

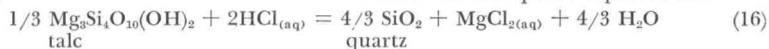
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ACID-BASE BUFFERS: USE OF Ag + AgCl IN THE EXPERIMENTAL CONTROL OF SOLUTION EQUILIBRIA AT ELEVATED PRESSURES AND TEMPERATURES

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ABSTRACT. A buffer has been developed and tested that allows the fugacity of HCl to be kept constant during hydrothermal experiments at elevated P and T. This is achieved by combining a fixed hydrogen fugacity, imposed by a conventional external hydrogen buffer, with a fixed chlorine fugacity, defined by the assemblage Ag + AgCl. This HCl buffer has been tested and calibrated, by using HCl-H₂O solutions and by measuring pH at room temperature and atmospheric pressure after quench. Values were obtained with Ni + NiO + H₂O and Fe₂O₄ + Fe₂O₃ + H₂O as hydrogen buffers for 1000 and 2000 bars. At higher temperatures there is reasonable agreement between calculated and measured values, but at lower temperature the two sets of data diverge. This is thought to be caused by the increasing dissociation of HCl at lower temperatures. Using this interpretation, a dissociation constant for HCl is derived as a function of temperature, which is then compared with Franck's data for the same constant obtained from conductivity measurement. The agreement is surprisingly good and well within the limits of errors of the two sets of data. This agreement is used as evidence that the Ag + AgCl assemblage successfully buffers the fugacity of HCl and that the values of f_{HCl} in the hydrothermal region are now well known. The Ag + AgCl acid buffer has been used to measure the talc-quartz equilibrium:



The great advantage of the Ag + AgCl acid buffer lies in the fact that it controls f_{HCl} at P and T and hence removes ambiguities associated with earlier methods based on quench pH measurements.

INTRODUCTION

The importance of solution equilibria in the formation of igneous and metamorphic mineral assemblages has recently been emphasized by a number of workers, following the pioneering studies of Morey and Hesselgesser (1951), Hemley (1959), and Orville (1963). Helgeson (1967) extended many of the approaches used by solution chemists into the supercritical region, while Carmichael (1969) interpreted metamorphic textures using exchange equilibria between domains, assuming conservation of aluminum. Eugster (1970) emphasized solution equilibria to predict reactions among K-spar-muscovite-Al-silicate assemblages, and Fisher (1970) explained metamorphic segregations in similar terms.

It is abundantly clear from these studies that the aqueous phase present in igneous and metamorphic rocks, be it a separate gas phase or a grain boundary phase, must be treated as a solution of charged as well as uncharged species. Salts, acids, and ionic species such as KCl, HCl, Na⁺ are essential constituents of such a phase, and they participate in many mineral reactions. Hence, if we desire to understand mineral assemblages and mineral textures, we need to know more about the role such species play. One way to find out is to measure equilibrium

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