CXXXVI.—*The Production of Fog in the Neutralisation of Alkali with Hydrogen Halides.*

By Henry Oscar Askew.

When a current of air carrying phosgene (carbonyl chloride) is passed through charcoal and then bubbled through an aqueous-alcoholic solution of sodium hydroxide, a fog appears in the flask containing the alkali as soon as the charcoal is saturated with phosgene. This fog persists even when the air in which it is suspended is passed through another similar absorption vessel.* If the phosgene is replaced by phosphorus oxychloride, similar observations are made.

A preliminary investigation of this phenomenon soon showed that neither the phosgene nor the charcoal was essential, and that a fog was readily produced when a stream of air carrying hydrogen chloride was bubbled through an absorption flask containing an aqueous solution of sodium hydroxide. It was found, indeed, that the phosgene (or phosphorus oxychloride) was effective only by virtue of the hydrogen chloride arising from the hydrolysis by moisture in the charcoal (compare Bohart and Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 523). If a column of zinc dust (which absorbs hydrogen chloride but not phosgene) was interposed between the charcoal column and the absorption flask, the production of fog in the latter ceased. Further, if the charcoal was first freed from the greater part of its moisture by heating for some time at 160°, phosgene produced no fog under the original conditions.

Preliminary experiments also made it clear that the production of fog was not dependent on the presence of alcohol in the alkaline absorbent, although the presence of alcohol or other organic substances undoubtedly intensifies the fog. This matter is discussed in greater detail later.

The investigation accordingly resolved itself into a careful examination of (1) the conditions of bubbling under which this fog formation occurs, (2) the amount of fog and its dependence on the concentration of the alkali, (3) the effect of adding organic and colloid substances to the alkali, (4) the nature and concentration of the acid present in the fog particles, and (5) the size and possible electric charge of these particles.

EXPERIMENTAL.

As a source of hydrogen chloride concentrated hydrochloric acid was used. Two wash-bottles, W (Fig. 1), were placed in series in

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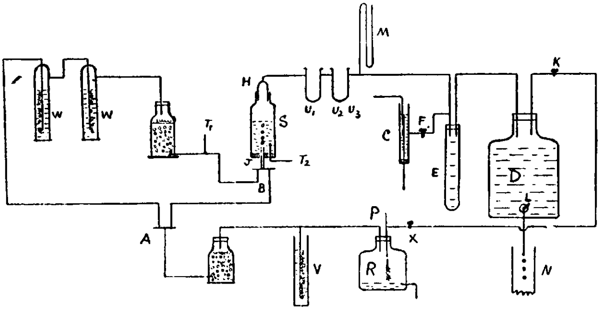
* The author's attention was directed to these facts by Prof. J. C. Philip.

a thermostat at 25·0°, and purified air from the reservoir, R, under a pressure of about 18 inches of water (kept constant by the water valve, V), was passed through the acid. The mixed gases, after being dried and filtered through several cm. of woolly asbestos in which the thermometer, T_1, was placed, passed to the three-way tap, B, and thence through the jet, J, to the vessel, S, which contained the alkaline solution and was fitted with a ground glass head, H, and an outlet tube. The fog was filtered out of the air by woolly asbestos in the tube U_1, which was kept in a box packed with cotton wool. (Special tests showed that the air from which the fog had been filtered out was free from chloride.) The moist air then passed to the tubes U_2 and U_3 containing calcium chloride. The dry air passed to the manometer, M, through the vessel, E, and then to the aspirator, D. The levels of the liquid in the limbs of M were kept the same throughout an experiment. In cases of difficulty in maintaining this setting, the constant-level arrangement, C, was set in operation by opening the tap, F, whereby, if the pressure shown by M was less than atmospheric, water entered the graduated vessel, E, until atmospheric pressure was restored; the volume of water entering E was deducted from that run out of the aspirator.

FIG. 1.



The graduated indicator card attached to the tap, L, on D allowed of duplicate settings being made, although in all cases exact check of the rate of outflow was kept by means of a stopwatch. The filter pump, P, was arranged so that it could be used for suction from the aspirator by opening the tap, K. When this was not desired, the air to be pumped into R entered through the inlet, X, on the pipe line. The thermometer, T_1, gave the temperature of the entering gas and T_2 that of the solution.

The various vessels, S, were of such sizes that, by always using the same volume of solution, the " depths " of liquid, as measured from the tip of the jet to the surface of the solution, were 7·5, 5·5, and 3·75 cm., respectively. Four jets were used, their radii being 1·81, 1·32, 1·08, and 0·82 mm., respectively. In order to prevent the solutions from creeping back into the barrels of the jets, the inside walls were coated with paraffin wax, but the tips were left clear.

All measurements of the rates of passage of the gas through the liquid are given in c.c. per minute. The alkali solutions were freed from carbonate, except where otherwise stated.

After the tube U_1 had been weighed, the asbestos was removed and extracted with water. The acidity as hydrogen chloride and the total chloride present were then estimated and invariably corresponded with one another. In the tables, " HCl % " refers to the percentage of acid by weight in the fog particles, both being given as mg. per litre of air. The standard quantity of air for an experiment was fixed at 2 l., as it was necessary to minimise the variation in concentration of the alkali.

Except where otherwise stated, the partial pressure of the hydrogen chloride is taken as 130 mm.

The amount of acid vapour which appears as fog varies between 0·8 and 12% of that passing through the jet, according to the solution used, the lower figure applying to simple aqueous solutions.

Conditions of Passage of Gas through the Solutions.—With aqueous solutions of sodium, potassium, and barium hydroxides an increase in the radius of the jet causes a greater production of fog, which, moreover, appears to attain a maximum at about 5·5 cm. depth, although, under similar conditions as to rate of passage, the amount of fog formed does not vary with depth by more than a few mg. per litre of air. In general, the concentration of acid in the particles is greatest when the depth of solution is 3·75 cm.

From Table I (giving mean values from 2 l. of gas), it will be seen that (1) the concentration of acid in the fog particles remains remarkably constant for a given jet; (2) the partial pressure of the water vapour in the air, after removal of the particles by the asbestos filter, is constant; and (3) increase in the rate of passage of the gas leads to an increase in the amount of fog. As the radius of the jet decreases and the depth of liquid increases, the relation between rate of passage and fog formation tends to become linear.

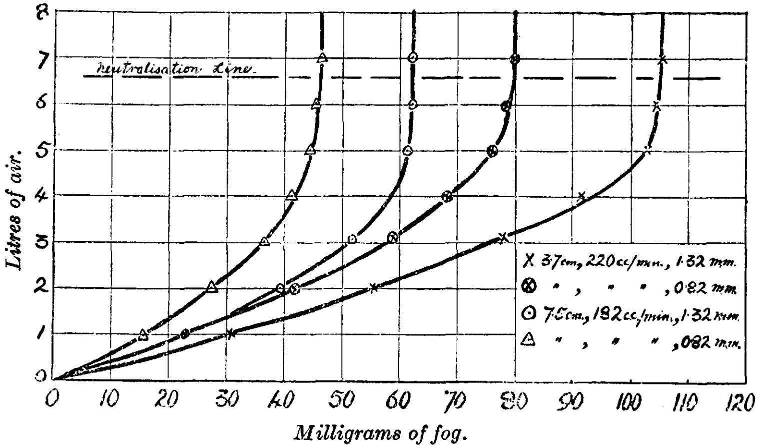
Concentration of Alkali.—Many experiments were made in which the same alkali solution was used until completely neutralised, the weight of fog formed being determined after each litre of air had been bubbled through the solution. As shown by Fig. 2 (for 0·614*N*-sodium hydroxide), the fog production falls off in every case as the alkali becomes weaker, and ceases when it is neutralised.

TABLE I.

Solution : 1·26*N*-NaOH. Depth : 7·5 cm. Air temp. : 20—23°.

Radius of jet, 1·81 mm.				Radius of jet, 1·32 mm.			
Rate (c.c./ min.).	Fog (mg.).	HCl %.	Partial press. of H_2O (mm.).	Rate (c.c./ min.).	Fog (mg.).	HCl %.	Partial press. of H_2O (mm.).
200	42·6	9·23	21·1	210	45·9	8·70	19·9
198	42·0	9·22	16·5	208	44·8	8·70	18·0
189	39·5	9·51	20·7	181	37·9	8·99	19·0
170	35·6	9·27	23·3	172	36·0	8·18	19·3
154	31·0	9·24	16·5	160	31·8	8·26	20·0
123	23·9	9·18	21·6	125	23·6	8·30	20·2
108	16·7	9·68	16·7	110	19·7	8·56	18·2

FIG. 2.



Solutions of potassium and barium hydroxides give similar results, although at corresponding concentrations less fog is obtained than with sodium hydroxide.

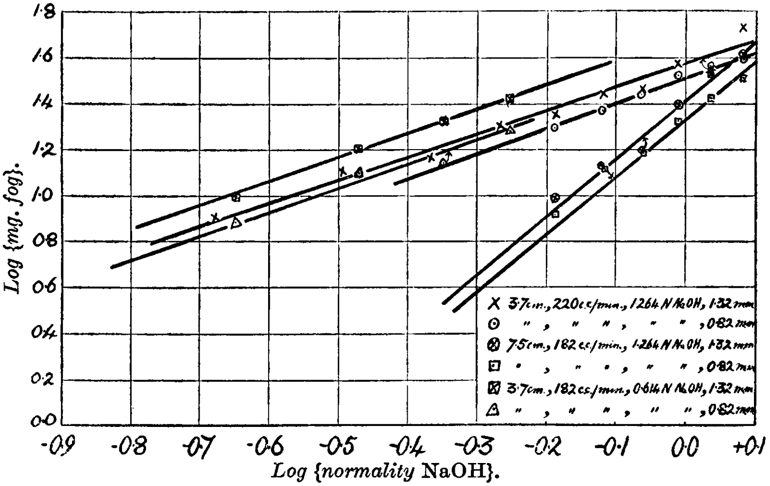
If the logarithm of the weight of fog obtained is plotted against that of the mean concentration of alkali during the passage of each litre of gas, a straight line is obtained. Moreover, under fixed conditions of depth and original concentration of alkali, the lines corresponding to the different jets are parallel, as shown in Fig. 3.

Table II shows the amount of fog formed at 20° (app.) in the first litre of air from different concentrations of sodium hydroxide (mean concentrations during each experiment). On plotting these figures it is seen that in dilute solutions the effect of the alkali is relatively great; in the more concentrated solutions, the amount of fog obtained is very nearly proportional to the alkali concentration.

TABLE II.

Depth of liquid (cm.).	Radius of jet (mm.).	Rate (c.c./min.).	Concentration.			
			0·07*N*.	0·26*N*.	0·56*N*.	1·21*N*.
3·7	1·32	220	14·0	22·2	30·9	49·2
		182	10·8	18·0	26·7	42·5
	0·82	220	9·9	16·4	22·8	39·4
		182	5·6	11·8	19·1	37·4
7·5	1·32	220	11·9	19·4	29·0	49·6
		182	9·6	15·6	22·8	40·7
	0·82	220	7·5	15·3	23·0	42·9
		182	4·8	8·6	15·8	32·4

FIG. 3.



In neutral or acid solutions of salts, dyes, and colloids (see later) and in water, in agreement with Fig. 2, all the hydrogen chloride is absorbed and no fogs are formed under the conditions of the present series of experiments. The incomplete absorption of the acid in alkaline solutions is not due to the rapid rates used, for in the presence of colloids and dyes thick fogs are obtained when only one bubble is formed every 2 or 3 seconds.

Solutions of the following salts of weak acids gave no fogs (in *N*-solution, except the diborate): Sodium acetate, sodium hydrogen carbonate, disodium hydrogen phosphate, sodium diborate (0·3*N*), and potassium dihydrogen phosphate. Thin fogs were formed with sodium carbonate and dense fogs with trisodium phosphate. The data in Table III were obtained for a depth of 7·5 cm. of solution, the rate being 225 c.c./min., the temperature 22°, and the jet radius 1·32 mm. They show clearly the changes in fog formation which

TABLE III.

Solution.	Air (l.).	Fog (mg.).	Solution.	Air (l.).	Fog (mg.).
N-Na_2CO_3.	1	9·7	N-Na_3PO_4.	1	25·5
	2	4·7		2	11·5
	3	4·1		3	1·3
	4	0·1		4	0·0

occur when the neutralisation has reached the hydrogen carbonate and disodium salt stages, respectively, and serve to emphasise the results of the foregoing experiments. Sodium carbonate is not so largely hydrolysed as trisodium phosphate and consequently its hydroxyl-ion concentration is somewhat less. This difference is plainly shown in the quantities of fog obtained. From the data in Table II, it is found that the concentrations of free sodium hydroxide which would give the same weight of fog under these conditions are $0·06N$ and $0·45N$, respectively; these are of the order of magnitude which would be expected from the degrees of hydrolysis. It has not been possible to fix a definite value for the hydroxyl-ion concentration at which fog formation begins, but it must be greater than $10^{-5}N$, since the other phosphates and sodium bicarbonate give no fog.

Addition of Organic and Colloidal Substances to the Alkali.—Ethyl alcohol, amyl alcohol, acetone, formaldehyde, and ether, especially when present in considerable amount, gave dense fogs, but no fog was obtained in the absence of alkali.

Experiments were made with the following "capillary-active" substances: *iso*Amyl alcohol, sucrose, gelatin, gum arabic, safranine, methylene-blue (hydrochloride), Congo-red, Orange G, glycerol, saponin, kaolin, aquadag, and purified clay. Solutions (or suspensions) of these substances in sodium hydroxide were made, and the fogs formed under different experimental conditions were investigated. As a typical example the results for gelatin solutions in $1·24N$-sodium hydroxide are given in Table IV, which also

TABLE IV.

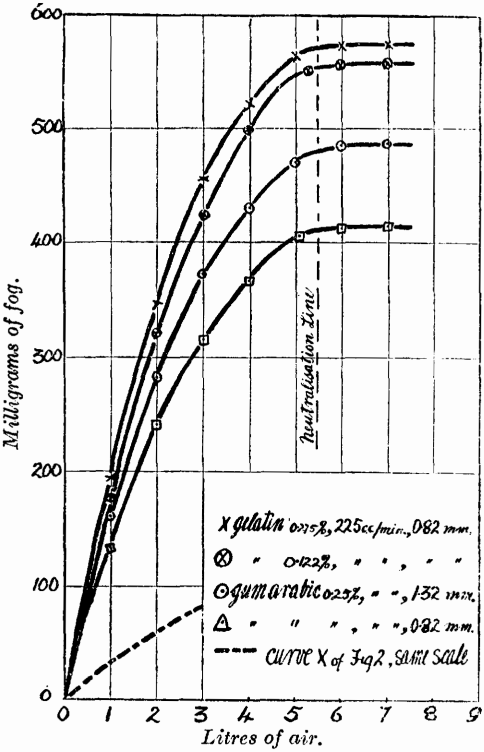
Rate : 208 c.c./min. Radius of jet : 1·32 mm. Depth : 7·5 cm.

Gelatin, %.	Fog (mg.).	Air temp.	Partial press. of H_2O (mm.).	Gelatin, %.	Fog (mg.).	Air temp.	Partial press. of H_2O (mm.).
0·0000	47·7	24·9°	21·7	0·041	141·4	25·8°	21·8
0·0032	63·0	25·3	21·9	0·081	153·8	25·1	22·2
0·0082	81·9	25·3	21·7	0·082	161·1	25·3	21·2
0·0163	102·9	25·7	22·3	0·098	167·3	23·9	19·7
0·041	137·7	24·5	22·3				

serves to show how constant and independent of the amount of fog formed is the aqueous vapour pressure of the air in contact with the particles.

In those cases where dense fogs are formed, the bubbles in passing up through the solutions become filled with fog and do not remain clear as in the case of the simple aqueous solutions. Addition of sodium chloride ($0{\cdot}5N$) to the gelatin solutions caused a slight increase in the amount of fog formed, but small alterations in the concentration of the alkali did not have much effect. A peculiarity, which appears with other solutions also (see Fig. 5), was found with gelatin, *viz.*, that at about 110 c.c./min. the curve showing the relation between rate of passage of the gas and fog formation undergoes a sudden change of direction.

FIG. 4.



When the alkali solutions were treated with the air–hydrogen chloride mixture until neutralised, the concentration of acid in the particles was found to be practically independent of the stage of neutralisation. This was true, not only for gelatin but in general, for the other substances also.

As mentioned above, none of the solutions gave any fog after neutralisation. Comparison of the curves in Fig. 4 with those in Fig. 2 shows the great effect of adding colloidal substances to the solutions, and also the rapid decrease in fog formation as the solution becomes neutralised.

Safranine and methylene-blue were particularly active in fog formation. The pronounced effect of the latter, even in extremely dilute solutions, is shown in Table X. Sucrose, up to 5%, had no effect on fog formation; glycerol caused a decrease, probably owing to viscosity effects, as the solutions used were somewhat concentrated. All the other substances mentioned caused great increases in the amount of fog obtained.

When the data from which Fig. 4 was constructed were plotted in the same manner as used in Fig. 3, the curves were again linear. The slopes of these lines did not vary greatly with the capillary-active substance employed; thus, under corresponding conditions the lines for two solutions of differing gelatin content, for the gum arabic, and for the amyl alcohol solutions were almost parallel; with saponin, the results were somewhat irregular, but this is not surprising in view of the excessive formation of froth in this case. It will be seen later that, when the alkali concentration is kept constant and that of the added substance is varied, each substance has its own specific effect, *i.e.*, the slopes of the curves vary greatly according to the compound employed.

From the considerable amount of data obtained, it may be stated that: (1) The concentration of acid in the particles tends to decrease as that of the capillary-active substance decreases; *e.g.*, under similar conditions with a china clay in 0·343% and 0·206% suspensions, the concentrations of acid were, respectively, 8·32% and 7·83%, whilst in the case of methylene-blue a steady decrease in acidity occurred as the dye concentration decreased; (2) for a given concentration of capillary-active substance, the concentration of acid in the fog droplets is independent of that of the sodium hydroxide solutions, *e.g.*, with gelatin in 0·61*N*- and 1·24*N*-sodium hydroxide, the acid concentrations are the same for fogs formed under similar conditions; and (3) the partial pressure of aqueous vapour in the air surrounding the particles is constant and independent of the amount of fog formed.

Experiments with Hydrogen Bromide.—Hydrogen bromide, although much more active than the chloride, resembles it in giving no fog with water or with neutral or acidic salt solutions.

The experiments with colloids in 0·59*N*-sodium hydroxide solution (Table V) were carried out under the following conditions: Radius of jet, 1·32 mm.; rate, 208 c.c./min.; depth of liquid, 7·5 cm.; air temperature 21·0—21·8°.

TABLE V.

Colloid.	Air (l.).	Fog (mg.).	HBr, % (mean).	Part. press. of H_2O (mm.).
Gelatin (0·122%).	1	180·2	21·8	21·2
	2	164·1		22·0
	3	132·6		21·6
	4	106·3		20·1
Gum arabic (0·25%).	1	148·7	21·9	18·6
	2	133·5		20·6
	3	114·3		20·6
	4	89·7		20·4

The % of hydrogen bromide in the particles is very large, but constant whether colloids are present or not; expressed as normalities, however, the concentrations are nearly the same as (in fact, a little higher than) in the case of hydrogen chloride.

The relation between alkali concentration and fog formation is the same as for hydrogen chloride, and when plotted, the lines for gelatin and gum arabic are practically parallel.

The partial pressures (about 59 mm.) of the hydrogen bromide in the air and acid mixtures in these experiments were considerably lower than with hydrogen chloride, yet the amount of fog formed under similar conditions was greater; this is probably due to the slower diffusion of the hydrogen bromide.

Alcoholic Solutions.—The weaker solution used did not give very dense fogs, but the stronger gave very dense ones; in the latter case, the bubbles, as they passed up through the solution, were filled with fog. With strong alcoholic solutions, the narrower the jet the greater is the amount of fog obtained. This is the reverse of that found for the simple aqueous solutions.

The solutions contained 7·6% and 33·0% by weight of alcohol, respectively, and were 1·223*N* and 1·238*N* with regard to sodium hydroxide.

The alcohol in the fogs was estimated by Benedict and Norris's method (*J. Amer. Chem. Soc.*, 1898, **20**, 293), in which a standard solution of potassium dichromate in concentrated sulphuric acid is used for oxidation, but since the presence of chloride in the solutions caused high results, the following modification was adopted. After extraction of the asbestos with water, the volume being kept as small as possible, the washings were run into a graduated flask to which an excess of 0·03185*N*-silver sulphate solution was added; after standing and being shaken for some time, the liquid was made up to volume. Portions were then filtered off for estimation of alcohol and of the excess silver. From the gross amount of alcohol found on analysis, a deduction was made for alcohol adsorbed by the asbestos, the latter having been determined by separate experiments.

An attempt was made to estimate separately the partial pressures of the alcohol and water vapours in the gas after filtering out the fog. Fresh calcium carbide, as described by Thomas (*J. Soc. Chem. Ind.*, 1922, **41**, 33T), was used for this purpose. The change in weight of a **U**-tube filled with carbide multiplied by 2·91 (experimental factor determined by blank experiments) gave the weight of water vapour in a given volume of air; the alcohol was absorbed in concentrated sulphuric acid, which, as shown by blank experiments, did not absorb acetylene. Hence the partial pressures of the water and alcohol vapours could be calculated.

The fogs produced at each stage of the neutralisation of the stronger solution were analysed: the composition of the particles with regard to both alcohol and acid content remained constant.

Series of experiments similar to those already described for other solutions were carried out. As shown in Fig. 5, there is a critical rate below which the amount of fog formed falls off rapidly as the rate decreases. Some of the results are in Table VI. It is seen that the lower the alcohol concentration the greater is the % of acid in the fog particles. Moreover, the percentages of alcohol in the fog particles are somewhat greater than those in the original solution. In view of the work of Kablukow (*Z. physikal. Chem.*, 1903, **46**, 399), however, it is probable that the vapour given off by the alkaline solutions is richer in alcohol than that given off by a simple aqueous solution of the same alcohol content. If a correction is applied to the usual vapour-composition data, assuming that sodium hydroxide has the same effect on the vapour composition as potassium iodide, it is found that the % of alcohol to be expected in the liquid in equilibrium with that vapour is close to that actually found.

TABLE VI.

Solution: Aqueous alcohol, NaOH 1·23-*N*. Depth of liquid: 7·5 cm.
Air temp.: 20·4—22·5°.

Alcohol, %.	Radius of jet (mm.).	Rate (c.c./min.).	Fog (mg./l. of air).	HCl, %.	Alcohol in fog, %.	Part. press. (mm.)	
						Alcohol.	H_2O.
7·6	1·32	191	44·7	8·42	9·40	7·86	24·8
		154	37·6	7·67	9·51	6·60	19·5
		149	35·8	7·77	9·76	7·11	22·4
		118	30·1	7·90	8·75	7·82	21·4
		101	24·0	10·59	10·85	6·50	21·6
33·0	0·82	222	132·7	5·16	41·9	18·2	—
		195	130·4	5·23	45·0	18·0	24·8
		192	127·8	5·11	44·4	18·2	24·9
		159	118·8	5·25	43·9	20·4	—
		126	113·2	4·94	43·6	21·2	22·3
		126	112·1	5·02	43·9	21·0	25·7
		74·5	76·6	4·85	41·8	21·4	20·9

Some experiments summarised in Table VII show what changes take place in a fog when bubbled through a second wash-bottle; in the examples given, the solution was 1·24*N*-sodium hydroxide in 50% (by vol.) alcohol. The symbols I and II refer to the first and

TABLE VII.

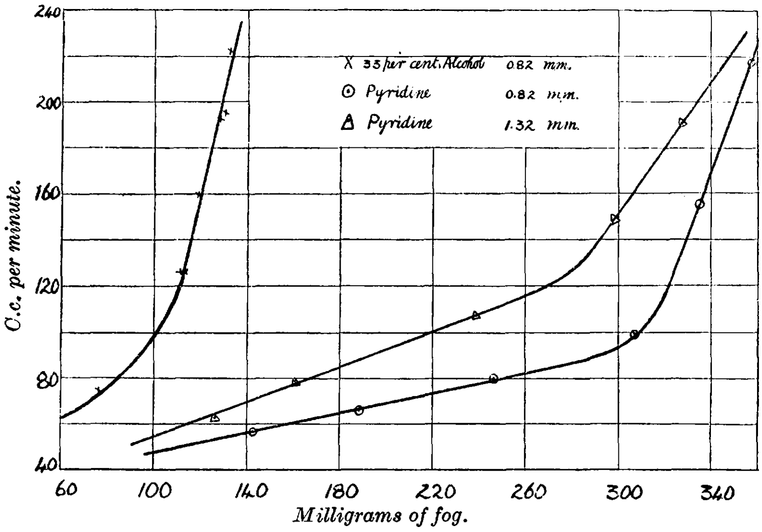
Radius of jet (mm.).		Rate (c.c./min.).	Fog (mg.).		Absorption, %.	HCl in fog, %.	
I.	II.		I.	II.		I.	II.
0·60	0·99	200	172	89·2	48·6	5·2	2·00
0·60	0·99	219	187	105·1	43·9	5·2	2·00
1·66	0·60	200	145	40·8	71·8	4·5	1·60

second wash-bottles, respectively. These figures clearly show how much more effective the narrower jets are for causing absorption of the particles. A great decrease in acid concentration is shown also, which can only be explained by condensation of vapour on the particles; whether this condensation is preferential or not has yet to be determined.

The alcoholic solutions follow the logarithmic law put forward in connexion with the other solutions.

Pyridine Solutions.—Pyridine was used to see whether an organic base would give fogs under the experimental conditions. (Aniline behaves in a similar manner to pyridine.) With an $M/2$-solution, very dense fogs were obtained in which the concentration of acid varied somewhat more than usual with the rate of passage of the gas, decreasing with decrease in the rate. The critical rate of about 110 c.c./min. is shown very distinctly in Fig. 5. During progressive neutralisation of the base, the concentration of acid in the particles remained steady, as also did the partial pressure of aqueous vapour. In this case also, as with the stronger alcoholic solution, the narrower jet was the more effective fog producer.

FIG. 5.



The pyridine solution follows the same law as do the simple aqueous solutions during the process of neutralisation.

The use of pyridine is complicated by its volatility, and this no doubt is one reason that fog was formed in the bubbles as they passed through the solution. This aspect of the question has been examined qualitatively, using solutions of ammonia and of hydrogen chloride of varying concentrations. If air carrying hydrogen chloride is passed through ammonia solutions, fogs are formed in all cases because even in dilute solutions ammonia has an appreciable vapour pressure. If, however, the vapour from even concentrated ammonia is passed through hydrochloric acid solutions, no fog is obtained until an acid solution is used of such high concentration that the partial pressure of the chloride rises above its infinitesimally small values in the dilute solutions. The formation of fogs begins in about 18% acid, and their density increases rapidly as the concentration of the acid rises above this.

Sizes of, and Charges on, the Particles.—Since the partial pressure of the water vapour and the concentration of acid in the fog particles remain practically constant, it would be expected, assuming the system to be in equilibrium, that the particles would all have the same radius, but this expectation is not completely fulfilled.

The apparatus used for studying the size of the fog particles consisted of an inner cylinder of thin, hard glass, surrounded by a thick one, the space between being sealed at each end. Wide-bore taps were used to minimise contact of the fog with surfaces. Light entered on one side by a narrow slit; on another slit at the front the level of the fog surface was read at intervals. The surface of the fog remained level during an experiment except when the densest fogs were being used.

The Stokes–Cunningham equation was used for calculating the radius of the particle from its rate of fall. The equation may be reduced to the form $r = x\sqrt{v}$, where r is the radius in cm., v is the velocity of fall in cm./sec., and x varies according to the viscosity of the medium and the density of the particle. For the aqueous, alcoholic (7·6 and 33·0%), and pyridine solutions with hydrogen chloride, and for the aqueous solutions with hydrogen bromide, x has been given the values 8·92, 9·00, 9·23, 8·92, and $8{\cdot}40 \times 10^{-4}$, respectively, the corresponding densities of the particles having been taken as 1·04, 1·02, 0·97, 1·04, and 1·17.

Experiment showed that the particles had the same radius at all stages of the neutralisation of the solution, but they increased somewhat rapidly in size during the time of settling, this being particularly noticeable in the case of those from the alcoholic solutions. With dense fogs, the particles appear to be smaller than in the other cases. Table VIII gives the radii of a number of dense fogs, 0·62*N*-sodium hydroxide being used (except with pyridine).

In general, the particles became larger as the concentration of

TABLE VIII.

Depth of liquid : 7·5 cm. Radius of jet : 1·32 mm.

Substance.	Conc.	Rate (c.c./min.).	Temp.	Radius (cm.) $\times 10^4$.
Methylene-blue ...	0·02%	210	25·3°	1·62
„ „ ...	0·004%	210	24·7	1·41
Gelatin	0·122% (with 0·5N-NaCl)	210	22·5	1·08
Buxton clay	0·186%	210	25·3	1·19
Pyridine	$M/2$	208	25·5	0·50—1·16
„	„	77	23·8	—1·19

colloid, etc., decreased, as the radius of the jet decreased (rate constant), and as the rate decreased (radius of jet constant). With the alcoholic solutions, the particles given by the stronger solution were somewhat smaller than those given by the weaker. In all cases the particles in the hydrobromic acid fogs were smaller than those obtained under similar conditions with hydrochloric acid.

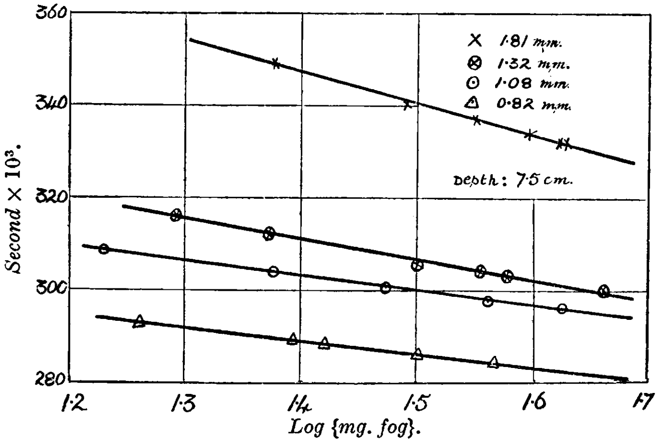
From the various data obtained, it appeared that the original size of the particles is possibly of the same order as for fogs from other reactions, *viz.*, 5×10^{-5} cm.,—pyridine has given particles originally of radius 5·0—7·2 $\times 10^{-5}$ cm., methylene-blue of 7×10^{-5} cm. These, however, are very unstable, often increasing rapidly to a mean radius of 2×10^{-4} cm. Whether the comparatively large particles (2—3 $\times 10^{-4}$ cm.) of the fogs from the simple aqueous solutions have grown from smaller particles, it is not possible to say. Apparently an equilibrium state is reached by the particles, since the partial pressure of the water vapour and the concentration of acid remain nearly constant and independent of the conditions of formation. It is hoped to investigate this matter further.

An attempt was made to determine the charges on the particles, but no definite evidence was obtained as to the presence of such charges. This is not surprising in view of the work of Bloch (*Ann. Chim.*, 1911, **22**, 370, 441 ; **23**, 28), who found that many organic liquids decreased or completely inhibited the formation of charges in a gas bubbling through aqueous solutions in which they were dissolved or on which they formed a layer.

Discussion.

For the rate of absorption of hydrogen chloride (or bromide) from bubbles containing the acid vapour we have $dw/dt = AKP_g$, in which A is the area of the bubble, P_g the partial pressure of the gas, and K the over-all diffusion constant (Lewis and Whitman, *Ind. Eng. Chem.*, 1924, **16**, 1215). Now $dw = -X \, . \, dP$, where X is a function of the molecular weight of the gas ; hence, $dP/dt = -AKP_g/X$, or $\log_e P_0/P_t = AKt/X$, where P_0 and P_t are the pressures at times 0 and t. Since in these experiments P_0 and the concentration of acid in the particles are constant, the equation becomes $K'' - K't = \log_e F$, where K'' and K' are constants, and F is the number of mg. of fog per litre of air. This requires that the relation between the time of contact of the bubbles with the solution and the logarithm of the weight of fog should be linear. Fig. 6 shows that this requirement is fulfilled. At the depth of 7·5 cm., as shown in Fig. 6, the lines get slightly steeper as the radius of the jet increases, but it has been found that the similar lines drawn for the depths 3·7 cm. and 5·5 cm. are practically parallel. Moreover, there is not a great difference between the slopes of the lines whatever the size of jet or depth of liquid.

Fig. 6.



On plotting the data obtained in the experiments where the concentration of capillary-active substance was varied, it is found that straight lines are obtained (Fig. 7) corresponding to the general equation $\log_{10} F = m \log_{10} C + K_1$, in which F is the weight of fog (in mg.) formed in the first litre of air used, C is the concentration % of added material, and m and K_1 are constants. The values thus found for m and K_1 for various solutions are given in Table IX, and some typical experimental and calculated values in Table X. It will be seen that the above expression satisfactorily represents the experimental results except for a few very dilute solutions.

The activities of the substances used extend over a wide range; the only generalisation which emerges is that basic substances (*e.g.*, safranine and methylene-blue) are more active than others (*e.g.*, gum arabic and Congo-red). The constant K_1 may be defined as the logarithm of the amount of fog which would be obtained

TABLE IX.

Substance.	Conc. of alkali (N).	m.	K_1.	Substance.	Conc. of alkali (N).	m.	K_1.
				Safranine	0·61	0·446	2·852
*iso*Amyl alcohol	0·59	0·274	1·938	Congo-red	0·61	0·385	2·237
Gelatin	0·61	0·284	2·532	Orange G.	0·61	0·370	2·326
Gelatin	1·24	0·287	2·522	Kaolin (1)	0·61	0·508	2·080
				Kaolin (2)	0·61	0·385	2·169
Gelatin $+0·5N$-NaCl	0·61	0·240	2·504	Aquadag (1)	0·61	0·286	2·352
				Aquadag (2)	0·61	0·390	2·667
Methylene-blue	0·61	0·218	2·700	Buxton clay	0·61	0·212	2·510

Kaolin and Aquadag (1) : partial pressure of HCl, 36·7 mm.
,, ,, ,, (2) : ,, ,, ,, 139·2 ,,

TABLE X.

Solution : $0·61N$-NaOH.

Substance.	%.	Fog (mg.). Found.	Fog (mg.). Calc.	Remarks.
Gelatin.	0·098	171·8	176	Points are scattered on both sides of the line drawn.
	0·073	156·2	162	
	0·052	142·4	147	
	0·049	143·2	145	
	0·024	123·8	118	
	0·008	87·1	87	
	0·0035	70·5	68	
	0·0016	52·9	54·5	
	0·000	23·4	—	
Methylene-blue.	0·0267	222·8	227	The last two points fall below the values required by the straight line.
	0·0133	195·0	195	
	0·0067	168·1	168	
	0·0027	146·7	138	
	0·0013	117·5	117	
	0·00067	98·1	102	
	0·00027	66·0	83	
	0·0000	31·9	—	
Aquadag (1).	0·194	142·0	141	All the points lie close to the line drawn through them.
	0·130	124·5	126	
	0·065	103·5	103	
	0·039	88·7	89	
	0·026	80·6	79	
	0·013	61·7	65	
	0·000	17·1	—	

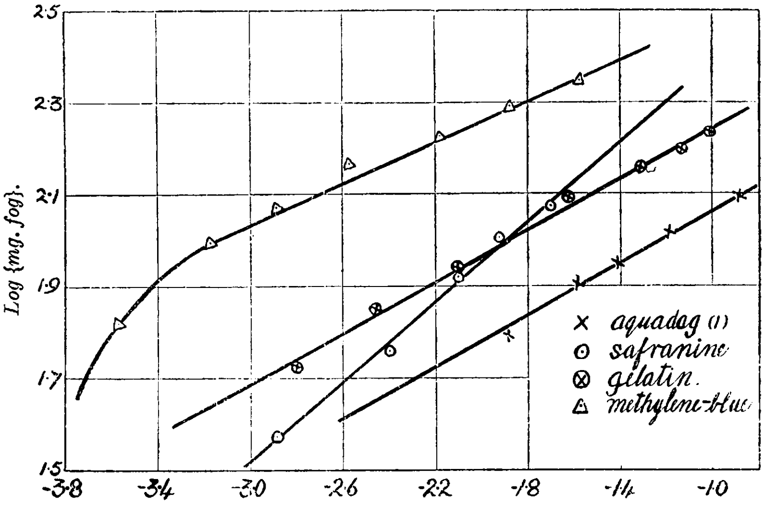
from a 1% solution, provided that the straight-line law held up to that point; K_1 is thus a measure of the activity of the given material. Fig. 7 shows that the slope of each line is a specific property of the corresponding substance, *i.e.*, that the rate of change of fog formation with change in concentration varies from one material to another.

The great capillary activity of such substances as gelatin and methylene-blue has been noticed in other directions (Donnan, *Rep. Brit. Assoc.*, 1923, Sect. B, 12), *e.g.*, *E.M.F.* (Šendera, *Rec. trav. chim.*, 1925, **44**, 480), cataphoresis (van der Grinten, *J. Chim.*

physique, 1926, **23**, 209), water-fall experiments (McTaggart, *Phil. Mag.*, 1914, **27**, 297). As the relation between the amount of material present and the effect it produces is of the same form as the "adsorption isotherm," it has generally been concluded that adsorption at the interface is the cause of the phenomena. The equation given above has the same form as the adsorption isotherm.

It is rather remarkable, however, that such great effects should be obtained, since the surface tensions of these solutions differ very little from that of pure water or of the alkali solutions used. That surface tension is probably not the controlling factor, at any rate so far as fog formation is concerned, is shown by the fact that although amyl alcohol causes great reductions in surface tension it is not very active as regards fog formation.

FIG. 7.



A survey of the possible causes of the decreased rate of absorption of the acid vapours brings out the fact that the seat of the phenomenon lies in the film round the bubble, and that this film is greatly altered by colloids, etc. Moreover, the peculiar properties of this film only appear in alkaline solution. A case of inhibited diffusion of a gas through an alkaline film has been noted by Taylor (*Fuel*, 1926, **5**, 195); in this case, the whole system was wet, so that it is not possible to say whether this film behaved towards water vapour in the same way as the alkaline films round the gas bubbles behaved in the present experiments.

A serious problem is that of explaining how all the moisture gets into the bubbles in order to form the great quantities of fog obtained in some cases. It may be that the film acts as a membrane which is readily permeable to water vapour but not so permeable to the acid gas.

In some of the experimental data it is noteworthy that the vapour pressures recorded are greater than correspond to saturation for air at the temperatures given. This is probably connected with the uncertainty attaching to the temperature, for it is difficult to control the heat effects arising from (i) the neutralisation process in the solution, and (ii) the condensation of water to form the fog particles. This uncertainty causes a complication in the attempt to correlate the size of the particles with their acid content. Rothmund (*Monatsh.*, 1918, **39**, 571) used an approximate form of the equation connecting vapour pressure with the radius of curvature of the particle by equating the increase in vapour pressure, due to the increased curvature, to the decrease brought about by dissolved material. The equation obtained finally was $r = 6{\cdot}1 \times 10^{-6}/ci$, where r is the radius of the drop, c the concentration of dissolved material, and i the van 't Hoff factor. With Rothmund's ozone fogs, the formula gives results of the right order, but if it is applied to the results of the present author and of others, the calculated values for the radii are very wide of those actually found. It is a remarkable fact that fog and cloud particles (whether liquid or solid), when formed by spontaneous condensation of vapour, all tend to have a radius of about 5×10^{-5} cm. None of the equations which have been put forward (such as Rothmund's given above, von Weimarn's equation of state, or the equation connecting vapour pressure and radius of curvature) gives any indication of such a "critical" radius. Donnan (*Z. physikal. Chem.*, 1903, **46**, 197) has deduced thermodynamically, however, that a critical radius of about 1×10^{-5} cm. should exist, and Lewis ("System of Physical Chemistry," 1920, I, 332) shows that with oil emulsions there is a distinct tendency for the particles to approximate to this size; but that the same radius should be found general for aerial colloids is certainly remarkable. The comparatively large particles found in the present experiments are probably the result of condensation of vapour on particles originally of this critical radius.

Many of the data recorded in the present investigation suggest that the fog droplets persist even in an unsaturated atmosphere. This is not unexpected, as it is well known that mists formed in the presence of ions can exist for long periods in highly unsaturated atmospheres. But in the present case the uncertainty as to temperatures precludes any definite conclusions on this matter. Further and more accurate information on this and other factors is required before the conditions of stability of these fogs can be completely understood.

Summary.

1. It has been shown that hydrogen chloride and hydrogen bromide vapours are incompletely absorbed by alkaline solutions, more particularly in presence of colloids and dyes. A limiting concentration of hydroxyl ions probably exists below which absorption is complete.

2. The relations between the amount of fog formed and alkali concentration, and also between the amount of fog and the concentration of capillary-active substance, are logarithmic and of the same form as the " adsorption isotherm."

3. The concentration of acid in the fog particles and the partial pressure of the water vapour in contact with them are practically constant.

4. The radii of the particles are smaller the denser the fog produced.

5. No electrical charges have been definitely detected.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
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