

IX. "On the Critical Point of Mixed Gases." By GERRARD ANSDELL, F.C.S. Communicated by Professor JAMES DEWAR, M.A., F.R.S. Received June 8, 1882.

Having on two previous occasions communicated to the Society papers on the physical constants of liquid hydrochloric acid gas and liquid acetylene, under which head I include the coefficients of compression and expansion, the critical points, and the volumes and tensions of the saturated vapour, it naturally led up to what promised to be a long investigation into the similar constants of other gases; and, amongst other things, the behaviour of two or more gases in presence of each other, more particularly with regard to the alteration of the critical point, appeared to me of especial interest.

These experiments, which I commenced nearly two years ago, were unavoidably interrupted at the time, and I have only now been able to resume them.

This subject has latterly engaged the attention of many physicists and chemists, and, amongst others, both Andrews and Cailletet have examined to a certain extent the behaviour of gaseous mixtures, the former finding both the critical point and vapour-tension of carbonic acid considerably modified by the introduction of a small quantity of pure nitrogen, and the latter ("Compt. Rend.," 90, 210) noting the peculiar behaviour of carbonic acid with one-fifth its volume of air, the former appearing to mix completely with the latter at 130 atmospheres pressure and $5^{\circ}5$ C., forming a homogeneous mixture. More recently Amagat ("Compt. Rend.," 89, 1879) and Roth ("Wiedemann," N.F., 2, 1880) have contributed exhaustive papers on the deviation of gases from Mariotte's law. Clausius and Van der Waals have introduced new formulæ for calculating the critical point, Winkelmann (Berichte, N.F., 2, 1880), Hannay ("Proc. Roy. Soc.," vol. 33) and others have been examining the relation between the different states of matter, and Ramsay and Pawlewski have investigated the behaviour of different liquid compounds with regard to their critical points, &c.; the former took equal weights of pure benzene and ether, and found that the critical temperature and pressure of the mixture was just between those of the individual bodies, but as he evidently experimented with only the one mixture, his results do not bear much upon the present problem, for which these experiments were undertaken, namely, the variation of the critical points of different percentage mixtures of two or more gases. Pawlewski's results, which seem to have an important bearing on the subject, I shall refer to more fully afterwards.

Before selecting any particular gases for investigation, there were

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several important points to be considered. In the first place, it was advisable to select those gases which could not only be easily prepared, but whose physical constants had been thoroughly investigated; it would be an advantage to use gases having comparatively low critical points, as the temperature would be much more easily kept constant, and would consequently contribute to the accuracy of the results; but above all those gases should be chosen which would not be likely to react upon each other in a liquid state, or at high temperatures and pressures, for this would modify the results considerably, from the probable formation of new compounds, &c. That this is likely to occur is shown in Professor Dewar's experiments on the behaviour of carbonic acid in presence of other bodies ("Proc. Roy. Soc.," 1880), where the carbonic acid often appeared to exist in a liquid state far above its critical point. This was no doubt due to the formation of a new compound; at least, as it could not be pure carbonic acid, we can only regard it as a compound of some kind formed under particular conditions of temperature and pressure, and this supposition seems to be confirmed by the experiment of carbonic acid in presence of camphor, where the camphor undoubtedly formed a new body, for we know how readily it combines with numerous substances such as hydrochloric acid, &c., to form unstable compounds. For these reasons I chose carbonic and hydrochloric acid gases, as they could be easily prepared, and their critical points had been very accurately determined, the former by Andrews, the latter by myself, besides being bodies most unlikely to be decomposed in each other's presence, more especially as they are chemically saturated bodies, and therefore according to the new chemical theory, most unlikely to form any addition or molecular compound.

The following method was adopted in the experiments, the Cailletet pump being used as described in my former papers. The carbonic acid was made by dropping pure strong sulphuric acid into a saturated solution of potash bicarbonate, being afterwards washed with distilled water, and dried by passing through four U-tubes with pounded glass and sulphuric acid. To check the readings of the air manometer (which was the same used in my former experiments) and also the purity of the gas, a tube was filled with the pure gas alone, and the tensions at different temperatures and the critical point were found to agree very well with Andrews' results. The hydrochloric acid gas was prepared by the action of strong sulphuric acid on pure chloride of ammonium, as described in my last paper ("Proc. Roy. Soc.," vol. 30), and was washed and dried with the usual precautions; a tube was also filled with the pure gas to begin with, and the critical point and tensions of the saturated vapour agreed as nearly as possible with those obtained by myself two years ago.

The purity of the individual gases and the accuracy of the air mano-

meter having thus been proved, an ordinary Cailletet tube was chosen, having a capillary part about 2 millims. in diameter, and a total capacity of about 50 cub. centims. This was accurately calibrated, and then filled with the hydrochloric acid gas, by passing it through in a regular stream for about four or five hours; after sealing off, the bent end was placed under pure dry mercury, under the receiver of an air-pump, and a sufficient quantity of the gas withdrawn to make room for any amount of carbonic acid gas required to be introduced; the introduction was effected by passing a very fine capillary tube, bent at a particular angle and through which pure carbonic acid was streaming, round the bend of the tube while it remained under mercury, great care being taken to prevent the slightest trace of air from getting in. When sufficient carbonic acid had been introduced the tube was transferred to one of the iron bottles containing pure dry mercury, which was connected with another iron bottle containing the air manometer, and with the pump in the usual way.

The critical point of the mixture was first determined, and then the tensions of the saturated vapour at different temperatures, together with the fractional volume to which the gas was reduced at the point of liquefaction, and also the relation between the liquid and gaseous volumes at different heights in the tube.

At the end of the experiments the tube was carefully lifted out of the bottle, the outside of it well cleaned and dried with bibulous paper, and the end of it placed under distilled water. The small quantity of mercury in the bend of the tube was shaken out, and the water allowed to rush up the tube and absorb the hydrochloric acid gas; the solution was afterwards made up to 500 cub. centims. with distilled water, and 50 cub. centims. titrated with standard nitrate of silver, which gave the quantity of chlorine equal to the amount of hydrochloric acid in the tube. The small residue of mercury was dried and weighed, and the space it occupied subtracted from the total capacity of the tube, the remainder, after correction for temperature and pressure, being of course the volume of the mixed gases; from this was subtracted the volume of the hydrochloric acid gas calculated from the amount of chlorine obtained by titration, the remainder being carbonic acid, with, of course, any slight impurity of air or other inert gas that might be present.

The following tables give the tensions of the saturated vapour, at different temperatures, of the different percentage mixtures of pure hydrochloric acid and carbonic acid gases. They are also plotted in the form of curves on Plate I.

I.		II.		III.		IV.	
T.	P.	T.	P.	T.	P.	T.	P.
0	.. 27·84	0	.. 28·86	0	.. 33·17	0	.. 31·89
15	.. 40·66	13·8	.. 39·86	16·3	.. 50·09	19·0	.. 51·93
27	.. 54·22	25·5	.. 52·77	25·4	.. 63·98	25·6	.. 60·46
37·5	.. 70·28	38·0	.. 67·36	34·0	.. 77·02		
46	.. 82·26	44·0	.. 76·23	43·2	.. 90·03		
C.P.=47·2	.. 92·21	45·5	.. 80·52	45·1		39·5	.. 80·28

V.		VI.		VII.	
T.	P.	T.	P.	T.	P.
0 32·72	0 34·56	0 34·65
17·5 50·73	18·8 55·79	18·8 56·44
26·6 63·31	25·5 65·68	24·9 67·27
35·0 76·64				
37·6 79·14				
C.P.=38·0 81·35	33·5 77·69	32·4 77·23

I=mixture containing 17·18 per cent. CO₂.

II=	"	"	19·37	"	"
III=	"	"	25·48	"	"
IV=	"	"	42·44	"	"
V=	"	"	45·67	"	"
VI=	"	"	74·18	"	"
VII=	"	"	82·14	"	"

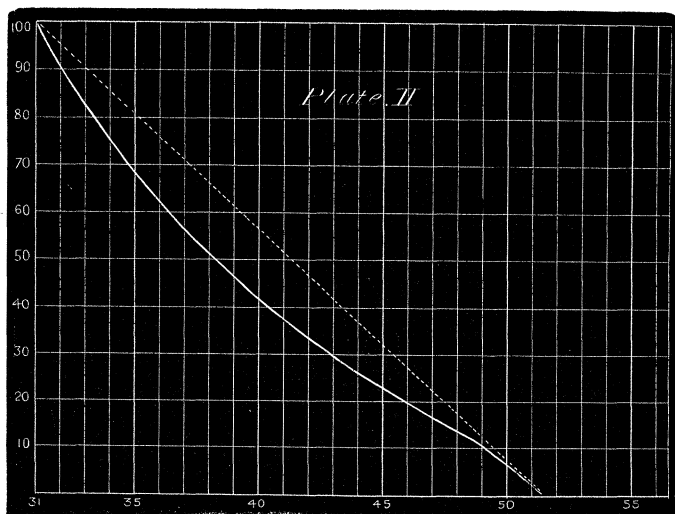
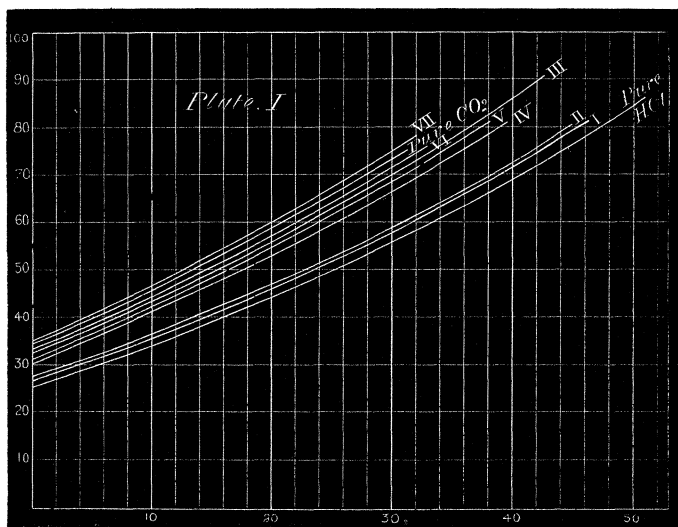
T=temperature of mixed gases.

P=pressure in atmospheres.

C. P.=critical point.

The critical points of the different mixtures are also plotted as a curve on Plate II, where the ordinates represent the percentage amount of carbonic acid in the mixture, and the abscissæ represent the temperature in degrees (centigrade). Now Pawlewski, in a short abstract of a paper ("Berichte," No. 4, 1882), describes a number of experiments he had made with the isomeric ethers, the alcohols, &c., and gives an equation to represent the critical point of mixtures of two or more liquids belonging to the same class of organic bodies, in terms of their respective critical points and relative weights, from which it would appear that the critical point of mixed bodies is directly proportional to the percentage composition of the mixture, when the origin of temperature taken is that of the body having the lowest critical point. He also mentions that this would probably be the case with the liquid form of substances which are gaseous at ordinary temperatures; but from our knowledge of liquefied gases, their physical constants are so much exaggerated with regard to their compression and expansion, &c.,

and the variation of their critical points is so much affected by small quantities of impurity, that we might naturally suppose gases having low critical points would not altogether follow this law, and the



results of my experiments seem to confirm this view. It will be seen from the diagram, Plate II, that instead of descending in a straight line as it ought to do, according to Pawlewski's formula, it forms a

very regular curve, all the values being below those of Pawlewski's, until a point is reached where the mixture contains about 17 per cent. of carbonic acid, within which limit it evidently approaches to Pawlewski's values. The reason for this apparent anomaly can only be explained by the assumption that a small trace of air or other impurity was present in the tube, for we know from Andrews' and my own experiments, that even the $\frac{1}{500}$ th part of air makes a considerable difference both in the critical point and tension of a gas.

It is also conceivable that a trace of air may have more effect in a mixture of two gases, than upon either individually, and this would consequently complicate matters considerably, when a mixture of several different gases is used. It was principally on this account that tensions of the saturated vapour of the mixture at different temperatures was taken, so as to judge of the amount of impurity in the gases, and whether it materially affected the results.

The curves on Plate I represent these tensions, the ordinates being the pressure in atmospheres, and the abscissæ the temperature in degrees C. The corresponding curves for pure hydrochloric acid and carbonic acid are also shown, but although all the curves for the different mixtures, except one, fall between the two, still the distances are evidently not strictly proportional to the percentage composition, which can only be explained by the presence of a small quantity of air; now, as this impurity must have been infinitesimal, it is interesting and curious to see how much it has modified the tensions of the saturated vapour. No. III should, of course, have come between No. II and No. IV, and must have had rather a larger amount of impurity than the others, and this is also the case in No. VII, which actually shows a tension higher than that of the most volatile constituent of the mixture, which, of course, is unprecedented.

Having satisfied myself that these apparent anomalies were really due to impurity, I filled another tube with extreme care, which contained the same relative proportions of the gases, within .2 of a per cent. as No. VII, and found that it now assumed its proper place below the curve for carbonic acid, the critical point, however, being scarcely altered at all, showing that an amount of impurity, sufficient to materially modify the tensions of the vapour, had very little effect on the critical point.

The present position of the question therefore appears to be, that the critical points of mixtures of liquefied gases cannot be expressed by Pawlewski's formula, the maximum difference between his calculated value and mine, which occurred in a mixture of equal volumes of the gases, being as much as $3^{\circ}6$ C. This is .2 or 25 per cent. of the whole difference between the critical points of the two gases, hydrochloric acid being $51^{\circ}25$, and carbonic acid 31° C.

But although these experiments seem to lead to this conclusion, more extended researches with other gases of the same nature, using the same precautions, will have to be made, before the real form of the curve can be ascertained.

This investigation has been carried out in the Laboratory of the Royal Institution.

X. "On an Arrangement of the Electric Arc for the Study of the Radiation of Vapours, together with Preliminary Results." By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received June 8, 1882.

In previous papers* we have described various devices for facilitating the study of the reversal of the lines of metallic vapour. The first series of observations were made by examining the spectrum of the interior of iron or porcelain tubes filled with vapour and heated to the highest temperature of a coke furnace, the subsequent series being eye or photographic records of the radiation of the electric arc surrounded by metallic vapour in the middle of blocks or tubes of lime or magnesia.

By inclosing the arc in a crucible of lime or magnesia we have found its steadiness very greatly increased, and the mass of metallic vapour which can be maintained at a temperature approaching to that of the arc much enlarged, but it cannot be said that that temperature is at all under control, and the walls of the crucible are almost always cooler than the contents. By the arrangement we have now to describe we are able to make observations through a long range of temperature, as the temperature rises and as it falls, and so to trace the influence of temperature in many cases in which the extent of that influence was before doubtful. The temperature attainable is doubtless far below that of the arc, but still it is quite sufficient to maintain iron and aluminium in the state of vapour, and show the reversal of the lines of these elements with singular sharpness. The temperature of the interior is sufficiently high to transform the diamond into coke, even in a current of hydrogen, and the result may be taken as proving that the temperature is above that of the oxyhydrogen flame.

The apparatus employed is thus constructed: A rod of carbon, *a* in the figure, 15 millims. in diameter, perforated down its axis with a cylindrical hole 4 millims. in diameter, is passed through a hole in a lime

* "Proc. Roy. Soc.," "On the Reversal of the Lines of Metallic Vapours," vols. 28, 29, 32.

Plate. I

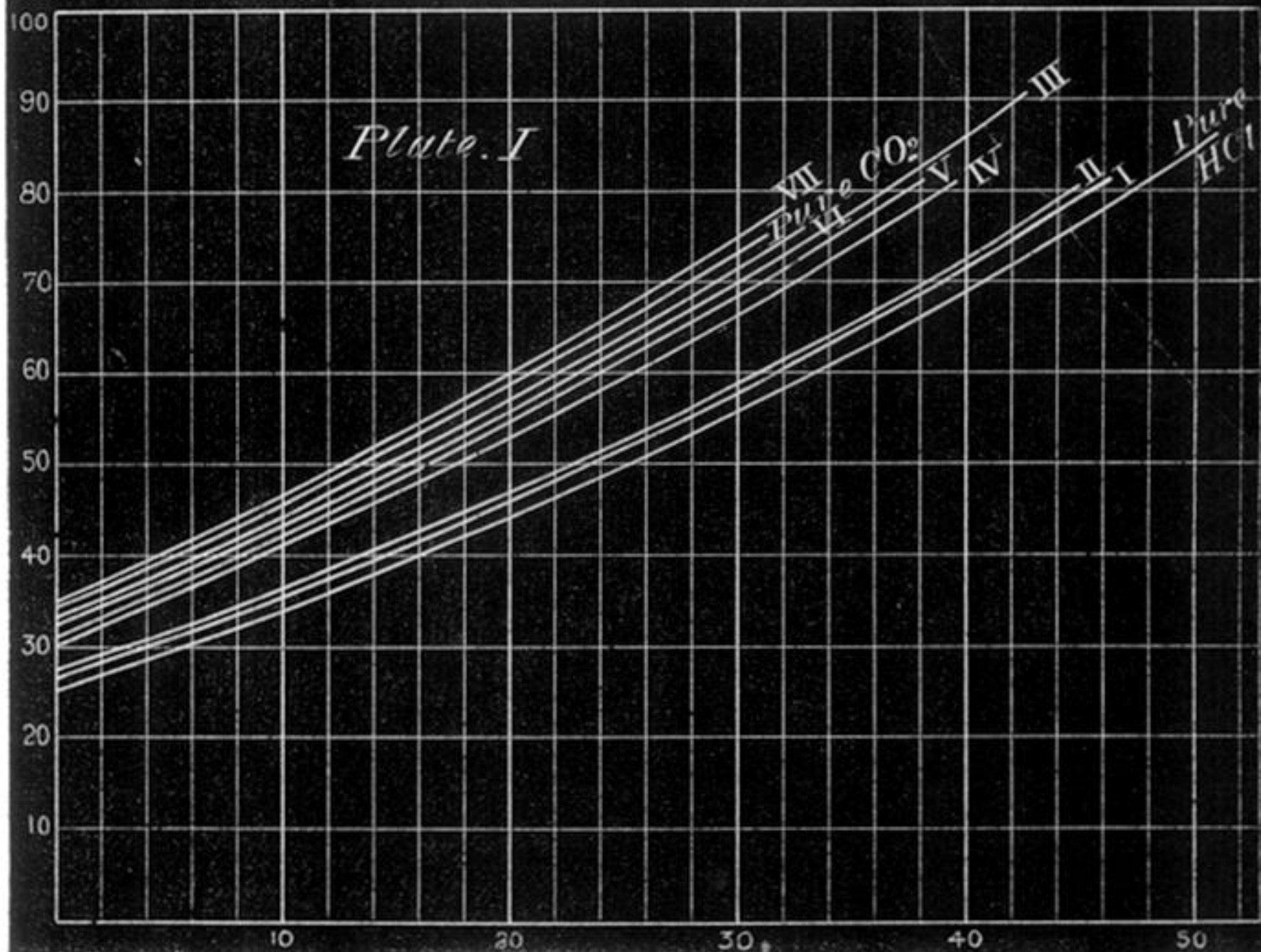


Plate II

