LXXII.—*The Budde Effect with a Mixture of Bromine Vapour and Air.*

By Ernest Brown and David Leonard Chapman.

Budde (*Pogg. Ann.*, 1871, **144**, 213) observed that chlorine expands on exposure to light, and suggested that the effect might be due to the dissociation of chlorine molecules into atoms; but later [*Pogg. Ann.* (*Ergb.*), 1873, **6**, 477], he showed that the expansion was accompanied by a rise in temperature, which was of sufficient magnitude to account for the increase in volume.

Several investigators have asserted that dry chlorine does not exhibit the Budde effect; but none, with the exception of Shenstone (J., 1897, **71**, 471), describes experiments in support of the assertion. Moreover, as the single experiment reported by Shenstone is unconvincing, there is not at present, in our opinion, sufficient reason for accepting the view that dry chlorine does not exhibit the Budde effect.

Recently, however, both Ludlam (*Proc. Roy. Soc. Edin.*, 1924, **44**, 197) and Lewis and Rideal (J., 1926, 583) have described

experiments which appear to demonstrate conclusively that a dry mixture of pure bromine vapour and air does not expand when exposed to light. Their published data show that the effect of desiccation becomes appreciable when the degree of dryness reaches that attainable by leaving a gas in contact with concentrated sulphuric acid, and that after thorough drying with phosphorus pentoxide no Budde effect at all can be detected.

Using rather different methods of experiment from those adopted by Ludlam and by Lewis and Rideal, and taking what appear to us to be reasonable precautions, we have obtained results which seem to indicate that the Budde effect with a mixture of air and bromine is not diminished to any measurable extent by drying.

Experimental.

The bromine was bought as pure, and was subjected to the process of purification recommended by Scott (J., 1913, **103**, 847). The last traces of chlorine (if any) were then removed by distilling it from a solution of potassium bromide (previously freed from iodine), and the last traces of hydrobromic acid by shaking it with a very dilute solution of potash, separating, and finally distilling it from moist zinc oxide.

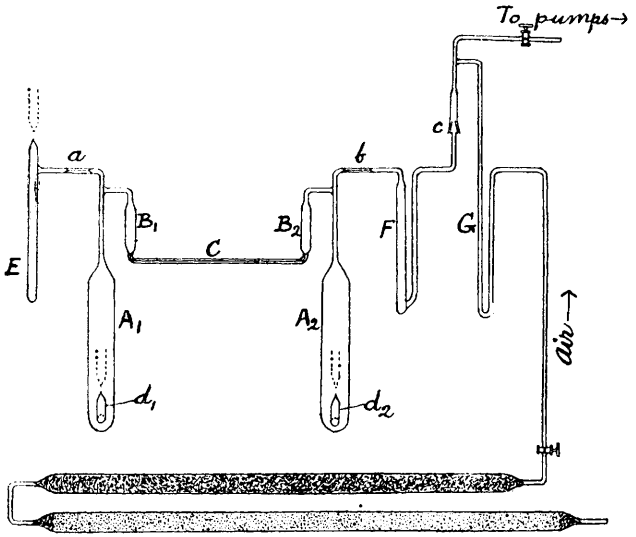
The phosphorus pentoxide was distilled in a current of oxygen, as described by Finch and Fraser (J., 1926, 117). The product was very pure, and the yield good. It melted to a perfectly clear liquid, did not reduce either silver nitrate or mercuric chloride, and contained a large proportion of the volatile form.

The apparatus is depicted in Fig. 1. The section to the left of the ground glass joint, *c*, was constructed of Pyrex glass. This was cleaned with chromic acid solution, washed with hot distilled water, and quickly dried. Whilst the glass was still warm, phosphorus pentoxide was introduced into the tube *E*, and into the tubes A_1 and A_2 through the tubulures d_1 and d_2. About 4 c.c. of bromine, which had been kept for some days in contact with phosphorus pentoxide, were introduced into *E*. *E*, d_1, and d_2 were then sealed by the blowpipe. The apparatus was next brought into connexion with the pumps by means of the ground glass joint, *c*, and the tube *E* and the U-tubes *F* and *G* were immediately afterwards surrounded with liquid air. The apparatus was then exhausted with a mercury-vapour pump backed by a Sprengel pump. After a high vacuum had been obtained, the lower portion of the tubes A_1 and A_2, to slightly above the level of the phosphorus pentoxide, were surrounded with water contained in shallow basins, and the rest of the apparatus, except the portions in the vacuum flasks, was strongly heated with the blowpipe while the pumps were in action. About 1 c.c. of the

bromine in E was then distilled into F. Air, which had already been freed from carbon dioxide and dried by phosphorus pentoxide, was then slowly admitted to the apparatus through the U-tube G. Most of the bromine contained in E was then distilled into A_1, and the portion of the apparatus between the short capillary tubes a and b was detached by sealing before the blowpipe.

Bromine " wets " phosphorus pentoxide and is rapidly drawn into the spaces between the crystals, and as the phosphorus pentoxide introduced into each of the tubes E, A_1, and A_2, was more than sufficient to absorb the whole of the bromine used, the drying of the liquid bromine must have been very rapid. To hasten the

FIG. 1.



process of desiccation the bromine was distilled backwards and forwards between the tubes A_1 and A_2 and the small bulbs B_1 and B_2, the distillation being effected by alternately cooling and warming B_1 and B_2 and the connecting capillary tube, C. The phosphorus pentoxide was not heated. The internal diameter of the tubes A_1 and A_2 was 3 cm., and that of the capillary tube, C, 1 mm.

For the purpose of comparison, a similar apparatus was constructed of the same Pyrex tubing and filled with 4 c.c. of moist bromine and air at atmospheric pressure.

With this apparatus the measurement of the Budde effect presented no difficulty. A_1 and B_1 were surrounded with aluminium foil which was painted black on the outside. A scale was attached to the capillary tube, C, which contained a thread of bromine about

1 cm. long. On exposure of A_2 to light, the thread of bromine moved rapidly towards A_1, and it returned to its former position on the light being shut off. All the measurements recorded below were made with the apparatus enclosed in a darkened thermostat filled with water at 26°, the light being admitted to the thermostat through an oblong window of such a size that about one-half of the central portion of the insolation vessel was illuminated. The source of light was a 1000-watt, gas-filled, tungsten-filament lamp, placed with its filament at a distance of 30 cm. from the centre of the insolation vessel. In making the measurements, the white light was filtered either through a 25% solution of ferrous ammonium sulphate or through a 5% solution of sodium dichromate contained in glass troughs with parallel plane faces, and of the same dimensions.

A typical result is recorded below:

Light filtered through ferrous ammonium sulphate solution.

Time of drying (days)	Wet	79	396
Expansion (scale divisions)	57	50·6	53·5

The ratios of the expansion caused by exposure to light which had been filtered through the solution of sodium dichromate to that occasioned by exposure to light transmitted through the solution of ferrous ammonium sulphate, after different periods of drying, is given in the following table.

Time of drying (days)	Wet	22	61	72	126	396
Ratio of expansions ...	0·40	0·39	0·44	0·41	0·38	0·35

Conclusion.

The almost complete removal of water vapour alone from a mixture of bromine vapour and air does not prevent the mixture from exhibiting the Budde effect.

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