CCXXXVIII.—*The Ternary System Lead Oxide–Nitrogen Pentoxide–Water.*

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As in the case of many other heavy metals, numerous basic nitrates of lead have been described in the literature; Mellor (" Treatise on Inorganic and Theoretical Chemistry," Vol. VII, p. 867) reports the methods of preparation and properties of the following :

$6PbO,N_2O_5,H_2O$; $4PbO,N_2O_5,xH_2O$; $3PbO,N_2O_5,3H_2O$; $2PbO,N_2O_5,H_2O$; $10PbO,3N_2O_5,4(\text{or } 5)H_2O$; $10PbO,3N_2O_5,H_2O$; $3PbO,N_2O_5,H_2O$; $2PbO,N_2O_5,2\frac{1}{2}H_2O$; $5PbO,N_2O_5$; $3PbO,N_2O_5$; $3PbO,2N_2O_5$.

None of the above compounds has been prepared according to phase-rule principles, and many of these probably represent merely mixtures of variable ratios of the components. Attempts to free the basic compound from adhering mother-liquor by washing, to eliminate water by drying in a water-bath, etc., have so often led to fallacious conclusions concerning the identity of basic salts that a systematic investigation of the three-component system lead oxide–nitrogen pentoxide–water at 25° and 50° was undertaken. The compositions of the solid phases were found by the " residue " method of Schreinemakers (*Z. physikal. Chem.*, 1893, **11**, 76), and Gibbs's triangular method was used in plotting results.

EXPERIMENTAL.

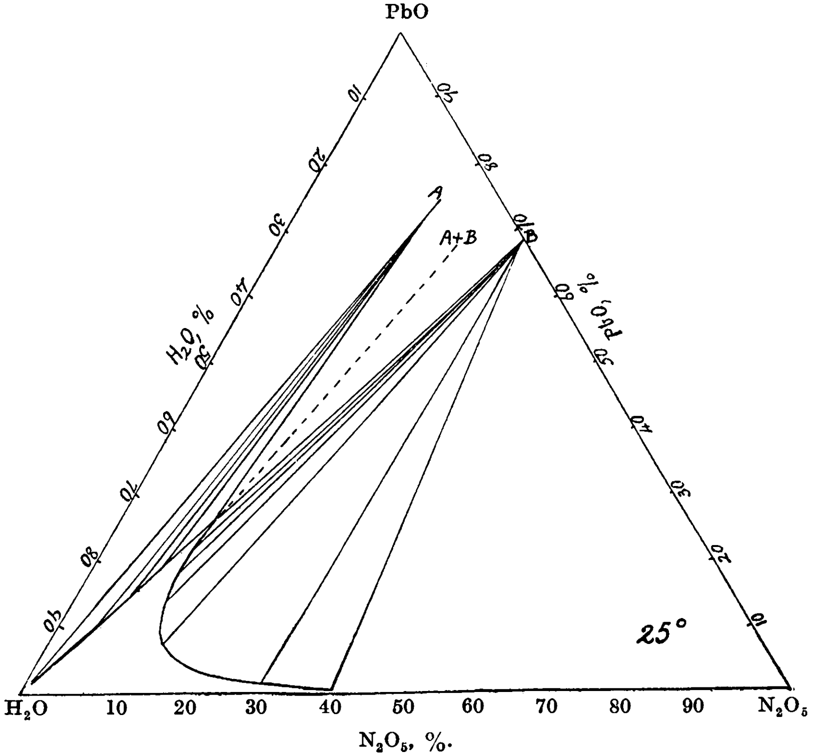
In the estimation of the lead, the solution was first neutralised with sodium hydroxide and then faintly acidified with acetic acid. The precipitation of lead chromate was then effected according to standard procedure. In the analysis of wet solids, solution was first effected in nitric acid and the above method subsequently followed. The nitric acid content was determined as in the preceding paper. Owing, however, to the precipitation of the lead in a very spongy form by Devarda's alloy, low results were at first obtained in blank tests. In order to overcome this the following procedure was adopted. The solution of lead salt was run into an excess of saturated sodium sulphate solution. Immediate coagulation of the lead sulphate ensued and the volume was then brought up to 200 c.c. by addition of water. Rapid settling took place. The supernatant clear liquid was decanted into a distilling flask, the precipitate washed with another 200 c.c. of water, and the filtrate added to the flask. The nitrate reduction then proceeded smoothly and quantitatively.

In making up complexes on the acid side of the graph, in many cases a saturated solution of lead nitrate was prepared at a temperature lying 40—50° above the final temperature of the experiment. To this hot solution sufficient nitric acid was added to bring the concentration approximately to the desired point. The bottle containing the complex was then sealed off, placed in the thermostat at 25° or 50°, and the shaker started. In other cases, a solution saturated with lead nitrate at the temperature of the thermostat was used, the necessary amount of nitric acid being then added to give the desired concentration. In such experiments the bottles were shaken for several days longer than usual. In all cases the solid–solution tie-lines intersected at the same point, irrespective of the method used in the preparation of the complex. Basic complexes were prepared from lead nitrate solution, saturated at a slightly higher temperature, to which freshly precipitated lead hydroxide had been added. The duration of the shaking varied from 3 days for the more concentrated solutions to a fortnight for the dilute solutions. The method of obtaining samples for analysis was substantially as described in the preceding paper. From the weights of lead and nitrogen found by analysis in a known weight of solution or of residue, the solution density (*D*) and percentage composition were calculated.

		Solution.			Residue.			
No.	*D*.	N_2O_5.	PbO.	H_2O.	N_2O_5.	PbO.	H_2O.	Solid phase.
				Data at 25°.				
1	1·022	0·71	2·09	96·20	15·64	65·64	18·72	A
2	1·134	4·67	9·77	85·56	15·77	63·98	10·25	A
3	1·223	7·68	15·03	77·29	15·39	60·71	23·90	A
4	1·287	8·80	18·39	72·81	15·98	62·98	21·04	A
5	1·433	12·20	25·70	62·10	16·63	61·35	22·02	A
6	1·452	12·27	26·38	61·35	23·06	67·63	9·31	A, B
7	1·408	11·54	23·61	64·85	26·93	58·31	14·76	B
8	1·387	11·70	22·61	65·69	24·45	52·90	22·65	B
9	1·328	11·83	18·88	69·29	28·77	59·74	11·49	B
10	1·257	12·06	14·09	73·85	27·00	55·50	17·50	B
11	1·194	14·30	8·16	77·54	27·32	51·91	20·77	B
12	1·192	14·60	7·40	78·00	28·84	56·60	14·56	B
13	1·236	30·59	1·59	67·82	32·25	56·74	11·01	B
14	1·243	30·70	1·38	67·92	32·06	25·26	42·68	B
15	1·290	40·05	0·49	59·46	35·56	40·73	23·71	B
				Data at 50°.				
1	1·022	0·60	2·69	96·71	15·50	64·64	29·86	A
2	1·059	2·01	5·28	92·71	16·00	64·00	20·00	A
3	1·117	4·39	8·99	86·62	17·00	67·47	15·53	A
4	1·133	4·72	10·27	85·01	15·67	62·56	21·77	A
5	1·229	7·24	15·81	76·95	16·10	63·27	20·63	A
6	1·322	9·55	20·47	69·98	17·22	72·15	10·63	A
7	1·436	11·60	25·45	62·95	16·53	65·67	17·80	A
8	1·480	12·27	27·16	60·57	17·10	64·60	18·30	A
9	1·562	13·95	29·92	56·13	17·21	63·43	19·36	A
10	1·590	14·47	31·00	54·53	23·00	66·23	10·77	A, B
11	1·511	14·22	26·05	59·73	28·84	61·10	10·06	B
12	1·443	14·19	24·72	61·09	29·20	60·83	9·97	B
13	1·420	14·33	23·42	62·25	30·10	63·40	6·50	B
14	1·357	14·22	19·77	66·01	29·52	59·28	11·20	B
15	1·323	14·80	17·69	67·51	29·35	61·20	9·45	B
16	1·279	15·08	15·64	69·28	29·97	62·13	7·90	B
17	1·258	16·08	12·79	71·13	27·73	53·35	18·92	B
18	1·234	17·92	10·08	72·00	30·09	62·00	7·91	B
19	1·221	19·18	7·93	72·89	29·00	54·94	16·06	B
20	1·211	23·75	4·27	71·98	28·92	44·04	27·04	B
21	1·233	29·95	2·41	67·64	31·07	44·81	24·12	B
22	1·244	32·32	1·74	65·94	32·04	51·30	16·66	B
23	1·261	35·91	0·51	63·58	33·35	46·16	20·49	B
24	1·308	45·33	0·04	54·63	37·69	39·00	23·31	B

The only solid phases which the graph indicates as capable of existence in stable equilibrium in the system at 25° and 50° are therefore Phase A ($2PbO,N_2O_5,2\frac{1}{2}H_2O$) and Phase B, $Pb(NO_3)_2$. The basic nitrate has been described by Senderens (*Bull. Soc. chim.*, 1894, **11**, 426; 1896, **15**, 214), who obtained it in the form of monoclinic needles by acting on a solution of lead nitrate with lead. Though it is possible that a temperature nearer the boiling point of the solution might lead to the appearance of another basic nitrate, the methods of preparation used by other workers do not suggest that the solids separated are likely to have been definite chemical compounds. This point will, however, be further tested. No evidence of the existence of a hydrated form of lead nitrate is to be

FIG. 1.



obtained from the graph, in agreement with the fact that no record in the literature of any such hydrate is to be found. The specific gravity–N_2O_5 graphs for the solutions show a well-defined break at the point of transition of the basic nitrate into the normal salt (Figs. 3 and 4).

Summary.

1. The composition of the solid phases in equilibrium with solutions in the system $PbO–N_2O_5–H_2O$ has been determined at 25° and 50°, the " residue " method of Schreinemakers being used.

FIG. 2.

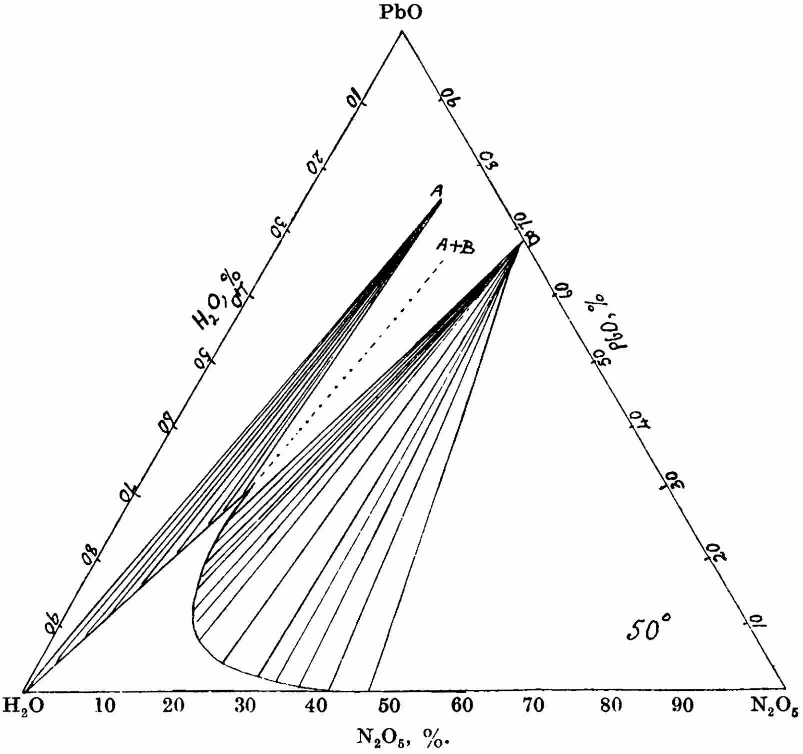


FIG. 3. (25°.)

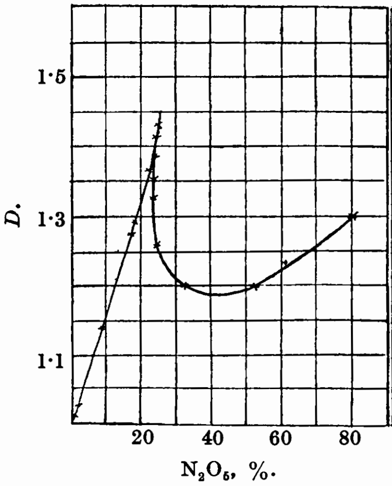
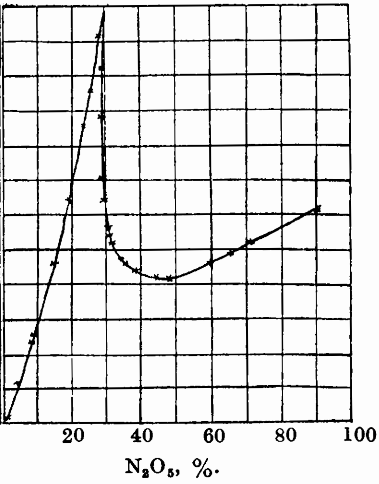


FIG. 4. (50°.)



2. The only basic nitrate at these temperatures is $2PbO,N_2O_5,2\frac{1}{2}H_2O$.

3. No evidence of the existence of a hydrate of the normal nitrate at these temperatures has been obtained.

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