Size-induced shifts in oxidation-reduction phase equilibria in nanophase transition metal oxides

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It is now well established that difference in surface energies can alter the relative free energies of different polymorphs, causing size driven thermodynamic crossovers in phase stability at the nanoscale. It has also been shown that, because oxyhydroxides generally have smaller surface energies than oxides, dehydration equilibria, e.g. goethite to hematite plus water, can shift to higher temperature by as much as 100 K at the nanoscale (4). A general formulation of the effect of particle size on chemical equilibria among solid phases is that increasing surface area will favor the phase assemblage of lower surface energy.

There is now new thermochemical evidence for strong thermodynamic shifts in the position of oxidation-reduction (redox) equilibria in oxides at the nanoscale. Using new calorimetric data on surface energies in the cobalt–oxygen system, we show that the thermodynamic phase field in oxygen fugacity–temperature space of the divalent rocksalt oxide CoO is substantially narrowed at the nanoscale, bringing the reduction to Co metal to higher oxygen fugacity and the oxidation to Co_3O_4 spinel to lower oxygen fugacity at a given temperature. Metals generally have lower surface energy than oxides and we present evidence that spinels have lower surface energy than rocksalt oxides. Thus the contraction of the stability field of the divalent oxide, MO, relative to the metal, M, and the spinel M_3O_4, is probably a general phenomenon. In the iron-oxygen system, wustite, $Fe_{1-x}O$, is thermodynamically unstable with respect to iron and magnetite, Fe_3O_4, below the melting point of bulk wustite (1650 K) for particle sizes below 16 nm, in contrast to being stable above 850 K for the bulk. These size-driven redox changes have implications for material preparation and characterization, catalysis and the splitting of water in the presence of transition metal oxide nanoparticles, as well as for environmental, geological, and biological redox reactions.

Thermodynamic issues in nanoscale actinide oxides

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Colloids, clusters, and nanoparticles provide major possible routes for the transport of radionuclides, including actinides, in the aqueous environment. Thus understanding the energetics of nanoscale oxides is critical to predicting their reactivity and dissemination. Two factors are particularly important - the dependence of energetics of a phase on its particle size (which can influence its solubility as well as its kinetics of dissolution/precipitation) and the influence of particle size on the thermodynamics of redox equilibria.

We have extended our studies of surface energies of nanophase oxides to thoria. The surface energy and enthalpy of water adsorption of thoria nanoparticles with cubic fluorite structure have been studied for the first time by direct calorimetric methods. Four samples with particle size 4.7, 5.9, 10.1, and 17.3 nm were prepared by co-precipitation method and surface enthalpy was determined from the variation in enthalpy of drop solution with surface area taking measured integral enthalpy of water adsorption (–81.1 ± 3.7 kJ/mol) into account. Surface enthalpies are 1.3 ± 0.4 J/m^2 for the hydrated surface and 1.9 ± 0.3 J/m^2 for the anhydrous surface. These preliminary values are similar to surface energies of C-type Y_2O_3 (1.3 ± 0.2 J/m^2 for the hydrated surface and 1.7 ± 0.1 J/m^2 for the anhydrous) as well as those of Y-doped zirconia with fluorite structure (0.8 – 1.3 J/m^2 and 1.2 – 1.8 J/m^2 for hydrous and anhydrous surfaces respectively for variable yttria content). Preliminary data for Y-doped HfO_2 (1.0 – 1.5 J/m^2 and 1.8 – 2.4 J/m^2 for hydrous and anhydrous surfaces respectively) also are similar to the values for ThO_2. Thus it appears that the surface energy of fluorite-structured oxides does not depend strongly on the nature of the cation (or the metal-oxygen distance, ionic radius, or lattice parameter) and we predict similar values for UO_2 and other tetravalent actinide oxides.

We recently found that differences in surface energies among phases of different oxidation state (e.g. Co metal, CoO, and Co_3O_4) can significantly changethe positions of redox equlibria. Though we do not yet have data for uranium phases, we suspect that similar effects will be seen, with small particle size thermodynamically favoring the phase assemblage of lowest surface energy. Whether such effects can significantly shift uraninite - uranyl mineral equilibria depends on the difference in surface energy between these phases, which we plan to measure in the future.