Solubility of Potassium Carbonate in Water between 384 and 529 K Measured Using the Synthetic Method

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The solubility of potassium carbonate in water at temperatures from 384 to 529 K is reported at the saturation vapor pressure of the solutions. Measurements were made using a visually-accessible apparatus consisting of a platinum cell with sapphire windows and gold seals. The results indicate that potassium carbonate remains prograde-soluble up to 529 K. At approximately 427 K the hydrate form of the solid changes as indicated by visual observation of the solid and a change in the solubility behavior. Solubilities determined at lower temperatures have been compared with literature data and are in good agreement.

Introduction

Supercritical water oxidation has been used to successfully treat a wide variety of wastes including organics (Thomason and Modell, 1984), halogenated organics (Swallow et al., 1989), biological and pharmaceutical wastes (Johnston et al., 1988; Hong et al., 1987), and surrogate mixed waste (Bramlette et al., 1990). However, when treating organic compounds containing chlorine, sulfur, phosphorous, and certain nitrogen groups, the products of oxidation include strong acids such as HCl (Swallow et al., 1989). The presence of these acids combined with the high temperatures and oxidizing media of the process create an extremely corrosive environment, resulting in degradation of structural materials. Even corrosion-resistant materials such as Hastelloy and Inconel may corrode at unacceptable rates (Bramlette et al., 1990). Corrosion in supercritical water oxidation is often most severe in the preheater and cool-down sections of the reactor where temperatures are below the critical temperature of water. Therefore, the measurements reported here focus on the subcritical region.

Methods to eliminate or minimize corrosion include use of inexpensive sacrificial reactor components (Buelow et al., 1990), ceramic liners (Garcia, 1996), and *in situ* neutralization (Thomason and Modell, 1984; Buelow et al., 1990; Swallow et al., 1990; Rofer and Streit, 1990). Of these methods, *in situ* neutralization is in principle the simplest and least expensive. *In situ* neutralization involves the addition of a base to the influent stream, which would neutralize acids as they form and before corrosion can occur. Carbonates, which would form CO_2 and salts as products of the neutralization reactions, are possible candidate compounds for *in situ* neutralization. Solubility and other thermodynamic data for these compounds in water at high temperatures are needed for designing and operating supercritical water reactors. However, very little literature data exist on the solubility of various carbonates in water at high temperatures. For potassium carbonate, solubility data are available only to 403.15 K (Linke and Seidell, 1965). These data indicate that potassium carbonate exhibits increasing solubility with increasing temperature (i.e., prograde solubility).

Solubility measurements of prograde-soluble salts present experimental difficulties. Direct sampling of a saturated solution held at constant temperature and pressure is impractical because of precipitation of salt in the sample lines and sample vessel. Early studies of prograde-soluble compounds used novel approaches for obtaining solubility data. For example, Waldeck et al. (1934) developed a bomb with an internal needle valve and sample container for direct sampling. The technique was very tedious and time consuming because the apparatus had to be cooled to room temperature, disassembled, and flushed for analysis for each datum. More recently, other techniques, including isopiestic studies (Robinson and Stokes, 1959) and the synthetic method (Marshall et al., 1954), have been used. Isopiestic methods involve solvent transfer between two solutions of nonvolatile solutes until the solutions have equal solvent activity. Major drawbacks of this method are that the time required for equilibrium to be reached is typically long, particularly at low temperatures, and an *in situ* weighing or high-temperature valve is required. The synthetic method entails the preparation of a solution of known composition and the visual determination of the temperature at which a phase transition occurs. The solution is typically sealed in a suitable visually-accessible container, with mechanical agitation to reduce the possibility of supersaturation. The accuracy of the measurement depends on the ability to detect the last trace of dissolving solid or first appearance of precipitating solid, accurate knowledge of the masses of salt and water, and the sensitivity of temperature control. The technique has been used in this laboratory by Marshall and co-workers (1954, 1974, 1981, 1985, 1990) and others (Clark et al., 1959; Barton et al, 1961; Lietzke and Marshall, 1983) for more than 40 years for determining solubility and liquid−liquid immiscibility and studying critical phenomena. In this work, the synthetic method was used to measure the solubility of potassium carbonate in water between 384 and 529 K.

Experimental Section

Apparatus. Figure 1 is a schematic diagram of the visually-accessible cell components. The main component is the platinum body piece. This piece is approximately 2.55 cm long with an internal volume of 0.15 cm^3. Sapphire windows, 0.64 cm thick (ESCO products, Oak Ridge, NJ), are sealed to each end of the cell body using gold washers seated inside the cell. The washers were made from 0.203 mm thick gold sheet and are annealed before each use. Additional gold washers are placed between the windows and follower pieces to prevent breakage of the windows. The stainless steel enclosure containing the cell is held together with four 6.35 mm bolts. A 1.6 mm hole was

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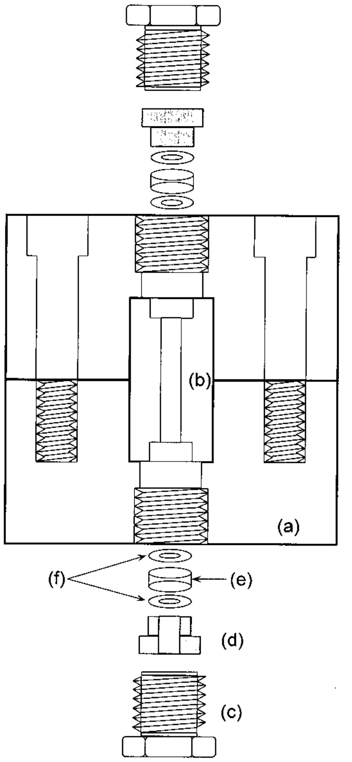

Figure 1. Visually-accessible cell for determining the solubility of salts in aqueous solutions: (a) stainless-steel cell body; (b) platinum cell core; (c) threaded retainers; (d) stainless-steel followers; (e) sapphire window; (f) gold washer seals.

drilled through the stainless steel shell and into the platinum body approximately 2.5 mm deep for use as a thermowell.

The visual cell assembly was mounted inside a Marshall tube furnace (40 cm long with a 6.35 cm bore) attached to a rocking frame to provide mixing in the cell and minimize equilibration times. At one end of the assembly, a Specwell 3× telescope was mounted for viewing the cell contents. A variable-intensity light was mounted at the other end. Two glass cylinders were placed on each side of the cell to provide a clear viewing path. Blanket ceramic insulation (Cooperheat, Piscateaway, NJ) was packed around the glass tubes to hold them in place and to reduce heat losses. Between observations of the cell contents, pieces of insulation were used to seal the ends of the furnace. A Barber-Colman 560 temperature controller was used to control the furnace temperature to ±1 K. Cell temperatures were monitored with a calibrated chromel-alumel thermocouple.

The entire assembly can be rocked through 45° in the horizontal or vertical position. Typically, the cell was rocked around the horizontal position between observations, and the cell contents were viewed while the apparatus was locked in the vertical position. In this position, salt crystals would collect on the bottom cell window and could be easily seen. Observing the reverse process, precipitation of solid from solution, was not possible because of extensive supersaturation of the solutions. A description of system test results with NaCl has been presented (Moore et al., 1994).

Materials and Procedure. Water purified using a Barnstead NANOpure Ultrapure Water System was used. Potassium carbonate 1.5 hydrate was purchased from J.T. Baker Inc. The material was dried overnight in vacuum at 413 K to give the anhydrous salt. Titration with standard HCl(aq) indicated the material was more than 99.99% pure.

Table 1. Molalities of Saturated K_2CO_3(aq) at Various Temperatures[a]

T/K	m_i/(mol·kg^{-1})	m_c/(mol·kg^{-1})
384	11.80	11.80
385	12.72	12.73
394	12.33	12.34
397	13.02	13.04
400	12.69	12.78
403	14.59	14.61
403	13.47	13.50
406	14.00	14.05
415	14.59	14.61
422	15.47	15.48
426	16.46	16.50
426	16.31	16.38
427	16.85	16.90
429	15.92	15.96
446	17.24	17.30
456	17.50	17.58
468	17.88	17.99
486	18.20	18.36
499	18.70	18.92
512	19.01	19.30
529	18.65	19.07

[a] Corrected molalities m_c calculated as described in the text.

The cell was charged gravimetrically with salt and solvent with a precision of ±0.0001 g. Salt solubility was determined by observing the phase change while increasing the cell temperature. The cell was rocked between observations to minimize equilibration time. Typically, the temperature was rapidly increased until only a small amount of solid remained. Near the phase change the temperature was increased at a rate of approximately 0.001 K·s^{-1}. Experiments were initially performed without rocking the cell. However, equilibration times were exceedingly long: on the order of a full day for one measurement. By rocking the cell, a single measurement could be taken in approximately 3−4 h. Duplicate solid-disappearance temperatures were recorded for every solubility point. All measurements were determined at the saturation pressure of the solutions.

Results and Discussion

The results from the solubility measurements for potassium carbonate are given in Table 1. The values given in column 2 were calculated on the basis of the masses of solid and water placed in the cell. The values in column 3 have been corrected to take into account water saturating the vapor space of the cell. The vapor space was estimated to be one-half of the total cell volume (0.075 cm^3), based on visually observing the liquid level in the cell while it was in the horizontal position. Solvent activity was estimated as equal to the mole fraction (ionized basis) of water in the solution as prepared. This correction procedure is discussed in some additional detail below. As indicated in Table 1, at temperatures less than approximately 450 K the correction to the data is less than 1% and is essentially negligible given the experimental uncertainty of the measurements. For higher temperatures, the correction becomes more significant. At the highest experimental temperature of 529 K, the correction amounts to slightly over 2% of the gravimetrically determined concentration.

The estimated accuracy of the temperature measurements is ±2 K. This value is based on the accuracy of temperature control and the reproducibility of the measurements. The accuracy of this method depends strongly on the temperature dependence of the salt solubility. Other factors affecting the accuracy of the results include the extent of temperature gradients within the cell, the pos-

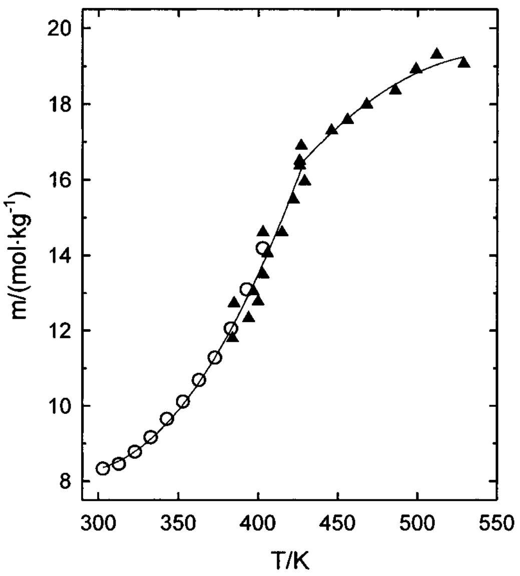

Figure 2. Molalities of K_2CO_3(aq) at solid saturation. ○, Linke and Seidell (1965); ▲, this study.

sibility that composition gradients may be established due to restricted diffusion within the solution, and the uncertainty in determining the final disappearance of the solid. It was not possible with the present apparatus to determine the temperature directly on the lower sapphire window, where the dissolution of the last of the solid phase was observed. The limited length of the solubility cell (less than 10% of the heated length of the furnace) and its location near the center of the furnace were designed to minimize temperature gradients across the cell. Concentration gradients, as indicated by changes in refractive index of the solution near the crystals, were not observed in any of the experiments. For potassium carbonate, large increases in solubility result from relatively small temperature changes. Therefore, the synthetic method is well suited to this particular compound.

Figure 2 is a plot of the experimental data along with literature data from the compilation of Linke and Seidell (1965). The lines drawn through the data represent polynomial fits and are presented only to guide the eye. In general there is good agreement with the literature values, with the solubilities determined in this work being slightly lower from 383 to 403 K. The literature indicates that the stable solid phase between 298 and 403 K is $K_2CO_3 \cdot 1.5H_2O$. No attempt was made in this work to identify the stable solid. However, a change in the crystal shape from a small granular shape to a larger, more cylindrical shape was observed at approximately 429 K. A change is also seen in the behavior of the solid solubility with temperature above 429 K. As illustrated in Figure 2, the temperature dependence of the solubility changes discontinuously above this temperature. This was taken as further evidence that a different stable solid was present. Higher temperature measurements were not possible with potassium carbonate and the current apparatus, as the high alkalinity of the solution combined with the high temperatures resulted in dissolution of the sapphire windows.

The approximations involved in correcting the compositions of saturated solutions for water vaporization have been described above. These approximations were made necessary by the lack of available vapor pressure data for K_2CO_3(aq) at high temperatures and concentrations. Water activities over carbonate solutions have been reported from 423.15 to 573.15 K by Matuzenko et al. (1982); the same work is referenced in the compilation of Zaytsev and Aseyev (1992). However, the values reported differ significantly between the two references, with Zatysev and Aseyev reporting activity coefficients to $m = 9$ mol·kg^{-1} and Matuzenko et al. reporting both solute activity coefficients and solvent activities at ionic strengths to $I = 9$ mol·kg^{-1}. If it is assumed that the derivative reference includes an error in translation, the water activities can be fitted as functions of temperature and composition using extended Debye−Hückel models for the excess Gibbs free energy on either the molality (Pitzer and Mayorga, 1973) or ionized mole fraction (Clegg et al., 1992) composition scale. Fits on the mole-fraction basis are then extrapolable, with some uncertainty, to solid saturation at each temperature. However, a comparison of water activities and solvent activity coefficients as functions of temperature and composition calculated from these analyses with K_2CO_3(aq) thermodynamic properties at temperatures to 368 K reported by Simonson et al. (1987) indicate significant differences in activity coefficients and water activities that cannot be resolved by a reasonable interpolation in the short (50 K) temperature interval between the two sets of results. Clegg et al. (1995) have reported water activities to supersaturated conditions for $(NH_4)_2SO_4$(aq), an electrolyte of similar charge type to K_2CO_3, near ambient temperatures. These results indicate water activities in these solutions remain near the "ideal" condition of $a_w \approx x_w = 55.508/(3m + 55.508)$ for molalities approaching 30 mol·kg^{-1}. This observation is the primary basis for the assumption of $a_w = x_w$ for the solvent-vaporization corrections to the present results as described above.

A primary use for solubility results is to calculate the solubility-product equilibrium constant as a function of temperature. However, given the lack of reliable information on the activity coefficient of saturated K_2CO_3(aq), we will not attempt to estimate equilibrium constants from the present data. It is expected that this question will be addressed in more detail in a future communication describing solubility results for mixtures including $\{K_2CO_3 + KCl\}$(aq) and $\{K_2CO_3 + KHCO_3\}$(aq).

Conclusions

When designing and operating supercritical water oxidation reactors, accurate thermodynamic data for salts in water at high temperatures are needed. In this work the synthetic method has been used to determine the solubility of potassium carbonate in water between 384 and 529 K. The accuracy of this technique depends strongly on the temperature dependence of solubility. The results indicate that potassium carbonate remains prograde-soluble to 529 K. At approximately 427 K a change in the stable solid phase was observed visually and was confirmed by noting a change in the dependence of the saturated solution composition on temperature. Higher temperature measurements for this compound will require replacement of the sapphire windows with diamond windows.

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