

CXXXIX.—*The Production of Fog in the Neutralisation of Alkali with Hydrogen Halides. Part II. The Significance of the Presence of Ammonia.*

By RICHARD WALTER ALDIS and JAMES CHARLES PHILIP.

THE earlier communication (Askew, J., 1927, 966) described an experimental study of the acid fogs obtained by passing a stream of air charged with hydrogen chloride or bromide through a solution of sodium hydroxide or other non-volatile alkali. Among the points investigated were the concentration of acid in the fog droplets, the dimensions of the latter, and the relation of the amount of fog formed to the concentration of the alkali solution. Further information on various aspects of the phenomenon was required, however, before the mode of production and the stability of the fogs could be adequately interpreted.

In the fresh work which was undertaken attention was first directed to the reproducibility of the results. Various minor modifications of the earlier apparatus and procedure failed to secure the desired degree of reproducibility, and it was only a fortunate circumstance which led to the discovery of the source of the difficulty. In two parallel series of experiments, designed to correlate the amount of fog produced with the concentration of the caustic soda solution, it was found that the quantities of fog obtained in the one series were throughout about twice as great as in the other. This serious discrepancy led to the recognition that the caustic soda solutions employed in the two series had been made up with distilled water from separate sources, and examination of the two waters showed that they differed appreciably in their content of ammonia, as proved by Nessler tests. This clue was followed up, and definite evidence was obtained that the production of fog under the given conditions was determined by the presence of traces of ammonia in the caustic soda solution. The quantitative results which support this view are set out below, but it may be stated that when ammonia is rigorously excluded or removed from the caustic soda solution the amount of fog produced is negligible.

EXPERIMENTAL.

*Apparatus and Procedure.*—The apparatus was in general the same as already described (Askew, *loc. cit.*), and it is necessary to refer only to a few modifications which have been introduced. It was thought desirable to improve the temperature control, and accordingly the vessel containing concentrated hydrochloric acid, in which the air current was saturated with hydrogen chloride, was

kept in a bath at 25°, and the dried mixture of gases was then passed through the fog production chamber, containing the alkali solution. This vessel, as well as the fog absorption tube, was immersed in the same thermostat as the hydrogen chloride saturator. Provision was made for renewing the acid in the saturator after each experiment.

The U-tube employed for collecting the fog was charged with asbestos wool and calcium chloride, so that the figures given below for "weight of fog" (in mg.) generally include the water vapour which accompanied the fog droplets. In some cases, where the composition of the fog itself was to be ascertained, the collecting tube was charged with asbestos wool only.

In the majority of the experiments the air-hydrogen chloride mixture was passed at a rate of about 200 c.c. per minute for 8—10 minutes, and this may be regarded as a standard run. The conditions were, of course, maintained constant in any one series of comparable experiments.

*Measurements and Observations.*—Following the discovery of the significance of traces of ammonia for the production of acid fogs under the conditions described above, the further investigation of the character and stability of the fogs was made with alkali solutions to which known quantities of ammonium chloride had been added initially. A series of experiments with increasing concentration of caustic soda, but the same initial concentration of ammonia in each case, showed that the amount of fog obtained in a standard run first increased, reached a maximum, and subsequently decreased. The results obtained in three such series are set out in Table I and represented graphically in Fig. 1.

TABLE I.

(a) $\text{NH}_3 = 0.00005\%$ .		(b) $\text{NH}_3 = 0.0005\%$ .		(c) $\text{NH}_3 = 0.002\%$ .	
Normality of NaOH.	Weight of fog (mg.).	Normality of NaOH.	Weight of fog (mg.).	Normality of NaOH.	Weight of fog (mg.).
0.1	10	0.1	102	0.1	158
0.5	50	0.4	170	0.48	250
1.2	65	0.85	192	0.55	264
2.4	50	2.0	155	0.88	250
4.8	5	3.5	78	2.0	198
				3.5	105

The figures in Table I indicate that the amount of fog increases as the ammonia concentration rises, but series of experiments carried out at constant caustic soda concentrations and with a much wider range of ammonia values show that the amount of fog tends to become steady. The results obtained in one such series, in which the sodium hydroxide was 0.84*N*, were as follows :

$\text{NH}_3$ , % .....	0.0001	0.00025	0.001	0.003	0.005	0.007
Weight of fog (mg.)	125	160	224	260	267	270

As already indicated, a number of experiments were made in which the fog, after being collected and weighed, was analysed for hydrochloric acid (by titration) and for ammonia (by Nessler tests). The strongly acid character of the fogs is proved by the figures in

FIG. 1.

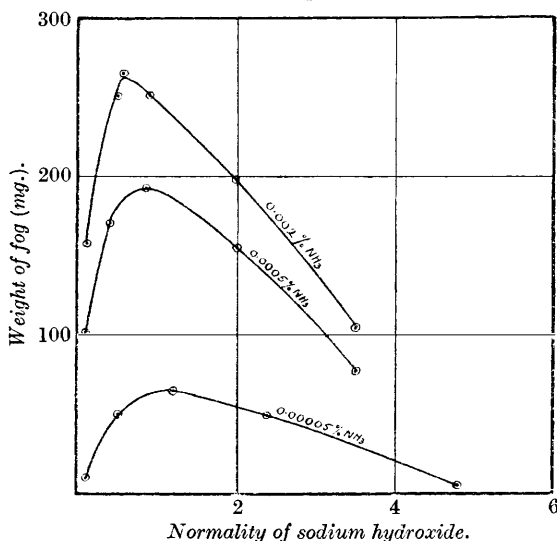


Table II, which show also that during each experiment a fair proportion of the ammonia was transferred from the caustic soda solution to the fog droplets.

TABLE II.

Normality of NaOH.	NH <sub>3</sub> initially, g.	Weight of fog (mg.).	Found in the fog.	
			NH <sub>3</sub> , g.	HCl, %.
0.39	0.00002	25	0.00001	5.9
0.39	0.00005	40	0.00002	5.9
0.39	0.0001	72	0.00005	5.8
0.39	0.0005	173	0.0003	5.8
0.39	0.001	246	0.0007	5.8
1.00	0.001	244	0.0005	6.4
3.90	0.001	106	0.0006	8.9

In some cases the passage of the acid-laden air stream was continued until fog formation practically ceased, and this was found to occur when the ammonia originally in the caustic soda had been transferred to the fog. Thus, for example, in one experiment the stream was bubbled through 100 c.c. of a 2.0N-caustic soda solution containing 0.002 g. of ammonia. When fog formation had practically ceased, after the passage of 12 litres of the gas mixture, the caustic soda solution was run out and found to be

1.75*N*, and to be free from ammonia. The fog formed during this experiment had been collected in a tube containing asbestos wool (previously shown to be free from ammonia). The wool was washed and the washings were made up to 200 c.c., aliquot portions being then tested with Nessler's solution. The total ammonia found in this way was equal to that originally present in the caustic soda solution.

In the earlier investigation it was observed that the amount of fog produced was markedly increased when small quantities of certain substances, such as gelatin and methylene-blue, were added to the alkali solution. These observations have been confirmed, and proof has been obtained that the substances in question owe their influence to the small quantities of ammonia liberated from them in caustic soda solution. It is noteworthy also that the ability to promote fog formation when an air-hydrogen chloride stream is passed through caustic soda is possessed, not only by ammonia, but by other volatile bases, such as methylamine and diethylamine.

The size of the droplets forming the fogs was estimated in the usual way by observing the rate of settling of the cloud. The value so obtained for the radius of the droplets varied somewhat according to the conditions under which the fog was produced, but was of the same order, *viz.*,  $10^{-4}$ — $10^{-5}$  cm., as that already recorded by Askew (*loc. cit.*). Definite evidence was obtained that the size of the droplets diminishes with increasing concentration of the caustic soda from which the fog was obtained.

Variation in the size of the droplets and the density of the fog, according to the vapour pressure of the surrounding medium, was further demonstrated by experiments in which thin fogs were passed through water. Thus, for example, a faint fog was obtained by bubbling the usual acid-air mixture through a concentrated (6*N*) caustic soda solution containing 0.002% of ammonia. This fog when bubbled through water became quite dense, but showed no change when bubbled through very concentrated solutions of potassium iodide or calcium chloride.

Further, when a fairly dense fog from the caustic soda solution was bubbled through concentrated sulphuric acid, it disappeared, but the inference that the fog had been absorbed was proved to be erroneous by subsequently passing the air stream through water, whereupon the fog reappeared, although in somewhat diminished intensity. The fact that concentrated sulphuric acid may render a fog invisible without absorbing it has been observed for ozone fogs (Rothmund, *Monatsh.*, 1918, **39**, 571), and for moist sulphur trioxide fogs (Remy, *Z. Elektrochem.*, 1922, **28**, 467).

Experiments carried out with the object of detecting any definite electrical charge on the fog droplets gave negative results. This is

in harmony with Askew's observations (*loc. cit.*, p. 978), as also with earlier investigations on the electrical condition of other chemical fogs (de Broglie and Brizard, *Compt. rend.*, 1909, **149**, 923; Rothmund, *loc. cit.*; Remy and Koch, *Z. anorg. Chem.*, 1924, **139**, 69).

#### *Discussion.*

The novel feature of the fogs described in this and the earlier communication is that they are strongly acid, although produced in an alkaline medium. Remy and his collaborators (*Z. angew. Chem.*, 1926, **39**, 147; *Z. anorg. Chem.*, 1927, **159**, 241), it is true, have shown that moist sulphur trioxide fogs can be bubbled through caustic potash solutions with only partial absorption, but these fogs were already formed before they came in contact with the alkaline medium.

Another important characteristic of the acid fogs described in the present paper is that their formation is conditional on the presence of ammonia (or other volatile alkali) in amounts which are very small compared with the quantity of acid contained in the droplets. The measurements and observations recorded above establish beyond doubt the significance of ammonia for the whole phenomenon, and warrant the view that the formation of ammonium chloride particles within the gas bubbles is the first and necessary stage in the production of the fog.

Such ammonium chloride particles, under the conditions prevailing, act as condensation nuclei, and droplets of solution are formed. These droplets then dissolve some of the hydrogen chloride in the gas bubble, and their vapour pressure is correspondingly lowered. This involves an increase in size by further condensation of water, the extent to which this takes place being determined mainly by the vapour pressure of the caustic soda solution surrounding the gas bubble.

Another consideration which is of significance in determining the stability of fogs such as those described above is the fact that the vapour pressure of a minute droplet of a liquid is greater than that at a plane surface. The bearing of this—as expressed by the Kelvin equation—on the stability of chemical fogs has been discussed by a number of earlier workers (Townsend, *Proc. Camb. Phil. Soc.*, 1899, **10**, 52; Rothmund, *loc. cit.*; Remy, *Chem. Zeit.*, 1928, **52**, 677). The vapour pressures for water droplets of radius  $10^{-4}$  and  $10^{-5}$  cm. are respectively about 0.1% and 1% greater than at a plane water surface at the same temperature. Hence, in an atmosphere saturated with water vapour in the ordinary way, such droplets would tend to disappear. They will be stabilised, however, even in such an atmosphere, if a compensating reduction of vapour pressure is effected by the presence of dissolved substances in the

droplets. Townsend (*loc. cit.*) has calculated that droplets of  $5 \times 10^{-5}$  cm. radius containing approximately 0.004 g. of sulphuric acid per g. of water would be stable in an atmosphere saturated with water vapour. It is assumed in the calculation that the sulphuric acid is completely ionised.

The fog droplets with which the present communication is concerned contain a much larger proportion of dissolved substance. Where the total amount of fog collected is small, the estimation of the acid which it contains is probably subject to a considerable error, but some of the figures recorded in Table II provide a basis for calculating the concentration of dissolved substance. The data of the experiment, for example, in which fog, weighing 246 mg., was produced from 0.39*N*-sodium hydroxide indicate that the droplets were approximately 1.5*N* as regards hydrochloric acid and 0.15*N* as regards ammonium chloride. Again, the solution constituting the droplets of the last experiment of Table II was approximately 2.5*N* as regards hydrochloric acid and 0.35*N* as regards ammonium chloride.

The fog droplets, of course, consist mainly of water, and the extent to which their concentration is altered by condensation or evaporation should be determined by the vapour pressure of water in the surrounding air. The measurements made so far and recorded above are not such as to permit the quantitative study of this adjustment, but attention is directed to one or two observations which are significant in this connexion. Thus, consideration of the last three experiments in Table II shows that, with increasing caustic soda concentration, the amount of acid in the droplets increases relatively to the water, and this means a lowering of the vapour pressure of the droplets. Again, an investigation of the size of the droplets obtained from caustic soda solutions of different concentrations showed a regular falling off with increasing alkali concentration.

It appears, however, that owing to the operation of certain factors, there are limits to the growth or shrinkage of droplets constituting a stable fog. If much water condenses on a droplet of radius  $10^{-4}$ — $10^{-5}$  cm., which is the stable range, it becomes so large as to settle very rapidly. If, on the other hand, a droplet within the stable range loses much water, the enhanced vapour pressure associated with high curvature may become the determining factor, with the result that the droplet becomes unstable and dries up. It is clear that further measurements are necessary in order to elucidate the relation between the vapour pressure of the droplets and that of the surrounding air.

The fact that the droplets, once formed inside the gas bubble, do not find their way to the surface of the bubble and get absorbed,

is probably due to their comparatively low mobility. The significance of this characteristic for the stability of chemical fogs has been discussed at length by A. Smith ("Text-book of Inorganic Chemistry," 1927, p. 482) and by Remy (*loc. cit.*, 1926 and 1927).

The character of the curves in Fig. 1 invites comment. The occurrence of a maximum is no doubt due to opposition between factors tending to increase the amount of fog and those which tend to diminish it. The vapour pressure of the ammonia in the caustic soda solution increases with increasing concentration of the latter, and this would lead to a larger number of nuclei and a greater weight of fog for a given run. Again, as the concentration of the caustic soda increases, it becomes more viscous, the air-acid mixture will form larger bubbles, and hence there is a greater chance of the droplets escaping in the air stream. The main factor operating in the reverse direction is the steady fall of water vapour pressure as the concentration of the caustic soda increases.

The observations recorded in this paper present one or two points of interest for the analytical chemist. The production of fog when an air-acid stream is passed through a solution of caustic soda is a sensitive test for small quantities of ammonia (or other volatile alkali) in the soda solution: the delicacy of the test approaches that of Nessler's solution. Further, it appears that the removal of hydrogen chloride from an air stream by passage through caustic soda solution is incomplete if the latter contains even small quantities of ammonia. In many of the experiments recorded above, as much as 10—15% of the hydrogen chloride escaped absorption in the caustic soda solution.

Under the conditions of the present work, where the factor of supersaturation is absent, the significance of hygroscopic nuclei for the production of fogs has been clearly demonstrated. In this connexion, it is interesting to note the view, now widely held by meteorologists, that atmospheric condensation does not normally commence on ordinary dust particles or on ions, but on hygroscopic substances. In view of the results of the present investigation, it seems possible that the small quantities of ammonia in the air may play a more important part in the production of atmospheric fogs than has been generally supposed.

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