

NOTES.

The Phosphorescent Flame of Arsenic. By HARRY JULIUS
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THE conditions under which the glow of arsenic occurs have been described by the author (J., 1927, 783). Since then it has been possible to photograph the spectrum of this flame, and to compare it with that of the normal flame. A suitable light source was obtained by heating about 3 g. of arsenic in a transparent silica tube (30 cm. long, 2 cm. internal diam.) wound over 15 cm. of its length with 30 turns of resistance wire (3 ohms/m.). A stream of air (200 c.c./min.) was passed down the tube from a side tube sealed on at one end, which was closed and worked in the blow-pipe so as to form a transparent window, through which the flame

was photographed. Under these conditions the tube above the arsenic was filled with a feebly luminous white cloud, the temperature of which, as measured by a mercury thermometer, varied between 250° and 360° . An exposure of 7 hours was needed with the large-aperture spectrograph already described (J., 1927, 788). The spectrum of the normal flame was photographed by igniting the arsenic, contained in the silica tube, in a stream of oxygen.

The spectrum of the phosphorescent flame was found to consist of an apparently continuous band between 4300 and 4900 Å. with its maximum intensity at about 4600 Å. There was no evidence of ultra-violet bands with this exposure. A $\frac{1}{2}$ -min. exposure of the normal flame gave a broad band closely resembling that from the low-temperature flame, and with its maximum in approximately the same position. With a 5-mins. exposure of the hot flame the continuous spectrum extended to 3200 Å., but there was no evidence of other bands in the ultra-violet. The correspondence between these spectra is in accordance with the fact that the chemical reactions are believed to be the same in the two flames.

Further experiments have also been made to determine if the phosphorescent arsenic flame can be inhibited by foreign vapours and gases in the same way as the flames of sulphur and phosphorus. In carrying out these tests, oxygen (dried by phosphoric oxide) was either passed directly over the arsenic (2 g.) heated in a U-tube, or the gas stream was diverted through two bubblers containing the organic liquid of which the inhibiting action was to be examined. The temperature was recorded by a mercury thermometer inside the U-tube. In making an observation, the glow was first obtained at as low a temperature as possible in an oxygen stream; the gas stream was then diverted through the organic liquid, and it was observed whether the glow became weaker or was diminished in intensity. The glow was found to appear at 220 — 245° , according to the conditions, and was completely extinguished at this temperature when the oxygen was saturated with the vapour of any of the following nine liquids: benzene, ethyl alcohol, hexane, acetone, chloroform, amyl acetate, ethyl acetate, methyl alcohol, and chlorobenzene. A temperature increase of 12 — 30° was needed to restore the glow, but it reappeared at the temperature at which it had been inhibited if the normal gas stream was once more passed, showing that no permanent change (*e.g.*, contamination of the surface) had taken place in the arsenic. If the glow was inhibited in oxygen saturated with, *e.g.*, benzene, and the gas stream was stopped, the glow reappeared in a few seconds, although there is no reason to think the inhibitor had been destroyed. On restarting the gas stream, the glow was once more swept out of the tube.

This observation suggests that there was a definite lag in the establishment of the glow in presence of the inhibitors, resulting in inhibition in a gas stream, but not in stationary gas. On comparing these results with those obtained previously on the inhibition of the glow of sulphur (J., 1928, 1942), it is seen that the effects with arsenic are very much weaker, though this phosphorescent flame apparently shows a phenomenon of exactly the same type.—
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Periodic Structures from Interacting Gases. By ERNEST SYDNEY HEDGES.

KOENIG (*J. Physical Chem.*, 1920, **24**, 466) has described the formation of bands of ammonium chloride when two litre flasks, containing respectively ammonia and hydrogen chloride, were connected by a narrow glass tube several metres in length. The bands were formed where the gases interacted in the connecting tube. Apart from the support given by this experiment to the view that the so-called specific function of the gel in the formation of Liesegang rings and other periodic structures has little or no significance, the observation is of some importance, since it is opposed to Wo. Ostwald's "diffusion-wave" theory of Liesegang rings (*Kolloid-Z.*, 1925, **36**, 380). According to this theory, the essential rôle is played by the second reaction product—potassium nitrate in the reaction between potassium dichromate and silver nitrate—which is said by its accumulation to reverse the reaction and dissolve the precipitate.

The combination of ammonia and hydrogen chloride is an example of a chemical reaction in which there is no second reaction product. Ostwald (*Kolloid-Z.*, 1926, **40**, 145), however, regards the reaction as $\text{NH}_4\text{OH} + \text{HCl} = \text{NH}_4\text{Cl} + \text{H}_2\text{O}$ and suggests that the water formed plays the part of the second product. It is doubtful whether ammonium hydroxide occurs even in moist ammonia gas, but it seemed desirable to repeat the experiment with dried gases.

Another point requiring investigation was whether the periodic structures produced in this way are genuine or are caused by fluctuations in temperature: apparently, Koenig used no temperature control, and a small variation in the temperature of one of the large flasks would move the boundary of the reacting gases in the narrow tube considerably.

In the present investigation, instead of using large globes containing the gases, solutions of ammonia and hydrochloric acid were put respectively into two bottles of 250 c.c. capacity and connected

by 2 m. of glass tubing (3 mm. diameter), no temperature control being used in the first experiments. Between the connecting tube and the bottles were inserted drying trains, containing phosphoric oxide on the hydrochloric acid side and lime on the ammonia side. After 2 days, irregular bands of ammonium chloride had formed in the tube. It was then found quite unnecessary to use so long a tube, for by varying the concentrations of the solutions the gases could be made to meet about half-way along the tube, and in subsequent experiments the bottles were kept close together and connected by 40—50 cm. of glass tubing suitably curved so as to occupy as little space as possible. The best concentrations were found to be 10*N*-hydrochloric acid and 2*N*-ammonia.

The experiment was repeated under constant temperature conditions by placing the two bottles side by side in a thermostat at 30°, the drying tubes also being immersed. The narrow connecting tube was above the level of the water and was protected from draughts by a wrapping of cotton wool. After 2 days, regularly spaced bands of ammonium chloride occupied a length of about 10 cm. of the tube, the mean distance between the bands being about 1 mm.

It is concluded that the interaction of gaseous ammonia and hydrogen chloride gives rise to a true periodic structure, that water plays no significant part in the formation of this structure, and that the "diffusion-wave" theory is inapplicable.—BEDFORD COLLEGE (UNIVERSITY OF LONDON), REGENT'S PARK, N.W.1.
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