heptyl and octyl alcohols. The interposition of another CH_2 group between the alcohol group and the triple bond reduces the inductive effect of the latter although its influence is still felt. 1-Hydroxy-3-octyne and 1-hydroxy-3-nonyne have moments about 0.09 unit higher than the aliphatic alcohols. Dioxane was used as the solvent for the determination of the moments of the alcohols. Hydrocarbons promote the association of hydroxyl compounds and for this reason are not as suitable as dioxane. As the moments of the alcohols reported in the literature were determined in benzene as a solvent it was felt advisable to determine the moment of heptyl alcohol in dioxane. The moment of 1.70 found in dioxane checks well with the value 1.71 found in benzene.

Summary

1. The moments of the acetylenic halides have been shown to be influenced by the position of the triple bond. The influence is least with the chloro compounds and the greatest with the iodo compounds.

2. The moments of the acetylenic alcohols are higher than those of the normal aliphatic alcohols. The inductive effect is felt although there are two carbon atoms between the acetylenic carbon and the hydroxyl group.

3. The moments of 1-hydroxy-3-octyne, 1-hydroxy-3-nonyne, 1-hydroxy-2-heptyne, 1-hydroxy-2-octyne, 1-chloro-2-heptyne, 1-chloro-2-octyne, 1-bromo-2-heptyne, 1-bromo-2-octyne, 1-iodo-2-heptyne, 1-iodo-2-octyne and 1-hydroxyheptane have been determined and reported.

NOTRE DAME, IND. RECEIVED FEBRUARY 7, 1935

[CONTRIBUTION FROM THE WALKER LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

The Binary System Lead Iodide–Lead Oxide[1]

BY HENRY S. VAN KLOOSTER AND ROBERT M. OWENS

Lead iodide, when heated in air, decomposes with the liberation of iodine and the formation of oxy-iodides.[2] None of the oxy-iodides which have been reported in the literature[3] have been examined from the standpoint of the phase rule. The authors decided therefore to determine the phase diagram of the binary system lead iodide–lead oxide by means of heating and cooling curves. The melting point of lead iodide has been previously found to be 412°.[4] The melting point of lead oxide has been recorded in the literature as high as 906°[5] and as low as 835°.[6] Quite recently Addink[7] determined the melting point of pure lead oxide in a platinum crucible and found the value 884 ± 1°, which has been used by the authors in this investigation.

Apparatus and Materials.—The apparatus was substantially the same as that used previously[4] to prevent the decomposition of the lead iodide. For the low-melting mixtures ordinary glass tubes were satisfactory, for those with more than 45% lead oxide Pyrex tubes were used. The 87 and 90% PbO mixtures were fused in stainless steel and in nickel tubes in which the bare thermocouple was inserted. The wires had to be rewelded after each experiment when used unprotected since they became badly corroded by the fused mixtures. The lead iodide and lead oxide were Baker C. P. products which were used without further purification. Undercooling on solidification was small in melts containing not over 50% of lead oxide and did not exceed more than 5 to 10°. In melts rich in lead oxide the undercooling and the resulting discrepancies in the values found on heating and on cooling were quite considerable as can be seen from the table. The data obtained from heating curves, therefore, were used exclusively for the construction of the diagram on the PbO side. This procedure, which has been recommended in cases where crystallization is slow and undercooling large,[8] was followed for another reason also, *viz.*, the attack on the glass wall and the porcelain thermocouple-tube by the molten mixtures rich in lead oxide. Since the heat ab-

(1) A thesis presented by Robert M. Owens in partial fulfilment of the requirements for the degree of Chemical Engineer at Rensselaer Polytechnic Institute.

(2) R. Brandes, *J. pharm. Chim.*, [2] **41**, 33 (1829).

(3) Mellor, "Treatise," Vol. VII, p. 766.

(4) Henry S. van Klooster and Edwin I. Stearns, THIS JOURNAL, **55**, 4121 (1933).

(5) Doeltz and Mostowitsch, *Metallurgie*, **4**, 289 (1907).

(6) R. Ruer, *Z. anorg. allgem. Chem.*, **49**, 365 (1906).

(7) N. W. H. Addink, *Proefschrift*, Utrecht, 57 (1933).

(8) Findlay, "The Phase Rule," 1927, p. 107.

sorption effects were, as a rule, quite small, no greater accuracy than ±10° can be claimed.

EXPERIMENTAL RESULTS

h indicates values taken from heating curves

Mole % PbO	Heat effects, °C. Primary		Secondary		Tertiary
0	412				
5.00	400		356		
10.03	393		360		
15.02	388		360		
20.00	377		366		
25.08	370				
30.00	364				
35.00	408		368		
40.00	435		363		
42.05		463h		370h	
45.00	505		350		
50.00	548		348		
52.00		593h		463h	
55.00		605h		465h	
60.00	610	614h		463h	354
61.87	553	616h		463h	348
65.00	615	619h	447	468h	341
67.04	613	620h	468	463h	
70.00	623	630h			
74.98	613	635h			
79.03	635	643h			
80.04	618	657h			
84.42		675h		651h	
87.01		735h			
90.00		770h			

Discussion of Results.—The phase diagram as drawn on the basis of the experimental data is given in Fig. 1 and indicates the existence of several compounds, one of which, made up of equimolecular quantities of the components, has an incongruent melting point at 465°. The compound $PbI_2 \cdot 2PbO$ melts at 620°, while the compound $PbI_2 \cdot 4PbO$ melts around 650°. The evidence in this case is not conclusive on account of possible errors due to contamination of the melts by the surrounding container. In fact, in some of the melts rich in oxide, tiny globules of lead collected at the bottom of the tube. The color of the brittle crystalline material was yellow-orange as far as about 60% oxide; melts containing 65, 67 and 70 mole per cent. of lead oxide were pale green and those with more than 70% lead oxide were reddish-orange. A comparison of this system with the analogous systems PbF_2–PbO, $PbCl_2$–PbO and $PbBr_2$–PbO, the first and third of which were investigated by Sandonnini[9] and the second by Ruer,[5] shows that, with the exception of the first, in which no compounds are formed, in all cases the ratios in which lead oxide combines with the lead halide are as 1:1, 1:2 and 1:4.

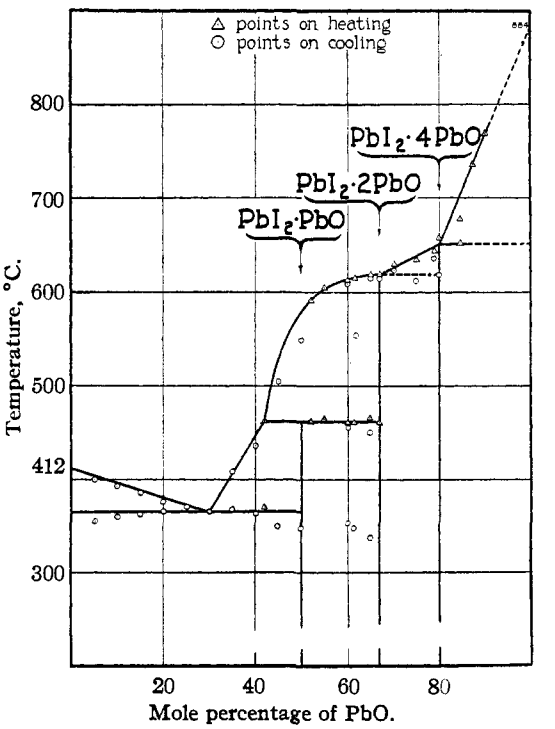

Fig. 1.—The system PbI_2–PbO: △, points on heating; ⊙, points on cooling.

Summary

The system PbI_2–PbO has been examined as far as 90% PbO. A eutectic was located at 30 mole per cent. PbO and 365°. The compound $PbI_2 \cdot PbO$ decomposes at 465° into a melt of 42% PbO content and the compound $PbI_2 \cdot 2PbO$. The latter melts around 620°. The existence of $PbI_2 \cdot 4PbO$, melting at 650° is tentatively indicated.

TROY, N. Y. RECEIVED FEBRUARY 8, 1935

(9) G. Sandonnini, *Atti accad. Lincei*, [5] **23**, I, 959 (1914).