HIGH TEMPERATURE REACTION CALORIMETRY APPLIED TO METASTABLE AND NANOPHASE MATERIALS

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Abstract

Materials with high surface areas and small particle size (nanophases), metastable polymorphs, and hydrated oxides are increasingly important in both materials and environmental science. Using modifications of oxide melt solution calorimetry, we have developed techniques to study the energetics of such oxides and oxyhydroxides, and to separate the effects of polymorphism, chemical variation, high surface area, and hydration. Several generalizations begin to emerge from these studies. The energy differences among different polymorphs (e.g., various zeolite frameworks, the α- and γ-alumina polymorphs, manganese and iron oxides and oxyhydroxides) tend to be small, often barely more than thermal energy under conditions of synthesis. Much larger contributions to the energetics come from oxidation-reduction reactions and charge-coupled substitutions involving the ions of basic oxides (e.g., K and Ba). The thermodynamics of hydration involve closely balanced negative enthalpies and negative entropies and are very dependent on the particular framework and cage or tunnel geometry.

Keywords: calorimetry, manganese oxide, nanophase, thermodynamics, zeolite

Introduction

Low temperature synthesis, whether in nature, industry, or the research laboratory, often produces a wealth of polymorphs. The phases produced are often of varying particle size, crystallinity, and hydration. Though often metastable and kinetically controlled, these materials offer a 'comparative laboratory' for the relation of structure and energetics far richer than the relatively small number of stable phases produced under high temperature equilibrium conditions. This paper discusses both the calorimetric methodology and the energetic trends seen in two groups of metastable oxides: zeolites and the oxides and oxyhydroxides of manganese, iron, and aluminum.

Calorimetric methodology

Our basic calorimetric technique involves dissolving a mineral, phase assemblage, or oxide mixture in molten lead borate at 700 or 800ºC [1, 2]. The difference in the heat of solution (if the sample is pre-equilibrated at calorimetric temperature

and then dissolved) or the difference in heat of drop solution (if the sample is dropped into the solvent from room temperature) between reactants and products gives the enthalpy of reaction. We first concentrated on developing oxide melt solution calorimetry as a means of studying phases containing water and carbon dioxide. The issue addressed was the final state of the H_2O or CO_2 evolved when a hydrous or carbonated mineral dissolved in the oxide melt. Using several thermochemical cycles, we showed that a thermodynamically reproducible final state, with the volatile evolved completely as gas and purged out of the calorimeter, could be achieved when a flowing gas stream (air, argon, or nitrogen) was passed through the calorimetric chamber continuously before, during, and after the dissolution process [3]. This development allowed the determination of heats of formation of a series of carbonates, amphiboles, micas, hydrous oxides and oxyhydroxides, zeolites, and clays [2].

We have fine-tuned the calorimetric procedures in a number of ways. First, by careful pressing and handling of oxide pellets, and the use of alumina pellets as calibrants [4], we have standardized dissolution procedures for 5, 10 and 15 mg samples and eliminated the need for sample encapsulation and the associated large heat effects associated with the capsule drops. We thus have much greater sensitivity, reproducibility, and accuracy for small samples. We can handle even smaller samples (1–2 mg) using a special ultrasensitive calorimeter [5].

The ability to dissolve small samples also lets us perform calorimetry on refractory oxides which were too slow to dissolve, or which formed local saturation and precipitated phases, when larger samples (20–50 mg) were used in earlier studies
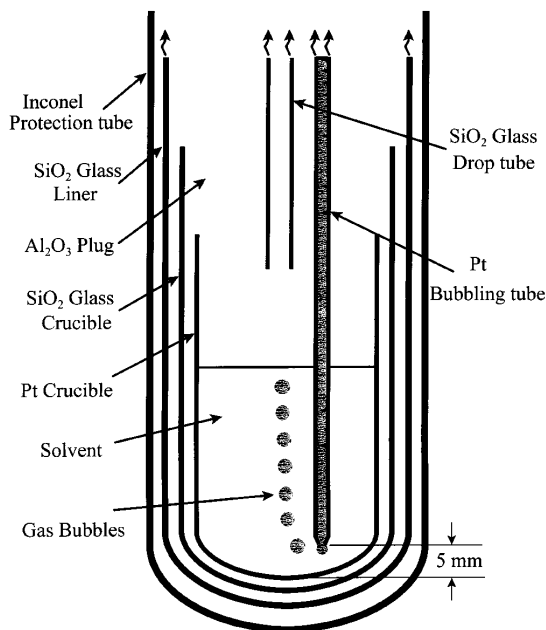

Fig. 1 Schematic representation of drop solution calorimetric arrangement with gas bubbling through and over solvent

(see [1] for a list, now very outdated, of materials which were considered unsuitable for lead borate calorimetry twenty years ago). We now are able to work with TiO_2, ZrO_2, and rare earth oxides, using lead borate as solvent [6, 7]. Another improvement has been the application of gas bubbling through (as well as over) the solvent (Fig. 1). This serves to control oxygen fugacity in the melt and, equally importantly, to stir the solvent effectively (and with no spurious calorimetric signals like those from mechanical stirring). Maintaining high oxygen fugacity by bubbling oxygen through the solvent also has led to success in an oxidative dissolution process for nitrides [8] and for Fe^{2+} bearing carbonates [9]. These improvements have greatly extended the chemical variety of systems for which we can obtain reliable thermochemical data.

Zeolites

Zeolites are framework aluminosilicates with interconnected structural pores through which cations, water molecules, gases, and organics can migrate. Synthetic zeolites form the basis of the multimillion dollar catalysis industry. Natural zeolite minerals can form massive deposits and are major phases at Yucca Mountain, Nevada, the proposed nuclear waste repository. Because of their sorption and ion exchange capacity, they are viewed as an important barrier to radionuclide migration.

To understand the thermodynamics of zeolites, one must consider their structural and compositional complexity as arising from a number of competing factors. We have chosen to consider, separately and systematically, the effects of framework type, of charge-balanced cation substitution, and of hydration. The effect of framework topology in the simplest possible chemical system, namely pure silica, was first studied [10]. The major finding (Fig. 2) is that the difference in energy among
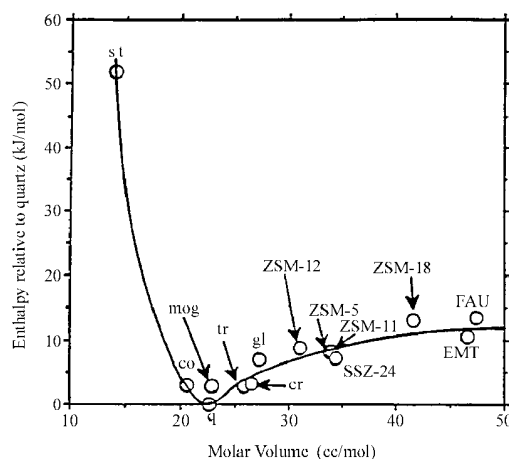
Fig. 2 Enthalpy of silica polymorphs relative to quartz; st – stishovite, co – coesite, q – quartz, mog – moganite, tr – tridymite, gl – glass, cr – cristobalite, other symbols (ZSM-12, ZSM-5, ZSM-11, ZSM-18, SSZ-24, EMT, FAU) refer to different zeolitic frameworks, all of SiO_2 composition

different frameworks is small SiO_2. Zeolites span an energy range of only about 7 kJ mol^{-1}, lying 7–14 kJ mol^{-1} above quartz and comparable in energy to amorphous silica. Similar small energy differences were found for aluminophosphate zeolites [11]. Even for anhydrous calcium aluminosilicate zeolites (metaleonhardite [4] and chabazite [12]) and sodium aluminum faujasites [13], the enthalpy difference between the zeolite framework and the dense aluminosilicate assemblage (feldspar plus quartz or nepheline plus feldspar), on a two-oxygen basis, is only 14–18 kJ mol^{-1}. The enthalpies of the calcium and sodium aluminosilicate anhydrous zeolites are comparable to those of the corresponding glasses. Thus such frameworks are modestly metastable with respect to dense isocompositional assemblages. Available entropy data suggest that the $T\Delta S$ term does not change these systematic trends significantly at 300–400 K.

The effect of charge-balanced substitution

$$Si^{4+} \rightarrow Al^{3+} + (1/n)\, M^{n+}$$
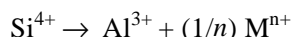
appears similar in zeolite frameworks and in aluminosilicate glasses [4, 12, 13]. Thus the large body of data amassed previously for aluminosilicate glasses is very useful in systematizing the effects of cation substitution and ion exchange in zeolites.

A major influence on zeolite stability, and the factor which is most variable for different frameworks and bulk compositions is hydration: its extent and energetics. The incorporation of water is generally exothermic in enthalpy and negative in entropy relative to bulk liquid water at 298 K. Data for some Ca zeolites are shown in Fig. 3. It is clear that hydration stabilizes the zeolite with respect to the dense anhydrous aluminosilicate phase as well as with respect to amorphous phases. This stabilization diminishes with increasing temperature because of the large negative entropy associated with water, especially water vapor above 373 K. Data for ion-exchanged leonhardites [14] and chabazites [12] show similar trends.
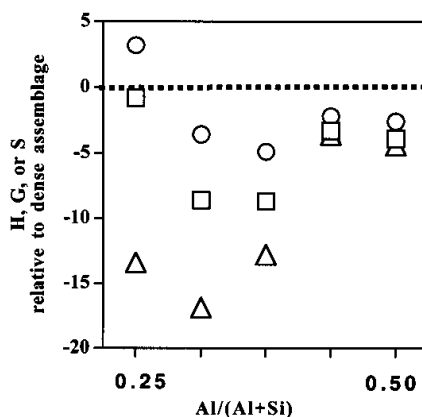
Fig. 3 Enthalpy, entropy, and free energy of formation of calcium aluminosilicate zeolites from anorthite ($CaAl_2Si_2O_8$), quartz (SiO_2), and water (H_2O) at 298 K. □ – enthalpy (kJ mol^{-1}), O – free energy (kJ mol^{-1}), △ – entropy (J mol^{-1} K^{-1})

Oxides and oxyhydroxides

Mineral surfaces are generally hydrated. Mineral dissolution often produces oxides and oxyhydroxides, often fine-grained or colloidal in nature. These phases containing iron, aluminum, and manganese are ubiquitous in the environment, in soils, streams, and sediments. They trap and/or transport pollutants. Polymorphism and poor crystallinity abound. Understanding the energetics of these phases and their surfaces is a starting point for understanding their transformations and rates and mechanisms of reaction. Manganese oxides are also important in batteries, catalysis, molecular sieves, and other materials applications. We began a calorimetric study of polymorphism in the Mn–O–H system. As in the zeolites, the enthalpy differences among MnO_2 and $MnOOH$ polymorphs are very small and do not vary systematically with tunnel size [15]. The oxidation state and tunnel cation have a larger effect on energetics, however [16, 17].

Similar studies have been done for some iron oxides and oxyhydroxides. The data (Figs 4 and 5) [18] show similar trends to the manganese oxides; energetic metastability of polymorphs is very small.
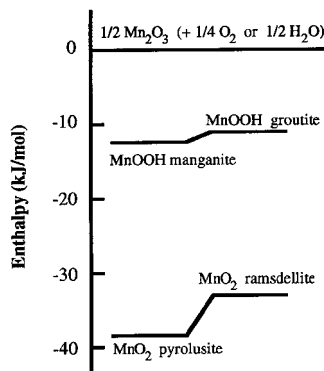

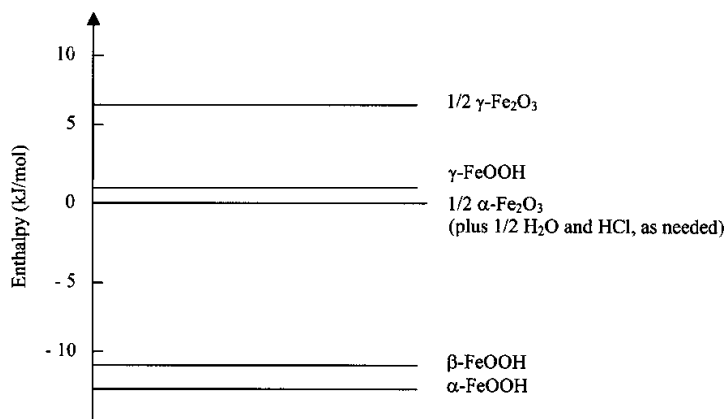**Fig. 4** Enthalpy relations among MnO_2 and $MnOOH$ polymorphs

Fig. 5 Enthalpy relations among Fe_2O_3 and FeOOH polymorphs

The effect of particle size (surface energy) on the energetics of competing polymorphs can be substantial. McHale *et al.* [19, 20] have demonstrated that nanophase γ-alumina is indeed energetically stable with respect to nanophase α-alumina because the spinel form has a lower surface energy than the corundum polymorph. Such energy 'crossovers' are suspected in other materials, notably Fe_2O_3, TiO_2, and ZrO_2.

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