

A DISCUSSION ON "MECHANISM OF SOLUTION OF QUARTZ IN PURE WATER AT ELEVATED TEMPERATURES AND PRESSURES"

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Recently Frederickson and Cox (1) have measured the solubility of quartz in water between 200 and 370° C. at a pressure of 300 bars. The solubility was determined by removing samples of the solution from the bomb at given P and T and determining the amount of solute by weighing the dry residue. An innovation in technique was introduced in that samples could be withdrawn from the top and near the bottom of the vertical bomb.

The important experimental finding reported by these workers in their studies on quartz and albite (2) is that the "solubility" differs in different parts of the bomb, being much greater at the bottom than at the top. Based on these findings a mechanism of solution is postulated. If the results are correct, they must throw considerable doubt on the "absolute" values of solubility as found by Kennedy (3) and Morey and Hesselgesser (4).

Unfortunately, some experimental data which are critical in evaluating the results of the experiments are not given in the paper. In particular, the volume of the samples withdrawn and the magnitude of the "temporary pressure drop" during sampling should have been recorded. If, however, the techniques and procedures used are as stated in the text of the paper, these may be calculated and if this is done we need not look far for an explanation of the solubility anomalies reported and certainly there is no justification for postulating any special mechanism of solution to explain the results.

There are a great number of experimental difficulties in determining the solubility of a substance in water at high pressures and temperatures. There are objections to the methods used by Kennedy and Morey and Hesselgesser, but both studies illustrate that some of the objectionable features are not significantly affecting the results. Such objections might be (a) diffusion out of the system along a cold gauge line is possible (a function of time); (b) there might be reaction with materials of the bomb (a function of time); (c) solution might be reprecipitated on the crystals during cooling (a function of the available surface and rate of cooling—a difficulty not encountered in Morey's work). In general, the data presented by these workers clearly shows that such effects under the conditions studied are trivial.

The inherent difficulty with sampling techniques lies in the possibility of changes in the system caused by the sampling. In this respect we must

look more closely at the experiments of Frederickson and Cox. We are told that a pressure of 300 bars at 200° C. was produced in the 195 cc. bomb by the degree of initial filling. The technique of sampling used was such that sufficient sample was removed at 200° C. to leave enough water to give a pressure of 300 bars at 250° C., this procedure being repeated at approximately 50° intervals till a temperature of 350–370° C. was attained. If this is the procedure used, then during sampling at each temperature, the state of the system will be profoundly changed. At 300 bars, at all temperatures a homogeneous fluid phase will exist in the bomb. If enough water is removed at each of the intervals mentioned above, then at the end of the sampling, and during much of the sampling, a liquid-vapor system will be created. In Table 1 are listed some calculations on this problem from *P.V.T.* data of Kennedy (5) and Keenan and Keyes (6).

TABLE 1

I	II	III	IV	V
T° C.	Vol. of water at <i>N.T.P.</i> to fill bomb	cc's removed in sampling	Vol. of water at <i>N.T.P.</i> to fill with satd. liquid	Minimum sample to enter liquid-vapor region
200	172.5 cc.	11.5 cc.	168.6 cc.	3.9 cc.
250	161.0	14.5	155.3	5.7
300	146.5	21.1	138.8	7.7
350	125.4	—	111.6	13.8

In column II are listed the volumes of water needed at *N.T.P.* to fill the 195 cc. bomb to give 300 bars at the temperatures of column I. In column III are listed the volumes of the samples removed if the successive sampling technique described is followed. In column IV are listed the volumes of water at *N.T.P.* needed to fill the bomb with liquid water at a pressure corresponding to the liquid-vapor equilibrium pressure. In column V are listed the maximum volumes of sample which could be removed without entering the liquid-vapor region. It is obvious when columns III and V are compared, that during much of the sampling, a vapor phase exists in the bomb. In each case this will occur when approximately $\frac{1}{3}$ of the sample has been removed. It is immediately obvious why the samples removed from the top of the bomb give lower solubilities than those removed from the bottom for much of these samples consist of vapor saturated with quartz and the solubility in the vapor will be small compared with that in the homogeneous fluid originally present. In the same way, the evaporation of part of the water will cause

rapid precipitation of silica which may be collected in the bottom sampling. The effects will occur independently of the order of sampling.

The removal of the samples will also cause pronounced cooling of the bomb, depending in part on the rate of sampling. If this is fast, then as the latent heat of vaporization of water is in the range 8–6 k. cal./gram mol over this temperature range, and as approximately a gram mol of water is removed at each sampling, then one might expect cooling of the order of 20–30° C. during the sampling. This effect will further tend to throw the system into the liquid-vapor region and the volumes of sample which could be removed without causing inhomogeneity of the fluid phase will be even smaller than indicated in column V of Table 1.

The conclusion which must be reached from the description of the experiments given by the authors is that the anomalous results for the solubility of albite and quartz found are in all probability related to the drastic changes in the state of the aqueous solvent caused by the sampling technique. With this doubt in mind it would be unwise to place too much weight on the deductions made from the experimental findings.

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DIRECTIONAL HARDNESS VARIATION IN TUNGSTEN CARBIDE (WC) MONOCRYSTALS

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INTRODUCTION

During a series of experiments designed to increase the hardness and density of tungsten carbide-cobalt alloys, microhardness tests were made on tungsten carbide single crystals.† Measurement of oriented micro-

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† Crystals supplied by Kennametal Inc., Latrobe, Pa.