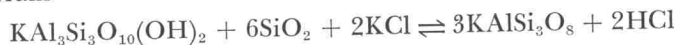


constants involving salts, acids, and ions and to compare the results with natural mineral assemblages. In other words, we must extend solution chemistry into the realm of metamorphic and igneous rocks.

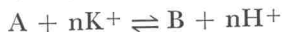
In the past, experimental petrologists concerned with metamorphic rocks have been preoccupied with reactions between minerals and stable gases or gas mixtures (for recent summaries see Greenwood, 1967; Eugster and Skippen, 1967). Hemley (1959), on the other hand, studied the equilibrium



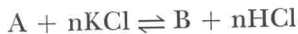
and measured pH and mKCl after quenching to room temperature and atmospheric pressure, expressing his results as a function of m_{HCl}/m_{KCl} of the solution. Measurements made after quench are used to determine the solution composition at P and T. This procedure is permissible, provided no significant reactions take place during and after quench. It appears that errors are small with respect to some solutions, such as KCl-HCl-H₂O, but there is very strong evidence that this is not the case for many solution compositions, such as MgCl₂-HCl-H₂O. Poty and Holland (1970) measured quench pH values of 1.0 and 6.5 respectively for the assemblages talc + quartz and forsterite + talc. To interpret these values, they were forced to assume dissociation of HCl° and reaction with Mg(OH)⁺ during cooling.

It is essential, then, that we devise a method for controlling or measuring solution species at P and T. One way would be to measure directly ion activities at P and T, but technical difficulties have not yet been overcome. Another possibility is to extend the buffering methods used so successfully for mixtures of uncharged gases (see for instance, Eugster and Skippen, 1967). In this approach the gas composition is held invariant by a suitable assemblage of solids, and the fugacities of individual gas species at P and T can then be calculated.

To achieve the bridge necessary from gas to solution equilibria, it seems most promising to buffer the fugacities of acids, such as HCl, H₂SO₄, HF at P, and T. This is obvious from the following considerations: Mineral-solution equilibria expressed in terms of ionic species can usually be balanced by hydrogen ions



Adding the dissociation equilibria, say with respect to chloride, we obtain



with the salts being balanced by acids. Hence by measuring salt concentrations, such as KCl, MgSO₄, NaF, after completion of an experiment, equilibrium constants can be calculated as a function of P and T. Reversibility can be tested by starting with salt concentrations below and above that of the equilibrium solution.

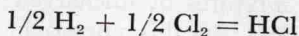
Data from fluid inclusions and from volcanic gases seem to indicate that chloride is probably the most common anion in natural supercritical

solutions. Hence, if we can find a way to buffer the fugacity of HCl, a very large number of geologically important reactions involving chloride solutions become amenable to experimental determination. f_{HCl} can be buffered most conveniently by combining conventional hydrogen buffers (Eugster and Skippen, 1967) with a chlorine buffer, such as an inert metal-metal chloride pair. Ag + AgCl offers the most promise. We have tested this buffer arrangement successfully and have used it extensively to measure equilibrium constants involving solutions of KCl, MgCl₂, CaCl₂ and the minerals muscovite, K-spar, andalusite, phlogopite, chlorite, talc, forsterite, tremolite, diopside, wollastonite, and quartz (Frantz, ms; Gunter, ms).

Ag and AgCl apparently behave as inert phases in H-O-Cl solutions, and therefore gas fugacities may not only be calculated from thermodynamic data, but they can readily be calibrated by quench pH measurements. In this paper we report the buffering method, its calibration, and its application to the talc-quartz equilibrium.

BUFFERING THEORY

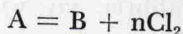
Consider a gas phase whose composition lies in the system H-O-Cl. At a given pressure and temperature, this gas phase has a variance of two. In order to make the system invariant, it is necessary to specify two additional intensive parameters, one of which may be the fugacity of hydrogen, f_{H_2} , controllable by standard techniques (Eugster and Skippen, 1967; Shaw, 1967). Use of an internal chlorine buffer, defining f_{Cl_2} , removes the remaining degree of freedom. Buffering f_{H_2} and f_{Cl_2} independently in turn fixes the fugacity of HCl, f_{HCl} , through the equation



It should be stressed, that this controls the fugacity of the associated uncharged HCl molecule (HCl°), regardless of any other species present. Through controlling HCl° the product $a_{\text{H}^+} \times a_{\text{Cl}^-}$ is also fixed, because of the equilibrium



In principle, any group of solids A + B related to each other by the reaction



can be used as a chlorine buffer. However, it is desirable that such solids be relatively insoluble and inert with respect to the phases to be investigated. We have found the pair Ag + AgCl to be most acceptable. One possible drawback is the low melting point of AgCl, 455°C at atmospheric pressure.

The dominant uncharged species present in a H-O-Cl gas are H₂O, H₂, O₂, HCl, Cl₂. For a given gas pressure, assuming it is equal to the total pressure, P_T, we have the following restrictions: