The Supersaturation and Nuclear Condensation of Certain Organic Vapours

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XII. *The Supersaturation and Nuclear Condensation of Certain Organic Vapours.*

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Condensation in Water Vapour.

The first precise measurements of the conditions causing condensation when dust-free air saturated with water vapour is expanded were made by C. T. R. Wilson.*

He calculated the cooling due to the adiabatic expansion, and then the supersaturation, which is the ratio of the actual pressure of the water vapour at the end of the expansion to the saturated vapour pressure of water at the temperature at the end of the expansion.

Mr. Wilson obtained the results given in the following table, in which v_2/v_1 is the ratio of the initial to the final gas pressure in the expansion apparatus :—

Gas.	Rain-like condensation.		Cloud-like condensation.	
	Expansion v_2/v_1.	Supersaturation.	Expansion.	Supersaturation.
Air	1·252	4·2	1·38 } 1·375	7·9
Oxygen	1·257	4·3	1·383	
Nitrogen	1·262	4·4	1·38	
Hydrogen	—	—	1·38	
Carbon dioxide . .	1·365	4·2	1·535	7·3
Chlorine	1·3	3·4	1·45	(5·9)

It was concluded from the size and number of the nuclei producing the cloud-like condensation that they were small aggregates of water molecules.

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* 'Phil. Trans.,' A, 189, p. 265 (1897).

With a large apparatus (with working parts of brass) WILSON* some time later showed, in the absence of (artificial) external ionising rays and of an electric field, that rain-like condensation took place in air saturated with water vapour at an expansion of 1·247, while with an electric field no drops were produced even by an expansion of 1·27. Thus the natural ions act as condensation nuclei for expansions of 1·25. The number of natural ions per cubic centimetre deduced from the number of drops is in agreement with the number obtained by other methods.

The simplest interpretation of WILSON'S experiments is that there are three kinds of nuclei concerned in condensation. Nuclei of one kind are naturally present in dust-free air, oxygen, nitrogen (hydrogen ?), carbon dioxide, and chlorine; they are increased in numbers by Röntgen and Becquerel rays, ultra-violet light acting on a negatively charged zinc plate, and they are electrically charged and produce condensation in water vapour when it is supersaturated at least 4·3 times; in short, these nuclei are ions. Another type of nuclei are uncharged and are possibly aggregates of water molecules, as mentioned above. A third kind are present near the surface of zinc, lead, and amalgamated zinc plates, are uncharged, and act as nuclei when the supersaturation is not less than 4·3.

The Comparative Efficiency of Positive and Negative Ions.

WILSON† showed in 1899, using air and water vapour, that the negative ions are more efficient in producing condensation than the positive, for he found that expansions greater than 1·247 caught the negative ions, while both the positive and negative were caught by expansions greater than 1·31. It is to be noticed that the second point (1·31) cannot be determined as readily or with the same accuracy as the first one (1·247).

Previous Work on Organic Vapours.—F. G. DONNAN‡ determined the expansion necessary to produce rain-like condensation, and a fog in dust-free air, saturated with the vapours of some carefully purified organic liquids.

K. PRZIBRAM§ has made observations on the condensation of organic vapours in ionised air. He has followed WILSON in carrying out his experiments. The piston of his expansion apparatus worked in paraffin oil, which would seem undesirable when using vapours soluble in that oil.

Experimental: The Expansion Apparatus.

Two modifications of the expansion apparatus have been tried. It was not easy to

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* 'Phil. Mag.,' June, 1904, p. 681.

† 'Phil. Trans.,' A, 193, pp. 289–308 (1900).

‡ 'Phil. Mag.,' March, 1902, p. 305.

§ 'Sitzungsber. d. kais. Akad. d. Wissen. in Wien,' Math.-naturw. Kl., Band 115 (1906).

obtain a durable piston for expansions up to $v_2/v_1 = 2$. The expansion apparatus as used is drawn in fig. 1.

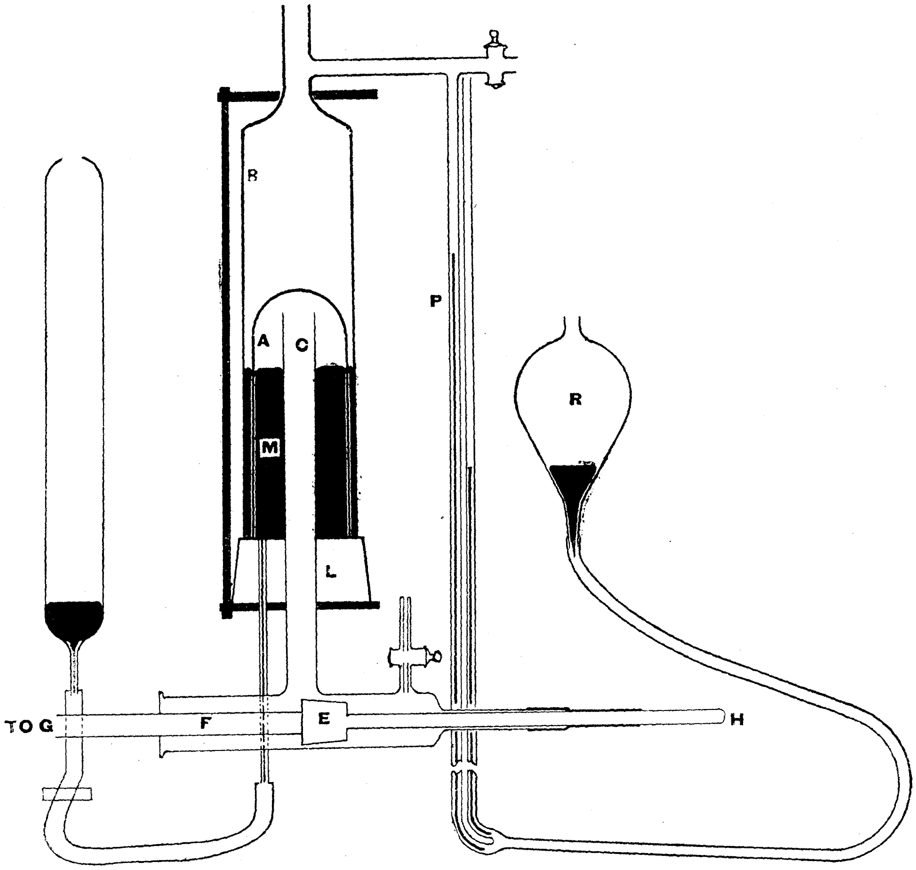

Fig. 1.

The glass piston A slides freely in B. By pulling the glass rod H, the rubber bung E is withdrawn from the mouth of the tube F, the air inside A flows suddenly into an exhausted globe G, the piston descends rapidly through the mercury M, and is suddenly brought to rest by the rubber bung L. Its ground edge remains in tight contact with the rubber, and so no mercury or gas escapes from B. As the action of the piston is very regular, as shown by the constant pressure after expansions, its dimensions may be worth mentioning. They are: height 13·2 cms., diameter 4·5 cms., weight 42 grammes. P is a mercury pressure gauge in communication with B. The reservoir is for emptying and adjusting the height of the mercury in B. This form of apparatus can be readily taken to pieces and cleaned, which was often necessary, since a number of liquids were used.

To obtain a given expansion, the piston A was adjusted in position until the initial pressure was the necessary one for that expansion.

The pressure in the 25-litre globe G, with which the tube F communicates, was kept below 80 mm. of mercury. With this pressure the piston falls rapidly—so rapidly, in fact, that a number of pistons were broken.

The amount of the expansion in any experiment is measured by

$$\frac{v_2}{v_1} = \frac{\text{the initial gas pressure}}{\text{the final gas pressure}} = \frac{B - \pi - s_1}{B - \pi - s_2},$$

where B is the barometric pressure, π the saturated vapour pressure of the liquid at the temperature of the experiment (*i.e.*, initially), and s_1 the initial and s_2 the final reading of the gauge P.

The Expansion Chambers.

The expansion chamber, used to find the least expansion to produce condensation in dust-free air saturated with the various organic vapours, is drawn in fig. 2. It was made so that only mercury and glass come in contact with the vapour. The test-tube T is fitted by the rubber cork R to the expansion apparatus E. Mercury and then the liquid to be used are admitted from M, until the liquid, which is always above the mercury, overflows into E and the lower part of the apparatus. When the apparatus is in use, the liquid L under examination lies above the mercury, as

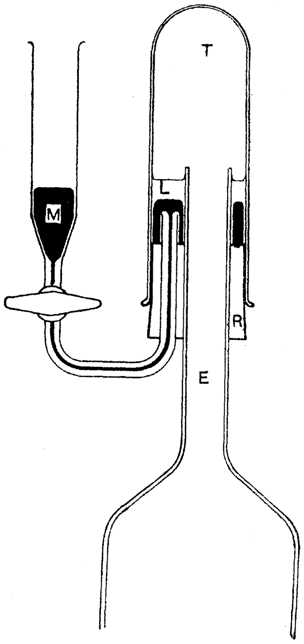

Fig. 2.

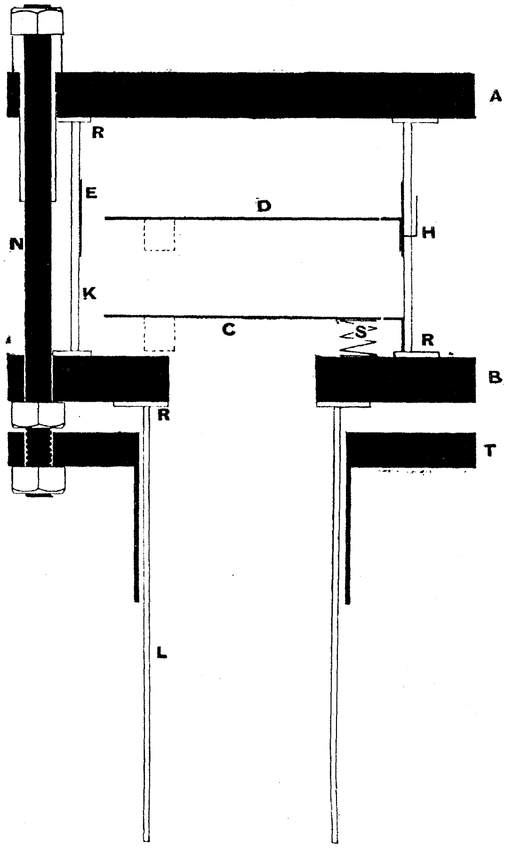

Fig. 3.

indicated in the figure. A thin film of the liquid also spreads over the interior surface of T, and so it is to be expected that the air in T is quickly saturated with its vapour. The beam of light, obtained from an incandescent mantle, I (see also the upper part of fig. 4), with a slit about 1 cm. wide, was focussed inside the test-tube T. All other light was excluded and a black background obtained by means of black velvet. Most of the drops formed by an expansion could be readily seen on looking from E.

Another expansion chamber was used to determine the sign of the charge of the more efficient ionic nucleus. It is drawn to scale in fig. 3. K is a portion of a glass tube, 3·1 cms. in length and 4·2 cms. in diameter, with ground edges. The ends of the chamber are thick aluminium discs, A and B. The joints between these and the glass cylinder K, and between L and B, are made by means of the rubber rings R. Three bolts such as N, insulated from A by vulcanite collars, press the aluminium ends A and B and the connector T against the rubber rings R. The joint obtained in this way is air-tight and remains so. The chamber is divided into an upper and lower half by a thin aluminium diaphragm, D, of 3·6 cms. diameter, supported by three projections pressing against E. Thus there is an annular space 3 mm. wide between the edge of the diaphragm and the wall E. In order to make the lower half of the chamber as similar as possible to the upper, a second diaphragm, C, of the same size as D, is placed over the outlet in the end B, and is connected to B by means of a spiral S of platinum wire. A ring of thin aluminium, E, 1 cm. in width, was placed symmetrically around D, in order to reduce the intensity of the secondary rays from the walls of the vessel, for it is here that the Röntgen rays (mentioned later) are incident. The ends A and B, &c., were made of aluminium with this object, and because the liquids used, when dry and pure, were found not to have any chemical action on aluminium. It it necessary to have the central diaphragm D electrically connected to the exterior of the vessel. A tapered aluminium wire filled a hole in the glass wall at H and was cleated down on the inside and sealing waxed on the outside. The cleated end is in contact with E, which supported D. This gives a joint which protects the sealing wax from the action of the liquids used.

Röntgen rays (see fig. 4) from a large bulb and coil pass through a horizontal slit between two lead blocks 2·8 cms. thick and 0·5 cm. apart. The narrow band of rays thus obtained passes through the ionisation chamber above and below the diaphragm D. The relative positions of the bulb, slit, and expansion chamber were finally adjusted by means of a barium-platino-cyanide screen placed at Y.

With these adjustments made, the shadow at Y of the diaphragm edge-on formed a dark line across the middle of the "image" of the slit.

Separation of Positive and Negative Ions.

The terminals of a two-volt cell were connected to a potentiometer wire (U of fig. 4) of 2000 ohms resistance (with contacts at every 20 ohms), which was connected at the middle to D and to earth. The potential of the top of the expansion chamber and the lower diaphragm C by connecting them to these contacts could be varied between +1 and −1 volt (in steps of 0·02 volt) with respect to the middle diaphragm D. In a number of experiments, the top in one expansion was at −1 volt, and the bottom at +1; in the next expansion the potentials of these plates were reversed.

When the Röntgen rays from the bulb R pass through the slit, they ionise above and below the diaphragm a thin layer of the mixture of air and the vapour present. The secondary rays produced by the primary inside the expansion chamber would produce a few ions throughout all the interior. With the diaphragm earthed, the top negatively and the bottom positively charged, the ions stream as indicated in fig. 4.

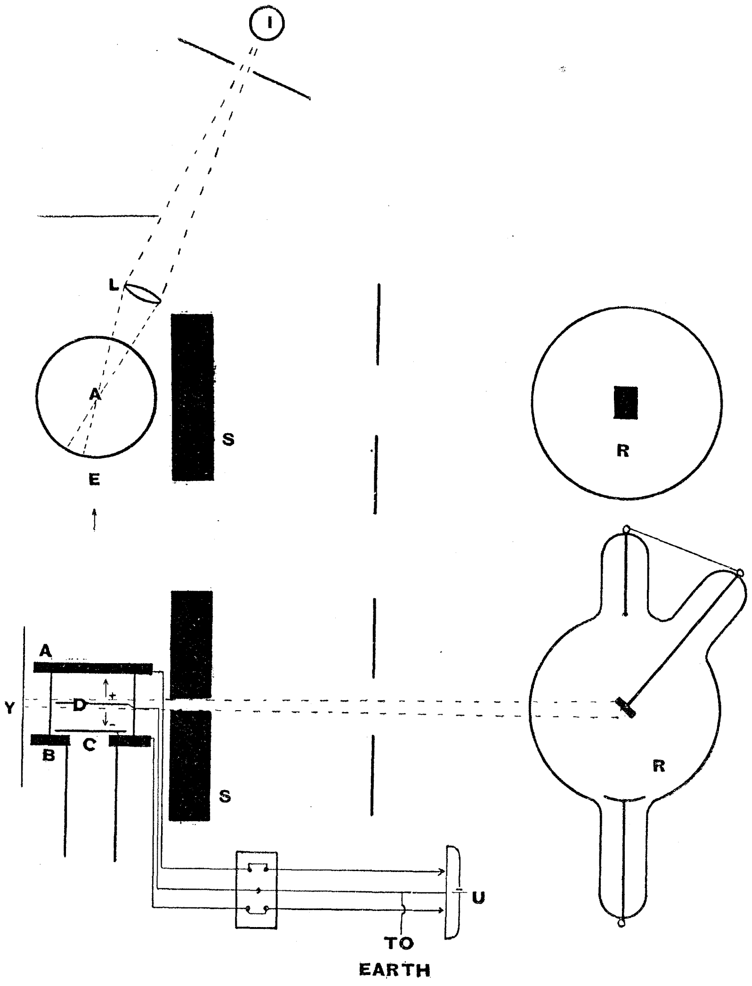

Fig. 4.

If then an expansion be made of the dust-free air and vapour (within one second) after cutting off the Röntgen rays, positive ions will be present in the top partition, and negative in the bottom, which will act as condensation nuclei. It is to be expected that in the top partition the negative ions formed by the secondary rays are removed by recombination with the more numerous positive ions present there.

Observation of the Drops.

The expansion chamber was observed from E (fig. 4) in a direction making a small angle with the beam of light (from the incandescent gas mantle I), which was brought to a focus inside the chamber by means of the lens L. With the eye on a level with the diaphragm D, drops in both the top and bottom partitions of the chamber could be observed at once on a background formed by black velvet.

The switch in the primary of the induction coil, which worked the X-ray bulb at R, was placed close to the handle for "firing" the expansion apparatus, and so with a metronome beating half-seconds the Röntgen rays could be cut off at given intervals before the expansion was made. This metronome was also used for timing the rate of fall of the drops.

Results with Air and Water Vapour.

The following results show that the expansion apparatus is capable of giving results suitable for absolute measurements. (The numbers represent expansions.)

Air Initially Saturated with Water Vapour. Test-tube Expansion Chamber.

No drops: 1·249, 1·253. Drops: 1·256, 1·329, 1·366 (many), 1·376 (fog). Therefore the least expansion for condensation on natural nuclei is 1·256 (1·247), and fog-point 1·376 (1·38).

Röntgen Rays. Expansion Chamber with Aluminium Electrodes.

1·232 no drops, 1·242 four drops seen, 1·246 many drops, 1·246 many. Expansion for Röntgen ray ions 1·246 (1·247).

The values in brackets are those obtained by C. T. R. Wilson. The agreement between the two sets of results is evidence that the expansion in the writer's apparatus is sufficiently rapid to give good results.

Selection of Liquids.

The writer wished to calculate from the results obtained with the liquids he used the supersaturation, and the radius of the nuclei causing condensation, as Mr. Wilson has done for water. To do this it is necessary to know the saturated vapour pressure, π, of the liquid at room temperatures and possibly 50° lower, and also its surface tension and density at this lower temperature. There are not very many liquids for which these have been found. YOUNG and THOMAS* have determined a number of constants for ten carefully purified esters. The data required exist or can be calculated for the formic to iso-valeric series of acids. A study of these esters and acids shows how homologous and isomeric compounds behave.

Liquids used.

All the liquids used were KAHLBAUM'S preparations. They were fractionated with a 12-bulbed (pear-shaped) still-head. The boiling-points, at 760 mm. pressure, given differ from those obtained by YOUNG and THOMAS and others partly on account of errors of the writer's thermometers. A more reliable criterion of purity is constancy of boiling-point.

Methyl formate: Dried with phosphorus pentoxide and then fractionated from it. The fraction used boiled from 31°·8 to 31°·9 C. (31°·9 C. YOUNG and THOMAS).

Methyl acetate: Dried with phosphorus pentoxide and fractionated from it. After three fractionations the portion boiling at 56°·9 (57°·15 to 57°·3 YOUNG and THOMAS) was collected and used.

Ethyl acetate: Fractionated from phosphorus pentoxide, the first portion rejected and that boiling at 77°·1 (77°·15 YOUNG and THOMAS) was collected.

Propyl acetate: Dried with phosphorus pentoxide; fractionated twice. The slightly hydrolysed distillate was treated with potassium carbonate, and then with phosphorus pentoxide, and distilled. Boiling-point 101°·4 to 101°·9 (101°·35 YOUNG and THOMAS).

Methyl butyrate: Fractionated; the portion boiling at 102°·9 (102°·8 YOUNG and THOMAS) was distilled from phosphorus pentoxide.

Methyl iso-butyrate: Fractionally distilled, treated with phosphorus pentoxide, and distilled, then with potassium carbonate, followed by phosphorus pentoxide. Boiling-point 92°·4 to 92°·6 (92°·3 YOUNG and THOMAS).

Ethyl propionate: Distilled from phosphorus pentoxide, and redistilled. Boiling-point 98°·9 to 99°·6 (99° YOUNG and THOMAS).

Formic acid: KAHLBAUM'S best acid was used direct from the sealed glass flask it was supplied in. Boiling-point 101°·1 (RICHARDSON 101°·3, SCHMIDT 100°·4, ROSCOE 101°, PERKIN 101°).

Acetic acid: Fractionated five times; final fraction boiled at 118°·5 to 118°·6, but the freezing-point appeared low, indicating the presence of water. The stock acid was then three times crystallised, twice distilled; it then gave a boiling-point of 118° to 118°·05 (118°·5 YOUNG'S "Fractional Distillation"), and a freezing-point of 16°·5 (16°·6 HOLLEMAN'S "Organic Chemistry").

Propionic acid was distilled from phosphorus pentoxide, and twice fractionated. The portion used boiled from 138°·9 to 139°·1 (140°·3 RICHARDSON).

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* 'Trans. Chem. Soc.,' 63, 1220 (1893).

n-Butyric acid was fractionated once, and the portion (nearly the whole of the original) boiling between 162°·5 and 162°·6 was used (162°·4 RICHARDSON).

Iso-butyric acid was fractionated. Boiling-point 152°·1 to 152°·6 (153° RICHARDSON).

Iso-valeric was treated with phosphorus pentoxide, and twice distilled. Boiling-point 175° to 176° (175°·3 RICHARDSON, 174°·9 SCHMIDT, 174°·5 LANDOLT).

Amyl alcohol: KAHLBAUM'S (pyridine free) " inactive,"

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

was fractionated. Boiling-point 130°·6 to 131° (131°·4 THORPE, 132° YOUNG and FORTEY, 130°·3 SCHMIDT). Some optically active alcohol was present in the final fraction which gave $[\alpha]_D = -0°{\cdot}5$; for active amyl alcohol $[\alpha]_D = +5°{\cdot}2$.

Least Expansion for Condensation in Air of an Organic Vapour exposed to Röntgen Rays.

The test-tube expansion chamber of glass and mercury, already described (see fig. 2), was used to find the least expansion to produce condensation in a mixture of air and an organic vapour when exposed to Röntgen rays. The air in the carefully cleaned apparatus was dried by placing an open tube containing phosphorus pentoxide inside B (fig. 1). In removing this tube less than 1 mgrm. of water as vapour gained admission to the apparatus. The organic liquid was then admitted by means of the stop-cock funnel (fig. 2) to above the mercury.

The dust present in the apparatus settled out on standing the vessel (say) overnight. It was more quickly removed by small expansions. It is worthy of remark that some vapours could be freed from dust by the latter method distinctly more quickly than others. Thus four or five expansions freed air and ethyl propionate from dust, while air and water vapour have always taken more expansions than that.

Since the writer has found, certainly in the case of some vapours, that the least expansion for condensation depends slightly on the intensity of the Röntgen rays, it is necessary to roughly specify the intensity of the rays used in the experiments to be described. A large bulb with a heavy water-cooled anti-cathode driven by a Marconi induction-coil was used as the source of the Röntgen rays. The alternative spark gap was from 5 to 10 cms. The anti-cathode was 46 cms. from the expansion chamber. The rays had to penetrate the wall—about 0·08 cm. thick—of the glass test-tube expansion chamber.

With some vapours the drops obtained were very minute, so were not readily seen, and did not settle out quickly. With such a vapour it was necessary, after an expansion giving a number of drops, to either wait some time for them to settle out, or to make a small expansion and so condense larger drops on these nuclei left over from the previous larger expansion.

Most of the vapours examined, especially the esters, gave only a few drops with the least expansion producing condensation, and on slightly increasing the expansion the number of drops did not increase as rapidly as they do in the case of water vapour. This makes the least expansion for condensation a less precise point with these vapours than it is with water and substances which behave like it in this respect.

Usually more than one series of experiments were made with each vapour. Examples of the nature of the results obtained are given below, where the different series of observations are combined together.

Air and Ethyl Propionate. Röntgen Rays.

No drops: 1·390, 1·409.

Drops: 1·404, 1·413, 1·426, 1·436, 1·456, 1·477, 1·497.

The apparatus was cleaned and refilled.

No drops: 1·314, 1·400, 1·400, 1·407, 1·408, 1·413, 1·418.

Drops: 1·416 (2 drops seen), 1·420, 1·422.

The first gives the condensation expansion as 1·404, the second as 1·416. Mean **1·410.**

Air and Acetic Acid. Röntgen Rays.

No drops: 1·414, 1·431, 1·439.

With drops: 1·441, 1·446, 1·454, 1·454, 1·497 (fog), 1·507 (fog).

Least expansion for condensation **1·441.**

The drops obtained in these expansions are very small. With feeble Röntgen rays a larger expansion than 1·441 was necessary. These feeble rays were from the same bulb, but the alternative spark gap was 5 cms. instead of 10 cms., and an aluminium screen 2·7 mm. thick was placed between the bulb and the expansion chamber.

Feeble Röntgen Rays.

No drops: 1·446, 1·446, 1·454, 1·471.

With drops: 1·460, 1·471, 1·474, 1·479, 1·482 (many drops).

Least expansion for condensation **1·471.**

This is distinctly larger than the expansion with the more intense rays.

This matter is being further investigated by using γ-rays from radium and from thorium, but the results so far obtained have often been contradictory.

Of the substances tried, acetic acid showed this effect of the intensity of the Röntgen rays on the least expansion for condensation the most.

Summary of Least Expansions for Condensation of Vapours in Air acted upon by Röntgen Rays.

Vapour.	Expansion.	Vapour.	Expansion.
Ethyl acetate	1·486	Formic acid	1·782
Methyl butyrate	1·334	Acetic acid	1·441
Methyl iso-butyrate	1·347	Propionic acid	1·343
Propyl acetate	1·310	*n*-butyric acid	1·380
Ethyl propionate	1·410	Iso-butyric acid	1·360
Iso-amyl alcohol	1·182	Iso-valeric acid	1·220

No very regular relationship can be seen between the constitution of the above vapours and the least expansion necessary to produce condensation in air saturated with them. The expansion, with some exceptions, decreases with increase of molecular weight. On calculating, however, the supersaturation, which exists in the vapour at the moment before condensation takes place, more regular relationships become evident.

Calculation of Supersaturation necessary for Condensation.

The calculation of the supersaturation which exists before condensation takes place has been made for gases saturated with water vapour by Mr. WILSON.* When air expands adiabatically, the final temperature is given by the relation

$$\theta_2/\theta_1 = (v_1/v_2)^{\gamma-1}, \quad \ldots \ldots \ldots \ldots \quad (1)$$

where v_1 and v_2 are the initial and final volumes, θ_1 and θ_2 the initial and final temperatures of the air, and γ the ratio of its specific heats; $\gamma = 1·404$.

We will assume (the assumption will be discussed later) that this relation gives the final temperature of the mixture of air and vapour in a condensation experiment.† This θ_2 then becomes the temperature of the air and vapour at the end of the expansion before any condensation has taken place.

The supersaturation, S, is conveniently defined as the ratio of the pressure of vapour

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[*] 'Phil. Trans.,' A, 189, p. 265, 1897.

[†] *Instantaneous Temperature by a Platinum Thermometer.*—When about half way through this investigation, the writer thought of using a platinum thermometer (after the manner CALLENDAR determines cylinder temperatures) to find the lowest instantaneous temperature produced by an expansion. There appears to be, however, an unsurmountable difficulty. A slight supersaturation would cause condensation on the thermometer wire itself, and the latent heat of condensation would heat the wire. I have seen such condensation actually take place on a hair in the apparatus. A stream of drops fell from it when the expansion was made. The presence of the wire would alter the conditions of the experiment. It certainly would be far more satisfactory to determine the lowest temperatures directly if it were possible.

finally at θ_2 before drops are formed to the pressure of vapour over plane surface of liquid at θ_2, so that

$$S = \pi_1 \frac{\theta_2}{\theta_1} \cdot \frac{v_1}{v_2} \bigg/ \pi_2 = \frac{\pi_1}{\pi_2} \cdot \frac{\theta_2}{\theta_1} \cdot \frac{v_1}{v_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where π_1 is the saturated pressure of the vapour at the temperature θ_1, and π_2 at θ_2. The expansion decreases π_1, to $\pi_1 \, . \, v_1/v_2$, and the temperature falls in the ratio θ_2/θ_1.

In deducing the above formula, and in using it to calculate supersaturations, it is assumed (A) that the final temperature when a mixture of air and vapour expands is given by the relation (I), and (B) that BOYLE'S and CHARLES' laws hold for the vapour. The assumption that BOYLE'S and CHARLES' laws hold for the vapours named on p. 455 seems unavoidable,* since the experimental data do not exist which would enable the supersaturations to be calculated without assuming these laws.

Consider assumption (A): for it to be true, the expansions must be (1) adiabatic, and (2) the formula $\theta_2 = \theta_1 (v_1/v_2)^{1 \cdot 404 - 1}$ must hold for the mixtures of air and organic vapour used.

(1) The expansion is believed to be adiabatic on these grounds: WILSON has most carefully tested the matter, using two very different apparatus, one of which had no piston. The piston of the other was light and the expansion must have been very rapid, certainly more rapid than in the first. The mean of a number of experiments, using air and water vapour gave with each apparatus the same value, 1·252, for the expansion which caught the natural ions present. The writer's result for this point was 1·256, both at the beginning and the end of his experiments. Let θ_2 be the final temperature in these three experiments, if the mean expansion (1·253) were adiabatic, and let the rise of temperature due to the ingress of heat by convection, conduction, and radiation from the walls of the expansion vessel in the different conditions of the three experiments be p, q, r. The actual final temperatures would then be θ_2+p, θ_2+q, θ_2+r, but since in each case these were the temperatures at which condensation just began, they were experimentally the same. Thus p, q, r are too small to be observed, and the expansions were adiabatic. Further, WILSON found $v_1/v_2 = 1 \cdot 38$ for fog-like condensation with air and water, and the writer's apparatus gave 1·376. In these two experiments we have the same final temperature, that necessary for fog-like condensation. The same final temperature is, however, only obtained from equal expansions of 1·38 in different apparatus, when the expansions are not only adiabatic, but are such that the whole lowering of temperature

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* To supply evidence that BOYLE'S and CHARLES' laws are applicable to supersaturated vapours would mean a separate and difficult research. I can think of no direct solution. Professor THOMSON'S determination of $-e$, the charge on a negative ion, is an indirect test of the applicability of these laws in the case considered, for in that method of determining $-e$ the quantity of water condensed by an expansion in ionised air and water vapour is calculated by an application of the gas laws. Dr. H. A. WILSON'S method for $-e$ does not assume those laws. The results of the two methods could be compared. They agree when water vapour is used. Both are subject to large errors.

takes place before any condensation occurs; for otherwise, when the expansion reaches (say, for example) 1·34, drops will be formed on the natural ions present and the temperature will rise with the liberation of the latent heat of condensation, and this rise of temperature will be different in different apparatus. Since actually the final temperatures were the same, we conclude that there was no rise of temperature in this manner and the expansions were strictly adiabatic.

(2) The formula $\theta_2 = \theta_1 (v_1/v_2)^{\gamma-1}$ is for air the expression of the observed results of LUMMER and PRINGSHEIM'S[*] and MAKOWER'S[†] experiments, in which θ_2, θ_1, v_1, v_2 were directly observed. With air in an engine cylinder CALLENDAR[‡] has observed with a platinum thermometer a change of temperature of as large as 244° C., that is, from $-34°{\cdot}4$ to 210° C.

A more exact calculation will now be given of θ_2 (for the conditions of experiment given in the next table) when air initially saturated with an organic vapour expands. RICHARZ calculated γ for a mixture of gases. The following indicates how his[§] result is obtained. Let the mixture and each component gas have the masses 1, $1-\mu$, μ, the densities (at 760 mm. and a common temperature) ρ, ρ', ρ'', the specific heats at constant volume c, c', c'', the ratio of specific heats, *i.e.*, C/c, γ, γ', γ'', and let R be the gas constant for a gram-molecule (M) of a gas. Then

$$c = c'(1-\mu) + \mu c'' = c' + \mu(c''-c'), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the specific volume of the mixture is

$$\frac{1}{\rho} = \frac{1}{\rho'}(1-\mu) + \mu\frac{1}{\rho''} = \frac{1}{\rho'} + \mu\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\mathrm{C} - c = \frac{\mathrm{R}}{\mathrm{JM}} = \frac{1}{\rho} k \quad (k = \text{const.}),$$

since M is proportional to ρ, and R and J are constant. Whence

$$\frac{1}{\gamma-1} = \rho c k', \quad \frac{1}{\gamma'-1} = \rho' c' k', \quad \frac{1}{\gamma''-1} = \rho'' c'' k' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By eliminating μ in (3) and (4), and re-arranging terms

$$\rho c(\rho''-\rho') = (\rho-\rho')\rho''c'' + (\rho''-\rho)\rho'c'.$$

Whence by (5)

$$\frac{1}{\gamma-1} = \frac{\rho-\rho'}{\rho''-\rho'}\frac{1}{\gamma''-1} + \frac{\rho''-\rho}{\rho''-\rho'}\cdot\frac{1}{\gamma'-1}.$$

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[*] SMITH, 'Cont. to Knowledge,' 1903.

[†] 'Phil. Mag.,' February, 1903, p. 226.

[‡] 'Proc. Inst. Civil Eng.,' 131, Pt. I., p. 170 (1897–8).

[§] RICHARZ, 'Ann. d. Phys.,' 19, 639 (1906).

This formula has been used to find γ as shown in the following table. In the calculations, as air is one of the component gases,

$$\rho'' = 0{\cdot}00130 \text{ gm./c.c.}, \quad \gamma'' = 1{\cdot}404, \quad \rho' = \tfrac{1}{2} \text{ molecular wgt.} \times 0{\cdot}00009 \text{ gm./c.c.},$$

$$\rho = [\pi_1\rho' + (760-\pi_1)\,\rho'']/760,$$

where π_1 has the values given in the table on p. 460, have been used.

γ for Air Saturated with a Vapour.

Vapour.	γ'. Observed for vapour.	γ. Calculated by formula.	S.	S_1 if $\gamma = 1{\cdot}404$.
Acetic acid	1·147	1·395	9·3	9·6
Methyl alcohol . . .	1·256	1·382	3·1	3·4
Ethyl alcohol . . .	1·133	1·367	2·3	2·6
Chloroform	1·11	1·264	3	—
Water	1·307	1·401	4·15	4·19

The supersaturation S_1 in the last column is that obtained when $\gamma = 1{\cdot}404$ is used in calculating it. The above values of γ' are from LANDOLT, BÖRNSTEIN, and MEYERHOFFER'S tables, and γ' could not be found for any of the other vapours used in these experiments. Assuming γ' is not less than 1·1* for propionic to iso-valeric acids and propyl to iso-amyl alcohols, it can be shown that S_1 for these substances would have closely the values (S) given in the table on p. 460. For the esters S_1 would be in the same ratio as the values of S given, but would be smaller. For formic $\gamma' = 1{\cdot}27$ has been assumed ;† it gives $S_1 = 25{\cdot}1$, while, if $\gamma = 1{\cdot}404$ is used, S = 26·1.‡

The values for the least expansion for condensation in the case of the alcohols are those of PRZIBRAM (except the value 1·182 for iso-amyl alcohol, which is the writer's), who used both radium and Röntgen rays as ionising agents. Though he does not explicitly state what ionising agent was used to obtain these particular values, it would appear the rays from radium were used in the case of ethyl, propyl, iso-butyl, and iso-amyl alcohols.

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[*] γ' for iso-butane with 14 atoms in the molecule is 1·108.

[†] γ' for penta atomic CH_4 is 1·27.

[‡] I admit that this application of Richarz' formula is open to criticism. Previously the presence of the vapour has not been taken into account at all. The calculations I give are intended to show that the values for S are not greatly altered when the presence of the vapour is taken into account. The paucity of data (such as the value of γ, and the association constant) for the vapours used in these experiments makes a satisfactory treatment impossible. It is trusted that the calculations given are not without value.

Discussion of Results.

The values of the expansion in the last table are thought by the writer to be accurate to 0·01. An error in a value of the expansion gives rise to a larger error in the value of the supersaturation derived from it. This will be seen on examining the figures for iso-amyl alcohol, for which an expansion of 1·218 means a supersaturation of 5·49, and an expansion of 1·182 an S of 4·02. In this case an error of 0·01 (0·8 per cent.) in the expansion gives rise to an error of 0·4 (8 per cent.) in the supersaturation; similar figures hold for the other vapours. Besides the error arising from an error in the expansion, another is introduced in the supersaturation in calculating it by the formula

$$S = \frac{\pi_1}{\pi_2} \cdot \frac{v_1}{v_2} \cdot \frac{\theta_2}{\theta_1};$$

for π_2, the saturated pressure of the vapour at the low temperature at the end of the expansion, has to be found in several cases by extrapolation. Though all the vapour-pressure data available have been used, and the inter- and extrapolations have been made with the greatest care by RAMSAY and YOUNG'S method, by the Kirchhoff-Rankine formula

$$\log p = A + B/\theta + C \log \theta,$$

and by graphical methods, it has not been possible to obtain very accurate values of π_2* in the case of the acids. We cannot expect, then, that the relation between the chemical constitution of a vapour and the supersaturation causing condensation in it to be very precise. Some general relationships, however, seem clear.

Supersaturation and Chemical Constitution.

In the case of the esters and acids the supersaturation decreases with increasing molecular weight. Ethyl propionate, and the isomers butyric and iso-butyric acids, are exceptions to this statement. Of the four isomeric esters, three, namely, methyl butyrate, methyl iso-butyrate, and propyl acetate, have (to quite as high a degree of accuracy as could be expected) the same supersaturation, namely, about 5·2. Ethyl propionate deviates from this value. The isomers *n*-butyric acid and iso-butyric acid have also approximately the same supersaturation.

In the case of the alcohols, after the first of the series the supersaturation increases regularly with the molecular weight, thus:—

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* Where π_2 had to be calculated, the extrapolation was made by two of the above-mentioned methods, and in every case these two results were found to agree as closely as the observations of different observers when extrapolated agreed among themselves.

LEAST Supersaturation for Condensation in Air Initially Saturated with Organic Vapours and Exposed to Röntgen Rays.

Vapour.	Formula.	Molecular weight.	Expansion, v_2/v_1.	$\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$.	θ_2	Temperature at end of expansion, t_2°.	Saturated vapour pressure.		Super-saturation, $= \frac{\pi_1}{\pi_2} \cdot \frac{v_1}{v_2} \cdot \frac{\theta_2}{\theta_1}$.
							π_1 at 17°.	π_2 at t_2°.	
Ethyl acetate	$C_4H_8O_2$	88·1	1·486	0·8521	247·1	−25·9	62·6	4·0	8·9
Methyl butyrate . . .	$C_5H_{10}O_2$	102·1	1·334	0·8901	258·1	−14·9	20·6	2·58	5·3
Methyl iso-butyrate . .	"	102·1	1·347	0·8866	257·1	−15·9	33·0	4·2	5·2
Propyl acetate	"	102·1	1·310	0·8966	260·0	−13·0	21·2	2·87	5·0
Ethyl propionate . . .	"	102·1	1·410	0·8704	252·4	−20·6	23·5	1·86	7·8
Formic acid.	CH_2O_2	46	1·782	0·795*	230·5	−42·5	26·3	0·479	25·1
Acetic acid	$C_2H_4O_2$	60	1·441	0·8656†	251·0	−22·0	9·8	0·63	9·3
Propionic acid	$C_3H_6O_2$	74	1·343	0·8877	257·4	−15·6	2·00	0·14	9·4
Butyric acid	$C_4H_8O_2$	88·1	1·380	0·8780	254·6	−18·4	0·52	0·022	15·0
Iso-butyric acid . . .	"	88·1	1·360	0·8832	256·1	−16·9	0·88	0·043	13·3
Iso-valeric acid . . .	$C_5H_{10}O_2$	102·1	1·220	0·9228	267·6	− 5·4	0·20	0·025	6·0

Expansions obtained by PRZIBRAM with Radium and Röntgen Rays.

Vapour.	Formula.	Molecular weight.	Expansion, v_2/v_1.	$\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$.	θ_2	Temperature at end of expansion, t_2°.	π_1 at 17°.	π_2 at t_2°.	Super-saturation.
Methyl alcohol. . . .	CH_4O	32	1·251	0·9181‡	266·2	− 6·8	78·3	18·4	3·1
Ethyl alcohol	C_2H_6O	46	1·175	0·9426§	273·4	0·4	36·9	12·9	2·3
Propyl alcohol	C_3H_8O	60·1	1·178	0·9360	271·4	− 1·6	12·6	3·31	3·0
Iso-butyl alcohol . . .	$C_4H_{10}O$	74·1	1·198	0·9296	269·6	− 3·4	6·8	1·44	3·6
P. Iso-amyl alcohol . .	$C_5H_{12}O$	88·1	1·218	0·9234	267·8	− 5·2	1·78	0·246	5·5
L. " " . .	"	88·1	1·182	0·9344	271·0	− 2·0	1·78	0·339	4·1
Chloroform	CCl_3H	119·4	1·54	0·8923‖	258·8	−14·2	143	27·9	3·0

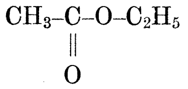
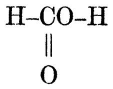
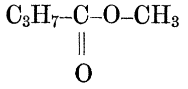
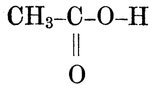
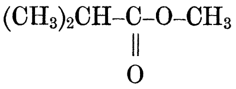
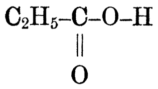
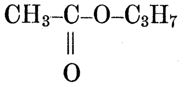
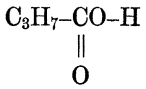
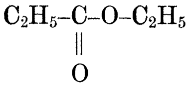
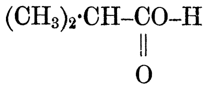
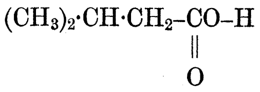
* $\gamma = 1·398$. † $\gamma = 1·395$. ‡ $\gamma = 1·382$. § $\gamma = 1·367$. ‖ $\gamma = 1·264$.

In all other cases $\gamma = 1·404$.

Alcohol.	Supersaturation.	Difference.
Ethyl[*]	2·56	—
Propyl	3·03	0·47
Iso-butyl	3·66	0·63
Iso-amyl	4·14	0·48

The acids and esters require a larger supersaturation to produce condensation in ionised air than the alcohols do. With the exception of iso-valeric acid, the acids require larger supersaturations than the esters—the supersaturation for formic and the butyric acids being extraordinarily large. One would have expected the association existing in the molecules of the vapour of acetic and some of the other acids to facilitate condensation.

The relations existing between chemical constitution and supersaturation will be seen from the following :—

Esters.	S.	Alcohols.	S.	Acids.	S.
(1)  $CH_3{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_2H_5$	8·9	(12) $CH_3{-}OH$	3·12	(6)  $H{-}\underset{\underset{O}{\|}}{C}O{-}H$	25·1
(2)  $C_3H_7{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_3$	5·3	(13) $C_2H_5{-}OH$	2·56	(7)  $CH_3{-}\underset{\underset{O}{\|}}{C}{-}O{-}H$	9·3
(3)  $(CH_3)_2CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_3$	5·2	(14) $C_3H_7{-}OH$	3·03	(8)  $C_2H_5{-}\underset{\underset{O}{\|}}{C}{-}O{-}H$	9·4
(4)  $CH_3{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_3H_7$	5·1	(15) $(CH_3)_2CH{\cdot}CH_2{-}OH$	3·66	(9)  $C_3H_7{-}\underset{\underset{O}{\|}}{C}O{-}H$	15·0
(5)  $C_2H_5{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_2H_5$	7·8	(17) $(CH_3)_2{\cdot}C_3H_5{-}OH$	4·14	(10)  $(CH_3)_2{\cdot}CH{-}\underset{\underset{O}{\|}}{C}O{-}H$	13·3
		$H{-}OH$	4·2	(11)  $(CH_3)_2{\cdot}CH{\cdot}CH_2{-}\underset{\underset{O}{\|}}{C}O{-}H$	6·0

The general nature of the affect of a given group of elements on the magnitude of S may be stated thus :—

Carbonyl, $>C = O$. The presence of this radical is associated with a large S, as shown by the acids and esters.

Alkyl-groups, CH_3–, C_2H_5–, C_3H_7–, $(CH_3)_2CH$–, $(CH_3)_2{\cdot}CHCH_2$–, C_5H_{11}–. The presence of these appears to contribute only a small amount to the value of S. The regular increment in S for ethyl, propyl, iso-butyl, and iso-amyl alcohols indicates that

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[*] Using $\gamma = 1{\cdot}404$ in each calculation.

the effect of these radicals, though small, is proportional to the number of carbon atoms in them. *Hydroxyl*, HO–. This group is present in the alcohols which have the smallest values of S, and in the acids which have the largest values. It may be that when the –OH group is combined with carbonyl carbon in a compound that compound has a large S, while when it is combined with alkyl carbon the value of S is small. S must be known for more varied compounds than the above before this action of hydroxyl can be tested.

Theory of Condensation on Ionic Nuclei.

The theory of the condensation of drops has been given by several writers. Lord KELVIN'S[*] well-known result showed that the surface tension makes the vapour pressure of a small drop greater than that of a large one. Professor J. J. THOMSON,[†] in 1886, deduced an expression for the diminution in the vapour pressure of a drop when it is charged electrically. The combined effect on condensation of the surface tension of a drop and the charge it receives when it condenses on an ionic nucleus has been given by J. J. THOMSON,[†] BLOCH and LANGEVIN,[‡] and C. T. R. WILSON.[§]

Size of Charged Drop in Equilibrium with Saturated Vapour.

Professor THOMSON finds that the vapour pressure of a drop as altered by its charge and surface tension is given by

$$\mathrm{R}\theta \log_e \frac{p}{\mathrm{P}} = \left(\frac{2\mathrm{T}}{a} - \frac{e^2}{8\pi \mathrm{K} a^4}\right)\frac{1}{\sigma}, \quad \ldots\ldots\ldots \quad (6)$$

when T is independent of a, where a is the radius, p the vapour pressure, θ the temperature, e the charge, σ the density, and T the surface tension of the drop; R is the gas constant for unit mass of the vapour, P the pressure of the vapour in equilibrium with a very large drop; K is the specific inductive capacity of the dielectric surrounding the drop.

When the drop is uncharged, *i.e.*, $e = 0$, it will evaporate in the unsupersaturated vapour. When it is charged it increases in size until $p/\mathrm{P} = 1$, *i.e.*, $\log_e(p/\mathrm{P}) = 0$, or, by (6), until

$$a = \sqrt[3]{\frac{e^2}{16\pi \mathrm{KT}}}$$

$$= \sqrt[3]{\frac{3{\cdot}4 \times 3{\cdot}4 \times 10^{-20}}{16 . \pi . 1.76}} = 3{\cdot}12 \times 10^{-8} \text{ cm.}$$

for water in C.G.S. units, taking $e = 3{\cdot}4 \times 10^{-10}$ electrostatic units.

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[*] 'Proc. Roy. Soc. Edin.,' 7, p. 63 (1870); also HELMHOLTZ, 'WIED. Ann.,' 27, 508 (1886).

[†] 'Applications of Dynamics to Physics and Chemistry,' London, 1888; 'Conduction of Electricity through Gases.'

[‡] 'Ann. Chem. et Phys.,' [8], IV., p. 135, January, 1905.

[§] 'Smithsonian Report,' p. 195 (1904).

I have calculated a for the following substances :—

RADIUS of Drop with Charge $3{\cdot}25 \times 10^{-10}$ Electrostatic Units in Equilibrium with the Saturated Vapour at 17° C.

a.	
	cm.
Water	$3{\cdot}02 \times 10^{-8}$
Ethyl acetate	$4{\cdot}4$
Methyl butyrate	$4{\cdot}4$
Methyl iso-butyrate	$4{\cdot}4$
Propyl acetate	$4{\cdot}4$
Ethyl propionate	$4{\cdot}4$
Formic acid	$3{\cdot}8$
Acetic acid	$4{\cdot}5$
Propionic acid	$4{\cdot}3$
Butyric acid	$4{\cdot}3 \times 10^{-8}$
Iso-butyric acid	$4{\cdot}5$
Methyl alcohol	$4{\cdot}5$
Ethyl alcohol	$4{\cdot}5$
Propyl alcohol	$4{\cdot}5$
Iso-butyl alcohol	$4{\cdot}5$
Iso-amyl alcohol	$4{\cdot}5$
Chloroform	$4{\cdot}3$

(Radius of N_2 molecule $1{\cdot}41 \times 10^{-8}$ cm., O_2 $1{\cdot}35 \times 10^{-8}$ cm.)*

The surface tensions used in calculating the above tables are from RAMSAY and SHIELDS'† and RAMSAY and ASTON'S‡ determinations, which were made with only the liquid and vapour present in the measuring apparatus.

This value of a is practically the same for the organic liquids, with exception of formic acid. The volume of one of these organic liquid drops would be three times that of the water drop in equilibrium with aqueously saturated air at the room temperature.

Calculated Supersaturation.

According to the theory we are considering, the presence of electrically charged nuclei in a vapour will cause it to condense and form small drops. The charge on these drops tends to make them grow larger, while their surface tension tends to make them evaporate. Their size, when in equilibrium with the vapour, depends on its pressure. There will be a pressure which will enable the drops to grow to such a size that the effect of surface tension will be overcome, and, if the vapour pressure be kept up, the drop will become very large. In a condensation experiment in which the expansion is just sufficient to cause condensation, the vapour pressure at the instant when the expansion ends is sufficient to make the very small (invisible) drops grow to a large size. Professor J. J. THOMSON§ has shown how this last vapour pressure may be found.

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* JEANS, 'Dynamical Theory of Gases,' Cambridge, 1904, p. 340.

† 'Phil. Trans.,' A, 184, p. 647 (1893).

‡ 'Roy. Soc. Proc.,' 56, p. 163 (1894).

§ 'Conduction of Electricity through Gases,' 2nd Edition, p. 180 (1906).

If c is the radius of a drop (with charge e) which is in equilibrium with the saturated vapour, and a its radius when in equilibrium with the vapour at a pressure p, then

$$\mathrm{R}\theta \log_e \frac{p}{\mathrm{P}} = 2\mathrm{T}x\,(1-x^3)\,\frac{1}{\sigma c},$$

where $x = c/a$.

For water at 10° C. we have $\mathrm{R} = 4{\cdot}62 \times 10^6$, $c = 3{\cdot}05 \times 10^{-8}$ cm., $\sigma = 1$, $\mathrm{T} = 74$ dynes/cm., so that for it

$$\log_{10}(p/\mathrm{P}) = 1{\cdot}61x\,(1-x^3).$$

The graph of this function (which is typical of the organic vapours as well) is given in fig. 5, where p/P, the supersaturation, is the ordinate, and the abscissa is the radius of the drop with a vapour pressure p. It will be seen that as p/P increases from a very small value to 1, the size of the drop changes very little. When p/P is 5·8, its maximum value, the radius of the drop is 1·6c. Any further increase in p/P makes the drop grow to a very large size, or visible condensation takes place. The AB portion of the curve represents unstable equilibrium, for a increases as p/P diminishes. For condensation to take place, p/P must be slightly greater than its value at A, which is the value of p/P in the above equation when $x\,(1-x^3)$ is a maximum, *i.e.*, when $1-4x^3 = 0$, or $x = 0{\cdot}63$ and $x\,(1-x^3) = 0{\cdot}472$.

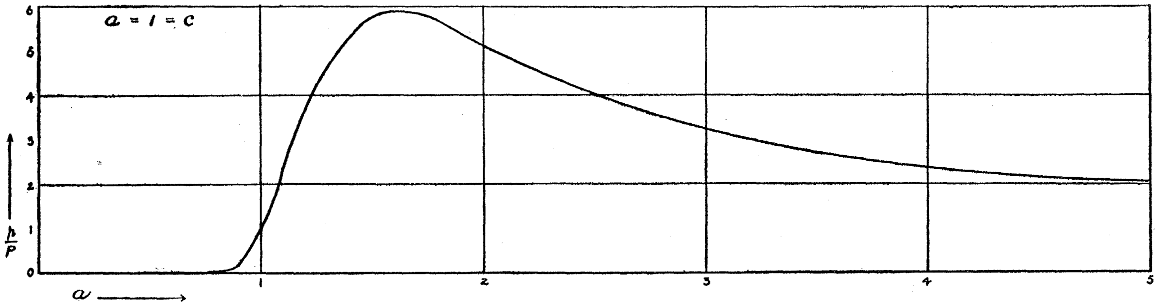

Fig. 5. Radius of charged drop in equilibrium with water vapour at various pressures.

Thus the value of p/P given by the expression

$$\log_{10}(p/\mathrm{P}) = \frac{1}{2{\cdot}3}\,\frac{2\mathrm{T}}{\mathrm{R}\theta c\sigma}\,x\,(1-x^3) = 0{\cdot}41\,\frac{\mathrm{T}}{\mathrm{R}\theta c\sigma}$$

is the least value which will cause condensation.

The values p/P which the equation gives are stated below for a number of esters, acids, and alcohols. T, the surface tension, was found at the required temperature by plotting Ramsay and Shield's, and Ramsay and Aston's* values of T at different temperatures; straight lines were nearly always obtained from which the required

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* *Loc. cit.*

SUPERSATURATION Necessary to make a Charged Drop Grow to a Large Size.

Liquid forming drop.	Condensation temperature, $t_2°$.	θ.	R.	σ at t_2, gm./c.c.	T at t_2, dynes/cm.	c at t_2, cm.	S or p/P. Calculated. $\log(p/P) = 0 \cdot 41 \frac{T}{R\theta c\sigma}$.	S or p/P. Observed.
Ethyl acetate	-26	247	$9 \cdot 44 \times 10^5$	$0 \cdot 956$	$31 \cdot 8$	$4 \cdot 04 \times 10^{-8}$	28	9
Methyl butyrate	-15	258	$8 \cdot 15 \times 10^5$	$0 \cdot 935$	$28 \cdot 2$	$4 \cdot 21$	25	$5 \cdot 3$
Methyl iso-butyrate	-16	257	$8 \cdot 15 \times 10^5$	$0 \cdot 931$	$26 \cdot 8$	$4 \cdot 28$	21	$5 \cdot 2$
Propyl acetate	-13	260	$8 \cdot 15 \times 10^5$	$0 \cdot 928$	$27 \cdot 3$	$4 \cdot 25$	22	$5 \cdot 1$
Ethyl propionate	-21	252	$8 \cdot 15 \times 10^5$	$0 \cdot 94$	$28 \cdot 1$	$4 \cdot 21$	25	$7 \cdot 8$
Formic acid	-43	230	$1 \cdot 81 \times 10^6$	$1 \cdot 29$	$43 \cdot 8$	$3 \cdot 63$	8	26
Acetic acid	-22	251	$6 \cdot 93 \times 10^5$	$1 \cdot 09$	$25 \cdot 9$	$4 \cdot 32$	$13 \cdot 5$	$9 \cdot 3$
Propionic acid	-16	257	$1 \cdot 12 \times 10^6$	$1 \cdot 03$	$29 \cdot 6$	$4 \cdot 14$	10	$9 \cdot 3$
Butyric acid	-18	255	$9 \cdot 44 \times 10^5$	$0 \cdot 997$	$29 \cdot 4$	$4 \cdot 15$	16	15
Iso-butyric acid	-17	256	$9 \cdot 44 \times 10^5$	$0 \cdot 987$	$27 \cdot 5$	$4 \cdot 24$	13	13
Methyl alcohol	-7	266	$2 \cdot 6 \times 10^6$	$0 \cdot 826$	$25 \cdot 4$	$4 \cdot 36$	$2 \cdot 6$	$3 \cdot 1$
Ethyl alcohol	0	273	$1 \cdot 81 \times 10^6$	$0 \cdot 81$	$23 \cdot 8$	$4 \cdot 45$	$3 \cdot 5$	$2 \cdot 3$
Propyl alcohol	-2	271	$1 \cdot 38 \times 10^6$	$0 \cdot 821$	$25 \cdot 3$	$4 \cdot 36$	6	$3 \cdot 1$
Iso-butyl alcohol	-3	270	$1 \cdot 12 \times 10^6$	$0 \cdot 823$	$24 \cdot 4$	$4 \cdot 42$	8	$3 \cdot 7$
Iso-amyl alcohol	-5	268	$9 \cdot 4 \times 10^5$	$0 \cdot 835$	$25 \cdot 2$	$4 \cdot 37$	13	$5 \cdot 5$
Chloroform	-14	259	$6 \cdot 97 \times 10^5$	$1 \cdot 58$	$31 \cdot 8$	$4 \cdot 04$	16	$3 \cdot 0$
Water	-8	265	$4 \cdot 62 \times 10^6$	$0 \cdot 999$	$76 \cdot 7$	$3 \cdot 01$	$7 \cdot 1$	$4 \cdot 2$

value of T could be found. The densities given* were corrected for temperature by using the observed coefficients of expansion. In this equation R for oxygen would be $2 \cdot 6 \times 10^6$, and for a gas of molecular weight M is $2 \cdot 6 \times 10^6 \times 32/M$. The molecular weight of acetic acid has been taken as 120, as found by BINEAU and RAMSAY and YOUNG.† The values of c, the radius of a drop with charge e in equilibrium with its saturated vapour, in the preceding table are slightly different to those given previously, for c varies a little with the temperature, which in this table is t_2, the temperature at which drops are formed in the expansion experiments.

Discussion of Calculated and Observed Supersaturations.

In calculating the supersaturation in the last table no account has been taken of the variation of surface tension with the thickness of the surface film. REINOLD and RUCKER'S observations show that the surface tension T of a water film begins to depend on the thickness when the film is about 10^{-5} cm. thick. For thicknesses less than this T diminishes, but passes through maxima when the film is $1 \cdot 2 \times 10^{-6}$ and when 6×10^{-7} cm. (Johannot) thick. Lord RAYLEIGH,‡ however, found that one interpretation of his experiments led to the conclusion that an oil film only one molecule thick still had surface tension. The equation $\log (p/P) = 0 \cdot 41 T/R\theta\sigma c$ has been applied above to drops of about 7×10^{-8} cm. radius. It is to be expected that T for the surface films of such drops has a smaller value than for thick films. This would lead to a calculated value of p/P, that is of S, which would be too large—a difference that the last table exhibits, for in all but two cases (formic acid and methyl alcohol) the calculated value of S is larger than the observed. On this view we would conclude that the surface tensions of acetic, propionic, butyric, and iso-butyric acids do not vary with the thickness of the surface film, since the calculated value of S for these acids agrees with the observed.

Condensation on Natural Nuclei.

The least expansion producing condensation in the absence of Röntgen rays was determined with the mercury sealed test-tube expansion chamber of fig. 2. The following is an example taken at random of the observations obtained.

Dust-Free Air Saturated with Ethyl Acetate. Natural Nuclei.

Expansions v_2/v_1.

Without drops: 1·390, 1·506, 1·511, 1·524, 1·526, 1·531.
With drops: 1·528, 1·534, 1·536, 1·542, 1·545, 1·556, 1·587.
Least expansion for condensation 1·528.

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* VAN NOSTRAND'S 'Chem. Ann.'

† 'Trans. Chem. Soc.,' 49, p. 790 (1886)

‡ 'Phil. Mag.,' October, 1899, p. 23

The results of these experiments, as a whole, were more regular than those obtained when the air and vapour were ionised by Röntgen rays. The number of expansions made in order to determine v_2/v_1 varied from 7 to 20 for the different substances, and on the average was 14.

After acetic acid had been exposed to the rays from radium or from thorium very inconsistent observations were obtained.

The vapour pressure π_1 of tertiary amyl alcohol was assumed to be between 5 and 15 mm. at 17° C.* in order to calculate the expansion.

Air and Water. Natural Nuclei.

No drops: 1·242, 1·242, 1·250, 1·252, 1·254.

Drops: 1·256, 1·258, 1·260, 1·262, 1·262, 1·266.

Least expansion for condensation **1·256.**

C. T. R. Wilson,† using a small apparatus, found 1·252. Immediately before the above experiments the following observations were obtained with the apparatus, the air and water vapour being exposed to Röntgen rays during the expansion.

Air and Water. Röntgen Rays.

No drops: 1·208, 1·218, 1·220, 1·224, 1·226, 1·230, 1·230, 1·234.

Drops: 1·236, 1·240, 1·240, 1·241, 1·252 (thin cloud).

Thus least expansion for condensation is 1·236; 1·247 (Wilson).‡ The least expansions for condensation found from experiments just described are given in the second column of the table on the following page.

The nuclei in the condensation we are considering must be the natural ones present in the dust-free air. Wilson found, as we saw earlier in this paper, the same expansion caught the natural nuclei as caught the nuclei produced by Röntgen, Becquerel, and other rays; and he showed also that the natural nuclei could be removed by an electric field, so they were the ions which normally exist in the air.

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* The vapour pressure of tertiary amyl alcohol at 17° C. has not been determined. It may be calculated thus: If ${}_{\mathrm{A}}\theta_{\pi}$ represents the absolute temperature when a liquid A has a vapour pressure π, then we know that

$${}_{\text{water}}\theta_{760}/{}_{\text{tertiary amyl alcohol}}\theta_{760} = 373/374\cdot8 = 0\cdot9975.$$

Now this ratio is known to vary only slightly with the temperature; for several alcohols it changes $+0\cdot0002$ per degree. Therefore the temperature of water when it has the same vapour pressure as tertiary amyl alcohol at 17° is

$${}_{\text{water}}\theta_{\pi} = {}_{\text{tertiary amyl alcohol}}\theta_{\pi} \times 0\cdot98 = 290 \times 0\cdot98 = 284°.$$

But at $273°+11°$ π for water is 9·8 mm. So, according to this reasoning, π for tertiary amyl alcohol at $273+17$ is 9·8 mm.

† 'Phil. Trans.,' A, 189, p. 265 (1897).

‡ 'Phil. Trans.,' A, 192, p. 408 (1899).

With the substances used by the writer in every case a larger expansion (as is shown in the following table) was necessary to cause condensation in air not acted on by Röntgen rays than in air so acted on.

LEAST Expansion for Condensation.

Vapour.	Without rays.	With Röntgen rays.	Difference.
Ethyl acetate	1·528	1·480	0·048
Methyl butyrate	1·364	1·334	0·030
Methyl iso-butyrate	1·387	1·347	0·040
Propyl acetate	1·334	1·310	0·024
Ethyl propionate	1·438	1·410	0·028
Formic acid	1·865	1·782	0·083
Acetic acid	1·508	1·441	0·067
Propionic acid	1·369	1·343	0·026
n-Butyric acid	1·463	1·380	0·083
Iso-butyric acid	1·403	1·360	0·043
Iso-valeric acid	1·256	1·220	0·036
Iso-amyl alcohol	1·210	1·182	0·028
Water	1·256	1·236	0·020

Natural and Röntgen-Ray Nuclei.

The differences between the expansions necessary to catch natural and Röntgen-ray nuclei arises partly probably from the size of the expansion chamber. We have seen (p. 445) that, by using a large apparatus, WILSON found for air and water vapour that the expansion for the natural nuclei was the same (1·247) as for Röntgen-ray ionic nuclei. Thus the differences in the table above must arise partly from the size of the apparatus. In the experiments made by the writer to determine the natural nuclei point in aqueously saturated air only a few drops were seen with the smaller expansions (1·256 one drop, 1·258 five or six drops, 1·260 one). Further, it was found that a drop may be formed and not be seen if the observer's eye has been exposed to anything but feeble light immediately before or during the experiment. Thus the small number* of natural nuclei (and consequently of drops) which are dealt with in these experiments lead to a value for the expansion required to catch the natural nuclei which is too large. This difficulty does not arise with the far more numerous Röntgen-ray nuclei. While it is thought that the above factors may account for the differences of 0·02 in the last table, they can scarcely account for the larger differences for formic (0·08), acetic (0·07), and butyric acids (0·08). These differences are very probably

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* The natural ionisation in hydrogen in a closed vessel is only 0·18 of that of air [WILSON, 'Proc. Roy. Soc.,' 69, p. 277 (1901)], and consequently WILSON did not observe condensation on the natural nuclei in it.

connected with the phenomena that the least expansion necessary to catch the nuclei produced in air and acetic acid vapour depends on the intensity of the Röntgen rays. Thus the least expansion for condensation in this acid with intense X-rays was found to be (see p. 454) 1·441, and with feeble rays 1·471. Now the radiation which produces the natural ionisation in air is largely due to a penetrating radiation* of very small intensity. It will be necessary to make a special investigation to clear up the question of the relative efficiency of the natural nuclei and the Röntgen-ray ionic nuclei in case of formic, acetic, and butyric acids.

Professor BARUS† observed, in 1906, that the intensity of the Röntgen rays similarly affects condensation in air and water vapour.

In the table on p. 470 the least supersaturations which will produce condensation on the natural nuclei have been calculated. $\gamma = 1{\cdot}404$ has been used in each case.

The values of π_2 used in this paper have been inter- and extra-polated by the method of RAMSAY and YOUNG, the Kirchhoff-Rankine formula, and graphically. π_2 of each substance is for a lower temperature in the table on p. 470 than in the case of the table on p. 460, and consequently the above values of the supersaturation are less accurate than those given in the latter table. For this reason the relation of S to chemical constitution is discussed for condensation in air ionised by Röntgen rays. It will be seen, however, that the supersaturation necessary for condensation on natural nuclei is related in essentially the same way to the chemical constitution of the vapour as in the case already discussed.

Sign of the Charge of the more Efficient Nucleus.

It has been mentioned how C. T. R. WILSON found that a smaller supersaturation gave condensation on the negative ion than on the positive in air initially saturated with water, or, in other words, how he found the negative ion to be the more efficient nucleus for water vapour.

The chief difficulty encountered in finding the more efficient ion for organic vapours was to make an expansion chamber of material which is unacted upon by them. Sodium silicate, lead oxide and glycerine, sealing wax, rubber dissolved in benzine, were tried as cements for the joint between the aluminium and glass in the apparatus described on p. 449; the two first, which were not acted upon by esters, failed to make a permanently gas-tight joint. Sealing wax and rubber are acted upon by many organic liquids. If, however, the vapour only of the ester (say) is allowed to come in contact with the rubber, the action is very slow and the rubber appears unaffected. A sensitive method of detecting the action of the ester on the rubber is to determine the expansion necessary to catch X-ray nuclei immediately after filling the apparatus with the ester, and then again twenty-four hours or so later; a change

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* McLENNAN, 'Phys. Rev.,' 16, p. 184 (1903); RUTHERFORD and COOKE, *ibid.*, 16, p. 183 (1903).

† 'Physical Rev.,' 22, 2, February, 1906.

LEAST Supersaturation for Condensation on Natural Nuclei in Dust-free Air Initially Saturated with Organic Vapours.

Vapour.	Formula.	Molecular weight.	Expansion, v_2/v_1.	$\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$, $\gamma = 1\cdot404$.	θ_2.	t_2.	π_1 at 17°.	π_2 at t_2.	Super-saturation, $S = \frac{\pi_1}{\pi_2} \cdot \frac{v_1}{v_2} \cdot \frac{\theta_2}{\theta_1}$.
Ethyl acetate	$C_4H_8O_2$	88·1	1·528	0·8426	244·4	−28·6	62·6	3·31	10
Methyl butyrate . . .	$C_5H_{10}O_2$	102·1	1·364	0·8821	255·8	−17·2	20·6	2·19	6
Methyl iso-butyrate . .	"	102·1	1·387	0·8762	254·1	−18·9	33·0	3·44	6
Propyl acetate . . .	"	102·1	1·334	0·8900	258·1	−14·9	21·2	2·47	5·7
Ethyl propionate . .	"	102·1	1·438	0·8635	250·4	−22·6	23·5	1·65	8·6
Formic acid	CH_2O_2	46	1·865	0·7774	225·4	−47·6	26·3	0·302	37
Acetic acid	$C_2H_4O_2$	60	1·508	0·8471	245·7	−27·3	9·8	0·407	13·5
Propionic acid . . .	$C_3H_6O_2$	74	1·369	0·8808	255·4	−17·6	2·00	0·128	10
Butyric acid	$C_4H_8O_2$	88·1	1·463	0·8575	248·7	−24·3	0·52	0·0125	25
Iso-butyric acid . . .	"	88·1	1·403	0·8721	252·9	−20·1	0·88	0·029	19
Iso-valeric acid . . .	$C_5H_{10}O_2$	102·1	1·256	0·9120	264·5	− 8·5	0·20	0·016	9

in the value of the expansion is an indication that the ester has acted on the rubber. Acetic acid and inactive amyl alcohol (iso-butyl carbinol), when tested in this way, and when tested directly, were not found to act on the rubber used in the writer's apparatus.

All the vapours tried condensed more readily in air on the positively charged nuclei than on the negative, as is seen below. Röntgen rays were the ionising agent.

Vapours which Condense with a Smaller Supersaturation on the Positive Nucleus than on the Negative.

Ethyl acetate, methyl butyrate, propyl acetate, acetic acid, amyl alcohol ("inactive").

Przibram (*loc. cit.*) has found in addition to the above :—

Methyl alcohol, ethyl alcohol, iso-amyl alcohol, heptyl alcohol, chloroform, ethyl iodide.

It is remarkable that there is only one vapour (water) so far known which condenses more readily on the negative than on the positive ion.

Bubbling Experiments.

Lenard* showed that when water splashes against a metal plate it charges the plate positively and the surrounding air negatively; a little later Lord Kelvin† observed the electrification produced by air in bubbling through water—the air became negatively and the water positively charged. The air near the Niagara Falls is known to be strongly negatively charged. Professor Thomson‡ has suggested a double-layer theory to account for these observations. "When air bubbles through water, or when the area of a drop is suddenly increased by the splashing of the drop against a plate, a virgin surface of the water is exposed to the air; if, as seems to be the case, a double layer of electricity is formed at this surface, and if the ions in the layer next the air come from the air, then there must be left in the air an excess of negative ions if the outer coating is positive, and of positive if the outer coating is negative." On this view for a water drop the negative layer is next to the water and the positive layer to the air.

Professor Thomson§ has further pointed out that if this double layer exists at the surface of an ionic condensation nucleus, and if the layers are in the same order on both positive and negative nuclei, then the relative efficiency of the nuclei will not be the same. For example, if the water nuclei have the negative layer inside, as indicated by the bubbling and dropping experiments, then the negative ion will be a

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* 'Wied. Ann.,' 46, p. 584 (1892).

† 'Roy. Soc. Proc.,' 57, p. 335 (1895).

‡ 'Conduction of Electricity through Gases,' 2nd Edition, p. 428.

§ *Loc. cit.*, p. 186.

more efficient nucleus for the condensation of water vapour than the positive, for in this case the field of the negative nucleus due to the ionic charge is in the same direction as that due to the double layer; while for the positive nucleus these fields are in opposite directions. In the first case the effect of the charge in making the ion efficient as a condensation nucleus is increased, and in the second it is diminished. Thus the double-layer theory requires, in order to account for the observed greater efficiency of the negative nucleus than the positive, that the negative layer on a water drop should be next to the water and the positive layer next to the air. This we have seen is also the arrangement of the layers to be expected from the fact that water becomes positively charged when bubbled. In other words, this theory requires that the sign of the charge acquired by air, when it is bubbled through a liquid, should be the same as the sign of the charge on the more efficient nucleus for the condensation of the vapour of that liquid.

The eleven liquids mentioned on p. 471 have been found by PRZIBRAM and myself to condense on the positive nucleus more readily than on the negative. In the case of these substances the theory requires that when air is bubbled through them the liquid should become negatively charged. When the liquids were bubbled, all that were tried, with exception of acetic acid, became negatively charged in agreement with the theory.

Ethyl alcohol is the only one of the liquids which had been previously examined in this way; LENARD found in two experiments with alcohol containing 9 per cent. of water the electrification on bubbling to be once $-0{\cdot}039$ and once $+0{\cdot}123$ in terms of his unit.

In the writer's experiments a small wide-mouthed bottle was insulated by attaching it with sealing wax to a disc of vulcanite. A foot bellows, which gave a sufficiently uniform pressure, forced air through two tubes containing cotton wool, calcium chloride, and solid caustic soda. The dust-free and dry air passed through a vulcanite tube insulator to a glass tube which dipped below the surface of the liquid in the bottle. When the bellows were in action, a steady stream of bubbles was formed in the liquid. The electrification produced was detected by attaching a wire dipping in the liquid to one pair of quadrants of a Dolezalek electrometer which gave from 4000 to 5000 mms. deflection per volt on a scale at about 2 meters. The bottle and wire were shielded from inductive effects by an earthed metal vessel. The drift of the spot was generally observed for four minutes while the air was bubbling through the liquid and for the same time without bubbling. The difference in the drift gave the electrification due to the bubbling. For nearly all the liquids tried the effect was larger the first time the liquid was bubbled than for subsequent bubblings. For methyl and ethyl alcohols the electrification was small and could just be detected with certainty.

It was found that different samples of KAHLBAUM'S I methyl alcohol, which had been distilled after drying over lime, became sometimes positively and sometimes negatively electrified. But when some of this alcohol was carefully purified—(1) by conversion into methyl oxalate and by subsequent hydrolysis, (2) by distillation after treatment with sodium—both products behaved alike and became negatively charged. The sign of the charge acquired by the liquids which have been examined when bubbled was as follows :—

Electrification on Bubbling.

Liquid.	Sign of charge acquired by liquid.	Liquid.	Sign of charge acquired by liquid.
Methyl alcohol	–	Methyl butyrate	–
Ethyl alcohol	–	Acetic acid	+
Iso-amyl alcohol	–	Chloroform	–
Ethyl acetate	–	Ethyl iodide	–
Propyl acetate	–		

Purification of Liquids.

Methyl alcohol : (1) Kahlbaum's alcohol was converted into methyl oxalate by anhydrous oxalic acid ; the resulting oxalate was washed and hydrolised by sodium hydrate. The alcohol obtained was distilled, and then distilled from lime. (2) The same initial alcohol was treated with metallic sodium, and distilled.

Ethyl alcohol : Distilled from lime from marble, and then from a small piece of sodium. Density at 12°, 0·7961 gms. per cubic centimetre. (Absolute alcohol has a density of 0·7962.)

Chloroform : Twice distilled, boiling point 61·7° to 61·8° at 777 mm.

Ethyl iodide : Once distilled.

The other liquids were the same as were used in the condensation experiments (see p. 452).

The result for acetic acid is not in agreement with the double-layer theory, though the acid used had been purified by fractional crystallisation and distillation. It has been mentioned that other anomalous results have been obtained with this acid.

Fog-like Condensation.

Some observations were made to find the expansion necessary for fog-like condensation in certain organic vapours. But the point at which this kind of condensation took place was not usually sufficiently well defined for the results to be very exact ; for, as the expansion was increased above that which caught the natural nuclei, the number of drops continuously increased. In this respect acetic, propionic, *n*-butyric, and iso-valeric acids, methyl butyrate, and propyl acetate are unlike water. Tertiary amyl alcohol behaves more like water : with it an expansion of 1·27 gives many drops, the condensation becoming fog-like when the expansion is increased 1·28.

Summary.

(1) The least expansion which causes condensation in air initially saturated with an organic vapour and ionised by Röntgen rays has been determined for five esters, six acids (formic to iso-valeric), and iso-amyl alcohol.

(2) In the case of acetic acid the expansion required was greater for feeble X-rays than for more intense ones.

(3) The supersaturation S existing at the end of each of the expansions mentioned in (1) has been calculated, and also for four alcohols and chloroform, from PRZIBRAM'S experiments.

(4) The acids are found, on the whole, to have the largest values of S and the alcohols the least. The isomers examined have the same value for S, with one exception. In the case of the alcohols, ethyl to iso-amyl, a fairly regular decrease in S accompanies the addition of a CH_2 group.

(5) The existing theory of condensation on ionic nuclei has been given, values of S have been calculated from it, and compared with S deduced from the observed expansions. The agreement in the case of acetic, propionic, *n*-butyric, and iso-butyric acids and methyl alcohol is very close.

(6) The expansion and supersaturation necessary for condensation on the natural nuclei have been determined for the same (dust-free) vapours. In the case of formic, acetic, and butyric acids a distinctly greater expansion is required to catch the natural nuclei than that required for the ionic nuclei produced by Röntgen rays.

(7) As the expansion was increased in the absence of artificial ionisation the number of drops usually increased continuously with it, so that the fog-point was ill defined, except in the case of tertiary amyl alcohol.

(8) Ethyl acetate, methyl butyrate, propyl acetate, acetic acid, iso-amyl alcohol were found to condense for a smaller supersaturation on the positive nucleus than on the negative. Water is the only known substance for which the negative ionic nucleus is more efficient than the positive.

(9) On bubbling air through methyl, ethyl, and iso-amyl alcohols, ethyl acetate, propyl acetate, methyl butyrate, chloroform, and ethyl iodide they became negatively electrified. This was the sign of the electrification to be expected from Professor THOMSON'S double-layer theory of the relative efficiency of ionic nuclei.

I wish to thank Mr. C. T. R. WILSON for most helpful discussion, and Professor THOMSON for many suggestions and his inspiring interest.