Studies on Metal Carbonate Equilibria. 13. On the Solubility of Uranium(IV) Dioxide, $UO_2(s)$

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The equilibrium constant K_{so}, i.e., the solubility product for the reaction $UO_2(s) + 4H^+ \rightleftarrows U^{4+} + 2H_2O$ and the standard potential $^*E_o$ for the redox equilibrium $UO_2^{2+} + 2e^- \rightleftarrows UO_2(s)$ have been determined at 25 °C in 3 M $NaClO_4$ at acidities greater than 10^{-3} M by measuring the potential of platinum and uranium(IV) dioxide electrodes versus a hydrogen half-cell. The results are as follows: $\log K_{so} = -1.2 \pm 0.1$; $^*E_o = 0.305 \pm 0.003$ V (in 3 M $NaClO_4$) and $\log K_{so} = -1.6 \pm 0.4$; $^*E_o = 0.301 \pm 0.005$ V (extrapolated to zero ionic strength).

In two previous papers,[1,2] we have shown that U(VI) is the stable oxidation state of uranium in carbonate-containing solutions under oxidizing conditions. If the redox potential of such solutions is gradually decreased, we obtain[3] a reduction of U(VI) to U(V) and U(IV), depending on the hydrogen ion concentration of the solution. In the range $9 < -\log [H^+] < 11$, all three oxidation states coexist according to the equilibrium $2UO_2(CO_3)_3^{5-} + 4HCO_3^- \rightleftarrows UO_2(CO_3)_3^{4-} + U(CO_3)_5^{6-} + 2CO_3^{2-}$. At $8 < -\log [H^+] < 9$ we can safely assume[4] that the reduction of U(VI) gives rise to U(IV) carbonate species only. (This may be important in groundwater systems under strongly reducing conditions.) $U(CO_3)_5^{6-}$ solutions of concentrations as high as 0.03 M were easily obtained in the course of our experiments.[4] This was unexpected, since the solubility product for $UO_2(s)$ reported in the literature indicated that $UO_2(s)$should precipitate under these conditions. Hence, we thought it was worthwhile to re-examine the solubility product, K_{so}, for the reaction

$$UO_2(s) + 4H^+ \rightleftarrows U^{4+} + 2H_2O \qquad (1)$$

for which Baes and Mesmer[5] report a value of $\log K_{so} = -1.8$, based on the standard free energies of formation of $UO_2(s)$, U^{4+} and H_2O: $\Delta G_f(UO)_2(s) = -1030.1$; $\Delta G_f(U^{4+}) = -545.6$; and $\Delta G_f(H_2O) = -237.2$ kJ/mol, respectively. A recalculation, using a more recent value of $\Delta G_f(UO_2(s))$ from CODATA[6] and $\Delta G_f(U^{4+})$ from Fuger and Oetting[7], gives $\log K_{so} = -4.6 \pm 0.4$. This value has also been reported in the compilations of Langmuir[8] and Lemire and Tremaine.[9] This solubility product refers to a crystalline, ceramic material. Langmuir also reported a solubility product for an amorphous solid, for which the standard free energy of formation was as much as 54 kJ/mol larger. It seemed reasonable to assume that the observed high solubility in our uranium carbonate system was related to the initial formation of such an amorphous $UO_2(s)$ phase.

Nikolaeva and Pirozhkov[18] reported $\log K_{so} = -3.2 \pm 0.2$ deduced from solubility measurements in the range $2.28 < -\log[H^+] < 4.09$. U(IV) is extensively hydrolyzed in this pH range and the numerical value of the solubility product is strongly dependent on the stoichiometry and equilibrium constants of the hydroxide complexes. No experimental values of the equilibrium constants for the predominant complexes,

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$U(OH)_3^+$ and $U(OH)_4$ have been reported and the log K_{so} value reported by Nikolaeva and Pirozhkov is based on *assumed* values of these constants.

Direct solubility measurements for the solubility product are difficult to perform because of the ease of oxidation of U(IV) to U(VI). The early study of Gayer and Leider[10] may have been influenced by such an oxidation, (cf. Ryan and Rai[11]). It is also necessary to correct the solubility data for hydrolysis, and precise data are known only at fairly high acidities where U^{4+} and $U(OH)^{3+}$ predominate. Another complicating factor in the experimental determination of K_{so} is the morphology and particle size of the solid phase. It is well known that amorphous and microcrystalline phases give higher solubilities than crystalline ones.

Parks and Pohl[19] have recently published a report on the hydrothermal solubility of uraninite which contains a review of the older literature and some new experimental data. The value proposed, log $K_{so} = -3.3 \pm 0.6$, agrees well with the value of Nikolaeva and Pirozhkov, but it is calculated by using estimated hydrolysis constants. In the present study, we attempted to measure the solubility product indirectly by using an emf method which circumvents some of the problems of direct solubility measurements. We use the following symbols in our report:

$B = [U(VI)]$, total concentration of uranium in the +6 oxidation state;
$b = [UO_2^{2+}]$, molar concentration of free uranium(VI);
$h = [H^+]$, molar concentration of protons;
$C = [U(IV)]$, molar concentration of uranium in the +4 oxidation state;
$c = [U^{4+}]$, molar concentration of free uranium(IV);
$K_{so} = c\,h^{-4} =$ the solubility product of $UO_2(s)$ in 3 M $NaClO_4$ ionic medium, i.e. the equilibrium constant of reaction (1) given above.

Method and calculations

The determination of the solubility product of $UO_2(s)$ was carried out at 25.00 °C in 3.00 M $NaClO_4$ ionic medium, by measuring with cell (A) the redox potential of UO_2^{2+} solutions equilibrated with solid UO_2 at acidities where the hydrolysis of UO_2^{2+} is negligible. In (A), TS (the test solution) has the composition TS = B M UO_2^{2+}, h M H^+, $(3.00-2B-H)$ M Na^+, 3.00 M ClO_4^- saturated with $UO_2(s)$, and RE is a reference half-cell of composition whose value, e_R, versus the normal hydrogen electrode, has been measured as described elsewhere.[4]

$$-\mathrm{Pt}\mid\mathrm{TS}\mid\mathrm{RE}+ \qquad \text{(A)}$$

$$\mathrm{RE} = \begin{array}{r|l|l} 3.00\ \mathrm{M} & 0.010\ \mathrm{M\ Ag^+},\ 2.99 & \mathrm{Ag,AgCl(s)} \\ \mathrm{NaClO_4} & \mathrm{M\ Na^+},\ 3.00\ \mathrm{M} & \\ & \mathrm{ClO_4^-} & \end{array}$$

The experiments were performed as titrations, in the course of which, h was kept constant, whereas B was varied. In a typical experiment, solid UO_2 was introduced into a known volume of deoxygenated solution of initial composition B_0 M UO_2^{2+}, H M H^+, $(3.00-2B_0-H)$ M Na^+, 3.00 M ClO_4^-.

Known volumes of a carefully deoxygenated titrant of higher $[UO_2^{2+}]$ and identical $[H^+]$ were then added. A stream of 99.998 % pure $N_2(g)$, after bubbling through washing bottles containing a Cr(II) solution on Zn/Hg and finally through 3 M $NaClO_4$, was led through the test and the titrating solutions to keep the oxygen content to a minimum.

After each addition of titrant, the emf of cell (A) was followed until it remained constant, within a few tenths of a millivolt, for several hours.

In our experiments, h ranged between $1 \cdot 10^{-3}$ to 0.1 M. At these concentrations, hydrolysis of U(VI) could be neglected and we could assume that $B = b$. The emf of cell (A), E, expressed in mV, is given by eqn. (2) where E_0 is the standard

$$E = e_R - E_0 - 29.58 \log (Bh^4c^{-1}) - 16.8\,h + E_j \qquad (2)$$

potential, referred to the normal hydrogen electrode in 3 M $NaClO_4$, for the semireaction:

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftarrows U^{4+} + 2H_2O \qquad (3)$$

The value 16.8 h is the liquid junction potential[12] due to the replacement of Na^+ with H^+ and E_j is the junction potential arising in (A) because of the replacement of Na^+ with UO_2^{2+} ions. In a separate experiment, described in detail below, (see Experimental), the relation (4) was found

$$E_j = -20.0\ B\ \text{mV} \tag{4}$$

which showed that E_j is a linear function of B, at least for $B \leq 0.1$ M.

When equilibrium between the test solution and solid UO_2 has been reached, the quantities h and c in eqn. (2) are no longer independent, but related to each other by K_{so}, the equilibrium constant of reaction (1), according to eqn. (5) If we

$$K_{so} = c\ h^{-4} \tag{5}$$

introduce eqns. (4) and (5) into eqn. (2), we obtain eqn. (6):

$$E = e_R - {}^*E_0 - 29.58 \log B - 16.8\ h - 20.0\ B \tag{6}$$

where

$$^*E_0 = E_0 - 29.58 \log K_{so}. \tag{7}$$

Eqn. (6) shows that under our experimental conditions, E depends only on the uranyl ion concentration, provided true thermodynamic equilibrium between solid UO_2 and UO_2^{2+} in solution is achieved. This was ascertained by performing back-titrations, as well as by changing h. The experimental data in the form of $Y(-29.58 \log B)_h$, with

$$Y = E + 16.8\ h + 20.0\ B - e_R = -{}^*E_0 - 29.59 \log B \tag{8}$$

are summarized in Table 1 and plotted in Fig. 1. The line has slope = 1 and represents the theoretical behaviour of the redox half-cell. The Y intercept yields, according to eqn. (8), the value of $-{}^*E_0$, which can be combined with E_0 to calculate K_{so}. From eqn. (7),

$$\log K_{so} = (E_o - {}^*E_0)/29.58. \tag{9}$$

The value of E_0 has previously[13] been determined at various ionic strengths and extrapolated to the infinite dilution standard state by using the specific interaction[14] and the Pitzer approach[15]. The results are summarized in the first row of Table 2, where E_0 and $^*E_0$, recall, are the standard potentials, referred to the normal hydrogen electrode, of the semireaction (3) and of the reaction

$$UO_2^{2+} + 2e^- \rightleftarrows UO_2(s). \tag{10}$$

respectively, in 3 M $NaClO_4$ ionic medium. In the second row of Table 2, we have reported the values of K_{so}, $^*E_0$ and E_0 extrapolated to zero ionic strength by using the specific ion interaction theory.[14] For a detailed description of the extrapolation of E_0 see Ref. 13.

Table 1. Summary of the $Y(-29.58 \log B)_h$ data.

$\log h = -1.29$

(Y,−29.58 log B): −253.33,51.24;−256.60,47.50; −259.25,45.00; −264.29,41.73; −269.65,38.22; −249.07,53.99 (back-tit); −242.58,59.86 (back-tit).

$\log h = -1.94$

(Y,−29.58 log B): −243.49,59.33; −256.67,49.82; −262.97,42.90; −268.33,36.82; −275.26,31.55; −268.07,38.47 (back-tit); −265.23,42.95 (back-tit).

$\log h = -3.00$

(Y,−29.58 log B): −263.65,42.95.

Experimental

Measurements were performed at 25.00 ± 0.02 °C in a paraffin oil bath. The equipment has been

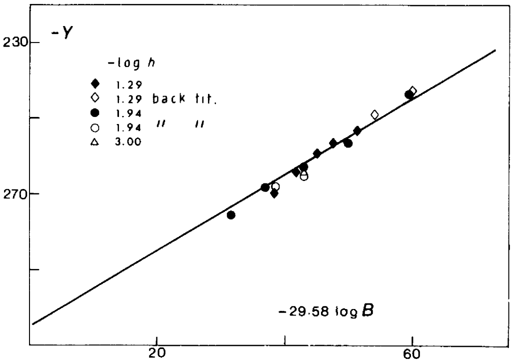

Fig. 1. Representation of eqn. (8). The symbols refer to measured values and the line to the theoretical potentials of solutions of UO_2^{2+} equilibrated with $UO_2(s)$. The Y intercept gives the standard potential of semireaction (10).

Table 2. Survey of the results.

Medium	K_{so}	$^*E_0$ (V)	E_o (V)
$NaClO_4$ (3M)	−1.2±0.1	0.305±0.003	0.2683±0.0003
Pure water	−1.6±0.4	0.301±0.005	0.254±0.006

described elsewhere.[4] The Ag/AgCl electrodes were prepared according to Brown.[16] Metrohm EA109 glass electrodes were used.

Reagents including Uranium(VI) perchlorate, perchloric acid, sodium perchlorate, sodium hydrogen carbonate and silver perchlorate solutions were prepared and analyzed as described in a previous paper.[1] Uranium(IV) perchlorate solutions were prepared by reducing acidic uranium(VI) perchlorate with $H_2(g)$ on a Pd catalyst. The preparation of the Pd catalyst has been described previously.[4] The preparation of *solid* UO_2 was one of the major difficulties of this study and is therefore described here in detail.

First, we attempted to precipitate UO_2 by partially reducing deoxygenated UO_2^{2+} solutions of $h \sim 10^{-2}$ M, *in situ* by electrolysis on a Pt cathode, by reduction with $H_2(g)$, as described above, or by addition of $NaHCO_3$, Na_2CO_3 or NaOH to acidic U(IV) solutions. A greenish amorphous solid was always obtained which rapidly turned black (solid 1). The redox potential of these heterogeneous solutions, measured by means of cell (A), tended to drift toward a decreasing $[U^{4+}]$; but after 3 to 4 weeks, stable, reproducible and reversible potentials were obtained. After that, much faster equilibria (1–2 hours per addition) were observed in the course of the titration. On one occasion, the solid and the solution were heated to the boiling point for a few minutes under a stream of $N_2(g)$; equilibrium was attained much faster (3 to 4 days).

In a series of experiments in 3 M $NaClO_4$, in which h ranged between 10^{-2} and $10^{-1.3}$ M and B from $10^{-2.4}$ to 10^{-1} M, we obtained for (solid 1): $\log K_{so} = 0.5 \pm 0.3$. A powder photograph of two-month-old $UO_2(s)$ equilibrated with a solution containing 0.1 M UO_2^{2+}, 2.8 M Na^+, 3.0 M ClO_4^- at $h \sim 10^{-2}$ M confirmed that the solid was UO_2; however, the few weak and broad lines indicated a rather poor crystallinity. In order to obtain a better crystalline solid, we changed the method of preparation of $UO_2(s)$.

Sodium hydrogen carbonate was added to an acidic U(IV) solution. The precipitate was allowed to settle and the supernatant was then replaced by 96% ethanol. The mixture was refluxed for a week. These operations took place under an uninterrupted flow of $N_2(g)$. The result was a growth in size of the precipitated particles which were microcrystalline when examined microscopically. The solid (solid 2) was rinsed several times with deoxygenated water and carefully transferred, still wet, into the measuring vessel where, after only a few days, it gave rise to stable and reversible potentials.

Finally, we also tested the possibility of using a pellet of nuclear fuel (O/U = 2.001) supplied by ASEA ATOM, as the solid phase (solid 3). Since the resistance of such a pellet is quite small, (UO_2 is a semiconductor), we used it to construct an electrode of a design similar to the one used by Johnson *et al.*[17] for different purposes. We used this electrode, in addition to the platinum foil in cell (A), after removing the brown oxidized surface layer by treating it first with a concentrated solution of $NaHCO_3$ and then with 0.1 M $HClO_4$. In this case also, a stable potential was obtained after a few days, with the Pt and the $UO_2(s)$ electrodes differing by not more than 1 mV.

It was obvious that the attainment of equilibrium between solid UO_2 and UO_2^{2+} in solution is slow even with crystalline uranium dioxide. To speed it up, we used Ag/AgCl(s) as a mediator in some experiments. We estimated that the potential of the semireaction

$$AgCl(s) + e^- \rightleftarrows Ag(s) + Cl^-$$

would not be too far from that of $UO_2^{2+}/UO_2(s)$ in solutions where $[Cl^-]$ is approximately 10^{-2} M. This electrode reaction is known to be fast. By introducing Ag(foil) and AgCl electrodes in cell (A), we found that the time for the attainment of equilibrium between UO_2^{2+} and $UO_2(s)$ decreased considerably – from days to hours. At equilibrium, the potentials of the Pt, the $UO_2(s)$, the Ag and the AgCl electrodes agreed within 2 mV. Hence, we concluded that both the solid UO_2 phases (2 and 3) have the same solubility within the 2 mV precision obtained in the emf measurements.

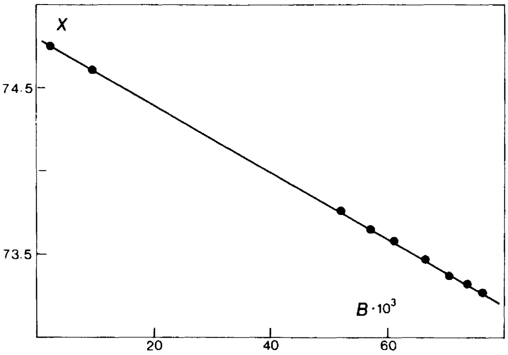

Fig. 2. Evaluation of the liquid junction potential, E_j, arising in cell (A) because of the replacement of Na^+ with UO_2^{2+}. The dots represent the experimental measurements by means of cell (D) [eqn. (11)]. The line has been calculated by assuming $E_j = -20\ B$.

Characterization of $UO_2(s)$ was done using three different methods. The UO_2(s) pellet had an average grain size of a few microns and a density that was ⩾ 95 % of the theoretical value. The precipitated UO_2 phase (solid 2) had X-ray diffraction patterns identical with those of the ceramic UO_2 except for a slight broadening of the diffraction lines in the Guinier photographs. The line broadening indicated that the material had a particle size close to that of the ceramic material.

Evaluation of E_j was carried out by measuring the emf of cell (D) where GE is the glass electrode

$$- \text{GE} \mid \text{TJ} \mid \text{RE} + \qquad \text{(D)}$$

and TJ is the test solution of composition TJ = B M UO_2^{2+}, 0.0526 M H^+, (2.947-2B) M Na^+, 3.00 M ClO_4^-. The evaluation was performed as a titration by varying B between $2 \cdot 10^{-3}$ and $8 \cdot 10^{-2}$ M while keeping h constant at a level where the hydrolysis of UO_2^{2+} is suppressed. The emf of cell (D) can be written:

$$E_D = E_D^0 - 59.16 \log h + E_j. \qquad (11)$$

The first and second terms on the right side of this eqn. are constants. Thus, any change in E_D is due to E_j under the reasonable assumption that the activity factor of H^+ is not affected by replacing at most 7 % of Na^+ with UO_2^{2+}. The plot of $X = E_D + 59.16 \log h$ vs B in Fig. 2 shows that the liquid junction potential, due to the replacement of Na^+ by UO_2^{2+}, can be represented by the previously quoted eqn. (4).

Discussion

There is a large discrepancy between the solubility product of UO_2(s) calculated from published thermodynamic data and the experimental values obtained by this study. The majority of the previous studies have been made by solubility measurements using UO_2(s). The free U^{4+} concentration was then calculated by using hydrolysis constants which were *estimated* by Baes and Mesmer.[5] By measuring the U(VI)/U(IV) redox potential, one circumvents the hydrolysis correction because $[U^{4+}]$ at equilibrium with UO_2(s) is obtained from the emf. Nikolaeva and Pirozhkov measured this redox potential in their solubility study[18] but did not use the data quantitatively. We have made a recalculation of their solubility data by using the following equilibrium constants

$$U^{4+} + 3H_2O \rightleftarrows U(OH)_3^+ + 3H^+ \qquad \log K_3 = -1.0 \pm 0.5$$

$$U^{4+} + 4H_2O \rightleftarrows U(OH)_4(aq) + 4H^+ \qquad \log K_4 = -4.0 \pm 0.5$$

which are estimated[21] from the data reported in Refs. 10 and 20. We obtain $\log K_{s0} = -1.2 \pm 0.5$ which is in fair agreement with the emf value arrived at directly in this study.

Another source of error in some of the reported solubility product data is in the standard free energy of formation of U^{4+}(aq) which is based on experimental determinations of the standard potential of the UO_2^{2+}/U^{4+} couple. Published data give values ranging from 0.334 to 0.268 V. Fuger and Oetting[7] proposed the value 0.273 ± 0.005 V, while we have proposed the somewhat lower value of 0.254 ± 0.006 V (see Ref 13 for further discussion).

The estimated error in the standard potential is equivalent to an error of ±0.2 in $\log K_{s0}$ and this is not sufficient to explain the differences observed. These are presumably due to differences in crystallinity between the various phases used in the solubility determinations and in the hydrolysis corrections. In this context, it is interesting to note that the different methods of preparation gave phases with nearly constant and reproducible properties after a few weeks of equilibration with the aqueous phase. However, a slightly more crystalline phase was obtained by refluxing the $UO_2(s)$ with ethanol. This is important in modelling the behaviour of $UO_2(s)$ in groundwater systems. The observed difference in solubility between the phases 2 and 3 and the thermodynamic value calculated for ceramic $UO_2(s)$ correspond to a difference in standard free energy of formation which is 17 kJ/mol – well within the limit proposed by Langmuir.[8] We also found that the solid 3, which was composed of crystalline $UO_2(s)$ in the form of a ceramic pellet, gave the same solubility product as the precipitated phase 2. This was unexpected and the only possible explanation is that the solubility was controlled by the presence of a small amount of grains of about the same size as those present in the solid 2. The difference in solubility product between the experimental values obtained in this study and the value calculated by using the CODATA value for the standard free energy of formation of UO_2 (ceramic) may also be due to surface oxidation of $UO_{2.001}$ to a form with a slightly higher oxygen content, (see Ref. 17). The agreement between the solubility data reported by Gayer and Leider[10] and Bruno *et al.*[20] is good in the range $0.4 \leq -\log h \leq 10$, indicating that the same (and reproducible) UO_2 form had been precipitated. The solubility product obtained was $\log K_{so} = 0.5 \pm 0.3$ which corresponds to the value found for the amorphous solid (solid 1) in the present study.

By using the hydrolysis constants proposed in this study on the solubility data of Ryan and Rai,[11] we obtained $\log K_{so} = -1.4 \pm 0.3$ which is in fair agreement with the value we found for the more crystalline UO_2 phase. Ryan and Rai used Zn(s) suspensions and sodium dithionate as reducing agents in their study. It is well known from the genesis of sedimentary uranium(IV) minerals that sorption of uranium on strongly reducing solids results in better crystallinity of the precipitated $UO_2(s)$.[22] This effect may explain the difference between the data of Gayer and Leider and those of Ryan and Rai. Unfortunately, no solid phase characterization was made by these authors.

From the value of the solubility product obtained in this study, we calculated that the maximum concentration of uranium(IV) in carbonate-containing solutions of the type we used previously in our studies[3,4] should be around 10^{-4} M. This value is much lower than the maximum concentrations actually observed. It is obvious that the initial solid phase formed in the precipitation must have been much less crystalline, i.e. had a much higher solubility than the phase used in the present study, an observation that is consistent with the known properties of hydrous oxides.

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References

1. Ciavatta, L., Ferri, D., Grenthe, I. and Salvatore, F. *Inorg. Chem. 20* (1981) 463.
2. Ferri, D., Grenthe, I. and Salvatore, F. *Acta Chem. Scand. A 35* (1981) 165.
3. Ferri, D., Grenthe, I. and Salvatore, F. *Inorg. Chem. 22* (1983) 3162.
4. Ciavatta, L., Ferri, D., Grenthe, I., Salvatore, F. and Spahiu, K. *Inorg. Chem. 22* (1983) 2088.
5. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations,* Wiley-Interscience, New York 1976.
6. *CODATA: Recommended Key Values for Thermodynamics, J. Chem. Thermodyn. 10* (1978) 903.
7. Fuger, J. and Oetting, F. L. *The Chemical Thermodynamics of Actinide Elements and Compounds. II. The Actinide Aqueous Ions,* International Atomic Energy Agency, Vienna 1976, p. 16.
8. Langmuir, D. *Geochim. Cosmochim. Acta 42* (1978) 547.
9. Lemire, R. J. and Tremaine, P. R. *J. Chem. Eng. Data 25* (1980) 361.
10. Gayer, K. H. and Leider, H. *Can. J. Chem. 35* (1957) 5.
11. Ryan, J. L. and Rai, D. *Polyhedron 2* (1983) 947.
12. Biedermann, G. and Sillén, L. G. *Arkiv Kemi 5* (1953) 425.
13. Bruno, J., Grenthe, I. and Lagerman, B. *Scientific Basis for Nuclear Waste Management, IX,* Werme, L. Ed. *Mat. Res. Soc. Symp. Proc. In press.*
14. a) Scatchard, G. *Chem. Rev. 19* (1936) 309; b) Guggenheim, E. A. *Application of Statistical Mechanics,* Clarendon Press, Oxford 1966; c) Biedermann, G. *The Nature of Sea Water,* Goldberg, E. E., Ed., Dahlem Konferenzen, Berlin 1975, p. 339.

15. Pitzer, K. S. *J. Phys.* 77 (1973) 268.
16. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
17. Johnson, L. H., Shoesmith, D. W., Lunansky, G. E., Bailey, M. G. and Tremaine, P. R. *Nucl. Technol.* 56 (1982) 238.
18. Nikolaeva, N. M. and Pirozhkov, A. V. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.* (1978) 82.
19. Parks, G. A. and Pohl, D. C. *Hydrothermal Solubility of Uraninite* Report DOE/ER 12016-1, Dec. 1985.
20. Bruno, J., Grenthe, I. and Muñoz, M. *Scientific Basis for Nuclear Waste Management IX* L. Werme, Ed. *Mat. Res. Soc. Symp. Proc. In press.*
21. Bruno, J. *To be published.*
22. Goldhaber, M. B., Mohagheghi, A. and Reynolds, R. L. *Origin of Coffinite in Sedimentary Rocks by a Sequential Adsorption-Reduction Mechanism* (Presented in Concentration Mechanisms of Uranium in Geological Environments, Nancy, France, October 1985). *To be published.*

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