[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

The System Ammonium Nitrate–Lithium Nitrate

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The system ammonium nitrate–lithium nitrate was redetermined using the micro-melt-thaw method for most of the points on the curve and the usual macro-cooling curve method for the eutectic points and some check points on the curves. The material used was very pure and dried under various conditions in such a manner as to eliminate the possibility of decomposition. The melts used in the cooling curve method were protected from moisture by a stream of dry nitrogen flowing over them during each run. The resulting phase diagram contained three solubility curves, one for ammonium nitrate I, a second for ammonium nitrate II and a third for lithium nitrate. A metastable eutectic point was found at 79.5° and composition of 25.3% lithium nitrate. Another eutectic was found between the curves of ammonium nitrate II and lithium nitrate at a temperature of 90.5° and a composition of 26.6% lithium nitrate. While the curve for both forms of ammonium nitrate agreed well with those previously reported, over corresponding sections, the curve for lithium nitrate did not agree at all. On account of the shape of the lithium nitrate curve and the impossibility of obtaining consistent data for it, the authors suggest that possibly a second form of lithium nitrate may exist or a molecular compound may be formed.

The phase diagram for the system ammonium nitrate–lithium nitrate has been determined previously by Perman and Harrison[2a] and also by Campbell.[2b] The former (Perman and Harrison) employed the conventional cooling curve technique and found a eutectic point between ammonium nitrate II and lithium nitrate at 97° and a composition of 25% lithium nitrate. The latter (Campbell) used a "refined technique" and confirmed the results of Perman and Harrison.

The authors of this paper were interested in redetermining the system using the micro-melt-thaw method that Holmes and Revinson[3] employed in their redetermination of the system ammonium nitrate–sodium nitrate. This technique was considered by them more accurate for points on the solubility curves than any other method. As it is not useful for the determination of the eutectic points, the usual cooling curve techniques were resorted to in order to find the temperature at which the eutectic points occur.

Materials: Ammonium Nitrate.—The ammonium nitrate for all determinations was supplied by the Committee on Eutectics of the Research Council originally and thereafter by Prof. Edward Mack, Jr., of Ohio State University. The analysis supplied with it showed that it contained 100.01% ammonium nitrate.

The lithium nitrate (Baker Co. analyzed) was purified by conversion to the carbonate by means of pure ammonium carbonate. The resulting lithium carbonate was twice washed with distilled water and then converted back into the nitrate by reaction with freshly distilled nitric acid. From the solution so obtained very pure crystals of lithium nitrate were separated. The resulting crystals were dried by suction, and then spread out in a thin layer on a watch glass which in turn was placed in a desiccator for several weeks. During this period, it was removed frequently, ground in an agate mortar and returned to the watch glass in the desiccator.

Some of the lithium nitrate so purified was dried in an oven at 150° for several hours and then preserved in a desiccator over Anhydrone. Other portions were dried immediately before using in a stream of dry nitrogen at 140° for two hours. No oxides of nitrogen could be detected under the above conditions of drying.

Those samples used to determine the eutectic point at 90.4° were dried at room temperature in a high vacuum system to avoid the slightest possibility of decomposition. The various methods of drying the samples are indicated in the tables.

Construction of Solubility Curves.—It was the intention of the authors to apply the method of least squares to the data for the various curves, imposing restrictions that they intersect at the proper eutectic temperatures, as did Holmes and Revinson.[3] However, in this case the degree of arbitrariness was so much greater, due to the presence of three cooling curves rather than two, and to the greater scattering of the points on the various curves, that it was finally decided not to use the method after all but to draw the curves so as to pass close to as many points as possible, and still preserve the requirement that they meet at the correct eutectic temperature.

Figure 1 shows the solubility curve of ammonium nitrate I, designated as (A), that for ammonium nitrate II as (B), and that for lithium nitrate as (C). The precise data on which these curves are based are available as an ADI Document.[4] The dotted curve is that of Perman and Harrison[2a] and is added for purposes of comparison.

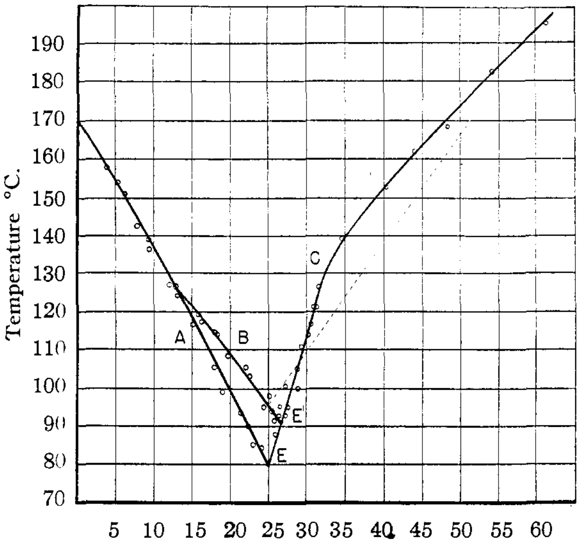

Fig. 1.

Interpretation of Results

One notices immediately that two new eutectic points have been discovered: a metastable one at a temperature of 79.5 (±0.3°) and 25.3% lithium nitrate; and another at 90.4 (±0.3°) and 26.6% lithium nitrate. The former (E) occurs at the intersection of the solubility curve for ammonium nitrate I (Curve A) and the solubility curve for lithium nitrate (Curve C) and the latter (E′) at the intersection of the solubility curve of ammonium nitrate II (Curve B) and that for the solubility of

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(1) Now Sr. Ernestine Marie.

(2) (a) E. P. Perman and W. R. Harrison, *J. Chem. Soc.*, **125**, 1709 (1924). (b) A. N. Campbell, THIS JOURNAL, **64**, 2680 (1942).

(3) Edward O. Holmes, Jr., and David Revinson, *ibid.*, **66**, 453 (1944).

(4) American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm with 1-inch size on 35 mm. film, or for 6 × 8 inch photocopies.

lithium nitrate (Curve C). Moreover, the latter eutectic point does not agree with that found by Perman and Harrison[2a] for these curves.

While curves (A) and (B) agree with those found by the above-mentioned authors over the corresponding parts of their ranges, curve (C) for lithium nitrate does not agree at all. Although curve (C′) is drawn as a continuous curve, it might as well have been drawn as two straight sections with a sharp break occurring at about 135° between them.

Experiments with cooling curves of pure lithium nitrate by the authors do not reveal any evidence of two forms of lithium nitrate. However, other experimenters have obtained results (private communications) that lead them to suspect a second form of lithium nitrate.

The authors feel that perhaps the difference between their results and those of former determinations on this system may be explained as a result of the extreme care that was taken to dry the samples thoroughly without any possibility of decomposition, and to keep them dry during the various determinations.

All samples used in the cooling curve method were dried in boats, either heating to a low temperature in dry air or nitrogen or keeping in a high vacuum until no further loss of weight occurred. The boats were then slipped into weighing bottles and stoppered, while still in the stream of dry nitrogen. Moreover, the tube in which the melts were made was pre-swept with dry nitrogen and continually bathed in this medium during each entire determination.

TABLE I

EUTECTIC POINT (E) FOR CURVES (A) AND (C) (COOLING CURVE METHOD)

%, $LiNO_3$	Temp., °C.	
23.53	79.5	Av. = 79.5°
23.75	79.5	Eutectic composition =
24.97	79.5	25.3 ± 0.3%
24.84	79.5	
Av.	79.5	

TABLE II

EUTECTIC POINT (E′) FOR CURVES (B) AND (C) (COOLING CURVE METHOD)

%, $LiNO_3$	Cor. eut. Temp., °C.	
19.7	90.2	Av. = 90.4 ± 0.3°C.
24.6	90.8	Eutectic comp. = 26.6
25.2	90.9	(±0.3%) $LiNO_3$
25.6	90.6	
26.0	90.2	
26.5	90.4	
27.4	89.9	
27.6	90.6	
29.0	89.2	
31.4	91.5	

Considerable difficulty was experienced in obtaining reproducible results by all methods used for the data of curve (C) as well as that of the eutectic point at temperature 90.4 ± 0.3° as the figures in Tables I and II will indicate. As the same methods gave good results for curves (A) and (B) and had previously been carefully proven on the system ammonium nitrate–sodium nitrate by Holmes and Revinson,[3] the trouble could be attributed to some as yet unknown peculiar property of lithium nitrate. If two forms existed in an equilibrium that shifted very slowly, the observed results might be explained, or possibly, a double salt with ammonium nitrate might be slowly formed.

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Chemisorption of Carbon Monoxide and the Heterogeneity of the Surface of Iron Catalysts

BY J. T. KUMMER AND P. H. EMMETT

Radioactive and non-radioactive samples of carbon monoxide have been added in succession as two separate fractions to a reduced iron synthetic ammonia catalyst at −195 or −78°. The chemisorbed carbon monoxide layer has then been removed by pumping and analyzed for $C^{14}O$. The results show that the second fraction of added carbon monoxide tends to desorb first. However, the results also show that a partial rapid exchange equivalent to a coverage of about 50% of the iron surface occurs between the two added fractions of chemisorbed carbon monoxide even if both fractions are added at −195°.

Many data have accumulated in the literature to indicate that metallic catalysts have heterogeneous surfaces. Some of the surface atoms appear capable of holding gas molecules much more tightly than do others. For example, measurements of the heats of adsorption of gases on metals usually show that the first few molecules picked up by the surface evolve considerably more heat per molecule than those picked up when the surface is partially covered with the chemisorbed gas.

Although this rapid falling off in the heat of chemisorption with fraction of the surface covered is usually taken as an indication of the heterogeneity of the surface, it might also be accounted for, as pointed out by a number of workers, by the influence of one adsorbed molecule on the adsorption of others. Thus it has been argued that even on a uniform surface one would expect that the exothermicity of adsorption would decrease as the surface became more and more covered with adsorbate molecules purely as a result of the tendency of adsorbed molecules to repel partially those that are being adsorbed in adjoining positions.

Several years ago, Roginskii and Todes[1] pointed out that these two explanations for the observed behavior of gases being adsorbed on solids could be

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(1) S. Z. Roginskii and O. Todes, *Acta Physicochim.* (*U. R. S. S.*), **21**, 519 (1946).