140. *A Thermal Analysis of the System Lithium Nitrate–Thallous Nitrate.*

By HENRY VINCENT AIRD BRISCOE, CARADOC EVANS, and PERCY LUCOCK ROBINSON.

SEVERAL binary systems in which thallous nitrate is one of the components have formed the subject of thermal analyses. Although the nitrates of sodium and of potassium have been paired with it, the system involving lithium nitrate had not been studied hitherto. We therefore describe this system, thus closing an obvious gap in our knowledge of the alkali-metal nitrates.

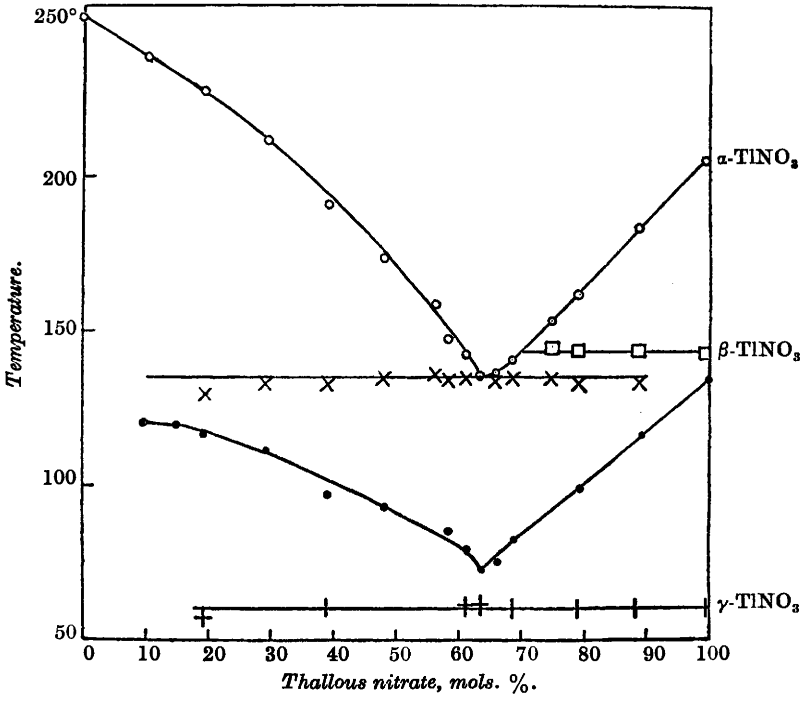
EXPERIMENTAL.

Preparation of Materials.—Anhydrous lithium nitrate was obtained from the trihydrate by keeping it for several days in thin layers on plates in an evacuated desiccator containing phosphoric oxide. That the resulting material was reasonably pure and free from moisture is evinced by the m. p., *viz.*, 252·0° ± 0·2° (Carnelley, J., 1876, **29**, 489, gives 267°; Carveth, *J. Physical Chem.*, 1898, **2**, 209, gives 253°). Thallous nitrate was prepared by dissolving pure metallic thallium in hot nitric acid (50% by vol.); the nitrate, which separated on cooling, was well washed with water, recrystallised six times from water, and finally dried as in the case of lithium nitrate. It melted at 206·0° ± 0·2° (Crookes, J., 1864, **17**, 112, gives 205°; Retgers, *Z. physikal. Chem.*, 1889, **4**, 593, 205°; Bergmann, *J. Russ. Phys. Chem. Soc.*, 1922, **54**, 200, 207°; Jaeger, *Z. anorg. Chem.*, 1917, **101**, 111, 206°), and the transitions from the α- to the β-form and from the β- to the γ-form occurred at 143·5° and at 61·0° respectively [compare 151° and 80° (Gossner, *Z. Kryst.*, 1903, **38**, 110); 125° and 80° (Wallerant, *Bull. Soc. Min.*, 1905, **28**, 311); 142·5° and 72·8° (van Eyk, *Z. physikal. Chem.*, 1905, **51**, 721); 144·6° and 75° (Bridgman, *Proc. Amer. Acad.*, 1916, **51**, 581); 142·5° and 78·5° (Bergmann, *loc. cit.*)].

Thermal Analysis.—Appropriate mixtures were made with weighed quantities of each component, the compositions being subsequently checked in the solidified melts by chemical analysis. For this purpose the centre portion of the melt only was employed, this being reduced to a coarse powder and made to yield three samples. About 1 g. was dissolved in 10 c.c. of warm water, and to it was added potassium iodide in minimal quantity to ensure complete precipitation of the thallous iodide. After settling over-night, the precipitate was collected on a tared Gooch crucible, washed free from precipitant with water, and dried to constant weight at 100° in an air-oven. The maximum difference in results for the three samples of one melt was never greater than 0·5%, and Table I records the mean value of the three analyses. The percentage of lithium nitrate was obtained by difference from 100.

The mixtures were melted in Pyrex test-tubes, 11″ × 1″, and were sufficient to give a depth of liquid not less than 1·5″. A cork carried a glass sheath, thin-walled and drawn to a fine point, which accommodated the thermocouple, and was also provided with a hole through which the handle of a glass ring-stirrer passed. The hot junction of the thermocouple was thus located slightly below the centre of the melt, whilst the cold junction was surrounded with melting ice. The *P.D.*'s were observed on a thermocouple potentiometer (laboratory pattern, Cambridge Instrument Company), and were converted into degrees by means of a graph obtained by calibrating the couple at the b. p.'s of water, naphthalene (218°), and sulphur (444°). An accuracy of ± 0·5° is claimed for the temperatures recorded in Table I.

The tubes were heated in a vertical cylindrical electric furnace suitably wound and lagged for the purpose, and when their contents were completely molten they were allowed to cool, the rates being approximately 0·7°/min. at 250°, 0·51°/min. at 180°, and 0·41°/min. at 150°. The rates of cooling were recorded on the Sayce inverse-rate curve tracer (*J. Sci. Inst.*, 1930, 7, 354), from which the periods of arrest at the eutectic temperature were subsequently ascertained. The various melts showed little tendency to supercool, but every effort was made to avoid this by first ascertaining the approximate temperature of each arrest at liquidus and solidus respectively, and in subsequent runs stirring the melt vigorously at about these points.



The results are in Table I and have been used to construct the equilibrium diagram (Fig.).

TABLE I.

		Mean arrest temperatures.				
$TlNO_3$, mols. %.	$LiNO_3$, mols. %.	1st arrest.	2nd arrest.	3rd arrest.	4th arrest.	Period of arrest at m. p. of eutectic (mins.).
0	100	252°				0
10·52	89·48	239	120°			14·20
19·65	80·35	228	130		57°	18·10
29·70	70·30	212	133·5			22·48
39·51	60·49	191	133		60	35·24
48·30	51·70	174	135			39·36
56·60	43·40	159	136			45·25
58·30	41·70	148	134			46·03
61·38	38·62	143	135		61	51·40
63·78	36·22		136		61	58·21
66·21	33·79	136·5	134			55·08
68·77	31·23	141	134·5		60	49·20
75·00	25·00	154	145	135°		
79·35	20·65	162	144	133	60	33·30
88·65	11·35	184	144	133·5	60·5	17·7
99·65	0	206	143·5		60·5	0

Discussion of Results.

The system has proved to be a simple one, very similar in character to that of sodium nitrate–thallous nitrate (van Eyk, *Z. physikal. Chem.*, 1899, **30**, 430). It gives no evidence of compound formation over the range of temperature observed, or of solid solutions such as those shown by potassium nitrate–thallous nitrate (*idem, ibid.*). The single eutectic has a composition 63·8 mols. % $TlNO_3$, 36·2 mols. % $LiNO_3$, and melts at 136·5°, whereas the lowest parts in the liquidus curve for the nitrates of sodium and potassium are 162° and 182° respectively. The eutectic point is observable over a range of 80% in composition and remains fairly constant except for the customary falling off in regions far removed from the eutectic composition. The periods of arrest which are shown in the figure reach a well-marked maximum at the eutectic composition. The temperature of transition from α- to β-thallous nitrate is not affected by the presence of the lithium salt, and as the liquidus does not appear to be modified in form by this change, any possibility of the formation of mixed crystals containing an appreciable proportion of lithium nitrate is excluded. The observed transition from β- to γ-thallous nitrate is much lower than previously recorded, but as this has been found in the pure material as well as in the mixtures, no significance attaches to it other than as a correction of previous observations.

Acknowledgment is made to the Research Committee of this College for grants which provided the potentiometer and the Sayce inverse-rate curve tracer used in this research.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.
[*Received, February 2nd,* 1932.]