} \quad \frac{p_2}{p_1} = \frac{1}{1{\cdot}252^{1{\cdot}41}} = {\cdot}728.$$

Condensation must therefore take place in air free from foreign nuclei when the pressure is reduced adiabatically to ·728 of the value which it has when the air is just saturated. The drops which are formed are, as we have seen, comparatively few. The fall of pressure required is sensibly the same for all values of the initial temperature between 28° and 15° C., and it is therefore probable that the result may be applied to considerably lower temperatures without any great error.

It is natural to suppose that when there is an upward current of moist air, the foreign nuclei will be left behind through becoming loaded with the water which condenses on them, and that the air which rises above the lower cloud layer thus formed will be dust-free and supersaturated.

It follows from the results of these experiments that condensation will again begin when the air reaches such a height that the pressure is reduced to about ·73 of that at the upper surface of the lower cloud.

It is not likely that the cloud-like condensation obtained with greater expansion has any meteorological significance. For it is unlikely that there can ever be such a sudden uprush of air as to enable any great degree of supersaturation to be maintained when drops have already begun to form.

Oxygen.

Preparation.—Potassium permanganate was heated in a small glass tube fused on to H (fig. 2). This was exhausted and then heated till the pressure considerably exceeded that of the atmosphere, and the process of alternate exhaustion and heating many times repeated.

The mercury reservoirs B, R_1 with the taps T_2, T_3 served as a pump.

Results.—Oxygen behaves exactly like air in these experiments. The expansion required to produce both rain-like and cloud-like condensation, is practically the same in both. The colour phenomena are also exactly alike.

EXPANSION required to produce Rain-like Condensation in Saturated Oxygen.

Pressures all given in millimetres of mercury. Correction for piston weight, $w = 1$ millim.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
May 8	769	17	14	594	1348	318	1072	1·258
„ 14	768	20	17	638	1388	357	1107	1·254
„ 15	768	21	18	579	1328	307	1056	1·258
							Mean	1·257

A fresh supply of oxygen was used each day.

EXPANSION required to produce Cloud-like Condensation in Oxygen.

	Date.	B.	$t°$ C.	π.	p_1.	P_1	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
	May 9	769	18·0	15	732	1485	318	1071	1·386
1	„ 14	767	20·5	18	659	1407	273	1021	1·378
2	„ 14	766	21·5	19	665	1411	273	1019	1·385
								Mean	1·383

Measurements were also made of the ratio v_2/v_1 when the colour produced by the expansion was the sensitive tint between the blue and red referred to in the account of the colour phenomena observed in the experiments with air.

EXPANSION required to produce the Sensitive Tint.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.	Colour.
March 6 . .	752	19·5	17	804	1538	347	1081	1·423	Violet
,, 7 . .	775	17·5	15	799	1558	341	1100	1·417	,,
							Mean	1·420	

Carbonic Acid.

Preparation.—Potassium bicarbonate was heated in a glass tube, fused directly to H. This was repeatedly heated and pumped out.

Results.—Carbonic acid shows, like air and oxygen, the two kinds of condensation, each requiring a definite minimum expansion for its production.

The measurements could not be made with the same accuracy in this case on account of the solubility of the gas in water. This caused a continual falling off in the pressure, necessitating the reading of the final pressure p_2 after each expansion.

On account of the difference in γ, the results with CO_2 are not directly comparable with those obtained with air, the same expansion corresponding to a different fall of temperature.

The colour phenomena were not looked for.

In the table which follows, the pressure readings corresponding to the greatest expansion which was made without condensation, as well as those of the least expansion which resulted in condensation, are given. In the case of the more insoluble gases, the difference between these only amounted to 2 millims.; here, as will be seen, it is considerably greater.

RAIN-LIKE Condensation in CO_2.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.	Result.
May 23	764	19	16	710	1457	333	1080	1·349	0
,, ...	764	19	16	700	1447	314	1061	1·364	Rain
May 25	775	17	14	605	1355	247	997	1·359	0
,, ...	775	17	14	612	1362	245	995	1·369	Rain
May 25	775	17	14	599	1349	242	992	1·360	0
,, ...	775	17	14	603	1353	240	990	1·367	Rain

Condensation begins when P_1/P_2 is between 1·36 and 1·37.

For pressure changes within these limits (between $1\frac{1}{2}$ and 2 atmospheres) BOYLE'S law is sufficiently nearly obeyed to justify us in saying that condensation begins when v_2/v_1 lies between 1·35 and 1·37. Regnault found* that if the pressure of the CO_2 was changed from 1 atmosphere to 2, the ratio of the initial to the final volume was 2 × 1·0076. The difference between P_1/P_2 and v_2/v_1 is therefore well within 1 per cent.

Cloud-like Condensation in CO_2.

Date.	B.	$t°$ C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.	Result.
May 25	775	17·5	15	738	1487	223	972	1·530	Rain
„	775	17·5	15	734	1503	230	979	1·535	Fog

All the above results were obtained with the same sample of CO_2. On absorbing the gas by KOH a bubble amounting to less than 1 part in 1000 of the whole remained. The gas had been in the expansion apparatus for three days and 50 expansions had been made. The contamination which takes place by air diffusing through the lubricating water round the piston is therefore certainly very slight. In the experiments with CO_2 the lubricating water was less frequently renewed, and a smaller quantity run in at a time than with the less soluble gases. There was, therefore, even less chance of contamination of the latter than of the CO_2.

Hydrogen.

This was prepared by passing steam over sodium. This method was used by Scott in his experiments on the composition of water.†

The apparatus for the preparation of the gas is shown in fig. 3.

The water was contained in the bulb A and the sodium in B, which was prolonged into a narrower tube C, fused directly to H in fig. 2. The vertical tube D served for the introduction of the water.

The sodium was previously heated in a tube, kept exhausted by the water pump. The tube was held for several minutes in a Bunsen flame, and the sodium then poured off into the clean part of the tube.

The water to be introduced into A was obtained free from dissolved gases by boiling rapidly down in a flask to about one-sixth of the original volume. This was drawn up through D without allowing it to cool, the end of D dipped under mercury and the apparatus immediately pumped out. The mercury rose in D, which now served as pressure-gauge and safety-tube.

The bulb A was now warmed till the pressure exceeded that of the atmosphere, and bubbles began to escape through the mercury in E.

The flame was then removed, and the apparatus again pumped out to as low a

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* 'Comptes Rendus,' vol. 23, p. 794 (1846).

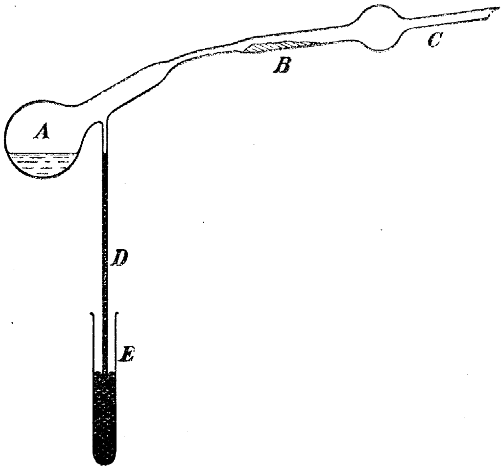
† 'Phil. Trans.,' 1893, p. 543.

pressure as possible. Hydrogen was thus generated and pumped out several times, and lastly a vigorous stream of hydrogen was allowed to escape through the water in the flask F (fig. 2) by opening the taps T_2 and T_3. The flame was then removed and T_2 closed, the gas which still continued to come off escaping through the safety-tube D. The hydrogen was then ready to be pumped into the expansion apparatus as required. Even in the cold, hydrogen is slowly formed by the water vapour reaching the sodium by diffusion, and escapes through the safety-tube. No further heating was therefore required when a fresh charge was wanted in the expansion apparatus.

Results.—The phenomena attending condensation in presence of hydrogen differed considerably from those observed with other gases.

As in air and oxygen, dense condensation begins when v_2/v_1 is between 1·37 and 1·38, and the number of particles rapidly increases with increasing expansion. With very slightly smaller expansions, however, the drops are excessively few, and if v_2/v_1 be less than 1·36, they are either absent altogether or at the most one or two scattered drops are seen. It was found impossible to get any consistent measurements of the minimum expansion required to make these drops appear. In no case was any condensation at all observed when v_2/v_1 was less than 1·30, while in one series of observations no condensation resulted when v_2/v_1 was as great as 1·356.

Fig. 3.



It is likely that this irregular condensation is due to impurities in the gas. For the observations in which no condensation whatever was observed, even when v_2/v_1 was not much below 1·36, were all made when the hydrogen was comparatively fresh, before it had been allowed to expand more than a very few times. The slight contamination which may take place by diffusion of air through the water lubricating the piston may account for their subsequent appearance. The contamination which can take place in this way must, as has been shown, be very slight; but it is quite possible that an exceedingly small trace of air would be sufficient to cause the slight condensation which is observed. It must be remembered that even if only one drop separates out it will be seen. Colours like those observed in the other gases made their appearance when the expansion exceeded that required to produce the dense condensation. Measurements, however, were not made of the expansion required to produce a given colour.

Expansion required to produce Dense Condensation in Hydrogen.

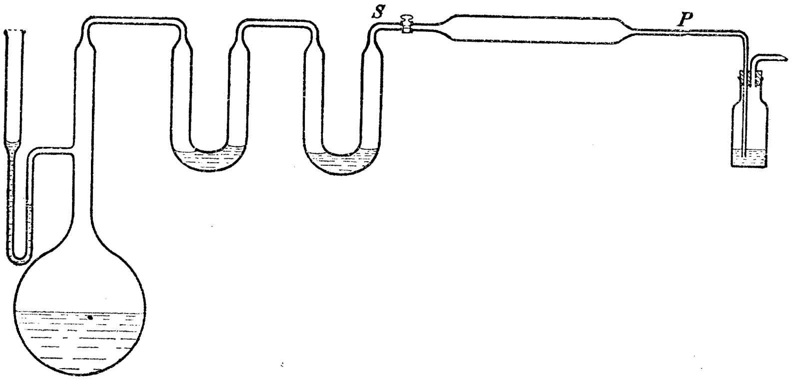
Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
Aug. 4	763	22·0	20	670	1412	283	1025	1·378
„ 6	767	20·5	18	661	1409	267	1015	1·388
„ 6	767	21·0	18	652	1400	269	1017	1·377
„ 6	767	21·0	18	653	1401	269	1017	1·378
							Mean	1·380

Chlorine.

This was prepared by heating hydrochloric acid with potassium bichromate.

The apparatus is shown in fig. 4. The U-tubes contained water. A supply of the gas was collected in the tube SP, by allowing a rapid stream to pass for about three-quarters of an hour, and then closing the stopcock, and sealing off at P with the blow-pipe.

Fig. 4.



The tube was then cut at S. The part from S to P was then removed, and the open end joined to L (fig. 2) in place of the stopcock T_2. The chlorine was then pumped into the expansion apparatus when required, the reservoir B (fig. 2) with the tubes connected to it being of course first completely filled with well-boiled water. The tube SP was throughout protected from the light by a wrapping of black paper.

After use, the chlorine was absorbed by driving KOH into the expansion chamber. (This was done by expelling the water from B, and drawing in potash in its place, and then opening T_1, while R_1 was raised sufficiently high to overcome the pressure in A.) The bubble which remained was then drawn up into the capillary tube for measurement.

Out of the three samples of chlorine used, two were analysed in this way. In both cases the volume of gas unabsorbed amounted to between 1 and 2 parts in 1000 of the whole.

Results.—Chlorine shows both kinds of condensation, each requiring a definite minimum expansion. With expansions greater than was necessary to produce cloud-like condensation, colour phenomena were observed like those exhibited by air and oxygen.

The solubility of the chlorine introduced difficulties of the kind experienced with CO_2, interfering considerably with the exactness of the measurements. The final pressure p_2 had to be measured after each expansion, no water being run in till after this measurement was completed.

The drops when the condensation was of the rain-like form appeared to the eye to be much more numerous in chlorine than in the other gases.

EXPANSION required to produce Rain-like Condensation in Chlorine.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.	Result.
August 20 . .	761	21·5	19	443	1184	166	907	1·306	Rain.
,, 20 . .	761	21·5	19	420	1161	153	894	1·299	0
August 24 . .	760	20	17	560	1302	257	999	1·304	Rain.
,, 24 . .	760	20	17	549	1291	252	994	1·299	0

Rain-like condensation begins when P_1/P_2 is about 1·30.

EXPANSION required to produce Cloud-like Condensation in Chlorine.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	P_1/P_2.
August 28	768	18	15	741	1490	280	1029	1·448
,, 28	768	18	15	660	1409	223	972	1·449

Cloud-like condensation begins when P_1/P_2 is about 1·45. The second observation was made with the condensing lens removed, the readings given being those corresponding to the least expansion required to make coloured rings appear. With greater expansions the size and brilliancy of the rings rapidly increased.

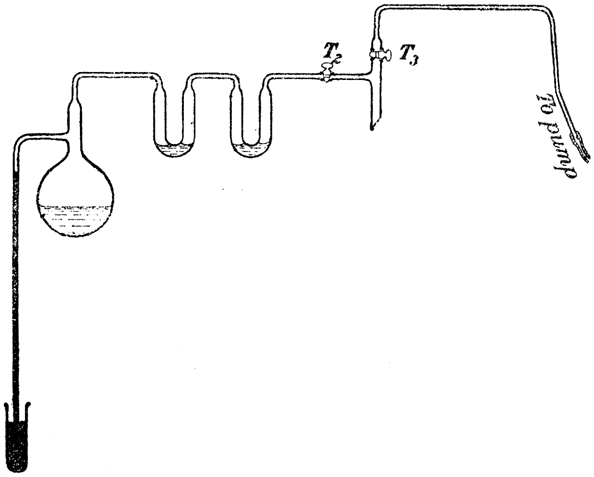
We cannot suppose that chlorine at the pressures and temperatures used in these experiments obeys BOYLE's law even approximately. It is not allowable, therefore, to put $P_1/P_2 = v_2/v_1$.

Nitrogen.

This was prepared by adding ammonium chloride to a nearly saturated solution of sodium nitrite, till no more would dissolve, and warming gently. In the first series of experiments a concentrated solution of potassium bichromate was added. This was omitted in the later experiments. The gas was allowed to pass through two U-tubes containing strong caustic potash solution.

The apparatus for the preparation of the gas is shown in fig. 5.

Fig. 5.



The liquid was drawn into the flask through the vertical tube. This was then made to dip below the surface of mercury contained in a small test-tube. The apparatus was then connected to the water-pump, and the liquid in the flask allowed to boil under very low pressure, by warming gently. This was allowed to continue for some time. The tap T_2 was then closed, and the heating continued till the pressure exceeded that of the atmosphere and the nitrogen began to escape through the safety-tube. T_2 was then again opened and the gas allowed to escape through T_2 and T_3. The temperature of the flask was never allowed to rise more than was sufficient to give a steady stream of the gas, which gradually ceased after the removal of the flame. Finally T_2 was closed and the heating discontinued. The nitrogen could then be pumped out when required.

Results.—The results are practically identical with those obtained with air and oxygen.

The experiments of October 6 were made with the same expansion apparatus as had been used with the other gases. This was unfortunately broken immediately afterwards and the apparatus made to replace it was much smaller, having a capacity of only 8 cub. centims., the length of the expansion chamber being 4 centims., and that of the piston 5 centims. The pressure required to balance the weight of the piston was about 2 millims. of mercury. The volume of the gas is, therefore, smaller, and the rate at which it expands slower than in the former machine.

EXPANSION Required to Produce Rain-like Condensation in Nitrogen.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
October 6	754	13	11	681	1423	390	1132	1·257
November 19	765	17·5	15	562	1310	289	1037	1·263
„ 19	764	17	14	546	1294	276	1024	1·264
„ 19	764	17	14	540	1288	275	1023	1·259
November 30	772	11	10	610	1370	321	1081	1·267
							Mean	1·262

The number of drops appeared to be small in nitrogen.

EXPANSION Required to Produce Cloud-like Condensation in Nitrogen.

Date.	B.	t° C.	π.	p_1.	P_1.	p_2.	P_2.	$P_1/P_2 = v_2/v_1$.
October 6	754	13·5	12	765	1506	350	1091	1·380
November 21	775	15·0	13	713	1473	307	1067	1·380
„ 21	775	15·0	13	709	1469	304	1064	1·381
							Mean	1·38

The colour phenomena were exactly like those observed in air.

Measurements were made of the expansion required to produce the sensitive tint.

Date.	t° C.	v_2/v_1.
October 6	13·5	1·417
November 28.	11·5	1·434
„ 28.	11·5	1·430
	Mean	1·427

The observations of November 28 were made with the smaller machine, those of October 6 with that which had been used for the experiments on the other gases.

Supersaturation Resulting from a Given Expansion.

By the supersaturation is here meant the ratio of the actual density of the vapour when the expansion has just been completed, and the minimum temperature has therefore been reached to the density of vapour which is in equilibrium over a flat surface of water at that temperature.

It is assumed in what follows that the expansion is completed before any appreciable amount of water has had time to condense on the walls, or in drops throughout the moist gas.

To find the lowest temperature reached we have the well-known equation for the cooling of a gas by adiabatic expression,

$$\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1},$$

where θ_1, θ_2, are the initial and final absolute temperatures, and γ is the ratio of the specific heat at constant pressure to that at constant volume. This has been assumed below to be the same as in the dry gas, the effect on γ of the small quantity of vapour present being neglected. The error introduced in this way, as pointed out by R. v. HELMOLTZ,[*] is inappreciable at temperatures below 30° C.

Knowing θ_1 and v_2/v_1, the ratio measured in these experiments, we can, therefore, calculate θ_2.

Let π_1, π_2 be the pressure of saturated vapour over a flat surface of water at the temperature θ_1, θ_2 respectively. π_1 is then the initial pressure of the vapour before expansion. The volume of the vapour is suddenly changed from v_1 to v_2. We cannot, however, calculate the resulting change in its pressure, there being no reason to suppose that BOYLE's law is even approximately obeyed by the highly supersaturated vapour. There is no such uncertainty, however, as to the density of the vapour, which must change inversely as the volume. It is for this reason that the supersaturation is here defined as the ratio of the actual to the equilibrium density over a flat surface, and not in terms of the corresponding pressure.

The supersaturation, according to the above definition, is equal to

$$S = \rho'/\rho_2,$$

where ρ' is the final density of the vapour before condensation takes place, and ρ_2 is the density of the saturated vapour at the temperature θ_2.

But $\frac{\rho'}{\rho_1} = \frac{v_1}{v_2}$, therefore, $S = \frac{\rho_1}{\rho_2} \times \frac{v_1}{v_2}$.

Now the actual density of saturated water vapour in the presence of air at ordinary atmospheric temperatures, has been shown by SHAW[†] to agree very closely with the

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[*] 'Wied. Ann.,' xxvii., p. 508 (1886).

[†] 'Phil. Trans.,' 1888, A, p. 83.

density calculated on the assumption that the vapour behaves like a perfect gas. We may, therefore, write

$$\frac{\rho_1}{\rho_2} = \frac{\pi_1}{\pi_2} \times \frac{\theta_2}{\theta_1}.$$

$$\text{Therefore, } S = \frac{\pi_1}{\pi_2} \times \frac{\theta_2}{\theta_1} \times \frac{v_1}{v_2} = \frac{\pi_1}{\pi_2} \times \left(\frac{v_1}{v_2}\right)^\gamma.$$

Supersaturation Required for Rain-like Condensation.

For convenience of comparison the calculations have been made for the case where the initial temperature t_1 is 20° C. As we have seen, the ratio v_2/v_1 when condensation just begins, is within the limits of experimental error, constant within the ordinary range of room temperature.

Chlorine is too far removed from the condition of a perfect gas for the fall of temperature to be calculated. The error from the same cause may also be considerable in the case of CO_2.

In the following table REGNAULT's numbers have been used for the vapour pressure at temperatures above the freezing point. The vapour pressures over water below the freezing point are from a paper by JUHLIN,* who has measured directly the pressure over water over a considerable range of temperature below the freezing point. t_1, t_2 are the initial and final temperatures Centigrade, $\theta_1 = t_1 + 273$, $\theta_2 = t_2 + 273$.

	θ_1.	π_1.	v_2/v_1.	γ.	θ_1/θ_2.	t_2.	π_2.	$S = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^\gamma$.
Air	293	17·39	1·252	1·41	1·097	− 5·8	3·02	4·2
Oxygen	293	17·39	1·257	1·41	1·098	− 6·2	2·93	4·3
Nitrogen	293	17·39	1·262	1·41	1·100	− 6·7	2·83	4·4
Carbonic Acid . .	293	17·39	1·365	1·31	1·101	− 6·9	2·78	4·2
(Chlorine . . .	293	17·39	1·30	1·32	1·087	− 3·5	3·58	3·4)

Hydrogen does not appear in this table, as no regular rain-like condensation was observed.

It will be noticed that the supersaturation required to cause condensation is practically the same in CO_2 as in the other gases, in spite of the great difference in v_2/v_1.

The supersaturation is in each case the greatest which can exist at the temperature t_2° C. without condensation resulting.

To find to what extent this depends upon the temperature, we may make use of the fact that v_2/v_1, when the resulting supersaturation is just sufficient to cause condensation, is in the case of air constant for temperatures between 15·5° C. and 28·8° C.

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* 'Bihang till K. S. Vet. Akad. Handlingar,' Bd. 17.

SUPERSATURATION required to cause Condensation in air at different temperatures.

t_1.	θ_1.	π_1.	v_2/v_1.	γ.	θ_1/θ_2.	t_2.	π_2.	$S = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^\gamma$.
15·5	285·5	13·12	1·252	1·41	1·097	− 10	2·197	4·35
20°	293	17·39	1·252	1·41	1·097	− 5·8	3·02	4·2
28·8	301·8	29·45	1·252	1·41	1·097	+ 2·2	5·377	4·0

Thus the maximum supersaturation is 4·35 at − 10° C. and 4·0 at + 2·2° C. It therefore diminishes with rising temperature at the rate of about ·03 per degree.

Supersaturation required to produce Cloud-like Condensation.

The calculations are again made for an initial temperature of 20° C.

The results for Air, Oxygen, Hydrogen, and Nitrogen are grouped together, the difference in the observed value of v_2/v_1 when the dense condensation begins being no greater than can be accounted for by experimental errors. In all these gases the least value of v_2/v_1 when the condensation first becomes cloud-like is about 1·38. In air, however, in which more exact measurements were attempted, the beginning of the change from the rain-like to the cloud-like form could be detected when v_2/v_1 only slightly exceeded 1·37.

The calculations have therefore been made taking $v_2/v_1 = 1{\cdot}375$. $t_1 = 20°$ C.

	θ_1.	π_1.	v_2/v_1.	γ_1.	θ_1/θ_2.	t_2.	π_2.	$S = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^\gamma$.
Air, O, H, N . .	293	17·39	1·375	1·41	1·140	− 15·8	1·41	7·9
CO_2	293	17·39	1·53	1·31	1·141	− 16·2	1·37	7·3
(Chlorine . . .	293	17·39	1·44	1·32	1·124	− 12·3	1·83	5·9)

If then by sudden cooling a supersaturation exceeding 7·9 be produced at a temperature of about − 16° C., the condensation, instead of taking place on a small number of scattered nuclei, as with a smaller degree of supersaturation, takes place upon a very large number, the number of nuclei which come into play increasing at a very rapid rate with increasing expansion. It will be noticed that the supersaturation required to produce either kind of condensation is practically the same in all gases, the rain-like condensation, however, being absent in hydrogen.

Supersaturation required to produce the sensitive tint.

At first sight it might seem that when the expansion is so great that a very large number of drops begin to grow before it is completed, the maximum supersaturation must be much less than is obtained by calculation according to the above method. It is difficult, however, to understand the constancy of the results obtained in the observations of the colour phenomena unless the supersaturation resulting from expansion of a given amount is always the same in spite of the variations which there must be in the rate of expansion. If the maximum supersaturation be independent of variations in the rate of expansion, it must be because the maximum supersaturation reached does not differ much from what would result from an infinitely rapid expansion.

This is, perhaps, not very surprising if we consider how little time the drops have to grow before the expansion is completed. To produce the sensitive tint in air v_2/v_1 must be made equal to 1·420. It is only while v_2/v_1 is increasing from 1·38 to 1·42, that the number of drops in process of formation is at all considerable, that is, when the piston has already completed nine-tenths of its journey. Now the piston must be moving with constantly increasing velocity; the whole distance moved by the piston amounts to less than 1·5 centimetres; the time taken to travel the last tenth of this, that is, less than 1·5 millimetres, must therefore be very short. We have seen that the time taken to travel the whole distance is itself very short. The growth of the drops too, as has already been pointed out, cannot be very rapid. It is quite likely therefore that even when they are very numerous, the quantity of water which separates out upon them before the expansion is complete may be too small to diminish appreciably the final supersaturation reached.

The supersaturation required to produce the sensitive tint in air is calculated below.

t_1.	θ_1.	π_1.	v_2/v_1.	γ.	θ_1/θ_2.	t_2.	π_2.	$S = \frac{\pi_1}{\pi_2}\left(\frac{v_1}{v_2}\right)^{\gamma}$.
20°	293	17·39	1·420	1·41	1·155	−19·2	1·07	9·9

On the number of the drops.

It is possible to obtain some information as to the number of the drops formed for a certain range of supersaturation from the colour phenomena. For from the colours we ought to be able to deduce the size of the full-grown drops, and the total quantity of water which condenses in consequence of the corresponding expansion may be calculated. With the exceedingly dense fogs with which we are now dealing there is no doubt that the water which condenses on the walls will be small in quantity compared with what condenses in the form of drops. From the quantity of water which separates, and the size of the drops, we may calculate the number, assuming the water to be equally divided among them.

It is assumed here that the cloud-particles are actually liquid drops and not ice-crystals, in spite of the fact that the condensation begins at temperatures much below the freezing point, and that the temperature when the particles are full grown is, as we shall see, also slightly below the freezing point.

Let us consider first the quantity of water which separates out in consequence of an expansion of a given amount. Let us suppose the expansion to be completed before the drops have grown to more than a very small fraction of their final size, so that the theoretical lowering of temperature results. Let t_1 be the temperature Centigrade before expansion, t_2 the lowest temperature reached.

In consequence of the condensation of the water, heat is set free, and the temperature of the moist air rises. A stationary state is reached at a temperature t_3, when just so much water has separated that the vapour remaining is in equilibrium in contact with the drops. The subsequent changes will be slow, being due to the inflow of heat and vapour from the walls. They appear to have little effect upon the size of the drops, for the colour changes very little, and only gradually fades away; evidently through the drops becoming unequal in size. This is not difficult to understand, for the air which comes in contact with the walls of the tube, since these are covered with water, must remain saturated in spite of its rise in temperature.

If we consider 1 cub. centim. of the moist gas, we have the following equation connecting the temperature t reached at any moment with the quantity of water q which has condensed,

$$\mathrm{L}q = \mathrm{CM}\,(t - t_2),$$

where M is the mass of unit volume of the gas and C its specific heat at constant volume. It will not introduce any serious error, for the present purpose, if we neglect the heat spent in raising the temperature of the small quantity of vapour present. L is the latent heat of vaporisation, which changes slightly as the temperature changes during the process, but may be considered with sufficient exactness as equal to 606, its value at 0° C.

Now,

$$q = \rho_1 - \rho,$$

where ρ_1 is the density of the vapour just before condensation begins, and ρ the mean density of the vapour remaining uncondensed at any moment.

Thus,

$$\mathrm{L}\,(\rho_1 - \rho) = \mathrm{CM}\,(t - t_2),$$

or

$$\rho = \rho_1 - \frac{\mathrm{CM}}{\mathrm{L}}\,(t - t_2).$$

If we consider the experimental results obtained with air on March 3rd, we have, when the violet colour results, $v_2/v_1 = 1{\cdot}420$, the initial temperature being 19° C., and the pressure, when the volume $= v_2$ and the temperature $= 19°$ C., being equal to 1039 millims. of mercury. The density of air at standard temperature and pressure is ·00129 grm. per cubic centimetre.

Therefore,

$$\mathrm{M} = {\cdot}00129 \times \frac{1039}{760} \times \frac{273}{292} = {\cdot}00165.$$

The lowest temperature calculated from the expansion is

$$t_2 = -\ 20{\cdot}2.$$

Also,

$$\rho_1 = \rho_0 \times \frac{v_1}{v_2},$$

where $\rho_0 =$ density of saturated steam at the temperature t_1.

When $t_1 = 19°$ C.

$$\rho_0 = {\cdot}0000162,$$

therefore,

$$\rho_1 = {\cdot}0000162 \times \frac{1}{1{\cdot}42} = {\cdot}000114.$$

Now C, the specific heat of air at constant volume $= {\cdot}167$.

We, therefore, find for the density of the vapour, when the temperature has risen from t_2 to t,

$$\rho = {\cdot}000014 - \frac{{\cdot}167 \times {\cdot}00165\ (t - t_2)}{606}$$

$$= {\cdot}000014 - 4{\cdot}55 \times 10^{-7}\ (t - t_2).$$

If we put $t = -\ 4°$ C., we obtain for ρ the value $4{\cdot}0 \times 10^{-6}$. Now, the density of the saturated vapour at that temperature is $3{\cdot}7 \times 10^{-6}$. More vapour would, therefore, condense, and the temperature would rise further.

If $t = -\ 3°$ C., ρ calculated from the above equation $= 3{\cdot}6 \times 10^{-7}$; but the density of saturated vapour at $-\ 3°$ C. is $4{\cdot}0 \times 10^{-7}$. Condensation will, therefore, not go so far as this, but only till the temperature rises to about $-\ 3{\cdot}5°$ C., and the density of the vapour has fallen to about $3{\cdot}8 \times 10^{-6}$ grm. per cubic centimetre.

This gives us for the quantity of water which separates out from each cubic centimetre

$$\rho_1 - \rho_2 = 11{\cdot}4 \times 10^{-6} - 3{\cdot}8 \times 10^{-6}$$

$$= 7{\cdot}6 \times 10^{-6} \text{ grm.}$$

In considering how far the condensation would go, the density of vapour in equilibrium when in contact with drops of the size of those actually present should have been used, not that over a flat surface. But for drops of 5×10^{-5} centim. in radius the difference, as calculated by Lord KELVIN'S formula, does not amount to more than 1 or 2 per cent., and is negligible for the present purpose.

The exact theory of the colour phenomena which are produced by clouds of small water drops such as are formed in these expansion experiments, has not, as far as I am aware, been worked out. This is especially true of the colours filling the centre of the field within the diffraction rings. Since the whole of the colour phenomena from the first appearance of small diffraction rings to the disappearance of all colour, except the bluish or greenish-white, are confined within quite a narrow range of expansions, the size of the drops evidently diminishes with great rapidity with increasing expansion.

When all diffraction colours disappear, and the fog appears white from all points of view, as it does when v_2/v_1 amounts to about 1·44, we cannot be far wrong in assuming that the diameter of the drops does not exceed one wave-length in the brightest part of the spectrum, that is, about 5×10^{-5} centim. That the absence of colour is not due to the inequality of the drops is evident from the fact that the colours are at their brightest when v_2/v_1 is only slightly less than 1·44, and from the perfect regularity of the colour changes up to this point.

Taking the diameter of the drops as 5×10^{-5} cub. centim., we obtain for the volume of each drop about 6×10^{-14} cub. centim., or its mass is 6×10^{-14} grm.

Now, we have seen that when the expansion is such as produces the sensitive tint (when $v_2/v_1 = 1·42$), the quantity of water which separates out is about $7·6 \times 10^{-6}$ grm. in each cubic centimetre. With greater expansions rather more must separate out. We, therefore, obtain as an inferior limit to the number of drops, when $v_2/v_1 = 1·44$,

$$\frac{7·6 \times 10^{-6}}{6 \times 10^{-14}} = 10^8$$

per cubic centimetre.

Effect of the Röntgen Rays on Condensation.

A statement of the results obtained when moist air is subjected to the action of the Röntgen rays, and then allowed to expand, has already been published,* but the experimental details were not given. The experiments were made with the second form of apparatus (fig. 2). A bulb which was giving out the X-rays energetically, as tested by a fluorescent screen, was fixed about 10 centims. from A. It was found that if expansion was made when the bulb was in action, or within a second or two after switching off the current from the induction coil, the number of drops produced was greatly increased if the expansion was such as would have caused rain-like condensation in the absence of the rays. Instead of a shower settling in one or two

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* 'Proc. Roy. Soc.,' vol. 59, p. 338, 1896.

seconds, a fog lasting for more than a minute was produced. If, however, v_2/v_1 was below 1·25, no condensation resulted, whether the rays were acting or not.

The same results were obtained when the expansion vessel was completely wrapped up in tinfoil, which was only removed after the expansion had been made and the current had been switched off. Direct electrical action was thus excluded.

The air inside A is probably sufficiently well shielded from electrical effects by the film of water which covers the inner surface of the walls. For it was afterwards found that no effect was produced on the condensation when A was placed directly between the terminals of an induction coil while the expansion was made.

The nuclei introduced by the X-rays only persist a few seconds. No effect is noticed if the expansion be made half a minute after the current has been turned off.

It will be noticed that in these experiments the rays had to pass through the glass walls of the tube, and must, therefore, have been very much reduced in intensity.

RICHARZ* has recently shown that the condensation of the steam-jet becomes dense under the action of the X-rays. The intensity of the radiation was probably much greater in his experiments, for the rays had merely to pass through aluminium.

Hydrogen.—The action of the X-rays when hydrogen was substituted for air was afterwards investigated. It was considered unnecessary in this case, for the reasons already mentioned, to take any precautions for shielding off direct electrical action. The arrangements were in other respects exactly as in the experiments with air. The hydrogen was obtained as already described.

In the first experiments the following results were obtained :—

v_2/v_1.		Result.
1·308	No X-rays	No condensation
1·296	X-rays	Fog

Several experiments were then made with the tube exposed to the rays, each expansion being made less than the preceding one. The number of cloud-particles was observed to diminish with diminishing expansion, till, when v_2/v_1 was made equal to 1·260, only a few drops were formed, and none were seen when v_2/v_1 was equal to 1·255.

Further measurements were now made of the smallest expansion required to cause condensation when the moist hydrogen was under the influence of the X-rays.

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[*] 'Wied. Ann.,' vol. 59, p. 592, 1896.

v_2/v_1.		Result.
1·326	No X-rays	No condensation
1·253	X-rays	Drops very few
1·309	X-rays	Fog
1·246	X-rays	No condensation
1·259	X-rays	Shower

With the X-rays on, condensation begins when v_2/v_1 lies between 1·246 and 1·253, the density of the condensation increasing rapidly with increasing expansion.

Fresh hydrogen was now prepared. The bulb was 30 centims. from the cloud chamber.

X-RAYS on in all Cases.

v_2/v_1.	Result.
1·251	No condensation
1·254	Very few drops
1·253	Very few drops
1·251	No condensation
1·258	Drops few
1·272	Dense shower
1·282	Fog

Thus it appears that condensation begins in hydrogen originally saturated when v_2/v_1 is between 1·251 and 1·253, if the gas be exposed to the action of the X-rays. Condensation therefore begins when the supersaturation reaches the same limit as is necessary for rain-like condensation in air, the supersaturation required to produce condensation under ordinary conditions being nearly twice as great.

As in the case of air the nuclei introduced by the RÖNTGEN rays only last a few seconds. Thus immediately after obtaining condensation when v_2/v_1 was as low as 1·253, if the expansion was made while the gas was exposed to the X-rays, an experiment was made in which the current was switched off half a minute before the expansion. Although v_2/v_1 was as great as 1·315, no condensation resulted. When, however, a similar expansion was made with only a few seconds' interval a slight fog resulted.

Since the X-rays make condensation begin in hydrogen, with a much smaller expansion than is necessary in their absence, it is much more easy to detect the effect of very weak radiation than in air, where only an increase in the number of the drops results from the action of the rays.

It was found that the effect of the rays was quite noticeable, even when the bulb producing them was at a considerable distance away. For example, quite a distinct shower was produced with the bulb 120 centims. off, when v_2/v_1 was equal to 1·326, while an expansion of the same amount made immediately afterwards with the current switched off from the coil caused no condensation.

When the bulb was as far away as this it was found necessary to make rather greater expansion to bring about condensation, than when stronger radiation fell on the expansion apparatus. With the bulb 120 centims. off condensation was first detected when v_2/v_1 was equal to 1·278, none being visible with smaller expansions.

Since every nucleus, capable of promoting condensation, in vapour supersaturated to the extent reached at the completion of the expansion, becomes visible by the growth of a drop around it, it is not surprising that even weak radiation should have a visible effect.

I have not yet made any experiments* to see if X-radiation, which has not been weakened by passing through glass, makes the condensation begin at a lower supersaturation or not. The experiments of RICHARZ, to which reference has already been made, do not give us any information on this point, as the extent of the supersaturation reached in a steam-jet is unknown.

Interpretation of the Results.

The view here taken as to the meaning of the phenomena described in this paper is briefly as follows :—

In aqueous vapour in the presence of air, oxygen, nitrogen, or carbonic acid, there always exists at any moment a small number of nuclei, capable of acting as centres of condensation when the density of the vapour reaches a certain value amounting at $-6°$ C. to about 4·2 times that of the vapour in equilibrium over a flat surface of water at the same temperature.

The nuclei capable of acting as centres of condensation when the supersaturation lies between this lower limit and another amounting at 16° to 7·9 are comparatively few, and their number depends on the nature of the gas, for they appear to be absent in moist hydrogen. No attempts have yet been made to count the drops produced when the supersaturation lies between these limits, but from the appearance of the resulting shower they almost certainly do not amount to nearly 100 in a cubic centimetre.

When the X-rays, or such components of the radiation as are able to pass through glass, act upon moist air or hydrogen, similar nuclei are produced in much greater numbers, those of them which are the most effective in helping condensation again requiring exactly the same minimum supersaturation in order that condensation may take place upon them.

The number of nuclei capable of acting as centres of condensation when the supersaturation, even slightly, exceeds the upper limit mentioned, is, whatever gas be present, very large, and the number which come into play increases with enormous

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* See note at the end of the paper.

rapidity as the supersaturation is increased, reaching in air, oxygen, or nitrogen probably many millions per cubic centimetre under a tenfold supersaturation. In the other gases the observations in the colour phenomena necessary for this estimate were not made. There is no indication in these experiments of any limit to the number of drops which could be formed by sufficiently increasing the supersaturation.

It is possible to make an approximate calculation of the size of the smallest drops which would be able to grow in vapour supersaturated to any given extent.

The formula given by Lord KELVIN* for the effect of curvature of a surface upon the pressure of the saturated vapour in contact with it only applies, in its original form, to cases where the curvature is not sufficiently great to make the density of the vapour over the curved surface differ more than very slightly from that over a flat surface. Here we wish to calculate the curvature necessary to make the equilibrium density of the vapour from four to eight times that over a flat surface.

If we assume that the supersaturated vapour obeys BOYLE's law, and that the surface tension retains its ordinary value in the case of the very small drops with which we are dealing, there is no difficulty in seeing how the formula must be modified to allow of its being extended to such cases as the present. Both of these conditions are, unfortunately, likely to be far from being satisfied.

If we make these assumptions, the formula becomes, when the density of the vapour is as in the present case small compared with that of the liquid, identical with that obtained in a different way by R. v. HELMHOLTZ,†

$$\log_e \frac{p}{\mathrm{P}} = \frac{2\mathrm{T}}{\mathrm{R}s\theta r},$$

where p is the vapour pressure in contact with drops of radius r, P that over a flat surface at the same temperature θ; T is the surface-tension, s the density of the liquid, and R the constant in the equation $p/\rho = \mathrm{R}\theta$. Since BOYLE's law is assumed to hold, p/P is equal to the ratio of the corresponding densities, that is, to what is here called the supersaturation S. We thus obtain for the radius of the drops just in equilibrium

$$r = \frac{2\mathrm{T}}{\mathrm{R}\theta \log_e \mathrm{S}},$$

since s in the case of water is equal to unity. R for water vapour is equal to $4{\cdot}6 \times 10^6$.

The results of the application of this formula are here given.

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* 'Proc. Roy. Soc.,' Edin., VII., p. 63 (1870).

† 'Wied. Ann.,' xxvii., p. 508 (1886).

RADIUS, in centims., of drops just large enough to grow in vapour supersaturated to the extent required to make rain-like condensation begin in the presence of Air.

$t°$ C.	θ.	T.	S.	r.
−10	263	77	4·35	$8{\cdot}7\times10^{-8}$
− 6	267	76	4·2	$8{\cdot}6\times10^{-8}$
+ 2	275	75	4·0	$8{\cdot}6\times10^{-8}$

r thus appears to be constant over the range of temperature − 10° C. to + 2° C. The value obtained for r is not changed by as much as 3 per cent. when the air is replaced by nitrogen, oxygen, or CO_2, or by hydrogen under the action of the X-rays.

RADIUS, in centims., of drops just large enough to grow when supersaturation is sufficient to make the dense condensation begin in Air, Oxygen, Nitrogen, or Hydrogen.

$t°$ C.	θ.	T.	S.	r.
−16	257	78	7·9	$6{\cdot}4\times10^{-8}$

If we consider the difference in the value found for S in CO_2 to be real, and not due merely to the error in the calculation of the cooling, due to deviation of CO_2 from the condition of a perfect gas, we find that r in CO_2 is about 3 per cent. greater than in these other gases.

RADIUS, in centims., of drops just large enough to grow when the supersaturation is such that the sensitive tint is produced in the presence of Air or Oxygen.

$t°$ C.	θ.	T.	S.	r.
−19	254	79	9·9	$5{\cdot}9\times10^{-8}$

The difference when nitrogen is substituted for Air or Oxygen is exceedingly small.

It cannot be assumed that the surface tension retains its ordinary value in drops of such small radii, which are not great compared with molecular dimensions. We know, in fact, from the behaviour of thin films, that it does not. These numbers therefore can only be considered as giving a very rough approximation to the absolute size of the water drops which would actually be in equilibrium in vapour of the various degrees of supersaturation.

They furnish, however, a convenient means of expressing the relative efficiency of the nuclei in helping condensation. Thus, the nuclei producing rain-like condensation are equivalent in their effect on the condensation, to water drops of radii between $6{\cdot}4 \times 10^{-8}$ and $8{\cdot}7 \times 10^{-8}$ centim. There are, as we have seen, certainly not more than 100 of these in each cubic centimetre of moist air, and they are absent in hydrogen. The nuclei equivalent to water drops whose radii lie between the narrow limits $5{\cdot}9 \times 10^{-8}$ and $6{\cdot}4 \times 10^{-8}$ centim. amount to many millions per cubic centimetre.

It is difficult to account for the immense number of these latter nuclei, otherwise than on the view that they actually are simply small aggregates of water molecules, such as may come into existence momentarily through encounters of the molecules. On this view the dimensions of the molecules cannot be small compared with 6×10^{-8} centim. BARUS* states that if it were possible to measure the supersaturation required to make steam condense in the absence of dust, the dimensions of the molecules could be calculated with the aid of LORD KELVIN'S formula. Probably he takes some such view as that here suggested.

The nuclei which bring about the rain-like condensation, and the greater number of which appear to be equivalent in their power of causing condensation to water drops of not much less than $8{\cdot}7 \times 10^{-8}$ centim. are probably of a different character. As, however, I am continuing these experiments, it would be premature at the present stage to discuss the various views that might be held as to their nature.

[*Note added July* 22, 1897.

Further Experiments on the Action of the X-rays.—I have lately repeated the experiments on air, using an expansion apparatus provided with a window of very thin aluminium, so arranged that the whole of the contents of the tube were exposed to the rays of a suitably placed Röntgen lamp.

This gave results identical with those already obtained, no condensation resulting when the air was expanded while exposed to the rays unless v_2/v_1 exceeded 1·25, while with expansions even slightly exceeding this, a comparatively dense fog resulted; only a few scattered drops appearing with similar expansions in the absence of the rays.

As was to be expected, much denser fogs were obtained under the action of the rays with this apparatus than with that formerly used.

A glass plate of 7 millims. thick, placed over the window, appeared to cut off the effect of the rays completely.]

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* 'Phil. Mag.,' vol. 38, p. 34 (1894); also "Report on the Condensation of Atmospheric Moisture." U. S. Department of Agriculture, Weather Bureau, 1895.