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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 25]

PHASE RELATIONS IN THE SYSTEM, SODIUM AMIDE-POTASSIUM AMIDE, AS DETERMINED FROM MELTING-POINT CURVES

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Introduction.—Franklin[1] has observed that in liquid ammonia solution sodium amide forms with potassium amide a relatively insoluble compound, the composition of which may be expressed by the formula, $NaNH_2.2KNH_2$. It is not possible to arrive at a conclusion regarding the constitution of this substance without further data as to its properties. It appeared worth while, therefore, to investigate the system, $NaNH_2$-KNH_2, in order to determine what compounds may be separated from the melt, as well as to obtain some information as to the relative stability of the compounds in the fused mixture of the amides.

Experimental Method and Apparatus.—Since the amides react readily with water vapor, carbon dioxide and oxygen,[2] it was found necessary to devise an apparatus for the purpose of preparing the amide mixtures and obtaining their cooling curves in an inert atmosphere.

The alkali metal was weighed in a small steel tube which was fitted with a cap for the purpose of excluding air. After weighing, the metal was introduced into the reaction tube, consisting of a steel cylinder of approximately 37 cm. length and 3.5 cm. diameter, and closed at the top by means of a cap. It was also provided with 2 valves, through one of which ammonia could be introduced and through the other the evolved hydrogen removed and thereafter collected.

After displacing the air in the apparatus by means of ammonia, the bomb was heated in an electric furnace to a temperature in the neighborhood of 300° in an atmosphere of ammonia vapor at a pressure of approximately 10 atmospheres. The higher pressure serves to accelerate the reaction between the metal and the ammonia vapor. The hydrogen formed was collected over water and served as a rough measure of the progress of the reaction. A mercury trap was inserted between the collecting apparatus and the bomb.

The melting point of the amide or of the amide mixture was determined by means of a thermocouple introduced through the cover of the reaction tube. After obtaining a cooling curve with a given mixture, another weighed quantity of metal was added and the process repeated.

Experimental Results.—The results obtained are given in the following table, which will require no further explanation.

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[1] Franklin, *J. Phys. Chem.*, **23**, 36 (1919).

[2] De Forcrand, *Compt. rend.*, **121**, 66 (1895). Drechsel, *Ber.*, **20**, 1456 (1887).

Table I

Melting Points of Mixtures of Sodium Amide and Potassium Amide

Wt. of Na	Wt. of K	Mol % of K	Temp. of solidification Initial ° C.	 Final ° C.
10.0880	0	0	206.4	None
	1.2535	6.4	189.5	..
	2.7996	14.0	155.0	92
	3.7528	18.2	145.1	92
	5.9480	25.1	120.5	92
	8.5552	32.9	97	97
	8.9517	34.3	97	97
	10.5280	38.0	100.3	92
	12.9373	43.2	110.5	92
0	8.7870	100	329.0	None
1.1060		82.4	231	120
2.0015		72.0	174	120
2.9830		64.1	120	None
4.4180		54.9	118.5	97

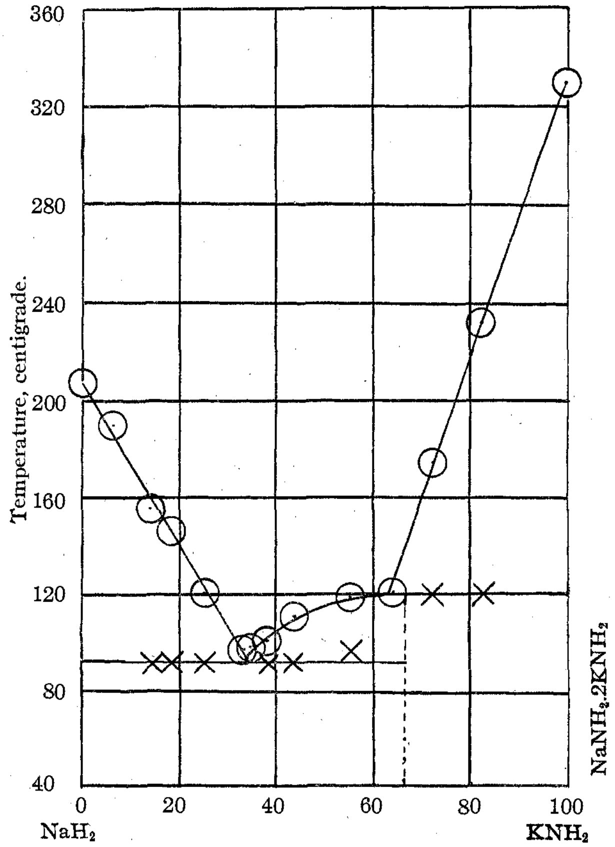

Fig. 1.—Melting-point diagram of NaNH$_2$–KNH$_2$.

Discussion.—As may be seen from the melting-point diagram shown in Fig. 1 a eutectic is formed which solidifies at approximately 92°, and which contains 33 mole per cent. of potassium amide. The curve joining the eutectic on the right indicates that a compound is formed having a transition point at 120°. This point lies at approximately 64 mole per cent. of potassium amide. From an extrapolation of the cooling curves the composition of the compound was fixed between 64 and 68 mole per cent. of potassium amide, which corresponds to the formula, $NaNH_2.2KNH_2$, thus confirming the results obtained by Franklin in liquid ammonia solutions.

It will be observed that the melting point of each constituent is greatly depressed on addition of the other, the curves in question being nearly rectilinear. The flatness of the melting-point curve of the compound indicates that it is largely dissociated in the melt. It is, of course, impossible to determine the nature of the products of dissociation from melting-point curves. It appears probable, however, that the compound dissociates into the constituent amides. As Franklin has pointed out, the compound may be formulated as a molecular compound of the 2 amides, as a dipotassium ammono-sodiate, with 2 molecules of ammonia of crystallization, or as an ammino compound according to Werner's system. The behavior of the amide mixtures at higher temperatures would appear to favor the view that the compound consists merely of an addition product of the two constituents. At all events, the ammonia in the compound is held very tenaciously, which is not characteristic of compounds containing ammonia of crystallization. The fused amide gives off no ammonia, even at relatively elevated temperatures and in a high vacuum. In other words, the properties of mixtures of sodium and potassium amides in a fused state correspond very closely with those of the pure constituents.

The amides prepared as described above were not quite free from impurities, as is evident from the melting points found for the pure constituents. According to Wöhler and Stanglund,[3] the melting point of sodium amide is 210° and that of potassium amide, 338°. The former value agrees closely with that of McGee.[4]

The eutectic temperature probably lies very near 92°, although in several of the runs a temperature of 97° was obtained. No obvious cause for this variation could be found.

The results given above were obtained in a preliminary investigation of the system in question. An apparatus was built for the purpose of making measurements under more favorable conditions. Unfortunately, that time, the laboratory supply of potassium was exhausted and could not be replenished. This put an end to the investigation and circum-

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[3] Wöhler and Stanglund, *Z. Elektrochem.*, **24**, 261 (1918).

[4] McGee, This Journal, **43**, 586 (1921).

stances since have prevented its resumption. In view of the absence of other data relating to the system here studied, it appeared that publication of these preliminary results might prove of interest.

Summary

The melting-point diagram of the system, sodium amide–potassium amide has been obtained by the method of thermal analysis. The diagram indicates the existence of a compound, $NaNH_2.2KNH_2$, having a transition point at approximately 120°. The eutectic between the compound and sodium amide lies at a point corresponding with a composition of 33 mole per cent. of potassium at a temperature in the neighborhood of 92°. The flatness of the melting-point curve of the compound indicates that it is largely dissociated in the melt.

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NOTES

The Bimetallic Electrode System Applied to Neutralization Reactions. —In the introductory part of the work on bimetallic electrode systems the expressions for the potential of an unattackable electrode dipping into an oxidizing solution were given.[1] It was pointed out at that time that the end-point in case of oxidimetric titrations carried out electrometrically with two metallic electrodes depended upon a differential solution pressure of absorbed gas becoming effective at the limiting ionic concentrations. From an inspection of the equations there seemed to be no reason why, if a neutral solution of an oxidizing agent were added to an acid solution of unknown strength, the bimetallic system should not serve as an indicator in the neutralization of the latter. A potential difference existing prior to the end-point should tend to disappear as the solution reaches exact neutrality, or the break should be downward. If the end-point were approached from the opposite direction, that is, alkaline to acid, the break should be upward. In brief, the end-point phenomenon of a neutralization reaction should be perfectly reversible.

A 0.1 *N* solution of hydrochloric acid was prepared and portions of it titrated with an approximately equivalent sodium hydroxide solution under various conditions. The usual electrometric arrangement was used, namely, 2 platinum wire electrodes with a polarizing voltage of 0.5 volt through an external resistance of 100,000 ohms. When the sample titrated contained only a dilute solution of hydrochloric acid the galvanometer was extremely sluggish in the region of the neutral point. An apparently enormous resistance was set up within the solution, the measuring instruments lost their sensitivity and no end-point was obtainable. The addition of potassium bromate did not improve matters. When,

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[1] Willard and Fenwick, THIS JOURNAL, **44**, 2516 (1922).