A NOTE ON THE EFFECT OF TEMPERATURE ON THE TRANSITION OF CALCITE TO ARAGONITE

R. Edman Greenfield, Chemist, State Water Survey, Urbana.

In a study of the solubility of the different forms of calcium carbonate in carbon dioxide solutions and its bearing on corrosion problems, some things were noted which led to a little study on the condition of change of one form to another. The studies on solubility were carried out by shaking carbon dioxide solutions with solid calcium carbonate in a constant temperature bath until equilibrium was reached. Over a week was always allowed for this reaction.

Bicarbonate alkalinity, which represented the calcium carbonate dissolved, and free carbon dioxide were determined on the resultant solution. The results at any one temperature when plotted on ordinary coordinate paper gave a smooth graft of an exponential form. It was found that if they were plotted on logarithm paper they gave straight lines within the limit of error. Results for 0°, 20° and 65°C are shown in Fig. 1. It will be seen that the solubilities of both forms increase with temperature from 0° to 20° and that aragonite is appreciably more soluble than calcite at all times. At 25° and 35° results were obtained not much different from those at 20°; if any thing they were a little lower in both cases than were the 20° results. These results are not shown in Fig. 1. At 65° the two forms were about the same solubility and were lower than even the 0° calcite. At first these results were considered to indicate a transition temperature between the two forms of calcium carbonate, but later experiments on mixtures and a study of Johnson's[1] article shows this to be impossible. They may well indicate that the solubilities of the two forms become quite close at this temperature. This is supported by certain conductivity data and solu-

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[1] J. Johnson, H. E. Merwith & Ed. Williamson, Am. J. Science, 4th ser. *41*, 473 (1916).
Studies conditions of formation of different forms of calcium carbonate under different conditions.

bility products obtained by H. W. Foote[2]. Of course it is also possible that at this high temperature the unstable aragonite has partly changed to calcite and that the equilibrium is established with the more insoluble form. A specific gravity of the undissolved residue was run, but the results were not conclusive as the sample had not been ground fine enough and a true specific gravity was not obtained.

Fifty percent mixtures of aragonite and calcite were ground together, covered with water containing carbon dioxide and exposed to various temperatures. These mixtures were allowed to react one week when they were ground and the specific gravity determined. Temperatures of 20°, 37°, 65° and 100° were used. The change in specific gravity in every case indicated that the aragonite was being changed quite rapidly to calcite and that the reaction was more rapid at 65° than at 25° and 37°. The specific gravity determinations of the material exposed to 100° were not very concordant and no very definite conclusions could be drawn. This rapid change is contrary to most of Johnson's[1] findings.

Certain of the samples which were allowed to react at 65°C cemented firmly together to form a mass which was quite strong and which showed rather large crystals of calcite mixed in a matrix of small crystals. Samples exposed to other temperatures, while they became much more granular than the original material, did not cement together. The samples which were finely ground did not form as strong a material as that which was more coarsely ground. The condition of packing seemed also to have some effect upon the strength of the material. An attempt was made to form this cemented material by the use of ground marble and the aragonite from ground oyster shell. This material recrystallized into a more granular form but did not cement together.

This formation of a cemented material, using as a binder only a more unstable crystalline modification,

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[2] .H. W. Foote, Zeitshr. Physikal, Chemie, *33*, 740 (1900) Uberdie Physikalish Chem. Beziechungen Zwischen Aragonit and calcit.

Showed by oxalate reaction and conductivity experiments that the solubility of calcite and aragonite approached each other with increasing temperature worked from 8° to 59° also show increase and then decrease. Aragonite at 50° still considerably higher than calcite.

may at times have been operative in nature, and might, if suitable material were available and if proper conditions of temperature, concentration of solution and state of subdivision were worked out, be of importance practically.