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Chemical Techniques for Measuring and Controlling the Thermodynamic Properties of Aqueous Fluids at High Pressures and Temperatures[1]

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Several chemical techniques have recently been developed for measuring and controlling the fugacities $f_{O_2}, f_{H_2}, f_{H_2O}$, and f_{HCl} in supercritical aqueous fluids. Experimental samples consisting of fluid components and solid chemical "sensors" or "buffers" are sealed in H_2-permeable noble metal (Pt or Ag–Pd alloy) capsules and reacted at high pressure and temperature. Hydrogen diffusion through the walls of the capsule(s) allows f_{H_2} to be controlled or measured. After quenching, the fluids and solids are analyzed to quantify one or more thermodynamic properties of interest. Methods for determining the activity–composition relations of H_2O in aqueous fluid mixtures are discussed.

KEY WORDS: activity-composition relations; aqueous fluid mixtures; hydrogen fugacity sensor; H_2O fugacity buffer; oxygen fugacity sensor; high pressures; high temperatures.

1. INTRODUCTION

Thermodynamic data for H_2O in fluid mixtures at high pressures and temperatures are extremely important for understanding and modeling a wide range of geochemical phenomena, such as ore deposits and explosive volcanism, and for geothermal energy evaluation and utilization. However, at the high pressures and temperatures relevant to the interior of the earth, standard techniques for measuring these properties are often impractical.

Recently, several chemical techniques have been developed for determining the thermodynamic properties of noble metal-encapsulated samples

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of aqueous mixtures in autoclaves at high pressures and temperatures. These techniques exploit the ability of noble metals to act as membranes semipermeable to H_2 and involve equilibria of the type

$$H_2(\text{gas}) + MY(\text{solid}) = H_2Y(\text{gas}) + M(\text{solid}) \tag{1}$$

where M and MY are a metal and a metal compound, respectively, whose thermodynamic properties are known, and where Y is either O or Cl_2. The presence of M and MY acts to fix the activity of species Y, and such assemblages are referred to as buffers, by analogy with buffers in aqueous chemistry. The semipermeable membrane allows the fugacity of H_2, f_{H_2}, to be fixed or measured externally to the system investigated. With appropriate experimental configurations the mole fraction, X, of one of the remaining species, MY, M, or H_2Y, will be the single remaining dependent variable. The nature of the reactions is such that they can be quenched by rapid cooling. By analyzing the quenched dependent variable (X_{H_2Y}, X_M, or X_{MY}) after the experiment, the equilibrium concentrations of species in Eq. (1) can be determined at known values of their chemical potentials at pressure and temperature.

2. THE f_{H_2O} BUFFER TECHNIQUE

The f_{H_2O} buffer, shown schematically in Fig. 1, works by simultaneously and independently buffering f_{O_2} and f_{H_2} in a noble metal-encapsulated fluid, thus buffering f_{H_2O} in the sample at a known value through the relation $H_2 + \frac{1}{2}O_2 = H_2O$ [1, 2]. The f_{O_2} is buffered by equilibrium of the type $M + \frac{1}{2}O_2 = MO$ (M = Ni, Co), and the f_{H_2} is controlled and measured externally to the sample by use of a H_2-permeable membrane [3]. This membrane consists of a sealed, internally supported, thin-walled metal alloy tube that is connected by stainless-steel capillary tubing to an external gauge and a hydrogen reservoir. The internal support is porous, and the metal alloy (palladium + 25 mass% silver) is highly permeable to H_2. The membrane is situated within 5 mm of the sample capsules, and at equilibrium the f_{H_2} inside each capsule is equal to the f_{H_2} in the membrane. For M = Ni, the overall equilibrium can be written as

$$H_2 + NiO = H_2O + Ni \tag{2a}$$

The equilibrium constant for this reaction is given by

$$K_{2b} = \frac{f_{H_2O}a_{Ni}}{f_{H_2}a_{NiO}} \tag{2b}$$

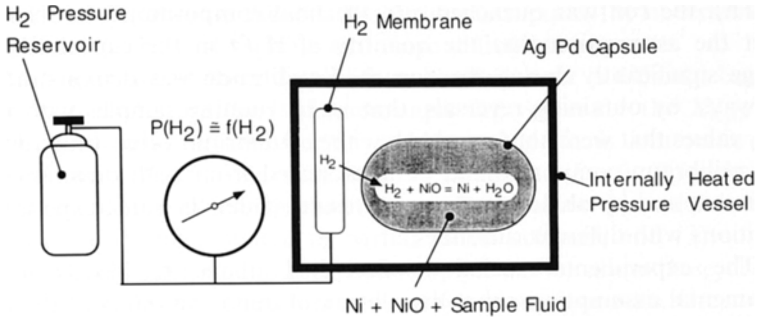

Fig. 1. A schematic diagram of the f_{H_2O} buffer [1, 2], in an $(Ar+H_2)$-pressurized internally heated pressure vessel. The H_2 membrane is situated in close proximity to the H_2-permeable capsules, and at equilibrium, the f_{H_2} in the capsules and the membranes will be equal to the P_{H_2} read on the external gauge. The combination of a fixed f_{O_2} (from the f_{O_2} buffer) and a fixed f_{H_2} (from the membrane) results in a fixed f_{H_2O} at equilibrium.

where K_{2b} depends only on the temperature. Given that the activities, a, of Ni and NiO are unity, and noting that $a_{H_2O} \equiv f_{H_2O}/f^0_{H_2O}$ ($f^0_{H_2O}$ is the fugacity of pure H_2O at P and T), Eq. (2b) yields the identity

$$a_{H_2O} = \frac{K_{2b} f_{H_2}}{f^0_{H_2O}} \tag{3}$$

Thus, buffered values of a_{H_2O} can be produced inside H_2-permeable capsules by externally imposing a fixed f_{H_2} in the presence of an f_{O_2} buffer. In this experimental design, the fluid composition is the dependent variable. During the experiment, the fluid reacts with the buffer to increase or decrease X_{H_2O} until the equilibrium composition corresponding to the experimentally set a_{H_2O} is achieved.

Activity–composition (a–X) data obtained with this technique for H_2O in H_2O–CO_2 fluids at 500 bar and 550°C are shown in Fig. 2. These experiments were conducted in an internally heated pressure vessel (IHPV) [4, 5], using premixed Ar–H_2 as the pressure medium. Ag–Pd capsules were loaded with a (metal + metal oxide) pair, a source of CO_2, and, in many cases, doubly distilled deionized H_2O, then sealed by arc welding. Silver oxalate ($Ag_2C_2O_4$) was used as a source of CO_2. The initial (loaded) composition was not the same as the final equilibrium composition and was generally chosen such that the equilibrium composition could be approached from either a low or a high X_{H_2O}. During an experiment, the equilibrium expressed by Eq. (2) proceeds to either the right or the left, depending on whether the f_{H_2} in the capsule is lower or higher than the f_{H_2} in the membrane. After sufficient time for equilibrium to be achieved (24 h to 72 h), the run was quenched and the final composition was measured under the assumption that the quantity of H_2O in the capsule did not change significantly during the quench. Equilibrium was demonstrated in two ways: by obtaining reversals, that is, by running samples with initial X_{H_2O} values that were above and below the equilibrium value, thus allowing the equilibrium composition to be approached from both directions in a single run; and by obtaining the same results under the same experimental conditions with different run times.

The experimental technique described above is based on two fundamental assumptions: that dissolution of minor amounts of the metal in the fluid has a negligible effect on the experimental results and that the X_{H_2O} of the experimental samples measured after the run is unchanged from the equilibrium X_{H_2O} under experimental conditions. The validity of these assumptions and other experimental details have been discussed previously [1, 2].

Extensive error analysis suggests that the uncertainty in the experimentally set value of a_{H_2O} is $\pm 9\%$. Much of this uncertainty is due to uncertainties in the free energy of formation of the metal oxide and of H_2O. The uncertainty in the determined value of X_{H_2O} is estimated to be

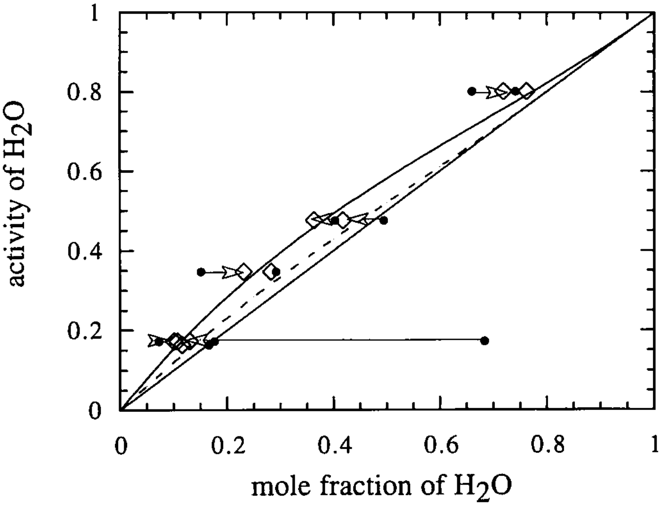

Fig. 2. An example of activity–composition data for H_2O–CO_2 mixtures obtained with the f_{H_2O} buffer technique at 500 bar and 550°C. [2]. The circles represent the starting compositions loaded into the capsule; the diamonds represent the final, equilibrium composition for the given a_{H_2O}. The dashed curve represents activity–composition data calculated from an expression of Greenwood [6].

~1%. However, because this is a bracketing technique, the uncertainty in the equilibrium X_{H_2O} is variable and more difficult to estimate.

A comparison of these data with volumetric data is difficult, because the primary data from the buffer technique are values for the X_{H_2O} at a given a_{H_2O} in a fluid mixture. For this to be calculated from volumetric data, one needs an isothermal data set that (1) extends to $P=0$, (2) includes a sufficient number of closely spaced compositions to allow the molar volumes to be accurately differentiated to partial molar volumes, and (3) consists of enough such determinations at various pressures to allow these derived partial molar volumes to be integrated as a function of pressure. Greenwood [6] measured V_m for H_2O–CO_2 mixtures up to $P=500$ bar and used smoothed values of the compressibility factor, Z, vs P to develop isothermal expressions for a_{H_2O} at 50 K intervals from $T=723.2$ to $T=1073.2$. An a–X curve calculated from one such expression is shown as the dashed curve in Fig. 2. Activities calculated from these expressions are systematically lower than the results from Ref. 2, particularly at the lower temperatures. The reasons for this are not entirely clear; however, at low pressure Greenwood's results indicate negative V^{ex}, whereas the volumetric results of other investigators at low pressure indicate only positive V^{ex}. Consequently, when integrated with respect to pressure, these excess volumes yield activities that may be lower than the true values.

The mismatch between the available volumetric data and the results of this study are the subject of ongoing research. Excess molar enthalpies, H_m^{ex}, calculated from these data are in good agreement with extrapolations of the results of direct measurement of H_m^{ex} for H_2O–CO_2 fluids by Wormald et al. [7] at lower pressures. However, a potential difficulty in applying the f_{H_2O} buffer technique at temperatures below ~400°C is that carbonate may form during the quench, this altering experimental results [2].

Many of the data collected with this technique are from experiments conducted at very high temperatures (550 to 1100°C) and pressures (2000 to 7000 bar). The few volumetric data at these conditions do not allow a meaningful comparison. However, at the highest temperatures the results of this technique demonstrate near-ideal mixing and are in accordance with predictions of the Kerrick and Jacobs MRK equation of state [8], which has been shown to be compatible with calculated mineral/fluid equilibria at similar pressures and temperatures.

3. THE Ag–AgCl ACID–BASE BUFFER

The Ag–AgCl acid–base buffer [9] was developed for the study of acid–base reactions at high P and T. Solid Ag and AgCl are added to an experimental sample which is sealed in a H_2-permeable Pt capsule. The Ag + AgCl buffers the f_{Cl_2}, and by buffering the f_{H_2} externally, the f_{HCl} of the sample is fixed by the overall equilibrium

$$AgCl + \tfrac{1}{2}H_2 = HCl + Ag \tag{4a}$$

and for which we may write

$$K_{4b} = \frac{f_{HCl}a_{Ag}}{(f_{H_2})^{1/2}\,a_{AgCl}} \tag{4b}$$

The f_{H_2} can be externally fixed either by using a membrane or by enclosing the H_2-permeable sample capsule in an outer Au capsule containing H_2O + an f_{O_2} buffer.

The Ag–AgCl buffer has been calibrated at high temperatures in hydrothermal solutions, and has been used in a variety of mineral solubility studies [10–12]. Several assumptions needed to apply this technique include the following.

(1) HCl mixes ideally in the aqueous fluid at concentrations up to several molar.

(2) The solubilities of Ag and AgCl in the solution of interest are negligible.

(3) Above ~450°C the AgCl melts. For experiments performed above this temperature it must be assumed that the solubilities of fluid species in the AgCl melt are negligible.

Because of these drawbacks the Ag–AgCl acid–base buffer has been superseded by several other techniques [13, 14] for determining solubilities of minerals and speciation in high-temperature hydrothermal solutions.

4. THE Ag–AgClH$_2$ SENSOR

The Ag–AgCl buffer described above is the basis for the Ag–AgClH$_2$ sensor [15], shown schematically in Fig. 3. The outer capsule is Au, which is impermeable to H_2 and ensures that the overall system is closed to H_2. This capsule contains the sample fluid whose f_{H_2} is to be measured, as well as a H_2-permeable sensor capsule (or capsules). This f_{H_2} measurement can be used to determine the thermodynamic properties of H_2O in the sample mixtures by including an f_{O_2} buffer such as the assemblage Ni + NiO in the outer sample capsule. At equilibrium, the f_{H_2} of the sample fluid will be proportional to the f_{H_2O}, as described by Eqs. (2a) and (2b). The inner f_{H_2} sensor capsule contains Ag + AgCl + H_2O. During the experiment, it equilibrates to the f_{H_2} imposed by the sample fluid, and reaction (4a) progresses until the f_{HCl} values reflect the f_{H_2} imposed by the sample. After quenching, the sample is recovered, and an analysis of the pH of the fluids in the inner capsules can be used to calculated the f_{H_2O} of the sample at experimental conditions from

$$f_{H_2O} = \frac{K_{2b}}{K_{4b}} \left(\frac{m_{HCl} \Gamma_{HCl} a_{Ag}}{a_{AgCl}} \right) \tag{5}$$

where m_{HCl} is the measured molality of HCl in the sensor, Γ_{HCl} is the fugacity coefficient for HCl, and the subscripts on the equilibrium constants indicate the equations in which they are defined.

The Ag–AgCl sensor has been used to measure a_{H_2O} in aqueous mixtures [16–18]. To circumvent uncertainties in K_{2b}, K_{4b}, and Γ_{HCl}, a reference capsule is included in the same experiment which contains two sensor capsules but only pure H_2O and Ni + NiO in the outer capsule. The $(f_{HCl})^{1/2}$ in this reference capsule is proportional to the $f^0_{H_2O}$. By ratioing the HCl measurements from the sample capsule to that measured for the reference capsule, K_{2b}, K_{4b}, and Γ_{HCl} can be eliminated from (5) [16], and a_{H_2O} can be solved for as

$$a_{H_2O} = \frac{f_{H_2O}}{f^0_{H_2O}} = \left(\frac{f^{\text{sample}}_{HCl}\, a^{\text{melt, reference}}_{AgCl}}{f^{\text{reference}}_{HCl}\, a^{\text{melt, sample}}_{AgCl}} \right)^2 \approx \left(\frac{m^{\text{sample}}_{HCl}}{m^{\text{reference}}_{HCl}} \right)^2 \tag{6}$$

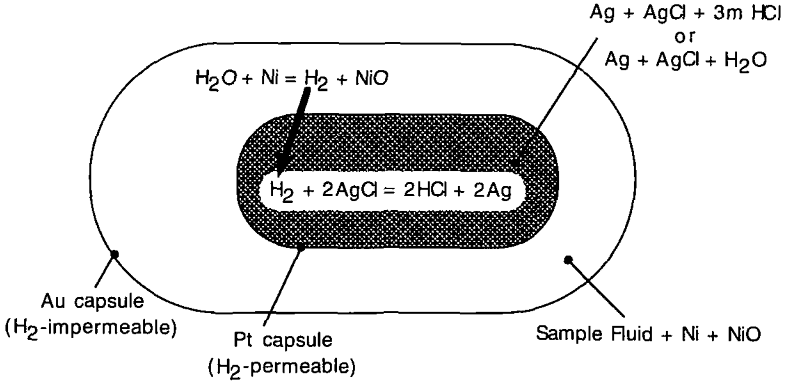

Fig. 3. A schematic diagram of the Ag + AgCl f_{H_2} sensor [15] configured for the experimental determination of a_{H_2O} of a fluid mixture. The outer capsule is Au, which ensures that the overall system is closed to H_2. This outer capsule contains Ni + NiO + the sample fluid. Under run conditions, this fluid reacts with the Ni-NiO to produce an f_{H_2} that is proportional to a_{H_2O}. In turn, the H_2 diffuses into the inner capsule and reacts with the AgCl to produce HCl. The resulting f_{HCl} in the inner capsules is proportional to $(f_{H_2})^{1/2}$ and, thus, to $(a_{H_2O})^{1/2}$.

However, several of the assumptions listed previously, particularly those expressed by Eqs. (1) and (3), have yet to be fully evaluated.

5. THE f_{O_2} SENSOR

Taylor et al. [19] have developed a new technique for measuring the f_{O_2} in high-pressure experiments (Fig. 4). The technique is based on previously calibrated f_{O_2} buffer equilibria ($Ni + \frac{1}{2}O_2 = NiO$, or $Co + \frac{1}{2}O_2 = CoO$), wherein the transition metal is allowed to alloy with Pd. The resultant lowering of the activity of the metal component displaces the equilibrium to more oxidizing conditions. Only small amounts of the alloy are used, which are incapable of buffering the redox conditions of the sample. Thus the assemblages (NiO + Pd1Ni alloy) and (CoO + Pd–Co alloy) represent f_{O_2} sensors. By inserting one of these sensors into a capsule that contains a sample fluid with an unknown f_{H_2O}, and by imposing a known f_{H_2}, the a_{Ni} measured after the run can be used to calculate the f_{H_2O} of the sample through

$$f_{H_2O}^{\text{sample}} = \frac{K_{2b} f_{H_2}}{a_{Ni}^{\text{sample}}} \tag{7}$$

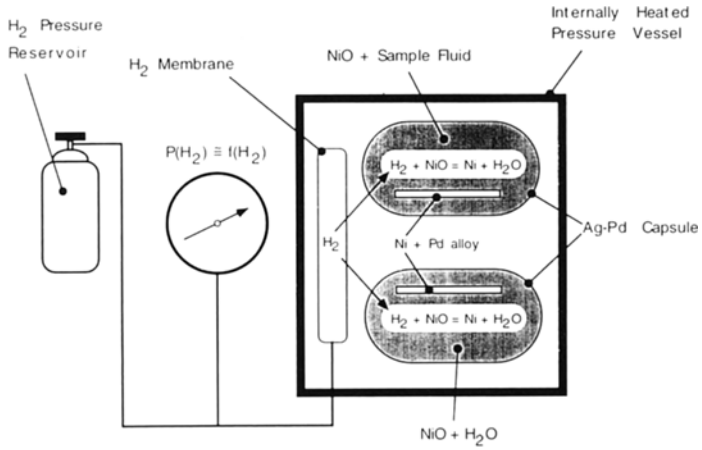

Fig. 4. A schematic diagram of the f_{O_2} sensor technique of Taylor et al. [19]. The sample capsule contains the fluid mixture with an unknown a_{H_2O}, as well as the f_{O_2} sensor assemblage (NiO and a small mass of Ni + Pd alloy). The reference capsule contains pure H_2O and the same sensor assemblage. The H_2-permeable capsules are equilibrated to the same f_{H_2}, then quenched. The alloys are then analyzed, and the a_{Ni} determined based on previously calibrated a–X relations for the alloy. The a_{H_2O} in the sample capsule is calculated as $a_{H_2O} = a_{Ni^*}/a_{Ni}$.

After the experimental is quenched, the alloy is analyzed, and the a_{Ni} is determined based on the concentration of Ni and previously calibrated a–X relations for the alloy.

A reference capsule containing H_2O as its only volatile component can be included in the same experiment with the sample capsules to eliminate uncertainties in K_{2b} and f_{H_2}. By ratioing the results from the sample capsule to the results from the reference,

$$a_{\mathrm{H_2O}}^{\mathrm{sample}} = \frac{a_{\mathrm{Ni}}^{\mathrm{reference}}}{a_{\mathrm{Ni}}^{\mathrm{sample}}} \tag{8}$$

The applicability of this techniques has been demonstrated down to 700°C, but the low-temperature behavior has not yet been investigated.

6. CONCLUSIONS

Several techniques involving metal–metal compound–hydrogen equilibria have been developed to determine the thermodynamic properties of aqueous fluids at high pressures and temperatures. These techniques rely on the unique capability of hydrogen to diffuse through semipermeable metal membranes and are capable of yielding accurate thermodynamic data on fluids under pressure–temperature conditions that are difficult to investigate by conventional means. Research into the low-temperature limits of these techniques is ongoing.

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