

1

Introduction

Water constitutes approximately 70% of the world's surface and 60% of the human body, where aqueous chemical reactions dominate the foundations of life. Even life itself is assumed to have originated in water. For many scientists, life and what has evolved around it are closely coupled to chemistry. For these reasons, the understanding of aqueous chemical systems is of great importance. However, no attempt has been made herein to try and grasp the whole subject of aqueous chemical reactions, but, instead, to focus on reactions associated with the self-ionisation of water and the reactions of water with cations. Such reactions are termed hydrolysis.

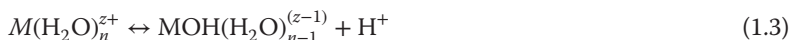
Water can self-ionise according to the reaction



for which the stability (protolysis) constant is given by

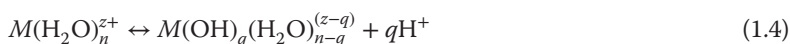
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] \quad (1.2)$$

Water can also hydrate ions present in an aqueous solution where, for example, a metal ion, M^{z+} , will be present as the hydrated ion $M(\text{H}_2\text{O})_n^{z+}$, where z is the charge of the metal ion and n is its coordination number in the aqueous solution. The water bound to the metal ion can also ionise (hydrolyse) to produce a proton and a metal hydroxide complex. The reaction can be written as



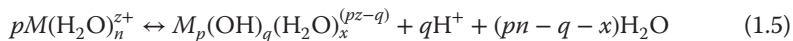
The conditions (i.e. pH) under which the metal ion will hydrolyse is dependent on its physical properties, in particular its ionic charge z and its ionic radius r . Typically, the larger the charge and the smaller the radius, the lower the pH at which the metal will hydrolyse.

Multiple hydrolysis steps are possible as the pH increases, with the species containing the largest number of hydroxide groups likely to be anionic. The reaction for the formation of these species can be expressed by



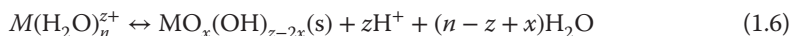
A reasonably unique feature of water bound to metal ions is its ability to ionise to produce polymeric hydrolysis species. A relatively large number of polymeric

species stoichiometries are possible, and those which can form for a particular metal ion are again related to the physical properties of the ion (size, charge, coordination number). These polymeric species are formed according to the reaction



The parameters p and q are the stoichiometric coefficients of the hydrolysis species that has been formed. In the formation of the polymeric species, some water molecules are lost from the reacting metal ion without being hydrolysed as shown in reaction (1.5).

Not only can soluble species be produced from the reaction between metal and hydroxide ions. At a given temperature and under appropriate pH and metal ion concentrations, the hydrated water molecules on the metal ion will hydrolyse, resulting in the formation of a solid hydroxide and/or oxide phase. The formation of such phases can be represented by reaction (1.6):



For odd charged metal ions, the value of x can be fractional having values of 0.5, 1.5 and 2.5 for metal charges of 1, 3 and 5, respectively. In these cases, no hydroxide ions would be in the phase formed, and the phase would be $MO_x(s)$ ($x = 0.5, 1.5$ or 2.5), which is equivalent to $M_2O_{2x}(s)$ (e.g. $AgO_{1/2}(s)$ is equivalent to $Ag_2O(s)$).

Highly charged metal ions (+4 to +6) hydrolyse water so strongly that in aqueous solution most cannot occur as the free metal ion, but appear as oxo-metal ions where one or two oxide ions are bound to the metal ion. Metal ions that fall into this group include titanium(IV), vanadium(IV), technetium(IV) and polonium(IV) (where the ion MO^{2+} is formed); vanadium(V), uranium(V), neptunium(V), plutonium(V) and americium(V) (where the ion MO_2^+ is formed), protactinium(V) (where the ion MO^{3+} is formed); and uranium(VI), neptunium(VI), plutonium(VI) and americium(VI) (where the ion MO_2^{2+} is formed). There are no pentavalent or hexavalent metal ions that exist as the free metal ion and only a few tetravalent ions (e.g. zirconium(IV), hafnium(IV), thorium(IV) and cerium(IV) and possibly tin(IV) and lead(IV)).

The ubiquity of water and metals that are ever present in the water means that hydrolysis reactions are essential aspects of many areas of science, industry and nature. Hydrolysis is an important component in water purification and treatment. In water treatment, many metals are removed from solution by precipitation as solid hydroxide phases which, in turn, may remove other metals and metalloids via adsorption onto the formed solids. In many countries, arsenic is removed from groundwater recovered for drinking via adsorption onto solid iron hydroxide, and knowledge of the precipitation behaviour of magnesium hydroxide is important in thermal desalination processes.

Gibbsite (aluminium hydroxide) is purified from bauxite (impure aluminium oxide) via the Bayer process, where the bauxite is reacted with sodium hydroxide to form the aluminium hydrolysis species, $Al(OH)_4^-$, from which gibbsite can then be recovered. Corundum (aluminium oxide) can then be obtained from the gibbsite via calcination. Pyrolusite (manganese dioxide) is often utilised in the

recovery of uranium, which occurs in ores principally in the form of uraninite (uranium dioxide). The manganese dioxide oxidises ferrous to ferric iron which, in turn, oxidises the uraninite to soluble uranium that is then separated from the ore tailings. The operation of some batteries relies on hydrolytic reactions. The oxidative process in a nickel hydride battery occurs via the interaction of nickel(II) hydroxide with hydroxide ions to produce nickel(III) oxyhydroxide. Conversely, in lithium batteries conditions are formulated such that the hydrolysis of the lithium does not occur. The non-reactivity of chromium alloys and stainless steels results because of the formation of oxide coatings on the surfaces of the alloys or steels.

There are a number of biological processes that rely on hydrolytic reactions. The regulation of iron in the body is carried out by the protein ferritin. This protein stores the iron in the form of a ferric oxyhydroxide phase, removing iron from the body when it is in excess and releasing it when the body is deficient in iron. Manganese has an essential role in photosynthesis. Manganese is a highly redox active metal, and it forms the strongest trivalent hydrolysis species that aids in the production of oxygen from water. Vanadium is an important metal for some marine organisms. These organisms convert vanadium(V) to either vanadium(III) or vanadium(IV), and hydrolysis is an essential component of this conversion process.

There are many different experimental techniques that can be utilised to obtain a hydrolysis constant. Each has advantages and disadvantages and no clear preference can be given to a particular technique, but use of a combination of techniques is generally desired since each can enable the derivation of the stability constants of different species for the single metal ion. However, few studies exist where multiple techniques have been employed successfully, where the relative strengths of each technique have been utilised under specific conditions, enabling a whole set of hydrolysis species (and their associated stability constants) to be derived, including all monomeric species that can be formed by the metal ion as well as all polymeric hydrolysis species.

There are two formulations by which stability or solubility constants can be expressed (see Section 2.1). The first is as a stoichiometric constant where the concentrations of the reacting and produced species are utilised. The second and more important formulation is as a thermodynamic constant where the activities of the species are used. An activity is the product of the concentration and the corresponding activity coefficient, and it is essential to understand models developed for determining activities as well as methods for deriving activity coefficients. Using derived activity coefficients, stoichiometric stability or solubility constants can be used to calculate the thermodynamic constants at the standard state, that is, at infinite dilution and a temperature of 25 °C and pressure of 10^5 Pa. The majority of critical reviews of the stability or solubility constants of metal hydroxide species and phases have derived thermodynamic stability constants.

There have been a number of reviews of hydrolysis reactions that have appeared in the literature. Baes and Mesmer (1976) produced a seminal review of the hydrolysis of metal ions. This was a fundamental study and compilation of hydrolysis

reactions and associated stability constants and derivation of thermodynamic stability and solubility constants. More recently, critical reviews have been undertaken on the thermochemistry of individual metals. The Nuclear Energy Agency of the Organisation for Economic Co-operation and Development began a series of reviews of the thermochemistry of elements related to nuclear waste management in 1992 on uranium (Grenthe *et al.*, 1992). Metals which were the focus of subsequent reviews have included americium, technetium, neptunium, plutonium, nickel, zirconium, thorium, tin and iron (Silva *et al.*, 1995; Rard *et al.*, 1999; Lemire *et al.*, 2001, 2013; Guillaumont *et al.*, 2003; Gamsjäger *et al.*, 2005, 2012; Brown, Curti and Grambow, 2005; Rand *et al.*, 2007). IUPAC also sponsored a series of reviews on environmentally relevant metal ions (Powell *et al.*, 2005, 2007, 2009, 2011, 2013) that included the metal ions mercury, copper, lead, cadmium and zinc. Other reviews have also been undertaken and thermochemical data for hydrolysis species derived. However, the focus of virtually all of these reviews has been on the selection of thermochemical data for the standard state (i.e. zero ionic strength, 25 °C and 10⁵ Pa). There is a dearth of selected information relating to stability and solubility constants relating to the wider range of temperatures over which liquid water exists (i.e. 0–375 °C).

The purpose of the current review was to critically evaluate the hydrolytic reactions of metal ions (cations) and select stability and solubility constants, where available, across the temperature range of 0–375 °C. In carrying out the review, an attempt has been made to be as thorough as possible and utilise as much data as are available in the literature as possible. However, it is not feasible to review all data that have been published on a given metal ion, and, undoubtedly, some studies have been missed. This certainly has not been by intention, and it is possible that the inclusion of some of these missing data may have led to different conclusions being reached for metals where little data exists. For those metals where substantial information is available, or for the protolysis constant of water, the exclusion of some data would unlikely affect the thermochemical data derived or the conclusions reached regarding the speciation of the metal ion.

References

- Baes, C.F. and Mesmer, R.E. (1976) *The Hydrolysis of Cations*, John Wiley & Sons, Inc., New York.
- Brown, P.L., Curti, E., and Grambow, B. (2005) *Chemical Thermodynamics of Zirconium*, vol. 8, Elsevier, Amsterdam, 512 pp.
- Gamsjäger, H., Bugajski, J., Gajda, T., Lemire, R.J., and Preis, W. (2005) *Chemical Thermodynamics of Nickel*, vol. 6, Elsevier, 617 pp.
- Gamsjäger, H., Gajda, T., Sangster, J., Saxena, S.K., and Voigt, W. (2012) *Chemical Thermodynamics of Tin*, vol. 12, OECD Publishing, Paris, 609 pp.
- Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., and Wanner, H. (1992) *Chemical Thermodynamics of Uranium*, vol. 1, North-Holland, 715 pp.
- Guillaumont, R., Fanghänel, T., Neck, V., Fuger, J., Palmer, D.A., Grenthe, I., and Rand, M.H. (2003) *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, vol. 5, Elsevier, Amsterdam, 919 pp.

- Lemire, R.J., Berner, U., Musikas, C., Palmer, D.A., Taylor, P., and Tochiyama, O. (2013) *Chemical Thermodynamics of Iron. Part I*, vol. **13a**, OECD Publishing, Paris, 1082 pp.
- Lemire, R.J., Fuger, J., Spahiu, K., Sullivan, J.C., Nitsche, H., Ullman, W.J., Potter, P., Vitorge, P., Rand, M.H., Wanner, H., and Rydberg, J. (2001) *Chemical Thermodynamics of Neptunium and Plutonium*, vol. **4**, Elsevier, Amsterdam, 845 pp.
- Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjöberg, S., and Wanner, H. (2009) Chemical speciation of environmentally significant metals with inorganic metals. Part 3: The $\text{Pb}^{2+} + \text{OH}^-$, Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} systems. *Pure Appl. Chem.*, **81**, 2425–2476.
- Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjöberg, S., and Wanner, H. (2011) Chemical speciation of environmentally significant metals with inorganic ligands. Part 4: The $\text{Cd}^{2+} + \text{OH}^-$, Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} systems. *Pure Appl. Chem.*, **83**, 1163–1214.
- Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjöberg, S., and Wanner, H. (2005) Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1: the $\text{Hg}^{2+} - \text{Cl}^-$, OH^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} aqueous systems. *Pure Appl. Chem.*, **77**, 739–800.
- Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjöberg, S., and Wanner, H. (2013) Chemical speciation of environmentally significant metals with inorganic ligands. Part 5. The $\text{Zn}^{2+} - \text{OH}^-$, Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} systems. *Pure Appl. Chem.*, **85**, 2249–2311.
- Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjöberg, S., and Wanner, H. (2007) Chemical speciation of environmentally significant metals with inorganic ligands. Part 2. The $\text{Cu}^{2+} - \text{OH}^-$, Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} systems. *Pure Appl. Chem.*, **79**, 895–950.
- Rand, M., Fuger, J., Grenthe, I., Neck, V., and Rai, D. (2007) *Chemical Thermodynamics of Thorium*, vol. **11**, OECD Publishing, Paris, 942 pp.
- Rard, J.A., Rand, M., Anderegg, G., and Wanner, H. (1999) *Chemical Thermodynamics of Technetium*, vol. **3**, Elsevier, Amsterdam, 544 pp.
- Silva, R.J., Bidoglio, G., Rand, M.H., Robouch, P.B., Wanner, H., and Puigdomenech, I. (1995) *Chemical Thermodynamics of Americium*, vol. **2**, Elsevier, Amsterdam, 374 pp.

