CLXXVII.—*The Effect of Gases on the Colour of Iodine Vapour, and the Solvent Action of Various Vapours on Solid Iodine.*

By Robert Wright and Thomas McGregor.

Dewar (P., 1898, 241) observed that the colour of iodine vapour was less dense in a vacuous flask than in one at the same temperature containing air, and that the colour in the latter case was more purple than in the former. It was suggested that this increase in depth of colour might be due to a greater volatility of iodine in air than in a vacuum, and Dewar's observation has been frequently cited as an example of the solubility of a solid in a gas under ordinary conditions of temperature and pressure.

A repetition of Dewar's experiment was carried out. Iodine was sealed in a vacuous bulb and heated in water to about 90°; the tip of the bulb was then broken. With the inrush of air the colour of the vapour at once deepened and became more purple. With a second bulb, containing *less iodine than would saturate the available space with vapour at the temperature of the experiment*, the same effect was observed; in this case, since no excess of solid was present, the effect cannot be attributed to the solubility of iodine in air.

A qualitative spectroscopic examination of the effect was also made. A small quantity of iodine was placed in a Lilburn flask, which was then evacuated to a pressure of about 1 mm. and sealed off. The sealed flask was held concentrically in a large beaker of water placed in front of the slit of a Hilger photographic spectroscope. The water was heated to 90° and a beam of light from a Point-o-lite lamp focused on the slit. Comparative photographs were then taken on a panchromatic plate, first with the iodine alone in the vacuous flask and then, at the same temperature, in the presence of air, the flask being opened and resealed between the exposures. The results showed an increase of absorption in the second case, the head of the absorption band in the green having moved towards the red end of the spectrum. The same effect was observed when less iodine was used than would saturate the available space with vapour at the temperature of the experiment. A further series of photographs was then taken in experiments in which the air was replaced by nitrogen, oxygen, carbon dioxide, and argon, and in all cases the same result was obtained. In order to compare more accurately the effect of the different gases, a small amount of iodine was placed in a 20 cm. polarimeter tube fitted with two side tubes; this was then placed in a glass-sided thermostat at 50° and arranged in front of the spectroscope. A series of four photographs

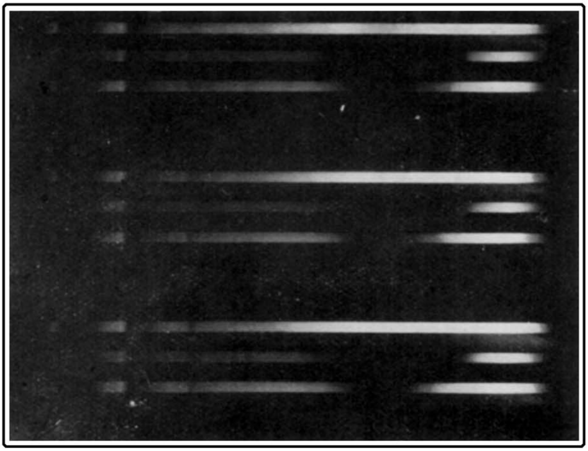


Plate I.

Air and vacuum.
Excess of I_2.

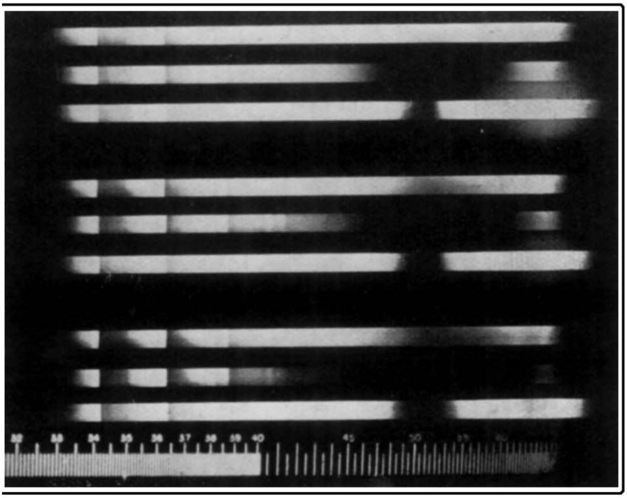


Plate II.

Argon and vacuum.
Excess of I_2.

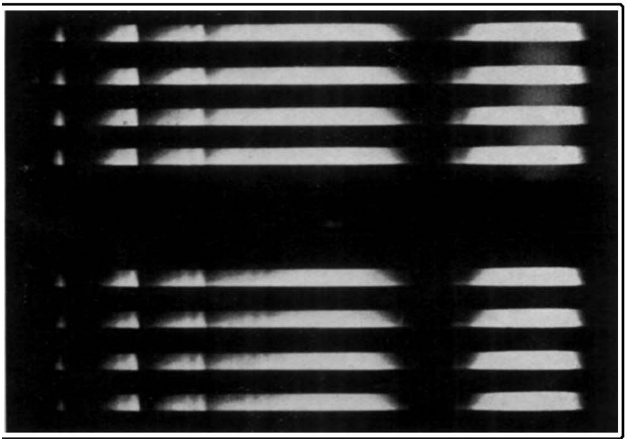


Plate III.

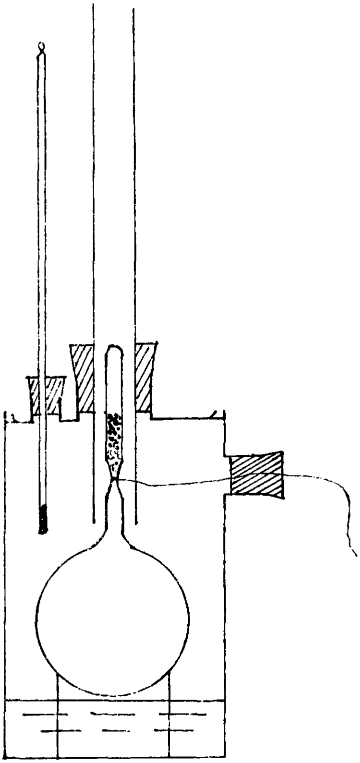
Spectra of I_2 *vapour in air, nitrogen, oxygen and* CO_2.

was taken in which the gas in the tube was successively air, nitrogen, oxygen, and carbon dioxide. The spectra were identical in all four cases, and this would seem to indicate that the colour change is not due to the solubility of the iodine in the gas used or to chemical action between the gas and the iodine vapour, but possibly to the effect of pressure on the iodine vapour.

In the accompanying photographs, Plate I shows three sets (with different exposures) of iodine absorption spectra in air and in a vacuum, with a comparison continuous spectrum in each case; Plate II shows three similar sets in argon and in a vacuum; and Plate III shows two sets taken in the 20 cm. tube with the four gases air, nitrogen, oxygen, and carbon dioxide.

It was thought of interest to try to determine the relative volatility of iodine in air and in a vacuum at 100° by measuring directly the quantity of iodine which would saturate a definite space with vapour under the two conditions. About 0·5 g. of iodine was placed in a flask of 130 c.c. capacity, the flask was sealed off, and while still hot the iodine was shaken into the neck, where it melted and adhered to the glass close to the sealed tip. (Under suitable conditions, only a small amount of iodine will sublime into the body of the flask, but if this amount is excessive it may be driven back by a prolonged heating of the bulb and cooling of the neck.) The flask was now placed in the steam-bath hown in Fig. 1 and heated at 100°. The steam-bath was constructed from a large lever-lidded paint tin fitted with a thermometer and a long brass tube to act as an air-condenser, the upper end of the condenser was attached to a large bottle and a manometer so that the pressure inside the vessel might be regulated and the temperature kept at 100°. After 5—7 hours' heating, the flask was removed from the bath and cooled quickly in a stream of water;

FIG. 1.



the iodine vapour condensed on the walls and, as diffusion of the vapour in air is slow, during the cooling hardly any iodine sublimed from the solid in the neck of the flask. The flask was now cut open, the amount of iodine in the bulb determined by titration with *N*/50-thiosulphate, and the volume of the flask measured by filling with water. For three consecutive determinations the quantity of iodine in 100 c.c. was found to be practically constant (see table).

When the same method was used with iodine in a vacuous flask the results obtained were much higher and were not constant. This was due to the sublimation of iodine from the neck into the cooling bulb during the removal of the flask from the bath. Various attempts were made to correct this and the most satisfactory result was obtained by breaking the neck of the flask while still in the heating bath, so that all sublimation due to the quicker cooling of the bulb was avoided. For this purpose a slight modification of the method was necessary. The neck of the flask was made of 5 mm. tube and a constriction was made about 3 cm. from the bulb; 3 cm. above the constriction there was a plug of glass wool, on the top of which were placed the fragments of iodine. The apparatus was now evacuated and sealed off. A loop of string was fastened to the constriction, and the flask placed in position in the heater. The end of the brass condenser tube was pushed well down over the neck of the flask past the constriction, the string passing through a slot cut in the end of the brass tube and then through a stopper in the wall of the heater. A period of 2 hours' heating was usually sufficient for the evacuated flask; the string was then pulled strongly, drawing the neck of the flask against the condenser tube until the former fractured. Steam entered the bulb and the broken end fell into the water of the heater. The bulb was now removed from the heater and its iodine content and volume were determined as before. The results for three consecutive estimations are shown in comparison with those obtained for air. They are not quite so regular but are always slightly higher, so there is no indication of iodine being soluble in air. The values for the vapour pressure of iodine at 100° are inserted in the table and are calculated on the assumption that iodine vapour obeys the gas laws and that the gram-molecular volume is 22·4 litres at N.T.P.

Weight (g.) of saturated iodine vapour in 100 c.c. at 100°.

	a.	*b.*	*c.*	Average.	V.p. (mm.).
In air	0·05032	0·05025	0·05060	0·05039	46·2
In a vacuum	0·05171	0·05182	0·05227	0·05193	47·5

A number of measurements were carried out to determine whether iodine is soluble in the vapours of those solvents in which, as liquids, it dissolves easily. The solvent vapours employed were benzene, toluene, alcohol, ether, carbon tetrachloride, and chloroform. The method and apparatus have already been described by one of us (J., 1915, **107**, 1527) for the determination of the vapour pressure of solid iodine. Purified air was first passed, at room temperature, through a weighed bubbler containing the solvent under investigation. The air and vapour then passed over iodine heated at 100° and the iodine carried over by the mixed gases was estimated. The volume occupied by the solvent vapour at 100° was calculated by application of the gas laws from the weight of solvent used, and the volume of air was measured after the removal of the solvent vapour by a suitable absorbent. The total amount of iodine carried over, less the amount due to the air alone, gives the quantity of iodine carried by the solvent vapour.

Although the quantity of iodine carried over by a litre of air at 100° was found by repeated estimations to be perfectly definite, no constant results could be obtained for the vapours. It was not infrequently found that, using the same iodine for a series of determinations, a litre of solvent vapour would carry over more iodine than a litre of air during the earlier determinations of the series, but this quantity would decrease in the later estimations and might even apparently become negative, *i.e.*, less iodine would be carried over by the mixture of air and solvent vapour than would be obtained by the air constituent of the mixture acting alone.

After prolonged exposure to the air–vapour mixture, the surface of the iodine frequently became moist, and in some cases the whole of the iodine melted. It would thus seem that the iodine was absorbing some of the solvent vapour and forming a solution which would of necessity have a lower iodine vapour pressure than the pure iodine, and this effect would mask any solvent action in the vapour phase. The positive results in the first determinations of a series were obtained before much of the vapour had been absorbed on the surface of the iodine.

Perman (J., 1903, **83**, 1168) found that the partial pressure of water vapour over aqueous ammonia was less than that of pure water; for although water vapour may be very soluble in ammonia gas, the presence of ammonia in the liquid phase lowers the water vapour pressure to such an extent that any solubility in the vapour phase is more than counterbalanced. It may, however, be suggested that solubility in the vapour phase is a factor in those positive deviations from the mixture rule which are sometimes obtained for the vapour pressures of binary liquid mixtures.

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