Pourbaix Diagrams at Elevated Temperatures ~A Study of Zn and Sn~

by

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#### Abstract

Metals in industrial settings such as power plants are often subjected to high temperature and pressure aqueous environments, where failure to control corrosion compromises worker and environment safety. For instance, zircaloy (1.2-1.7 wt.% Sn) fuel rods are exposed to aqueous 250-310 °C coolant in CANDU reactors. The Pourbaix ( $E_{H}$ -pH) diagram is a plot of electrochemical potential versus pH, which shows the domains of various metal species and by inference, corrosion susceptibility. Elevated temperature data for tin +II and tin +IV species were obtained using solid-aqueous phase equilibria with the respective oxides, in a batch vessel with *in-situ* pH measurement. Solubilities, determined via spectroscopic techniques, were used to calculate equilibrium constants and the Gibbs energies of Sn complexes for E-pH diagram construction. The SnOH<sup>3+</sup> and Sn(OH)<sup>5</sup> species were incorporated, for the first time, into the 298.15 K and 358.15 K diagrams, with novel G<sup>o</sup> values determined at 358.15 K.

**Key words:** Pourbaix diagrams, E<sub>H</sub>-pH, elevated temperatures, solubility, equilibrium, metal oxides, hydrolysis, redox potential, pH, thermochemical data, tin, zinc, zircaloy, corrosion, passivity.

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# List of Abbreviations and Symbols

Notation	Meaning
α	Activity
А	Davies equation parameter
AA	Atomic absorption
aq	Aqueous phase
atm	Atmosphere (unit)
b	Davies equation parameter, y-intercept of a generic line
BWR	Boiling water reactor
°C	Celsius (unit)
C <sup>o</sup>	Concentration at standard state (i.e., $1 \text{ mol} \cdot L^{-1}$ )
C <sub>p</sub>	Heat capacity at constant pressure
CANDU	CANada Deuterium Uranium
E <sub>H</sub> or E	Electrochemical potential
Eo	Standard electrochemical potential
F	Faraday's constant (96485.3 $C \cdot mol^{-1}$ )
FAAS	Flame atomic absorption spectroscopy
G	Gibbs energy
G°	Standard Gibbs energy
g	Gas; gram (unit)
h	Hour (unit)
Н	Enthalpy
H <sup>o</sup>	Standard enthalpy
HECC	Hydrogen electrode concentration cell
HKF	Helgeson-Kirkham-Flowers
HTS	Heat transport system
i	General species
Ι	Ionic strength
ICP-MS	Inductively-coupled plasma mass spectroscopy
ICP-OES	Inductively-coupled plasma optical emission spectroscopy
J	Joule (unit)
Κ	Kelvin (unit)
K <sub>cond</sub>	Conditional equilibrium constant $(I \neq 0)$
Ko	Thermodynamic equilibrium constant (I=0) at a constant
	temperature
1	Liquid
L	Liter (unit)
LOCA	Loss-of-coolant accident

m	Slope of a generic line
М	General notation for any metal; concentration $mol \cdot L^{-1}$ (unit)
mg	Milligram (unit)
mol	Mole (unit)
MPa	Megapascal (unit)
MS	Mass spectrometry
n	Number of electrons; mole (unit)
ORNL	Oak Ridge National Laboratory
Р	Pressure
ppb	Parts per billion (unit)
ppm	Parts per million (unit)
ppt	Parts per trillion (unit)
PWR	Pressurized water reactor
Q	Reaction quotient
R	Ideal gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$ )
r	Reaction (used as subscript)
S	Second (unit)
S	Entropy
S <sup>o</sup>	Standard Entropy
SCC	Stress corrosion cracking
SHE	Standard hydrogen electrode
SS	Stainless steel
Т	Temperature
UV-vis	Ultraviolet-visible
V	Volume
wt.%	Weight percent (unit)
γ	Activity coefficient
YSZ	Yttria-stabilized zirconia
Z	Ionic charge

# **1 INTRODUCTION**

The importance of metals as materials is evident across a variety of industrial sectors, whether it is oil and gas production, nuclear and fossil fuel-based power generation, chemical processing, or hazardous waste management. In particular, the applications of metals and alloys often involve corrosive, aqueous, high temperature, and pressure environments. A key example of this is the primary heat transport system (HTS) of a CANDU<sup>\*</sup> nuclear reactor, where the temperature of aqueous coolant ranges from around 523.15 K at the core inlet headers to 583.15 K at the outlet, and a pressure boundary of 10 MPa [1] to suppress boiling outside the steam generators. In such conditions, components such as fuel rods, feeder tubes and headers, and feedwater heaters are composed of zirconium alloys, carbon steels, and copper alloys, respectively. The use of metals in such severe conditions on an industrial level requires an in-depth knowledge of their properties. An improper choice of materials (i.e., not suitable for the system design and operating conditions) can lead to failure of the equipment and compromised worker safety.

A prime example of such a situation is the recent near-miss loss-of-coolant accident (LOCA) in 2002 at the Davis Besse pressurized water reactor (PWR) site in Oak Harbor, Ohio. The cracking of several nickel alloy control rod nozzles resulted in a leak of borated reactor coolant onto the pressure vessel head [2], shown in Figure 1.1(a). Upon exposure to the boric acid environment, the mostly carbon steel head was highly susceptible to corrosion, which continued through nearly 15 cm (six inches) until reaching the inner stainless steel liner. The resulting cavity in the vessel head is shown in

<sup>\*</sup> CANDU, short for CANada Uranium Deuterium, is a Canadian-designed pressurized heavy water reactor and a registered trademark of Atomic Energy of Canada Limited.

Figure 1.1(b). Although stainless steel is corrosion resistant under acidic conditions, it was not intended to provide long-term structural integrity to the vessel [2]. If the stainless steel liner had failed before the leak was discovered, a loss-of-coolant accident (LOCA) would have taken place.



Figure 1.1(a) Pressure vessel head flange area showing boric acid deposits, (b) cavity in the carbon steel portion of the reactor head [2].

# 1.1 Aqueous Corrosion and Passivity

Corrosion is the destruction of a metal due to chemical or electrochemical reaction with its environment [3]. Consequently, aqueous corrosion refers to the series of chemical and electrochemical reactions that occur between a metal and a bulk solution medium. It can be subdivided into several categories based on the environmental factors such as: concentration of various dissolved species; fluid flow; stress; and temperature. In general, corrosion can be expressed in terms of half-cell reactions. In the anodic half-cell the metal is oxidized, producing electrons and aqueous species as indicated by equation 1.1. The electrons released during the oxidation are used by the corresponding cathodic half-cell. If the solution is oxygenated, the dissolved  $O_2$  gas is reduced to hydroxide ions, (equation 1.2), while in anoxic conditions, protons are reduced to form hydrogen gas (equation 1.3). The former is favoured in neutral or alkaline conditions,

while the latter is more likely to be the cathodic reaction in acidic solutions. Figure 1.2(a) shows active corrosion under oxygenated conditions where the metal is removed (so-called "eating away") by dissolving into the surrounding solution.

anode: 
$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^-$$
 1.1

cathode: 
$$0_{2(g)} + 2H_2 O_{(l)} + 4e^- \rightarrow 40H_{(aq)}^-$$
 1.2

cathode: 
$$2H_{(aq)}^+ + 2e^- \rightarrow H_{2(q)}$$
 1.3

In addition to producing aqueous products, corrosion can lead to the growth or deposition of solid oxides on the surface of the metal. Figure 1.2(b) illustrates a scenario where an oxide layer forms on the surface of the base metal. The term oxide is generally used to represent any oxygen-bearing phase of a metal, M, in the system M-O-H, which includes oxyhydroxides, and hydroxides [4]. Depending on properties of the oxide, this layer can protect the surface from further oxidation - a phenomenon known as passivity. For instance, a non-porous film can prevent the direct contact between the metal and solution. Factors such as temperature, solution pH, and redox potential affect the stability of the passive layer, dictating whether it will dissolve and lead to further corrosion, or continue to protect the metal.



Figure 1.2 A graphical summary of (a) general metal corrosion under aerobic conditions,(b) passivity via metal oxide formation in aqueous solution.

The Davis Besse incident is merely a single example highlighting that corrosion can be detrimental. In order to mitigate corrosion in such large-scale, industrial systems, accurate elevated temperature prediction tools are necessary. The basic objective of the thermodynamics of corrosion is to foresee the conditions at which a metal will react with its environment, leading to the formation of dissolved ions or solid reaction products [5]. The accumulation of thermodynamic data for metal species provides information on stable phases in equilibria, ion concentrations in the aqueous phase, and directions of change of the systems to the most stable phase.

# **1.2 Elevated Temperature Corrosion Systems**

In the context of nuclear reactors, when conditions do not permit the use of stainless steels, two major alloy systems, brass and zircaloy, are used at the elevated temperatures. These alloys and their main constituent elements are briefly discussed here with respect to their various corrosion and mechanical properties.

#### 1.2.1 Copper and Brass

Although the high corrosion resistance of copper makes it an attractive material for various industrial applications, pure copper metal is quite soft and malleable [6]. Alloying additions of zinc, tin, and nickel can be made to increase strength, while maintaining the corrosion resistance properties of the original metal. For instance, common brass alloys are a combination of copper and 10-50% zinc, with trace amounts of tin, iron, manganese, arsenic, and lead. Admiralty brass, consisting of 70-73% copper,  $\sim$ 1% tin, 0.02-0.10% arsenic, and the balance being zinc, is used for the low pressure

feedwater heaters<sup>\*</sup> (operating temperature between 80-100 °C) and condensers in the CANDU secondary side heat transport system [7].

Zinc

Unalloyed zinc is characterized by a lower hardness and strength than copper, and a poor resistance to long-term deformation under constant applied stress, referred to as creep [8]. While such properties do not make pure Zn convenient for most high stress and elevated temperature applications, the combination of zinc and copper produces brass alloys with better mechanical properties than either of the pure metals. However, a high zinc content (>50%) increases the potential for Zn diffusion or dezincification, a dealloying process in mediums where zinc is the more corrosion susceptible constituent [6].

A noteworthy application of unalloyed zinc at elevated temperatures is its injection into the light water coolant of pressurized and boiling water reactors (BWRs) since the mid-1980s [9]. A major consequence of the addition is a decrease in the build-up of radionuclides, specifically cobalt-60, a strong gamma ray emitter with a long half-life (approximately 5.3 years) [10], into reactor piping systems. It has been shown that the protective oxide layers that develop in the presence of zinc are thinner than those in its absence and they incorporate a smaller amount of Co-60 activation product [9]. An additional effect of the presence of Zn is mitigation of intergranular stress corrosion cracking (SCC) of the nickel alloy (Inconel) components. It has been proposed that zinc cations replace Ni<sup>2+</sup> and Fe<sup>2+</sup> in the inner (Fe-Ni-Co,)Cr<sub>2</sub>O<sub>4</sub> chromite spinel oxide on the alloy surface, to form a new Zn-spinel with improved corrosion protection [1]. The

<sup>&</sup>lt;sup>\*</sup> Water collected from the turbine condensers is reheated from approximately 33 °C to 100 °C in the low pressure heaters followed by heating up to ~175 °C in the high pressure heaters. This lessens the thermal shock of feedwater entering the ~250 °C steam generator {{90 CANTEACH}}.

desire to better understand the mechanism and advantages of Zn action in brass alloys and as a coolant additive in reactor settings prompted the investigation of the thermochemical properties of zinc species over the past two decades (see section 2.1.1).

#### 1.2.2 Zirconium and Zircaloys

The low-neutron-capture cross section, corrosion resistance in high temperature aqueous environments (573.15-623 K), and strong mechanical properties of zirconium make it an attractive choice for use in the fuel region of nuclear reactor cores. Specific areas include: fuel cladding, grid spacers, guide tubes, pressure tubes, and calandria tubes [11,12]. However, the strength and corrosion resistance of unalloyed zirconium are insufficient for more severe in-reactor conditions, such as those encountered in a loss-of-coolant accident [11]. To improve upon these properties, zirconium alloys are used. With the exception of zircaloy-2.5Nb, where niobium is the main alloying component, Zr alloys (zircaloys) are essentially a binary combination of zirconium and tin. The compositions of Zr-2, Zr-4<sup>\*</sup>, and Zr-2.5Nb, which are used for calandria tubes, fuel cladding, and pressure tubes in the CANDU primary heat transport system, respectively, are summarized in Table 1.1.

Table 1.1 Chemical Specification for Standard Zircomann 741095 [11,12].						
Element	Zircaloy-2	Zircaloy-4	Zircaloy-2.5% Nb			
Tin (Sn)	1.2-1.7%	1.2-1.7%				
Iron (Fe)	0.07-0.2%	0.18-0.24%				
Nickel (Ni)	0.03-0.08%	0.007%				
Chromium (Cr)	0.05-0.15%	0.07-0.13%				
Niobium (Nb)			2.4-2.7%			
Zirconium (Zr)	Balance	Balance	Balance			

Table 1.1 Chemical Specification for Standard Zirconium Alloys [11,12].

Note: Amounts are reported in weight percent.

<sup>&</sup>lt;sup>\*</sup> The numbers in zircaloy nomenclature indicate chronological order of manufacturing, with Zr-1created first and compositional variations around it leading to the Zr-2 alloy, etc.

Although tin is a soft and malleable metal [13], alloying Sn with zirconium works to improve the creep resistance in zircaloys [11]. However, due to the lowered corrosion resistance when tin is present in larger amounts than shown in Table 1.1, only small additions are made. As will be discussed in subsequent sections, much of the thermochemical data on the tin system remains uncertain, specifically at elevated temperatures.

# **1.3 Pourbaix Diagrams**

The comprehensive prediction of aqueous corrosion and speciation of metals was first introduced by Marcel Pourbaix in the 1950s via the development of predominance area diagrams, which plot electrochemical potential, E, versus pH. The diagrams, named in honour of Pourbaix, show corrosion behaviour of a metal, M, based on the equilibrium reactions between its various species and phases. The domain of thermodynamic stability for each form of the metal is expressed as a function of solution pH on the abscissa and electrochemical potential on the ordinate. To construct an E-pH diagram, all known existing aqueous and solid substances such as the metal itself, its oxides, hydrides, hydroxides, and various dissolved ions should be considered<sup>\*</sup>. The boundary lines separating any two domains represent the equilibria between the inhabiting species and are plotted based on available thermochemical data at the desired conditions. A collection of Pourbaix diagrams for M-H<sub>2</sub>O systems at standard, ambient temperature and pressure (298.15 K, 1 atm) was published in the Atlas of Electrochemical Equilibria in

<sup>&</sup>lt;sup>\*</sup> The full procedure of constructing a Pourbaix diagram, while essential, is not the main scope of the current work. The reader is, instead, directed to additional literature for a more thorough walk-through of the process {{122 Verink, E.D., Jr. 2011; 120 Thompson, W.T. 2011}}.

Aqueous Solutions [14], and includes over 70 metals. A diagram at 298.15 K for tin, constructed from the available thermochemical data on the Sn system [15] using the species in the original work of Pourbaix [14] is shown in Figure 1.3.



**Figure 1.3** Classical E-pH diagram for tin at 298.15 K and an aqueous species concentration of 10<sup>-6</sup> mol·L<sup>-1</sup>.

An E-pH diagram is a highly useful organizational tool for understanding the corrosion susceptibility of a metal in aqueous solution and establishing which metals are expected to exhibit passivity over a particular range of pH and potential conditions [16]. Pourbaix diagrams can be subdivided into immunity, corrosion, and passivity regions, based on the identities of the dominant species in a particular region. In the immunity

area, the most stable species is the unreacted metal itself. At the electrochemical potential and pH coordinates in this region, the metal cannot thermodynamically undergo oxidation [14]. As previously discussed, in the regions where solid corrosion products such as metal oxides are dominant, passivity of the metal surface can occur, thus preventing further oxidation. Lastly, the areas of the diagram where aqueous ions are stable represent active corrosion conditions. The concentration of dissolved metallic species used in Pourbaix diagrams is usually, if not specified,  $10^{-6}$  mol·L<sup>-1</sup>. This value was stipulated by Pourbaix as the practical limit for corrosion, depending greatly on the detection limits of metal content-determining instrumentation at the time that the Atlas of Electrochemical Equilibria in Aqueous Solutions was assembled [14]. Thus, at metal concentrations greater than 10<sup>-6</sup> mol·L<sup>-1</sup>, active corrosion is assumed, while at less than  $10^{-6}$  mol·L<sup>-1</sup>, where quantitative measurements are difficult even with modern techniques, it is considered that corrosion is not occurring. Thus, in order to determine if an aqueous metal system is likely to passivate, corrode, or be immune at particular pH and potential conditions, access to accurate Pourbaix diagrams at the desired temperature is essential.

#### 1.3.1 General Construction of a Pourbaix Diagram

To create a Pourbaix diagram, all possible reactions between the species that exist in a system are analyzed. More specifically, the coordinates of stability boundaries are determined using the standard Gibbs energies of the various equilibria. For any chemical reaction, r, the change in Gibbs energy,  $\Delta G_{r,T}$ , at a particular temperature, T, can be related to the standard Gibbs energy change,  $\Delta G_{r,T}^{o}$ , and the reaction quotient, Q, by:

$$\Delta G_{r,T} = \Delta G_{r,T}^{o} + 2.303 \text{RTlog}Q_{T}, \qquad 1.4$$

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where R represents the ideal gas constant (8.314  $J \cdot K^{-1} \cdot mol^{-1}$ ), and T represents the temperature, which at standard ambient conditions is 298.15 K, and Q represents the ratio of product of the concentrations or pressures of the products over those of the reactants, where each species is raised to the power of the appropriate stoichiometric coefficient according to the balanced reaction. For a system at equilibrium, the sum of the individual Gibbs energies of the products is equal to those of the reactants, thus  $\Delta G_{r,T}$  is equal to zero. Equation 1.4 can be re-written to express the standard Gibbs energy, at a temperature, T, as a function of the thermodynamic equilibrium quotient,  $K_T$ , as follows:

$$\Delta G_{r,T}^{o} = -2.303 RT \log_{10} K_{T}, \qquad 1.5$$

with  $K_T$  is expressed analogously to the reaction quotient, Q, but in terms of product and reactant activities,  $\alpha$ . Likewise, each activity would be raised to the power of the appropriate stoichiometric coefficient based on the particular equilibrium:

$$K_{\rm T} = \frac{\alpha_{\rm products}}{\alpha_{\rm reactants}} = \frac{C_{\rm products}}{C_{\rm products}^{\rm o}} \gamma_{\rm products} / \frac{C_{\rm reactants}}{C_{\rm reactants}^{\rm o}} \gamma_{\rm reactants}$$
 1.6

where  $\gamma$  represents the activity coefficient, C represents the concentration (e.g., units of mol·L<sup>-1</sup>), and C<sup>o</sup> represents the concentration at standard state of 1 mol·L<sup>-1</sup> such that the activities and, subsequently, equilibrium constant are dimensionless. In an ideal dilute solution, the activity of a solute, i, approaches the concentration and it is reasonable to set the activity coefficient to 1 (i.e.,  $\alpha_i \rightarrow C_i$  as  $\gamma_i \rightarrow 1$ ). While the ideal solution model assumes solute-solute, solvent-solvent, and solute-solvent interactions all to be the same, this is not true for solutions containing electrolyte species, which readily release ions. The difference is due to the strong Coulombic interactions (i.e., electrostatic repulsion or

attraction) between ions. Unlike the relatively simple metal-water systems modelled by E-pH diagrams, aqueous metal environments often involve interactions between metal ions and high concentrations of ionic species in electrolyte solutions. In such high ionic strength media, activity coefficients quantify the deviations from ideality ( $\gamma \neq 1$ ). If the activity coefficients are known, thermodynamic properties obtained at various ionic strengths can be easily compared once extrapolated to the ideal (negligible electrostatic interaction) dilute solution reference state via activity coefficients. The models used to determine the activity coefficients for metal ions vary depending on the magnitude of ionic strength and will be discussed in more detail in sections 3.1.1.

The parallel sloping dotted lines, labelled *a* and *b* in Figure 1.3, limit the electrochemical stability area of water at standard pressure of gaseous species. The upper line represents equilibrium between water and oxygen gas above which water is oxidized to  $O_{2(g)}$  as shown by the reverse of the cathodic process written in equation 1.2, while the lower boundary represents equilibrium with  $H_{2(g)}$ , below which hydrogen gas evolution occurs according to equation 1.3. It should be noted that although it is actually heavy water,  $D_2O$ , which is in contact with the zircaloy in CANDU reactors, the small chemical distinction between  $D_2O$  and  $H_2O$  does not detectably affect the construction of Pourbaix diagrams [15]. The reactions on an E-pH diagram are subdivided into chemical and electrochemical categories. The former are vertical lines and indicate purely chemical processes in which no electron transfers take place. These equilibria can either be between a solid and dissolved substance, or two aqueous species. An example using the tin system from Figure 1.3, is the dissolution of tin(II) oxide to produce the Sn<sup>2+</sup> ion:

$$\operatorname{SnO}_{(s)} + 2\operatorname{H}_{(aq)}^{+} \leftrightarrow \operatorname{Sn}_{(aq)}^{2+} + \operatorname{H}_{2}\operatorname{O}_{(l)}$$
 1.7

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The pH coordinate of the vertical line on the E-pH plot that represents this equilibrium can be determined using the standard Gibbs energy of the reaction and the activities of aqueous species, where the activities of water and solid tin(II) oxide are assumed to be one:

$$\Delta G_{r,T}^{o} = -2.303 \text{RT} \log_{10} \frac{\alpha_{\text{H}_2\text{O}} \alpha_{\text{Sn}^{2+}}}{\alpha_{\text{Sn}\text{O}} \alpha_{\text{H}^{+}}^2} = -2.303 \text{RT} \log_{10} \frac{\gamma_{\text{Sn}^{2+}}[\text{Sn}^{2+}]}{\gamma_{\text{H}^{+}}^2[\text{H}^{+}]^2}$$
 1.8

$$pH = \left(-\frac{\Delta G_{r,T}^{o}}{2.303 \text{RT}} - \log_{10} \alpha_{\text{Sn}^{2+}}\right)/2 = \left(-\frac{\Delta G_{r,T}^{o}}{2.303 \text{RT}} - \log_{10} \gamma_{\text{Sn}^{2+}}[\text{Sn}^{2+}]\right)/2 = 1.9$$

Horizontal boundaries represent electron-transfer reactions, while diagonal lines indicate equilibria in which both a proton and electron exchange occurs. For any equilibrium involving electrons, the electrochemical equivalent of the standard Gibbs energy, the standard thermodynamic potential,  $E^{o}$ , is used. The two are related via:

$$\Delta G^{o}_{r,T} = -nFE^{o}_{T}, \qquad 1.10$$

where n represents the number of electrons involved, and F, the Faraday constant (96484.5  $\text{C}\cdot\text{mol}^{-1}$ ). For instance, the oxidation of tin metal with water to tin(II) oxide (equation 1.11) is plotted as a linear equation where the electrochemical potential is a function of the pH, as shown in equation 1.12. Note, in equation 1.12, for the given example, n=2:

$$Sn_{(s)} + H_2O_{(l)} \leftrightarrow SnO_{(s)} + 2H^+_{(aq)} + 2e^-$$
 1.11

$$E_{\rm T} = E_{\rm T}^{\rm o} - \frac{2.303 {\rm RT}}{{\rm nF}} \cdot 2 {\rm pH}$$
 1.12

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#### 1.3.2 Elevated Temperature Diagrams

As many applications of metals and alloys involve super-ambient temperature conditions, it is essential to adapt corrosion prediction tools to accurately model realistic conditions. In general, the same procedure is applied for Pourbaix diagram construction at standard ambient (T = 298.15 K, P = 1 atm), and elevated temperature conditions. However, the latter requires knowledge of thermodynamic properties at the desired temperature from either empirical data or calculations using the relationships provided by thermodynamics [17]. An example of the effect of temperature on equilibria can be seen from the location of the neutral pH line, labeled N, in Figure 1.3. Due to the T-dependence of the ion product constant of water (H<sub>2</sub>O<sub>(1)</sub>  $\leftrightarrow$  H<sup>+</sup><sub>(aq)</sub> + OH<sup>-</sup><sub>(aq)</sub>, K<sub>w,T</sub> =  $\alpha_{H^+}\alpha_{OH^-}$ ), the neutral pH changes with the temperature according to:  $pH_{neutral} = \frac{1}{2}pK_{w,T}$ , and is thus specified on each diagram.

The Gibbs energy at any given temperature, T, is related to the enthalpy, H, and entropy, S, state functions according to:

$$G = H - TS$$
 1.13

In order to determine an expression for the Gibbs energy of a substance at any temperature and pressure,  $G_T^P$ , a convenient reference state at which G, H, and S are well known is necessary. The values of the thermodynamic properties in equation 1.13 are then calculated as changes from that reference temperature and pressure ( $T_{ref}$ ,  $P_{ref}$ ) to the desired conditions. To reach the desired temperature, a constant pressure, or isobaric, step is needed, while changing the pressure from  $P_{ref}$  to P requires a constant temperature, or isothermal step [18]. The total differential, dG, can be written as:

$$dG = VdP - SdT, 1.14$$

which, evaluated at constant temperature, is:

$$\left(\frac{\partial G}{\partial P}\right)_{T} = V \qquad 1.15$$

The combination of isobaric and isothermal steps to produce  $G_T^P$  can be expressed as:

$$G_{T}^{P} = G_{T}^{P_{ref}} + \int_{P_{ref}}^{P} \left(\frac{\partial G}{\partial P}\right)_{T}$$
 1.16

Substituting equations 1.13 and 1.15 to calculate  $G_T^{P_{ref}}$  and determine the pressure effect, respectively leads to:

$$G_{T}^{P} = \left(H_{T}^{P_{ref}} - TS_{T}^{P_{ref}}\right) + \int_{P_{ref}}^{P} V_{T} dP$$
1.17

The temperature dependences of the entropy and enthalpy, assuming no phase changes occur over the temperature interval and a constant pressure can be written as follows:

$$H_{T}^{P_{ref}} = H_{T_{ref}}^{P_{ref}} + \int_{T_{ref}}^{T} C_{P_{ref}} dT$$
1.18

$$S_{T}^{P_{ref}} = S_{T_{ref}}^{P_{ref}} + \int_{T_{ref}}^{T} \frac{C_{P_{ref}}}{T} dT, \qquad 1.19$$

where the heat capacity at constant pressure,  $C_P$ , is as polynomial temperature function:

$$C_P = a + bT + cT^2 + dT^{-2} + \cdots,$$
 1.20

with fitting parameters a, b, c, and d. Equations 1.16-1.20 can be combined in equation 1.21 to show the temperature and pressure dependence of the Gibbs energy. As most

thermochemical data is available at ambient conditions of 298.15 K and 1 atm, this is often chosen as the reference state:

$$G_{T}^{oP} = H_{298.15 \text{ K}}^{o} + \int_{298.15 \text{ K}}^{T} C_{P_{\text{ref}}} dT - T \left( S_{298.15 \text{ K}}^{o} + \int_{298.15 \text{ K}}^{T} \frac{C_{P_{\text{ref}}}}{T} dT \right) + \int_{1 \text{ atm}}^{P} V_{T} dP = 1.21$$

If the final pressure does not greatly exceed 100 atm, the effect of P on Pourbaix diagram construction can be assumed negligible [15]. Thus, the VdP term in equation 1.21 is removed, and  $P_{ref}$  is simply referred to as P:

$$G_{T}^{o} = H_{298.15 \text{ K}}^{o} + \int_{298.15 \text{ K}}^{T} C_{P} dT - T \left( S_{298.15 \text{ K}}^{o} + \int_{298.15 \text{ K}}^{T} \frac{C_{P}}{T} dT \right)$$
 1.22

To emphasize, the CANDU primary HTS pressures of 10 MPa is equivalent to approximately 99 atm, thus the pressure effect can be neglected even when simulating reactor conditions.

# 1.3.3 Challenges with Elevated Temperature Thermodynamic Data

Corrosion-predicting Pourbaix diagrams have been constructed for most metals at a reference temperature of 298.15 K and pressure of 1 atm due to the large body of thermodynamic data that has been gathered at these conditions [14]. While several M-H<sub>2</sub>O systems have been very well characterized (e.g., Al, Ca, Ga, Ge, Mg, Si, and Zn) at elevated temperatures such that the data are not likely to change from currently accepted values, results for other industrially significant metals (e.g., Cr, Cu, Ni, Ti, and Sn) are still controversial or insufficient [4]. Specifically, systems with greater complexity due to multiple stable oxidation states are more poorly understood. The contact between an aqueous phase in the range 523.15 K to 583.15 K and the zircaloy fuel rods creates a situation where knowledge of the effects of temperature on thermodynamic-based, corrosion prediction methods is necessary. This also highlights the general need for experimental, elevated temperature thermochemical research to improve corrosion modelling of metals and alloys in harsh aqueous conditions. The present work focuses on developing an elevated temperature Pourbaix diagrams for the tin system due to its presence in fuel cladding and, the unavailability of thermodynamic data for multiple Sn species [15]. The extensive collection of data on the Zn system makes it an ideal candidate for method and data analysis verification in the current work.

One of the issues in creating elevated-temperature E-pH diagrams is the unavailability of the temperature dependencies of the thermodynamic properties. For instance, if the  $C_p(T)$  power function for a substance is known along with its standard enthalpy of formation,  $\Delta H_f^o$ , and entropy, S<sup>o</sup>, at a reference temperature (i.e., 298.15 K), the use of equations 1.18 and 1.19 to calculate the enthalpies and entropies of a substance at any desired temperatures is quite straightforward. For solids, elements, and neutral compounds, the experimentally-derived fitting parameters of the heat capacity polynomials are often tabulated in the literature [17]. However, in the case of many aqueous species such C<sub>p</sub> functions are often unavailable due to insufficient experimental data. The approach used to determine the temperature dependence of thermodynamic properties is a key to accurate Pourbaix diagram construction. In an effort to fill in the missing data for hydrothermal (T  $\geq$  373.15 K) metal systems, specifically for aqueous species, a combination of experimental and theoretical work is necessary. The next chapter will provide a review of the current knowledge of the tin and zinc systems

considered in detail in this work, and the methods currently used to evolve our understanding of the elevated temperature thermochemistry of M-H<sub>2</sub>O systems in general. The advantages and challenges of techniques are presented along with how the present research aims to contribute to this multidisciplinary work.

#### 1.3.4 Combining Modelling and Experimentation

While extrapolating thermochemical data at ambient conditions up to elevated temperatures is often necessary for estimating the temperature effect on a system with limited information, it is not a complete substitute for experimental work. On the other hand, there are often discrepancies in the experimental data collected due to challenges with instrumentation, accuracy of measurements, and data analysis at high temperatures. The solution is to combine the two approaches. More available measured data for a system allows for accurate construction of E-pH diagrams and improved fitting parameters for models. Better correlations lead to more accurate predictions at conditions that have not been previously studied. This work aims to contribute to the continuous effort to close the gap between experimental and theoretical approaches by developing efficient and accurate equipment and an optimized procedure that can be extended to studying the solubility equilibria of any system at the desired temperature.

The exposure of zircaloy fuel rods to an aqueous, 523.15-583.15 K coolant in the CANDU primary heat transport system provides a scenario where corrosion-predicting tools such as Pourbaix diagrams must be effective at super-ambient conditions [15]. The elevated temperature E-pH diagrams for tin are investigated both due to its presence in fuel cladding (1.2-1.7 wt.%), as shown in Table 1.1, and the large unavailability and unreliability of thermodynamic data for aqueous tin species. Much of the

thermochemical information on tin +IV complexes are conflicting even at 298.15 K, which is compensated with heavy estimation based on known data for  $\text{Sn}^{2+}$  and other similar +IV ions. For instance, the similar sizes of the tin +II and +IV species allows an analogous heat capacity – the energy required to increase the temperature by one temperature degree (i.e., K) to be assumed for the two ions. However, there is still limited information on the temperature dependence of some of the Sn +II dissolved species. This indicates a need for specialized instrumentation and a simple, effective way to obtain more information on both oxidation states of the Sn-H<sub>2</sub>O system at super-ambient conditions.

Solubility experiments are a simple and effective method of using solid-aqueous phase equilibria to obtain thermochemical data on the aqueous species involved. In particular, the equilibrium constants and subsequent Gibbs energies of these elevated temperature dissolution and hydrolysis reactions are used to re-calculate portions of Pourbaix diagrams at the temperature of interest. The Gibbs energies of individual complexes can also be extracted based on the known  $G_T^o$  values of other species involved in the reactions under study. This allows for the re-construction of super-ambient E-pH diagrams by substituting experimental data in place of the predicted values and improving subsequent correlations to higher temperatures. There is also an opportunity to produce novel, elevated temperature data for aqueous species in the Sn system, on which little experimental work is available. Furthermore, zinc, which is used to mitigate SCC in PWRs and cobalt-60 accumulation in CANDU reactors, is an ideal choice to verify experimental setup and data analysis due to the well-established thermodynamic data for the Zn-H<sub>2</sub>O system up to 573.15 K.

# 1.4 Objectives

The overall goal of this project is divided into three parts:

1. Validate the instrumentation and data analysis process by examining the solubility of a well-studied system, where the resulting data can be compared to literature. The dissolution equilibria of zinc oxide will be investigated at 358.15 K using a constant volume, batch reactor system with *in-situ* pH measurement.

2. Investigate the solubilities of tin(II) and tin(IV) oxides at various temperatures (i.e., 298.15 K, 358.15 K, and 378.15 K) to obtain previously unavailable experimental insight on the Sn system. The measured data will be used to calculate the standard Gibbs energies for the various solubility and hydrolysis reactions. The results will be compared to any existent experimental and extrapolated data and used to re-construct portions of tin E-pH diagrams at the examined temperatures.

3. Recommend optimizations and additions to the method and equipment used in the present work to facilitate higher temperature experiments, able to simulate the harsh (523.15-583.15 K) conditions of the CANDU heat transport system.

# **2** REVIEW OF RELEVANT LITERATURE

#### 2.1 Current Thermodynamic Data for Select Aqueous Systems

The focus on zinc and tin in the present work requires an overview of the key sources of thermodynamic properties for the Zn-H<sub>2</sub>O and Sn-H<sub>2</sub>O systems. The following is a general summary of the investigations that have contributed to data compilations for tin and zinc, as reported in various thermochemical databases [19-29], with particular attention to solubility studies. The major challenges encountered in the literature and the subsequent issues with missing properties are highlighted.

# 2.1.1 Speciation and Thermodynamic Data for the Zn-H<sub>2</sub>O System

ZnO is the dominant oxide in the zinc system, as zinc only has the one stable oxidation state of II (i.e., species of the form  $Zn^+$  and  $Zn^{3+}$  or  $Zn^{4+}$  have not been observed, unlike, for example, iron where  $Fe^{2+}$  and  $Fe^{3+}$  exist or copper with  $Cu^+$  and  $Cu^{2+}$  possible). The solid hydroxide,  $Zn(OH)_2$  is metastable relative to ZnO [30]. The  $Zn^{2+}$  ion is coordinated to several waters of hydration, which undergo splitting or hydrolysis to produce a proton and various metal hydroxide aqueous species (see section 3.1.2). The hydrolytic reactions of  $Zn^{2+}$  form the  $ZnOH^+$ ,  $Zn(OH)_2^0$ , and  $Zn(OH)_3^-$  complexes. Polynuclear species (containing multiple metal ions) are generally not considered at metal concentrations less than  $10^{-3} \text{ mol} \cdot L^{-1}$  [10]. Over the past several decades, the identities of Zn species and their subsequent reactions in aqueous environments at various temperatures have been extensively studied with good reproducibility. The solubility product constant of ZnO and the subsequent  $Zn^{2+}$  hydrolysis reactions have been investigated at various pH conditions via flow-through and batch vessels at temperatures up to 623.15 K [30-36]. The corroborating studies by

Hanzawa *et al.* [33] and Benezeth *et al.* [36] resolved the conflicting data that had been previously reported for the ZnOH<sup>+</sup> hydrolysis product by Khodakovskyi and Yelkin [30] and incorporated into the geochemical database SUPCRT92 [29] by Shock and workers [37]. The source of the discrepancies, due to the narrow pH stability range of the complex, was resolved by the advancement of *in-situ* pH measurements. Thus, the thermodynamic properties for the Zn system are readily available at 298.15 K along with their experimentally derived temperature dependence. The thermochemical data for the

Zn system are presented in Table 2.1.

Species	$\Delta H_{298\;K}^{°}$	$S_{298 K}^{\circ}$	$C_P = a + bT + cT^2 + dT^{-2} (J \cdot mol^{-1} \cdot K^{-1})$			
1	$(J \cdot mol^{-1})$	$(J \cdot mol^{-1} \cdot K^{-1})$	a	b	c	d
Zn <sub>(s)</sub>	0	41.63	21.334	0.011648	0	54000
ZnO <sub>(s)</sub>	-350460	43.65	45.338	0.007289	0	-573000
Zn <sup>2+</sup> <sub>(aq)</sub>	-153640	-109.8	-25.8	0	0	0
$ZnOH^{+}_{(aq)}$	-384220	-22.06	10.0	0	0	0
$Zn(OH)_{3(aq)}^{-}$	-881520	2.98	94.0	0	0	0

Table 2.1 Thermochemical Data Necessary for Zn Pourbaix Diagram Construction [29,35].

#### 2.1.2 Speciation and Thermodynamic Data for the Sn-H<sub>2</sub>O System

Stable compounds in the tin system have oxidation numbers of II and IV, where the dominant Sn oxides are  $SnO_{(s)}$ , and  $SnO_{2(s)}$ . It has been shown [38,39], that the solid hydroxides  $Sn(OH)_{2(s)}$  and  $Sn(OH)_{4(s)}$  are unstable and easily dehydrate to their respective anhydrous forms, which is also consistent with the data presented by Pourbaix [14]. The +IV ion is the prevalent oxidation state in oxygenated aqueous systems, while Sn +II exists under more reducing conditions [40]. Both Sn<sup>2+</sup> and Sn<sup>4+</sup> ions undergo hydrolysis reactions that result in a variety of charged and neutral tin complexes.

# Tin (II) Speciation

Work on the solubility product constant for tin(II) oxide/Sn<sup>2+</sup> equilibrium was done by Silen [41] and corroborated by Djurdjevic et al. [39]. Early hydrolysis speciation of Sn<sup>2+</sup> was carried out by Gorman [42] and Garret and Heiks [38], respectively. Data from the former have been criticized for errors due to oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup>. While Garret and Heiks controlled the redox chemistry, there was inadequate attention to the stability ranges of various hydrolysis species when calculating equilibrium constants [43]. In the work of Vanderzee and Rhodes [44], the use of chlorinated solutions required a correction for the formation of tin(II)-halide complexes. Since then Tobias, Djurdjevic et al., and Pettine et al. [39,43,45] have studied Sn<sup>2+</sup> hydrolysis electrochemically under a nitrogen atmosphere to prevent oxidation and have The  $\text{SnOH}^+$ ,  $\text{Sn}(\text{OH})_2^0$ , and  $\text{Sn}(\text{OH})_3^-$  mononuclear achieved consistent results. hydrolytic complexes have been confirmed for the +II oxidation state [46]. The trinuclear species  $Sn_3(OH)_4^{2+}$  has been proposed by Djurdjevic *et al.* [39] and Tobias [43] as the principle hydrolysis product instead of SnOH<sup>+</sup>. It has, however, generally been found that polynuclear metal complexes are only stable in high concentration solutions of  $\geq 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  [4,46]. There is occasional disagreement over the stoichiometry of the final  $\text{Sn}^{2+}$  hydrolysis product,  $\text{Sn}(\text{OH})_3^-$ , with some compilations reporting it as the oxyanion  $HSnO_2^-$ , in reference to the classification in the original Sn E-pH diagram in Pourbaix's Atlas [14]. The difference between these notations is simply one water molecule:  $HSnO_2^- + H_2O = Sn(OH)_3^- [47,48]$ . Original Pourbaix conventions dictated that the terminal hydrolysis products of all metal cations are oxyanions, i.e., MO<sub>v</sub><sup>m-</sup>, for which complete removal of the waters of hydration has occurred, and only

oxygen atoms are coordinated. However, literature on metal cation hydrolysis since then suggests that these species are unlikely for cations with a charge  $\leq$  IV [47]. The hydroxide notation is in agreement with recent reviews of the tin system [46] and was used in the present work.

# Tin (IV) Speciation

The proposed solubility product constant for tin(IV) oxide reported in Pourbaix's Atlas [14] has recently been confirmed by Rai et al. [40] with good agreement. However, thermodynamic data for Sn<sup>4+</sup> hydrolysis products are limited even at reference conditions and with either no confirmatory sources or reported equilibrium constants that differ by several orders of magnitude [4]. Many of the solubility studies used to obtain hydrolysis constants were based mostly on pH regions where tin concentrations are at or near the detection limit, or from a time when some of the newer analytical and speciation techniques or data interpretation models were not available, making it difficult to obtain reliable values [40]. According to Pourbaix, the only stable soluble +IV species are Sn<sup>4+</sup> and the oxyanion  $SnO_3^{2-}$  [14]. Although the latter is sometimes replaced by  $Sn(OH)_6^{2-}$  in the literature [40], it is quite likely that the terminal hydrolysis complex for a +IV cation is an oxyanion [47]. Macchi and Pettine [49] have identified several possible hydrolytic complexes such as  $SnOH^{3+}$ ,  $Sn(OH)_2^{2+}$ ,  $Sn(OH)_4^0$ , and  $Sn(OH)_5^-$ , however, no equilibrium constants were reported for their formation reactions. Amaya et al. [50] suggested hydrolysis constants for the equilibria between the  $Sn(OH)_4^0/Sn(OH)_5^-$  and  $Sn(OH)_5^{-}/Sn(OH)_6^{2-}$  complexes, however, these values have not yet been confirmed. Due to the extremely low solubility of  $SnO_2$  over the stability range for  $Sn(OH)_4^0$ , reported data on this species [50,51] vary by several orders of magnitude, as a result of
instrumental detection limits. The recent SnO<sub>2</sub> solubility study by Rai *et al.* at 298.15 K over a pH range of 0.03-14 reports stability constants for the proposed hydrolysis complexes, SnOH<sup>3+</sup>, Sn(OH)<sub>5</sub><sup>-</sup>, and Sn(OH)<sub>6</sub><sup>2-</sup> (alternately SnO<sub>3</sub><sup>2-</sup>) at standard ambient conditions [40]. However, no corroborating data are available for comparison, nor are there studies at elevated temperatures. Thus in addition to the Sn<sup>4+</sup> and SnO<sub>3</sub><sup>2-</sup> forms retained in the original Pourbaix diagram, this work will consider the SnOH<sup>3+</sup> and Sn(OH)<sub>5</sub><sup>-</sup> species.

## Thermodynamic Data Summary

The thermodynamic properties of solid and aqueous Sn species are presented in Table 2.2 as reproduced from Table 9.1 in the work of Kaye and Thompson on modelling the tin elevated temperature E-pH diagram [15]. The following is a brief summary of key points from their critical literature review [14,23,24,52]. The data in Table 2.2 that are in italics represent estimations in accordance with practices that have been applied to many other high temperature Pourbaix diagram computations [15,53]. The partial molar heat capacity function of Sn<sup>4+</sup> was taken to be the same as that of Sn<sup>2+</sup>, while the entropy at 298.15 K was estimated based on chemical similarities with other +IV ions such as U<sup>4+</sup>. The enthalpy for Sn<sup>4+</sup> was calculated based on a restriction on its standard Gibbs energy in relation to the  $G_{298.15 \text{ K}}^{0}$  of Sn<sup>2+</sup>, such that the electrochemical potential of 0.151 V versus the standard hydrogen electrode (SHE) at 298.15 K would be respected for the reaction:

$$\operatorname{Sn}_{(aq)}^{4+} + 2e^{-} \leftrightarrow \operatorname{Sn}_{(aq)}^{2+}, \quad E^{o} = 0.151 \text{ V (SHE) at 298.15 K},$$
  
 $E_{298.15 \text{ K}}^{o} = -\frac{G_{298.15 \text{ K}}^{o}}{nF}$ 

30

In the case of the aqueous ions  $HSnO_2^-$  and  $SnO_3^{2-}$ , as there was no basis for estimation, the partial molar heat capacities were set to zero. The enthalpies of these species were taken from the data for the Sn diagram in the Pourbaix Atlas [14], while the entropies were estimated by Kaye and Thompson. As there is no corroborated thermodynamic data for the Sn(IV) hydrolysis complexes described in the previous section, they were not included in the table below. Treatment of these species towards the Sn E-pH diagram in the present work is further discussed in section 3.4.

Species*	$\Delta H_{298 \text{ K}}^{\circ}$	S <sub>298 K</sub>	$C_P = a + bT + cT^2 + dT^{-2} (J \cdot mol^{-1} \cdot K^{-1})$			
species	$(J \cdot mol^{-l})$	$(J \cdot mol^{-1} \cdot K^{-1})$	а	b	c	d
Sn <sub>(s)</sub>	0	51.195	21.5936	0.01810	0	0
SnO <sub>(s)</sub>	-285767	56.484	39.9572	0.01464	0	0
$SnO_{2(s)}$	-580739	52.300	73.8894	0.01004	0	-2158944
$\mathrm{SnOH}^{+}_{(\mathrm{aq})}$	-285767	50.208	-94.0103	0.22864	0	7137904
Sn <sup>4+</sup> (aq)	-56856	-410.000	-54.8690	0.09394	0	6755486
Sn <sup>2+</sup> <sub>(aq)</sub>	-10042	-24.686	-54.8690	0.09394	0	6755486
HSnO <sub>2 (aq)</sub>	-523834	10.000	0	0	0	0
$SnO_{3(aq)}^{2-}$	-724228	10.000	0	0	0	0

**Table 2.2** Thermochemical Data Used to Construct the Sn Pourbaix Diagram [15].

<sup>\*</sup> Italics indicate that the data have been estimated as described above.

In order to emphasize the effect of estimating thermochemical data, the 378.15 K diagram for tin was determined using the information presented in Table 2.2, but varying the entropy of  $\text{SnO}_3^{2-}$  at 298.15 K. Two different estimates for the standard entropy were used to calculate Figure 2.1, (i.e.,  $\text{S}_{298.15 \text{ K}}^0 = 10$  and  $100 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ), and the standard enthalpy (i.e.,  $\Delta H_{298.15 \text{ K}}^0$ ) values were changed accordingly to preserve the desired value of  $G_{298.15 \text{ K}}^0$ . The resulting change in the stability fields of  $\text{SnO}_3^{2-}$  and  $\text{HSnO}_2^-$  when the entropy was increased to  $100 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  (green lines) shows the importance of accurate thermodynamic data for Pourbaix diagram construction.



**Figure 2.1** E-pH diagram for tin at 378.15 K and a concentration of  $10^{-6}$  mol·L<sup>-1</sup> showing the effect of varying the S<sup>o</sup><sub>298.15 K</sub> value of SnO<sub>3</sub><sup>2-</sup>[15].

# 2.2 Modelling Methods for Elevated Temperature Equilibria

One approach for super-ambient E-pH diagram construction is using available standard thermodynamic properties such as the heat capacity, enthalpy, or entropy, at reference conditions to extrapolate a system to elevated temperatures. In particular, the focus of such correlations is usually on aqueous ions, for which partial molar properties at temperatures other than 298.15 K are scarce [5]. Some extensively used models are

the early entropy correspondence principle of Criss and Cobble [54,55] and the semiempirical model developed and modified by Helgeson and co-workers [56-59] referred to as the revised Helgeson-Kirkham-Flowers (HKF) equation of state. The former involves extrapolation of standard entropies based on an assumption of linear temperature dependence, while the latter, electrostatic correlation, incorporates partial volumes of ions, relative permittivity of the solvent, and electrostatic radii to determine heat capacities as a function of temperature [57]. The following section summarizes how challenges in selecting a correlation, estimations within a particular set of equations, and knowledge of speciation for a system affect the accuracy of the extrapolated, elevated temperature Pourbaix diagrams.

### 2.2.1 Model Selection

An extensive range of extrapolation techniques, with modifications continuously formulated, creates an issue with consistency across the literature. While more complex models can be quite successful in correlating data, simpler expressions with weaker theoretical foundations are often used to avoid the rigorous calculations. In the reconstructions of the iron Pourbaix diagram over the temperature range 298.15-573.15 K, Beverskog and Puigdomenech used the revised HKF equation to determine the temperature dependence of the standard Gibbs energies of reactions based on C<sub>p</sub> and S<sup>o</sup> data for ions at 298.15 K [60]. However, the authors point out that the majority of the previous Fe E-pH diagrams were constructed via the correspondence principle of Criss and Cobble, resulting in dispersion of the literature data. The estimated linear dependence of entropy on temperature, and the derived heat capacity expression have been criticized by Helgeson and co-workers to have poor correlation above 423.15 K, not

agreeing well with experimental data for  $M^{2+}$  and some  $M^{3+}$  cations [57]. In order to be truly useful, a model must not only describe as many systems as possible, but also be flexible enough to cover a wide range of conditions. Although the correlation of Criss and Cobble is rapidly being replaced with more sophisticated models, its relative simplicity allows it to remain an attractive contender. A recent computation of the Pourbaix diagrams for cobalt at 298.15-423.15 K by Chivot *et al.* [61] justifies the use of the correspondence principle as being effective for temperatures up to 473.15 K [55]. With increasing computational capabilities, even the well-established HKF model is criticized for weak theoretical origins and lower accuracy when extrapolating toward the critical point of water, specifically for non-electrolyte solutes [62,63]. Overall, models with lower correlation accuracy are still widely used in modern E-pH extrapolations due to practicality, although the consequence is inconsistency of extrapolated properties across the literature.

#### 2.2.2 Estimations within a Model

Even when a single extrapolation expression is considered, thermodynamic properties required for initial parameters are often limited or uncertain. If basic thermodynamic measurements at reference conditions are unknown, predictions from theoretically sound models can still be unreliable. An advantage of the HKF equation is estimation correlations for species on which little experimental information is available [17]. However, more than one type of estimation is often used when the issue of missing data is encountered. For instance, when heat capacity data for a substance is unavailable at 298.15 K, it is often estimated to either be zero, constant at all temperatures, or based on chemical similarities with other species. In the work of Kaye and Thompson on the

computation of high temperature E-pH diagrams focused on tin and zirconium [15], the heat capacity function parameters for  $\text{Sn}^{4+}$  were taken to be the same as that of  $\text{Sn}^{2+}$ . Furthermore, the entropy of  $\text{Sn}^{4+}$  at 298.15 K was similarly approximated according to that of the U<sup>4+</sup> ion. In their work on chromium at 298.15-573.15 K, Beverskog and Puigdomenech indicate that the calculated Pourbaix diagrams at T >298.15 K are tentative due to the uncertainty in the reference thermodynamic data for the Cr<sup>2+</sup> and Cr<sup>3+</sup> cations and hydrolysis products [64]. Specifically, the entropy for Cr<sup>3+</sup> has been reported in the range of -370 to -270 J·K<sup>-1</sup>·mol<sup>-1</sup> in the literature due to inconsistency in the estimations. Thus, the use of different approximations to account for missing reference data can produce discrepancies even when the same overall model is used for the elevated temperature extrapolation.

## 2.2.3 Species Selection

In addition to error introduced from the selection between models and approximations within a correlation, many existing E-pH diagrams deviate in the choice of species included. Although there are well-established E-pH diagrams at various temperatures for thoroughly investigated metals, often the species considered are based on the original diagrams published by Pourbaix [14]. It is necessary to critically evaluate the forms of the metal which are expected to exist in a system before they are allowed to be the basis of thermodynamic calculations. In chromium diagrams recalculated from 298.15-573.15 K by Beverskog and Puigdomenech [64], it is pointed out that the stoichiometric compositions of the Cr +III species are not well known in alkaline conditions. The  $Cr(OH)_4^-$  complex is assumed to be the identity of the chromite ion for the purpose of calculating the E-pH diagram. However, as the temperature extrapolation

used by Beverskog and Puigdomenech depends on the electric charge of the aqueous species, uncertainty in the charge of the actual chromite ion introduces error into the generated data and subsequent Pourbaix diagrams. Similarly, as information on the Cr +II hydrolysis speciation is unavailable, the authors included only the  $Cr^{2+}$  aqueous cation in the diagrams. Thus, calculations based on wrong species or omission of forms of a metal provides misleading information on chemical equilibria, which can lead to false stability regions and expectations of corrosion or passivity.

# 2.3 Elevated Temperature Solubility Equilibria

Alternatively to the modelling method, thermodynamic properties can be extracted from measurements made directly at the desired temperature. The benefit of this approach is the ability to obtain reliable data while avoiding the errors from extrapolations. For example, although iron is a well-studied metal with established elevated temperature E-pH diagrams, the availability of new solubility measurements for magnetite (Fe<sub>3</sub>O<sub>4(s)</sub>) at 373.15-573.15 K allowed Beverskog and Puigdomenech to reconstruct and revise the diagrams [60]. Although each branch of experimental thermodynamics (e.g., calorimetry, densimetry, and solubility) has its own benefits and disadvantages, the techniques are complementary and can be used in conjunction towards constructing elevated temperature Pourbaix diagrams. Properties such as enthalpy, heat capacity and volume, which can be determined from calorimetric and volumetric experiments, are necessary for extrapolations of the Gibbs energy to elevated temperatures (equation 1.22). Solid-aqueous phase solubility equilibria established at a particular set of conditions (i.e., pH, redox potential, temperature) can be used to obtain the equilibrium constant, and thus, standard Gibbs energy of reaction. Subsequently,

Gibbs energies of individual species at the temperature of interest can be extracted and applied toward re-calculating portions of a super-ambient Pourbaix diagram. This section emphasizes the importance of equipment design, accurate control of parameters, and analysis instrumentation for elevated temperature solubility studies.

## 2.3.1 Selecting an Apparatus

Similar to the different thermochemical models available for E-pH calculations, the variety of instrumental designs that exist in each branch of super-ambient experimental work makes it difficult to achieve consistent data across different laboratories. In flow-through solubility studies, the experimental solution is continuously circulated through a thick-walled column or pipe packed with the metal oxide. A sophisticated delivery system allows for automatic mixing and sampling, shorter equilibration times, and flushing of contaminants with large volumes of solution. Flowthrough systems have been used extensively for the past decade at Oak Ridge National Laboratories (ORNL) for several oxides/hydroxides, including Al(OH)<sub>3</sub>, MgO, CuO, and ZnO up to 573.15 K [32,65-67], as well as in the well-cited data on magnetite and nickel oxide produced by Tremaine and Leblanc [68,69]. However, the large total surface area of components (i.e., main reaction vessel, tubing, pump internals, etc.) requires extra effort to prevent corrosion, including the use of gold and platinum as materials. The high cost and design requirements of flow-through systems often result in the selection of an alternate setup.

In batch reactors, the volume of solution is fixed in a sealed pressure vessel at the desired temperature. These simpler systems lack the finesse of circulation, instead relying on inexpensive additions and modifications such as overhead stirring or a rocking

autoclave system, first described by Bourcier and Barnes [70], where the entire vessel assembly continuously oscillates. The batch reactor of Byrappa and Yoshimura [71] circumvents the need for a pump in the sampling system via a platform, such that the solid and solution are separated during cooling once the vessel is inverted at the end of the experiment. However, failure to reach equilibrium and precipitation and re-equilibration in the sample lines of static systems can lead to inconsistencies when compared to flow-through measurements. For instance, in the study by Benezeth and coworkers on zinc oxide solubility up to 573.15 K [34,35], precipitation of ZnO in the sample line was suspected to be the result of the falsely low solubility data due to re-equilibration at the lower temperature [35]. Overall, the choice of design must balance cost and ability to obtain self-consistent data for a system.

## 2.3.2 Establishing Solution pH

An essential factor of working at elevated temperatures is effective control of experimental parameters. In particular, for metal oxide dissolution equilibria establishing solution pH is essential due to its influence on aqueous metals speciation and solubility. Although the use of buffers appears to be an obvious solution, only select ones are stable at super-ambient conditions. Furthermore, the formation of metal-buffer complexes can control the solubility behaviour of a compound, producing misleading data. In examining the solubility of gibbsite, an aluminum oxide, at 298.15 K-323.15 K, Wesolowski *et al.* discovered that one of the aluminum species formed a highly stable complex with the chosen Tris buffer [72]. When possible, buffer-controlled experiments are overlapped with known, non-complexing acids or bases. Examples of such reagents including sodium hydroxide, acetic acid, and triflic acid, have been extensively used at ORNL.

Hydrochloric acid, although convenient for establishing highly acidic environments, requires caution due to the interfering metal-Cl complexes that readily form. The strength of interaction with the metal species depends on a variety of factors including concentration of the pH controlling agent, electronegativity of the conjugate acid or base species, and temperature. However, if the solubility data can be sufficiently deconvoluted, the formation constants of metal-solvent complexes can be extracted from those of the free metal species [4]. For instance, Wesolowski and workers conducted a study on the solubility of ZnO and the complexation of  $Zn^{2+}$  by chloride and sulphate in solutions up to 563.15 K [34]. Meanwhile, in their investigation of the solubilities of copper and zinc oxides in phosphate buffer up to 573.15 K, Ziemniak *et al.* have determined formation constants for copper and zinc-phosphate complexes [32,66]. In summary, overcoming the challenges of controlling solution properties at elevated temperatures is crucial for ensuring accurate thermochemical data are obtained.

## 2.3.3 Measurement of pH at Elevated Temperatures

As pH is one of the independent variables in solubility work, it is necessary to accurately determine both the initial value and monitor its evolution during the length of an experiment. Over the past several decades, several types of pH determining instrumentation suitable for measurements in aqueous, elevated temperature solutions have been developed. Some of the criteria for an effective pH sensor include: resistance to chemical degradation, thermal stability, and ability to produce steady and reproducible measurements [73].

Glass membrane electrodes, common to ambient temperature environments, have been used to measure pH up to 627.15 K with the silver-silver chloride (Ag/AgCl) reference electrode [74]. As one of the few thermally stable reference electrodes, the silver-silver chloride (Ag/AgCl) probe, which is stable at around 373.15 K for longer periods, has also been used at up to 573.15 K for shorter durations [73]. Prolonged use in harsh conditions results in decomposition of the Ag/AgCl electrode. However, as welldefined, thermally stable pH buffers are limited [65], calibration of glass electrodes for use at high temperatures is difficult, regardless of the choice of reference electrode [73]. The hydrogen electrode concentration cell (HECC), first introduced by Mesmer et al. [75], is a pressure vessel with two platinum electrodes inserted into Teflon cups separated by a porous Teflon plug. While the inner cup contains a solution of known proton concentration, acting as a reference, the outer cup is filled with analyte. The difference in measured potential between the electrodes, described by the Nernst equation, allows the concentration of H<sup>+</sup> in the analyte to be determined. In order to apply the HECC for solubility work, modifications such as a sampling line are required. The hydrogen electrode concentration cell provides highly precise pH measurements over a wide range of conditions and has been used to investigate a variety of metal oxide systems including ZnO, MgO, and CuO, however the cost of such an instrument can be quite high.

The yttria-stabilized zirconia (YSZ),  $ZrO_2(Y_2O_3)$ , membrane electrode has been used at elevated temperatures in both static [33] and flow-through systems [76]. A main advantage is the high operating temperature (423.15-773.15 K), which exceeds the range of the HECC. The sensor is an oxygen-ion conducting ceramic that resembles the structure of a standard glass electrode. The vacancies in the  $ZrO_2$ , are used to conduct  $O^{2-}$ from oxygenated solution, where the equilibrium between oxygen ions in the zirconia lattice, and the protons and water in solution (H<sub>2</sub>O  $\leftrightarrow$  H<sup>+</sup> + O<sup>2-</sup>) is used to determine pH [73,77,78]. A common reference electrode is a metal/metal oxide, such as the Hg/HgO, which has higher temperature stability than the conventional Ag/AgCl [73]. Furthermore, unlike the HECC, the YSZ can be used under oxidizing conditions [79]. However, these electrodes suffer from relative complexity of the design, brittleness, and variability in performance and reproducibility [73]. For instance, in the  $Zn^{2+}$  hydrolysis investigation by Hansawa *et al.* the YSZ electrode did not work at temperatures below 448.15 K and broke at 548.15 K, thus restricting the temperature range at which measurements were made [33].

Although the HECC can measure pH with greater precision, the YSZ electrode is stable at high subcritical and supercritical conditions. Overall, the cost and complex design of the yttria-stabilized zirconia probes makes the glass membrane electrode an attractive choice at moderately elevated temperatures (i.e., < 473.15 K).

# 2.3.4 Metal Ion Detection and Speciation Techniques

In order to extract the standard Gibbs free energy of reaction from a metal oxide solubility equilibrium at a known pH, it is necessary to determine the metal concentration in solution (e.g., equations 1.8 and 1.9). Spectroscopic methods such as inductively-coupled plasma optical emission spectroscopy (ICP-OES), atomic absorption (AA), and ultraviolet-visible (UV-vis) are used to detect and quantify total metal content with a high level of precision. Measuring absorption in the ultraviolet and visible regions of the electromagnetic spectrum is one of the oldest quantification techniques for inorganic species [80]. However as many metal ions are colourless in solution, complexation with a colour-developing reagent, which is not available for all metallic species, is required.

In AA spectroscopy, the absorption of a discrete wavelength of radiation, specific to the analyte, is used to determine total metal concentration via a calibration curve constructed from a set of standards of known concentrations. Meanwhile, ICP-OES is based on measuring the light emitted by a sample at a specific wavelength after excitation by a plasma source. Both technique are independent of the chemical form of the analyte, meaning that any variation in the chemical identity due to pH adjustment or temperature changes after a solubility experiment is complete (i.e., complexation, hydrolysis), will not affect the measured total metal content. While both instruments can detect trace amounts, atomic absorption spectrometers generally have higher precision, while ICP-OES has a lower detection limit. However, as the Zn sensitivity of AA is in the ppb range, while that of ICP-OES is only in the ppm range, the former is often chosen for ZnO solubility studies [33-35]. An advantage of ICP-OES is the higher temperature of the plasma (9300-10300 K) in comparison to the flame in atomic absorption spectroscopy (2000-2800 K) [80], which can easily decompose any refractory, i.e., high melting point (> 1700 K), metal oxides that form during the atomization stage. Accordingly, metals such as tin and zirconium that can form refractory compounds are analyzed with ICP-based methods [40,81]. Furthermore, the drawback of lower sensitivity can be circumvented by coupling with a mass spectrometer (MS), where the ions from the plasma are separated according to their mass-to-charge ratio. While the ICP detection limit for tin is around 1 ppm, ICP-MS has been used to quantify concentrations in the ppt range [40].

Although the solubility behaviour of a system at well-controlled conditions can be used in conjunction with a predicted hydrolysis or complexation scheme to confirm or disprove the presence of certain species, the validity of the model and its assumptions are often uncertain. Thus, a direct method to distinguish the identities of aqueous species is preferable. However, the main objective of the above spectroscopic techniques is determination of the total metal content, not separation of the different forms of a metal, whether redox states or hydrolysis complexes.

Raman spectroscopy, a technique based on the excitation of molecules to a higher electronic level via a monochromatic laser light source and subsequent relaxation to produce a vibrationally excited species, which produces a signature spectrum upon scattering light [80], has been used extensively to identify aqueous metallic hydrolysis species such as Al(OH)<sub>4</sub><sup>-</sup>, VO<sub>3</sub><sup>4-</sup>, and Si(OH)<sub>6</sub><sup>2-</sup> [82], and study the hydration of metal cations (e.g., Zn, Cd, Mg, Al) prior to hydrolysis [83-86]. Unlike AA and ICP-OES, Raman spectroscopy is not performed at a fixed wavelength, but is rather a measurement of an entire spectrum over a range of wavelengths. Both qualitative and quantitative information is extracted by comparing factors such as peak position and ratio of intensities of the analyte to a reference spectrum. Furthermore, the development of high temperature cells for Raman spectroscopy has allowed for *in-situ* determination of speciation at the desired temperature. For instance, Raman speciation studies have been performed on gold-chloride complexes, and zinc hydrolysis and speciation in sulfuric acid up to 573.15 K [87,88]. However, a limitation of this approach is the detection limit due to the low solubilities of most metal oxides at near-neutral pH conditions and thus low concentrations of some hydrolysis complexes. Overall, accurate measurement of metal content in solution is necessary for solubility work, with ion speciation often necessary to support or reformulate existing hydrolysis equilibrium models.

#### **3** ZINC AND TIN SYSTEM EQUILIBRIUM MODELS

# 3.1 Thermodynamic Equilibrium Constant

Conditions of phase equilibria can be used to extract thermochemical data of the reactants and products involved. In the case of solid-aqueous equilibria, which are the focus of the present work, solubility measurements at super-ambient conditions provide the means of determining the temperature dependence of Gibbs energies of dissolution and hydrolysis reactions and by inference, the  $G_T^o$  values of select aqueous species.

### 3.1.1 Ionic Strength Correction

In addition to dependence on variables such as temperature, the position of most aqueous equilibria is also influenced by the presence of ionic species in solution. The effect of added electrolytes is generally not governed by the chemical identities of the ions, assuming they are not common with those in the equilibrium reaction, but depends only on their concentrations and charges, known as the ionic strength [89]. The expression for ionic strength, I, is:

$$I = \frac{1}{2} \sum z_i^2 [C_i], \qquad 3.1$$

where z represents the charge of the ions and [C] represents the concentration of species i in mol·L<sup>-1</sup> with respect to a standard state of  $C^{\circ} = 1 \text{ mol} \cdot L^{-1}$  (i. e.,  $[C_i] = \frac{C_i}{C^{\circ}}$ ). As described in section 1.3.1, the activity,  $\alpha$ , is used to account for the Coulombic effects of electrolyte species. Thus, similar to the format of equation 1.6, the relationship between the activity,  $\alpha_i$ , and the dimensionless concentration,  $[C_i]$  can be written as:

$$\alpha_{i} = \gamma_{i}[C_{i}], \qquad 3.2$$

where  $\gamma_x$  represents the dimensionless activity coefficient, which is dependent on the ionic strength. At very dilute electrolyte concentrations, solutions are assumed to be 44

ideal such that activity coefficients equal unity as ionic strength approaches zero and concentrations can be approximated to equal the activities ( $\alpha_i \rightarrow [C_i]$  and  $\gamma_i \rightarrow 1$ , as  $I \rightarrow 0$ ). Using the dissolution reaction of a solid compound,  $X_m Y_{n(s)} \leftrightarrow m X_{(aq)} + n Y_{(aq)}$ , as an example, the equilibrium constant based on analytically measured concentrations of the products is  $K_{cond} = C_X^m C_Y^n$ . In real, non-ideal electrolyte solutions, this constant is referred to as conditional since it will vary according to the ionic strength effect on the magnitude of the solubility of  $X_m Y_n$ . The thermodynamic equilibrium constant, expressed in terms of activities, is independent of the ionic strength and can be related to  $K_{cond}$  via activity coefficients as follows:

$$K^{o} = \alpha_{X}^{m} \alpha_{Y}^{n} = [C_{X}^{m}] \gamma_{X}^{m} [C_{Y}^{n}] \gamma_{Y}^{n} = K_{cond} \gamma_{X}^{m} \gamma_{Y}^{n}$$
3.3

If  $K_{cond}$  is determined from concentration measurements in very dilute electrolyte solutions, it will approach the true, thermodynamic constant, i.e.,  $K_{cond} \rightarrow K^o$  as  $I \rightarrow 0$ . Thus,  $K^o$  is often termed the zero ionic strength or infinite dilution equilibrium constant. However, as instrumental detection limits and pH control make work in very dilute solutions difficult, solubility studies, including the current work, are often performed in high ionic strength mediums. In order to compare experimental equilibrium constants determined in solutions of various electrolyte concentrations to literature values, correction to the thermodynamic value is necessary. One approach is using the linear relationship between  $K_{cond}$  and ionic strength to extrapolate a curve of measured constants at various ionic strengths to I=0. Alternately, in this project, calculated activity coefficients are used to correct the  $K_{cond}$  at a known ionic strength to  $K^o$  via equation 3.3.

Experimentally, only the average effects of all ions in the solution can be determined, whereas single ion coefficients can be estimated based on theoretical or semi-empirical equations. Models such as the Debye-Huckel, extended Debye-Huckel, and Davies equations, which have provided good approximations of activity for ionic strengths up to 0.01 mol·L<sup>-1</sup>, 0.1 mol·L<sup>-1</sup>, and 0.5 mol·L<sup>-1</sup>, respectively, depend only on the ionic charge and strength of the medium [89]. More sophisticated expressions take into account the individual characteristics of the electrolyte solution, and can be used for higher electrolyte concentrations [90]. However, this requires knowledge of the interaction coefficients between the metal ion and the solution electrolyte species of interest. In the present work, as the ionic strengths of most of the analyte solutions range from 0.05 to 0.2 mol·L<sup>-1</sup>, the Davies equation was used, where the activity coefficient of an ion, i, of charge z is:

$$\log_{10} \gamma_{i} = -Az_{i}^{2} \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - bI \right), \qquad 3.4$$

where, A represents the Debye-Huckel constant and b represents a fitting parameter often taken to be 0.2 or 0.3. While the linear bI term has no theoretical justification, it has shown to improve activity coefficient results at higher ionic strengths [90]. The values of the A term are listed as a function of temperature in Table A1 (Appendix A).

#### 3.1.2 Metal Ion Hydrolysis

As can be seen on an E-pH diagram (e.g., Figure 1.3), the stability region of a metal oxide has both an acidic and alkaline limit. For a redox-independent oxide dissolution reaction, the pH range of the solubility minimum is ruled by the hydrolysis equilibria of the aqueous metal ion [4]. Deviation from the pH boundaries of the oxide stability window results in higher solubility. In solution, water molecules are coordinated to metal cations via the oxygen atoms, resulting in a hydrated aqua complex,

 $[M(H_2O)_n]^{m^+}$ . The metal-oxygen, ion-dipole interactions strengthen with increasing cation charge and decreasing ionic radius [47]. Strong M-O attractions draw electron density from the O-H bonds of the H<sub>2</sub>O ligands, consequently weakening them. The hydrated cation behaves as a Lewis acid, where the hydrolysis or splitting of a water molecule releases a proton [47]. A new metal species is also formed in the process:

$$[M(H_2O)_n]^{m+} \leftrightarrow [MOH(H_2O)_{n-1}]^{m-1} + H^+$$
3.5

This can continue through several stages with each successive reaction replacing a water of hydration with a hydroxide group. The extent of hydrolysis is dependent on pH, with proton dissociation more favourable in alkaline conditions.

# **3.2 Zinc System Equilibrium Model**

The hydrolytic reactions of the  $Zn^{2+}$  cation in aqueous solutions of increasing pH are shown below. For simplicity, all metal ions are written excluding the aquo ligands:

$$\operatorname{Zn}_{(\operatorname{aq})}^{2+} + \operatorname{H}_2O_{(1)} \leftrightarrow \operatorname{ZnOH}_{(\operatorname{aq})}^{+} + \operatorname{H}_{(\operatorname{aq})}^{+} 3.6$$

$$\operatorname{Zn}_{(aq)}^{2+} + 2\operatorname{H}_2\operatorname{O}_{(1)} \leftrightarrow \operatorname{Zn}(\operatorname{OH})_{2(aq)}^0 + 2\operatorname{H}_{(aq)}^+$$
 3.7

$$Zn^{2+}_{(aq)} + 3H_2O_{(l)} \leftrightarrow Zn(OH)^-_{3(aq)} + 3H^+_{(aq)}$$
 3.8

In a given solubility experiment, the total concentration of zinc in equilibrium with ZnO at any particular pH is the sum of all products of the hydrolysis reactions in equations 3.6- 3.8:

$$\sum Zn = [Zn^{2+}] + [ZnOH^+] + [Zn(OH)_2^0] + [Zn(OH)_3^-]$$
 3.9

Although the complexes shown above are present in solution, some can be considered negligible in certain limiting conditions [4]. The pH stability ranges of the hydrolysis complexes of a particular metal at a known temperature can be determined from the thermodynamic data of the various species. The identity of the metal ion in equilibrium with the solid oxide dictates the extent of solubility and the amphoteric behaviour seen on Pourbaix diagrams. The distributions of the  $Zn^{2+}$  hydrolytic products in equilibrium with solid ZnO as a function of pH at 298.15 K and 358.15 K are presented in Figure 3.1. The plots are calculated from the available thermochemical properties of the Zn system, summarized in Table 2.1. As the species  $Zn(OH)_2^0$  is not included in Table 2.1, data were obtained separately [35,37]. To simplify and isolate the species involved in a solubility reaction, experiments can generally be restricted to specific pH conditions according to hydrolysis distribution plots.



**Figure 3.1** Distribution of zinc hydrolysis species as a function of pH at 298.15 K and 358.15 K.

In order to account for the stepwise hydrolysis of the metal cation, a model for the dissolution of an oxide that consists of a series of solubility equilibria is necessary. At progressively higher pH, the solubility of zinc oxide is controlled by the reactions:

$$\operatorname{ZnO}_{(s)} + 2\operatorname{H}^{+}_{(aq)} \leftrightarrow \operatorname{Zn}^{2+}_{(aq)} + \operatorname{H}_2O_{(l)}$$
 3.10

$$\operatorname{ZnO}_{(s)} + \operatorname{H}^{+}_{(aq)} \leftrightarrow \operatorname{ZnOH}^{+}_{(aq)}$$
 3.11

$$ZnO_{(s)} + H_2O_{(l)} \leftrightarrow Zn(OH)^0_{2 (aq)}$$
 3.12

$$\operatorname{ZnO}_{(s)} + 2\operatorname{H}_2\operatorname{O}_{(l)} \leftrightarrow \operatorname{Zn}(\operatorname{OH})^-_{3(aq)} + \operatorname{H}^+_{(aq)}$$
 3.13

The conditional equilibrium constants for reactions 3.10-3.13 are given below, remembering that the concentration of  $ZnO_{(s)}$  and  $H_2O_{(1)}$  are taken as 1:

$$K_{sp \ cond} = [Zn^{2+}]/[H^{+}]^{2}$$
 3.14

$$K_{1 \text{ cond}} = [ZnOH^+]/[H^+]$$
 3.15

$$K_{2 \text{ cond}} = [Zn(OH)_{2}^{0}]$$
 3.16

$$K_{3 \text{ cond}} = [Zn(OH)_{3}^{-}][H^{+}],$$
 3.17

where square brackets represent concentrations (mol·L<sup>-1</sup>). As previously discussed, constants based on measured concentrations are subject to the influence of ionic strength on the solubility equilibria and must be corrected to I=0 via activity coefficients. The thermodynamic equilibrium constants for the above reactions, written in terms of activities,  $\alpha$ , are presented in equations 3.18-3.21. The activities of water and solid zinc oxide are assumed to be one at the temperatures studied and have been excluded.

$$K_{sp}^{o} = [Zn^{2+}]\gamma_{Zn^{2+}}/\alpha_{H^{+}}^{2}$$
 3.18

$$K_1^o = [ZnOH^+]\gamma_{ZnOH^+}/\alpha_{H^+}$$
 3.19

$$K_2^{o} = [Zn(OH)_2^{o}]\gamma_{(ZnOH)_2^{o}}$$
 3.20

$$K_3^{o} = [Zn(OH)_3^-]\gamma_{Zn(OH)_3^-} \alpha_{H^+}$$
 3.21

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## Interpreting a Hydrolysis Distribution Plot

Using the distribution plot in Figure 3.1, in order to investigate only the ZnO/Zn<sup>2+</sup> equilibrium in equation 3.10 at 358.15 K (blue line), the pH region where Zn<sup>2+</sup> is dominant, meaning ~100%, is needed (i.e., pH $\leq$ 6). As can be seen from the appearance of the ZnOH<sup>+</sup> field (6<pH<9), at more alkaline conditions than pH 6, the ZnO/ZnOH<sup>+</sup> reaction in equation 3.11 begins to contribute to the existent solubility equilibria. Furthermore, the lower ~  $\leq$ 50% dominance of this species over its stability range relative to the high, near 100% fields of Zn<sup>2+</sup> and Zn(OH)<sup>-</sup><sub>3</sub>, makes isolating solely the ZnO/ZnOH<sup>+</sup> equilibrium difficult. Thus, hydrolysis complexes with large stability pH ranges, over which only one species is present at ~100%, are preferred for isolating solubility reactions. In the present work, the experimental pH domains are chosen accordingly.

# 3.3 Tin(II) System Equilibrium Model

The  $Sn^{2+}$  cation undergoes hydrolysis with increasing pH, such that the total tin concentration in equilibrium with tin(II) oxide at any given acidity can be expressed as:

$$\sum Sn = [Sn^{2+}] + [SnOH^+] + [Sn(OH)_2^0] + [Sn(OH)_3^-]$$
 3.22

The predicted complex distribution for the  $\text{Sn}^{2+}$  hydrolytic products in equilibrium with solid SnO as a function of pH at 298.15 K and 358.15 K, based on the available thermodynamic data [15], is shown in Figure 3.2. The issue of limited reported data for the  $\text{Sn}(\text{OH})_2^0$  complex was circumvented by following the technique recommended by Shock *et al.* [37] to estimate the thermochemical properties. Due to the pH-independence of the  $\text{SnO}/\text{Sn}(\text{OH})_2^0$  equilibrium (equation 3.25),  $\text{Sn}(\text{OH})_2^0$  was not used in the construction of the Sn Pourbaix diagram and was not included in Table 2.2.



**Figure 3.2** Distribution of tin(II) hydrolysis species as a function of pH at 298.15 K and 358.15 K.

The equilibrium model for the solubility of SnO in conditions of increasing pH consists of the following reactions:

$$\operatorname{SnO}_{(s)} + 2\operatorname{H}_{(aq)}^{+} \leftrightarrow \operatorname{Sn}_{(aq)}^{2+} + \operatorname{H}_{2}\operatorname{O}_{(l)}$$
 3.23

$$\operatorname{SnO}_{(s)} + \operatorname{H}^{+}_{(aq)} \leftrightarrow \operatorname{SnOH}^{+}_{(aq)}$$
 3.24

$$\operatorname{SnO}_{(s)} + \operatorname{H}_2\operatorname{O}_{(l)} \leftrightarrow \operatorname{Sn}(\operatorname{OH})^0_{2 (aq)}$$
 3.25

$$\operatorname{SnO}_{(s)} + 2\operatorname{H}_2\operatorname{O}_{(l)} \leftrightarrow \operatorname{Sn}(\operatorname{OH})^-_{3(aq)} + \operatorname{H}^+_{(aq)} \qquad 3.26$$

and their respective thermodynamic equilibrium constants at I=0:

$$K_{sp}^{o} = [Sn^{2+}]\gamma_{Sn^{2+}}/\alpha_{H^{+}}^{2}$$
 3.27

$$K_1^o = [SnOH^+]\gamma_{SnOH^+} / \alpha_{H^+}$$
 3.28

$$K_2^{o} = [Sn(OH)_2^{o}]\gamma_{(SnOH)_2^{o}}$$
 3.29

$$K_3^0 = [Sn(OH)_3^-]\gamma_{Sn(OH)_3^-} \alpha_{H^+}$$
3.30

51

2 20

\_

### 3.4 Tin(IV) System Equilibrium Model

The total tin concentration in equilibrium with tin(IV) oxide at any given acidity can be defined as a sum of the species described in section 2.2:

$$\sum \text{Sn} = [\text{Sn}^{4+}] + [\text{SnOH}^{3+}] + [\text{Sn(OH)}_4^0] + [\text{Sn(OH)}_5^-] + [\text{SnO}_3^{2-}]$$
 3.31

The general model for metal cations in aqueous solutions dictates that every step of hydrolysis adds a hydroxide ion to the metal cation. However, due to the tendency of high charge ( $\geq$  +IV) metal cations to form oxyanions [47], the final hydrolysis complex is taken to be SnO<sub>3</sub><sup>2-</sup> as proposed by Pourbaix [14], instead of Sn(OH)<sub>6</sub><sup>2-</sup>. The distribution for the Sn<sup>4+</sup> hydrolytic products in equilibrium with solid SnO<sub>2</sub> as a function of pH at 298.15 K is presented in Figure 3.3 based on the constants reported by Rai *et al.* [40]. However, due to the lack of solubility and hydrolysis data at T > 298.15 K, the thermochemical properties for the proposed primary and secondary hydrolysis complexes are unknown at elevated temperatures. A speciation plot at 358.15 K such as the ones produced for Zn<sup>2+</sup> and Sn<sup>2+</sup> cannot be constructed without heavy estimation, and, therefore, is not shown.



Figure 3.3 Distribution of tin(IV) hydrolysis species as a function of pH at 298.15 K.

The solubility scheme for tin(IV) oxide consists of equilibria with the +IV hydrolysis products according to increasing pH:

$$\operatorname{SnO}_{2(s)} + 4\operatorname{H}_{(aq)}^{+} \leftrightarrow \operatorname{Sn}_{(aq)}^{4+} + 2\operatorname{H}_{2}\operatorname{O}_{(l)}$$
 3.32

$$\mathrm{SnO}_{2(s)} + 3\mathrm{H}^{+}_{(\mathrm{aq})} \leftrightarrow \mathrm{SnOH}^{3+}_{(\mathrm{aq})} + \mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$$
 3.33

$$\text{SnO}_{2(s)} + 3\text{H}_2\text{O}_{(l)} \leftrightarrow \text{Sn(OH)}_{5(aq)}^- + \text{H}^+_{(aq)}$$
 3.35

$$\text{SnO}_{2(s)} + \text{H}_2\text{O}_{(l)} \leftrightarrow \text{SnO}_{3(aq)}^{2-} + 2\text{H}_{(aq),}^+$$
 3.36

where the corresponding thermodynamic equilibrium constants at zero ionic strength are:

$$K_{sp}^{o} = [Sn^{4+}]\gamma_{Sn^{4+}}/\alpha_{H^{+}}^{4}$$
 3.37

$$K_1^{o} = [SnOH^{3+}]\gamma_{SnOH^{3+}} / \alpha_{H^+}^3$$
 3.38

$$K_2^{o} = [Sn(OH)_4^{o}]\gamma_{(SnOH)_4^{o}}$$
3.39

$$K_3^0 = [Sn(OH)_5^-]\gamma_{(SnOH)_5^-} \alpha_{H^+}$$
 3.40

$$K_4^{o} = [SnO_3^{2-}]\gamma_{SnO_3^{2-}} \alpha_{H^+}^2$$
 3.41

53

#### **4 EXPERIMENTAL METHODS AND MATERIALS**

#### 4.1 Chemicals

Zinc oxide ( $\geq$  98.5), tin(II) oxide ( $\geq$  99%), and tin(IV) oxide (99.9%) powders were purchased from Sigma Aldrich and used without further purification. The chemical impurities, where available, are listed in Table A2 in Appendix A. Experimental solutions were prepared using the ACS grade reagents: 50 % w/w sodium hydroxide, hydrochloric acid, trifluoromethanesulfonic (triflic) acid, and glacial acetic acid from Fischer Scientific. Deionized distilled water was used in all solution preparations. Ultra high purity grade nitrogen gas (99.998%) was obtained from Praxair.

## 4.2 Apparatus

All experiments at super-ambient conditions were conducted in the batch, boltedclosure type reaction cell shown in Figures 4.1(a) and 4.1(c). The main body of the vessel is a 25.4 cm (ten inch) long section of schedule 40 stainless steel pipe with an internal diameter of 10.2 cm (four inches) and a maximum volume capacity of two liters. A small headpace (~200 mL, or ~10% of the available volume) was maintained by using a working volume of approximately 1.8 liters. The inside of the reactor vessel is lined with Teflon, insuring that there is no contact between the steel pipe wall and the solution. This also prevents the degradation of the vessel and subsequent cross-contamination of the samples. The cell design is symmetrical, such that both ends of the pipe are sealed with 316 stainless steel, Teflon-lined blind flanges via bolts to create a closed system. The top blind flange acts as a housing for the pH and redox electrodes and the pressure gauge as shown in Figure 4.1. All three elements are inserted into the vessel with 19 mm (¼ inch) NPT stainless steel Swagelok fittings.



Figure 4.1(a) 1. Teflon-lined vessel; 2 & 3. 316 SS blind flanges; 4. band heater; 5. K-type thermocouple; 6, & 7. elevated temperature pH and ORP electrodes; 8. Pressure gauge; (b) photo of pH electrode; (c) photo of vessel and control panel.

The vapour pressure versus temperature curve for light water is shown in Figure 4.2. Based on this diagram, the saturation pressure inside the closed system of the reaction cell will not greatly exceed 1 atm for the solution to remain in the liquid state even at the maximum experimental temperature of 378.15 K used in the present work.



Figure 4.2 Vapor pressure of light water as a function of temperature [91].

An external 900 watt band heater from O.E.M. Heaters surrounded the vessel body and ensured even heat distribution. A K-type (Chromel-Alumel) thermocouple from Omega Engineering measured the outer cell temperature. Both the thermocouple and heater were connected to a proportional-integral-derivative (PID) temperature controller from Love Controls. Based on the signal measured from the thermocouple, the heater was programmed to periodically turn on and off to maintain the vessel temperature at the user-defined set-point for the desired length of time. The internal solution 56 temperature was measured via a resistance temperature detector, RTD ( $\pm$  0.5 K), housed inside the pH electrode. A ceramic fiber Kaowool<sup>\*</sup> blanket (2.5 cm thick) insulated the outside of the vessel, minimized heat loss, decreased the time required to reach the set-point, and aided in keeping a stable temperature over the duration of an experiment.

The pH was measured *in-situ* with an insertion, T-handle, elevated temperature pH electrode from Omega Engineering ( $\pm 0.01$  pH unit) shown in Figure 3.1(b). The probe was designed for continuous exposure to temperatures from 268.15 to 408.15 K and pressures up to 3.4 MPa (33.6 atm). The glass membrane indicator electrode and a double junction (KCl/AgCl, KNO<sub>3</sub>) silver/silver-chloride reference probe were combined inside a polymer (thermoplastic) housing. A resistance temperature detector (Pt, 1000 ohm), also contained inside the glass electrode body, measured solution temperature and allowed for automatic temperature compensation to changes in electrode sensitivity due to the elevated conditions. The pH probe was calibrated against dilute NIST standard buffers (pH 4, 7, and 10) before each experiment. An Omega Engineering meter was used to monitor both the *in-situ* solution pH and temperature. At highly alkaline conditions, a deviation between the measured and actual pH can occur due to the presence of Na<sup>+</sup> at the cation sites of the glass membrane, where sodium ions are counted as protons and a falsely low pH is reported. The effect is more prominent with increasing time and higher temperatures. However, electrodes that are rated to be full range (0-14) by the manufacturer, such as the probe from Omega Engineering, use a glass membrane with smaller lithium ions, which enables the presence of  $Li^+$  and  $H^+$  but reduces response to Na<sup>+</sup> thus, lowering alkaline error in sodium-containing solutions [89].

<sup>&</sup>lt;sup>\*</sup> Kaowool blanket (melting point of 1760 °C) is produced from kaolinite, a naturally-occurring aluminasilica clay mineral, and trace amounts of titanium and ferric oxides.

An oxidation-reduction potential (ORP) elevated temperature electrode from Omega Engineering ( $\pm$  0.01 mV), was used to determine the redox potential of the system. The ORP was measured at an inert platinum indicator electrode versus a silver/silver-chloride (Ag/AgCl) reference probe, both in the same housing. An inert working electrode acts as a source or sink for electrons and is effective in determining the ratio of oxidized to reduced species for fast redox processes via the Nernst equation [89]. Thus, the state of oxidation or reduction of species in a system with multiple redox states (e.g., Sn<sup>2+</sup> and Sn<sup>4+</sup>) was determined from the redox potential of the solution. All potential measurements, made against the silver/silver chloride reference electrode were converted to the standard hydrogen electrode scale, where the potential versus the SHE = potential versus the Ag/AgCl + 0.222 V [80].

## 4.3 Typical Experimental Run and Analysis

## 4.3.1 General Solution Preparation

Solubility experiments were conducted over a wide range of pH values (0 to 14). Highly (0-2) and moderately (2.5-3.5) acidic environments were established via triflic, CF<sub>3</sub>SO<sub>3</sub>H, and acetic, CH<sub>3</sub>COOH, acids, respectively. Both triflic and acetic acid have been shown to not form complexes with dissolved metal species in dissolution studies [4,35]. For comparison, hydrochloric acid, which is reported to easily complex with most metals [4], was used to reach pH 0-3.5 in separate experiments. Intermediate pH ranges (4 to 6) were achieved with acetate buffer and pure deionized water, while moderately (8-9.5) and highly alkaline conditions ( $\geq$  10) were established using acetate and sodium hydroxide bases, accordingly. Table 4.1 summarizes these controlling agents.

Species	Formula	pН	Description
Triflic acid	CF <sub>3</sub> SO <sub>3</sub> H	0-2	Strong organic acid, non- complexing
Hydrochloric acid	HC1	0-3.5	Strong acid, complexing
Acetic acid	CH <sub>3</sub> COOH	2.5-3.5	Weak acid, non-complexing
Acetate buffer	CH <sub>3</sub> COOH/ CH <sub>3</sub> COONa	4-6	Buffer, non-complexing
Sodium acetate	CH <sub>3</sub> COONa	8-9.5	Weak base, non-complexing
Sodium hydroxide	NaOH	≥10	Strong base, non-complexing

Table 4.1 Summary of Acids and Bases Used to Establish Solution pH

The pH ranges required to anchor the hydrolysis scheme for each metal ion to a single, prevalent species were chosen based on the stability domains of the various complexes as shown in Figures 3.1, 3.2, and 3.3. Furthermore, as both tin and zinc oxide solubilities are quite low at near-neutral pH, most of the experiments were conducted in the lower acidic or upper basic ranges to ensure that the measured metal concentrations were above instrumental detection limits, unless confirmation of the solubility minimum was required.

For each run, approximately five grams of metal oxide sample were added to the reaction vessel at the desired pH and temperature. While the mass of the oxide used was noted, it had no effect on the chemistry of the system as long as it was present in excess of the amount that would dissolve at equilibrium. Adjustments were not made to the pH during the experiments. Furthermore, all experiments were performed under aerated conditions unless otherwise stated. Where indicated, several runs were purged with  $N_{2(g)}$  to control the redox potential of the system.

## 4.3.2 Zinc Oxide Reaction Conditions

Table 4.2 summarizes the reaction conditions for the ZnO solubility experiments. From the 358.15 K distribution plot in Figure 3.1, the lower limit acidic run (sample Zn1) was chosen to isolate the  $Zn^{2+}$  species prior to hydrolysis of the cation. Thus, the solubility of ZnO can be modelled by equation 3.10. The same principle applies to sufficiently alkaline conditions (sample Zn4), where only the terminal hydrolysis species,  $Zn(OH)_3^-$ , is stable and equation 3.13 represents the dissolution reaction. The solubility minimum of ZnO was investigated with the intermediate pH ~ 7 and pH ~ 10.70 runs.

Tuble 1.2 Reaction Conditions for Zine Oxfac Boldonity Experiments					
Run	Reaction	Temperature	Desired	Concentrations of pH	
Number	Time (h)	(K)	рН <sub>358.15 К</sub>	Controlling Agents	
Zn1		358.15	5.00	$5.2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3 \text{COOH}$ $9.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3 \text{COONa}$	
Zn2	8		6.00-7.00	Deionized H <sub>2</sub> O	
Zn3	0		11.00	$1.0 \ge 10^{-3} \mod L^{-1} \operatorname{NaOH}$	
Zn4			12.00	$1.0 \ge 10^{-2} \mod L^{-1} \mod$	

**Table 4.2** Reaction Conditions for Zinc Oxide Solubility Experiments

## 4.3.3 Tin(II) Oxide Reaction Conditions

The pH ranges for solubility runs were chosen to simplify the number of aqueous species in equilibrium with solid SnO according to the predicted stability regions of the hydrolysis complexes in Figure 3.2. The solubility was studied over a period of 28 hours at 358.15 K at the lower acidic (pH  $\sim$ 3) and upper alkaline (pH  $\sim$ 9) limits established by HCl and NaOH, respectively. The relatively large range over which the first hydrolysis product, SnOH<sup>+</sup>, is dominant, allows the equilibrium constant to be evaluated

unambiguously for equation 3.24. The acidic environment was repeated using acetic acid to test for interfering Sn-Cl complexes. An additional acidic run (sample Sn(II)3) was conducted by initially bubbling nitrogen gas through the solution to remove dissolved oxygen and control the redox chemistry of  $\text{Sn}^{2+}$  species. The reaction conditions for all tin(II) oxide solubility experiments are summarized in Table 4.3.

Tuble the Redection Conditions for Tim(ii) Oxide Solidonity Experiments					
Sample Number	Reaction Time (h)	Temperature (K)	Desired pH <sub>358.15 K</sub>	Concentration of pH Controlling Agent	
Sn(II)1			3.00	6.7 x 10 <sup>-2</sup> mol·L <sup>-1</sup> CH <sub>3</sub> COOH	
Sn(II)2			3.00	2.0 x 10 <sup>-3</sup> mol·L <sup>-1</sup> HCl	
Sn(II)3	28	358.15	3.00	$6.7 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3 \text{COOH}$ (N <sub>2</sub> bubbled through solution initially)	
Sn(II)4			9.00	3.8 x 10 <sup>-5</sup> mol·L <sup>-1</sup> NaOH	

Table 4.3 Reaction Conditions for Tin(II) Oxide Solubility Experiments

### 4.3.4 Tin(IV) Oxide Reaction Conditions

As seen from the speciation plot in Figure 3.3, extreme pH conditions (< -1.86) are required to isolate the unhydrolyzed  $\text{Sn}^{4+}$  species at 298.15 K. The stability window of the first hydrolysis complex is less acidic (-1.86 < pH < 0.83) and broad enough to explicitly establish the  $\text{SnO}_2/\text{SnOH}^{3+}$  solubility equilibrium according to equation 3.33. Likewise, the wide pH range over which  $\text{Sn}(\text{OH})_5^-$  is dominant, allows both reactions 3.35 and 3.36 to be investigated unambiguously. The solubility of  $\text{SnO}_2$  was studied over a period of 48 hours at 298.15 K at the low acidic and upper alkaline pH limits established by triflic acid and NaOH, accordingly.

Without sufficient thermochemical data for a distribution plot of the hydrolysis products at T > 298.15 K, the temperature effect on the stability regions was estimated for experiments at 358.15 K and 378.15 K. More acidic pH conditions than those at 298.15 K were selected to account for the general shift to the left of all stability areas at elevated temperatures [15]. The solubility of SnO<sub>2</sub> at 358.15 K was investigated for 48 hours. The low acidic environment was repeated using hydrochloric acid to determine the effect of Sn-Cl complexes on the solubility behaviour. The pH of one of the alkaline runs was established via a combination of acetate and sodium hydroxide to investigate possible interference from Sn-CH<sub>3</sub>COO complexes. Two moderate acidity (pH  $\sim$  3) experiments used either acetic or hydrochloric acid to confirm the solubility minimum. The acidic and alkaline 378.15 K batch runs were established with CF<sub>3</sub>SO<sub>3</sub>H and NaOH, respectively. Table 4.4 outlines the reaction conditions for the SnO<sub>2</sub> experiments.

Run Number	Reaction Time (h)	Temperature (K)	Desired pH <sub>T</sub>	Concentration of pH Controlling Agent
Sn(IV)1			0.50	0.21 mol·L <sup>-1</sup> CF <sub>3</sub> SO <sub>3</sub> H
Sn(IV)2	48	298.15	11.00	1.0 x 10 <sup>-3</sup> mol·L <sup>-1</sup> NaOH
Sn(IV)3			13.00	$0.20 \text{ mol} \cdot \text{L}^{-1} \text{ NaOH}$
Sn(IV)4			0.00 - 0.30	$0.60 \text{ mol} \cdot \text{L}^{-1} \text{ HCl}$
Sn(IV)5			0.00 - 0.30	$0.48 \text{ mol} \cdot \text{L}^{-1} \text{ CF}_3 \text{SO}_3 \text{H}$
Sn(IV)6			3.00	$1.2 \text{ x } 10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{ HCl}$
Sn(IV)7	48	358.15	3.00	6.7 x 10 <sup>-2</sup> mol·L <sup>-1</sup> CH <sub>3</sub> COOH
Sn(IV)8			11.00	$0.37 \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3 \text{COONa}$ 5.0 x 10 <sup>-3</sup> mol · L <sup>-1</sup> NaOH
Sn(IV)9			12.00	$2.9 \text{ x } 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ NaOH}$
Sn(IV)10			12.50	6.3 x 10 <sup>-2</sup> mol·L <sup>-1</sup> NaOH
Sn(IV)11	19	279 15	0.00 - 0.30	0.48 mol·L <sup>-1</sup> CF <sub>3</sub> SO <sub>3</sub> H
Sn(IV)12	4ð	3/8.13	11.00	1.0 x 10 <sup>-3</sup> mol·L <sup>-1</sup> NaOH

Table 4.4 Reaction Conditions for Tin(IV) Oxide Solubility Experiments

# 4.3.5 Equilibration and Sample Preparation

The dissolution reactions were allowed to proceed for several hours or days in order for equilibrium to be attained, evidenced by consistency in the composition of collected samples over time [5]. Zinc oxide runs were maintained for eight hours (Table 4.2) analogous to previous studies, which indicated that ZnO equilibria in various pH conditions are reached relatively quickly (<12 hours) [36]. As the experimental data on the tin system is rather limited, longer reaction times of one to two days were chosen.

At 358.15 K, both zinc and tin oxide solubility studies were conducted inside the reaction vessel, where 50-100 mL grab samples were directly withdrawn at regular intervals. The temperature inside the vessel did not, on average, decrease by more than approximately 0.5 K during sampling. The tin(II) and tin(IV) oxide systems were also examined at two additional temperatures of 298.15 K and 378.15 K to investigate the temperature dependence of the solubility reactions. The former were carried out in glass volumetric flasks on the bench top, while the latter were conducted inside the reaction vessel. The system was undisturbed for the entire length of a 378.15 K run with an aliquot only withdrawn at the end. As the current setup did not permit direct sampling above 373.15 K, the vessel was cooled to 358.15 K to obtain a sample. At the end of the various equilibration periods for studies at all temperatures, the aliquots were filtered with Fisherbrand filters to ensure the solid oxide was separated from solution. The filters were initially treated with solution at the same pH and temperature as the samples to prevent changes in solubility during the filtration. If required (i.e., anticipated analyte concentrations were predicted to exceed the upper detection limit of the instrument), samples were diluted before analysis.

## 4.3.6 Sample Analysis

#### Inductively-Coupled Plasma Emission and Atomic Absorption Spectroscopies

In atomic absorption spectroscopy, an aqueous sample is converted into free atoms by a high temperature (2000-2800 K) flame [80]. A hollow cathode lamp, composed of the metal being analyzed, provides discrete wavelengths of electromagnetic radiation, one of which is isolated by a monochromator. The total energy absorbed by the electrons at this wavelength is proportional to the number of analyte atoms in the flame. Based on the calibration curve generated from standards of known concentrations, the absorption intensity of the sample is used to calculate the concentration of metal ions. Inductively-coupled plasma emission spectroscopy involves the conversion of a carrier gas (commonly argon) to plasma at 9300-10300 K [80], in which the atomized sample undergoes excitation. The number of photons emitted when the excited electrons relax to a lower energy level is used to determine emission spectrum and accordingly, the concentration of analyte based on a calibration curve analogous to AA spectroscopy.

For the zinc oxide solubility, the total metal concentration was determined via inductively-coupled plasma emission spectroscopy, ICP-OES, (Varian Vista-MPX) or flame atomic absorption spectroscopy, FAAS, (Varian AA240FS) depending on the range of expected concentrations. As the atomic absorption spectrometer has a higher sensitivity for zinc (0.1 ppm/~1.5 x 10<sup>-6</sup> mol·L<sup>-1</sup>) in comparison to the ICP-OES ( $\geq 0.5$  ppm/~4.0 x 10<sup>-6</sup> mol·L<sup>-1</sup>) lower detection limit, the former can accurately measure lower Zn concentrations. The upper limit signifies an oversaturation of the instrument when analyte concentrations are too high. For both ICP-OES and AA spectroscopy, this upper limit is approximately 10<sup>-3</sup> mol·L<sup>-1</sup>.

All tin content analyses were performed with ICP-OES. In comparison to the flame of the AAS, the high temperature of the ICP is preferred for studies involving high melting point refractory compounds such as tin oxides. For the samples containing solid SnO (melting point 1323.15 K) or SnO<sub>2</sub> (melting point 1903.15 K) due to precipitation, the higher temperatures of the ICP ensures that there is no difficulty dissociating the oxides into free atoms. This avoids the possibility of measuring falsely high tin concentrations. The lower detection limit of the ICP-OES for tin is approximately
4.5 x  $10^{-6}$  mol·L<sup>-1</sup>. In both techniques, a set of standards of known concentration were prepared for each analysis and a calibration curve was calculated based on the measured absorbances or intensities. A precision of 5%-10% in terms of the relative standard deviation was routinely achieved in replicate analyses of samples and standards for concentrations above 4.5 x  $10^{-6}$  mol·L<sup>-1</sup> for tin via ICP-OES and > 1.5 x  $10^{-6}$  mol·L<sup>-1</sup> for zinc using flame AA spectroscopy. The total metal concentrations from the experimental runs were used to determine equilibrium solubility constants for both zinc and tin oxides according to an equilibrium speciation model unique to each system.

# A Typical Calibration Curve

The relationship between the ICP-OES or AA spectroscopy measured response (dependent variable), and the total metal concentration of a sample (independent variable), is linear in the form  $y = m \cdot x + b$ , where y represents the instrumental response, x represents the concentration, m represents the slope, and b represents the y-intercept. A calibration curve, obtained from the analytical response of a number of standards of known concentrations, was constructed for each analysis. A typical ICP-OES calibration curve, based on the standards used to quantify tin(II) oxide solubility in the alkaline regime for sample Sn(II)4 (Table 4.3), is shown in Figure 4.3. The concentrations of the tin standards were chosen such that the analyte would fall roughly in the middle of the range and are summarized in Table 4.5. The effectiveness of the linear regression fit to the data is indicated on the graph by the R<sup>2</sup>, where a value closer to unity indicates minimal variation from the fit. The resulting linear equation is also shown on the plot. The standard errors in the slope and y-intercept,  $\sigma_m$  and  $\sigma_b$ , respectively, are provided in Table 4.6.

	Sample Sn(II)4	
Standard Number	Concentration (mg·L <sup>-1</sup> )	Measured Intensity $(c \cdot s^{-1})$
1	1.00	6.25903
2	5.00	27.05594
3	10.00	52.10394
4	15.00	83.33964

 
 Table 4.5 Tin ICP-OES Standard Data for Sample Sn(II)4

**Table 4.6** Data for the Calibration Curve in Figure 4.3

	Coefficient	Standard Error
slope (m)	5.5	0.2
y-intercept (b)	-0.1	1.9



Figure 4.3 Typical ICP-OES calibration curve constructed to determine total tin concentration based on four standard solutions.

A sample calculation based on a measured sample intensity of 10.87654 counts per second,  $c \cdot s^{-1}$ , after 28 hours (Table A3, Appendix A) to obtain a concentration of 2.016 mg·L<sup>-1</sup> or 1.698 x 10<sup>-5</sup> mol·L<sup>-1</sup> is shown below:

$$y = 5.4609x - 0.1323$$
$$x = \frac{10.87654 + 0.1323}{5.4609}$$
$$x = 2.016 \text{ mg } \text{L}^{-1} \left(\frac{1\text{g}}{1000 \text{ mg}}\right) \left(\frac{1}{118.69 \text{ g} \cdot \text{mol}^{-1}}\right)$$
$$x = 1.7 \times 10^{-5} \pm 3 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1},$$

where  $118.69 \text{ g} \cdot \text{mol}^{-1}$  is the molar mass of tin used to convert from units of mg·L<sup>-1</sup> to mol·L<sup>-1</sup>. A similar calibration curve and calculation procedure was performed to extract total metal concentration data from all ICP-OES and atomic absorption analyses for tin and zinc content, accordingly. In the cases where it was difficult to anticipate analyte concentration, a larger number of samples were prepared over a wider range of concentrations. An outline of a typical propagation of the uncertainty in the concentration of an analyte through a calibration curve is presented in Appendix B.

# Raman Spectroscopy

In order to obtain a Raman spectrum, the analyte is irradiated with a laser source of monochromatic, visible or near-infrared radiation. As the light passes through the sample, molecules in the ground and excited vibrational states absorb a photon and are excited to an electronic energy level [80]. The emitted energy that is of either a lower or higher frequency from the incident photon, known as inelastic scattering, is used to produce a spectrum of the sample. The analyte can then be identified by comparing the observed Raman peaks to reference spectra. Although solids are commonly characterized via Raman spectroscopy, liquid samples can be analyzed as well.

A RM Renishaw Raman microscope with an argon ion (514 nm) laser was used to collect spectra for the solid zinc, tin(II) and tin(IV) oxides before any solubility experiments were performed. Samples of the oxides were also characterized after solubility runs to confirm that the solid phase had not undergone any changes.

### **5 RESULTS AND CALCULATIONS**

5.1 Zinc Oxide Solubility Results

The zinc concentrations and pH measurements over each eight hour ZnO run at 358.15 K are reported in Table 5.1 according to the sample numbers from Table 4.2 (section 4.3.2). The total Zn content in various pH conditions is plotted versus time in Figure 5.1. The solubilities were determined via atomic absorption spectroscopy with a Zn instrument detection limit of approximately  $1.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ . The Raman spectrum of the solid zinc(II) oxide used in this work, prior to solubility experiments, is presented in Figure C1 in Appendix C, with the assigned peaks and the known shifts of ZnO in listed in Table C1. The thermodynamic equilibrium constants at 358.15 K, extrapolated to I=0 via the Davies equation (equation 3.4), are shown in Table 5.3 for the lower and upper pH limit reactions alongside the constants obtained from literature [34,35,37].

Sample Number	Reaction time (h)	I (mol·L <sup>-1</sup> )	$\frac{pH_{358.15\ K}}{\left(\pm\ 0.01\right)^{*}}$	$[Zn]_{Total} (mol \cdot L^{-1})^*$
	2		5.45	$5.752 \times 10^{-3} \pm 2 \times 10^{-6}$
7 1	4	$0.2 10^{-2}$	5.41	$1.9201 \ge 10^{-2} \pm 2 \ge 10^{-6}$
Zni	6	9.3 X 10	5.43	$6.832 \times 10^{-3} \pm 2 \times 10^{-6}$
	8		5.41	$1.1293 \times 10^{-2} \pm 2 \times 10^{-6}$
	2		6.99	$7 \ge 10^{-6} \pm 1 \ge 10^{-6}$
7)	4	$1.0 \times 10^{-7}$	6.98	$8 \ge 10^{-6} \pm 1 \ge 10^{-6}$
Zn2	6	1.0 X 10	6.94	$7 \ge 10^{-6} \pm 1 \ge 10^{-6}$
	8		6.98	$9 \ge 10^{-6} \pm 1 \ge 10^{-6}$
	2		10.76	$7 \ge 10^{-6} \pm 4 \ge 10^{-6}$
72	4	$1.0 \times 10^{-3}$	10.70	$7 \times 10^{-6} \pm 4 \times 10^{-6}$
Z115	6	1.0 X 10	10.66	$5 \times 10^{-6} \pm 4 \times 10^{-6}$
8	8		10.67	5 x $10^{-6} \pm 4 x 10^{-6}$
	2		11.46	$1.36 \ge 10^{-4} \pm 2 \ge 10^{-6}$
77 4	4	$1.0 \times 10^{-2}$	11.45	$1.35 \times 10^{-4} \pm 2 \times 10^{-6}$
<b>Z</b> 114	6	1.0 X 10	11.39	$1.32 \times 10^{-4} \pm 2 \times 10^{-6}$
	8		11.40	$1.34 \times 10^{-4} \pm 2 \times 10^{-6}$

Table 5.1 Zinc Oxide Solubility Data at 358.15 K

Uncertainty represents one standard deviation  $(1\sigma)$ .



Figure 5.1 The evolution of zinc oxide solubility in varying pH environments over a period of eight hours at 358.15 K.

Reaction	Sample Number	log <sub>10</sub> K <sup>o*</sup>	Source	Medium	
		$8.38 \pm 0.01$	This work	CH <sub>3</sub> COOH/ CH <sub>3</sub> COONa	
$ZnO + 2H^+ \leftrightarrow Zn^{2+} + H_2O$ (equation 3.10)	Zn1	8.31	[37]	CH <sub>3</sub> COOH/ CH <sub>3</sub> COONa	
		8.42	[34]	CF <sub>3</sub> SO <sub>3</sub> H	
		$-15.32 \pm 0.01$	This work	NaOH	
$LnU + 2H_2U \leftrightarrow Ln(UH)_3 + H^{-1}$	Zn4	-15.39	[37]	NaOH	
(040000 5.15)		-15.46	[35]	NaOH	

Table 5.2 Logarithm of Zinc Oxide Solubility Constants at 358.15 K

<sup>\*</sup> Uncertainty represents one standard deviation  $(1\sigma)$ .

### 5.2 Tin (II) Oxide Solubility Results

The final tin concentration, pH, and redox potential data for each 28 hour 358.15 K run (Table 4.2), are presented in Table 5.3. The solubility results from all tin(II) oxide experiments are plotted as a function of time in Figure 5.2. Tin content was determined via ICP-OES with a detection limit of 4.0 x  $10^{-6}$  mol·L<sup>-1</sup>, which is indicated by the solid line on the solubility plot. The Raman spectrum of an original tin(II) oxide sample, prior to solubility experiments, is shown in Figure C2 (Appendix C), with the peak assignments summarized in Table C2. Peak assignments are reported in Table 5.4 for the Raman spectra of the SnO samples recovered from an oxygenated (sample Sn(II)2) and N<sub>2(g)</sub> purged (sample Sn(II)3) run, shown in Figure 5.3(a) and 5.3(b), respectively.

Sample	Reaction	$I(mol \cdot I^{-1})$	рН <sub>358.15 К</sub>	Redox Potential	[Sn] <sub>Total</sub>
Number	time (h)		$(\pm 0.01)^*$	$(mV \pm 0.01)^*$	$(\text{mol} \cdot \text{L}^{-1})^*$
	8		3.29	396.8	$1 \ge 10^{-6} \pm 3 \ge 10^{-6}$
$S_{n}(II)1$	18	$1.1 \times 10^{-3}$	3.25	407.0	$1 \ge 10^{-6} \pm 3 \ge 10^{-6}$
511(11)1	24	1.1 X 10	3.23	404.5	$1 \ge 10^{-6} \pm 3 \ge 10^{-6}$
	28		3.23	432.3	$1 \ge 10^{-6} \pm 3 \ge 10^{-6}$
	8		3.09	567.8	$1 \ge 10^{-6} \pm 5 \ge 10^{-6}$
$S_{m}(II)$	18	1.0 x 10 <sup>-3</sup>	3.02	561.4	$1 \ge 10^{-6} \pm 5 \ge 10^{-6}$
511(11)2	24		2.99	562.7	$1 \ge 10^{-6} \pm 5 \ge 10^{-6}$
	28		2.99	544.8	$1 \ge 10^{-6} \pm 5 \ge 10^{-6}$
	8		2.92	274.4	$1 \ge 10^{-6} \pm 8 \ge 10^{-6}$
$G_{m}(\mathbf{H})$	18	1.1 x 10 <sup>-3</sup>	2.89	272.2	$1 \ge 10^{-6} \pm 8 \ge 10^{-6}$
Sn(11)3	24		2.95	241.2	$1 \ge 10^{-6} \pm 8 \ge 10^{-6}$
	28		2.94	244.8	$1 \ge 10^{-6} \pm 8 \ge 10^{-6}$
	8		8.82	141.2	$1.8 \times 10^{-5} \pm 3 \times 10^{-6}$
$\mathbf{S}_{m}(\mathbf{H})\mathbf{A}$	18	$1.0 \times 10^{-2}$	8.87	135.8	$2.1 \times 10^{-5} \pm 3 \times 10^{-6}$
Sn(11)4	24	1.0 X 10	9.01	143.6	$1.8 \ge 10^{-5} \pm 3 \ge 10^{-6}$
	28		8.98	128.3	$1.7 \ge 10^{-5} \pm 3 \ge 10^{-6}$

Table 5.3 Tin(II) Oxide Solubility Data at 358.15 K

<sup>\*</sup> Uncertainty represents one standard deviation  $(1\sigma)$ .



Figure 5.2 Tin(II) oxide solubility in varying pH environments over a period of 28 hours at 358.15 K determined by ICP-OES.

Sample Number	Raman Shift (cm <sup>-1</sup> )	Peak Assignment	Reference
	116	SnO	[92]
	134	*SnO <sub>x</sub>	[92]
	162	SnO <sub>x</sub>	[92]
Oxygenated (a) Sn(II)1	203	SnO	[92]
	473	$SnO_2$	[93]
	619	$SnO_2$	[93]
	682	$SnO_2$	[94]
N <sub>2</sub> Purged (b)	110	SnO	[92]
Sn(II)3	205	SnO	[92]

Table 5.4 Raman Shift Assignments for SnO After Solubility Runs

\* For SnO, 1<x<2.



Figure 5.3 Raman spectra of tin(II) oxide samples recovered after 358.15 K solubility experiments for (a) sample Sn(II)1, (b) Sn(II)3.

The experimental equilibrium constants at 358.15 K for the first and terminal hydrolysis complex solubility reactions, as modelled by equations 3.24 and 3.26, respectively, are shown in Table 5.5. The thermodynamic data presented in Table 2.2 were used to calculate the predicted constants, shown alongside values from this work.

Reaction	Sample Number	log <sub>10</sub> K <sup>o*</sup>	Source	Medium
$SnO + H^+ \leftrightarrow SnOH^+$ (equation 3.24)	Sn(II)1	-3 ±2	This work	HC1
	Sn(II)2	-3 ±2	This work	CH <sub>3</sub> COOH
	Sn(II)3	-3 ±3	This work	CH <sub>3</sub> COOH + N <sub>2</sub>
		-0.32	[15]	
$\text{SnO} + 2\text{H}_2\text{O} \leftrightarrow \text{Sn(OH)}_3^- + \text{H}^+$	Sn(II)/	$-13.75 \pm 0.08$	This work	NaOH
(equation 3.26)	511(11)4	-13.08	[15]	

Table 5.5 Logarithm of Tin(II) Oxide Solubility Constants at 358.15 K

<sup>\*</sup> Uncertainty represents one standard deviation  $(1\sigma)$ .

# 5.3 Tin (IV) Oxide Solubility Results

Tin(IV) oxide solubilities at 298.15 K and various pH are reported in Table 5.6 and plotted in Figure 5.4 over the 48 hour reaction time. The Raman spectrum of a sample of SnO<sub>2</sub> before solubility runs is reported in Figure C3. The shifts from the spectrum are summarized alongside the known values for SnO<sub>2</sub> from the literature in Table C3. The experimental, thermodynamic equilibrium constants (I=0) at 298.15 K are reported in Table 5.7 for the first, tertiary, and terminal hydrolysis complex solubility reactions, modelled by equations 3.33, 3.35, and 3.36, respectively. For comparison, the constants determined by Rai and workers [40] and those calculated from the thermochemical data in Table 2.2 are also presented.

Sample Number	Reaction time (h)	$\frac{I}{(\text{mol} \cdot I^{-1})}$	$pH_{298.15 \text{ K}}$ (+ 0.01)*	$[Sn]_{Total}$				
Tunioei	time (ii)		(± 0.01)					
	8		0.48	$1 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
Sn(W)1	18	0.21	0.52	$1 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
511(1 v )1	22	0.21	0.52	$1 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
	48		0.54	$1 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
	8		10.80	$7 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
Sn(W)2	18	$1.0 \times 10^{-3}$	10.74	$7 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
511(1 V )2	22	1.0 X 10	10.74	$8 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
	48		10.74	$6 \ge 10^{-6} \pm 7 \ge 10^{-6}$				
	8		13.14	$4.5 \ge 10^{-5} \pm 3 \ge 10^{-6}$				
Sn(IV)3	18	0.20	13.17	$7.2 \times 10^{-5} \pm 3 \times 10^{-6}$				
	22	0.20	13.13	$8.6 \ge 10^{-5} \pm 3 \ge 10^{-6}$				
	48		13.14	$8.8 \times 10^{-5} \pm 3 \times 10^{-6}$				

Table 5.6 Tin(IV) Oxide Solubility Data at 298.15 K

<sup>\*</sup> Uncertainty represents one standard deviation  $(1\sigma)$ .



**Figure 5.4** Tin(IV) oxide solubility in acidic and alkaline pH ranges over a period of 48 hours at 298.15 K determined by ICP-OES.

Reaction	Sample Number	log <sub>10</sub> K <sup>o*</sup>	Source	Medium
$\text{SnO}_2 + 3\text{H}^+ \leftrightarrow \text{SnOH}^{3+} + \text{H}_2\text{O}$	$\mathbf{S}_{m}(\mathbf{W})$	$-6 \pm 2$	This work	CF <sub>3</sub> SO <sub>3</sub> H
(equation 3.33)	Sn(IV)I	-6.52	[40]	
$\text{SnO}_2 + 3\text{H}_2\text{O} \leftrightarrow \text{Sn(OH)}_5^- + \text{H}^+$	Sn(IV)2	$-16.0\pm0.5$	This work	NaOH
(equation 3.35)		-17.58	[40]	
		$-30.88\pm0.02$	This work	NaOH
$SnO_2 + H_2O \leftrightarrow SnO_3^{2-} + 2H^+$ (equation 3.36)	Sn(IV)3	-28.66	[40]	
		-30.27	[15]	

Table 5.7 Logarithm of Tin(IV) Oxide Solubility Constants at 298.15 K

Uncertainty represents one standard deviation  $(1\sigma)$ .

The measured tin concentrations and pH values from the 358.15 K and 378.15 K SnO<sub>2</sub> experiments are shown in Table 5.8. The 358.15 K solubility data from the acidic and alkaline pH regions are presented in Figures 5.6 and 5.7, respectively, versus time for 48 hours. The measured tin content of the batch experiments performed at 378.15 K (Table 4.3) is reported in Table 5.8, where only single samples withdrawn at the end of the 48 hour equilibration times. The Raman spectrum of a sample of SnO<sub>2</sub> recovered after one of the solubility runs (sample Sn(IV)7) is shown in Figure 5.7, with the assigned peaks summarized in Table 5.9. The 358.15 K and 378.15 K constants from this work are summarized in Tables 5.11 and 5.12, accordingly. As thermodynamic properties are not available for certain tin(IV) species, comparison values could not be calculated for all reactions considered.

Sample Number	Reaction time (h)	$I \pmod{L^{-1}}$	$pH_{358.15 \text{ K}}$ (±0.01)*	Redox Potential $(mV \pm 0.01)^*$	$[Sn]_{Total}$ $(mol \cdot L^{-1})^*$
Sn(IV)4	8 18 22 48	0.61	0.11 0.12 0.18 0.15	548.1 525.9 635.7 632.5	$\begin{array}{c} 1.21 \text{ x } 10^{-4} \pm 4 \text{ x } 10^{-6} \\ 1.59 \text{ x } 10^{-4} \pm 4 \text{ x } 10^{-6} \\ 1.74 \text{ x } 10^{-4} \pm 4 \text{ x } 10^{-6} \\ 1.55 \text{ x } 10^{-4} \pm 4 \text{ x } 10^{-6} \end{array}$
Sn(IV)5	8 18 22 48	0.48	0.02 0.03 0.06 0.05	316.7 321.5 322.2 324.8	$7 x 10^{-6} \pm 9 x 10^{-6} 5 x 10^{-6} \pm 9 x 10^{-6} 5 x 10^{-6} \pm 9 x 10^{-6} 4 x 10^{-6} \pm 9 x 10^{-6} 4 x 10^{-6} \pm 9 x 10^{-6} $
Sn(IV)6	8 18 22 48	1.2 x 10 <sup>-3</sup>	3.08 3.07 3.08 3.08	440.7 420.9 409.5 411.4	$4 x 10^{-6} \pm 4 x 10^{-6}  3 x 10^{-6} \pm 4 x 10^{-6} $
Sn(IV)7	8 18 22 48	1.0 x 10 <sup>-3</sup>	3.06 3.04 2.98 3.03	398.6 407.5 387.0 394.0	$1 \times 10^{-6} \pm 2 \times 10^{-6}$ $1 \times 10^{-6} \pm 2 \times 10^{-6}$
Sn(IV)8	8 18 22 48	0.37	10.40 10.36 10.39 10.38	140.9 136.6 125.3 129.5	$\begin{array}{c} 1.5 \text{ x } 10^{-5} \pm 7 \text{ x } 10^{-6} \\ 2.1 \text{ x } 10^{-5} \pm 7 \text{ x } 10^{-6} \\ 2.6 \text{ x } 10^{-5} \pm 7 \text{ x } 10^{-6} \\ 2.2 \text{ x } 10^{-5} \pm 7 \text{ x } 10^{-6} \end{array}$
Sn(IV)9	8 18 22 48	2.9 x 10 <sup>-2</sup>	11.09 10.73 10.70 10.68	179.2 179.1 178.9 179.0	$2.24 \times 10^{-5} \pm 8 \times 10^{-7}$ $1.10 \times 10^{-5} \pm 8 \times 10^{-7}$ $2.10 \times 10^{-5} \pm 8 \times 10^{-7}$ $1.87 \times 10^{-5} \pm 8 \times 10^{-7}$
Sn(IV) 10	8 18 22 48	6.3 x 10 <sup>-2</sup>	11.50 11.18 11.19 11.20	94.5 99.9 88.5 88.1	$2.26 \times 10^{-5} \pm 8 \times 10^{-7}$ $2.60 \times 10^{-5} \pm 8 \times 10^{-7}$ $2.89 \times 10^{-5} \pm 8 \times 10^{-7}$ $3.34 \times 10^{-5} \pm 7 \times 10^{-7}$
Sample Number	Reaction time (h)	$I \pmod{(mol \cdot L^{-1})}$	$\begin{array}{c} pH_{378.15\ K} \\ \left(\pm 0.01\right)^{*} \end{array}$	$\frac{\text{Redox Potential}}{(\text{mV} \pm 0.01)^*}$	$[Sn]_{Total}$ $(mol \cdot L^{-1})^*$
Sn(IV) 11	48	0.48	0.07	303.9	$4 \ge 10^{-6} \pm 3 \ge 10^{-6}$
Sn(IV) 12	48	6.3 x 10 <sup>-2</sup>	11.01	64.6	$4.2 \times 10^{-5} \pm 2 \times 10^{-6}$

 Table 5.8 Tin(IV) Oxide Solubility Data at 358.15 K and 378.15 K

\* Uncertainty represents one standard deviation  $(1\sigma)$ .



**Figure 5.5** Tin(IV) oxide solubility in acidic pH conditions over a period of 48 hours at 358.15 K determined by ICP-OES.



**Figure 5.6** Tin(IV) oxide solubility in alkaline pH conditions over a period of 48 hours at 358.15 K determined by ICP-OES.



Figure 5.7 Raman spectra of a tin(IV) oxide sample recovered after a 358.15 K solubility experiment in a pH 3.03 (CH<sub>3</sub>COOH) medium.

Raman Shift (cm <sup>-1</sup> )	Peak Assignment	Reference
116	$SnO_2$	[93]
205	SnO	[92]
473	$SnO_2$	[93]
619	$SnO_2$	[93]
773	$SnO_2$	[93]

**Table 5.9** Raman Shift Assignments for an SnO<sub>2</sub> Sample

 After a Solubility Run

Reaction	Sample Number	$\log_{10} \mathrm{K}^{\mathrm{o}^*}$	Source	Medium	
$SnO_2 + 3H^+ \leftrightarrow SnOH^{3+}$ (equation 3.33)	Sn(IV)4	$-5.29\pm0.02$	This work	HCl	
	Sn(IV)5	$-6.8 \pm 0.9$	This work	CF <sub>3</sub> SO <sub>3</sub> H	
$SnO_2 + 3H_2O \leftrightarrow Sn(OH)_5^- + H^+$ (equation 3.35)	Sn(IV)8	$-15.2 \pm 0.1$	This work	NaOH/ CH <sub>3</sub> COONa	
$\text{SnO}_2 + \text{H}_2\text{O} \leftrightarrow \text{SnO}_3^{2-} + 2\text{H}^+$	Sn(IV)	$-27.30\pm0.03$	This work	NaOH	
(equation 3.36)	10	-26.22	[15]		

Table 5.10 Logarithm of Tin(IV) Oxide Solubility Constants at 358.15 K

<sup>\*</sup> Uncertainty represents one standard deviation  $(1\sigma)$ .

Table 5.11 Logarithm of Tin(IV) Oxide Solubility Constants at 378.15 K	
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Reaction	Sample Number	$\log_{10} \mathrm{K}^{\mathrm{o}^*}$	Source	Medium
$SnO_2 + 3H^+ \leftrightarrow SnOH^{3+} + H_2O$ (equation 3.33)	Sn(IV) 11	$-6.8 \pm 0.3$	This work	CF <sub>3</sub> SO <sub>3</sub> H
$\text{SnO}_2 + \text{H}_2\text{O} \leftrightarrow \text{SnO}_3^{2-} + 2\text{H}^+$	Sn(IV)	$-26.85 \pm 0.02$	This work	NaOH
(equation 3.36)	12	-25.17	[15]	

Uncertainty represents one standard deviation  $(1\sigma)$ 

# 5.4 Tin Pourbaix Diagrams

### 5.4.1 Gibbs Energy Calculations

Based on the experimental equilibrium constants for both the tin(II) and tin(IV) systems, the standard Gibbs energies of reactions pertinent to the Sn E-pH diagram are summarized in Table 5.12. The values calculated from the thermochemical data in Table 2.2 and Rai *et al.* are also presented where available. To guide the reader along in the calculation process, the exact equilibrium constants chosen from Tables 5.6, 5.8, 5.11, and 5.12 in order to obtain the Gibbs energies of each reaction at the specified

temperature, are listed in Table 5.12. A sample calculation is shown for the reaction in equation 3.26 using equation 1.5 and the equilibrium constant reported in Table 5.5 (sample Sn(II)4):

As previously mentioned, the error propagation procedure is outlined in Appendix A, and is not further focused on in this section.

Reaction	T (K)	Sample Number	log <sub>10</sub> K <sup>o*</sup>	$\Delta G_{r,T}^{o} \text{ this work}$ $(J \cdot \text{mol}^{-1})^{*}$	Ref $\Delta G_{r,T}^{o}$ (J · mol <sup>-1</sup> )
$SnO + H^+ \leftrightarrow SnOH^+$ (equation 3.24)	358.15	Sn(II)3	-3 ±3	$2 \times 10^4 \pm 2 \times 10^4$	2.218 x 10 <sup>3</sup> [15]
$SnO + 2H_2O \leftrightarrow Sn(OH)_3^- + H^+$ (equation 3.26)	358.15	Sn(II)4	$-13.75 \pm 0.08$	$9.43 \times 10^4 \pm 5 \times 10^2$	8.969 x 10 <sup>4</sup> [15]
	298.15	Sn(IV)1	$-6 \pm 2$	$3 \ge 10^4 \pm 1 \ge 10^4$	3.7 x 10 <sup>4</sup> [40]
$SnO_2 + 3H^+ \leftrightarrow SnOH^{3+} + H_2O$ (equation 3 33)	358.15	Sn(IV)5	$-6.8 \pm 0.9$	$4.7 \ge 10^4 \pm 6 \ge 10^3$	N/A
(equation 5.55)	378.15	Sn(IV)11	$-6.8 \pm 0.3$	$5.0 \ge 10^4 \pm 2 \ge 10^3$	N/A
$\text{SnO}_2 + 3\text{H}_2\text{O} \leftrightarrow \text{Sn(OH)}_5^- + \text{H}^+$	298.15	Sn(IV)2	$-16.0 \pm 0.5$	$9.2 \times 10^4 \pm 3 \times 10^3$	1.0 x 10 <sup>5</sup> [40]
(equation 3.35)	358.15	Sn(IV)8	$-15.2 \pm 0.1$	$1.042 \text{ x } 10^5 \pm 9 \text{ x } 10^2$	N/A
	298.15	Sn(IV)3	$-30.88 \pm 0.02$	$1.763 \times 10^5 \pm 1 \times 10^2$	1.6 x 10 <sup>5</sup> [40] 1.728 x 10 <sup>5</sup> [15]
$SnO_2 + H_2O \leftrightarrow SnO_3^{2-} + 2H^+$ (equation 3.36)	358.15	Sn(IV)10	$-27.30 \pm 0.03$	$1.872 \times 10^5 \pm 2 \times 10^2$	1.798 x 10 <sup>5</sup> [15]
	378.15	Sn(IV)12	$-26.85 \pm 0.02$	$1.944 \ge 10^5 \pm 2 \ge 10^2$	1.822 x 10 <sup>5</sup> [15]

Table 5.12 Standard Gibbs Energies of Various Tin(II) and Tin(IV) Equilibria

<sup>\*</sup> Uncertainty represents one standard deviation  $(1\sigma)$ .

Using the experimentally derived  $\Delta G_{r,T}^{o}$  data in Table 5.12 and the known Gibbs energies for the other components in a reaction, the  $G_{T}^{o}$  value for a particular species can be back-calculated. A sample calculation is provided to guide the author using the example of the standard Gibbs energy of SnOH<sup>3+</sup> at 358.15 K from equation 3.26 (SnO + 2H<sub>2</sub>O  $\leftrightarrow$  Sn(OH)<sub>3</sub><sup>-</sup> + H<sup>+</sup>):

$$\Delta G_{r,T}^{o} = \sum G_{products,T}^{o} - \sum G_{reactants,T}^{o}$$

 $\Delta G_{r\ 358.15\ K}^{o} = \left(G_{H,^{+}\ 358.15\ K}^{o} + G_{Sn(OH)_{3}^{-},\ 358.15\ K}^{o}\right) - \left(2G_{H_{2}O,\ 358.15\ K}^{o} - G_{H,^{+}\ 358.15\ K}^{o}\right)$ 

$$G_{\text{Sn}(\text{OH})_{3}^{-}, 358.15 \text{ K}}^{\text{o}} = \Delta G_{\text{r} 358.15 \text{ K}}^{\text{o}} + 2G_{\text{H}_{2}\text{O}, 358.15 \text{ K}}^{\text{o}} + G_{\text{SnO}, 358.15 \text{ K}}^{\text{o}} - G_{\text{H},+ 358.15 \text{ K}}^{\text{o}},$$

where the 358.15 K Gibbs energies of all other species can be extrapolated based on established thermochemical properties (e.g., Table 2.2). The temperature dependence data for auxiliary species are listed in Table 5.13 and are used to calculate the Gibbs energies at the desired condition according to equation 1.22. Using this data, the Gibbs energies of H<sub>2</sub>O<sub>(1)</sub> and H<sup>+</sup><sub>(aq)</sub> at 358.15 K are:  $G^{0}_{H_2O_{,358,15 K}} = -3.109 \times 10^5 \text{ J} \cdot \text{mol}^{-1}$ and  $G^{0}_{H,+358,15 K} = 0 \text{ J} \cdot \text{mol}^{-1}$ , respectively. The Gibbs energy of SnO<sub>(s)</sub>,  $G^{0}_{SnO_{,358,15 K}} = -3.062 \times 10^5 \text{ J} \cdot \text{mol}^{-1}$ , was calculated using the thermochemical data in Table 2.2. The  $\Delta G^{0}_{r,T} = 9.43 \times 10^4 \pm 5 \times 10^2 \text{ J} \cdot \text{mol}^{-1}$  was taken from Table 5.12.

Pourbaix Diagram [15].							
Species	$\Delta H_{298 \ K}^{\circ}$	S <sub>298 K</sub>	$C_P = a +$	$bT + cT^2 + c$	$cT^2 + dT^{-2} (J \cdot mol^{-1} \cdot K^{-1})$		
Species	$(J \cdot mol^{-l})$	$(J \cdot mol^{-1} \cdot K^{-1})$	а	b	с	d	
$H_2O_{(l)}$	-285830	69.950	-203.1190	1.52070	-0.0032	3848758	
$H^{+}_{(aq)}$	0	0	0	0	0	0	

 Table 5.13 Thermochemical Data for Auxiliary Species Necessary to Construct the Sn

 Pourbaix Diagram [15].

$$G^{o}_{\text{Sn(OH)}_{3}, 358.15 \text{ K}} = (9.43 \text{ x } 10^{4} \pm 5 \text{ x } 10^{2} \text{ J} \cdot \text{mol}^{-1}) + 2(-3.109 \text{ x } 10^{5} \text{ J} \cdot \text{mol}^{-1}) + (-3.062 \text{ x } 10^{5} \text{ J} \cdot \text{mol}^{-1}) - (0 \text{ J} \cdot \text{mol}^{-1})$$

$$G_{\text{Sn}(\text{OH})_{3}}^{\text{o}}$$
, 358.15 K =  $-5.228 \text{ x } 10^5 \pm 5 \text{ x } 10^2 \text{ J} \cdot \text{mol}^{-1}$ 

The standard Gibbs energies for various aqueous tin(II) and tin (IV) species are presented in Table 5.14.

Table 5.14         Standard Gibbs Energies of Various Tin(II) and Tin(IV) Species					
Species	T (K)	$G_{T}^{o}$ this work $(J \cdot mol^{-1})^{*}$	$\operatorname{Ref} G_{\mathrm{T}}^{\mathrm{o}}$ $(\mathbf{J} \cdot \mathrm{mol}^{-1})$		
SnOH+	358.15	$-2.8 \times 10^5 \pm 2 \times 10^4$	-3.040 x 10 <sup>5</sup> [15]		
$Sn(OH)_3^-$	358.15	$-5.228 \times 10^5 \pm 5 \times 10^2$	-5.274 x 10 <sup>5</sup> [15]		
SnOH <sup>3+</sup>	298.15	-2.6 x $10^5 \pm 1 x 10^4$	-2.5 x 10 <sup>5</sup> [40]		
	358.15	$-2.39 \times 10^5 \pm 6 \times 10^3$	N/A		
	378.15	$-2.36 \times 10^5 \pm 2 \times 10^3$	N/A		
C (OU)=	298.15	$-1.422 \times 10^6 \pm 3 \times 10^3$	-1.4 x 10 <sup>6</sup> [40]		
$SII(OH)_5$	358.15	$-1.4251 \ge 10^6 \pm 9 \ge 10^2$	N/A		
Sn0 <sub>3</sub> <sup>2–</sup>	298.15	$-7.237 \ge 10^5 \pm 1 \ge 10^2$	-7.272 x 10 <sup>5</sup> [15] -1.6 x 10 <sup>6</sup> [40]		
	358.15	$-7.204 \ge 10^5 \pm 2 \ge 10^2$	-7.279 x 10 <sup>5</sup> [15]		
	378.15	$-7.158 \ge 10^5 \pm 2 \ge 10^2$	-7.280 x 10 <sup>5</sup> [15]		

\* Uncertainty represents one standard deviation  $(1\sigma)$ .

## 5.4.2 Pourbaix Diagrams Based on the Current Work

The Pourbaix diagrams in Figures 5.8 and 5.10 are included for comparison to the current literature diagrams. The former is calculated using the properties in Table 2.2 [15] and the 298.15 K data from Rai and coworkers [40] for the SnOH<sup>3+</sup> and Sn(OH)<sup>5</sup> complexes [40]. Meanwhile, the latter is plotted using the 358.15 K extrapolations [15] of the original Sn E-pH diagram [14], excluding SnOH<sup>3+</sup> and Sn(OH)<sup>5</sup>, as previous elevated temperature data on these species are not available. The tin Pourbaix diagram is re-constructed at 298.15 K and 358.15 K based on the  $\Delta G_T^0$  data from this work in Figures 5.9 and Figures 5.11, 5.12, respectively. The 358.15 K diagram is presented both with, Figure 5.11, and without, Figure 5.12, the alkaline pH data extracted from the tin(II) oxide system (reactions 3.24). An E-pH diagram was not constructed at 378.15 K due to the uncertainties in the data acquired at this temperature associated with the sampling procedure (section 4.3.5).



**Figure 5.8** E-pH diagram for tin at 298.15 K and an aqueous species concentration of  $10^{-6}$  mol·L<sup>-1</sup> constructed using the thermochemical summary of the tin system.



Figure 5.9 E-pH diagram for tin at 298.15 K and an aqueous species concentration of  $10^{-6}$  mol·L<sup>-1</sup> constructed using data from present work.



**Figure 5.10** E-pH diagram for tin at 358.15 K and a concentration of 10<sup>-6</sup> M constructed using thermochemical data for the tin system [15] [40].



**Figure 5.11** E-pH diagram for tin at 358.15 K and a concentration of 10<sup>-6</sup> M constructed using experimental data from the present work, including tin(II) oxide alkaline pH solubility data.



**Figure 5.12** E-pH diagram for tin at 358.15 K and a concentration of 10<sup>-6</sup> M constructed using experimental data from the current work excluding tin(II) oxide data.

# **6 DISCUSSION**

#### 6.1 Zinc System

The Raman spectrum of the zinc oxide powder used in this work (Figure C1, Appendix C) is in good agreement with the literature spectra for ZnO, as summarized in Table C1. The evolution of zinc solubility versus time plot in Figure 5.1 shows that fairly constant solution compositions were achieved within the eight hour reaction period. This is in agreement with several elevated temperature studies [35,36], where zinc oxide equilibria were attained within approximately twelve hours, both in acidic and alkaline conditions. Although as demonstrated by previous investigations, more consistent solubility measurements can be achieved with longer reaction times, the purpose of studying the ZnO system was to validate the equipment and data analysis procedures. Thus, a more time-efficient, cursory investigation was performed.

The 358.15 K equilibrium constants summarized in Table 5.2 indicate that the acidic (pH 5.41) and alkaline (pH 11.40) limits chosen using the  $Zn^{2+}$  hydrolysis distribution plot (Figure 3.1) were effective in isolating the  $Zn^{2+}$  and  $Zn(OH)_3^-$  complexes. The constant for the acidic pH ZnO/Zn<sup>2+</sup> equilibrium (equation 3.10) obtained from this work,  $log_{10} K_{sp}^0 = 8.38 \pm 0.01$ , corresponds well to the literature values of  $log_{10} K_{sp}^0 = 8.31$  [37] and  $log_{10} K_{sp}^0 = 8.42$  [34]. Likewise, the equilibrium with the terminal hydrolysis complex according to equation 3.13 resulted in a constant of  $log_{10} K_3^0 = -15.32 \pm 0.01$  that is analogous to the -15.39 from Shock *et al.* [37] and -15.46 from Wesolowski and workers [34]. The challenge lies in solubility measurements at pH values between the acidic and alkaline limits. As can be seen in Table 5.1, the pH 10.67 run (sample Zn3) , which falls into the stability domain of the Zn(OH)<sub>2</sub><sup>0</sup> complex at

358.15 K, resulted in zinc concentrations that are at or below the atomic absorption spectrometer detection limit (~1.5 x  $10^{-6}$  M). Such solubility data could only be used to suggest an upper limit for the value of the Zn(OH)<sup>0</sup>/ZnO equilibrium constant. Furthermore, the narrow stability window of ZnOH<sup>+</sup> (8<pH<8.5) indicated on the hydrolysis distribution plot requires a large number of measurements surrounding and encompassing that range, along with accurate knowledge of the solubility product constant, to unambiguously determine the equilibrium constant involving the primary hydrolysis species (equation 3.11). However, the work in the acidic and alkaline regions has demonstrated that the equipment setup, data analysis, and equilibrium model could produce values that were comparable to literature data. Temperatures other than 358.15 K were not considered for the Zn system, as it was not the primary focus of this work.

## 6.2 Tin (II) System

The Raman spectrum for the tin(II) oxide powder prior to solubility runs, (Figure C2, Appendix C) is analogous to the previously reported SnO spectra (Table C2). As very little of the thermodynamic data on the tin(II) oxide system has come from solubility studies [38], a reaction period of 28 hours was arbitrary chosen for the 358.15 K investigations summarized in Table 5.3.

### 6.2.1 SnO Solubility in Oxygenated Conditions

The  $\log_{10} K_1^0 = -3 \pm 2$  (Table 5.5) constant for the SnO/SnOH<sup>+</sup> equilibrium shown extracted from the pH 2.99 HCl solubilities, modelled by equation 3.24, is an order of magnitude lower than the expected -0.32 calculated from the available Sn+II thermodynamic data [15]. Upon suspicion of interference from Sn-Cl complexes, the run 92 was repeated using acetic acid to establish the solution acidity instead. Although the tin content from the HCl experiment was slightly higher, both data sets fell below the instrument detection limit. The  $\log_{10} K_1^0 = -3 \pm 3$  constant obtained from the pH 3.23 CH<sub>3</sub>COOH experiment remained lower than the anticipated value, implying that an alternate source of interference was present. Furthermore, as tin concentrations measurements were under the instrument detection cut-off, it is unclear if the data reached a constant plateau and 28 hours was a sufficient equilibration period.

In comparison to the Raman shifts observed for SnO prior to a solubility run shown in Figure C2 in Appendix C, the spectrum of the sample after reaction in an oxygenated solution (Figure 5.3(a)) had several distinct differences. According to the literature spectra for tin(II) oxide [92], the increase from two to four peaks in the 100-200 cm<sup>-1</sup> range indicates the formation of compounds with stoichiometries intermediate of tin(II) and tin(IV), e.g.,  $SnO_x$ , where 1<x<2. Furthermore, the peaks at 473 cm<sup>-1</sup> and 620 cm<sup>-1</sup> correspond to tin(IV) oxide [93], which is in agreement with the original SnO<sub>2</sub> sample from this work (Figure C3). These changes to the SnO spectrum suggest that a transformation in the oxidation state has occurred. This is further supported by comparing the 358.15 K pH ~ 3 SnO solubility data both in CH<sub>3</sub>COOH and HCl (samples Sn(II)) and Sn(II) in Table 5.3) to the tin content measured from  $SnO_2$ runs at the same conditions (samples Sn(IV)6 and Sn(IV)7 in Table 5.8). Total tin concentrations obtained from all four runs, plotted together in Figure 6.1 as a function of time, show very similar concentrations around 10<sup>-6</sup> mol·L<sup>-1</sup>, despite the expected  $\sim 10^{-4}$  mol·L<sup>-1</sup> solubility calculated for SnO at this pH using the data in Table 2.2. The combination of the Raman and solubility data suggests that the observed ~400 mV vs.

SHE redox potential of the oxygenated solutions (Table 5.3), prompts the SnOH<sup>+</sup> to readily oxidize to Sn<sup>4+</sup> or similar +IV hydrolysis products. As the SnO measurements correspond to the anticipated extremely low solubility of tin(IV) oxide, the Sn +IV species are likely precipitating as SnO<sub>2</sub> according to the mechanism in Figure 6.2. Thus, the low tin concentrations obtained from the SnO investigations are a result of SnO<sub>2</sub> controlling the solubility equilibrium.



**Figure 6.1** Tin(II) and tin(IV) oxide solubilities in acidic conditions over a period of 48 hours at 358.15 K determined by ICP-OES.



**Figure 6.2** Model for tin +II oxide oxidation to tin +IV via dissolved oxygen, and subsequent precipitation to SnO<sub>2</sub>.

### 6.2.2 SnO Solubility in Nitrogen Gas Purged Conditions

As dissolved oxygen from the atmosphere controls the redox potential of water and directly affects the oxidation state of aqueous species [95], the acetic acid run was repeated by purging the solution with nitrogen gas prior to the run to remove the  $O_{2(aq)}$ . Once  $N_{2(g)}$  was bubbled through the solution, the redox potential decreased from the regular ~400 mV vs. SHE in the presence of dissolved oxygen, to ~250 mV vs SHE, as shown in Table 5.3. However, in a similar fashion to the previous two oxygenated experiments at this pH, i.e., samples Sn(II)1 and Sn(II)2, the SnO/SnOH<sup>+</sup> equilibrium constant,  $log_{10} K_1^0 = -3 \pm 3$ , remains an order of magnitude lower than anticipated. Although the Raman spectrum of tin(II) oxide after the  $N_{2(g)}$  purged solubility experiment, shown in Figure 5.3(b), resembles that of the original SnO sample (Figure C2), the measured tin(II) oxide solubility obtained from the deoxygenated run (sample Sn(II)3) was still much lower than expected. As the concentrations involved in metal oxide solubility equilibria are in general quite low ( $\leq 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ), the amount of Sn<sup>4+</sup>, and accordingly SnO<sub>2</sub>, produced during the Sn<sup>2+</sup>  $\rightarrow$  Sn<sup>4+</sup> transition is very small. Thus, the SnO<sub>2</sub> signal, which was present weakly in the oxygenated run in Figure 5.3(a), is likely not intense enough to appear on the Raman spectrum of the N<sub>2(g)</sub> sparged trial in Figure 5.3(b). Even at the lower redox potential of ~250 mV, tin +II species are unstable and readily convert to the +IV state. This is highlighted in Figure 6.3 below, where the (pH, potential) coordinates of the 358.15 K tin(II) oxide experiments (samples Sn(II)1-4) are superimposed on the tin Pourbaix diagram originally presented in Figure 5.12. It is clear that the tin(II) runs, shown as circles, are in the domain of tin +IV, along with the tin(IV) data points (samples Sn(IV)4-10), shown as squares.



**Figure 6.3** The (pH, potential) coordinates of the tin(II) oxide and tin(IV) oxide solubility runs with the superimposed on the 358.15 K Sn E-pH diagram (Figure 5.12).

The 358.15 K solubility runs were not repeated at 298.15 K or 378.15 K as similar interference from  $SnO_2$  was predicted. In order to mitigate this issue, considerably more reducing conditions, via the addition of a non-complexing reducing agent, are required to ensure SnO remains in equilibrium with only +II aqueous species.

### 6.3 Tin(IV) System

The Raman shifts of the original tin(IV) oxide sample (Figure C3, Appendix C) correspond well with the SnO<sub>2</sub> peaks previously identified in the literature, as shown in Table C3. In a recent study of the solubility of tin(IV) oxide at 298.15 K for periods up from 7-49 days, it was noted that equilibrium was reached in less than seven [40]. To maintain a practical reaction time, two day (48 hour) runs were performed in this work at all temperatures.

# 6.3.1 SnO<sub>2</sub> Solubility in Acidic Conditions

# Experiments at 298.15 K

Unlike the original Sn<sup>4+</sup> speciation model proposed by Pourbaix [14], hydrolysis schemes since then have suggested that the cation goes through several intermediate complexes before reaching the SnO<sub>3</sub><sup>2-</sup> form. The likelihood of highly charged metal cations to hydrolyze even under acidic conditions [47,50] supports the existence of the SnOH<sup>3+</sup> product (equation 3.33) despite the low pH over which it is assumed to dominate (Figure 3.3). The 298.15 K log<sub>10</sub> K<sub>1</sub><sup>0</sup> = -6 ± 2 (Table 5.7) constant for the SnO<sub>2</sub>/SnOH<sup>3+</sup> equilibrium is higher than the -6.52 reported by Rai and workers [40]. As this is the only tin(IV) oxide study that incorporates the SnOH<sup>3+</sup> complex into the solubility scheme, there are no other sources to corroborate either result. However, as the measured tin concentrations in this work are just under the ICP-OES detection limit, it is likely that the true solubility is lower than the value determined in this investigation and the equilibrium constant is accordingly closer to the proposed -6.52. Although it is possible to mitigate this issue with additional runs at progressively lower acidities, conditions that are much more extreme than the pH 0.54 used in the present work are destructive to the reaction apparatus and electrodes. An alternate solution is a measuring technique with a lower tin detection limit than the ICP-OES and AAS, such as the ICP-MS used by Rai *et al* [40], which can analyze concentrations down to the  $10^{-8}$  mol·L<sup>-1</sup> range.

# Experiments at 358.15 K

The work at 358.15 K in triflic acid resulted in a constant of  $\log_{10} K_1^0 = -6.8 \pm 0.9$ for the equilibrium with the first hydrolysis product (Table 5.11). Repetition of the 0.05 pH CF<sub>3</sub>SO<sub>3</sub>H run with HCl resulted in a higher value of  $\log_{10} K_1^0 = -5.29 \pm 0.02$ . The apparent increase of SnO<sub>2</sub> solubility in hydrochloric acid, as shown in Figure 5.5, supports the postulated interference of Sn-Cl complexes at high chloride concentrations. Tin content determined in the acidic regime was above the detection limit for samples in both media, eliminating this as a potential source of error. The CF<sub>3</sub>SO<sub>3</sub>H derived equilibrium constant is considered valid due to the extensive solubility work that has been done in triflic acid without indication of metal-CF<sub>3</sub>SO<sub>3</sub> products [4]. Although there is no elevated temperature SnO<sub>2</sub> solubility work available for comparison, according to the trend of decreasing metal oxide solubility in acidic conditions with increasing temperature [4,47], the equilibrium constant at 358.15 K is expected to be lower than the 298.15 K value. This tendency is observed in the present work, where the 358.15 K  $SnO_2/SnOH^{3+}$  constant of  $log_{10} K_1^0 = -6.8 \pm 0.9$  is lower than the  $log_{10} K_1^0 = -6 \pm 2$  at 298.15 K. Lastly, the Raman spectrum of a sample of SnO<sub>2</sub> after a solubility run in a pH  $\sim$ 3 environment (sample Sn(IV)7, Figure 5.7) matches to that of the sample analyzed prior to the experiment. The locations of the 473 cm<sup>-1</sup>, 619 cm<sup>-1</sup>, and 773 cm<sup>-1</sup> peaks correlate with the expected assignments for SnO<sub>2</sub> as shown in Table 5.9. A weak signal at ~100 cm<sup>-1</sup> is sometimes observed for tin(IV) oxide [93] and is likely the cause of the
116 cm<sup>-1</sup> peak. The additional absorption at 205 cm<sup>-1</sup> is identified as possibly belonging to SnO [92], however, it is too weak to indicate a considerable transformation in the redox chemistry has occurred.

# 6.3.2 SnO<sub>2</sub> Solubility in Intermediate Conditions

# Experiments at 358.15 K

Similar to the issue of extremely low metal concentrations in the stability regions of the  $Zn(OH)_2^0$  complex in the Zn system, the solubility data from the pH range where the Sn(OH)<sup>0</sup><sub>4</sub> is dominant falls below the Sn detection limit of the ICP-OES (~4.0 x 10<sup>-6</sup> M). However, as shown in the 298.15 K speciation plot in Figure 3.3, the Sn(OH)<sup>0</sup><sub>4</sub> stability window is quite broad, thus generally limiting the pH conditions under which SnO<sub>2</sub> solubility data can be extracted without encountering instrumental detection limits. Analogously, at elevated temperatures, even after assuming a general shift to the left of the various stability areas, most of the pH scale remains dominated by  $Sn(OH)_4^0$ . This is clearly shown by both the 358.15 K hydrochloric acid (sample Sn(IV)6) and acetic acid (sample Sn(IV)7) solubility results presented in Table 5.8, where concentrations are under the detection limit, particularly in the case of the latter. A similar issue was observed in the ambient temperature work of Rai and workers [40], where no reliable value for the  $SnO_2/Sn(OH)_4^0$  reaction (equation 3.34) could be obtained from their data in the range of pH 3.5-8 even with the lower instrument detection cut-off of the ICP-MS [40]. Although it is possible that the increased solubility of the sample run in HCl is due to tin complexation with Cl, the detection limit does not allow a concrete conclusion to be made.

# 6.3.3 SnO<sub>2</sub> Solubility in Alkaline Conditions

## Experiments at 298.15 K

Similar to the incorporation of SnOH<sup>3+</sup> into the hydrolysis speciation, the  $Sn(OH)_5^-$  complex is also added as a preceding step to the terminal  $SnO_3^{2-}$  anion. From the 298.15 K pH domains shown in Figure 3.3, the pH 10.74 run was used to isolate the equilibrium with  $Sn(OH)_5^-$ , represented by equation 3.35. The ambient temperature equilibrium constant,  $\log_{10} K_3^0 = -16.0 \pm 0.5$  (Table 5.7) is higher than the observed -17.58 by Rai and workers [40], however, as seen in Figure 5.6, the measured tin concentrations remained constant and above the detection limit over the 48 hour reaction time. The pH 13.14 trial is far into the alkaline regime, such that the  $SnO_2/Sn(OH)_5^$ equilibrium was assumed to be established unambiguously. The  $\log_{10} K_4^0 = -30.88 \pm 0.02$ constant for equation 3.36, is in good agreement with the -30.27 value reported by Pourbaix [14]. However, Rai and workers observed a higher solubility and a constant of -28.66 [40]. It was initially believed that the pH chosen by the authors to ascertain the equilibrium with the terminal hydrolysis product (~11.7) was not alkaline enough to prevent interference from the previous hydrolysis complex, Sn(OH)<sub>5</sub>, and lead to a mixed constant.

## Experiments at 358.15 K

At 358.15 K, an equilibrium constant of  $\log_{10} K_3^0 = -15.2 \pm 0.1$  was obtained for reaction 3.35 using the pH 10.38 (sample Sn(IV)8) run. Although there is no literature data available for Sn(OH)<sup>-</sup><sub>5</sub> at elevated temperatures, there is an increase in the constant from the  $\log_{10} K_3^0 = -16.0 \pm 0.5$  at 298.15 K. This corresponds to the predicted trend of greater solubility, and subsequently higher equilibrium constants at elevated temperatures

in alkaline environments [15,47]. The  $\log_{10} K_4^0 = -27.30 \pm 0.03$  constant for the SnO<sub>2</sub>/SnO<sub>3</sub><sup>2-</sup> equilibrium obtained using the pH 11.20 experiment does not show good agreement with the  $\log_{10} K_4^0 = -26.22$  (Table 5.10) value extracted from the temperature dependences of the SnO<sub>3</sub><sup>2-</sup> thermodynamic data [15]. As the model used by Pourbaix did not take into account any species other than SnO<sub>3</sub><sup>2-</sup> in the alkaline regime, the pH conditions used to extract this constant were likely not in the true stability window of the terminal hydrolysis product. The hypothetical constants for the SnO<sub>2</sub>/Sn(OH)<sub>5</sub><sup>-</sup> and SnO<sub>2</sub>/SnO<sub>3</sub><sup>2-</sup> reactions were calculated using the pH 10.38, 10.68 and 11.20 data and summarized in Table 6.1. The  $\log_{10} K_4^0 = -26.1 \pm 0.1$  obtained for equation 3.36 using the pH 10.38 data, corresponds well with the temperature-extrapolated constant, -26.22, (Table 5.10) reported by Kaye and Thompson [15].

Reaction	Sample Number	$\log_{10}$ K <sup>o</sup> *
	Sn(IV)8 (pH 10.38)	$-15.2 \pm 0.1$
$SnO_2 + 3H_2O \leftrightarrow Sn(OH)_5^- + H^+$ (equation 3.35)	Sn(IV)9 (pH 10.68)	$-15.47 \pm 0.02$
	Sn(IV)10 (pH 11.20)	$-15.77 \pm 0.03$
	Sn(IV)8 (pH 10.38)	$-26.1 \pm 0.1$
$SnO_2 + H_2O \leftrightarrow SnO_3^- + 2H^-$ (equation 3.36)	Sn(IV)9 (pH 10.68)	$-26.39\pm0.02$
	Sn(IV)10 (pH 11.20)	$-27.30\pm0.03$

 Table 6.1 Logarithm of the 358.15 K Tin(IV) Oxide Solubility Constants

 Calculated Using the Alkaline pH Data

\* Uncertainty represents one standard deviation  $(1\sigma)$ .

The variation in the  $\text{SnO}_2/\text{SnO}_3^{2-}$  constant as pH was increased indicates that more than one process is occurring over the range investigated, supporting the presence

of the  $Sn(OH)_5^-$  species. However, unlike the anticipated increase in the solubility, and thus equilibrium constant, which is expected with progressively more alkaline pH, Table 6.1 shows that the value of  $log_{10} K_4^0 = -27.30 \pm 0.03$  at pH 11.20 is lower than that obtained at pH 10.38 (-26.1 ± 0.1). Furthermore, the solubility data in Table 5.8 indicate that instead of an increase in tin total concentration, a plateau is established. The total tin content at the end of the three runs is summarized in Table 6.2.

 Table 6.	<b>.2</b> Final 358.15	K Alkaline Rang	ge Solubility Data
Sample	Reaction	Final pH	[Sn] <sub>Total</sub>
 Number	Time (h)	$(\pm 0.01)^{*}$	$(\text{mol} \cdot L^{-1})^*$
 Sn(IV)8		10.38	$2.2 \times 10^{-5} \pm 7 \times 10^{-6}$
Sn(IV)9	48	10.68	$1.87 \ge 10^{-5} \pm 8 \ge 10^{-7}$
Sn(IV)10		11.20	$3.34 \ge 10^{-5} \pm 7 \ge 10^{-7}$

 Table 6.2 Final 358.15 K Alkaline Range Solubility Data

 $\frac{\text{Sn(IV)10}}{\text{*} \text{Uncertainty represents one standard deviation (1<math>\sigma$ )}}

The unexpected decrease in the constants for reaction 3.36 as pH is increased suggests the presence of a reaction additional to the  $SnO_2/SnO_3^{2-}$  equilibrium. A similar trend of a plateau in the tin concentrations was observed at 298.15 K by Rai *et al.* for pH > 11.7 [40]. The authors postulated that this phenomenon is due to the formation of a Na-Sn salt, namely Na<sub>2</sub>SnO<sub>3</sub>, which dictates the solubility behaviour in high alkaline conditions. Several crystalline Na-Sn compounds including Na<sub>2</sub>Sn(OH)<sub>6(s)</sub>, Na<sub>2</sub>SnO<sub>3(s)</sub>, and Na<sub>2</sub>Sn<sub>2</sub>O<sub>5(s)</sub> have been reported by the International Center for Diffraction Data [40], but the exact stoichiometry has not yet been identified. The solubilities determined at 298.15 K and 358.15 K pH 13.14 and pH 11.20 experiments, respectively are likely due to the Na<sub>2</sub>SnO<sub>3(sy</sub>/Na<sub>2</sub>SnO<sub>3(aq)</sub> equilibrium:

$$\operatorname{Na}_{2}\operatorname{SnO}_{3(s)}^{2-} \leftrightarrow \operatorname{Na}_{2}\operatorname{SnO}_{3(aq)}^{2-}$$

$$6.1$$

A solubility of  $\sim 1.15 \times 10^{-5}$  to 5.1 x  $10^{-6}$  mol·L<sup>-1</sup> at 298.15 K was attributed to this reaction by Rai and workers [40]. In comparison, values of 8.8 x  $10^{-5} \pm 3 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ and 3.34 x  $10^{-5} \pm 7 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$  were observed at 298.15 K and 358.15 K, respectively, in the most alkaline pH experiments in this work (samples Sn(IV)3 and Sn(IV)10 in Tables 5.7 and 5.9). In order to be certain of the pH value at which the stability domain of the proposed Na<sub>2</sub>SnO<sub>3(s)</sub> begins and ends at either temperature, additional runs under more alkaline conditions are required both at 298.15 and 358.15 K. Thus, the solubility behaviour of the pH 11.20 run, used to generate the constant for the  $SnO_2/SnO_3^{2-}$  reaction (Table 5.10), and the subsequent line on the 358.15 K E-pH diagram (Figure 5.11), does not conform with the predicted model outlined in equations (3.33-3.36). As no thermochemical data are yet available on Na-Sn compounds [40], it is difficult to incorporate such a compound into the Sn E-pH diagram or a hydrolysis distribution plot. The regime of the  $SnO_3^{2-}$  must be replaced with  $Na_2SnO_{3(s)}$ , however, to determine the locations of the solid-aqueous phase equilibria lines for a Pourbaix diagram involving this compound, further investigation is necessary.

## 6.3.4 SnO<sub>2</sub> Solubility at 378.15 K

The inability to withdraw solution samples directly at temperatures over 373.15 K or a means to separate the solid and aqueous phases during the quenching, introduces error into the 378.15 K solubility data (samples Sn(IV)11 and Sn(IV)12, Table 5.8). As the temperature of the vessel and solution are brought down to conditions that permit a grab sample to be taken (358.15 K), the solubility equilibrium begins to re-establish at the

new conditions. Due to the slow reaction kinetics of most metal oxide equilibria [4], it is possible that these samples do not deviate too much from the true 378.15 K solubilities. However, this process can result in mixed data between the two temperatures and is not recommended. The 378.15 K SnO<sub>2</sub>/SnOH<sup>3+</sup> (sample Sn(IV)11) and SnO<sub>2</sub>/SnO<sub>3</sub><sup>2-</sup> (sample Sn(IV)12) constants  $\log_{10} K_1^o = -6.8 \pm 0.3$  and  $\log_{10} K_4^o = -26.85 \pm 0.02$ , obtained from 48 hour batch runs, are very similar to the respective  $\log_{10} K_1^0 = -6.8 \pm 0.9$  and  $\log_{10} K_4^0 = -27.30 \pm 0.03$  at 358.15 K. Although the  $\log_{10} K_1^0$  values follow the predicted trend of decreased tin concentration and equilibrium constant in acidic conditions [15], the small difference between the two supports the possibility of re-established solubility during cooling to the 358.15 K sampling temperature. On the other hand, the  $\log_{10} K_4^0$ data show a substantial increase in the constants with higher temperature, as expected according to the elevated temperature effect in alkaline conditions [15]. However, these data cannot be reported with certainty without either a direct sampling procedure at 378.15 K, or separation of the aqueous and solid phases during the quenching process to corroborate the result.

## 6.4 Tin Pourbaix Diagrams

As the standard Gibbs energies of reactions are derived from the measured tin concentrations and subsequent equilibrium constants, discrepancies in the constants are carried through to the Pourbaix diagram. For instance, the failure to establish adequate redox conditions for tin(II) oxide resulted in  $\Delta G_{r,T}^{o}$  values that deviated greatly from the calculated data and thus, could not be sensibly incorporated into the diagram. In particular, the Gibbs energy extracted for the primary hydrolysis complex, SnOH<sup>+</sup> differed greatly from the expected value and lead to heavy skewing of the diagram. On

the other hand, the higher solubility of  $\text{SnO}_2$  in the alkaline regime, and thus similarity to predicted SnO, masked the interference of the  $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$  oxidation and precipitation process. The resulting Gibbs energy of reaction for equation 3.26,  $\Delta G_{r,T}^0 = 9.43 \times 10^4 \pm 5 \times 10^2 \text{ J} \cdot \text{mol}^{-1}$ , does not deviate far from the extrapolated value of 8.969 x 10<sup>4</sup> J · mol<sup>-1</sup> [15]. Thus, although the alkaline 358.15 K SnO solubility could be incorporated into the E-pH diagram as shown in Figure 5.11, it is not truly representative of the equilibrium under consideration. The E-pH diagram is also shown without the SnO data obtained in the present study in Figure 5.12.

The standard Gibbs energies of the tin +IV equilibria showed reasonable agreement with the literature, where available, as can be seen by comparing the 298.15 K E-pH diagram based on the data of Kaye and Thompson [15] and Rai and workers in [40] (Figure 5.8) to the re-constructed version from this work (Figure 5.9). The moderate deviation between the 3.2 x  $10^4$  J·mol<sup>-1</sup> and 3.7 x  $10^4$  J·mol<sup>-1</sup> Gibbs energies for the SnO<sub>2</sub>/SnOH<sup>3+</sup> reaction determined from the present work and the data of Rai *et al.* [40], respectively, manifests itself as shifting of the Sn<sup>4+</sup>/SnOH<sup>3+</sup> and SnO<sub>2</sub>/SnOH<sup>3+</sup> equilibrium lines. The most dramatic alteration to the predicted diagram is the new location of the SnO<sub>2</sub>/SnO<sup>2</sup><sub>3</sub><sup>-</sup> boundary. As previously discussed, it can be rationalized that the interference of a solid compound such as Na<sub>2</sub>SnO<sub>3(s)</sub> [40], previously unaccounted for on E-pH diagrams, has the lead to the decreased solubility in the alkaline pH range. Subsequently, the standard Gibbs energy of SnO<sup>2</sup><sub>3</sub><sup>-</sup> at 298.15 K (Table 5.14),  $\Delta G_{SnO^2_3-298.15 \text{ K}}^{\circ} = -7.237 \times 10^5 \pm 1 \times 10^2$ , obtained in this work is lower than the -1.66 x  $10^5$  J·mol<sup>-1</sup> value extracted from the investigation of Rai and workers, where a

less alkaline pH range was selected to avoid interference from  $Na_2SnO_{3(s)}$  and establish the  $SnO_2/SnO_3^{2-}$  equilibrium [40].

In general, the temperature dependence of standard Gibbs energies (Table 5.12) manifests itself as several trends in E-pH diagrams. The stability areas of aqueous ions decrease at acidic pH and increase at alkaline pH as temperature is raised [4]. In particular, at higher temperatures, the fields for the aqueous species tend to shift to the left. This change in the domains of species can be seen by comparing the Pourbaix diagrams for tin at 298.15 K (Figure 5.9) and 358.15 K (Figure 5.12). The  $Sn(OH)_5^-/SnO_3^{2-}$  boundary line moves to less alkaline pH at 358.15 K, thus decreasing the stability window of tin(IV) oxide and increasing solubility. While the  $SnO_2/SnO_3^{2-}$  boundary leftwards as the temperature is raised, the magnitude of the shift exceeds that of the other equilibria. This is a product of the deviations between the determined and anticipated Gibbs energies of  $SnO_3^{2-}$ . Likewise, the  $SnO_2/SnOH^{3+}$  and  $SnOH^{3+}/Sn^{4+}$  equilibria shift to the left, with the latter moving to the even more extreme pH = -2.83 compared to -2.41 at 298.15 K. This consequently enlarges the  $SnO_2$  domain in acidic conditions, indicating reduced solubility.

## 7 CONCLUSIONS AND FUTURE WORK

#### 7.1 Summary

The experimental method and data analysis process, including activity coefficient considerations, were verified by investigating the well-known zinc oxide system. The 358.15 K constants for the ZnO solubility equilibria with the primary and terminal hydrolysis complexes from this work are in good agreement with the values extracted from previous elevated temperature studies [34,37].

The solubilities of the tin(II) and tin(IV) oxide systems were investigated from 298.15 K-378.15 K. Difficulties with controlling the redox chemistry were encountered during the 358.15 K investigations of SnO both under oxygenated and nitrogen gas purged conditions. As predicted by the original Sn Pourbaix diagram [14], the redox environments for the SnO and SnO<sub>2</sub> predominance regions differ greatly. The oxidation of Sn<sup>2+</sup> species to Sn<sup>4+</sup> and the subsequent precipitation of tin(IV) oxide was confirmed by the presence of SnO<sub>2</sub> peaks in the Raman spectra of tin(II) oxide samples taken after solubility experiments (Figure 5.3). Thus, in order for species in the +II oxidation state to remain stable, highly reducing conditions, which could not be obtained by only purging the solution with nitrogen gas, were required. As further consideration of a suitable reducing agent that will not complex with the analyte is necessary before proceeding, the present work on tin(II) oxide was only performed at 358.15 K.

Results from the alkaline experiments, although also controlled by SnO<sub>2</sub> equilibria, were incorporated into the final Sn E-pH diagram shown in Figure 5.11 to indicate that interference from various factors, i.e., complexation, failure to control redox chemistry, etc., is not always readily evident.

A thorough investigation of tin(IV) oxide across several temperatures and a wide pH range was performed, producing novel data for Sn +IV aqueous species. As some of the solubility results for the SnO<sub>2</sub>/SnOH<sup>3+</sup> equilibrium fell at or below instrument detection limit, these can only be interpreted as an indication of the upper solubility limit for future work. Similarly, as the SnO<sub>2</sub>/Sn(OH)<sup>5</sup> solubility reaction has also not been previously studied at elevated conditions, new values for the 358.15 K constant and standard Gibbs energy were determined. In comparison to the 298.15 K constant, the 358.15 K value shows an increase that is in accordance with the predicted temperature dependence of solubility in the alkaline regime [15]. The observed plateau in the tin concentrations in the pH > 10.38 alkaline pH regime at 358.15 K is in agreement with the previously observed trend for pH > 11.7 at 298.15 K [40]. The presence of a Na-Sn salt, as suggested by Rai and workers [40], is predicted to control the solubility behaviour via a Na<sub>2</sub>SnO<sub>3(s)</sub>/Na<sub>2</sub>SnO<sub>3(aq)</sub> equilibrium.

Lastly, the combination of data from the tin(II) and (IV) oxide studies were used to re-construct portions of the tin Pourbaix diagram at 298.15 K and 358.15 K as shown in Figures 5.9, 5.11, and 5.12. The general trends of solubility increasing with temperature at alkaline pH and decreasing in acidic conditions was observed in the tin +IV system. Furthermore, the SnOH<sup>3+</sup> and Sn(OH)<sup>5</sup> species, which were not included in earlier E-pH diagrams, have been used in present calculations both at 298.15 K and 358.15 K based on the measurements from this work. The Na<sub>2</sub>SnO<sub>3(s)</sub>/Na<sub>2</sub>SnO<sub>3(aq)</sub> are not included in the diagrams pending further solubility investigations in the alkaline pH range.

## 7.2 Future Recommendations

In accordance with the final objective of this project, the following recommendations are suggested for future, higher temperature investigations that will be able to simulate the conditions of the CANDU heat transport system (523.15 K-573.15 K). It is essential that the procedure and instrumentation can be applied to not only further investigate tin, but any M-H<sub>2</sub>O system.

# 7.2.1 Apparatus and Equipment

As Teflon decomposes at 573.15 K, the inner liner of the reaction vessel (Figure 4.1) requires replacing. Possible options include platinum or Hastelloy, which have been used successfully in both flow-through cells at ORNL and in batch reactors for temperatures up to 573.15 K. While the pH and redox electrodes from Omega Engineering featured in the present work can operate only up to 408.15 K, current developments in glass electrodes allow them to function until 473.15 K. For more extreme temperatures, an yttria stabilized zirconia (YSZ) probe with a suitable reference electrode such as Hg/HgO or Ag/AgCl is necessary. In order to obtain samples that are representative of the solid-aqueous phase equilibrium at a temperatures > 373.15 K, one of two modifications is necessary. A possible option is a sampling system with a tube, secured using pressure fittings, extending into the vessel. A pump to withdraw aliquots of the analyte and a high-temperature filter are needed, followed by a cooling stage. Any precipitation that occurs after filtration can be accounted for by adjusting the pH of the samples.

An alternative approach is physically separating the two phases inside the reaction vessel once equilibrium is established. For instance, analogous to the addition made by

Byrappa and Yoshimura [71], an inverted platinum cup with a filter that contains the solid sample can be incorporated to the bottom of the vessel. Once the reaction is terminated, the entire cell is inverted, such that the solid oxide and solution are no longer in contact while quenching occurs. The cup and solid can then be withdrawn separately from aqueous samples. Lastly, the addition of an overhead stirrer would insure that there are no temperature gradients inside the vessel and increase time required for equilibration. A pressure seal would be necessary for any components added to the cell, including the sampling tube, to maintain a closed system.

## 7.2.2 Sample Analysis

One of the major limitations of solubility work is due to instrumental detection limits. The use of an ICP-MS is recommended specifically for the tin systems, as Sn concentrations as low as  $10^{-8}$  mol·L<sup>-1</sup> have been measured [40], in comparison to the ~4.0 x  $10^{-6}$  mol·L<sup>-1</sup> limit of the ICP-OES. Furthermore, an investigation of the hydrolysis complexation of metal cations would be complementary to the solubility studies. As described in section 2.5.4, Raman spectroscopy, has been used for *in-situ* high temperature metal speciation. This would be of interest for future work on the tin system due to the disagreement over the stoichiometry of some Sn hydrolysis complexes, such as the terminal hydrolysis product, SnO<sub>3</sub><sup>2-</sup>, and the existence of others.

# Appendix A: Supplementary Data

$\log_{10} \gamma_i = -Az_i^2 \left( \frac{\sqrt{I}}{-1} - bI \right)$			
Temperature (K)	A	$\frac{1+\sqrt{1}}{b}$	Source
298.15	0.5085		
323.15	0.5319	0.2	[00]
358.15	0.568	0.2	[90]
378.15	0.607		

Table A1 Davies	Equation	Constant	S
		$\sqrt{I}$	١

**Table A2** Chemical Impurities of Zinc Oxide (Sigma Aldrich)

Metal Oxide	Anion Impurities	Cation Impurities
ZnO (>98.5%)	Chloride (Cl <sup>-</sup> ): $\leq 50 \text{ mg} \cdot \text{kg}^{-1}$ Sulfate (SO <sub>4</sub> <sup>2-</sup> ): $\leq 500 \text{ mg} \cdot \text{kg}^{-1}$	Arsenic (As): $\leq 3 \text{ mg} \cdot \text{kg}^{-1}$ Cadmium (Cd): $\leq 10 \text{ mg} \cdot \text{kg}^{-1}$ Iron (Fe): $\leq 10 \text{ mg} \cdot \text{kg}^{-1}$ Lead (Pb): $\leq 50 \text{ mg} \cdot \text{kg}^{-1}$

Table A3 ICP-OES Measured Intensities for 358.15 K Tin(II) Oxide Solubility Experiment: Sample Sn(II)4

Time (h)	Intensity $(c \cdot s^{-1})$	Concentration $(mg \cdot L^{-1})$
8	11.23974	2.082
18	13.70214	2.533
24	11.77044	2.180
28	10.87654	2.016

# Propagation of Uncertainty Through a Calibration Curve

This section outlines how the uncertainty in the ICP-OES or AA spectroscopy measured concentration of an analyte is propagated through a general, linear calibration curve in the form

$$y = m \cdot x + b$$
,

where y is the measured intensity (ICP-OES) or absorbance (AA spectroscopy), x is the analyte concentration, m is the slope, and b is the y-intercept. With replicate samples taken by the instrument, where measured signal is within the calibrated range of the instrument (interpolation), the uncertainty in the concentration, x, taken to be one standard deviation ( $\sigma_x$ ) is given by:

$$\sigma_{\rm x} = \frac{\sigma_{\rm xy}}{m} \sqrt{\frac{1}{r} + \frac{1}{n} + \frac{(y_{\rm meas} - \bar{y})^2}{m^2 \sigma_{\rm xx}}},$$

where  $\sigma_{xy} = \sum_{i=1}^{n} ((x_i - \bar{x})^2 (y - \bar{y})^2)$  and  $\sigma_{xx} = \sum_{i=1}^{n} (x_i - \bar{x})^2$  represent the sum of cross products of standard concentrations and instrument responses and the sum of squares of standard concentrations functions, respectively,  $\bar{x}$  represents the average of the concentrations of the standards,  $\bar{y}$  represents the average of the instrument responses of the standards, n represents the number of standards, r represents the number of replicates, and  $y_{meas}$  represents the experimental signal from the instrument for which x is to be determined. Using the standard data presented in Figure 5.1 as a typical example, specifically for the 28 hr data point (2.016 mg·L<sup>-1</sup>, 10.87654 c·s<sup>-1</sup>) for sample Sn(II)4 (Table 5.3), the relevant calculation variables are summarized in Table A1.

		0
Variable	Symbol	Value
slope	m	5.461
number of standards	n	4
number of replicates	r	3
measured analyte response	<b>y</b> <sub>meas</sub>	10.87654
average of standard concentrations	$\overline{y}$	42.1896
sum of squares of standard concentrations	$\sigma_{xx}$	1.11 x 10 <sup>3</sup>
sum of cross products of standard concentrations and instrument responses	$\sigma_{xy}$	2.11

**Table B1** Statistical Data for the Calibration Curve in Figure 5.1

$$\sigma_{\rm x} = \frac{2.11}{5.461} \sqrt{\frac{1}{3} + \frac{1}{4} + \frac{(11.2397 - 42.1896)^2}{(5.461)^2(1.11 \, {\rm x} \, 10^3)}} = 0.4 \, {\rm mg} \cdot {\rm L}^{-1}$$

Converting both the concentration,  $x = 2.016 \text{ mg} \cdot \text{L}^{-1}$  and the standard deviation above to mol·L<sup>-1</sup>, as indicated in section 4.3.6, the final concentration is reported as follows (Table 5.3):

$$1.7 \ge 10^{-5} \pm 3 \ge 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

In cases where the measured value for the sample was outside the measured range of the calibration curve (extrapolation), a modified expression for the standard deviation was used to calculate the standard deviation:

$$\sigma_{x,E} = \frac{\sigma_{xy}}{m} \sqrt{\frac{1}{r} + \frac{1}{n} + \frac{\bar{y}^2}{m^2 \sigma_{xx}}}$$

## Propagation of Uncertainty Through an Equilibrium Constant

Using the example of the Sn(II)4 sample run (Table 4.3), the logarithm of the 358.15 K thermodynamic (I=0) equilibrium constant and its standard deviation for the reaction SnO +  $2H_2O \leftrightarrow Sn(OH)_3^- + H^+$  (equation 3.26) are calculated as follows:

$$\begin{split} \mathrm{K}_{3}^{0} &= [\mathrm{Sn}(\mathrm{OH})_{3}^{-}]\gamma_{\mathrm{Sn}(\mathrm{OH})_{3}^{-}} \,\alpha_{\mathrm{H}^{+}} \\ \mathrm{log}_{10} \,\mathrm{K}_{3}^{0} &= \mathrm{log}_{10} [\mathrm{Sn}(\mathrm{OH})_{3}^{-}] + \mathrm{log}_{10} \,\gamma_{\mathrm{Sn}(\mathrm{OH})_{3}^{-}} - \mathrm{pH} \\ &= \mathrm{log}_{10} \big( (1.7 \, \mathrm{x} \, 10^{-5} \, \pm \, 3 \, \mathrm{x} \, 10^{-6} \, )(0.992) \big) - 8.98 \pm 0.01 \\ \sigma &= 0.434 \, \bigg( \frac{3 \, \mathrm{x} \, 10^{-6} \, (0.992)}{1.7 \, \mathrm{x} \, 10^{-5} \, (0.992)} \bigg) = 0.08 \\ &= (-4.77 \, \pm 0.08) - (8.98 \pm 0.01) \\ \sigma_{\mathrm{K}_{3}^{0}} &= \sqrt{(0.08)^{2} + (0.01)^{2}} = 0.08 \\ &\qquad \mathrm{log}_{10} \,\mathrm{K}_{3}^{0} = -13.75 \pm 0.08, \end{split}$$

where  $\gamma_{Sn(OH)_3^-}$  is determined using the Davies expression (equation 3.4) using the appropriate constants for 358.15 K (Table A1, Appendix A) and the ionic strength reported in Table 5.3. The uncertainty in the pH measurement is  $\pm 0.01$  pH unit (1 $\sigma$ ) as described in section 4.2. The  $\sigma$  values, including the final  $\sigma_{K_3^0}$ , are determined according to standard error propagation formulae for logarithmic and addition operations.

Appendix C: Reference Raman Spectra



Figure C1. Raman spectrum of zinc(II) oxide prior to solubility experiments.

Assignments for $ZnO_{(s)}$ [96]		
Raman Shift (cm <sup>-1</sup> )	Peak Assignment	
329	ZnO	
436	ZnO	
582	ZnO	
1151	ZnO	

Table CI. Reference Li	terature Raman Shift
Assignments fo	r ZnO <sub>(s)</sub> [96]
Raman Shift (cm <sup>-1</sup> )	Peak Assignment



Figure C2. Raman spectrum of tin(II) oxide prior to solubility experiments.

<b>Table C2.</b> Reference Literature Raman Shifts for $SnO_{(s)}$ [92]		
Raman Shift (cm <sup>-1</sup> )	Peak Assignment	
110	SnO	
208	SnO	



Figure C3. Raman spectrum of tin(IV) oxide prior to solubility experiments.

<b>Table C3.</b> Reference Literature Raman Shift Assignments for $SnO_{2(s)}$ [93]		
Raman Shift (cm <sup>-1</sup> )	Peak Assignment	
121	$SnO_2$	
472	$SnO_2$	
631	$SnO_2$	
772	$\mathrm{SnO}_2$	

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