Chapter 10
pH-Metric Determination of the Equilibrium Constants in Aqueous Heterogeneous Systems

Igor Povar
Institute of Chemistry, Moldova

Oxana Spinu
https://orcid.org/0000-0002-3166-1931
Institute of Chemistry, Moldova

Alfonso Mucci
https://orcid.org/0000-0001-9155-6319
Department of Earth and Planetary Sciences, McGill University, Canada

ABSTRACT

In this chapter, original methods for determining thermodynamic properties such as the equilibrium activity product or solubility product of sparingly soluble compounds and the stability constants of complexes are described. Methods for determining concentration product and solubility are based solely on pH measurements of the saturated aqueous solutions for a known initial composition of the heterogeneous mixture and the equilibrium constants of an arbitrary set of possible side reactions in the solution. In the case of sparingly soluble acids or hydroxides, the determination of the solubility (Sol) and solubility product (KS) is also possible in the presence of other acids and bases of known concentrations. Sol and K^S were calculated from known experimental pH data for a series of hydroxides, acids, neutral and acidic salts $MmHxAy^{(S)}$, as well as basic/mixed salts $Mm(OH)xAy^{(S)}$ of arbitrary composition.

DOI: 10.4018/978-1-7998-7356-3.ch010

INTRODUCTION

We describe the original method for determining thermodynamic characteristics in multicomponent heterogeneous systems such as the equilibrium activity product (K_S^0) or solubility product, equilibrium concentration product (K_S) of sparingly soluble compounds, and the stability constants of complexes. The methods for K_S and solubility (S*ol)* determining are based solely on pH measurements of saturated aqueous solutions for a known initial composition of the heterogeneous mixture and the equilibrium constants of an arbitrary set of possible side reactions in the solution. In the case of sparingly soluble acids or hydroxides, the determination of the solubility *Sol* and solubility product K_S is also possible in the presence of other acids and bases of known concentrations. The quantities of *Sol* and K_S have been calculated from the known experimental pH data for a series of hydroxides, acids, neutral salts $M_mA_{y(S)}$, acidic salts $M_mH_xA_{y(S)}$ and basic/mixed salts $M_m(OH)_xA_{y(S)}$ of arbitrary composition. The elaborated methods for determining the solubility and solubility product of slightly soluble compounds of different nature and arbitrary composition based on pH-metric data allow an essential simplification of the experimental measurement procedure.

The research of the thermodynamic characteristics of complex chemical equilibria and the thermodynamic properties of substances provokes a continuous interest and attracts attention, because the thermodynamic data have both scientific and practical importance (Bénézeth et al., 2018; Gácsi et al., 2016; Sandeepa et al., 2018; Scholz & Kahlert, 2015). Their reciprocal relations with different physicochemical properties constitute the basis for the systematization of experimental material, the substantiated search for the optimal conditions of technological processes or the repression of unwanted or unknown laws, as well as for solving other practical or theoretical tasks. Thus, for example, the regulation of thermodynamic parameters allows to turn the different processes in the desired direction and to synthesize the substances with certain properties. At the same time, for optimal realization of process and the regulation of the composition of a system, it is necessary that in the field of optimal concentrations it would have a minimum sensitivity and high buffering action in relation to the substance in force (Tenno et al., 2018; Zhang et al., 2015). The thermodynamics of equilibrium processes play an essential role in the design of technological schemes for the synthesis and purification of substances (Pohl, 2020). Due to the complexity and large volume of experiments, a current task is to develop and apply the thermodynamic research methods to describe the complex experiments and predict them in those cases where the experiment is impossible or difficult to perform.

The solubility method is one of the oldest research methods of the processes of complexes formed in solution. The general methods for measuring solubility are well described in the literature (Pazukhin & Kudryavtsev, 1990; Schwertmann, 1991). The exact composition of precipitate must be known in the solubility method and remain unchanged during the experiment. Although the measurement of solubility usually includes the analysis of saturated solution, the experiments were also performed to mix the solutions of known concentration with the subsequent determination of the mass of precipitate formed (Pazukhin & Kudryavtsev, 1990). The composition and stability of insoluble and soluble species are determined by the mathematical analysis of the solubility curve.

In the general case, two types of experimental data were used: a) solubility as a function of the initial concentrations of substances in solution or b) measurement of solubility is accompanied by the determination of one or several additional functions of the solution composition, more commonly pH. The determination of the solubility product is essentially simplified if, at the same time as the solubility, the