CLXIX.—*The Effect of a Gas upon the Pressure of a Vapour.*

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The work of Regnault (*Ann. Chim. Phys.*, 1845, **15**, 129; *Mem. Acad. Sci.*, 1862, **26**, 679) and others shows quite conclusively that the pressure of a saturated vapour in equilibrium with its liquid is lowered by the presence of an indifferent gas. Campbell (*Trans.*

Faraday Soc., 1915, **10**, 197), in particular, in a study of the saturated vapour pressures of eight different liquids in contact with air, hydrogen, and carbon dioxide, observed and measured this effect and showed that in certain cases it attained a considerable magnitude, the vapour pressures of chloroform and methyl alcohol in an atmosphere of carbon dioxide, for example, being only about three-quarters of the values in the absence of the gas.

It follows that the concentration of a saturated vapour in a gas is not a true measure of the vapour pressure of the liquid and, therefore, that the very large number of "vapour pressure" measurements which have been made by the gas-saturation method are subject to an error, unknown in extent but, in some cases at least, of very considerable magnitude.

Campbell advanced the theory that the low values he obtained were due to the adsorption of gas at the liquid–gas interface, and we have sought, in the work now reported, to apply a crucial test of the validity of his view, according to which, evidently, in the absence of liquid a gas should have no effect on the pressure of a vapour. We have therefore measured independently both the concentration and the pressure of a vapour in the presence and in the absence of a gas, the gas used being carbon dioxide and the vapour either (1) ether or (2) pentane. It seems rather remarkable that, though many so-called measurements of vapour pressure (being in fact measurements of vapour concentration in a gas) have given results differing in a systematic fashion from those of true vapour-pressure measurements in the absence of gases, there is no recorded case of the precise measurement simultaneously of the pressure and the concentration of a vapour. Admittedly the experimental difficulties of such measurements are considerable, but the results are likely to be of great interest.

The method here described is so laborious as to be unsuitable for the investigation of a large number of cases. Attempts are therefore being made to develop a simpler and more speedy technique without substantial loss of accuracy. Meanwhile the present results are recorded, as they appear definitely to contradict the view that the diminution of vapour pressure of a liquid in presence of a gas can be wholly attributed to the effects of solution or adsorption of gas in the liquid.

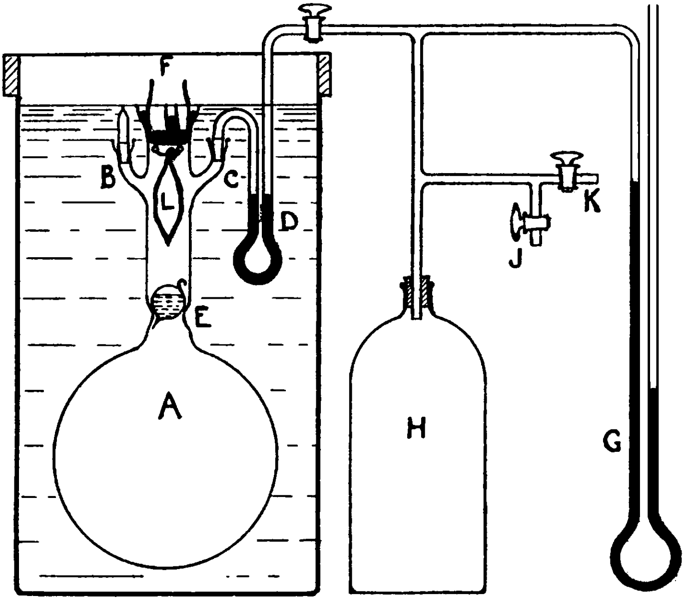
EXPERIMENTAL.

The ether used was prepared from a specially good commercial sample, supplied by Messrs. McFarlane, by repeated fractional distillation from metallic sodium after standing for some months over solid caustic potash and potassium permanganate. Carbon dioxide was prepared from marble in a Kipp's apparatus, well washed, and dried over phosphoric oxide.

To determine the concentration : pressure ratio for ether, precisely known weights of the liquid were taken in evacuated sealed glass bulbs, these were broken in a glass flask of known volume, previously either evacuated or filled with carbon dioxide at a known pressure, and the resulting pressure change was measured.

Thin-walled glass bulbs having a capacity of 3—10 c.c. were charged with various quantities of ether by the method of Briscoe and Little (J., 1914, **105**, 1326). Each bulb was weighed against a tare to 0·01 mg. before and after filling and sealing, a correction being applied for the weight of air excluded from the bulb when finally weighed.

FIG. 1.



The apparatus used is shown diagrammatically in Fig. 1. A flask, A, of about 1200 c.c. capacity, had the neck indented at E to support the bulbs and was closed by a mercury-sealed ground glass stopper F. The stopper carried two sealed-in platinum wire loops, from which a chisel-ended glass hammer, L, was suspended by means of a bridge of tin fuse-wire. By connecting the platinum leads to a 6-volt accumulator the tin wire suspension could be fused at will, thus releasing the hammer, which smashed the bulb and (if all went well) was itself held by the indentations.

Two side tubes carrying mercury-sealed ground joints were provided: B was used for evacuation or introduction of gas, and C was connected through the mercury-filled isoteniscope, D, to a large bottle, H, and the manometer G. The pressure in H could be regulated with nicety by evacuation at J or admission of air at K. The flask and isoteniscope were immersed in a large glass-sided thermostat maintained electrically at 25·00° ± 0·002° and a microscope was used to observe equality of pressure on the two sides of the isoteniscope, the cross-wire being set upon the images of the menisci while both sides were open to the atmosphere. The pressure in H, when shown in this way to be equal to that in A, was observed, by means of a good cathetometer reading to 0·02 mm., on the manometer, G, the limbs of which were made of 9 mm. internal diameter in order to minimise capillary errors.

In determining unsaturated vapour pressures in the absence of gas, the flask was first thoroughly evacuated through B and this tube was sealed off. Then the pressure in H was reduced until the levels of mercury in the isoteniscope D were exactly equal, and the pressure was read on the manometer. The bulb was then broken and when, after the lapse of 3—4 hours, the pressure in A had become constant, the pressure in H was again adjusted to precise equality with that in A and read on the manometer.

The difference in the manometer readings, corrected to 0°, then measured the unsaturated vapour pressure due to a known weight of ether contained in a space given by the internal volume of the flask and side tubes *less* the volumes of the hammer and the broken glass of the bulb. The gross internal volume of the flask was ascertained by weighing it filled with water in the usual way.

Determinations of unsaturated vapour pressures in the presence of carbon dioxide were made in a similar way, except that the flask was first filled with carbon dioxide at a pressure of approximately 500 mm., which was accurately read after it had attained a constant value. Then the bulb of ether was broken as before and, after the pressure had become constant (8—10 hours), the pressure in the flask was again read. In cases where the pressure within the flask was greater than that of the atmosphere, compressed air was introduced through the tap K. The observed rise in pressure within the flask was slightly less than the true pressure exerted by the ether vapour, because when the bulb was broken the carbon dioxide had increased in volume by an amount equal to the internal volume of the bulb. Thus, in a typical case :—

Pressure of CO_2 before breaking of bulb = 495·58 mm. Hg.
Internal volume of bulb = 3·28 c.c.
Final total volume of CO_2 + ether vapour = 1208·89 c.c.
Pressure of CO_2 alone in the volume occupied by ether vapour and $CO_2 = 495{\cdot}58 \times \dfrac{1208{\cdot}89 - 3{\cdot}28}{1208{\cdot}89} = 494{\cdot}24$ mm. Hg.

Stress is laid upon the necessity for this correction, because it appears to have been overlooked by Campbell (*loc. cit.*) in his application of a method similar in principle to that now described.

The experiments with pentane were performed in a precisely similar manner to those with ether. The pentane was a pure sample supplied by Messrs. Kahlbaum.

	No.	Corrected net volume of flask (c.c.).	Initial pressure (mm. Hg at 0°).	Final pressure (mm. Hg at 0°).	Vapour pressure (mm. Hg at 0°).	Weight of vapour (g.).	Vapour pressure of 1 g. vapour per litre.
Ether in vacuum	1	1208·30	1·82	44·87	43·05	0·20374	255·3
	2	1208·54	0·38	106·81	106·43	0·51787	247·8
	3	1208·97	0·56	108·38	107·82	0·52624	247·7
	4	1208·62	0·76	173·11	172·35	0·83987	248·0
	5	1208·47	0·31	243·39	243·08	1·18576	247·7
	6	1208·53	0·50	445·01	444·51	2·20679	243·4
Ether in carbon dioxide	7	1208·89	*494·24	537·07	42·83	0·20552	251·9
	8	1208·36	*499·81	710·46	210·65	1·04588	243·4
	9	1208·48	*497·21	757·19	259·98	1·29962	241·8
Pentane in vacuum	10	1205·96	0·05	137·51	137·46	0·65710	252·3
	11	1205·98	0·05	368·79	368·74	1·78672	248·9
	12	1208·46	0·12	534·31	534·19	2·48909	259·4
	13	1206·09	2·54	520·28	517·74	2·52863	247·0
Pentane in carbon dioxide	14	1206·25	*497·14	782·47	285·33	1·48577	231·7
	15	1206·31	*497·70	954·47	456·77	2·27006	242·7

* Corrected for internal volume of weighing bulb.

The results of these experiments are shown in the above table and, although in the case of ether they are less consistent than was to be expected from the precautions taken, yet they show a definite lowering of the unsaturated vapour pressure in the presence of carbon dioxide at a pressure of approximately 50 cm. of mercury. The effects of adsorption of ether upon the walls of the flask are very evident in that the unsaturated vapour pressure exerted by 1 g. of vapour in 1 litre of space diminishes progressively as the actual concentration of vapour increases. In this connexion it should be noted that the flask received the same treatment before each determination; it was scoured with a solution of chromic and nitric acids, washed thoroughly with pure water, alcohol and ether, and dried by passing through it a current of pure air.

In comparing the unsaturated vapour pressures in a vacuum with those in carbon dioxide it is necessary, therefore, to consider corresponding vapour concentrations. Thus, if the results here recorded are plotted on a graph, the lowering of unsaturated vapour pressure on the basis of 1 g. of vapour per litre will be seen to vary from a minimum of 3·4 mm. to a maximum of approximately 5·9 mm. of mercury for ether in carbon dioxide at a pressure of approximately 50 cm. of mercury.

In the case of pentane there is a grave irregularity in the results obtained which is difficult to understand. It would appear, however, that the lowering of the unsaturated vapour pressure of pentane in presence of carbon dioxide is distinctly greater than the corresponding lowering of unsaturated vapour pressure of ether, but the results are put forward merely as indicating a general tendency.

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