[CONTRIBUTION FROM U. S. NAVAL RESEARCH LABORATORY]

The Solubility of Quartz in Sodium Carbonate Solutions at High Temperature

BY I. I. FRIEDMAN[1]

This work was undertaken as a preliminary investigation of the system at 300, 350, 400 and 450°, and is restricted to solutions in equilibrium with quartz.

To define completely this system at the liquidus it would be necessary to fix three independent variables. The usual variables which are experimentally controllable are the temperature and two others, such as total pressure, the partial pressure of one of the components of the vapor, and the liquid or vapor composition. The apparatus available did not permit sampling the liquid or vapor phases, nor was it possible to get accurate pressure measurements. However, while the following data do not define the system completely, they provide a valuable preliminary basis for such investigations.

Experimental

The runs were made by placing weighed blocks of quartz in 18-ml. pressure bombs together with weighed amounts of sodium carbonate, pipetting in 10 ml. of distilled water, sealing the bombs and allowing them to remain at a predetermined temperature. The bombs were continuously rocked to provide agitation. Further details of the equipment are given in a previous paper.[2] After equilibrating for from forty to one hundred and fifty hours, the bombs were removed from the furnaces and quenched by directing a stream of cold water onto them. The sodium carbonate was reagent grade, and was dried at 120° for several hours. Quartz slabs (2.5 × 1.5 × 0.5 cm.), cut from piezo-electric grade natural quartz were used throughout.

Results and Discussion

It was noted in many runs at 400° and in all runs at 450° that considerable pressure was released upon opening the bombs after quenching. Evidently at these temperatures silica displaces carbon dioxide from the sodium carbonate, resulting in a high partial pressure of carbon dioxide in the vapor. This parallels the results of Morey and Fleischer[3] in the system K_2O–SiO_2–H_2O–CO_2, who found that the distribution ratio of carbon dioxide between the liquid and vapor increased in the direction of the vapor at 500° and K_2O–SiO_2 ratios above 1:1.

As a check on the solubility curves many runs were equilibrated at 450° and slowly cooled to various temperatures from 425 to 300°. They were then allowed to equilibrate at the lower temperature and quenched. In all cases all of the excess quartz recrystallized on the remains of the original quartz block. This indicated that: (1) The curves represent true equilibrium values; (2) Quartz can be grown from sodium carbonate solutions by slowly cooling a saturated solution of quartz in sodium carbonate in contact with a quartz seed plate.

Figure 1 shows the solubility of silica in sodium carbonate solution as a function of sodium carbonate concentration at various temperatures. The spread of experimental points, particularly at 450° can be explained by the high temperature dependence of the solubility at the higher temperatures. The bombs that were used varied slightly (5% max.) in the size of the chamber. This variation in the degree of filling would also contribute to the error.

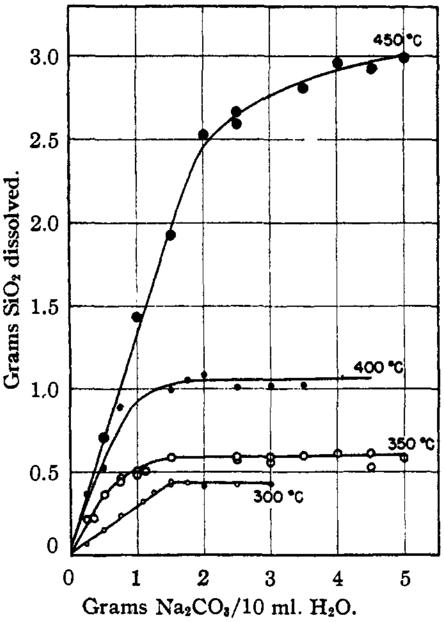

Fig. 1.

The leveling off of the solubility curves with increasing sodium carbonate concentration might be due to the formation of a solid phase containing sodium oxide. Sodium carbonate crystals were found in most runs, but it is not clear if the crystals formed during the quench or represent a stable solid phase at the temperature of the runs.

Upon opening the quenched runs a hard water-soluble glass was found in most of the bombs in addition to the liquid and crystalline phases. The glass was not found in runs made at 300° that contained less than 1.5 g. of sodium carbonate, nor was it observed in runs made at 450° that contained over 3.5 g. of sodium carbonate. These glasses are similar in character to the glasses observed in the Na_2O–SiO_2–H_2O system,[2] and can be assumed to have been liquid at the temperature of the runs. It seems quite probable that the liquid immiscibility reported in the Na_2O–SiO_2–H_2O sys-

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[2] Tuttle and Friedman, THIS JOURNAL, **70**, 919 (1948).

[3] Morey and Fleischer, *Bul. Geo. Soc. Am.*, **51**, 1035 (1940).

tem extends into the $Na_2O-SiO_2-H_2O-CO_2$ system. However the correctness of this assumption will have to be checked by a more elaborate investigation of this system.

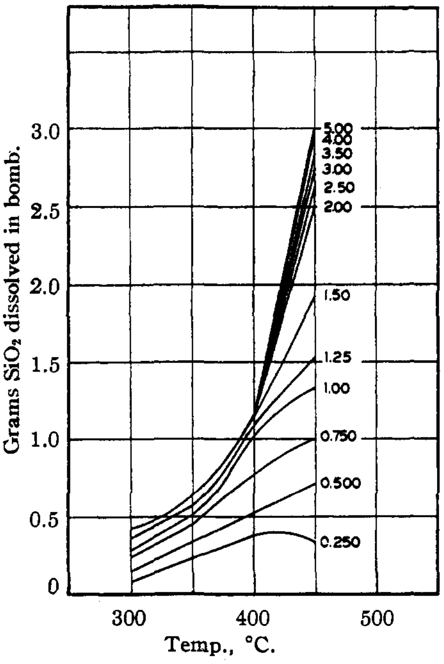

Fig. 2.

As can be seen from Fig. 2, this system would be a desirable one from which to grow quartz. The steep slope of the Solubility *vs.* Temperature curve would be favorable for growing quartz by the temperature lowering as previously stated, while the low solubility of quartz in sodium carbonate solutions as compared to its solubility in sodium hydroxide solutions, as shown in Table I, suggests that carbon dioxide might be used to displace quartz from sodium hydroxide solutions at constant temperature.

TABLE I

Temp., °C.	% Na_2O	Solubility, of quartz, g./l.	
		NaOH solutions	Na_2CO_3 solutions
	1	20	5
300	5	135	28
	15	514	43
	1	25	13
350	5	152	50
	15	515	60
	1	35	22
400	5	155	90
	15	560	105
	1	35	24
450	5	163	124
	15	560	285

The author again wishes to emphasize the preliminary nature of the present paper. Much careful experimentation remains to be done before our understanding of equilibrium in multicomponent systems containing volatile and non-volatile components can be extended very far.

The assistance rendered by Mr. Charles Jackson was of great aid in carrying out the experimental work.

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Heats of Combustion of Some Organic Nitrogen Compounds

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The need for accurate values of heats of combustion for thermodynamic calculations has often been emphasized, and the lack of such data seems especially noticeable for organic compounds containing nitrogen. We therefore record here heats of combustion, determined with relatively high accuracy, of eight such compounds: cyanamide, dicyandiamide, melamine, 3-cyanopyridine, phthalonitrile, dimethylol urea, diisopropyl cyanamide, and diisopropyl carbodiimide.

Experimental

Apparatus and Procedure.—The bomb calorimeter used was modeled after that of Dickinson,[2] being a replica of that of Huffman and Ellis,[3] and of Richardson and Parks[4]; the calorimeter was in fact made in the shops of the California Institute of Technology.

The samples were burned in a Parr bomb (380 ml. capacity), containing initially 1 ml. of water and commercial tank oxygen at 30 atm. pressure at about 24°. The air was usually flushed out by two fillings with oxygen to 15 atm. pressure when solid samples were burned, but no flushing was made with liquids. The weight of water for the calorimeter, usually 2770 g., was measured to 0.05 g. on a high capacity balance.

Pellets of solid samples were weighed in a platinum crucible to 0.05 mg. on an analytical balance, after they had been kept in a desiccator over phosphorus pentoxide for several days. As far as is known, the compounds are not hygroscopic (except cyanamide, discussed below), and no changes in the heats of combustion with drying times of three to ten days were noticed. For liquids, thin-walled soft glass ampoules were completely filled by means of a fine hypodermic syringe, through a single stem, which was then sealed off. The liquids were not freed of any dissolved air.

Either of two methods of firing the sample have been employed, the platinum wire-string fuse of Richardson and Parks,[4] or the usual iron wire. In the former, the electrical energy (*EIT*) introduced was obtained by accurate measurements of voltage, current, and time. These

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(1) Present address: Guymon, Oklahoma.

(2) Dickinson, *Bull. Bureau of Standards*, **11**, 243 (1915).

(3) H. M. Huffman and E. L. Ellis, THIS JOURNAL, **57**, 41 (1935).

(4) J. W. Richardson and G. S. Parks, *ibid.*, **61**, 3543 (1939).