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

W. S. Fyffe, Institute of Geophysics, University of California, Los Angeles, California.

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 An innovation in technique was introduced in that samples could be withdrawn from the top and near the bottom of the vertical bomb.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 In particular, the volume of the samples withdrawn and the magnitude of the "temporary pressure drop" during sampling should have been recorded.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 at-
tained. If this is the procedure used, then during sampling at each tem-
perature, 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 sam-
pling, 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>
<thead>
<tr>
<th>T° C.</th>
<th>Vol. of water at N.T.P. to fill bomb</th>
<th>cc's removed in sampling</th>
<th>Vol. of water at N.T.P. to fill with satd. liquid</th>
<th>Minimum sample to enter liquid-vapor region</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>172.5 cc.</td>
<td>11.5 cc.</td>
<td>168.6 cc.</td>
<td>3.9 cc.</td>
</tr>
<tr>
<td>250</td>
<td>161.0</td>
<td>14.5</td>
<td>155.3</td>
<td>5.7</td>
</tr>
<tr>
<td>300</td>
<td>146.5</td>
<td>21.1</td>
<td>138.8</td>
<td>7.7</td>
</tr>
<tr>
<td>350</td>
<td>125.4</td>
<td>—</td>
<td>111.6</td>
<td>13.8</td>
</tr>
</tbody>
</table>

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 sam-
pling technique described is followed. In column IV are listed the vol-
umes 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 re-
moved 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 ap-
proximately ½ of the sample has been removed. It is immediately obvi-
ous why the samples removed from the top of the bomb give lower solu-
bilities 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 sam-
ppling. 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. cals/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 sam-
ping technique. With this doubt in mind it would be unwise to place too
much weight on the deductions made from the experimental findings.

References
1. Frederickson, A. F., and Cox, Joseph E., Mechanism of “solution” of quartz in pure
3. Kennedy, George C., A portion of the system silica-water: Economic Geology, 45, 629
(1950).
4. Morey, G. W., and Hesselgesser, J. M., The solubility of quartz and some other sub-
stances in superheated steam at high pressures: Transactions of the A.S.M.E., 865
(1951).
5. Kennedy, George C., Pressure-volume-temperature relations in water at elevated
Sons (1936).

DIRECTIONAL HARDNESS VARIATION IN TUNGSTEN
CARBIDE (WC) MONOCRYSTALS

J. A. Kohn,* Perry G. Cotter, and R. A. Potter,

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-

* Present address, Chemical-Physics Branch, Signal Corps, Engineering Laboratory,
Pt. Monmouth (Hexagon) N. J.
† Crystals supplied by Kennametal Inc., Latrobe, Pa.