Thermodynamic properties of kornelite ($Fe_2(SO_4)_3{\cdot}{\sim}7.75H_2O$) and paracoquimbite ($Fe_2(SO_4)_3{\cdot}9H_2O$)

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Hydrated ferric sulfates are abundant phases in many areas affected by acid mine drainage waters, in anoxic soils, and industrial waste. The precipitation of these phases exerts a control not only over Fe and sulfate ions in the waters but also over toxic metals and metalloids by coprecipitation or adsorption. Understanding the formation and stability of these phases plays an important role in estimating and modelling their solubility relationships and hence the scavenging effect of hazardous ions. In this work, we measured enthalpies of formation of kornelite ($Fe_2(SO_4)_3{\cdot}7.75H_2O$) and paracoquimbite ($Fe_2(SO_4)_3{\cdot}9H_2O$) by acid solution calorimetry at $T = 298.15$ K. The samples were characterized chemically, and structurally by single-crystal, in-house powder, and synchrotron powder X-ray diffraction. From the single-crystal diffraction data, we were also able to locate the H atoms and decipher the H-bonding system in kornelite. The measured enthalpies of formation from the elements (crystalline Fe, orthorhombic S, ideal gases O_2 and H_2) at $T = 298.15$ K are -4916.2 ± 4.2 $kJ{\cdot}mol^{-1}$ for kornelite and -5292.7 ± 4.2 $kJ{\cdot}mol^{-1}$ for paracoquimbite. We have used several algorithms to estimate the standard entropy of the two phases. Afterwards, we calculated their Gibbs free energy of formation and constructed a phase diagram for kornelite, paracoquimbite, $Fe_2(SO_4)_3{\cdot}5H_2O$, and $Fe_2(SO_4)_3$ as a function of temperature and relative humidity of air. Our calculations show that the topology of the phase diagram is very sensitive to the entropy estimates and a reliable construction of a phase diagram must await better constraints on entropy or Gibbs free energy of formation. A possible remedy of this problem is the measurement of entropy, even though it is difficult owing to the high H_2O concentration within the structures of these compounds.

Air quality in a changing climate

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Changes in the climate of our planet will be accompanied by changes in the major meteorological factors affecting air quality: temperature, vertical stability of the atmosphere, precipitation, humidity, cloudiness and wind patterns. To assess these climate change impacts, we have developed the Global-Regional Climate-Air Pollution modelling System (GRE-CAPS) by coupling global and regional models of air quality and meteorology. The GRE-CAPS system is capable of predicting ozone and particulate matter (PM) mass concentrations and is currently being extended to treat mercury and ultrafine particle number concentrations as well.

Climate change is expected to make the ozone pollution problems faced by developed and developing regions worse, causing more frequent and severe pollution episodes and a longer ‘ozone season’. Major factors contributing to the degradation in ozone air quality include shifts in the PAN-NOx equilibrium at higher temperatures, increased emissions of biogenic VOCs, increased HOx abundance under more humid conditions, and increases in background ozone due to higher methane levels. In contrast, the situation for particulate matter (PM) is much more complex and the sign and magnitude of the climate effects will vary regionally and seasonally. Climate change will likely force additional emissions reductions to improve or maintain current air quality.