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).

however, a neutral solution of hydrogen peroxide[2] was added the normal sensitivity continued throughout; a potential difference persisted to within 0.3 to 0.4 cc. of 0.1 *N* titrating solution of the end-point, then began slowly to decrease and at the neutral point a clear, sharp, downward break occurred. With the reversed titration a rise preceded the end-point which was marked by an upward break of about 100 mv. A slight excess of acid caused the voltage to fall. In both cases the point of maximum velocity of potential change was exactly coincident with the "green point" of bromothymol-sulfonephthalein which corresponds to a P_H value of 6.8. In neither case was the end-point permanent. The rapid stirring of the solution favored the absorption of carbon dioxide to such an extent that variable results were obtained in consecutive titrations approaching the neutral point from the alkaline side. With the approach on the opposite side the crawl as the end-point was passed was not sufficient to impair seriously the clarity of the break.

The method seems to offer very favorable possibilities for an extensive development of a new type of hydrogen electrode that is unique in its independence of an external gas supply. In view of further work along this line, the publication of which must be delayed, it is desired to call brief attention at this time to this application.

CONTRIBUTION FROM THE
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A Glass-to-Metal Joint.—In constructing a thermostat it became necessary to make a connection between ordinary soft glass and copper tubing. Platinizing, copper plating and soldering according to the method described by McKelvy and Taylor[1] was unsuccessful with soft glass tubing 8 mm. in diameter, as such joints had a tendency to break after they were finished, because of heating strains produced in the glass by the hot solder. A satisfactory joint, free from such strain, was finally constructed in the following manner.

The end of the glass tube was drawn down so that it fitted easily into the copper tube for about a centimeter. It was then platinized and heavily copper plated, over a length of 3 or 4 cm., in the usual manner. The coppered end was polished until it fitted tightly into the copper tube. By

[2] The hydrogen peroxide used was the ordinary 3% commercial solution; 100 cc. was neutralized with sodium hydroxide, using bromothymol-sulfonephthalein as the indicator, and diluted to 250 cc.; 5 cc. of this solution was added to each sample titrated.

A solution of hydrogen peroxide prepared by neutralizing sodium perborate with hydrochloric acid failed to give satisfactory results. No explanation is advanced for this unexpected behavior.

[1] McKelvy and Taylor, THIS JOURNAL, **42,** 1364 (1920).

a suitable arrangement copper was again deposited on both tubes across the joint until they were completely united by a solid mass of deposited copper. It was found very convenient to use as a plating vessel a short section of glass tubing, 3 cm. in diameter, closed at the bottom with a 1-hole rubber stopper. That part of the glass tube to be plated extended through the hole in the stopper into the bath. By sliding the tube up or down through the stopper and by adjusting the height of the liquid, it was very easy to regulate the deposit to the desired position and extent. A copper-sulfate acid bath was used and the current density was kept below 0.1 ampere per sq. cm. It was necessary to remove the tube from the bath and file the deposit occasionally until it became perfectly smooth across the joint. Such a connection is perfectly solid and the glass is free from all heating strains.

A joint of this type was built into a thermostat regulator a year ago and has been entirely satisfactory. A similar joint was made between copper-plated steel tubing, 6 mm. in diameter, and soft glass of the same size. The metal end was soldered shut and the glass tube sealed directly to a manometer system in which a vacuum of less than 1 mm. was produced. During a week of observation no trace of a leak was evident.

Violent changes of temperature, because of the different coefficients of expansion of the glass and metal, evidently tend to weaken the vacuum tightness of the joint. It will stand a reasonable amount of heat, however, as shown by the fact that the above joint became quite hot when the metal tube was soldered within 7.5 cm. of the glass.

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[CONTRIBUTION FROM THE LABORATORY OF PLANT CHEMISTRY, UNIVERSITY OF WISCONSIN]

EXPERIMENTS ON AZULENE[1]

BY ROLAND E. KREMERS

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Historical

The blue pigment which is associated with the high-boiling fractions of certain volatile oils has long been known to chemists. Various conjectures as to its nature have been put forward and, indeed, the problem was at one time considered settled by the discovery of copper salts in oils distilled through untinned copper condensers. Even in recent years, no definite knowledge was at hand, and the substance was considered to contain

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[1] An abstract based on part of a monograph submitted by Roland E. Kremers to the Graduate Faculty of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1921.