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SOLUBILITY OF, AND HYDROGEN ION ADSORPTION ON, SOME METAL OXIDES IN AQUEOUS SOLUTIONS TO HIGH TEMPERATURES

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Abstract

The solubility of boehmite (AlOOH), ferrous hydroxide ($Fe(OH)_2$) / magnetite (Fe_3O_4), zincite (ZnO), and brucite ($Mg(OH)_2$) have been measured over a range of temperatures (depending on the oxide: AlOOH, 100 - 290°C; $Fe(OH)_2/Fe_3O_4$, 100 - 250°C; ZnO, 50 - 290°C; $Mg(OH)_2$, 60 - 200°C) using a unique approach involving *in situ* pH measurements. A hydrogen-electrode concentration cell was employed for this purpose and the range of pH investigated was dependent on the nature of the oxide. The solubility results for boehmite are the most extensive and are given here mainly to demonstrate the viability of the experimental method, whereas those for zincite are mainly restricted to mildly acidic to neutral pH where Zn^{2+} predominates in solution. The corresponding magnetite (presumably coated with $Fe(OH)_2$) solubilities extend from pH values greater than five and, because of their importance to general water/steam cycles of power plants, are compared here in some detail with the results of previously-published studies. The same cell was used to investigate the surface adsorption-desorption thermodynamics of hydrogen ions on rutile (TiO_2) and zincite to 290°C. The former was chosen for the initial study in view of its low solubility which provided an ideal, unambiguous test case for this high temperature potentiometric approach. The behavior of the pH at zero-point-of-charge, pHzpc, as a function of temperature and the application of the Stern-three-layer model were determined for this solid. The zincite study is still incomplete and the preliminary results show trends that can be rationalized only qualitatively at the present time with the zero-point-of-charge being apparently affected by hydration of the surface in basic solutions and specific absorption of sodium ions under the same conditions.

Introduction

The desire to control the pH of boiler water to minimize the solubility of magnetite should possibly be tempered by the effect of pH on the adsorption of cations/anions that could lead to fouling problems. However, there appears to be an approximate correlation between the pHzpc and the pH at the solubility minimum of a given metal oxide. However, no reliable measurements of the former have been performed above 100°C. This article presents results of laboratory measurements of the solubility of a number of important metal oxides and the first surface titration data with rutile as the test case using the approach of direct pH measurement.

Traditionally, solubility studies have been the principal means of obtaining unique thermodynamic properties of sparingly soluble metal ions, as well as providing much needed information on the behavior of metals, their oxides and hydroxides, in both industrial and environmentally important settings.[1] Such experimental investigations are fraught with difficulties, some of which have not as yet been successfully overcome. The principal variables that must be controlled and/or measured in a given solubility experiment are: pH, temperature, pressure, ionic strength, H_2 fugacity (for redox experiments), concentration of possible complexing agents, and the concentration of metal ions in solution.[1,2] Other key considerations include a thorough characterization of the solid material before and after the solubility experiment was carried out, as well as a determination of particle size to ensure that no ultra-fine particulates were present which could lead to enhanced solubility.

Of the solution properties that must be measured, pH has proven to be the most difficult, except in strongly acidic or basic solutions where the concentration of free hydrogen or hydroxide ions are sufficiently high that the pH may be calculated from mass and charge balance equations. At intermediate to neutral pH, where hydrolysis is generally changing and the solubility minimum occurs, calculation of pH is subject to large uncertainties and is affected to an unknown degree by the presence of hydrolyzable impurities and surface adsorption/desorption of hydrogen ions, and requires knowledge of the speciation of the metal ions in solution. Measurement of the quenched pH has more credibility, but it is still subject to the same restrictions. Another approach, which is used more frequently for experiments at ambient conditions, involves using pH buffers to control, and permit calculation of, the pH assuming that the temperature/ionic strength behavior of the hydrolysis constant of the buffer is known. However, in reality, the components of buffers often tend to complex the metal ions, thus enhancing the apparent solubility of the solid, an effect that increases dramatically as the critical temperature of water is approached. Moreover, many common buffers tend to decompose at high temperatures and may also be specifically adsorbed to the metal surface.

The approach taken here is to measure the pH of the solution directly, utilizing the established hydrogen-electrode concentration cell,[3,4] thus obviating many of the problems discussed above. Other direct advantages of this method are that monitoring pH often provides a sensitive measure of the attainment of equilibrium (in some cases - see the case of brucite below - knowledge of pH alone was sufficient to determine the solubility thermodynamics) and the approach to equilibrium (i.e., from either under- or supersaturation) can be readily varied by addition of acidic and basic titrants. The required presence of a hydrogen atmosphere within the cell provides control of the redox potential, which is essential in the study of magnetite, for example. The working range of the cell is 0 to 300°C, pressures from that of water saturated vapor to several hundred bars of hydrogen, depending on the temperature, and ionic strengths from *ca.* 0.01 molal to virtual saturation with respect to the supporting electrolyte.

This presentation outlines four solubility studies, each involving different chemistries that highlight different aspects of the experimental method. In the main these studies are ongoing at the present time. Similarly, two surface adsorption investigations are summarized, indicating the potential usefulness of this approach to the advancement of modeling efforts and applications to industrial environments. In the case of zincite, the solubility and surface adsorption studies are interrelated as the dissolution of zinc affects the calculation of the hydrogen ion concentration balance equation. As suggested to occur for magnetite, both solubility and surface adsorption can be affected by surface hydration effectively sealing off the bulk solid from the solution and thereby imposing its own thermodynamics.

Experimental Technique

Hydrogen-electrode concentration cells in various forms have been used in the solubility and surface titrations described here, but all have the same basic configuration, namely,

$$\underbrace{H_2,Pt \mid NaX,(HX \text{ or } NaOH)}_{\text{reference compartment}} \parallel \underbrace{NaX,(HX \text{ or } NaOH),\text{solid} \mid Pt,H_2}_{\text{test compartment}}$$

where X is either Cl^- or trifluoromethanesulfonate ($F_3CSO_3^-$) and $\parallel$ represents the liquid junction, or salt bridge separating the two solutions. The original cell design was reported 27 years ago by Mesmer et al.[5] and the modifications to allow solution samples to withdrawn are described by Palmer et al.[6] Generally these cells operate in the range of 0 to 300°C (±0.1). Essentially, the concentration cell contains two hydrogen electrodes in two solutions of matching ionic strength interconnected by a salt bridge. The reference solution is of known **pH (defined as the negative logarithm of the hydrogen ion molality)** so that from the measured potential reading of the cell, corrected for the liquid junction potential, which itself is minimal due to the similarity in ionic strengths across the salt bridge, the pH in the second (test) solution can be determined accurately (typically ± 0.001) from the Nernst expression. The hydrogen pressure in the cell is determined from the measured total pressure and can be varied from less than one bar to about 100 bars; an important feature in experiments involving magnetite.

The solid is suspended in the test solution by mechanical stirring and samples of the solution are withdrawn through inert tubing into syringes containing excess acid to be analyzed later by ion chromatography, AA, or ICP. The sampling tube is fitted with a platinum filter at the high temperature end and a commercial Gelman PVDF 0.2μm filter at the other. Constant potential readings and metal ion analyses are the criteria for the attainment of equilibrium. Acidic or basic titrant (again at matching ionic strength) is then metered into the cell in known increments and the potential is monitored until equilibrium is again reestablished.

Samples of the solid phases are taken before and after the experiments and subjected to a battery of analyses to ascertain the crystallinity, composition, grain size and surface features of the material.

Discussion

The following discussion is broken down into the four solubility studies and two surface-adsorption studies, which are all summarized at the conclusion with an outline of the advantages and limitations of the experimental technique.

Solubility Studies

Brucite. This study[7] involved the precipitation of $Mg(OH)_{2\,(cr)}$ from homogeneous magnesium chloride solutions at ionic strengths of 0.1 and 1.0 molal NaCl at temperatures of 60, 100, 150, and 200°C. The dominant reaction under these conditions was:

$$Mg^{2+} + 2H_2O \rightleftharpoons Mg(OH)_{2\,(cr)} + 2H^+ \qquad (1)$$

whereby the extent of reaction was determined based solely on the potential reading as basic titrant (NaOH) was added to magnesium chloride solutions. The hydrolysis of Mg^{2+} to yield $Mg(OH)^+$ was studied independently[8] and represents a negligible contribution of hydrogen ions to the overall reaction (1). X-ray diffraction patterns of the precipitated material showed it to be pure, crystalline brucite. The "titration curves" resulting from the precipitation by the addition of base into Mg^{2+} solutions are shown in Figure 1. As illustrated by the 200°C isotherm in Figure 1, addition of acidic titrant upon precipitation of brucite established that reaction (1) is readily reversible within the time-frame of these titrations, i.e., several hours. Although many precipitation reactions lead to the formation of metastable, or even amorphous phases, the formation of brucite represents an example of a reaction that is ideally suited to the potentiometric method, whereby very precise results can be obtained expediently. The excellent agreement found between the logarithm of the equilibrium constant for reaction (1) fitted as a simple linear function of the reciprocal temperature in Kelvin and corrected to the standard infinite-dilution reference state, and those reported by McGee and Hostetler[9] (10-90°C) and Walther[10] (350°C) attests to the reliability of the results obtained by potentiometry.[7] Thus, from this work the formation of brucite is defined thermodynamically from 0 to 350°C at saturation vapor pressure.

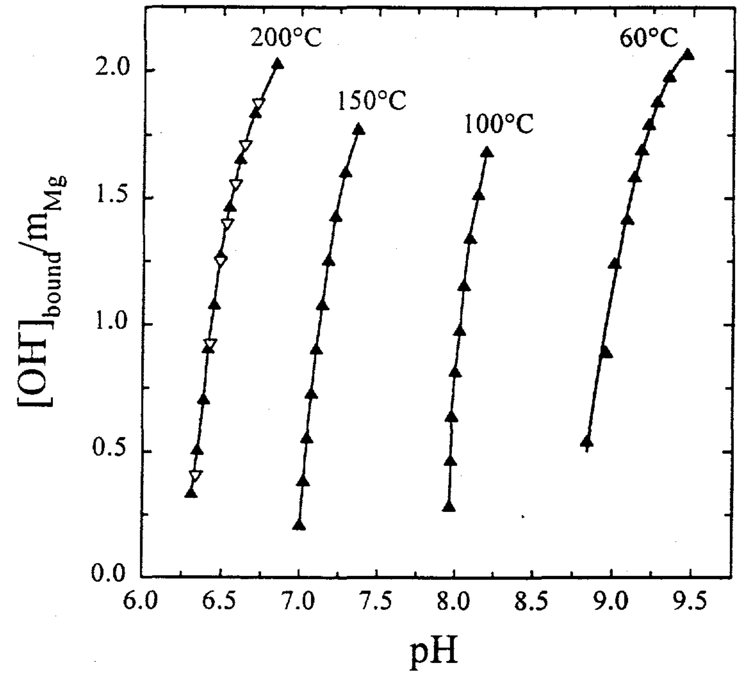

Figure 1
Titration curves of $5\cdot10^{-3}$ molal Mg^{2+} solutions at 0.1 molal ionic strength depicting the molal concentration of hydroxide ions bound (missing from solution) per total stoichiometric concentration of magnesium (e.g., a value of two is equivalent to the formation of $Mg(OH)_2^0$): where △ represents a titration with addition of base and ▽ involves addition of acid.[7]

Boehmite. The aqueous chemistry of aluminum has received considerable attention in the past decade due largely to its industrial importance, toxicity and ubiquitous presence in the earth's crust. The chemistry is exceedingly complex, such that despite the amount of research devoted to it, the thermodynamics of this highly-charged ion are controversial, particularly above 100°C. Below this temperature, where gibbsite - $Al(OH)_{3\,(cr)}$ - is the stable phase, recent conventional solubility studies in our laboratory have established the free energies of the Al^{3+} ion and its mononuclear hydrolysis products, $Al(OH)_n^{3-n}$, $n = 0$-4, to ionic strengths as high as five molal.[11-14]

The most complete study carried out thus-far utilizing the new potentiometric technique involves the solid phase boehmite, which is stable from *ca.* 100 to 400°C. These experiments were performed in NaCl solutions from 0.03 to 5 molal ionic strength. The equilibria between the solid and solution involve monomeric aluminum species, which are formed according to the generalized reaction:

$$AlOOH_{(cr)} + (3\text{-}n)H^{+} \rightleftharpoons Al(OH)_n^{(3-n)+} + (2\text{-}n)H_2O \qquad (2)$$

A typical solubility profile is illustrated in Figure 2, which summarizes the results of six independent experiments beginning on the acid branch of the profile and proceeding to high pH by the addition of basic titrant after establishing equilibrium at each point. From the reverse experiment it can be seen that although equilibrium was approached from supersaturation on the basic branch, identical solubilities were found as obtained from the undersaturation condition. X-ray diffraction and SEM images showed the boehmite to be well crystallized and increasing in grain size during the experiment (i.e., Ostwald ripening effect). The study of boehmite is reported here in order to establish, (1) the utility of the potentiometric approach, (2) that attainment of equilibrium can be established expediently leading to the free energies of the species Al^{3+} through $Al(OH)_4^-$, which in general are in reasonable agreement with the earlier work of Castet et al.[15]at low ionic strengths (see Figure 2) from 100 to 290°C; and (3) that certain

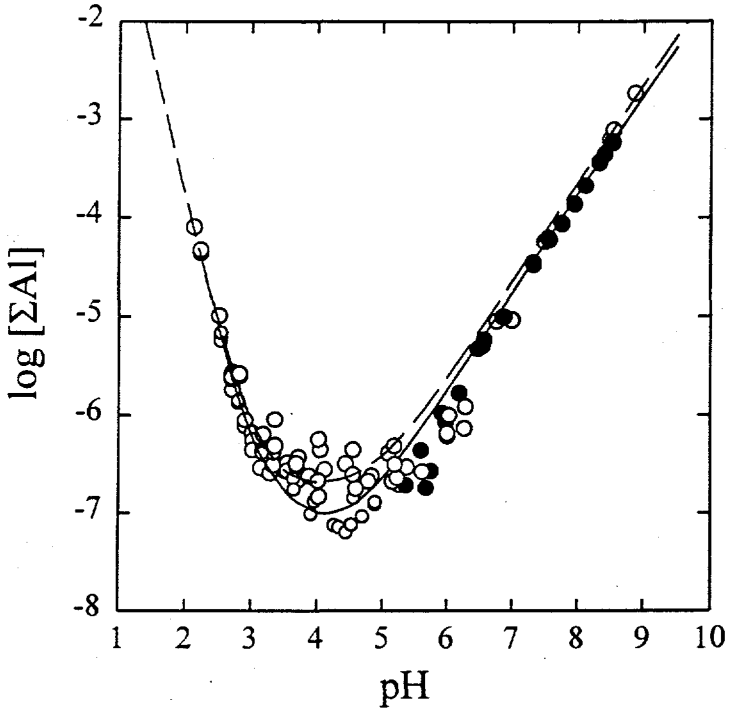

Figure 2
Solubility profile for AlOOH illustrating the dependence of the logarithm of the total aluminum molality on pH at 152.4°C, 0.03 molal ionic strength (NaCl) and saturation vapor pressure. The open symbols summarize six independent titrations begun on the acid branch, whereas the filled symbols correspond to an experiment initiated on the base side. The solid curve represents a fit to these data and the dashed curve was taken from Castet et al.[15], adjusted from infinite dilution to 0.03 molal ionic strength using an extended Debye-Hückel expression.

general trends observed in this system should be applicable to other metal oxides/hydroxides, for which less detailed results need to be gathered. These general trends can be summarized as follows: (i) The acid arm of the solubility profile, corresponding to cations of aluminum being dominant in solution, moves to more acidic pH with increasing temperature; (ii) the solubility minimum, corresponding to the maximum influence of the neutral $Al(OH)_3^0$ species, becomes broader, moves to lower pH, and raises slightly with increasing temperature; (iii) the anionic, tetrahedral aluminate ion, $Al(OH)_4^-$, becomes more dominant from basic to near-neutral/slightly acidic solutions with increasing temperature; (iv) increased ionic strength has the effect of increasing the stability field of the highly-charged Al^{3+} ion at the expense of the lesser-charged and neutral species, such that the solubility of the aluminum solid phases can be eventually described over most of the pH range by the two end-member ions, viz., Al^{3+} and $Al(OH)_4^-$.

Magnetite/Ferrous Hydroxide. The iron oxide/water system has received considerable attention during the past 27 years [2,16-20] and solubility studies with the hydrogen-electrode concentration cell are now in progress in our laboratory. The first results obtained with this approach were most puzzling in that despite equilibrating a small quantity of magnetite in dilute acidic solutions (0.1 molal ionic strength using sodium trifluoromethanesulfonate as the unreactive - fully dissociated - supporting electrolyte) under *ca.* **20 bars of H_2** pressure at temperatures in excess of 100°C, the solid material obtained upon opening the cell was 100% crystalline **hematite (Fe_2O_3)**. Magnetite (or $Fe(OH)_2$) should be the stable phase even in the presence of <1 bar H_2). After demonstrating that this process was reproducible, it was concluded that in acidic solutions, the kinetics of dissolution of ferrous ion by the transformation reaction,

$$Fe_3O_{4\,(cr)} + 2H^+ \rightleftharpoons Fe^{2+} + Fe_2O_{3\,(cr)} + H_2O \qquad (3)$$

must exceed those of the reduction reaction:

$$Fe_3O_{4\,(cr)} + H_2 + 6H^+ \rightleftharpoons 3Fe^{2+} + 4H_2O \qquad (4)$$

This phenomenon has immediate implications as to the design of experiments aimed at measuring the equilibrium solubility of magnetite, and should also have a bearing on the removal of magnetite scales from boiler tubes by acid washing. In other words, in regards to the latter, chemical cleaning of boilers with the intrinsic condition of large surfaces of exposed magnetite may well leach out ferrous ion and leave a layer of less reactive hematite. In regards to the experimental conditions for magnetite solubility determinations in the concentration cell, a lower pH limit of five was set to avoid the preferential formation hematite, although it was still observed under special circumstances. The results of a number of titrations of magnetite from basic pH conditions are summarized in Figure 3, together with the regressed data from a number of independent previous studies, which were recalculated for the condition of 0.1 molal ionic strength using the extended Debye Hückel expression.

On the acid arm, the previously-determined solubilities of magnetite are in very good agreement,[16-19] noting that the curve attributable to Shock et al.[20] was derived from the HKF equation of state and was based mainly on the work of Sweeton and Baes.[16] At higher pH, where

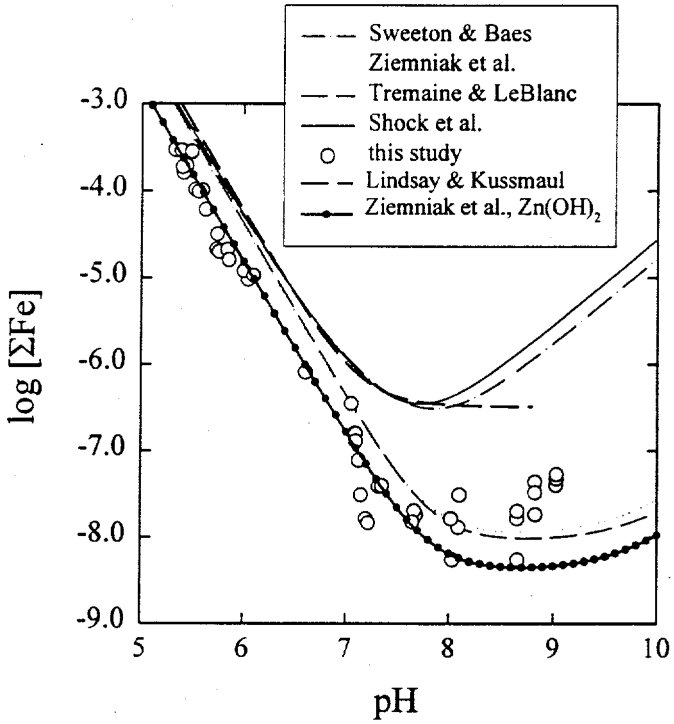

Figure 3
Solubility profile for Fe_3O_4 and $Fe(OH)_2$ illustrating the dependence of the logarithm of the total iron molality on pH at 150°C, calculated at 0.1 molal ionic strength and 20 bar H_2 pressure (neutral pH = 5.668).

hydrolysis of Fe^{2+} becomes significant, these studies diverge into two groups, with the higher curve probably being due largely to unmeasured contributions from ferric hydroxides in solution (H_2 pressure was not varied in these experiments). Tremaine and LeBlanc[17] mentioned the formation of $Fe(OH)_3$ in their packed-column experiments at high pH, indicating that the relatively high insolubility of this phase may tend to stabilize it even under moderatly reducing conditions.

It is immediately apparent that the data obtained in our experiments are consistent with the $Zn(OH)_{2\,(cr)}$ curve calculated from Ziemniak et al.[17] indicating that the surface of the magnetite grains may have been reduced to $Fe(OH)_2$ according to the reaction:

$$Fe_3O_{4\,(cr)} + H_2 + 2H_2O \rightleftharpoons 3Fe(OH)_{2\,(cr)} \tag{5}$$

This is consistent with the free energies of these to phases with the partial pressure of hydrogen corresponding to this transition being 1.2 bar.[17] Thus, it is interesting that the two transformation reactions (3) and (5) occur at the same operating conditions, differing only in pH. The extent of reduction of the magnetite grains in base solutions is currently under investigation by XPS and

TEM surface characterization techniques. However, it is sufficient to note at this time that the solubilities shown in Figure 3 for $Fe(OH)_2$, and at the other temperatures studied, were readily reproducible between different experiments and by reversing the direction of approach to equilibrium.

Experiments are continuing in this mode to elucidate the thermodynamics of the ion / water system and at lower hydrogen pressures, in an attempt to work in the stability field of magnetite and thereby determine its solubility, particularly in basic solutions where the controversy exists.

Zincite and Zinc Hydroxide. We have recently completed a solubility study of ZnO in acidic solutions from 50 to 290°C over a range of ionic strengths (0.03 - 1 molal) where the dominant ion in solution was Zn^{2+}.[21]

$$ZnO_{(cr)} + 2H^+ \rightleftharpoons Zn^{2+} + H_2O \qquad (6)$$

The equilibrium was found to be readily reversible (i.e., the same equilibrium constant, K_{s0}, was obtained when equilibrium was approached from super- and undersaturation), independent of the source of zincite, and totally consistent with the recently-published work of Ziemniak et al.[22] at infinite dilution. Once again, a simple linear function of log K_{s0} versus the reciprocal temperature in Kelvin was sufficient to represent these results from 0 to 300°C.

However, when these potentiometric experiments were initiated from basic solutions, a distinctly different, higher solubility constant was obtained on the acid arm of the solubility profile, where reaction (6) should dominate. These studies are still in progress and the detailed investigation of the solid zinc oxide material retrieved from these latter runs is incomplete, but initial indications are that the higher solubilities obtained in acidic solutions may be attributable to the formation of hydrated zinc oxide on the surface upon exposure to basic solutions. Indeed the solubilities reported for $Zn(OH)_{2\,(cr)}$ by Ziemniak et al.[22] are in excellent agreement with the "apparently hydrated" ZnO results found in our experiments. The immediate reaction to this finding is that the kinetics of hydration of a metal oxide are apparently pH dependent and not readily reversible in this case, and may therefore mask the equilibrium solubilities of the underlying parent oxide.

Surface Adsorption of Hydrogen Ions

Much has been written concerning the link between surface adsorption and the formation of scales on metal oxide surfaces.[23,24] These interactions are generally electrostatic in nature and therefore depend on the charge on the surface, which in turn is dictated by the pH of the solution. The pH at which these surface charges cancel is known as the point-of-zero-charge, or pHzpc, above which cations are attracted to the negative charge on the surface, whereas anions are bound at lower pH values. The adsorption of hydrogen ions can be represented by the equilibrium:

$$\text{-}SOH_s^{-1/2} + H^+ \rightleftharpoons \text{-}SOH_{2s}^{+1/2} \qquad (7)$$

with the equilibrium constant, K_H, equivalent to pHzpc. Potentiometry provides a means of measuring the pHzpc from the pH at which the acid-base titration curves exhibit a common cross-over value at varying ionic strengths. Such measurements have been restricted to <100°C until our recent study of hydrogen ion adsorption onto rutile, TiO_2, which extended to 250°C using the hydrogen-electrode concentration cell.[25] Subsequently, these measurements were extended to 290°C when the rutile system was reinvestigated. Currently hydrogen ion adsorption on ZnO is under investigation and magnetite will be studied in the near future.

Rutile Rutile was chosen for the first study because: (1) its low solubility over a wide range of pH simplifies the interpretation of the results; (2) the pHzpc lies in the near-neutral pH region where the sensitivity of the pH measurement is greatest to changes caused by adsorption; (3) considerable data already exists in the literature at temperatures <100°C; and (4) the system is immune to reduction by the hydrogen atmosphere within the cell.

The initial study[25] was conducted from 25 to 250°C (0.01 to 1 molal ionic strength, NaCl) and led to the following observations and conclusions: (1) the pH of zero net surface charge decreased with temperature from 5.7 at 25°C to 4.50 at 200°C (note that the pH of zero electrophoretic mobility for this sample of rutile was found independently to be 5.65 at 25°C); (2) the difference, pHzpc - ½pKw, was constant at -1.1 ± 0.2 over the entire temperature range, which supports the use of this "isocoulombic" extrapolation method employed for systems where high temperature data are unavailable (see below); (3) the adsorption capacity increases significantly with increasing temperature on the basic side of the pHzpc (i.e., adsorption of hydroxide ions) consistent with increased interaction with (or shielding by) sodium ions in the second layer; (4) these results could be fitted by a three-layer Stern model from which binding constants for Na^+ and Cl^- interactions with the surface (see equations 8 and 9) and the their Stern layer capacitances could be calculated.

$$-SOH_s^{-1/2} + Na^+ \rightleftharpoons -SOH_sNa^{+1/2} \qquad (8)$$

$$-SOH_s^{+1/2} + Cl^- \rightleftharpoons -SOH_sCl^{-1/2} \qquad (9)$$

A second study of this system was recently completed from 25 to 290°C (0.03 to 1 molal NaCl) on a rutile solid that had been pretreated hydrothermally (200°C for two weeks) in order to minimize surface defects, hydrolytic adsorbed impurities, etc. This pretreatment had the effect of reducing hysteresis between the forward and reverse titrations, improving the reproducibility of pHzpc determinations, and lowering the adsorption capacity of the surface even after correction for the slightly reduced surface area. Additional experiments were performed using tetramethylammonium chloride as the supporting electrolyte and showed that the build-up in surface charge was reduced markedly above the pHzpc, indicative of the larger cation interacting more weakly with the surface. Modeling of these more precise results is now in progress and this will pave the way to studies of the competitive adsorption of other cations and anions on this "ideal" (well behaved) surface.

Zincite. Surface titrations have been carried out at ionic strength of 0.03, 0.1 and 1 molal ($NaCF_3SO_3$) at 50 to 250°C. Apparently due to the combination of strong sodium ion interaction with the surface in basic to neutral solutions and the high solubility of ZnO in mildly acidic solutions, a common cross-over point of the titrations curves at different ionic strengths was not observed unambiguously. Therefore the pHzpc was determined from the inflection point in the titration curve with somewhat greater uncertainty than could be obtained for rutile, for example. Nevertheless, a general trend in pHzpc with increasing temperature to lower values following the change in ½pKw was observed, reflecting the behavior clearly seen in the case of rutile. In addition, the effect of the strong interaction of the negative surface with sodium ions is to shift the pHzpc to lower values. Finally, the majority of these surface titrations originated from basic solutions, but reverse titrations begun in mildly acidic solutions superimposed precisely within the combined experimental uncertainty on the former titration curves, indicating that the adsorption/desorption reaction was readily reversible.

Conclusions

1. Solubility of brucite was studied to 200°C by precipitation from solution and was found to undergo rapid precipitation/dissolution. Extrapolation to existing data at 350°C was achieved with a simple expression.
2. An extensive study of boehmite dissolution equilibria demonstrated the use of direct pH measurement of solubility with the promise of future applications to the study of dissolution kinetics. Combined with earlier low temperature data obtained in this laboratory, the thermodynamics of aqueous aluminum in dilute solutions are now defined from ambient conditions to 300°C.
3. Measurements of magnetite solubility from 100 to 250°C in the hydrogen-electrode concentration cell under partial pressures of H_2 in excess of 10 bars, suggest that ferrous hydroxide controls the solution behavior. At pH values below five, hematite was formed in a rapid transformation reaction, which has implications to acid cleaning of boilers.
4. The solubility of zincite was studied to 290°C in dilute acidic solutions where Zn^{2+} predominated in solution and the solubility constant, which was in excellent agreement with the work of Ziemniak et al.[22] was treated with a similar simple function that accounted for the brucite data. Higher pH solubility data suggest the possible formation of $Zn(OH)_{2\,(cr)}$, but this is still under investigation.
5. An extensive series of surface adsorption titrations were carried out from 25 to 290°C on rutile resulting in the quantification of the decrease in the pHzpc with increasing temperature and the increase in capacitance for secondary adsorption of sodium ions at pH greater than the pHzpc. Similar experiments in progress on zincite, which were complicated by high solubility in acidic solutions and the existence of strong interactions with sodium ion, showed a similar trend in the pHzpc. The pHzpc was effectively shifted to lower values by the adsorption of sodium ions.
6. The hydrogen-electrode concentration cell has the advantages alluded to in 1-5, but it can not be used for systems that either are readily reduced by the prevailing hydrogen atmosphere in the cell, or exhibit sluggish kinetics of dissolution (weeks to months).

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