

Gas adsorption microcalorimetry: Probing energetics of oxide surfaces

S.V. USHAKOV, N. DALALO AND A. NAVROTSKY

Thermochemistry Facility and NEAT ORU, University of California at Davis, One Shields Avenue, Davis, CA 95616, USA (anavrotsky@ucdavis.edu)

There is a paucity of data on direct measurement of energies of gas adsorption on mineral surfaces. Two new approaches for volumetric static and pulse dynamic adsorption microcalorimetry were developed at the UC Davis Thermochemistry Facility. The dynamic technique for chemisorption microcalorimetry implemented based on Netzsch 449 instrument, providing differential scanning calorimetry (DSC) and thermogravimetry (TG) capabilities. Pulses of the adsorbate are introduced in a gas constantly flowing through the sample chamber. The adsorbed amount is recorded as a sample weight change. Heat of adsorption is derived from the DSC trace.

The instrumental design for static volumetric adsorption microcalorimetry consists of a modified commercial surface area analyzer (Micromeritics ASAP 2020) and a Calvet-type twin microcalorimeter (Setaram DSC 111). The surface area analyzer provides automated dosing and measurement of adsorbed amounts of water vapor or gas of interest. The microcalorimeter records corresponding heat effects. The sensitivity of the instruments enables measurements on the samples with total surface area less than 5 m².

Examples of application of both methods will be given. For monoclinic zirconia and hafnia samples annealed at 800 °C in vacuum, heats of water adsorption on most energetic sites were measured using volumetric adsorption technique and found to be in the range -274 to -291 kJ per mole of water. For tetragonal ZrO₂ and HfO₂ treated in the same conditions, the initial heat values were measured as -156 and -119 kJ per mole of water. Smaller heats of water adsorption on the surface of tetragonal phases of ZrO₂ and HfO₂ support arguments on the thermodynamic nature of their stabilization at ambient by a surface energy term. Complementing oxide-melt solution calorimetry techniques with adsorption microcalorimetry data allows for experimental measurements of surface energies.

The surfaces of iron-bearing minerals: Key reactive substrates in Earth systems

D.J. VAUGHAN, R.S. CUTTING AND P.L. WINCOTT

School of Earth, Atmospheric and Environmental Sciences, and Williamson Research Centre for Molecular Environmental Science, University of Manchester, Manchester M13 9PL, UK
(David.Vaughan@manchester.ac.uk)

As the most geochemically abundant of the transition metals, iron occupies a unique position in Earth systems science. The richness and diversity of the mineral chemistry of iron is particularly well illustrated by the binary oxides/hydroxides and the sulfides of this metal, phases which also span a key redox boundary in much of the near-surface sedimentary environment.

Recent experimental studies in Manchester have been concerned with exploring the nature of iron oxide and sulfide mineral surfaces at the molecular scale, using both imaging and spectroscopic methods. The surface structures and reactivities of well crystallized phases such as magnetite, haematite and pyrrhotite have been clarified by careful scanning probe studies in UHV; this has included direct observation of reactions with oxygen, water and simple organic molecules such as formic acid, pyridine and carbon tetrachloride. On the other hand, reactions at the mineral – aqueous solution interface of very fine particle oxyhydroxides (such as goethite) and sulfides (such as mackinawite) with a wide range of dissolved metals have been studied more indirectly, using techniques such as X-ray absorption and X-ray photoelectron spectroscopies. Systems investigated have included those involving reaction with certain transition metals (eg Mn, Co, Ni, Cu), heavy metals (eg Cd, Hg) and nuclear metals (eg U, Np). What emerges from these studies is a diversity of behaviour, with phenomena including surface complexation, partial and total replacement reactions, and precipitation (in some cases involving redox processes).

This behavioural diversity is further extended when the reactions entail the activities of micro-organisms, and one goal of current work is to understand the mechanisms of the *direct* reactions between the solid mineral surface and microbes such as *Geobacter*. Examples of the surface chemistry of iron-bearing minerals will be presented, and the current state of knowledge discussed.