

ARE CHEMICAL MODELING AND CHEMICAL THERMODYNAMICS SYNONYMS?

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ABSTRACT

The value of equilibrium constant for a chemical reaction at a specified temperature and pressure can be calculated from the thermodynamic data of the substances involved in the reaction. But in practice it seldom happens that the calculated and experimentally measured values of the constant for a reaction in an aqueous solution at high temperatures and pressures are close together. A comparison of experimental values of the dissociation constant of water (K_w) with the values used in computer programs suggests that the inconsistency in the values of equilibrium constant is one of reasons that the programs do not function well for different types of system. Similarly there is no agreement between experimental and theoretical values of K_w except at 25°C.

A critical analysis of the experimental methods used for the determination of K_w suggests that the values of K_w at high temperature and pressure are not reliable. The thermodynamic data of aqueous species are determined through the experimental values of equilibrium constant. Therefore, the approaches, chemical modeling and chemical thermodynamics should be synonymous. In actuality, the thermodynamic data are not updated for the latest measurement of the equilibrium constants as it is seen for the most important aqueous reaction, the dissociation of water.

INTRODUCTION

Ultimate goal in geochemistry is to understand the physical-chemical processes responsible for the origin and evolution of systems like water-bodies, volcano, mineral alteration and deposit, hydrothermal system, etc. through chemical composition of fluids and rock-mineral assemblages in them. Two synonymous approaches are used in order to formulate and solve reaction mechanisms and processes in the system: *chemical modeling* and *chemical thermodynamics*. In chemical modeling the values of experimental equilibrium constants for a reaction are interpolated to the specified temperature.

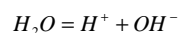
A number of commercial softwares are available which were developed using this approach. Norstrom et al (1979) reviewed over 30 computerized chemical modeling softwares. Every modeling program had been developed for specific purposes; therefore it had its own capacities and limitations. One of the fundamental limitations was the form of alkalinity input and the non-carbonic alkalinity correction and pH calculation. This limitation is still not resolved completely in the improved versions of these commercial computer-software. Although this aspect is extremely important, but it is not a subject of this work.

The alternative approach for calculation of the equilibrium constant is based on the use of chemical thermodynamic data (Helgeson, 1969; Chatarjee, 1991, and others). The approach is more versatile, because it can provide the value of equilibrium constants at any temperature and pressure. A system is not necessarily always be along the saturation curve. Verma (1997) demonstrated through PVT characteristics of water that there would always be a liquid phase in a chemical reaction vessel when the total specific volume is less than the critical volume of water. Additionally, this approach can even be used to calculate the equilibrium constant of reactions that are not feasible to perform in laboratory.

Unfortunately it is rare that the thermodynamically calculated values of equilibrium constant for a reaction in an aqueous solution at higher temperatures (and pressures) are in agreement with the experimentally measured values. To understand this controversy between the approaches and elucidate reasoning for this discrepancy between the calculated and experimental values of equilibrium constant, the self-dissociation of water is considered as an example in this work.

DISSOCIATION CONSTANT OF WATER

In all the aqueous solutions the self-dissociation of water into H^+ (more accurately $\Sigma H(H_2O)_n^+$) and OH^- is the most important chemical reaction. The reaction can be written as



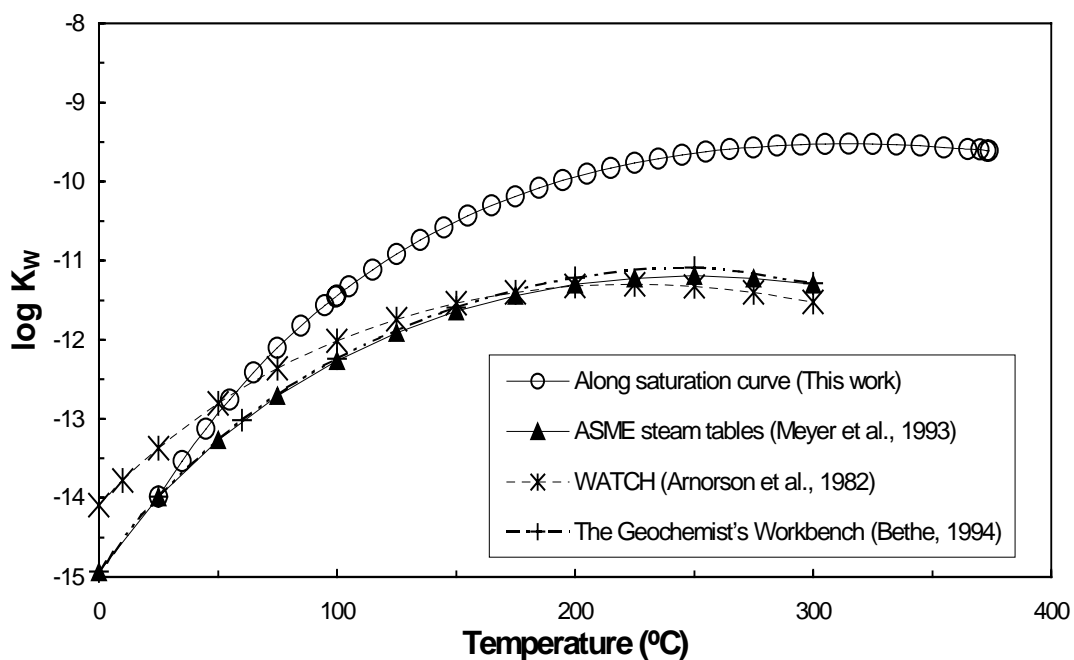


Fig. 1. Experimental values of dissociation constant of water (K_w) together with the polynomials used in the computer softwares WATCH and "The Chemist's Workbench". The thermodynamically calculated values agree only at 25°C.

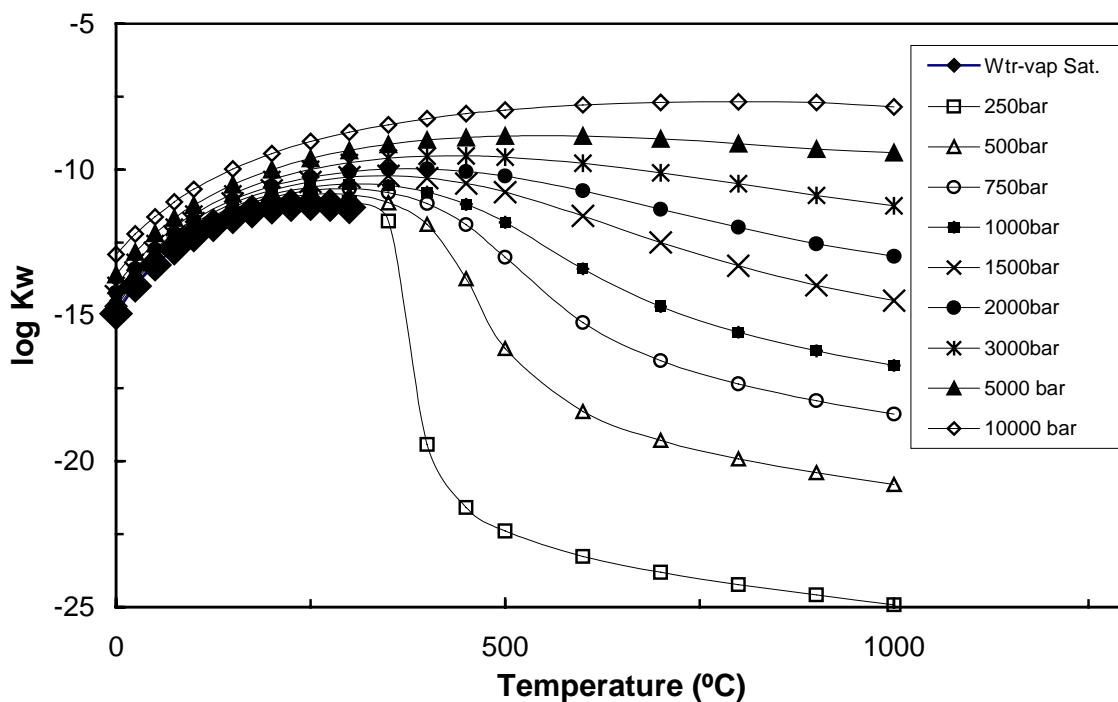


Fig. 2. Most accepted experimental values of the dissociation constant of water (K_w) along the water-vapor saturation curve and in compressed liquid region (Meyer et al., 1993).

The equilibrium constant of this reaction is known as dissociation constant of water (K_w) and may be expressed as

$$K_w = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = [H^+][OH^-]$$

Where the activity of water is taken as unity and the activity coefficients for H^+ and OH^- ions are considered as 1. The term inside the [] represents molar concentration of the specie.

Knowledge of the dissociation constant of water at a specified temperature and pressure is a fundamental parameter in dealing the chemical modeling of any aqueous system in the laboratory or in nature. The values of K_w have been measured experimentally by many workers (ref. cited in Meyer et al., 1993). The most accepted values along the saturation curve up to 370°C are from Sweeton et al. (1974). Meyer et al. (1993) compiled and refitted the dissociation constant values for wide range of temperature and pressure.

Figure 1 shows the temperature dependence of dissociation constant of water along the water-vapor saturation. The data used in "The Geochemist's Workbench" are in good agreement with the experimental values, whereas the polynomial expression for K_w used in WATCH (Arnorsson, 1982) fits better with the experimental values in the temperature range 150-200°C, but there is considerable discrepancy at lower and higher temperatures. Probably, this is one of the reasons that the different computer programs work well for different situations.

The most recent experimental values of K_w along the water-vapor saturation and in the compressed liquid region (Meyer et al., 1993) are plotted in Figure 2. It can be observed that there is increase in K_w with increase in pressure and there are irregularities with temperature. For example, there is drastic drop in K_w around 400°C for the curve corresponding to 250 bar. It is well known that pressure and temperature produce, in general, adverse effect on the physical and chemical properties of any substance with some exceptions. The dissociation constant of water increases with temperature, it should decrease with increase in pressure. In case of K_w the values are increasing with temperature as well as with pressure. The dissociation of water with increasing pressure does not seem reasonable. If it is true, one has to know the basic concept governing this behavior of water, which is never been stated in the literature.

CRITICISM ON THE DETERMINATION OF K_w

From knowledge of K_w and its temperature dependence one can calculate the thermodynamic changes ΔG° , ΔH° , ΔS° and ΔC_p of the standard ionization reaction of water. Conversely, from knowledge of ΔC_p and its temperature dependence and one value of ΔH° and one value of either ΔG° or

ΔS° , K_w and its temperature dependence can be calculated (Clever, 1968). In other words, the values of equilibrium constant and thermodynamic data of any reaction are complementary to each other. Therefore we have to know the reasons for the discrepancy in the values of K_w calculated with the two approaches at higher temperatures.

Three mostly used techniques for determination of K_w are *conductivity*, *emf of cells without transference*, and *thermal measurements* (Clever, 1968). In all the methods, a salt solution like of KCl is used and the measured properties are extrapolated to the zero salt effect, as it is difficult to measure the properties of pure water. The true number of points for extrapolation is very less. For example, Figure 3 shows the experimental values of K_w with the ionic strength of solution as measured by Sweeton et al. (1974). For a neutral KCl aqueous solution with $I=0.5$ m, the concentration of the species K^+ , Cl^- , H^+ , OH^- at room temperature (25°C) will be in the order 0.5, 0.5, 10^{-7} and 10^{-7} m, respectively. The contribution of H^+ and OH^- should be very small even at $I=0.5$ m. So any measured property of solutions having $I>0.5$ m, the contribution of H^+ and OH^- is practically negligible. If we look in Figure 3, there are only two points for each temperature, which have $I<0.5$ m. Therefore, there is still need of creating more reliable experimental data in order to obtain values of equilibrium constant for the most important aqueous solution reaction (i.e. dissociation of water).

Let us look for the second point, the discrepancy between the experimental and theoretical values for K_w . The thermodynamic data are taken from Naumov et al. (1971) and Robie et al. (1978). It is conventional that all the thermodynamic properties of H^+ are considered to be zero at all temperatures and pressures. The properties of OH^- are only reported by Naumov et al. (1971). So, the thermodynamics properties of OH^- are based on the earlier data on the measurement of K_w . Therefore, it is needed to update the thermodynamic data tables. Besides all these facts both the approaches are synonymous as the experimental values of equilibrium constant are used to calculate the thermodynamic properties of all the aqueous species, but the experimental data for K_w and thermodynamic data for OH^- are still needed to be revised for geochemical modeling of any system.

CONCLUSIONS

The chemical modeling and chemical thermodynamics are synonymous, but the values of equilibrium constant and the thermodynamic properties of aqueous species are not always correct and consistent. This is a fundamental limitation of chemical computer softwares that those do not work well for different types of systems. The computer programs are only efficient and fast way of solving

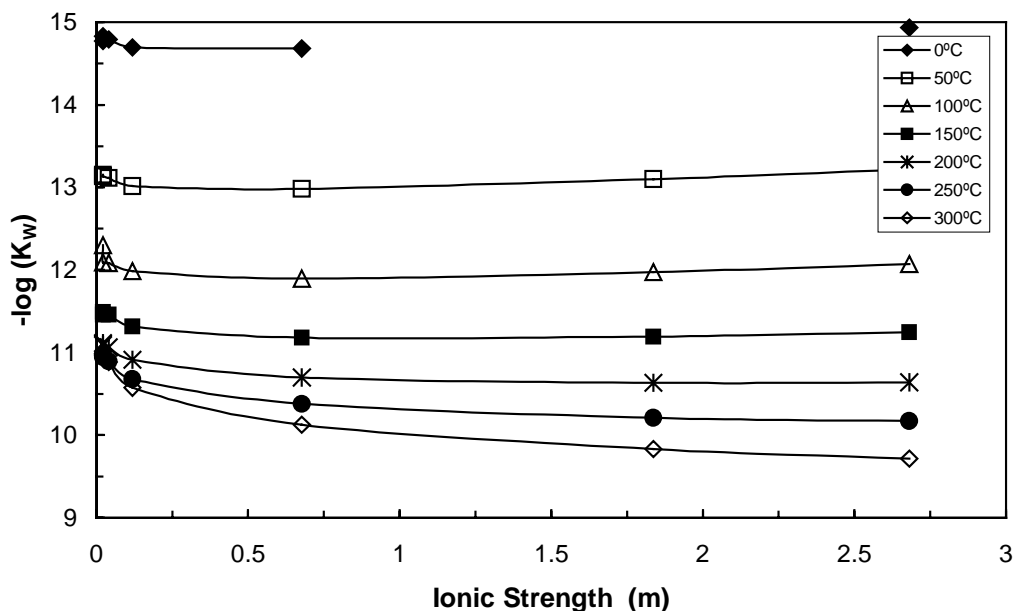


Fig. 3. Values of the dissociation constant of water (K_w) measured by Sweeton et al. (1974) at different ionic strength of solution.

mathematics associated with the chemical equilibrium calculations.

The values of equilibrium constant and thermodynamic data of the most important aqueous solution reaction, the dissociation of water are not reliable and consistent at high temperature and pressure.

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