CXC.—*The Influence of Glass upon Vapour Pressure.*

By JACOBUS RINSE.

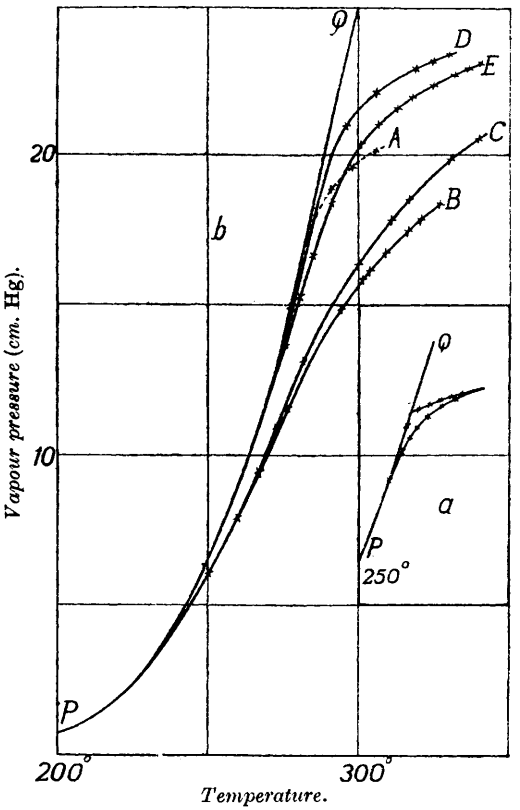
IN determining the dissociation of mercuric iodide by means of glass-spring indicators (*Rec. trav. chim.*, 1928, **47**, 35), we observed that the vapour pressure–temperature curves were of an unusual form : instead of changing abruptly to the linear form on passing the saturation point, as required by Gay Lussac's law, the curves were continuous. Moreover, it was frequently noticed that the vapour pressure at that temperature at which the gas should be just unsaturated was too low—in many cases more than 10% and once 14% below the calculated value. A similar phenomenon has been described by McHaffie and Lenher (J., 1925, **127**, 1559; 1926, 1785; 1927, 272) in the adsorption of water and benzene on glass, quartz, and platinum surfaces. Frazer, Patrick, and Smith repeated and extended these experiments (*J. Physical Chem.*, 1927, **31**, 897), and found continuous curves under certain conditions. These results, however, are probably of a different type from those now to be described.

(*a*) *Reaction between the Glass Wall and Mercuric Iodide.*—The passage to the Gay Lussac curve was continuous if the indicators had been previously heated above 500°; if, however, the indicator was evacuated without being heated during the pumping, a break was obtained immediately after evacuation, as shown in Fig. 1a. If the apparatus was then heated at 600° for 30 minutes, the vapour-pressure curve determined during the subsequent cooling was continuous. Although the glass never appeared to be attacked, even in indicators which had been used for a long time, experiments were made to determine whether an excess of either mercury or iodine was responsible for the continuity, but the results showed that they were not. Moreover, mercurous iodide gave curves showing a break. Further experiments giving negative results on this point are described in section (*d*).

(*b*) *The Influence of Drying.*—As it had been observed that the effect was greatest when the glass-spring indicators had been evacuated and heated simultaneously for a long time, during which

some mercuric iodide distilled off, experiments were made to decide whether adsorbed water had any influence. A manometer was constructed to which a bulb containing fine phosphoric oxide was connected by a wide tube. The apparatus was filled in the same way as for the intensive drying experiments in this laboratory (J., 1926, 2657). The indicator was left for 14 days and occasionally heated. The phosphoric oxide bulb was then removed and the

FIG. 1.



vapour-pressure curve determined: it showed only a continuous transition over a short range, and a second similar experiment had the same result. Therefore water is probably not the cause of the phenomenon.

(c) *The Influence of Glass.*—Some glass powder (1·68 g.), made from the same high-melting Jena combustion glass as the indicators, was introduced, and the apparatus evacuated during 30 minutes and heated meanwhile. The curve subsequently determined is

represented by A (Fig. Ib) and shows a gradual transition over the range 285—310°. After ½ hour's heating at 560°, curve B was obtained, which shows a much longer range. As a small amount of gas was liberated during the heating (probably it had been adsorbed by the glass powder), the indicator was again evacuated, by breaking a point which was connected by a rubber tube to the pump, and resealed. The volume was thus diminished, whilst the amount of mercuric iodide remained the same as before; accordingly the new vapour-pressure curve C now lies above B. After the determination of C the glass was freed from mercuric iodide by heating the lower part of the manometer. The glass powder was shaken into the end of a tube which was sealed off. Curve D was then obtained, which is much less straight than C. The influence of the glass was therefore distinctly demonstrated. After heating again at 550—600° for 1½ hours, curve E was obtained. The points on all these curves were found both with increasing and with decreasing temperatures, and the equilibrium was established very rapidly.

A second experiment, in which a definite amount of mercuric iodide was used, gave the same results. 1·5 G. of glass powder were placed in an indicator of about 13 c.c. capacity. A part of the iodide sublimed during the evacuation and heating. The normal values of the pressure can be calculated from Gay Lussac's law, and hence the lowering of the vapour pressure was found to be as follows :

Temperature	241°	250°	259·5°	269·5°	276·5°	286·5°	303°
Pressure (calc.)	4·7	6·7	9·0	11·8	14·3	18·0	27·0
,, (obs.)	4·2	5·75	7·35	9·0	10·35	12·7	16·3
Lowering	0·5	0·95	1·65	2·8	3·95	5·3	10·7
Lowering, %	11	14	18	24	27·5	29·5	40

We see from this table that a decrease of 40% can occur. In the same way a lowering of 14% was found when no glass powder was used.

At higher temperatures the decrease diminished till the theoretical curve was reached. This was verified in indicators of known volume with a known amount of mercuric iodide.

For the further investigation of the phenomenon the apparatus shown in Fig. 2 was constructed. The bulbs, of about 30 c.c. capacity, were connected by a tube, in which a capillary was made, and 5 g. of glass powder were introduced in one of them. The apparatus was then evacuated and heated in an electric furnace at 550—600° for ½ hour. After cooling, 200 mg. of mercuric iodide were rapidly placed in the second bulb. The whole was evacuated again, the glass powder heated, and the connecting tube to the pump finally sealed off. The apparatus was again placed in the

furnace and heated to 600°. Then it was put in a bath of an equimolecular mixture of potassium and sodium nitrates and heated to a temperature at which, as found by calculation, the vapour ought to be just unsaturated. The apparatus was now raised so that the capillary was above the surface of the liquid and could be sealed off, thus separating the bulbs. The volume and weight of mercuric iodide in each were then determined. In this way it was found that the vessel which contained glass powder had more iodide than the other. On one occasion this difference amounted to 12·5%, and in another case to 5·5%. In these experiments it is necessary to evacuate carefully and to heat the glass powder strongly; otherwise, no excess of iodide is found in the vessel with glass powder.

To complete these experiments it was desirable to measure the pressure. Fig. 3 shows the apparatus used. The procedure of filling was the same as in the preceding experiments. Glass powder was introduced in the space immediately below the spring, the apparatus was evacuated and heated to 600°, mercuric iodide was introduced, and the apparatus again baked out and sealed at *a*. In Fig. 4, A is the vapour-pressure curve first determined. This is continuous from about 300° to 330°. At 308°, where the pressure is 27·5 cm., the capillary *b* was raised out of the bath and sealed off. The subsequent vapour-pressure curve B is now much higher than the former and shows less deviation from the third curve in the figure, which is the saturation curve.

FIG. 3.

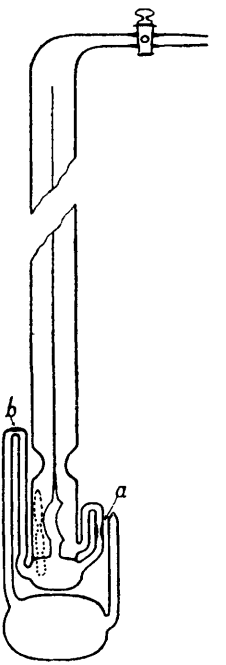
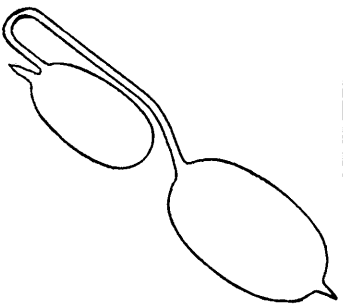


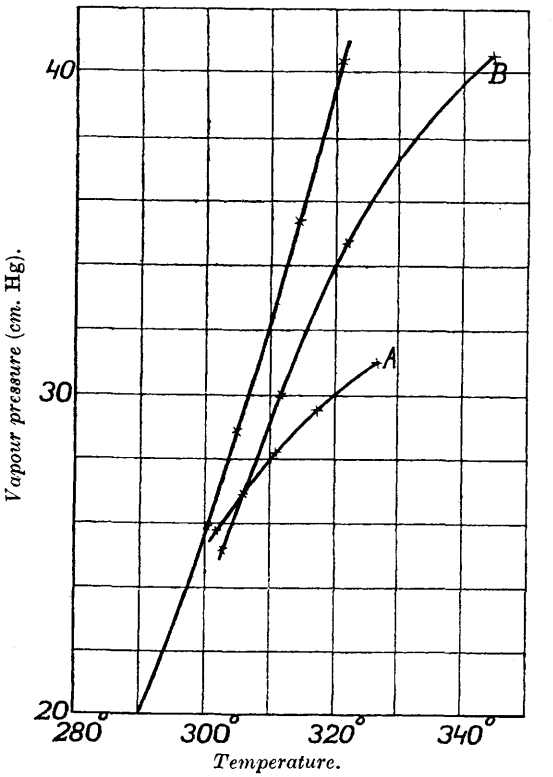
FIG. 2.



This experiment was repeated under more quantitative conditions, glass powder now being placed in the big bulb. This time the manometer was evacuated first through a capillary sealed to the large bulb, and then through the capillary which connected the two sides of the spring. A part of the mercuric iodide, which was introduced in the space immediately below the spring, was distilled off during the second evacuation. The apparatus was then heated to 600°,

after which a continuous vapour-pressure curve was obtained (A, Fig. 5). The bath was then kept constant at 303°, corresponding to the middle of the bend in curve A, and the capillary was brought 1 cm. above the liquid and sealed off, the glass powder thus being separated from the manometer. The new vapour-pressure curve is represented by B (Fig. 5). Then the two parts of the original apparatus were opened and weighed, the volume and weight of

FIG. 4.



mercuric iodide being determined. From these values the corresponding theoretical curves C and D could be derived, and it is seen that without glass powder the maximum lowering is 10·2% (curves B and D at 285°), and with powder 29·5% (curves A and C at 300°).

(*d*) *The Roughness of the Surface.*—During this investigation the paper of Frazer, Patrick, and Smith appeared (*loc. cit.*), dealing with the thickness of adsorbed vapour films. The authors show that for water and toluene the smoothness of the surface is very important,

the reaction between water and glass being largely responsible for the results of McHaffie and Lenher. With toluene and a plane surface no adsorption could be detected by vapour-pressure determinations.

The roughness of the surface might therefore account for the phenomenon with mercuric iodide. To test this an indicator was made that had not been in contact with water or aqueous vapour: it was blown through a tube containing phosphoric oxide, and then

FIG. 5.

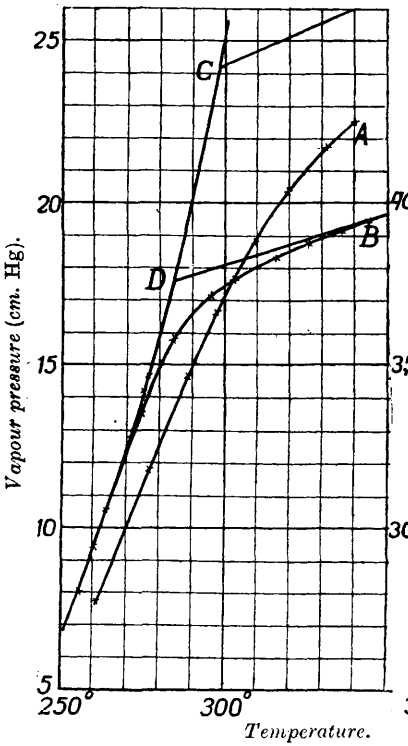
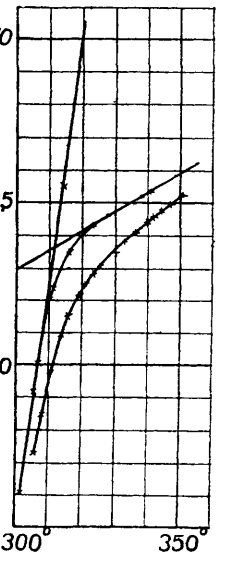


FIG. 6.



heated in a stream of very dry oxygen until the glass softened, and is therefore believed to have a plane surface such as Frazer and his co-workers found necessary. Into this apparatus were rapidly introduced 48 mg. of mercuric iodide, which was heated in a vacuum until a part distilled off, and the observations represented in Fig. 6 were made. The higher curve was obtained immediately after the evacuation, and the lower after heating for 2 hours at 580°. The maximum decrease is 12%. This experiment proves that the effect with mercuric iodide cannot be explained in the same way as that

with toluene. Assuming that adsorption has occurred, we can calculate the thickness of the adsorbed vapour layer. The internal surface of the glass-spring indicator used is about 20 sq. cm., the amount of mercuric iodide used in the last case is about 40 mg., and the surface occupied by a mercuric iodide molecule in a layer of the tetragonal crystal is $4{\cdot}4^2 \times 10^{-16}$ sq. cm. (Bijvoet, Claassen, and Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 529; Huggins and Magill, *J. Amer. Chem. Soc.*, 1927, **49**, 2357). Therefore to produce one layer of iodide molecules on the inner surface of the manometer we need $20/4{\cdot}4^2 \times 10^{-16} = 10^{16}$ molecules, *i.e.*, $10^{16} \times 454/6{\cdot}06 \times 10^{23} = 0{\cdot}75 \times 10^{-5}$ g. Since we found a decrease of 12% of 40 mg., about 5 mg. should be adsorbed on the wall, and the thickness of the layer would be $(5 \times 10^{-3})/(0{\cdot}75 \times 10^{-5})$, *i.e.*, more than 500 molecules. Such a result is very improbable, for it cannot be understood why the glass wall should exert its influence on molecules separated from it by so many layers. Hence we may conclude that adsorption is probably not the cause of the behaviour of mercuric iodide.

To determine whether a slight reaction between glass and mercuric iodide was responsible for roughening the glass surface or for the formation of mercury silicate at higher temperatures, the following experiments * were carried out. In a bulb of combustion glass of about 25 c.c. capacity 5·6 g. of powdered glass of the same origin were heated above 600° in a vacuum to remove adsorbed water and air; a known amount of mercuric iodide was rapidly introduced, and the bulb was evacuated again and sealed off. The tube was then heated in an electric furnace at 600—650°, and mercuric iodide was sublimed in the point of the vessel, which was broken off, weighed, heated until all the iodide was driven off, and weighed again.

(1) Introduced 139·4 mg., heated for 24 hours at 650°, regained 139·7 mg.

(2) Introduced 101·8 mg., heated for 20 hours at 600°, regained 101·6 mg.

Since in the experiments with glass-spring indicators the heating was at 550—600° and lasted only for 1 hour, it is evident that not the slightest reaction could have taken place in that case.

(*e*) *Behaviour of Other Substances.*—It was desirable to know if other substances showed similar phenomena when treated in the same way. Accordingly preliminary experiments were made with mercuric chloride and bromide, iodine, mercurous chloride, and

* These two tests were done in the chemical laboratory (Remsen Hall) of the Johns Hopkins University. I am indebted for this part of the work and also for the interest they have taken in this paper to Drs. Patrick and Frazer.

mercury; the first three showed continuous transformations to the Gay Lussac curve, especially mercuric bromide, which showed decreases up to 25% even without glass powder. The other two substances, on the other hand, showed sharp breaks, and no decreases were observed even after heating for some hours at 600°. These experiments are being continued.

Summary.

1. Mercuric iodide exhibits a continuous passage from the saturation curve to the Gay Lussac line, similar to that found by McHaffie and Lenher for water and benzene and by Frazer, Patrick, and Smith for toluene. The deficiencies in vapour pressure for mercuric iodide and certain other substances are, however, much larger.

2. No reaction could be detected between glass and mercuric iodide.

3. The effect is independent of the degree of dryness.

4. The introduction of glass powder into the vessel augments the effect.

5. A plane glass surface does not prevent the phenomenon, contrary to the results of Frazer, Patrick, and Smith with toluene and water.

6. Adsorption cannot explain the phenomenon, for the layers would have to be more than 500 molecules thick, and this is regarded as very improbable.

I take this opportunity to thank Prof. Dr. A. Smits and Dr. J. M. Bijvoet for the interest they have taken in this paper.

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