[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# The Solubility of Sodium Carbonate in Fused Sodium Hydroxide

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This investigation is the first step in a series essential to the planning and interpretation of some experiments on reactions in and with fused sodium hydroxide. It is reported now because the data obtained differ from those previously reported, and may be of practical value since all commercially available sodium hydroxide contains carbonate. Neumann and Bergve[1] reported that sodium hydroxide and sodium carbonate form a continuous series of solid solutions with a minimum in the melting point curve at 280°. The experiments reported here indicate little or no solid solution formation and a eutectic point at 286°. The data of Halla and Tompa[2] are qualitatively in agreement. The later investigators did not, however, determine the composition nor, very definitely, the temperature at the eutectic point.

**Experimental Method.**—Because of the fairly high temperatures required, the freezing point method was chosen. Cooling curves were taken with mixtures of sodium carbonate and sodium hydroxide of varying composition. A known weight of sodium hydroxide was placed in a nickel cylinder 4 cm. in diameter and 7 cm. in height. The cylinder in use was placed in an electric furnace to melt the material and regulate the rate of cooling. A hole 1 cm. in diameter in the top permitted addition and removal of material. Two small nickel tubes also passed through the top, one closed at the bottom to serve as a thermocouple well, and the second open at the bottom to permit blowing a stream of dry nitrogen through the fused mixture to stir it and to remove evolved moisture. After observing each cooling curve, weighed amounts of sodium carbonate were added and the procedure repeated.

The temperatures were measured with a chromel–alumel thermocouple, potentiometer, and galvanometer. The thermocouple was calibrated at the freezing points of tin, cadmium and lead. A second thermocouple in the furnace but not in the cylinder served to detect the appearance of a new phase. When this occurs a sudden increase in the difference between the temperatures recorded by the inner and outer thermocouples is observed. No appreciable supercooling was noticed. While it was possible to read the temperatures somewhat more closely, they were reproducible in general to ±1°, so the recorded temperatures are given to the nearest degree. The addition of sodium carbonate was carried only to 35% because the purpose of the investigation was to measure solubilities in the neighborhood of the melting point of sodium hydroxide.

The sodium hydroxide used was a "Reagent Grade" found by analysis to contain 0.4% sodium carbonate. This material also contained 2–3% water but when heated to 450° for an hour in a stream of dry nitrogen lost this much in weight and gave a constant and reproducible freezing point. Although not completely protected from the atmosphere in the apparatus, it was found that, if kept hot, the sodium hydroxide could be left for several days without absorbing enough water or carbon dioxide to cause a detectable change in its freezing point.

**Results.**—Table I gives the composition of the various mixtures employed and the observed freezing, transformation, and eutectic temperatures. The several blank spaces in the last column are due to failure, for lack of time, to carry the cooling down to the eutectic temperature. They are shown graphically in the accompanying temperature–composition diagram. The freezing points of Neumann and Bergve[1] are shown on the diagram for comparison.

TABLE I

TEMPERATURE-COMPOSITION DATA

| $Na_2CO_3$, wt. % | Freezing temp., °C. | Transition temp., °C. | Eutectic temp., °C. |
|---|---|---|---|
| 0.4 | 319 | 294 | |
| 2.4 | 316 | 294 | |
| 4.3 | 313 | 294 | 286 |
| 7.1 | 307 | 294 | |
| 9.7 | 301 | 294 | 286 |
| 12.2 | 295 | | |
| 14.6 | 292 | | 286 |
| 19.0 | 288 | | 286 |
| 22.8 | 292 | | 286 |
| 25.3 | 320 | | 286 |
| 26.6 | 333 | | |
| 27.9 | 342 | | 286 |
| 29.4 | 354 | | |
| 30.8 | 367 | | |
| 33.1 | 381 | | |
| 35.1 | 395 | | 286 |

The data indicate the freezing point of pure sodium hydroxide to be 320°.

The data tabulated below allow comparison with previously reported freezing and transition temperatures for sodium hydroxide.

| | Fr. pt., °C. | Trans. pt., °C. |
|---|---|---|
| Ref. 1 | 296 | ... |
| 2 | 328 | 295 |
| 3 | 318 | 299 |
| 4 | 322 | 304 |
| This report | 320 | 294 |

(1) Neumann and Bergve, *Z. Elektrochem.*, **20**, 271 (1914); "International Critical Tables," Vol. IV, p. 67.

(2) Halla and Tompa, *Z. anorg. Chem.*, **219**, 321 (1934).

(3) von Hevesy, *Z. physik. Chem.*, **73**, 667 (1910).

(4) Antropoff and Sommer, *ibid.*, **133**, 165 (1926).

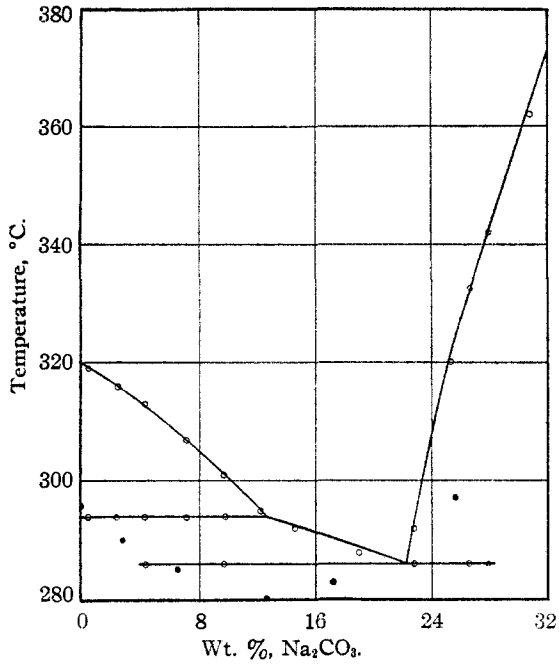


Fig. 1.—Temperature-composition diagram: O, this report; ●, Neuman and Bergve.

The very low freezing point of Neumann and Bergve[1] and their failure to even record the transition temperature indicate that their measurements on the sodium hydroxide–sodium carbonate system may be considerably in error. The fact that additional carbonate does not lower the transition temperature indicates that solid solution formation must be slight. If the logarithm of the mole fraction of sodium hydroxide is plotted against the reciprocal of the freezing temperatures where the solid phase is sodium hydroxide, the first four points lie on a straight line from the slope of which the heat of fusion of sodium hydroxide is calculated to be 1670 cal. per mole in agreement with 1600 cal. obtained by von Hevesy[3] by an independent method. From the heat of fusion of sodium carbonate as given by Kelley,[5] 7000 cal., and its melting point, the calculated solubility of sodium carbonate at 320° is 7 mole % compared to the observed solubility of 11 mole %. Since 320° is more than five hundred degrees below the m. p. of sodium carbonate, this calculation is of no quantitative significance but indicates that the solution under consideration is not far from ideal. This calculation is based on the assumption that the solid phase at 320° is sodium carbonate, which seems likely but has not been proved since the maximum content of carbonate employed was only 35%.

## Summary

Freezing point measurements have been made on sodium hydroxide–sodium carbonate mixtures up to 35% carbonate. The freezing point of sodium hydroxide was found to be 320° and the transformation point 294°. The addition of sodium carbonate reduces the freezing point until a eutectic at 286° with a sodium carbonate content of 22% is reached. The heat of fusion of sodium hydroxide was calculated to be 1670 cal. per mole.

(5) Kelley, "U. S. Bureau of Mines," Bulletin 393 (1936).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON STATE COLLEGE]

# The Secondary Ionization and Activity Coefficients of Selenic Acid*

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## Experimental

Electromotive forces of cells of the type QH: $H_2SeO_4$, $Ag_2SeO_4$: Ag have been measured at 25 ± 0.02°.

**Preparation and Purification of Materials.**—The preparation of selenic acid has been described previously.[1] The acid was twice recrystallized and gave a melting point of 58°. Stock solutions of the acid, approximately 0.2 molar, made from the crystalline acid and conductivity water, were standardized by titration with standard alkali. Solutions of various concentrations were made by dilution of the stock solution with conductivity water.

Molal concentrations were calculated from the densities at the concentrations studied. Density determinations were made at 25°, using a 25-ml. Weld specific gravity bottle. All weights were corrected to vacuum. The values are shown in Table I.

**Quinhydrone Electrodes.**—The quinhydrone was a laboratory preparation which was recrystallized and compared with good commercial samples. Results of such comparison were identical.

Electrodes were of heavy platinum foil, 0.005 inch in thickness, sealed into Pyrex glass tubing. Several methods of cleaning the electrodes were tried before reproducible

* Original manuscript received August 12, 1940.

(1) Gilbertson and King, THIS JOURNAL, 58, 180 (1936).