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Condensation Nuclei
Produced in the Laboratory

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CONDENSATION NUCLEI PRODUCED IN THE LABORATORY *

In a recent publication S. TWOMEY and the writer described experiments on the production of condensation nuclei by ultraviolet light in moist laboratory air and other gases.⁽¹⁾ The experiments seemed to show that the radiation acted on ammonia present as an impurity in these gases. The addition of ammonia caused a great increase in the number of nuclei produced by a given exposure. The limiting wavelength for nucleus production was not altered by the addition of ammonia. The gas NO_2 , which also absorbs in the critical region, might also have contributed to the effect. Further experiment would be required to see if this is so.

The nuclei can remain in equilibrium with unsaturated air and must therefore be droplets of an aqueous solution of some substance either formed by the light or present originally as an impurity in the gas and activated by it so as to cause condensation of the water molecules. In the above paper (Ref. 1) it was suggested that the ammonia, raised to a higher energy level by the light quantum, possessed a high dipole moment and was thus capable of attracting a small cluster of water molecules and that these clusters grew, by collision and attraction of more H_2O molecules, until large aggregates of 10^5 or 10^6 molecules were formed. These aggregates were the condensation nuclei which were able to remain in equilibrium with the unsaturated air on account of the lowering of the equilibrium vapour pressure by the dissolved substance. The equilibrium of these hygroscopic nuclei has been examined by WRIGHT,^(2, 3, 4) whose formula enables us later to make an estimate of the concentration of the dissolved substance in nuclei of a given radius when they are in equilibrium with air of known relative humidity.

Some further experiments, hitherto unpublished, have been done in the laboratory of the Physics Department at University College, Cork, in an attempt to throw some light on the important initial step in condensation, viz. the attraction of a group of H_2O molecules by a molecule of the soluble substance to form a cluster. In these experiments different chemical substances, unexposed to radiation, were added to moist air which was then examined for the presence of nuclei by the ionization method.⁽⁵⁾ In this method condensation nuclei in an air-stream are sent through a region of intense ionization produced by alpha rays. The nuclei collide with 'small' ions and become 'large' ions of much lower mobility. The large ions pass through the space between two coaxial cylinders at different potentials and the ionization current is measured for different values of the potential difference. The ionic mobilities are calculated from the values of the potential difference required for saturation of the current. The radii of the ions, and hence of the nuclei may be calculated from the mobilities using the STOKES-CUNNINGHAM law for the resistance offered to a moving sphere by a viscous medium. In practice, we calculated the radii from the mobilities by means of a table prepared by NOLAN and KENNY.⁽⁶⁾ In this method the saturation current divided by the electronic charge gives the number of large ions reaching the electrodes in one second. This enables the number of nuclei per cc. to be estimated. A similar method, with stationary instead of streaming air, was recently used by VASSAIL.⁽⁷⁾

* Substance of a lecture delivered to the Dublin Meteorological and Geophysical Seminar on 4th December, 1952.

FIG. 1.

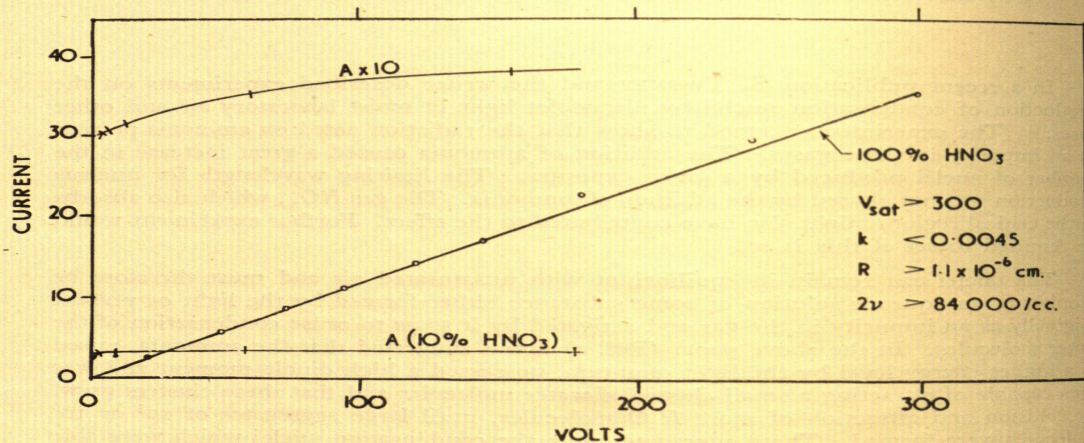
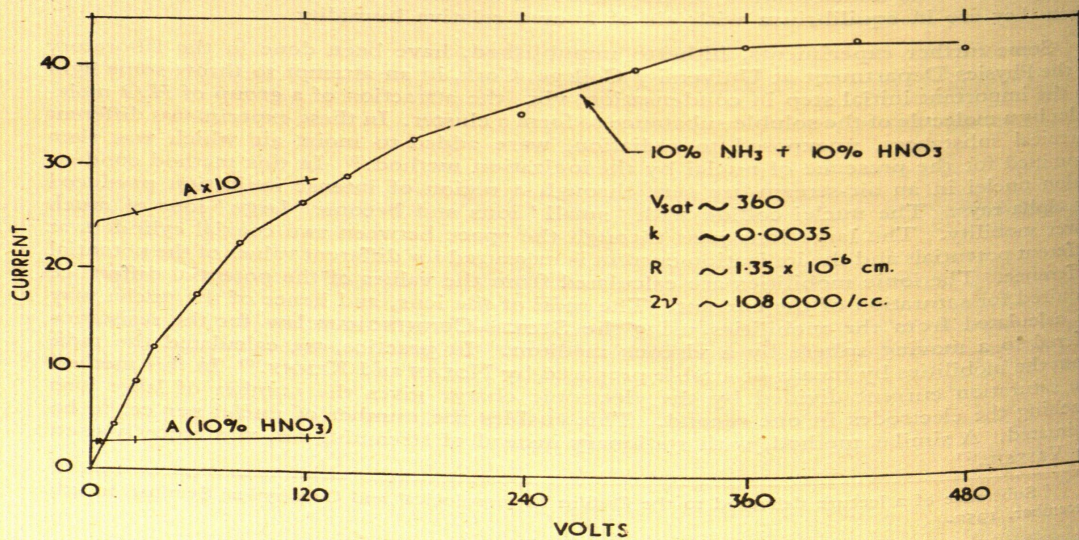


FIG. 2.



AIR PASSED OVER HNO_3

When no nuclei are present the small ions recombine rapidly and the current reaching the electrode is small and saturates at a low voltage. When filtered moist air passes over concentrated nitric acid, nuclei are formed. The resulting large ions, with lower losses by diffusion and recombination, give an increased current which saturates at a higher voltage. *Fig. 1* shows an incomplete ionization curve for this case, shown here because the straight line graph of current against difference of potential indicates the presence of ions of only one size. Saturation is not reached at 300 volts. It was calculated that the mobility was less than 0.00454 cms per sec per volt/cm, and the radius greater than 1.1×10^{-6} cm. Curve A of *Fig. 1* shows the ionization currents obtained when 10% nitric acid is used instead of the concentrated acid. In this case the lower saturation currents and voltage show that all or nearly all the ions are small, so that no nuclei, or very few, are formed over the diluted acid. Our concentrated acid contained 64.4% of HNO_3 by weight. The equilibrium pressure of HNO_3 over it is 1.1 mm Hg. The 10% acid of approximately 6% by weight gives a much smaller equilibrium pressure of HNO_3 . A 45% solution gives a HNO_3 pressure less than 0.1 mm Hg.

AIR PASSED OVER NH_3

When the nitric acid of the last experiment is replaced by ammonia solution, concentrated or 10%, no large ions are found and consequently no nuclei are formed. The concentration of gaseous NH_3 in the air stream in this case was much higher than that of HNO_3 in the last experiment. The pressure of NH_3 gas in equilibrium with our concentrated solution was 148 mm Hg and that with our 10% solution was 14 mm Hg. Weaker solutions, giving an equilibrium ammonia pressure of 1.14 mm Hg had been used by S. TWOMEY and the author (Ref. 1). No nuclei were then detected by the NOLAN-POLLAK nucleus counter until the mixture of air, ammonia and water vapour had been exposed to ultraviolet radiation.

These experiments show that mere solubility in water is not sufficient to promote 'clustering' and nucleus formation. If it were, we should expect many more nuclei to be formed by ammonia than by nitric acid, on account of its greater solubility in water and the greater concentration used in the air stream.

 HNO_3 AND NH_3 TOGETHER

It has been shown that no nuclei were formed when moist laboratory air was passed over a 10% HNO_3 solution. The same result held for a 10% NH_3 solution. When the air passed over both solutions copious nuclei were formed. *Fig. 2* shows the ionization curve obtained in the last case. Curve A in this figure shows the values of the current obtained when only the HNO_3 solution was present. With both substances in the air stream, and therefore with the formation of nascent NH_4NO_3 , saturation occurred at about 360 volts. This gave a mobility 0.0035 and radius 1.35×10^{-6} cm. The non-linear graph indicates either that smaller ions were also present, or ions of the same size with different multiple charges. Assuming single charges the number of large ions per cc. was approximately 108,000.

VASSAIL's work on condensation nuclei (Ref. 7) is on parallel lines to our own. He finds that when the nuclei are produced by ultraviolet light and transformed to large ions by the addition of small ions produced by gamma rays, they are apparently all of one size. Groups of different ionic mobilities are found but the differences in mobility are, according

to VASSAIL, to be attributed to multiple charges. One result of his is at variance with the evidence given by us (Ref. 1) : he includes NH_3 in the list of 'neutral' substances, whose addition to air makes no difference to the number of nuclei produced by ultraviolet radiation. We found a 10-fold increase when NH_3 was added to a pressure of 1.14 mm Hg. Another result of his is of interest in connection with our experiment in which NH_3 and HNO_3 were added to the air together. When he added NH_3 and NO_2 (without radiation) a blue cloud of visible nuclei was formed of mobilities between 10^{-4} and 10^{-5} , and radius $> 10^{-5}$ cm. In this case the formation of NH_4NO_3 and NH_4NO_2 is possible according to the equation $2NH_3 + 2NO_2 + H_2O = NH_4NO_3 + NH_4NO_2$.

CONCENTRATION OF SOLUTE IN THE NUCLEI

In order that a nucleus of radius 1.35×10^{-6} cm may be in equilibrium in unsaturated air it must, it seems, consist of a highly saturated solution. The NH_4NO_3 nuclei to which Fig. 2 refers were collected as large ions about 8 seconds after they were formed. It is not certain that they had grown to full size so as to be in equilibrium with the water vapour in the air stream. In spite of this it is of some interest to calculate the concentration of the NH_4NO_3 in the nucleus, assuming equilibrium with the moisture of the air which in this case had a relative humidity of 57%. The mass m of dissolved NH_4NO_3 may be calculated from the formula given by WRIGHT (Ref. 2, 3, 4) :

$$\text{Supersaturation } S = \frac{\text{actual vapour pressure}}{\text{sat. vapour pressure}} = \exp (P/r) - Q/r^3.$$

Here $P = \frac{2\sigma M}{RT}$, where σ , M , ρ are the surface tension, molecular weight and density of the liquid and R and T are the molar gas constant and absolute temperature. Q is $\frac{750 m C}{\pi \rho W}$, where m is the mass of solute of molecular weight W , ρ the solution density.

C is a constant of the solution given by the equation $C = \frac{p_0 - p}{M' p_0}$ in which p_0 and p are the saturation vapour pressures over solvent and solute and M' the concentration of the solution in gram-molecules of solute per 1,000 gms. of solution. Small r in WRIGHT's formula is the drop radius. Using $C = \text{approx. } \frac{1}{80}$ (found by extrapolation from Int. Crit. Tables, vol. 3, p. 292) ; $r = 1.35 \times 10^{-6}$ cm. and relative humidity = 57%, WRIGHT's curves (Ref. 3) give the mass m of dissolved NH_4NO_3 as 37.5×10^{-18} gm. The volume of the nucleus is 10.3×10^{-18} cm.³ and this gives a rough estimate of the mass of water in the nucleus as 10.3×10^{-18} gm.

The ratio of the number of molecules of ammonium nitrate to the number of molecules of water in the nucleus is then $\frac{37.5 \times 18}{10.3 \times 80}$, which is approximately 0.82. The number of NH_4NO_3 molecules in the nucleus is $6.03 \times 10^{23} \times \frac{37.5 \times 10^{-18}}{80}$ which $\approx 300,000$.

The calculated concentration of the ammonium nitrate is improbably high and would indicate a supersaturated droplet. In spite of the assumptions made about equilibrium, the calculation indicates that the nuclei are quite concentrated solutions and are formed by the collision of a large number ($\sim 300,000$) of 'clusters'. Each cluster consists of a small number of H_2O molecules about a molecule of NH_4NO_3 . In our experiment the H_2O and NH_3 partial pressures were of the same order of magnitude so that molecules

of H_2O and of NH_3 collided with the growing clusters with similar frequencies. It is probable then that NH_3 as well as NH_4NO_3 was dissolved in the nucleus, which might explain the high solute concentration found.

Clusters similar to those postulated here are formed about the ordinary 'small' ions (mobility ~ 1.5). These are now accepted to be groups of about 10 water molecules about a gaseous ion, the water dipoles being held together by the attraction of the electric charge. Recombination of positive and negative small ions destroys this attraction so that the clusters evaporate and no large aggregates are formed. When two uncharged solution-nuclei coalesce the concentration of the solute is unchanged and hence the term Q/r^3 in WRIGHT's equation. The P/r term is diminished on account of the increase in r and hence the supersaturation required for equilibrium must diminish. If the vapour pressure is kept constant the drop will grow by addition of water. Lowering of the surface energy will cause two colliding spherical nuclei to coalesce, since the surface area is reduced by about one fifth when the spheres are equal.

THE COMPOSITION OF ATMOSPHERIC NUCLEI

A paper by H. CAUER⁽⁸⁾ seems to indicate that ammonia and its compounds may play an important role in producing condensation of water vapour in the atmosphere. In the Institut für Chemische Klimatologie, Hohenberg a.d. Eger, he has made quantitative microanalyses of the substances found in condensation nuclei in the atmosphere. Readings were apparently taken all over Germany. On the average ammonia and its compounds come next in importance to the chlorides. The mass of ammonia found is three times greater than that of the SO_4 group, and thus, taking the molecular weights into account, ammonia occurs in nuclei seventeen times more often than sulphates. More striking than this: the ammonia group is the only one never absent from nuclei. His results are given in Table I, the units γ/m^3 being micrograms per cubic metre of air.

TABLE I.
ANALYSIS OF CHEMICAL SUBSTANCE FOUND IN CONDENSATION NUCLEI

Group	Mean Concentration (γ/m^3)	Variations (γ/m^3)
Mg	3.1	0 - 65.2
Cl	32.2	0 - 964
SO_4	2.6	0 - 732
NH_3	7.9	2.5 - 54.4
NO_2	1.0	0 - 21.6
H_2O_2	0	0 - 0
HCHO	0.5	0 - 16

CAUER mentions ammonia as a potent nucleus-producing substance which comes into action long before saturation of the water-vapour occurs. In experiments not yet published

(in 1949) he found condensation of water vapour on ammonia to begin at a relative humidity of 70%. As stated above we failed to detect nuclei produced by NH_3 at partial pressures between 1.14 and 148 mms. Hg. With the lower pressure produced by a dilute solution of ammonia in the closed chamber of a NOLAN-POLLAK counter the relative humidity must have exceeded 70%, even before expansion, and no nuclei were detected.

In Japan OGIWARA and OKITA⁽⁹⁾ have used the electron microscope to examine the nuclei of cloud, fog and haze particles. They found hygroscopic and non-hygroscopic nuclei and some of the former lost their hygroscopic nature on electron bombardment, presumably by evaporation. Several types of hygroscopic nuclei were found. Both hygroscopic and non-hygroscopic nuclei were supposed by these workers to originate in combustion. Neither sea-salt nor pure sulphuric acid was found to be a significant source of condensation nuclei.

A considerable amount of work has been done on the concentration of ammonia and of nitrates in the atmosphere and in rain, fog and mist. The published results are being reviewed in a paper by ERIKSSON⁽¹⁰⁾ on the composition of atmospheric precipitation. The proportion of ammonia nitrogen is much higher than that of nitrate nitrogen in rain-water. Fog, dew, frost and condensed water are as a rule much richer in ammonia than is rain-water. The results are not inconsistent with the view that a considerable amount of condensation of water in the atmosphere is due to ammonia and nitrates. The WRIGHT equation would explain why a higher concentration of solute is found in the small fog particles than in the larger rain drops. In the equation $S = \exp(P/r) - Q/r^3$ with constant S , when r increases the term $\exp(P/r)$ diminishes. The term Q/r^3 must diminish by the same amount and this is proportional to the concentration of the solute.

An effect of ammonia which is of interest here is the property of reactivating AgI nuclei (used in seeding clouds) which have been fatigued by ultra-violet rays⁽¹¹⁾.

Assuming then that our result is correct, and that no nuclei are produced in moist air containing ammonia of partial pressure between 1.14 and 148 mm Hg, the question arises: why is ammonia unable, in spite of its great solubility, to form nuclei. Nitric acid does so apparently and we have found nascent NH_4NO_3 very efficient in nucleus production. All three substances are soluble in water and if solubility were the only requisite property for condensing H_2O vapour we should have expected ammonia to be the most efficient.

It is possible that the nuclei formed by concentrated nitric acid arise from the combination of the HNO_3 with NH_3 present as an impurity in the air. If this is so we should expect the rate of formation of nuclei to be proportional to the product of the partial vapour pressures of NH_3 and HNO_3 .

One property of a soluble molecule which might enable it to attract and hold a cluster of H_2O molecules is a high dipole moment. Another possibility is the ability to form a hydrogen bond with the OH group of water. The H -bond,⁽¹²⁾ intermediate in strength between a valency and a Van der WAALS bond is formed between a hydroxyl or amino group and an easily polarizable group of the same or a different molecule. It can only occur between hydrogen and an atom possessing π -electron pairs which do not take part in a valency bond. The effect is consequently entirely confined to the elements F , O , N , and C only if one of its valence links is double-bonded.

HIGH DIPOLE MOMENT — NITROBENZENE

To try if a molecule with high dipole moment formed nuclei we passed air over nitrobenzene. No nuclei were found. The odour of nitrobenzene was noticeable at the exit tube but the partial pressure must have been low. The dipole moment of nitrobenzene is about 3.9 DEBYE units, compared with 1.8 D for water.

HYDROGEN BOND — PYRIDINE

The attraction between the *N* of pyridine (C_5H_5N) and the hydrogen of an *OH* group is known to be particularly strong (KELLNER, Ref. 12). Further it boils at 105°C and has therefore a saturation vapour pressure similar to that of water at the same temperature. We passed moist laboratory air over pyridine, but again no nuclei resulted.

SUMMARY

Experiments are described on the production of condensation nuclei by the addition of nitric acid or other chemicals to moist air. The mechanism of nucleus formation is discussed. A review of the literature of the subject seems to show that the effect of ammonia and of nitrates in promoting atmospheric precipitation has been minimized and that of sea-salt and sulphuric acid exaggerated.

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