

84. Conditions for the Production of Fog in the Neutralisation of a Volatile Acid or Alkali.

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THE work described in two earlier papers (J., 1927, 966; 1930, 1103) has shown that when an air stream carrying hydrogen chloride is bubbled through a sodium hydroxide solution (the alkali being in excess of the amount required for neutralisation) a fog is very commonly formed above the solution. The fog so produced consists of minute droplets with a strongly acid reaction, and its formation is conditional on the presence of traces of volatile alkali (ammonia) in the sodium hydroxide solution. The concentration of volatile alkali required to give the effect is extremely small: unless stringent precautions are used to exclude traces of ammonia from the water used in preparing the alkali solution, the formation of fog under the conditions stated will be observed. Such formation of fog appears, indeed, to be as delicate a test for ammonia as Nessler's reagent.

The liquid fog droplets, as already stated, have a strongly acid reaction and contain as much as 6—7% HCl by weight; under the bubbling conditions adopted, quite an appreciable fraction, 5—10%, of the hydrogen chloride in the air stream may escape absorption by the sodium hydroxide solution, if the latter contains a small quantity of ammonia. The fog droplets contain also ammonium chloride, and the work described in this communication was concerned in the first place with the extent of transference of the ammonia from the alkaline liquid to the fog droplets. An attempt was further made to elucidate the mechanism of fog formation by experiments in which the vapour pressure of the alkaline liquid in the fog chamber was varied within wide limits.

Formation of fog is observed also when a stream of air carrying ammonia is bubbled through a strongly acid solution, containing sufficient hydrochloric acid to give a small partial pressure of the latter compound. The conditions under which fog formation occurs in this case have been explored, and it is found that the fog droplets again contain ammonium chloride and hydrochloric acid, the amount of the latter being far greater than is obtained when the same volume of *ammonia-free* air is passed through the acid solution. The quantity of ammonium chloride in the fog droplets is considerable and as much as 9% of the total ammonia passed during a standard run may escape absorption by the acid solution.

EXPERIMENTAL.

(a) *Experiments in which Air-Hydrogen Chloride Mixtures were passed through Sodium Hydroxide Solutions.*—The apparatus and procedure used were in all essentials the same as

those already described (*loc. cit.*) and only one or two minor modifications need be mentioned. The air passed in a standard run was kept under control by forcing it in at a constant pressure and allowing it to leave at another constant pressure, care being taken to maintain the resistance of the apparatus train as steady as possible.

The jet through which the air stream bubbled into the alkaline liquid had an internal diameter of about 1 mm., and was usually 5—6 cm. below the surface. Some trouble was experienced with creeping back in the jet, an occurrence which seriously affected the reproducibility of the results. When, however, the apparatus is perfectly air-tight, and when the tube leading to the jet is absolutely free from soluble gas before the fog chamber is attached, this source of trouble is eliminated.

The earlier work had demonstrated the significance of small quantities of ammonia for the formation of fog when an air-hydrogen chloride stream is bubbled through sodium hydroxide solution; accordingly, in the further study of this phenomenon only ammonia-free water was used in preparing the solutions. The fog chamber was charged with ammonia-free sodium hydroxide solution, to which were added, as required, known amounts of a standard ammonium chloride solution. Special procedure was adopted for the preparation, dilution, and mixing of the solutions so that the risk of contamination with ammonia should be reduced to a minimum.

The U-tubes for collecting the fog produced in a standard run contained Gooch-crucible asbestos and calcium chloride, so that the increase of weight recorded covers both the fog droplets and the water vapour carried by the air stream. The standard run consisted in the passage of 3½ litres of air (*a*) through concentrated hydrochloric acid, (*b*) through the sodium hydroxide solution in the fog chamber—both at 25°—and then (*c*) through the U-tube. The duration of the run was about 8 minutes, and the weight of hydrogen chloride passed during this time under the conditions stated was about 250 mg., equivalent to 69 c.c. of *N/10*-acid. The fog chamber was charged with 80 c.c. of sodium hydroxide solution, and as the latter was never weaker than *N/10*, it is clear that the alkali was always in excess of the amount required for neutralisation. It should be further stated that the air stream was filtered through cotton-wool before entering the hydrochloric acid-saturator, and that between the saturator and the fog chamber the air stream passed through a sulphuric acid bubbler and then through an empty glass spiral, both immersed in the constant-temperature bath.

With the elimination of ammonia from the stock sodium hydroxide solutions, it became possible, by the addition of small known quantities of ammonium chloride, to determine exactly the significance of ammonia for the fog production and for the acidity of the fog droplets. The mean results of experiments on these lines, carried out with *N/10*-sodium hydroxide as absorbent, are set out in Table I.

TABLE I.

NH ₃ in 80 c.c.			NH ₃ in 80 c.c.		
NaOH, mg.	Fog + water	Found in the	NaOH, mg.	Fog + water	Found in the
After	vapour	fog, mg.	After	vapour	fog, mg.
Initi- standard	collected,	HCl NH ₃ (as	Initi- standard	collected,	HCl NH ₃ (as
ally. run.	mg.	(free). NH ₄ Cl).	ally. run.	mg.	(free). NH ₄ Cl).
0	94	0 0	0·4	293	13·8 0·27
0·008	0·0064	3·5 0·0017	0·8	325	16·3 0·62
0·04	0·024	7·3 0·016	1·2	338	17·7 0·90
0·08	0·04	8·5 0·04	4·0	396	18·6 3·2
0·24	0·10	11·7 0·14			

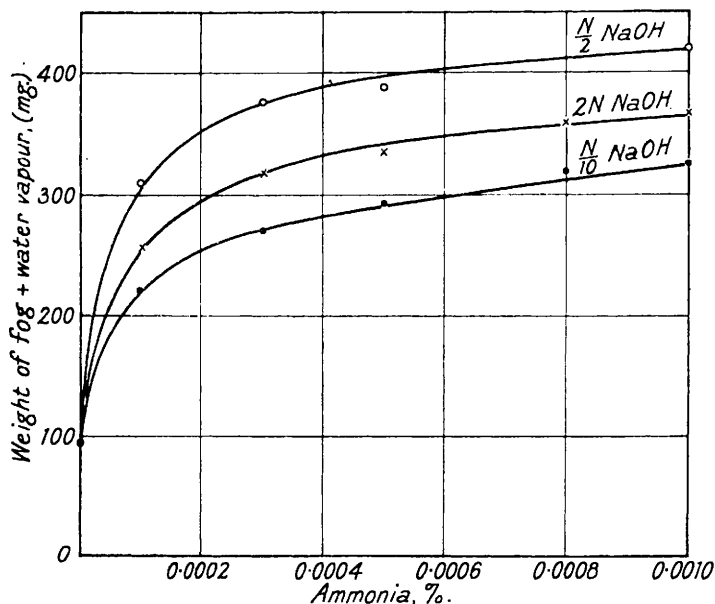
The increase in the weight of the U-tube recorded in the first line of the foregoing table, *viz.*, 94 mg., is due to the water vapour carried by the air stream and corresponds closely with what is to be expected under the conditions of the standard run. The loss of ammonia in the sodium hydroxide solution is, of course, due to its removal in the fog, and Nesslerisation both of the sodium hydroxide solution after the run and of the contents of the U-tube showed that the difference of the figures in the first two columns of Table I was exactly accounted for by the amount found in the fog.

The results set out in Table I are typical of many others obtained with different concentrations of sodium hydroxide, which need not be recorded in detail. The general character, however, of the variation in the amount of fog with the strength of the sodium hydroxide and with the amount of ammonia present, is important, and is shown by Fig. 1, which covers the results obtained with *N/10*-, *N/2*-, and *2N*-sodium hydroxide.

The curves, the relative position of which should be particularly noted, show clearly the

rapid rise in the amount of fog with small additions of ammonia, while the later additions have a relatively small effect.

FIG. 1.



The very significant fact (cf. J., 1930, 1105) that for a given initial amount of ammonia the fog production reaches a maximum in a certain concentration of sodium hydroxide is emphasised by Fig. 2; the subsequent notable diminution with increasing sodium hydroxide concentration is undoubtedly connected with the vapour pressure conditions. This point is elaborated on p. 345.

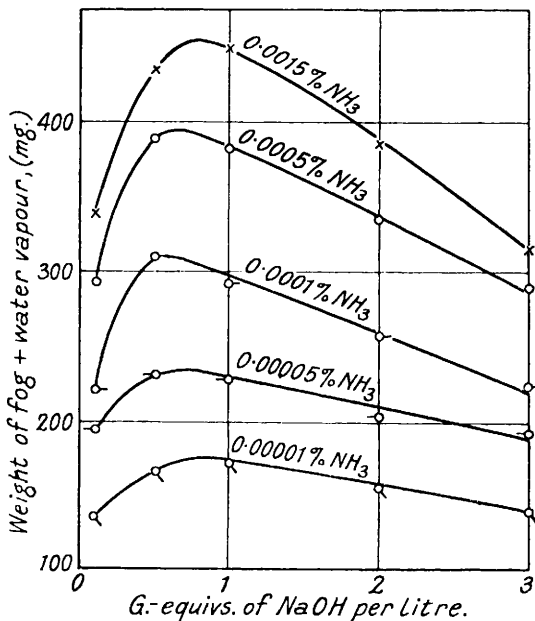
(b) *Experiments in which Air-Ammonia Mixtures were passed through Acid Solutions.*—The apparatus and experimental procedure used in this part of the work were similar to those already described.

When an air stream carrying volatile alkali is bubbled through a solution of sulphuric or phosphoric acid containing volatile acid (hydrogen chloride), extensive formation of fog is observed, under the conditions set out below. The fog droplets, collected as before in a U-tube charged with Gooch asbestos and calcium chloride, contain ammonium chloride (although the liquid in the bubbler remains acid) and free hydrochloric acid.

The undried air-ammonia stream employed in most cases was obtained by forcing air through a 2.07N-solution of ammonia. The partial pressure of ammonia over this solution at 25° is approximately the same—ca. 30 mm.—as that of hydrogen chloride in the air-acid stream used in the earlier experiments.

The quantity of ammonia passed into the fog chamber during a standard run was about 90 mg., and the amount of acid in the fog chamber was in every case in excess of that required for the neutralisation of the ammonia.

FIG. 2.



Under the conditions adopted, the absorption of ammonia was found to be complete when the fog chamber contained only sulphuric or phosphoric acid, also when hydrochloric acid was present up to 4.5%. At this point, however, visible fog began to be formed, which increased in amount as the hydrogen chloride concentration in the fog chamber was raised to 15%, the highest concentration employed. The hydrogen chloride partial pressure even over this solution is extremely low, and it is important to note that in a standard run with a stream of pure air, instead of an air-ammonia stream, the quantity of hydrogen chloride removed from a 15% solution in the fog chamber was too small to be detected.

Numerous quantitative runs were carried out with hydrochloric acid (*a*) mixed with sulphuric acid, (*b*) mixed with phosphoric acid, or (*c*) alone, in the fog chamber. The character of the results obtained will be sufficiently indicated by quoting one case in detail and setting out others graphically. Table II records the results of a series of measurements in which the contents of the fog chamber were throughout *N* as regards phosphoric acid. The acidity of the fogs was determined by titration with *N*/500-sodium hydroxide (methyl-red as indicator), and the chloride content by titration with *N*/100-silver nitrate.

FIG. 3.

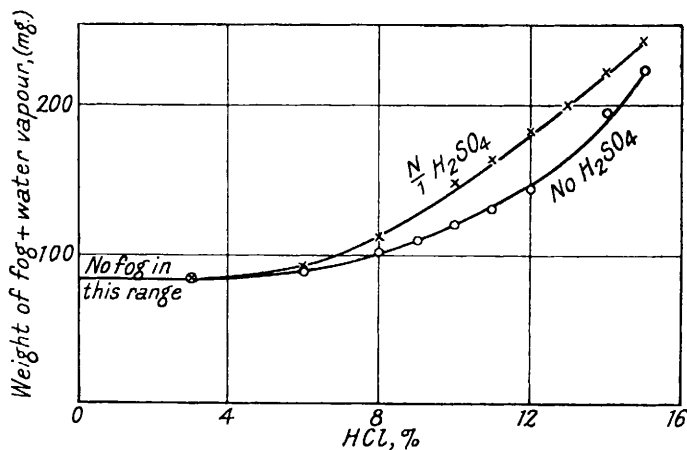


TABLE II.

HCl, %, in H ₃ PO ₄ solution.	Fog + water vapour (in mg.).	HCl in fog, mg.	NH ₄ Cl in fog, mg.	HCl, %, in H ₃ PO ₄ solution.	Fog + water vapour (in mg.).	HCl in fog, mg.	NH ₄ Cl in fog, mg.
0	86	—	—	12	165	6.7	15.4
4	102	1.0	4.4	13	184	9.8	18.2
8	131	3.2	8.7	14	209	12.9	21.0
11	147	4.8	11.7	15	217	15.5	25.8

In Fig. 3 the weight of fog + water vapour is plotted against the percentage of hydrogen chloride in the liquid of the fog chamber, with and without sulphuric acid. Curves generally similar to the right-hand half of those in Fig. 3 are obtained when the weight of hydrogen chloride or that of ammonium chloride in the fog droplets is plotted against the percentage of hydrogen chloride in the liquid of the fog chamber. It should be noted that under the conditions specified an appreciable proportion—up to 8 or 9%—of the ammonia passed into the acid may escape absorption.

As stated above, when the partial pressure of ammonia in the air-ammonia stream is 30 mm., no visible fog is formed unless the concentration of hydrogen chloride in the liquid of the fog chamber is at least 4.5%. If the partial pressure of the ammonia in the air stream is reduced, then the minimum concentration of hydrogen chloride necessary for visible fog formation rises. On the other hand, an air stream rich in ammonia will yield a fog even with a dilute hydrochloric acid solution. Similar observations are made when conditions are reversed and air-hydrogen chloride streams of varying hydrogen chloride content are passed into caustic soda solutions containing ammonia. It seems as if the product of the partial pressures of ammonia and hydrogen chloride in the gas bubbles must reach a certain minimum value for fog formation to occur.

(c) *Effects of varying the Water-vapour Pressure of the Liquid in the Fog Chamber.*—On p. 343, attention was directed to the fact that when an air–hydrogen chloride stream is passed through caustic soda solutions of different concentrations, but with the same ammonia content, the amount of fog increases up to a point with increasing alkali concentration but subsequently falls off (see Fig. 2). This is paralleled by the effects observed when an air–ammonia stream is passed through sulphuric or phosphoric acid solutions of varying strengths but with constant hydrogen chloride content. More striking still are the results obtained when the air–ammonia stream is passed through salt solutions of various concentrations, but of constant hydrogen chloride content. These results are illustrated by the figures in Table III, obtained with calcium chloride as the salt and 12% hydrogen chloride concentration throughout.

TABLE III.

CaCl ₂ , g.-equiv./l.	Weight of fog + water vapour (in mg.).	Found in the fog.		CaCl ₂ , g.-equiv./l.	Weight of fog + water vapour (in mg.).	Found in the fog.	
		HCl, mg.	NH ₄ Cl, mg.			HCl, mg.	NH ₄ Cl, mg.
0	145	3·5	11·4	2·0	201	13·5	25·8
0·5	163	7·1	13·9	2·5	181	13·3	31·5
1·0	184	9·4	17·7	3·0	124	9·2	38·0
1·5	209	12·0	22·0				

It is evident that the quantity of fog obtained in the standard run passes through a maximum value as the calcium chloride concentration is progressively increased, and a similar result has been obtained with sodium chloride in place of the calcium chloride.

It further appears from the figures in cols. 3 and 4 of Table III that while the ammonia content of the fog rises steadily with increasing calcium chloride concentration the hydrogen chloride content reaches a maximum and definitely falls off in the strongest calcium chloride solutions. The reality of this difference in regard to the constituents of the fog is confirmed by a series of experiments with an air–hydrogen chloride stream passed into solutions which were all *N* as regards sodium hydroxide and 0·001% as regards ammonia, but contained varying proportions of sodium chloride. Determinations of the weight of the fogs and their composition gave the results set out in Table IV.

TABLE IV.

NaCl, g.-equiv./l.	0	1·0	2·0	3·0	4·0	5·0
Wt. of fog + water vapour (mg.)	467	457	389	310	217	140
Found in fog { HCl (free), mg.	35·9	37·0	33·4	28·4	18·9	12·0
{ NH ₃ (as NH ₄ Cl), mg.	0·64	0·64	0·65	0·65	0·66	0·66

It is plain that as the fog obtained in a standard run gets thinner, its acidity markedly decreases, whereas the amount of ammonia carried over (as ammonium chloride) increases slightly. The figures, indeed, suggest that the amount of hydrogen chloride carried over depends on the water content of the fog droplets, and that if it were possible to reduce the water-vapour pressure of the liquid in the fog chamber much further, nuclei of ammonium chloride would still be produced, but dry and neutral.

A thoroughly dried air–hydrogen chloride stream was accordingly passed through a gas-washing bottle charged with 50% sodium hydroxide, containing 0·001% of ammonia, then through two bubblers with concentrated sulphuric acid, and then into the air. Fog was not visible above the sodium hydroxide solution, but appeared at the point of issue of the gas stream into the air, and could be intensified by bubbling through water. Examination of this fog showed that it carried no free acid.

A parallel experiment, in which an air–ammonia stream, dried by passage over barium oxide, was bubbled through a saturated solution of zinc chloride in *N*-sulphuric acid, containing 4% of hydrogen chloride, gave a similar result. Fog was not visible over the acid solution, but appeared at the point of issue into the air.

(d) *Experiments in which Air–Sulphur Dioxide Mixtures were passed through Sodium Hydroxide Solutions.*—Air was forced through a freshly prepared sulphurous acid solution of such concentration (0·15*N*) that the partial pressure of sulphur dioxide in the stream was comparable with that of the hydrogen chloride or the ammonia in the earlier experiments. Under certain conditions this stream, when passed through a sodium hydroxide solution containing ammonia, gave rise to a fog, the droplets of which contained ammonium sulphite and free ammonia. In the main series of experiments, in which the sodium hydroxide solution in the

fog chamber was 5*N*, and provision was made for determining both the sulphur dioxide and the ammonia in the fog, it was found that the minimum concentration of ammonia in the sodium hydroxide solution required for the production of visible fog was about 0.25*N*. With less ammonia the absorption of the sulphur dioxide was complete, but, on the other hand, when the ammonia concentration was 1.5*N*, a copious fog, carrying away as much as 12% of the sulphur dioxide, was formed.

These fogs are less stable and persistent than those which originate in the formation of ammonium chloride nuclei, described in the previous sections.

DISCUSSION.

On the basis of the earlier work (J., 1930, 1103) in which an air-hydrogen chloride stream was bubbled through alkaline solutions containing a trace of ammonia, the view was expressed that the formation of ammonium chloride particles within the gas bubbles is the first stage in the production of the fog. Such ammonium chloride particles act as condensation nuclei, and droplets of solution, in which the hydrogen chloride dissolves, are formed. The extent to which water condenses on these nuclei would obviously depend on the water-vapour pressure of the medium surrounding the bubble.

The measurements and observations recorded in the present communication, covering experiments not only with air-hydrogen chloride streams, but also with air-ammonia streams bubbled through media containing hydrogen chloride, give definite support to the views previously expressed. In particular, the variation of the water-vapour pressure of the medium surrounding the bubbles has shown definitely that the hydrogen chloride gets into the fog, not by direct primary adsorption on the ammonium chloride particle, but by solution in a droplet already formed by the condensation of water on the particle.

The general conditions in which these ammonium chloride nuclei are produced are the same as those shown by Rothmund (*Monatsh.*, 1918, 39, 571) to prevail in the case of ozone fogs. Where a volatile substance in the solution reacts with a constituent of the gas stream to form a non-volatile soluble product, the formation of fog is observed. Thus when a stream of ozonised oxygen is passed through sodium bisulphite solution or an acid solution of potassium iodide, fog is formed, the non-volatile soluble products which act as the nuclei of the fog droplets being sulphuric acid and iodic acid respectively. The analogue of these substances in the experiments of the present investigation is ammonium chloride (or ammonium sulphite).

From the available data it is possible to make a rough estimate of the quantity of ammonium chloride constituting the nucleus of a droplet. Earlier observations on the rate of settling of these ammonium chloride fogs (J., 1927, 977; 1930, 1106) indicated that the radius of the droplets was 10^{-4} – 10^{-5} cm. On the assumption that the droplets in a given case are of uniform size, the known weight and composition of the fog permit a calculation of the ammonium chloride in each droplet. For example, it was found in a standard run with an air-hydrogen chloride stream passed through *N*-sodium hydroxide containing 0.001% of ammonia that the weight of the fog was 343 mg., and that the quantities of ammonium chloride and free hydrochloric acid carried over in this fog were 2.01 mg., and 27.5 mg. respectively. If the radius of the droplets is taken as 10^{-5} cm., then the total number of droplets was between 10^{13} and 10^{14} and the weight of ammonium chloride per droplet was between 10^{-16} and 10^{-17} g. This means that the number of ammonia molecules taking part in the formation of each nucleus was of the order 10^6 .

These figures are naturally only rough, and it must be borne in mind that the size of the droplets is to some extent dependent on the conditions under which the fog is produced. The mere fact of the stability of the fogs means that there must be vapour-pressure equilibrium between the droplets and their environment, and account must be taken of the greater vapour pressure of minute water droplets as compared with that of water at a plane surface (Kelvin's equation). The significance of these considerations has been emphasised both by Townsend (*Proc. Camb. Phil. Soc.*, 1899, 10, 52) and by Rothmund (*loc. cit.*), who calculate the radius of the droplets in a "chemical" fog by combining the Kelvin equation for the increase of vapour pressure with the Raoult equation for the lowering of vapour pressure due to the substances dissolved in the droplet. If the data

of the experiment quoted above are considered on these lines they lead to a value between 10^{-5} and 10^{-6} cm. for the radius of the droplets, definitely lower than the figure calculated from the rate of settlement of the fog cloud (cf. Remy, *Chem.-Ztg.*, 1928, **52**, 679). No specific reason for this discrepancy in the values calculated for the radius of the droplets has yet been discovered. It may be that one or other of the assumptions underlying the calculations, as, *e.g.*, the assumption (made in the second case) that vapour pressure equilibrium has been completely established, is not warranted.

SUMMARY.

1. The amount and composition of the fog produced when an air-hydrogen chloride stream is passed through sodium hydroxide solutions containing a trace of ammonia have been determined, and the results considered more especially in relation to the vapour pressure of the sodium hydroxide solution.

2. Similar observations and measurements have been made in the case where an air-ammonia stream is passed into hydrochloric acid.

3. The part played by ammonium chloride nuclei in the formation of these fogs is elucidated.

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[Received, February 1st, 1934.]
