

STUDIES OF SOLUBILITY IN SYSTEMS CONTAINING
ALKALI AND WATER: I. GENERAL INTRODUCTION.
II. A FILTER AUTOCLAVE FOR SOLUBILITY MEAS-
UREMENTS AT ELEVATED TEMPERATURES AND
ATMOSPHERIC PRESSURE. III. SOLUBILITY OF
NaOH IN A SATURATED Na_2CO_3 SOLUTION BETWEEN
60 AND 70° C.

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ABSTRACT.

The application of physico-chemical principles to the problems of pegmatite formation and the hydrothermal alteration of minerals requires knowledge of the solubility or fusion surface of the system, $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, at temperatures below about 600° C. As a first step toward gaining this knowledge a new type of autoclave has been designed for solubility studies by the analytical method. With it a mixture of solid and liquid at a constant temperature can be stirred in a silver vessel and then filtered through a platinum felt, after which the filtrate is cooled and analyzed. Such an autoclave for use at atmospheric pressure has been perfected during investigation of part of the system, $\text{NaOH}-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$, at elevated temperatures. The liquidus temperatures along the boundary curves $\text{NaOH}\cdot\text{H}_2\text{O}-\text{Na}_2\text{CO}_3$ and $\text{NaOH}-\text{Na}_2\text{CO}_3$ between 60 and 70° now are reported, together with the optical properties of $\text{NaOH}\cdot\text{H}_2\text{O}$ and NaOH .

I. GENERAL INTRODUCTION.

Various problems concerning the natural occurrence of minerals have been solved by the application of physical chemistry. Of the many minerals whose origins are still little understood, analcite ($\text{H}_2\text{NaAlSi}_2\text{O}_7$), muscovite ($\text{H}_2\text{KAl}_3\text{Si}_3\text{O}_{12}$), and natrolite ($\text{H}_4\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{12}$) are examples that are quaternary compounds in the system, $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Orthoclase (KAlSi_3O_8), nephelite (NaAlSiO_4), and pyrophyllite ($\text{H}_2\text{Al}_2\text{Si}_4\text{O}_{12}$) are ternary compounds in the same system. In the endeavor both to explain the paragenesis of the former group and to predict the action of hot aqueous solutions on the latter group, it is necessary to begin by the formulation of the phase relations in this five-component system—which relations sometimes are complicated by interaction with carbon dioxide. Only by such a systematic procedure can we equal the success attained by van't Hoff and his coworkers¹ in unraveling the

¹ van't Hoff, J. H., *et al.*: Untersuchungen über die Bildungsverhältnisse der Ozeanischen Salzablagerungen insbesondere des Stassfurter Salzlagere; Akademische Verl., Leipzig, 1912.

mysteries of the Stassfurt salt deposits or that attained more recently by Bowen² in predicting the composition of residual liquids of crystallizing magmas as exemplified by rhyolites, trachytes, and phonolites. To follow an opposite course by undertaking more hydrothermal syntheses of minerals would produce no results beyond additions to a sixty-year-old accumulation of information that cannot of itself be systematized. Once the phase relations are known, however, they should provide the explanation of the results³ of individual hydrothermal syntheses.

After the completion of the first quantitative investigation of phase equilibria in the system, alkali—alumina—silica—water (the study⁴ of the system, $\text{H}_2\text{O}—\text{K}_2\text{SiO}_3—\text{SiO}_2$, in this Laboratory twenty years ago), it was realized that before the work could be extended, it would be necessary to examine the two limiting ternary systems that do not contain water. Thanks to the work done since then by several investigators,⁵ mostly in this Laboratory, the phase relations in the systems, $\text{Na}_2\text{O}—\text{Al}_2\text{O}_3—\text{SiO}_2$ and $\text{K}_2\text{O}—\text{Al}_2\text{O}_3—\text{SiO}_2$, are understood, except near the two binary borders $\text{Na}_2\text{O}—\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}—\text{Al}_2\text{O}_3$. With the aid of this knowledge, it has been possible to resume

² Bowen, N. L.: This Journal, 33, 1-21, 1937.

³ For an annotated bibliography of hydrothermal syntheses, see Morey, G. W., and Ingerson, Earl: Econ. Geol., 32, 607-761, 1937.

⁴ Morey, G. W., and Fenner, C. N.: J. Am. Chem. Soc., 39, 1173-1229, 1917.

⁵ SiO_2 . Fenner, C. N.: This Journal, 36, 331-384, 1913; Wietzel, R.: Z. anorg. allgem. Chem., 116, 71-98, 1921; Greig, J. W.: This Journal, 13, 1-44, 1927.

$\text{Al}_2\text{O}_3—\text{SiO}_2$. Bowen, N. L., and Greig, J. W.: J. Am. Ceram. Soc., 7, 238-254, 1924; Bowen, N. L., Greig, J. W., and Zies, E. G.: J. Wash. Acad. Sci., 14, 183-191, 1924.

$\text{Na}_2\text{O}—\text{SiO}_2$. Morey, G. W., and Bowen, N. L.: J. Phys. Chem., 28, 1167-1179, 1924; D'Ans, J., and Löffler, J.: Z. anorg. allgem. Chem., 191, 1-35, 1930; Kracek, F. C.: J. Am. Chem. Soc., 52, 1436-1442, 1930; Kracek, F. C.: J. Phys. Chem., 34, 1583-1598, 1930.

$\text{K}_2\text{SiO}_3—\text{SiO}_2$. Kracek, F. C., Bowen, N. L., and Morey, G. W.: J. Phys. Chem., 33, 1857-1879, 1929; Goranson, Roy W., and Kracek, F. C.: J. Phys. Chem., 36, 913-926, 1932; Kracek, F. C., Bowen, N. L., and Morey, G. W.: J. Phys. Chem., 41, 1183-1193, 1937.

$\text{Na}_2\text{SiO}_3—\text{K}_2\text{SiO}_3—\text{SiO}_2$. Kracek, F. C.: J. Phys. Chem., 36, 2529-2542, 1932.

$\text{Na}_2\text{SiO}_3—\text{Na}_2\text{Si}_2\text{O}_5—\text{NaAlSiO}_4$. Tilley, C. E.: Mineralog. petrog. Mitteilungen (Z. Krist., Abt. B) 43, 406-421, 1933.

$\text{NaAlSiO}_4—\text{KAlSiO}_4$. Bowen, N. L.: This Journal, 43, 115-132, 1917; Bowen, N. L., and Greig, J. W.: This Journal, 10, 204-212, 1925.

$\text{NaAlSiO}_4—\text{KAlSiO}_4—\text{SiO}_2$. Rice, B. A.: J. Am. Ceram. Soc., 6, 525-547, 1923; Schairer, J. F., and Bowen, N. L.: Trans. Am. Geophys. Union, 16, 325-328, 1935.

KAlSiO_4 . Morey, G. W., and Bowen, N. L.: This Journal, 4, 1-21, 1922.

the inquiry into the two quaternary systems, $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, with attention limited at present, for the sake of simplicity, to constituent binary and ternary systems.

METHODS OF STUDY OF PHASE EQUILIBRIA.

A problem as broad as this one must be attacked piecemeal by a variety of methods. In working out the phase relations in the anhydrous systems just mentioned, the two standard procedures were quenching⁶ and thermal analysis.⁷ The former was employed in the determination of liquidus temperatures and the latter in the determination of phase changes in the solid state. The modification⁸ of thermal analysis for use with substances having a high vapor pressure probably can be used when necessary in studying solid phases in the systems involving water. The quenching method already has been modified in several respects for use in those regions of the system, alkali—alumina—silica—water, in which crystallization is sluggish, so that a small sample just above the liquidus temperature can be quenched to a glass. In the study of the system, $\text{H}_2\text{O}-\text{K}_2\text{SiO}_3-\text{SiO}_2$, most of the measurements were performed by the "hydrothermal quenching method,"⁹ in which the quenching took place in a bomb in the presence of the water vapor that had been in equilibrium with the melt. A number of other samples were quenched in an ordinary quenching furnace through which steam was passed at atmospheric pressure. By means of the former procedure the isothermal polybaric saturation curves were obtained in the temperature range 200 to 600°, and by means of the latter the isobaric polythermal saturation curve at one atmosphere was obtained. Recently a considerable advance has been made by the development of apparatus¹⁰ for the simultaneous extension of the method of quench-

⁶ Introduced by Shepherd. [Shepherd, E. S., Rankin, G. A., and Wright, F. E.: *This Journal*, 28, 293-333, 1909; p. 308.]

⁷ For a description of its application to a silicate, see Kracek, F. C., Bowen, N. L., and Morey, G. W.: *J. Phys. Chem.*, 33, 1857-1879, 1929 (pp. 1874-1878); 41, 1183-1193, 1937 (pp. 1187-1191).

⁸ Kracek, F. C.: *J. Phys. Chem.*, 34, 225-247, 1930 (p. 228).

⁹ Reference 4, pp. 1181-8. The success of the hydrothermal quenching method in this system was made possible by the low temperatures and pressures prevailing at saturation and by the ease of quenching a liquid to a glass from these low temperatures. There may be no other system in which the same favorable characteristics would be combined over such a wide range of compositions.

¹⁰ Morey, G. W., and Ingerson, Earl: *This Journal*, 35A, 217-225, 1938.

ing in steam to higher temperatures and high pressures. This new technique, it is hoped, will make possible the exploration of the saturation curves in that part of the system, alkali—alumina—silica—water, containing little water.

A related research that is being conducted by Goranson¹¹ concerns the effect of large hydrostatic pressure on the fusion temperature of silicate—water systems. Still another type of information is being sought in a study¹² of the distribution of water and carbon dioxide between the liquid and vapor phases in the system, $K_2O—SiO_2—H_2O—CO_2$, at temperatures above the liquidus.

None of these methods is conveniently applicable to regions in which compounds crystallize readily at relatively low temperatures (below say 500°). Furthermore, the synthetic method of solubility determination in a sealed tube, which was used successfully up to about 500° in the system boric oxide—water,¹³ will not yield accurate measurements in systems containing alkali, because of corrosion of the glass tube.

The behavior of saturated aqueous solutions at temperatures below about 600° C. is especially interesting because of its bearing on several problems of petrography. The formation of pegmatites is ascribed¹⁴ generally to crystallization at a late stage during the cooling of an intrusive magma, by which time the percentage of water in the magma had increased considerably because of the crystallization of anhydrous phases. The aqueous solutions remaining from the crystallization of pegmatites, containing a still higher percentage of water at a still lower temperature, occasioned hydrothermal alteration of previously solidified minerals and finally left deposits of secondary minerals in veins. The temperature at the beginning of the pegmatitic stage is a matter of speculation; but it seems likely that the temperature at the end was not far from 500° C. Thus that portion of the fusion surface of the system, alkali—alumina—silica—water, that lies at temperatures below 600° is concerned directly in any attempt to explain the order of crys-

¹¹ Goranson, R. W.: *Trans. Am. Geophys. Union*, 17, 257-9, 1936; *This Journal*, 35A, 71-91, 1938.

¹² By G. W. Morey and M. Fleischer, cited in the *Annual Report of the Acting Director of the Geophysical Laboratory, Carnegie Institution of Washington Yearbook No. 36*, p. 115, 1937.

¹³ Kracek, F. C., Morey, G. W., and Merwin, H. E.: *This Journal*, 35A, 143-171, 1938.

¹⁴ For a comprehensive but not critical review of the opinions on the genesis of pegmatites, see Albert Johannsen: *A descriptive petrography of the igneous rocks*; Univ. of Chicago, Chicago, 1932; Vol. 2, pp. 77-84.

tallization at the end of the pegmatitic stage and during the entire course of the periods of hydrothermal alteration and of deposition in veins. In connection with these latter processes it is important to emphasize that a high degree of solubility of a solid phase in the aqueous solution was not required for considerable reaction to have taken place: all that was required was that the products of the reaction should have been removed in some manner,—as by deposition elsewhere,—the presence of the material in the solution having been merely an intermediate step.

ANALYTICAL METHOD OF SOLUBILITY DETERMINATION.

In the effort to find a suitable method for the study of such solutions in the system, alkali—alumina—silica—water, the readiness to crystallize that makes difficult the use of the quenching method was turned to account by trying the analytical method of solubility determination, in which ease of crystallization is a prerequisite to success. Although a complete bibliography of the various applications of the analytical method would be very long, it would include few attempts to apply this method to alkaline solutions at high temperatures.

Koenigsberger and Müller¹⁵ constructed an apparatus that in principle would have served for solubility determinations by the analytical method, although the only use they made of it was for the separation of the solid phase in hydrothermal syntheses of alkaline silicate minerals. This apparatus was similar in some respects to that which had been used by Tilden and Shenstone¹⁶ in the determination of the solubility of a number of salts in water between 100 and 200° C. The reaction vessel was a cylindrical steel bomb (inside dimensions: 25 x 400 mm.) lined with platinrhodium. It fitted inside an insulated electric furnace that was mounted in a framework in such a way that it could be shaken three times a second by an eccentric driven by an electric motor. A device for filtration inside the reaction chamber consisted of two platinrhodium tubes, each half as long as the reaction chamber but of different diameters. The larger, which was the filter tube proper, fitted snugly inside the

¹⁵ Koenigsberger, J., and Müller, W. J.: *Centr. Mineral. Geol.*, 1906, 339-348; 353-372; Müller, W. J., and Koenigsberger, J.: *Z. anorg. allgem. Chem.*, 104, 1-26, 1918; Koenigsberger, J.: *Fortschr. Mineral. Krist. Petrog.*, 11, 41-48, 1927.

¹⁶ Tilden, W. A., and Shenstone, W. A.: *Trans. Roy. Soc. (London)*, 175, 23-36, 1884.

reaction chamber. One end, which was at the top of the chamber when the apparatus was in the normal position, was open; and the other end was covered with a fine platinum sieve. One end of the smaller tube (5 mm. diameter) was fastened through the center of the sieve; and the other end, which extended almost to the bottom of the chamber, was covered also with a platinum sieve. After the reaction mixture had been agitated for the desired length of time, the furnace (and therefore the reaction tube also) was turned upside down. The reaction mixture then rested on the sieve covering the filter tube. As the liquid phase dripped slowly through the sieve, the smaller tube permitted gas to displace it in the upper half of the chamber. After filtration had been completed in six to 24 hours, the furnace was cooled slowly to room temperature, the bomb was opened, and the two phases were separated. The three chief objections to this design (if the apparatus were to be used for solubility determinations) are: (a) the agitation of the reaction mixture is inadequate; (b) temperature uniformity is difficult to maintain (a difference of 3° between the two ends of the bomb was found by Koenigsberger and Müller); and (c) the time of filtration is much too long.

Waldeck, Lynn, and Hill¹⁷ used a bomb constructed of 18-8 stainless steel in the determination of the solubility of NaCO_3 in water up to 348° and of isotherms in the system, $\text{Na}_2\text{CO}_3\text{—NaHCO}_3\text{—H}_2\text{O}$, up to 200° . The bomb (capacity, 135 cc.) was oscillated in an air thermostat until equilibrium was reached. A sampling tube, set into the head of the bomb (in the later model) and operated externally by a needle valve, permitted removal of part of the liquid phase after the solid phase had settled. Bombs of this same design were used by Schroeder and his coworkers¹⁸ in measurements of the solubility equilibria of sodium sulphate in solutions of sodium hydroxide and other sodium compounds up to 350°C . They added a blow-off valve at the bottom, in order to secure a sample of dry solid phase. The chief objections to this design are: (a) the agitation of the reaction mixture is inadequate; (b) contamination by corrosion is present; (c) the solid phase of a slightly viscous mixture or of one containing very fine crystalline particles (a

¹⁷ Waldeck, W. F., Lynn, George, and Hill, A. E.: *J. Am. Chem. Soc.*, 54, 928-936, 1932; 56, 43-47, 1934.

¹⁸ Schroeder, W. C., Gabriel, Alton, and Partridge, E. P.: *J. Am. Chem. Soc.*, 57, 1539-1546, 1935; Schroeder, W. C., Berk, A. A., and Gabriel, Alton: *J. Am. Chem. Soc.*, 58, 843-849, 1936; 59, 1783-1790, 1937.

desirable condition in itself) would not be removed completely from the liquid phase because of the lack of a filter; (d) removal of the filtrate from the sampler would be difficult, if it solidified in it, as would some filtrates obtained at high temperatures; and (e) precise temperature control of such a large apparatus in an air thermostat is difficult.

The reaction vessel used by Seyer and Todd¹⁹ in the determination of the solubility of Na_2CO_3 up to 173° consisted of an iron tube with a side-arm. After the mixture had been agitated by rotation of the tube and then allowed to settle, some of the solution was decanted into the side-arm. Vasil'ev²⁰ in the determination of the solubility of Na_2CO_3 and of K_2CO_3 up to 200° used a glass tube of somewhat similar design. Neither arrangement would furnish accurate results with alkali—water systems at high temperatures, because of contamination by the products of corrosion, the lack of active agitation, and the lack of complete filtration.

Hitchen²¹ devised an apparatus to study hydrothermal solubility and used it to measure the solubility of silica in water from 128 to 336° . A large reaction chamber (volume, 1365 cc.) made of 18-8 stainless steel was supported in an electrically-heated air thermostat. To the head of this pressure vessel was attached a re-entrant thermocouple well and a connection to a pressure gauge. The large size of reaction chamber had been chosen so that a number of 100-cc. samples could be taken for analysis without renewing the charge. Each was withdrawn from the bottom of the chamber through a needle valve that was connected to a weighed steel sampling tube surrounded by a water jacket. The hole leading from the bottom of the reaction chamber into the needle valve was covered with a filter cup that contained graded layers of particles of some inert material—silica in the experiments on the solubility of silica. Although this design was satisfactory for researches with solutions of silica, its use for alkaline solutions, for which its originator had hoped to employ it later, is attended by several objections: (a) lack of agitation of the reaction mixture (equilibrium in a silica solution at 300° was reported to have been reached in ten hours without agitation); (b) contamina-

¹⁹ Seyer, W. F., and Todd, Eric: *Trans. Roy. Soc. Can.*, 23-III, 67-70, 1929.

²⁰ Vasil'ev, B. B.: *Trans. State Inst. Applied Chem. (U. S. S. R.)*, No. 23, 110-117, 1935.

²¹ Hitchen, C. S.: *Bull. Inst. Mining Met.*, Nos. 364, 366, and 375, 1935. Printed also in *Trans. Inst. Mining Met.*, 44th session, 1934-1935, pp. 255-336.

tion by corrosion (only very slight with the silica solutions); (c) crystallization of filtrate in the needle valve during filtration; and (d) change of composition of the solution by the evaporation that would accompany the decrease of pressure during sampling.

Successful application of the analytical method of solubility determination requires:

(1) A containing vessel that does not contaminate the solution by products of its corrosion.

(2) Active agitation of the solution to facilitate the attainment of equilibrium.

(3) Precise control and measurement of the temperature of the solution during agitation.

(4) A means of filtration that removes every trace of solid phase without disturbing the equilibrium either by a temperature change or by altering the liquid-vapor equilibrium.

(5) A means of bringing the filtrate to atmospheric pressure and temperature without changing its composition.

(6) Accurate analysis of the filtrate.

(7) Identification of the solid phase or phases that had been present in equilibrium with the solution.

With non-corrosive reaction mixtures near room temperature, these conditions are fulfilled easily. In the several forms of apparatus that have just been reviewed, one or more of these requirements had not been met, as already has been pointed out. For the investigation of solubility equilibria in alkaline solutions at elevated temperatures, all of them have been satisfied by the filter autoclave and technique that will be described in Part II of the present paper.

APPLICATION OF THE FILTER AUTOCLAVE.

During the development of the filter autoclave as a precision instrument, we chose to work with the system, $\text{NaOH—H}_2\text{O}$, because the vapor pressures of solutions saturated with respect to NaOH are less than atmospheric pressure; and therefore the basic principles of the autoclave could be perfected without the complication of high pressures. The ease of analysis of filtrates in this system also influenced our choice. Inasmuch as it is impossible without working in a vacuum to obtain and keep NaOH free of carbonate, it was decided to find out how much effect CO_2 has on the solubility of NaOH at high temperatures. The information gained concerning the system, $\text{NaOH—Na}_2\text{CO}_3\text{—H}_2\text{O}$, which in itself is of general chemical interest.

will be helpful in the subsequent study of alkali—water systems of greater complexity.

Since the autoclave has been perfected, it has been used to determine the boundary between the NaOH and Na_2CO_3 fields in the system, $\text{NaOH}—\text{Na}_2\text{CO}_3—\text{H}_2\text{O}$. So soon as the determination of the isotherms in the field of NaOH up to 300° has been completed, these results will be published. The determination of the solubility of $\text{NaOH}·\text{H}_2\text{O}$ in a saturated Na_2CO_3 solution, which is described in Part III of the present paper, is an especially severe test of the method, for although a change of two per cent in the composition of the solution alters the liquidus temperature only one degree, it was possible to obtain a smooth liquidus curve that shows the rise of only two and one-half degrees from the eutectic temperature to the maximum temperature along the curve of double saturation.

An earlier form of this autoclave had been used by Morey²² to determine the 125° isotherm in the system, $\text{Na}_2\text{O}—\text{SiO}_2—\text{H}_2\text{O}$. We have performed experiments in this system at higher temperatures; but they were unsuccessful, because the vapor pressure of the solution was sufficiently above atmospheric pressure for a considerable quantity of water vapor to leak out past the stirrer shaft, thereby progressively changing the composition of the solution. For the study of such systems a high-pressure-steam filter autoclave is now under construction. It will be a pressure vessel with an oil-sealed stuffing box for the stirrer shaft, and it will be connected to a steam boiler kept at a constant temperature in a separate furnace, whereby steam at a constant pressure will be supplied during stirring and filtration. With this new apparatus it is hoped that solubility determinations can be carried out at temperatures up to 500°C . and at pressures up to 200 bars in large regions of the systems, $\text{NaOH}—\text{Na}_2\text{CO}_3—\text{H}_2\text{O}$, $\text{Na}_2\text{O}—\text{SiO}_2—\text{H}_2\text{O}$, $\text{Na}_2\text{O}—\text{Al}_2\text{O}_3—\text{H}_2\text{O}$, and the corresponding potassium systems.

II. A FILTER AUTOCLAVE FOR SOLUBILITY MEASUREMENTS AT ELEVATED TEMPERATURES AND ATMOSPHERIC PRESSURE.

The filter autoclave that was designed to meet the requirements for solubility measurements in alkaline solutions at elevated temperatures, as set forth in Part I of this paper, is shown

²² Morey, G. W., quoted in Vail, James G.: Soluble silicates in industry; Chem. Catalog Co., New York, 1928, pp. 116-7.

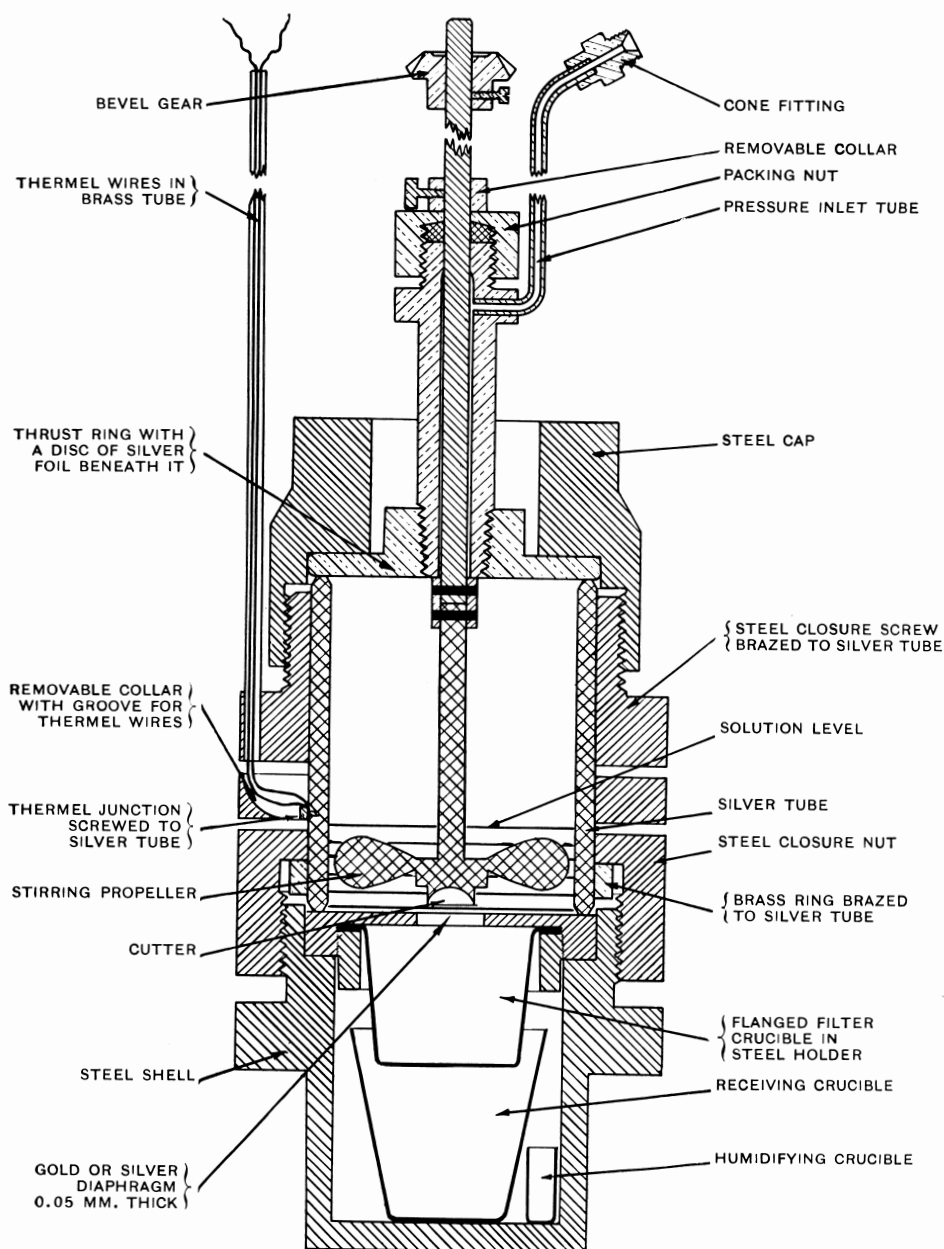


Fig. 1. Filter Autoclave.

in cross-section in Fig. 1. It consists of three principal units: a lower chamber that contains a platinum crucible (capacity, 25 cc.) to receive the filtrate, a reaction chamber in which the mixture of solid and liquid is stirred by a propeller, and a combination stirrer-shaft-bearing and gas inlet tube that is fastened to the top of the reaction chamber by means of a steel cap.

A steel disc with a 13-mm. hole in its center rests on a shoulder inside the top of the steel shell that forms the lower chamber. To its under side is attached a flanged platinum filter crucible²³ by means of a lens ring that is screwed into a recess in the disc. The joint is made tight by a silver gasket (0.10 mm. thick) beneath the flange. The perforated bottom of the filter crucible is covered with a highly burnished platinum felt. A silver tube forms the walls of the reaction chamber. A steel closure nut that encircles this tube screws on the top of the lower steel shell. Thus, when the autoclave is assembled, the diaphragm (0.05 mm. thick) that forms the bottom of the reaction chamber is held tightly between the face of the steel disc and the beveled end of the silver tube. Before assembly of the autoclave at the beginning of an experiment, the end of the silver tube and the face of the steel holder are polished with very fine emery on a lapping plate. Tests with prussian blue at various times have shown that after these parts have been polished, the line of contact between them is continuous.

After some experiments at 180° and higher temperatures, it was found that the silver diaphragm had become welded to the end of the silver tube, and had to be cut away. Gold diaphragms of the same thickness were tried; but welding still took place. Because of their color, the pieces of gold that adhered to the silver tube could be seen easily, and therefore could be cut away without damage to the tube. Hence gold diaphragms have been used in many of the experiments at temperatures above 180°.

The stirrer shaft is stainless steel except for the part inside the reaction chamber, which is pure silver. To its lower end is screwed a pure silver propeller, and below that a cutter with which to cut a hole in the silver diaphragm to let the mixture pass from the reaction chamber into the filter crucible. The cutter, which operates like a cork-borer, was made from an

²³ A "Munroe crucible." For its history and for incomplete directions for the formation of the platinum felt, see W. O. Snelling: *J. Am. Chem. Soc.*, 31, 456-61, 1909.

alloy²⁴ containing 90 per cent Ag and 10 per cent Ni that was cast especially for this purpose. Its sharpened end has a circular cross-section with a diameter of 9 mm. Above the reaction chamber the stirrer shaft passes through a bearing tube on top of which is a stuffing box and packing nut. The packing is an asbestos cord impregnated with graphite. The lower end of the bearing tube is fastened into a thrust ring that is held against the top of the silver tube by a screw cap. The joint is made tight by a silver gasket (0.20 mm. thick) beneath the thrust ring. The stirrer shaft is kept in position by a shoulder that bears against the under side of the thrust ring at the same time that a removable collar bears against the top of the packing nut. Just below the stuffing box a small copper tube has been brazed to the bearing tube. It is bent upward parallel to the stirrer shaft, and has a cone fitting on its upper end in order that a connection can be made to a tank of compressed nitrogen.

Furnace. The autoclave is heated in an air bath, formed by a hollow brass cylinder with a thick brass bottom (outside diameter, 12.2 cm.; inside diameter, 8.8 cm.; inside depth, 16.6 cm.; outside length, 19.7 cm.; weight, with cover, 11.3 kg.). This brass cylinder fits snugly inside a refractory furnace tube (wall thickness, 1.5 cm.; length, 37 cm.), on the outside of which has been wound a heater of nichrome wire. The furnace tube sits within a sheet-metal shell (diameter, 25.6 cm.; height, 37.5 cm.), the annular space being filled with powdered magnesia. A wooden box (top, 39 x 39 cm.; height, 43 cm.) surrounds the furnace. A brass cover fits over the air bath just above the steel cap of the autoclave; and the furnace tube and wooden box have separate covers, the center sections of which are removable. The furnace is bolted to a steel casting (diameter, 44 cm.; thickness, 2.3 cm.), to which is attached also a steel bar that serves as a pillar on the top of which a motor is pivoted at such a height that a bevel gear on its shaft can engage another on the upper end of the stirring shaft of

²⁴ This alloy apparently has not been described previously. According to the phase equilibrium diagram of Petrenko [Petrenko, G. J.: *Z. anorg. allgem. Chem.*, 53, 212-5, 1907, reproduced (with some temperatures corrected) in *Int. Crit. Tables*, Vol. 2, p. 422, and in Hansen, M.: *Der Aufbau der Zweistofflegierungen*, Berlin, 1936, p. 43] this alloy consists of a matrix of pure silver in which is dispersed a few per cent of a solid solution containing 96 per cent Ni and 4 per cent Ag. We intend to study further the alloy system silver-nickel.

the autoclave. The speed of stirring is thirty revolutions a minute.

The furnace heater is connected to a 115-volt line through a "Variac."²⁵ Because the voltage of the current is kept constant by the main laboratory voltage regulator and because the furnace is so well insulated, it has been possible to dispense with an automatic temperature controller. A particular setting of the Variac will cause attainment of the same temperature within a degree or two on different occasions. Infrequent manual variation of the power input keeps the temperature of the autoclave constant within 0.1° C.

Thermocouples. The temperature of the autoclave is measured with a platinum vs. platinum (90)—rhodium (10) thermocouple junction that is held by a screw tightly against the outside of the silver tube about one centimeter from the bottom. A removable collar that is fastened around the tube protects the junction from convection currents and from radiation from the furnace wall. The wires leading from the junction, insulated by two concentric porcelain tubes, pass up through a 4-mm. brass tube that fits in a hole through the rim of the top steel closure screw of the autoclave. The temperature of the brass cylinder that forms the air bath is measured separately with a glass-enclosed platinum vs. platinum-rhodium junction in a well ten centimeters deep.

These two thermocouple junctions are connected to a cold junction that has a common platinum-rhodium wire. The cold junction, which is imbedded in paraffin in a glass tube, is kept in melting ice and distilled water in a vacuum-jacketed bottle. The connections between the leads from the hot junctions and the corresponding ones from the cold junction, which are held together by spring clips, are protected from draughts by a small wooden box.

The emf. of each thermocouple is measured with a modified Wolff-type potentiometer (No. 3530), used in conjunction with a Weston galvanometer (Model 99, No. 3) and an Eppley unsaturated standard cell that is packed in glass wool in a wooden box.

The galvanometer sensibility has been adjusted to 0.5 μ v per scale division. Deflections, which are kept less than 6 μ v, are estimated to the nearest 0.1 μ v. The small corrections found in a calibration of the potentiometer coils in May, 1936 are

²⁵ A variable transformer (type 200), made by the General Radio Co.; Cambridge, Mass.

applied to all readings. Under these conditions an emf. can be measured to $\pm 0.5 \mu\text{v}$.

The potentiometric system is doubly shielded as recommended by White,²⁶ with the inner shield connected to the case terminal of the galvanometer. There is also an internal battery shield. Inasmuch as the autoclave is connected electrically to the thermocouple, it has been necessary to insulate the motor shaft from the autoclave by a hard rubber bushing. With these precautions the galvanometer circuit shows no deflection when either the motor circuit or the heating circuit is broken. The small internal parasitic emf. (less than $1 \mu\text{v}$) is circumvented by a combination selector-eliminating switch with an all-copper circuit, designed by W. P. White.

The thermocouple in the shell of the air bath has not been calibrated. The thermocouple connected to the autoclave (Th. 372/370B) and another new thermocouple (Th. 374/370A) were calibrated simultaneously in April, 1937 at the ice, steam, tin, and lead points with a maximum uncertainty of $\pm 1 \mu\text{v}$. At the same time the difference in emf. between them at these different fixed points was measured directly. After this calibration Th. 374/370A was preserved as a reference standard. It was recalibrated in January, 1938 at the same fixed points. The greatest difference between the two sets of results was $0.6 \mu\text{v}$.

The results of all calibrations are expressed in the form of deviations from the "standard emf. values" listed in Adams' table,²⁷ which is used in this research to convert the emf. of a thermocouple to a temperature on the scale of the Geophysical Laboratory. This scale differs from the International Temperature Scale²⁸ by not more than 0.4° at temperatures below 600° .

Immediately after the calibration of Th. 372/370B and Th. 374/370A, they were compared with each other while the hot junction of the former was screwed to the outside of the autoclave tube in its normal position and the hot junction of the latter, enclosed in a very thin glass tube, rested on the diaphragm inside the autoclave. In lieu of a reaction mixture, sodium chloride was placed around this junction to a depth of fifteen millimeters. The autoclave was heated in the air bath to a constant temperature, and the difference in emf. between the two thermocouples was measured five times at intervals of

²⁶ White, W. P.: *J. Am. Chem. Soc.*, 36, 2011-2020, 1914.

²⁷ Adams, L. H.: *J. Am. Chem. Soc.*, 36, 65-72, 1914; *Int. Crit. Tables*, Vol. 1, p. 57, 1926.

²⁸ Burgess, G. K.: *Bur. Standards J. Research*, 1, 635-640, 1928.

ten minutes. The maximum difference observed at any of four temperatures between 100 and 327° was 0.5 μv , which is equivalent to a difference of only 0.05° between the temperature measured in the usual way and that indicated inside the autoclave.

A series of four similar experiments was performed, with the hot junction of Th. 374/370A passing through a hole in the diaphragm and resting on the bottom of the filter crucible. Under these conditions the temperature measured in the usual way was a little lower than that measured with the thermocouple in the filter crucible. The difference was almost directly proportional to the temperature of the autoclave, reaching 0.6° at 280°.

Even this maximum difference in temperature between the reaction mixture and the filter crucible cannot affect the accuracy of the measurements. A calculation based on the heat capacities of the crucible and of ten grams of filtrate shows that if the total excess heat of the crucible corresponding to a temperature difference of 0.6° were absorbed by the filtrate, the temperature of the latter would be increased less than 0.1°. This increase can do no harm; on the contrary, it furnishes assurance that no precipitation occurs during filtration.

After Th. 372/370B had been in use several months, it was recalibrated against Th. 374/370A, with the latter resting on the diaphragm on the inside of the autoclave just as during the initial comparison. When Th. 372/370B had been new, its emf. was slightly greater than the standard value for a given temperature (1.5 μv at 2000 μv); but at the time of the second calibration its emf. was lower (3.3 μv at 2000 μv). At four subsequent calibrations during the next nine months, the fluctuations of the deviation curve amounted to less than ± 2 μv throughout the range 400 to 2600 μv .

The change from one period of calibration to the next is so slight that the total uncertainty introduced in a temperature measurement by the uncertainty of the calibration is not more than $\pm 0.1^\circ$. Hence, the maximum relative uncertainty of the equilibrium temperature during a solubility determination with the filter autoclave is $\pm 0.2^\circ$, when the maximum observed variation of temperature during the period of equilibrium is $\pm 0.1^\circ$ (as is usually the case). The maximum uncertainty of any temperature with respect to the thermodynamic temperature scale, however, is $\pm 0.5^\circ$, because of the uncertainty of interpolation²⁹ between fixed points.

²⁹ Roeser, W. F., and Wensel, H. T.: *J. Research Nat. Bur. Standards*, 14, 247-282, 1935; Table 9, p. 280.

Corrosion. During the development of the autoclave, the first cutter of the present type that was tried was made of Monel metal. In an $\text{NaOH—Na}_2\text{CO}_3$ solution at 180° it corroded badly, producing a pale green color in the filtrate, because of the presence of ferrous iron. When the filtrate was dissolved in water, the iron became oxidized to $\text{Fe}(\text{OH})_3$, which was precipitated. Metallic copper in the mixture inhibited the attack on the iron in the Monel metal; but finely divided copper was precipitated on the cutter and also appeared in the filtrate. When the filtrate was dissolved, the copper reacted to form blue cupric ions. The corrosion seemed not to affect the Na_2O content of the filtrate very much; but it did increase by one part in thirty the amount of CO_2 present at double saturation at 180° . Also the values obtained for the CO_2 content when corrosion was present were more irregular than those obtained in the absence of corrosion.

Even with a reaction chamber that is completely silver-lined (except for the silver-nickel alloy of the cutter) some corrosion of the metal occurs, as evidenced by the whitening of the silver at temperatures above 100° . In some of the experiments at high temperatures in which a gold diaphragm was used, it became covered with a layer of silver thick enough to cause a perceptible whitening of the surface.

Technique. The use of the filter autoclave may be described in terms of the standard procedure that is being used in the determination of solubilities in the system, $\text{NaOH—Na}_2\text{CO}_3\text{—H}_2\text{O}$. In a typical experiment a charge of total weight between 35 and 40 grams was made up from NaOH pellets, $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$, and H_2O in proportions to give between 5 and 10 grams of solid phase at equilibrium. The charge was sealed in the autoclave late one afternoon, with a cap on the pressure inlet tube, and the autoclave was placed in the preheated furnace overnight.

Early the next morning the stirrer was started by means of a time switch. A measurement four hours later showed that the temperature was a few degrees above the desired equilibrium value (in a companion experiment the "Variac" was set to give a temperature a few degrees below the equilibrium value). The furnace was cooled rapidly for a short time, and then more slowly as the autoclave approached the equilibrium temperature, which was reached in about two hours. Stirring had been continued during the period of cooling; and it was continued four hours longer, during which time the tempera-

ture remained within 0.1° of the equilibrium value as shown by observations made every ten minutes.

At the end of the period of constant temperature, stirring was stopped; the cap was removed from the pressure inlet tube; and a hole was cut in the diaphragm by loosening the collar on top of the packing nut and pushing down on the stirring shaft while rotating it slowly. The melt was allowed to drain through the hole for two minutes. A pressure of 20 lb. of nitrogen was applied through the pressure inlet tube in the course of one-half minute and then was maintained for five minutes, to force the solution through the filter.

Evaporation during filtration was prevented by having the same pressure of water vapor in the lower chamber as had existed in the reaction chamber at equilibrium. This was accomplished by having in the lower chamber a small crucible (the "humidifying crucible" in Fig. 1), in which at the start of the experiment had been placed a one-gram charge that contained a few centigrams of water in excess of the approximate composition of the liquidus. When the autoclave had been heated, some of the water had evaporated and had filled the lower chamber, remaining in equilibrium with the saturated solution in the humidifying crucible, so that at the time of filtration the proper humidity was present there. This precaution probably was not important at temperatures below 200° ; but at higher temperatures it contributed to the accuracy of the measurements.

The nitrogen gas itself did not change the composition of the filtrate, because of the preliminary period of drainage, and because of the slowness with which the gas was admitted. Under these conditions the nitrogen became warmed in the upper chamber before it came in contact with the melt in the filter crucible.

After the nitrogen pressure had been applied for five minutes, it was released and the autoclave was removed from the furnace. It was cooled quickly first by having a fan blow air on it and then by placing it in running water. After the autoclave had been at room temperature for about 15 minutes, it was opened. The platinum crucible containing the filtrate, which had solidified on cooling, was removed from the lower chamber and placed quickly in a stoppered flask. The filtrate was weighed to ± 1 mg.

During the cooling no change in composition of the filtrate could occur, because the air that was drawn into the autoclave

had to pass through the filter crucible before it reached the filtrate: the pores of the filter retained enough NaOH to remove the small quantity of CO₂ and H₂O present in atmospheric air. After the autoclave was opened, however, an undetermined amount of CO₂ and H₂O was absorbed by the surface of the filtrate, by the time the crucible had been placed in the solution flask. The air of this flask also contained a little of these gases. Nevertheless, the total amount absorbed probably did not exceed a few milligrams. The observed weight of filtrate was not corrected to the time of removal of the filtrate from the autoclave, for the leading error was the actual weight of CO₂ absorbed (which subsequently was measured in the analysis) and not the proportional increase in weight of the filtrate.

After an experiment the autoclave was cleaned and the inside of the silver tube was polished. The platinum filter crucible was filled with 20 per cent HNO₃. After the acid had dripped through, the filter was washed with distilled water by suction. Washing was continued until the filtrate gave no reaction with either phenolphthalein solution (absence of NaOH) or methyl orange (absence of HNO₃). The filter was dried in an oven at 125° for not less than three hours or at 400° for one-half hour. It was stored in a desiccator until the autoclave was assembled for the next experiment.

The solidified filtrate was dissolved in CO₂-free distilled water the next morning; and the solution was analyzed in duplicate for Na₂O and CO₂. The percentages of Na₂O and CO₂ found, together with the equilibrium temperatures, constituted the data obtained by this one experiment.

The total elapsed time required for a single experiment is about fifty hours, of which on the average the actual working time is fifteen hours, counting the time spent in keeping the apparatus in proper order, securing materials, and collating the data. By dovetailing several experiments, it is possible to complete three or four in a week.

III. SOLUBILITY OF NaOH IN A SATURATED Na₂CO₃ SOLUTION BETWEEN 60 AND 70° C.

PREVIOUS INVESTIGATIONS.

The solubility of sodium hydroxide monohydrate in water has been measured by Pickering³⁰ and by R. Dietz at the Reichs-

³⁰Pickering, S. U.: J. Chem. Soc., 63, 890-909, 1893.

anstalt.³¹ The former showed that $\text{NaOH}\cdot\text{H}_2\text{O}$ is the stable phase above 12°C ., that it melts congruently at 65° , and that it forms a eutectic with anhydrous NaOH at a temperature not much below its melting point. The latter's seven measurements (by the analytical method) in the range 0 to 64° gave a percentage of NaOH about one per cent less than that reported by Pickering at each of the same temperatures. Freeth,³² in his determination (by the analytical method) of the isotherms in the system, $\text{NaOH}\text{—}\text{Na}_2\text{CO}_3\text{—}\text{H}_2\text{O}$, at 0, 15, 30, 45, and 60° , did not carry his measurements all the way to the $\text{NaOH}\text{—}\text{H}_2\text{O}$ border, but made use there of the data of Pickering. His work demonstrated that Na_2CO_3 is the stable phase in alkaline solutions containing more than 35 per cent NaOH above 30°C ., and that at 60° the boundary between the $\text{NaOH}\cdot\text{H}_2\text{O}$ and Na_2CO_3 fields lies very close to the $\text{NaOH}\text{—}\text{H}_2\text{O}$ border.

In order to furnish a bridge between our contemplated measurements of the solubility of NaOH at elevated temperatures and the results of others at lower temperatures, we decided to extend our measurements to 60°C ., thus taking in a portion of the double saturation curve of $\text{NaOH}\cdot\text{H}_2\text{O}\text{—}\text{Na}_2\text{CO}_3$ on both sides of the maximum temperature. We were interested also to find out how the filter autoclave would behave near a congruent melting point and near a eutectic point.

EXPERIMENTAL PROCEDURE.

The solubility measurements were made with the filter autoclave, employing the technique outlined in Part II of the present paper.

Reagents. The starting material was C. P. NaOH in the form of pellets from the J. T. Baker Chemical Co. The label analysis on the bottle was as follows: Assay (NaOH), 98.7 per cent; Na_2CO_3 , 0.8 per cent; PO_4 , 0.0005 per cent; SO_4 , 0.002 per cent; Cl , 0.003 per cent; N , 0.0005 per cent; Fe , 0.001 per cent; heavy metals (as Ag), 0.001 per cent; SiO_2 and NH_4OH ppt., 0.00 per cent. Samples from this bottle were analyzed in duplicate for Na_2O and CO_2 , with these results: 98.36 per cent NaOH and 0.51 per cent Na_2CO_3 . The monohydrated sodium carbonate was of "reagent quality" from the Mallinckrodt Chemical Works. A fifty-gram sample of

³¹ Mylius, F., and Funk, R.: *Wiss. Abhandl. physik.-tech. Reichsanstalt*, 3, 449-458, 1900; p. 450.

³² Freeth, F. A.: *Trans. Roy. Soc. (London)*, 223 A, 35-87, 1923.

this same batch had been analyzed by E. G. Zies of this Laboratory, January, 1930, with the following results: SiO_2 , 0.0006 per cent; Cl as AgCl , 0.0008 per cent; SO_4 as BaSO_4 , nil; Fe_2O_3 and Al_2O_3 , 0.001 per cent; CaO , 0.001 per cent; MgO , nil; residue after neutralizing with HCl , 0.0003 per cent.

Preliminary Crystallization. When $\text{NaOH} \cdot \text{H}_2\text{O}$ was to be the solid phase, the charge was heated in the autoclave to 70° with stirring for an hour or two, and then cooled quickly to about 40° . After that the autoclave was returned to the furnace and heated overnight in the usual manner. In this way it was made certain that crystals of $\text{NaOH} \cdot \text{H}_2\text{O}$ would be present at equilibrium.

Thermocouple Calibration. Thermocouple Th. 372/370B, which had been recalibrated just prior to this series of measurements, was calibrated again near the end of them, Th. 374/370A having been used as the standard in both cases in accordance with the procedure described in Part II. In order to improve the accuracy of the temperature measurements between 60 and 65° , Th. 372/370B was calibrated at three temperatures within this range against a copper-constantan thermocouple³³ that had been calibrated at the Bureau of Standards (Test No. 62303; November, 1930). The correction to Th. 372/370B obtained by interpolation of the results of the calibration against Th. 374/370A agreed within 0.1° with that determined by this special calibration. On the basis of this agreement and the reliability of the calibration of a copper-constantan thermocouple,²⁹ we assign to the liquidus temperatures reported in Part III a maximum relative uncertainty of $\pm 0.2^\circ$, and a maximum uncertainty of $\pm 0.3^\circ$ with respect to the thermodynamic temperature scale.

Determination of Sodium. Analysis of the filtrate was started by dissolving it in CO_2 -free water (prepared by passing CO_2 -free air through boiling distilled water for half an hour) and diluting the solution until it contained approximately 3.93 per cent Na^+ . This concentration was chosen because 10 ml. of such a solution yield 1 g. of NaCl after neutralization. The total amount of solution was weighed to ± 1 mg.

For the determination of sodium two 10-gram samples of solution were weighed from a weight burette into 30-ml. platinum evaporating crucibles with flared tops. To each were

³³ We are indebted to R. E. Gibson of this Laboratory for the loan of this thermocouple.

added 3 ml. of concentrated HCl. Each solution was evaporated on a steam bath to about one-fourth its original volume. The evaporation was interrupted while another 3-ml. portion of concentrated HCl was added to each (whereupon fine crystals of NaCl were precipitated), and then it was continued to dryness. The crucibles were placed in a furnace preheated to slightly over 100°. The temperature was raised to 600° in the course of an hour and was maintained there for two hours. The crucibles were weighed after having been cooled in a desiccator for 30 minutes. The percentage of Na₂O in the original filtrate was computed from the mean amount of NaCl found.

Drying of Sodium Chloride during Analysis. At the beginning of this research a series of experiments was performed to find out the best temperature at which to dry NaCl. It has been suggested³⁴ that the NaCl be heated to incipient fusion in a covered crucible. Such a procedure will give a result that is too low. We found that the volatility of NaCl at its melting point (800° C.) is so great that in a covered crucible heated in an electric furnace the loss on fusion of previously fused NaCl amounts to at least 0.2 mg.

After having tried a number of different temperatures, we chose 600° for the final drying because it is high enough to dehydrate NaCl completely in two hours, but low enough so that there is no loss by sublimation from a covered crucible.

Determination of Carbon Dioxide. The determination of CO₂ was made in a gas-evolution type of apparatus by neutralization of the solution with dilute H₂SO₄. The evolved CO₂ was absorbed in "ascarite," after having been dried by concentrated H₂SO₄ and "anhydrone." Two separate determinations were made whenever sufficient solution remained after the sodium determinations.

Weighing. Weighings of the weight burette containing the solutions for the sodium determinations, of the evaporating crucibles containing NaCl, and of the absorption tubes containing CO₂ were made by the method of substitution on a Ruetprecht balance. The rest point could be estimated to ± 0.05 mg., as proved by a series of ten weighings of an empty platinum crucible. The weights had been calibrated with an uncertainty of ± 0.05 mg. by the method of Richards.³⁵

³⁴ For example, see Hillebrand, W. F., and Lundell, G. E. L.: *Applied inorganic analysis*; Wiley, New York, 1929, p. 521.

³⁵ Richards, T. W.: *J. Am. Chem. Soc.*, 22, 144-9, 1900.

TABLE I.
Liquidus Temperatures and Compositions.

Expt. No.	Temperature ^a Equilibrium	Initial	Stirring ^a (hours)	Gross Na ₂ O	Comp. ^b CO ₂	Composition of Na ₂ O	Filtrate ^c CO ₂
<i>Solid Phases: NaOH.H₂O and Na₂CO₃</i>							
104	60.1°	59.5°	6.2	49.8%	0.34%	48.75%	0.116%
129	62.0	59.5	6.0	50.6	0.55	49.61	*0.152
106	63.1	63	5.3			51.16	*0.120
128	*63.9	64.1	7.1	51.4	0.55	51.27	
107	*64.4	63	6			51.78	0.116
124	*64.7	64.2	5.7	52.0 ^d	0.55	52.24	
120	64.5	56	5.9	52.5	0.54	53.34*	*0.133
113	*64.7	64.5	4.1	52.9	(Analysis of residue—no filtrate.)		
122	*64.9	64.7	4.3	53.3	(Analysis of residue—no filtrate.)		
119	*64.9	63.4	5.5	52.7 ^f	0.55	53.72	
115	64.8	64.6	5.2	53.6	0.55	54.67*	0.206 ^g
111	64.4	63.9	6.3	54.0	0.55	55.17	0.159
101	*63.4	62.9	6.0	54.6	0.35	55.94	0.158
110	*62.3	68.7	11.5	54.6	0.55	55.39*	0.155
114	62.4	62.6	6.5	54.5	0.55	56.57	
103	62.6	62.4	5.0	55.7	0.26	56.63	*0.132
<i>Solid Phases: NaOH and Na₂CO₃</i>							
93 ^h	60.2	60.4	4.3	56.6	0.16	56.46	
112 ^h	61.4	66.5	10.8	58.1	0.57	56.59	0.159
97	62.6	62.7	5.0	60.4	0.17	56.60	
91	64.9	68.9	10.3	62.2	0.15	56.73	*0.107
92	65.1	61.6	8.5	62.2	0.15	56.75	*0.106
89	69.8	88	10.3	62.7	0.21	56.92	*0.144
90	69.9	65.2	8.9	62.2	0.15	56.99	*0.127

^a The *initial temperature* was that at the beginning of stirring. The period of *stirring* was the total time; during the last 4.0 hr. of stirring, the temperature was maintained at the *equilibrium* value. When the equilibrium temperature is preceded by an asterisk, the observed variation from the mean was $\pm 0.05^\circ$; in all other experiments it was $\pm 0.1^\circ$. The relative uncertainty, however, as already mentioned, was $\pm 0.2^\circ$ in all cases, because of the uncertainty in the thermocouple calibration.

^b The *gross composition* of each mixture (except in Expts. 113 and 122) was computed from the known composition of the ingredients; but each value for Na₂O may be too small by as much as one per cent because of loss of water by evaporation during mixing of the ingredients.

^c Each Na₂O percentage listed under *composition of filtrate* is the mean of duplicate determinations. Each has been corrected for non-volatile matter in the HCl used in the analysis (correction, -0.003 per cent), and for air buoyancy (correction, -0.01 per cent). The probable error was taken as the square root of the sum of the squares of (1) the mean deviation of the two determinations; (2) the systematic error in the weight calibration; and (3) an estimated systematic error of ± 0.005 per cent in the correction for air buoyancy. The absolute magnitude of the individual probable errors ranges from ± 0.008 per cent (Expts. 107 and 120) to ± 0.044 per cent (Expt. 89). The root mean square error for the 21 experiments being ± 0.021 per cent.

Each CO₂ percentage marked with an asterisk is the mean of duplicate

EXPERIMENTAL DATA.

The information gained from a single experiment was the composition of the liquid in equilibrium with two solid phases— Na_2CO_3 and either NaOH or $\text{NaOH}\cdot\text{H}_2\text{O}$ —at a measured temperature. Because the NaOH pellets contained slightly more Na_2CO_3 than such a doubly saturated solution between 60 and 70° , it was not possible to make experiments with solutions in the $\text{NaOH}\cdot\text{H}_2\text{O}$ field containing less than the saturation amount of Na_2CO_3 . In order to be certain that the reaction mixture contained an abundance of solid Na_2CO_3 at equilibrium, a small amount of $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ was added to it, except in the first few experiments.

The composition of the liquid at equilibrium is listed for each experiment in Table I. In several cases there was sufficient solid phase to form a mush that did not flow easily through the hole in the bottom of the reaction chamber into the filter crucible; with the result that there was not sufficient filtrate³⁶ for a CO_2 determination. Because of the small CO_2 content of these filtrates, between three and four grams of filtrate were needed for analysis in order that five milligrams of CO_2 might be weighed.

The lack of complete data on the CO_2 content of the filtrate does not seriously affect the value of these solubility determinations; because the CO_2 content is both small and practically independent of the temperature along the boundary between the $\text{NaOH}\cdot\text{H}_2\text{O}$ and Na_2CO_3 fields above 60° . There seems to be a tendency for a maximum CO_2 content at the maximum temperature; but it is not well-defined. The occurrence of such a maximum would not be surprising, for it would mean merely that in the ternary diagram the boundary between the $\text{NaOH}\cdot\text{H}_2\text{O}$ and Na_2CO_3 fields curves around the melting point

³⁶ In Experiments 113 and 122 no filtrate at all was obtained for the same reason. Analysis of a sample of the residue in the reaction chamber fixed a point above which the liquidus temperature must lie at that particular Na_2O content. The results of these two experiments are in agreement with the other results.

determinations. The deviation from the mean ranges from ± 0.001 per cent (Expt. 106) to ± 0.007 per cent (Expt. 91), the root mean square deviation for the 8 experiments being ± 0.005 per cent.

^d Analysis of residue in reaction chamber: 52.77 per cent Na_2O .

^e No solid phase present because of undercooling. See text, p. 210.

^f Analysis of residue in reaction chamber: 53.62 per cent Na_2O .

^g Results may be a little too high, because platinum felt in filter crucible disintegrated at end of this experiment.

^h NaOH metastable.

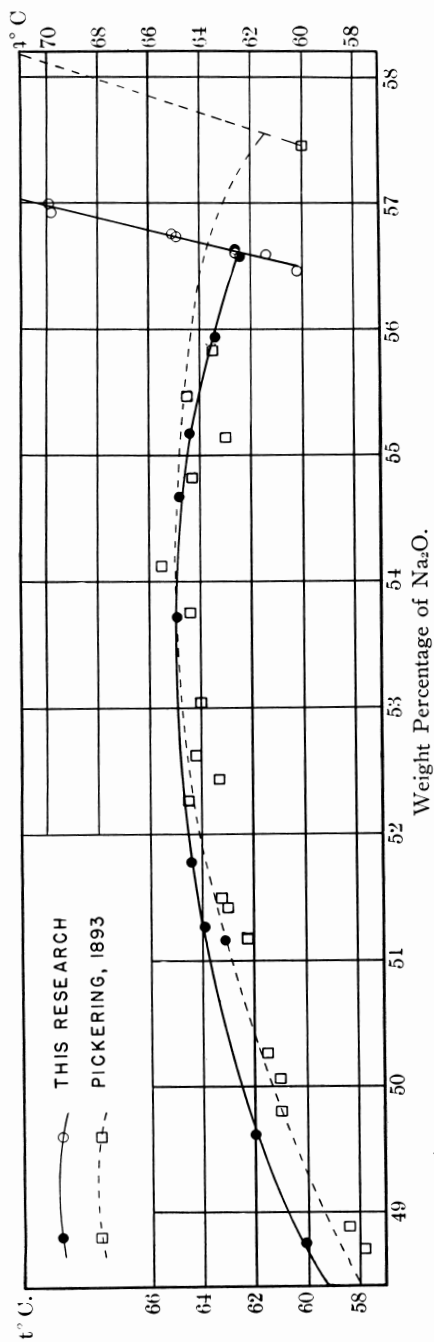


Fig. 2. Na_2O content along the boundary between the Na_2CO_3 field and the $\text{NaOH} \cdot \text{H}_2\text{O}$ and NaOH fields in the system $\text{NaOH}-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}$.

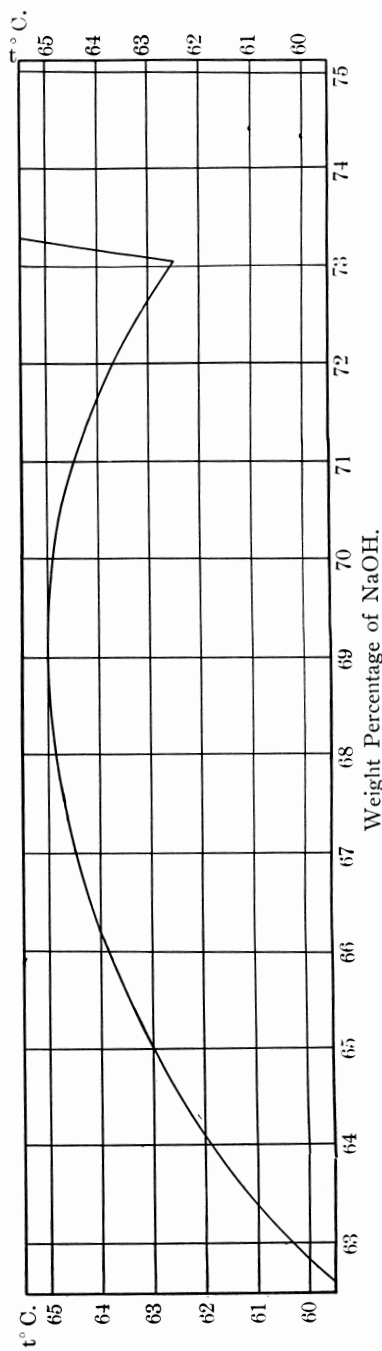


Fig. 3. Solubility of NaOH in water (solution saturated with CO_2 , and total alkali computed as NaOH).

of $\text{NaOH.H}_2\text{O}$. In the absence of more precise information, however, the best we can do is to suggest 0.14 ± 0.04 per cent as the most probable value of the CO_2 content along this boundary curve above 60° . Along the boundary between the NaOH and Na_2CO_3 fields, our data are adequate.

Na₂O Content as a Function of Temperature. The values of the Na_2O content (except for that in Expt. 106) are very self-consistent, as shown in Fig. 2 by the way they fall on a smooth curve. This curve gives the Na_2O content as a function of the temperature along the boundary between the Na_2CO_3 field and the $\text{NaOH.H}_2\text{O}$ and NaOH fields of the liquidus surface.

The point of maximum temperature along the curve must occur at the composition determined by the intersection of the $\text{NaOH.H}_2\text{O}$ — Na_2CO_3 join and the boundary curve between the $\text{NaOH.H}_2\text{O}$ and Na_2CO_3 fields in a ternary diagram. Assuming a CO_2 content of 0.14 per cent along the boundary curve (see above), the corresponding Na_2O content has been computed³⁷ analytically to be 53.45 per cent. In drawing the curve in Fig. 2, the maximum was made to occur at this composition, the maximum temperature having been determined by the shape of the curve itself as fixed by the experimental results. It is $65.0 \pm 0.5^\circ \text{C}$.

Ternary Eutectic. The position of the ternary eutectic between $\text{NaOH.H}_2\text{O}$, NaOH , and Na_2CO_3 is indicated in Fig. 2 at a temperature of $62.5 \pm 0.5^\circ \text{C}$. and a Na_2O content of 56.60 ± 0.05 per cent. Linear extrapolation of the CO_2 content along the boundary between the NaOH and Na_2CO_3 fields (Expts. 89, 90, 91, and 92, Table I) gives 0.093 per cent at 62.5° . This is a little lower than that indicated by the determinations (especially Expt. 103) along the $\text{NaOH.H}_2\text{O}$ curve. We select 0.11 ± 0.02 per cent as the mean CO_2 content at the ternary eutectic. The H_2O content, by difference, is 43.29 per cent. When the components are changed, this same composition becomes: NaOH , 72.85 ± 0.10 per cent; Na_2CO_3 , 0.27 ± 0.05 per cent; and H_2O , 26.88 ± 0.15 per cent.

Comparison with Data of Pickering. The points determined by Pickering³⁸ also have been plotted in Fig. 2, together with the smooth curve that he had drawn through them. Pickering had recorded his data as the percentage of NaOH in a solu-

³⁷ For the method of computation, see Morey, G. W.: *J. Phys. Chem.*, 34, 1745-50, 1930.

³⁸ Reference (30): Table I, p. 900; Fig. 1, facing p. 890.

tion whose freezing point he measured; but in the absence of any reference to efforts made to prepare CO_2 -free NaOH or to work in a CO_2 -free atmosphere, we assume that actually he measured the freezing points along the $\text{NaOH} \cdot \text{H}_2\text{O}$ — Na_2CO_3 boundary. For plotting his data, we have converted his recorded NaOH percentages to Na_2O percentages by multiplying by the factor 0.7748.

Although the reproducibility of Pickering's measurements was not as great as that of ours, it was remarkably good in view of the simple experimental method that he had used—merely a thermometer in a test tube. The portion of his measurements reproduced in Fig. 2, however, seems to have been affected by a systematic error in the determination of the composition of the solutions. Although he reported the same maximum temperature that we have found, the composition at this temperature was 54.2 per cent Na_2O instead of 53.45 per cent. Similarly for corresponding temperatures throughout the curve, the composition he reported was greater³⁹ than that which we have found. That Pickering's results rather than our own are in error is established by the fact that shifting the maximum of his curve to the theoretical percentage⁴⁰ of 53.45 per cent Na_2O would cause disagreement between the curve and his experimentally determined points.

Comparison with Data of Dietz. The difference just noted between our data and those of Pickering is the same as that between his data and those of Dietz⁴¹ throughout the course of the solubility curve of $\text{NaOH} \cdot \text{H}_2\text{O}$. A direct comparison between our data and those of Dietz is possible only at the maximum on the solubility curve, for his next highest temperature was 53° , and the curvature of the curve is too great to permit accurate interpolation. Dietz placed the maximum temperature at $64 \pm 1^\circ$, and we have placed it at $65.0 \pm 0.5^\circ$, at the same composition, which is good agreement.

Undercooling. Experiments 110 and 120 are interesting because they illustrate the ease of undercooling a solution that

³⁹ The difference cannot be ascribed to a difference in atomic weights; for Pickering mentioned (p. 894) that $\text{NaOH} \cdot 3\text{H}_2\text{O}$ contains 42.55 per cent NaOH , and the percentage on the basis of the 1938 International Atomic Weights is 42.53 per cent.

⁴⁰ If Pickering really measured the solubility of NaOH in water in the absence of CO_2 , the maximum of the curve should have been at 53.43 per cent Na_2O (or at 69.0 per cent NaOH , instead of at 70.0 per cent as shown on his graph).

⁴¹ See p. 202.

has a composition close to that of $\text{NaOH} \cdot \text{H}_2\text{O}$, provided that all crystals of $\text{NaOH} \cdot \text{H}_2\text{O}$ have been melted.

In Expt. 110 the reaction mixture was placed in the autoclave that had been preheated to about 65° , and then was heated overnight to 68.7° . In the morning it was cooled with stirring to the equilibrium temperature of 62.3° , and kept there for 4.0 hours before filtration. No solid material remained in the reaction chamber after filtration; and the composition of the filtrate was not far from that of the starting material. Contrasted with this result was that shown in Table I for Expt. 114, which was a duplicate experiment except that crystals of $\text{NaOH} \cdot \text{H}_2\text{O}$ were formed by a preliminary freezing after the reaction mixture had been dissolved.

In Expt. 120 the usual procedure was modified as follows. The reaction mixture was placed in the autoclave that had been preheated to about 60° , and stirring was started immediately. After 0.9 hr. the temperature had reached 64° , and at the end of 2.0 hr. it had reached 64.5° . It was maintained at $64.5 \pm 0.05^\circ$ for 4.0 hr., after which the diaphragm was cut and the mixture was filtered. No solid material remained in the reaction chamber after filtration; and again the composition of the filtrate was close to that of the starting material. Apparently all the NaOH had dissolved to form a solution from which no $\text{NaOH} \cdot \text{H}_2\text{O}$ crystallized because the solution never was undercooled sufficiently.

Further evidence of the reluctance of $\text{NaOH} \cdot \text{H}_2\text{O}$ to crystallize was observed in several experiments near the ternary eutectic. After a reaction mixture had been dissolved by stirring in the autoclave at about 65° , it was cooled slowly with stirring until it froze. Table II gives the temperature at which freezing started when the solution was cooled at the rate of a few tenths of a degree a minute. The solid phase that appeared

TABLE II.
Undercooling of Solutions of NaOH .

Expt.	Gross Composition	Minimum Temperature	Undercooling
92	62% Na_2O	55.9°	6.6°
93	56%	57.4°	5.1°
95	62%	57.0° ; 55.0°	5.5° ; 7.5°
96	57%	51.4°	11.1°
100	55%	51° ^a	11.5°

^a Solution not stirred during cooling.

in Expt. 93 must have been NaOH, judging from the composition of the filtrate that was obtained (see Table I), for the mixture had not been heated above 60.4° after it had melted. In the other experiment (Expt. 112) along the metastable prolongation of the solubility curve for anhydrous NaOH the reaction mixture first was stirred at 66.5° and then was cooled to the equilibrium temperature of 61.4° .

EXTRAPOLATION OF THE SOLUBILITY DATA.

A saturated solution of NaOH between 60 and 70° will be saturated also with respect to Na_2CO_3 , unless some special process is employed for making the solution from NaOH that truly is carbonate-free. Hence it is of no practical importance that our data concerning these solutions cannot be extrapolated

TABLE III.
Composition of Solutions Saturated with Respect to
 Na_2CO_3 and $\text{NaOH}\cdot\text{H}_2\text{O}$ or NaOH.

Temp. ^a ($^{\circ}\text{C}.$)	Na_2O (wt. pct. $\pm 0.03\%$)	Total alkali computed as NaOH (wt. pct. $\pm 0.05\%$)	NaOH (wt. pct. $\pm 0.1\%$)	Na_2CO_3 (wt. pct. $\pm 0.05\%$)	Solid Phases ^b
60.0	48.67	62.81	62.5	0.35	A & C
61.0	49.10	63.37	63.1	0.35	A & C
62.0	49.66	64.09	63.8	0.35	A & C
63.0	50.37	65.01	64.7	0.35	A & C
64.0	51.29	66.19	65.9	0.35	A & C
65.0	53.45	68.98	68.7	0.35	A & C
64.0	55.50	71.63	71.4	0.35	A & C
63.0	56.27	72.62	72.4	0.30	A & C
62.5	56.60	73.05	72.8 ₅	0.27	A, B, & C
63.0	56.63	73.09	72.9 ₀	0.27	B & C
64.0	56.68	73.15	72.9 ₅	0.28	B & C
65.0	56.74	73.23	73.0 ₀	0.29	B & C
70.0	56.97	73.53	73.3 ₀	0.33	B & C

^a This temperature scale is only relative. A temperature may differ from the thermodynamic scale by $\pm 0.5^{\circ}$ at a particular composition.

^b Solid phases: A = $\text{NaOH}\cdot\text{H}_2\text{O}$; B = NaOH; and C = Na_2CO_3 .

to the border of the ternary diagram to yield the true solubility of NaOH in water. That temperature-solubility curve presumably would not be far different from that which we have obtained for the doubly saturated solution; although the maximum temperature (which would be the true melting point of NaOH.H₂O) might be raised by as much as five degrees by the absence of carbonate, although such a large change is not likely.

Instead of attempting an extrapolation based on insufficient evidence,—and the work required to secure more evidence would scarcely be justified,—we have prepared a table (Table III) that shows the composition of the doubly saturated solutions as actually encountered in laboratory practise. The first column of the table gives the Na₂O content as read from the smooth curve in Fig. 2. The second column gives the total alkali content of the solutions computed as NaOH by multiplying the percentage of Na₂O by 1.2906. These values are shown graphically in Fig. 3. The third and fourth columns of Table III give the amounts of the separate alkalis in the saturated solutions, as computed from the Na₂O content and the CO₂ content.

OPTICAL PROPERTIES OF NaOH AND OF NaOH.H₂O.

The phase relations were so simple in the part of the system, NaOH—Na₂CO₃—H₂O, that we have investigated, that it was not necessary to make optical examinations in order to identify the solid phases present at equilibrium. But since the optical properties of neither NaOH nor its monohydrate have been published heretofore, we thought this an appropriate time to do so. Our colleagues Dr. Merwin and Dr. Ingerson kindly consented to make the examinations. The results they obtained are presented in Table IV.

SUMMARY.

We have made a precise determination of the position of the boundary between the field of Na₂CO₃ and the fields of NaOH.H₂O and NaOH in the ternary system, NaOH—Na₂CO₃—H₂O, in the temperature range 60 to 70°. The liquidus temperature varies little as long as NaOH.H₂O is the solid phase along with Na₂CO₃, reaching a flat maximum of 65° at 53.45 per cent Na₂O. The ternary eutectic is at 62.5° and 56.60 per cent Na₂O. From this point the temperature

TABLE IV.
Optical Properties of NaOH and of NaOH.H₂O.

	NaOH ^a	NaOH.H ₂ O ^b
Crystal system	Orthorhombic (or pseudo-orthorhombic?) ^c	Orthorhombic (or monoclinic?) ^c
Habit and orientation	Blades: flattened (001) Plates: flattened (001) Nearly equant grains	Blades: flattened (001), elongated <i>a</i> , and terminated by (110) and (110) and by (110) and (110) at interior angle of $92 \pm 2^\circ$. Edges frequently beveled by slightly developed domal and pyramidal faces
Cleavage	Eminent, (001) Imperfect, (110), angles about 90°	Good, (001)
Color	Colorless	Colorless
Extinction	Extinction directions on cleavage flakes nearly or quite bisect the angles of the other cleavages	Parallel to elongation
Refractive indices and Optical orientation	$\left\{ \begin{array}{l} \alpha(?) = 1.45_7 \\ \beta(?) = 1.47_0 \\ \gamma(c) = 1.47_2 \end{array} \right.$	$\left\{ \begin{array}{l} \alpha(c) = 1.435 \pm 0.004 \\ \beta(a) = 1.470 \pm 0.004 \\ \gamma(b) = 1.475 \pm 0.004 \end{array} \right.$
Optical character	Biaxial negative	Biaxial negative
Optic axial angle	$2V = 50 \pm 10^\circ$	$2V = 45 \pm 5^\circ$
Dispersion of optic axes		None apparent
Interference figure	Cleavage flakes normal to obtuse bisectrix	Cleavage flakes normal to acute bisectrix

^a Examination by H. E. Merwin.^b Examination by Earl Ingerson.^c The probability that this substance is not orthorhombic is very slight.

Remarks on the Optical Examinations. Three types of crystalline NaOH were studied. Radiating blades were obtained by melting and quenching the nearly pure hydroxide. Plates and nearly equant grains, which had grown in aqueous solutions at 270° in the course of solubility determinations, were obtained as lumps cemented together by solidified mother liquor. Powdering the lumps under paraffin oil to secure clean surfaces was accompanied by deformation and the development of strain-birefringence. Cutting or chopping with a sharp scalpel gave the best fragments. Interference figures obtained from fragments cut normal to the cleavage showed marked effects of distortion. Because of the ease of deformation of the crystals, the optical properties

risks rapidly with increase of Na_2O content, NaOH being the second solid phase.

As a demonstration of the worth of the new type of filter autoclave for solubility measurements that was described in Part II of this paper, these experiments were very satisfactory. Even close to the maximum of the solubility curve it was possible to make determinations by careful control of the gross composition of the reaction mixture. For the determination and composition of the ternary eutectic, the autoclave was especially well suited.

The optical properties of NaOH and $\text{NaOH}\cdot\text{H}_2\text{O}$ have been measured by H. E. Merwin and Earl Ingerson, respectively, using samples that we prepared.

This study, which is part of a comprehensive research program concerning water in alkali silicate melts, has been aided by means of special funds made available to the Carnegie Institution of Washington by the Carnegie Corporation of New York.

could not be measured as accurately as otherwise would have been possible; and for the same reason it could not be determined whether the optic axes are dispersed. It was noticed that the crystals themselves were more dispersive than the paraffin oils used as immersion media.

The $\text{NaOH}\cdot\text{H}_2\text{O}$ that was examined consisted of residues from several of the experiments near the melting point. In the measurement of the refractive indices and in the study of the interference figures, the flakes of $\text{NaOH}\cdot\text{H}_2\text{O}$ were crushed under oils to secure fresh surfaces. In the study of the crystal habit, crystals were grown in aqueous mother liquor in a shallow glass cell on the microscope stage.