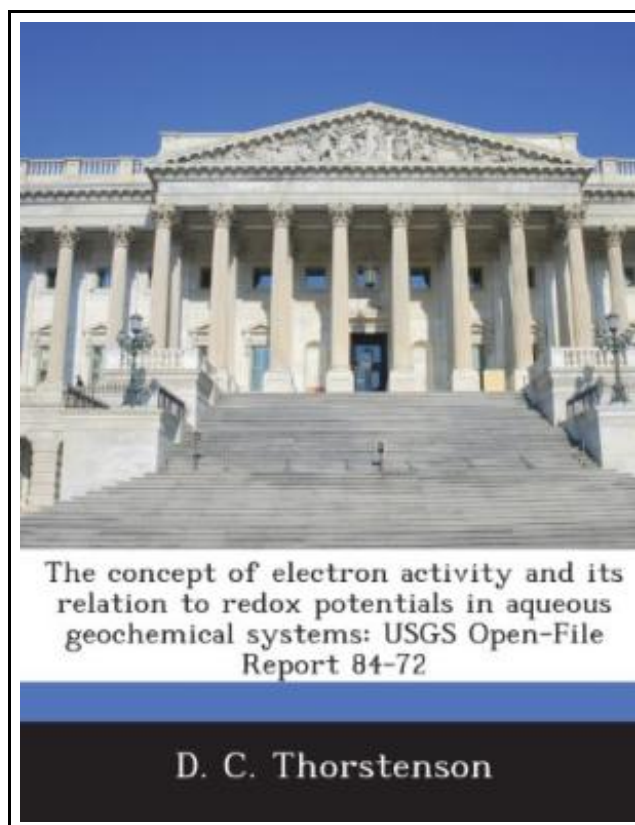


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Bibliogov, United States, 2013. Paperback. Book Condition: New. 246 x 189 mm. Language: English . Brand New Book ***** Print on Demand *****.The definition of a formal thermodynamic activity of electrons in redox reactions appears in the literature of the 1920 s. The concept of p_e as $-\log$ (electron activity) was introduced by Jorgensen in 1945 and popularized in the geochemical literature by Sillen, who considered p_e and pH as master variables in geochemical reactions. The physical significance of the concept of electron activity was challenged as early as 1928. However, only in the last two decades have sufficient thermodynamic data become available to examine this question quantitatively. The chemical nature of hydrated electrons differs greatly from that of hydrated protons, and thermodynamic data show that hydrated electrons cannot exist at physically meaningful equilibrium concentrations under natural conditions. This has important consequences for the understanding of redox processes in natural waters. These are: (1) the analogy between p_e and pH as master variables is generally carried much further than is justified; (2) a thermodynamically meaningful value of redox potential cannot be assigned to disequilibrium systems; (3) the most useful approach to the study of redox characteristics is the analysis and study of multiple redox couples in the system; and (4) for all practical purposes, thermodynamically defined redox potentials do not exist (and thus cannot be measured) in natural waters. The overall implication for natural systems is that, in terms of redox reactions, each case must be considered on an individual and detailed basis. Field studies would appear to be a mandatory part of any site-specific study; conclusions regarding redox processes cannot be based solely on electrode measurements or thermodynamic stability calculations.



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