

The aqueous chemistry of uranium minerals. Part I. Divalent cation zippeïte

DAVID F. HAACKE AND PETER A. WILLIAMS

Department of Chemistry, University College, Cardiff, CF1 1XL

SYNOPSIS

FREE energies of formation of divalent metal ion zippeïtes, $M_2(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot n\text{H}_2\text{O}$, $M = \text{Mg, Co, Ni, Zn}$ have been determined from solution studies and metal speciation calculations, in water. It is found that in the compounds, the number of molecules of water of crystallization is equal to 8. This is at variance with a previous report (Fron del *et al.*, 1976), but it has been found that some at least of the water content of zippeïte is either non-essential or very loosely bound in the structure. Based on the octahydrate formulation, ΔG_f° values are -13506 , -12695 , -12683 and -12870 ± 4 kJ mol⁻¹ for the Mg, Co, Ni and Zn end-members, respectively. Almost all of the differences in the ΔG_f° values are accounted for by those values for the metal ions alone with the exception of Zn-zippeïte where a discrepancy of some 22 kJ mol⁻¹

is found. Even this value is small however, and the chemical studies indicate that extensive mutual solid solution between all end members is to be expected. These findings agree perfectly with observations on the composition of naturally occurring zippeïte minerals of this group.

REFERENCE

Fron del (C.), Ito (J.), Honea (R. M.), and Weeks (A. M.), 1976. *Can. Mineral.* **14**, 429-36.

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THE AQUEOUS CHEMISTRY OF URANIUM MINERALS.

PART I. DIVALENT CATION ZIPPEITE

D.F. Haacke and P.A. Williams

Department of Chemistry, University College,
Cardiff, CFI 1XL.

Summary. Mg-, Co-, Ni- and Zn-zippeite have been synthesised and their ΔG_f° values determined by solution chemistry. ΔG_f° values are -13506, -12695, -12683 and -12870 (± 4) kJ mol⁻¹ respectively. The differences largely arise from the individual cations and a chemical basis for previously suggested solid solution between the end-members has been shown. Divalent cation zippeite appears to contain at least some extraneous water in the natural state and it is suggested that this series should be viewed in the light of the compounds' retention of 8 moles of water of crystallization.

Introduction. The uranium sulphates were among the first naturally occurring uranium minerals to be recognised and were known in the early part of the nineteenth century. John (1821) described the first mineral of this group and the name zippeite was conferred upon a basic sulphate-containing uranium mineral by Joachimsthal by Heisinger (1845). While zippeite and zippeite-like minerals have since been described from numerous localities, the exact chemical nature of the species has long been in doubt. Much confusion was caused by the belief that zippeite was a hydrated basic uranyl sulphate. It has since been shown, however, that early analyses were incomplete and the zippeite contains various mono- and divalent cations as well as the uranyl ion in the crystal lattice. The mineralogy has been put on a firm footing with the recent work of Prondel et al. (1976), who carried out a systematic study of the zippeite group and confirmed their conclusions through comparisons of naturally-occurring material with synthetic phases.

In these laboratories, we have recently begun a number of studies of the secondary minerals of uranium with a view to establishing their stability, the chemical basis of interconversion of one into another, and the aqueous solution chemistry of the many and various compounds which are known to occur. In this paper, the first of a series, we report results of a study of the chemical stability of zippeite containing a variety of divalent alkaline earth and transition metal cations.

Experimental. Magnesium-, cobalt-, nickel- and zinc-zippeite were prepared using the methods of Prondel et al. (1976). It was found that the minerals could most easily be obtained by precipitation from solutions that were nearly saturated with uranyl sulphate as well as the corresponding divalent metal sulphate. The compounds were filtered at the pump, washed well with cold water and dried over silica gel at atmospheric pressure.

Powder X-ray studies were carried out on samples in 0.3mm capillaries using Ni-filtered Cu-K_α radiation with a 114.5mm camera. All four compounds are isomorphous and agree well with the published data of Prondel et al. (1976). Thermogravimetric analyses were performed using a Stanton Redcroft TG750 temperature programmed thermogravimetric balance.

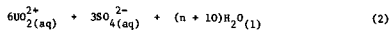
For the solution studies boiled-out, CO₂-free distilled water was added to pre-cleaned, tightly-stopped flasks which contained more than sufficient solid mineral to saturate the solutions and a magnetic follower. No gaseous phase was added to the flasks for the duration of the experiments. The reaction vessels were placed in a thermostatted water bath (25.0 ± 0.10) and stirred occasionally until equilibrium was reached (about 2-3 weeks, defined by constant pH reading). Samples of the solutions were then removed, the pH recorded using an Orion 470A pH meter, and aliquots filtered through pre-washed Whatman GF/F fibreglass filter papers to remove any particles greater than 0.7 microns in size. The solutions were then analysed using a Varian AA-6 atomic absorption spectrophotometer fitted with a carbon rod analyser for the appropriate divalent cations. The total concentrations of dissolved species were calculated from the stoichiometry of the mineral. Analytical results are given in Table 1. Separate experiments establish that the overall errors in the calculated ΔG_f° values of the minerals (below) are less than 4 kJ mol⁻¹.

In order to derive ΔG_f° values for the zippeite phases species distributions in the solutions in equilibrium with the solids were calculated using the well-tested programme COMICS (Ferrin and Sayce, 1967). Species included in the calculations were UO₂(OH)₂, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₆⁴⁺, UO₂SO₄, UO₂(SO₄)₂²⁻, UO₂(SO₄)₃⁴⁻, HSO₄⁻ and MOH⁺ (M = Mg, Co, Ni, Zn), M(OH)₂²⁺, M(OH)₃³⁺ and H₂O₂²⁺ (M = Co, Ni, Zn), M₂(OH)₄⁴⁺ (M = Mg, Co, Ni), Zn₂(OH)₆²⁺ and HSO₄⁻. Values of the equilibrium constants for the hydrolysed metal species were taken from Bass and Messer (1976). Other values are those given in Truesdell and Jones (1974), Smith and Martell (1976), Langmuir (1978), and Helgeson (1967). For the reaction (1), a value of log K = 5.0 was chosen. Accurate values for this equilibrium

$$UO_2^{2+}(aq) + 3SO_4^{2-}(aq) \rightleftharpoons UO_2(SO_4)_3^{4-}(aq) \quad (1)$$

constant at zero ionic strength are not available. At ionic strength 1.0 mol dm⁻³, and at 200, a log K value of 3.7 has been reported (Smith and Martell, 1976). In any case, the computed species distributions (below) indicate that the equilibrium concentrations of UO₂(SO₄)₃⁴⁻ are practically negligible and hence errors in the value for log K likely to be involved have no bearing upon the conclusions of this study.

Because of the low concentrations of dissolved species no corrections to the equilibrium constants used in the COMICS calculation were made for ionic strength, although in the final calculation of ΔG_f° for the dissolution reactions individual ionic activity coefficients were included. These were estimated using the modified Debye-Hückel equation of Truesdell and Jones (1974). Thermodynamic calculations were carried out in the following way. Once the free metal ion concentrations had been computed, the equilibrium constant, K, for the reaction (2) was calculated. (3), the hydrogen ion activity, a_{H⁺}, being directly available from the pH measure-

$$M_2(UO_2)_6(SO_4)_3(OH)_{10}nH_2O(s) + 10H^+(aq) \rightleftharpoons 2M^{2+}(aq) +$$


ments. ΔG_f° values for the reactions were then calculated from the values

$$K = \frac{(a_{M^{2+}}^2 a_{UO_2^{2+}}^6 a_{SO_4^{2-}}^3 a_{OH}^{10} a_{H_2O}^{n+10})}{(a_{H^+}^{10})} \quad (3)$$

(a_i refers to the activity coefficient of the ion i.)

TABLE 1. Total and calculated species distributions^a in solutions in equilibrium with solid zippeite phases, used for calculation of ΔG_f° values at 298.2K.

| Species | Mg-zippeite | Co-zippeite | Ni-zippeite | Zn-zippeite |
|--|-------------------|-------------|-------------|-------------|
| pH | 5.15 | 5.10 | 5.05 | 4.95 |
| [UO ₂ ²⁺] | 15.1(-6) | 16.8(-6) | 18.6(-6) | 55.0(-6) |
| [SO ₄ ²⁻] ^{tot} | 7.50(-6) | 8.40(-6) | 9.30(-6) | 27.5(-6) |
| [H ⁺] ^{tot} | 5.00(-6) | 5.60(-6) | 6.20(-6) | 18.5(-6) |
| [UO ₂ SO ₄] | 5.30(-6) | 6.43(-6) | 7.84(-6) | 17.8(-6) |
| [UO ₂ SO ₄] ²⁻ | 4.99(-6) | 5.59(-6) | 6.19(-6) | 18.2(-6) |
| [SO ₄ ²⁻] | 7.47(-6) | 8.36(-6) | 9.24(-6) | 27.1(-6) |
| [HSO ₄ ⁻] | 5.13(-9) | 6.44(-9) | 7.99(-9) | 29.5(-9) |
| [UO ₂ OH ⁺] | 1.19(-6) | 1.28(-6) | 1.39(-6) | 2.52(-6) |
| [(UO ₂) ₂ (OH) ₂ ²⁺] | 1.35(-6) | 1.57(-6) | 1.86(-6) | 6.04(-6) |
| [(UO ₂) ₃ (OH) ₆ ⁴⁺] | 1.97(-6) | 1.97(-6) | 2.01(-6) | 7.45(-6) |
| [UO ₂ SO ₄] ⁰ | 20.9(-9) | 28.3(-9) | 38.1(-9) | 254(-9) |
| [UO ₂ (SO ₄) ₂ ²⁻] | 4.70(-12) | 7.14(-12) | 10.7(-12) | 208(-12) |
| [UO ₂ (SO ₄) ₃ ⁴⁻] | < ^b | < | < | 35.4(-15) |
| [M ₂ (OH) ₄ ⁴⁺] | 6.45(-9) | 10.7(-9) | 12.0(-9) | 118(-9) |
| [MOH ⁺] | 2.56(-12) | 158(-12) | 95.8(-12) | 1780(-12) |
| [M(OH) ₂ ²⁺] | n.c. ^c | 14.0(-15) | 7.79(-15) | 1820(-15) |
| [M(OH) ₃ ³⁺] | n.c. | < | < | < |
| [M ₂ (OH) ₄ ⁴⁺] | n.c. | < | < | < |
| [M ₂ (OH) ₆ ⁶⁺] | n.c. | < | < | 29.5(-15) |
| [M ₂ (OH) ₄ ⁴⁺] | n.c. | < | < | n.c. |
| [M ₂ (OH) ₆ ⁶⁺] | n.c. | n.c. | n.c. | < |

^a Concentrations in mol dm⁻³ given 15.1(-6) mean 15.1 × 10⁻⁶ mol dm⁻³.

^b Less than 10⁻¹⁵ mol dm⁻³.

^c Not calculated in species distribution.

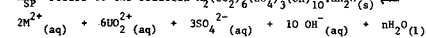
of K and these, together with standard thermodynamic parameters for the other species involved (Barner and Scheuerman, 1978) were used in turn to estimate ΔG_f° for the four zippeite minerals concerned.

Results and Discussion. The species distributions for the solutions in equilibrium with the four zippeites are also given in Table 1. Species whose concentrations were calculated at less than 1 × 10⁻¹⁵ mol dm⁻³ are not included. Values of ΔG_f° for the four minerals, together with those parameters for the free metal ions involved, as aqated ions are given in Table 2.

TABLE 2. ΔG_f° values calculated in this work and from Barner and Scheuerman (1978).

| | Mg-zippeite | Co-zippeite | Ni-zippeite | Zn-zippeite |
|---|---|-----------------------------|-------------|-------------|
| ΔG_f° / kJ mol ⁻¹ | -13506 | -12695 | -12683 | -12870 |
| log a_{SP}^{2+} (298.2K) | -146.1 | -145.9 | -145.6 | -153.0 |
| | Mg | Co | Ni | Zn |
| ΔG_f° / kJ mol ⁻¹ | -456.5 | -51.5 | -46.3 | -146.9 |
| ΔG_f° [Mg-zippeite] | - ΔG_f° [Co-zippeite] | = -811 kJ mol ⁻¹ | | |
| ΔG_f° [Mg-zippeite] | - ΔG_f° [Ni-zippeite] | = -823 kJ mol ⁻¹ | | |
| ΔG_f° [Mg-zippeite] | - ΔG_f° [Zn-zippeite] | = -636 kJ mol ⁻¹ | | |
| $2\Delta G_f^\circ$ [Mg ²⁺] | - $2\Delta G_f^\circ$ [Co ²⁺] | = -810 kJ mol ⁻¹ | | |
| $2\Delta G_f^\circ$ [Mg ²⁺] | - $2\Delta G_f^\circ$ [Ni ²⁺] | = -820 kJ mol ⁻¹ | | |
| $2\Delta G_f^\circ$ [Mg ²⁺] | - $2\Delta G_f^\circ$ [Zn ²⁺] | = -614 kJ mol ⁻¹ | | |

a_{SP}^{2+} refers to the reaction $M_2(UO_2)_6(SO_4)_3(OH)_{10}nH_2O(s) \rightleftharpoons$



We have calculated our thermodynamic parameters on the basis of zippeite as an octahydrate. While the choice of the number of moles of water of crystallization makes no difference as far as the change in ΔG_f° upon converting from one phase into another, the magnitude of the ΔG_f° values reflect the number of waters included. It has earlier been reported that the divalent metal ion zippeite crystallise as hexa-decahydrates (Prondel et al., 1976). We find that while our X-ray data is, within experimental error, the same as these authors', thermogravimetric analyses of our synthetic material do not support the formulation of 16 moles of water per mole of compound. Weight losses upon heating (N₂ atmosphere, flow-rate 25cm³min⁻¹, heating rate 100 min⁻¹, sample weight 8-10 mg) for each of the four zippeites considered here are very similar indeed. These weight losses are summarized in Table 3. Three transitions are observed up to 1000°. The first occurring between 600° and 1600° corresponds to a loss of 5 molecules of water. The remaining 3 molecules of water are lost more slowly as is the H₂O corresponding to hydroxyl decomposition. SO₃ is liberated from all samples between 680° and 880° and the final residues correspond to metal(II) oxide and U₂O₇. Excellent agreement between observed and calculated weight losses are found. These results indicate that the additional 8 waters of crystallization reported earlier may not be essential to the structure or at least are not very strongly bound in the lattice. The previous

workers do not give details of any drying procedures for either their natural or synthetic zippeites. One further experiment has cast some light on this problem. When a sample of solid Zn-zippeite octahydrate was allowed to remain during 48 hours in an atmosphere of H₂O-saturated air, an additional 17 of H₂O by weight was taken up. Experiments were not continued to discover whether, given enough time, water corresponding to 8 molecules of water could eventually be gained, but it is evident that there can be some variation in the H₂O contents of the divalent metal ion zippeites. In this connection it is interesting to note that Frondel (1958) comments on the fact that the water content of zippeite may vary zeolitically.

The results of the thermodynamic studies, given in Table 2, lead to several conclusions as to the chemical nature of zippeites containing divalent metal cations. There is some variation in the free energies of formation for the variously substituted phases. However, reference to the ΔG_f° values for the substituting ions alone (Table 2)

TABLE 3. Results of thermogravimetric analyses with weight losses calculated for an octahydrate.

| Compound | Transition | Temp. (°C) | cumulative weight loss (%) | |
|-------------|--------------------------------------|------------|----------------------------|----------|
| | | | calculated | observed |
| Mg-zippeite | -5H ₂ O | 73-159 | 4.0 | 3.8 |
| | -8H ₂ O | 190-560 | 10.3 | 10.5 |
| | -(3SO ₃ +O ₂) | 690-850 | 22.3 | 22.0 |
| Co-zippeite | -5H ₂ O | 66-152 | 3.9 | 4.0 |
| | -8H ₂ O | 160-549 | 10.0 | 10.3 |
| | -(3SO ₃ +O ₂) | 690-860 | 21.6 | 22.0 |
| Ni-zippeite | -5H ₂ O | 66-146 | 3.9 | 4.0 |
| | -8H ₂ O | 180-485 | 10.0 | 10.4 |
| | -(3SO ₃ +O ₂) | 680-830 | 21.6 | 21.9 |
| Zn-zippeite | -5H ₂ O | 80-159 | 3.8 | 3.9 |
| | -8H ₂ O | 200-560 | 10.0 | 10.0 |
| | -(3SO ₃ +O ₂) | 680-880 | 21.5 | 21.4 |

show that with very close agreement, these differences arise purely from those in free energies of the appropriate metal ions. The only exception to this pattern is in Zn-zippeite where a difference of some 22kJ mol⁻¹ is found. Even this difference however is very small.

Complete solid solution between the Mg, Co and Ni end-members is predicted by these studies. Reference to the solubility products of these three phases shows $K_{sp} = -145.9 \pm 0.3$ at 25°. Zn-zippeite is very slightly less soluble, but extensive Zn-substitution would also be expected in the divalent metal ion zippeite lattice.

These chemical results simply mean that should the activity of any of the four ions Mg²⁺ (aq), Co²⁺ (aq), Ni²⁺ (aq) or Zn²⁺ (aq) achieve a level greater than any other, then that ion will be incorporated into the mineral. The findings therefore agree perfectly with the careful mineralogical studies of Frondel et al. (1976). Co-zippeite and Ni-zippeite from the Happy Jack mine, Utah, was shown to have occupancy of the divalent cation sites (mole %) of (Ni₃₉Co₂₄Mg₁₈Fe₁₃Mn₆) and (Ni₃₂Co₃₄Mg₁₈Fe₁₁Mn₅) in two separate samples. Material from Joachimsthal had Ni:Co as 10:3 with minor Fe and Zn. Mg-zippeite from the Lucky Strike No. 2 mine, Utah, contained 1.4% COO and Zn-zippeite from the Hillside Mine, Arizona, contained 0.87% MgO. It was suggested that "a complete series may extend between the Mg-Co-Ni end-members", a conclusion we readily concur with, and would extend to include the Zn end-member.

These are the first chemical stability studies of the zippeite family to be reported to our knowledge. We are encouraged by the excellent correlation between field and laboratory studies and will report results of other related systems in the near future.

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