Solubility of Uranium (IV) Oxide in Alkaline Aqueous Solutions to 300°C

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The solubility of carefully characterized UO_2 in pOH 1.5 and pOH 2.5 aqueous solutions has been determined from 25°C to 300°C using a flow apparatus. Data were analyzed in terms of the reaction

$$UO_2 + 2H_2O + OH^- = U(OH)_5^-, \quad \log K = -5.86 + 32/T$$

The extreme sensitivity of both the UO_2 surface and aqueous U(IV) to oxidation is discussed.

1. INTRODUCTION

The solubility of UO_2 under reducing conditions is an important parameter in modelling fission product and actinide releases from irradiated nuclear reactor fuel in reactor primary coolant circuits (250-300°C) and in deep underground waste vaults. Under acidic conditions, the solubility behavior can be estimated with some certainty[1,2] because thermodynamic data have been reported for UO_2, U^{4+}, and the hydrolyzed species,[3] $U_6(OH)_{15}^{9+}$ and UOH^{3+}, the latter to 150°C.[4] Only one study has been reported for alkaline conditions, the uranium hydroxide solubility measurements of Gayer and Leider[5] at 25°C. Their data are of considerable importance since they provide a value for the formation constant for the species $U(OH)_5^-$, from which the intermediate hydrolysis constants can be derived.[1-3] Here we report the results of a similar study in which we measured the solubility of carefully characterized UO_2 in alkaline solutions to 300°C.

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2. EXPERIMENTAL

Sintered spheres of natural UO_2, $\sim$ 250 μm in diameter and density 10.3 g cm^{-3}, were obtained from the Commercial Directorate of the United Kingdom Atomic Energy Authority. The oxide stoichiometry was calculated by measuring its X-ray diffraction unit cell parameter, a_o = 5.4704 ± 0.003 Å at 22°C, from which we calculate[6] the formula $UO_{1.999 \pm 0.012}$. An emission spectral analysis showed the major impurity to be 450μg-g^{-1} Al. All other elemental impurities were less than 50μg-g^{-1}. The oxide was left overnight in a hydrogen atmosphere at 900°C to remove higher surface oxides before being quickly transferred to the solubility apparatus. During the course of the solubility measurements, oxide samples could be taken from the solubility apparatus under an argon atmosphere (less than 40 ppm O_2), for analysis by X-ray photoelectron spectroscopy (XPS). Details of the XPS analysis are reported elsewhere.[7]
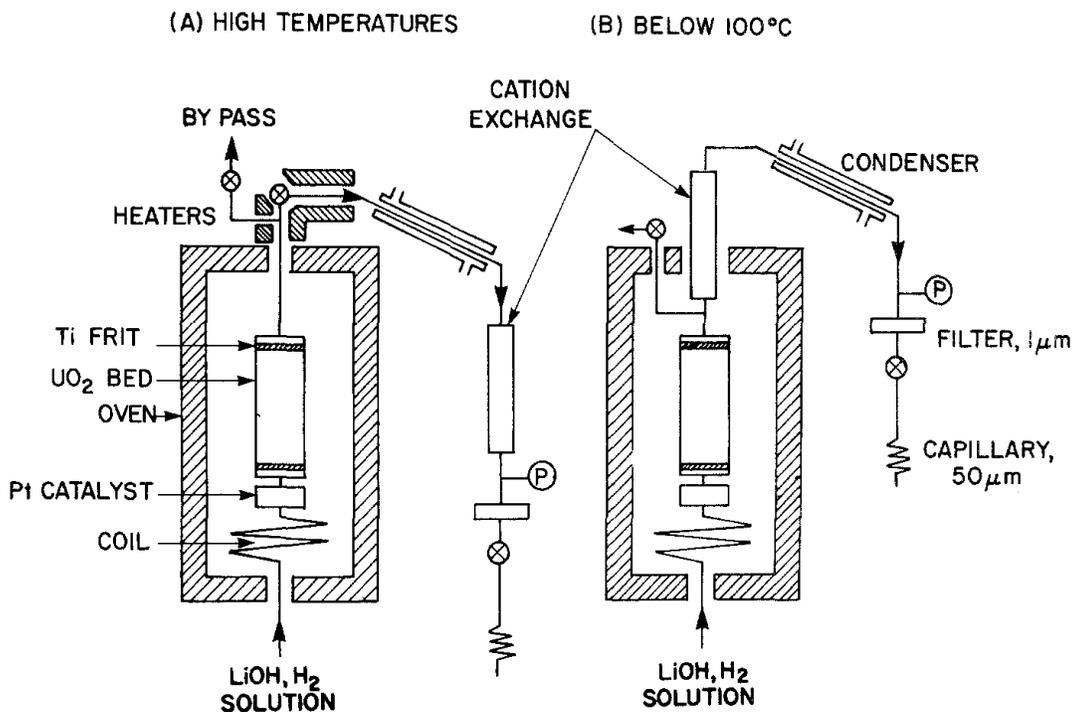

Fig. 1. The flow solubility apparatus in two of the configurations used.

Our procedures for preparing oxygen-free, hydrogen-saturated standard alkaline solutions for the solubility measurements were identical to those used previously[8] except that LiOH, rather than NaOH, was used to minimize interference with the neutron activation analysis. Solutions were prepared by weight, using Fisher reagent grade LiOH·

H_2O from freshly opened bottles. Contamination by Li_2CO_3 in the final solutions was estimated to be less than 1% from potentiometric titrations with a standard HCl solution and by precipitation as $BaCO_3$.

The flow solubility apparatus described in Ref. 8 was used in three configurations, two of which are shown in Fig. 1. The apparatus pumped hydrogen-saturated LiOH solution at a rate of 2 cm^3-min^{-1} or less through three parallel systems, two of which contained about 180 g of UO_2 each (about 0.4 m^2 geometric surface area); the third system contained no UO_2, as a control. The configuration shown in Fig. 1A allowed the saturated solution to be diverted through a condenser and cation exchange resin (Amberlite IR120 in the protonated form) after the UO_2 bed had been equilibrated with the flowing solution for several hours. Uranium precipitated in the condenser or exchanged on the resin was then eluted with 200 ml of 2 m HNO_3 for analysis. The second configuration (Fig. 1B) allowed the hot solution to be passed isothermally into the resin without passing through the condenser or the 10 cm length of tubing which connected the condenser to the cell through the oven wall. This arrangement, which minimized losses of uranium by sorption or precipitation on the wall of the tubing, was limited to temperatures below about 100°C because of the thermal instability of the resin. Some measurements near room temperature were also made by passing the saturated solutions from the UO_2 bed directly into a sample bottle, then acidifying with HNO_3 before analysis. The efficiency of the apparatus was tested at several temperatures by inserting aliquots containing 10 μg and 100 μg of uranium into the system, upstream of the condenser and ion exchange column. Recovery of the uranium was quantitative, within the error limits of the analysis ($\pm$ 10% and $\pm$ 6%, respectively) as long as the resin was unsaturated with respect to Li^+. Continuing to run the system past this point caused the solutions leaving the resin to be sufficiently alkaline to strip uranium from the column.

At the much lower concentrations observed during solubility runs, there is a danger that a substantial amount of uranium might have been irreversibly sorbed by the TiO_2 microcrystalline layers on the walls of the apparatus or on the ion exchange resin, so that it could not be eluted. After several months of operation, when about 800 kg of solution had passed through, the system downstream of the oxide bed was cut up for analysis. Scrapings of the tube walls were analyzed by emission spectroscopy and electron microscopy with an energy dispersive X-ray spectrometer. The remainder of the tubing upstream of the condenser was eluted with 2 m HNO_3 for analysis by neutron activa-
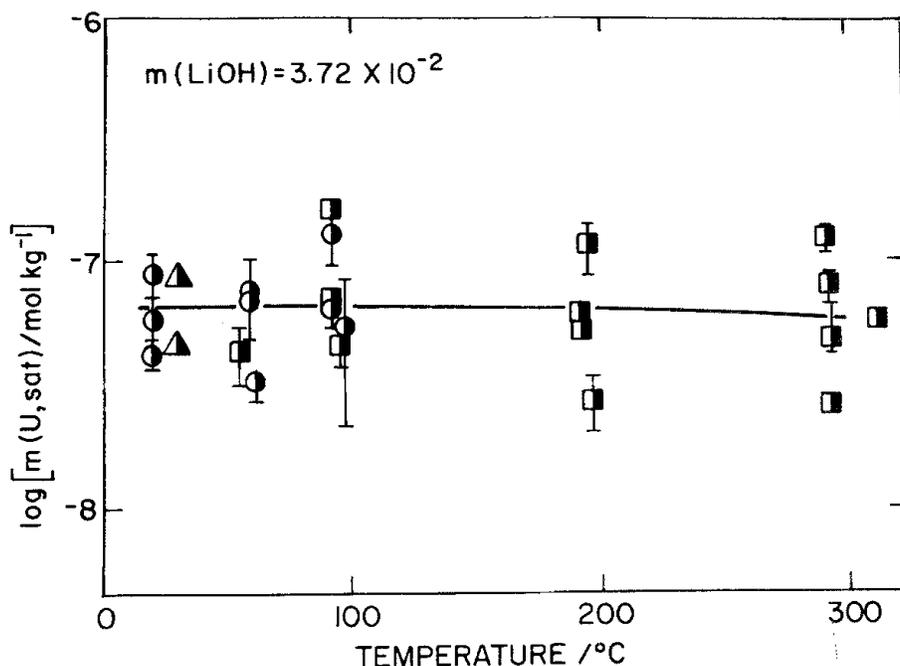
Fig. 2. The solubility of UO_2 at pOH 1.5 as a function of temperature from the flow system: ▢ , configuration 1a; ◑ , configuration 1b; ▲ ,direct measurement of the uranium molality without using an ion exchange resin.

tion. Also, 2 *m* HNO_3 was left standing in the condenser and ion exchange resin for 48 hours in order to determine whether additional uranium might be eluted. The total inventory of uranium was 30 μg from the elutions and less than 500 μg from the emission spectrum, calculated from the detection limit (300 μg-g^{-1}) and the maximum thickness of the TiO_2 layer on the system components. Sorption losses over the course of the experiments therefore averaged $< 2 \times 10^{-9}$ *m*.

Some room-temperature static experiments, similar to Gayer and Leider, were carried out in a sealed glass cell, purged with presaturated, deoxygenated hydrogen and containing 1.4 g UO_2, (31 cm^2 surface area). A stopcock arrangement allowed solution to be forced out by the hydrogen overpressure for analysis.

The acidified uranium solutions were analyzed by instrumental neutron activation analysis using the WR-1 irradiation facility at the Whiteshell Nuclear Research Establishment, which has a thermal neutron flux of 1 x 10^{14} n-cm^{-2}s^{-1}. Evaporated 200 μl aliquots were irradiated for five minutes and the 75 keV γ-ray associated with the $^{238}U(n,\gamma)^{239}U$ reaction was counted for five minutes using a Ge(Li)γ spectrometer. Of the group 1A elements, lithium interferes least with this method. Nevertheless, the Li/U ratio in our samples was so large that sensitivity was limited by a high-intensity, 511 keV annihilation γ-ray from ^{18}F produced by the $^6Li(n,\alpha)^3H$ and $^{16}O(^3H,n)^{18}F$ reactions.[9] The detection limit of this technique for uranium was 1 to 5 ng.
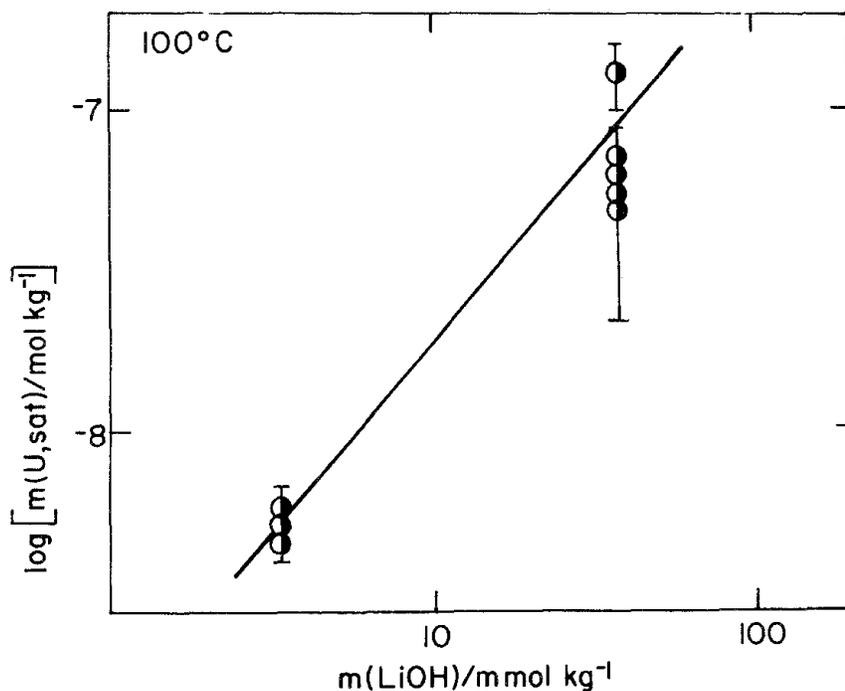
Fig. 3. The solubility of UO_2 as a function of m(LiOH) at 100°C.

3. RESULTS

Solubility results from the three flow apparatus configurations are shown in Figs. 2 and 3, as a function of temperature in 37 x 10^{-3} m LiOH and as a function of alkalinity at 100°C, respectively. The uranium molalities in the eluent samples were so low that several of the lower solubility results in Fig. 2 were indistinguishable from the corresponding blank runs taken from the empty flow system. These did not exceed 5 x 10^{-8} m at pOH 1.5. Our analysis in the previous section showed irreversible sorption losses to be small. This was confirmed by the very nearly identical results obtained at low temperatures using isothermal sampling with and without the ion exchange resin. We therefore conclude that, while the results in Figs. 2 and 3 may be upper limits, they do not underestimate the uranium molality of the solution leaving the sample bed.

The analytical difficulties prohibited meaningful flow rate studies which would have determined whether equilibrium had occurred. Earlier studies[8] established that transition metal oxide solutions do have time to reach saturation in this system under the conditions used here. The first-order rate constant required to achieve 99% of saturation[8] at a flow rate of 2 cm^3-min^{-1} is 0.02 m^{-2}-s^{-1}, which corresponds to an initial dissolution rate of 3 x 10^{-11} mol-m^{-2}s^{-1}.

The XPS spectra of the surface of UO_2 and higher oxides have
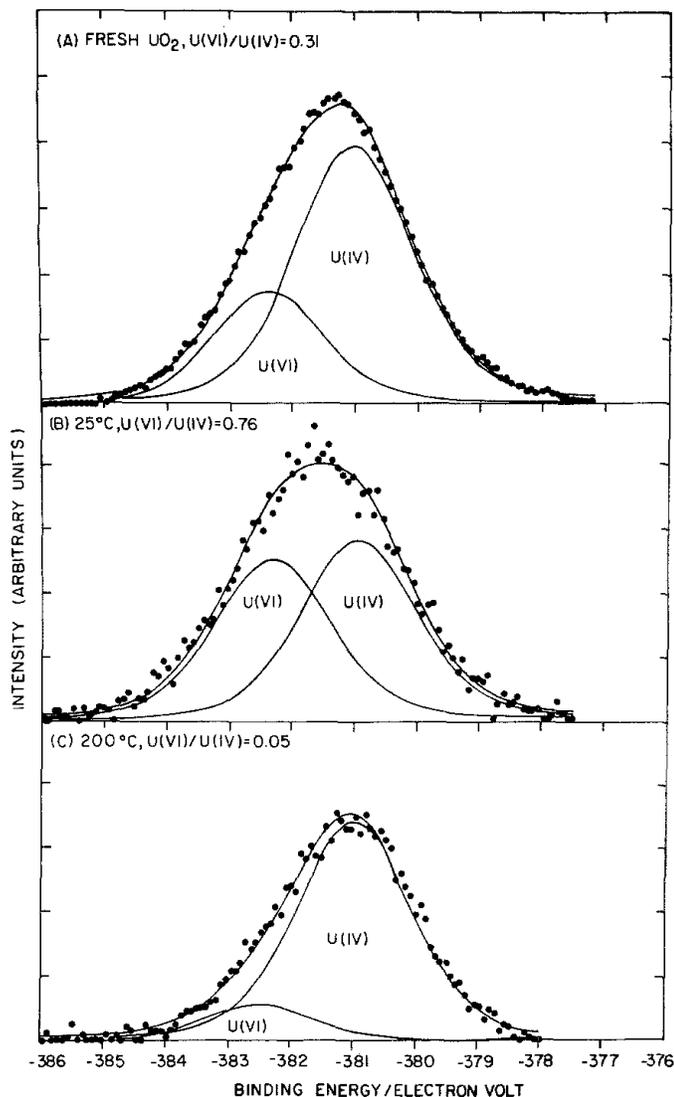
Fig. 4. X-ray photoelectron spectra of the UO_2 surface before and after 6 weeks exposure to pOH 1.5 solutions at the temperature shown.

been studied in detail.[7,10,11] Spectra of samples from our studies are presented in Fig. 4. The U(VI)/U(IV) ratios in the figure were obtained by deconvoluting the spectrum into the two Gauss-Lorentz component peaks and subtracting the residual baseline correction, according to the detailed procedure of McIntyre *et al.*[7] The spectrum of the freshly reduced oxide, Fig. 4A, showed a U(VI)/U(IV) ratio of approximately 0.3 which would correspond to a two-monolayer surface film of UO_3 or a thicker layer of a lower oxide, for example, U_2O_5.[7] This presumably formed during the brief exposure to air during transfer to the solubility apparatus.

The spectra in Figs. 4B and 4C show the effects of exposure to flowing room-temperature and high-temperature (200°C to 300°C) solutions, respectively, each for a six-week period. Contact with the 25°C solution caused further oxidation of the UO_2 surface while temperatures above 200°C were sufficient to reduce the initial oxide layer leaving a surface of nearly pure UO_2.
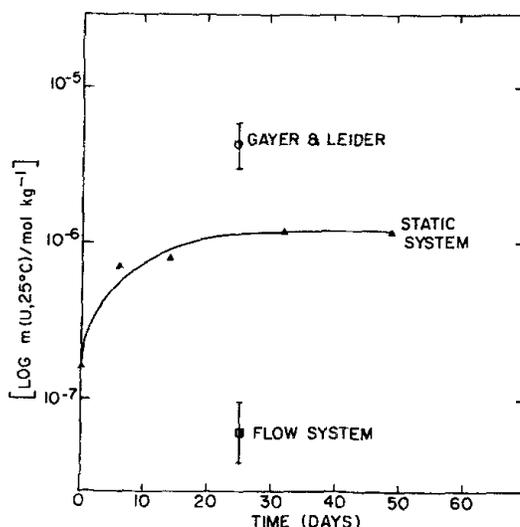

Fig. 5. Dissolution of UO_2 in the static system as a function of time at 25°C and pOH 1.5 Equilibrium solubilities reported by Gayer and Leider[5] and from the flow system (Fig. 3) are shown for reference.

Finally, the results of the static dissolution experiments at 25°C are presented in Fig. 5 with Gayer and Leider's data and results from the flow system for reference. After one month the uranium molality reached a constant value of 1 x 10^{-6} m, a factor of 10 higher than results from the flow system and somewhat lower than Gayer and Leider's results. The XPS spectrum taken after the run showed a surface composition $U(VI)/U(IV) = 0.2$, probably indicating no significant change in the initial oxidized layer. The first-order rate constant for the dissolution process in the static system was 5 x 10^{-4} m^{-2}-s^{-1}.

4. DISCUSSION

UO_2 is known[7,12] to be extremely sensitive to oxidation by gaseous or dissolved oxygen. The XPS results show the presence of a thin oxide layer, probably U_2O_5, which undergoes continuous slow oxidation below 100°C due to residual traces of oxygen (< 5 ng-g^{-1}) in the solutions. This is consistent with kinetic studies[7] which show that, even though UO_2 is the thermodynamically stable oxide in hydrogen-

saturated solutions,[1,2] residual dissolved oxygen is so aggressive that oxidation takes place. Isotopic exchange and electrode experiments[8,13] suggest that the kinetics of hydrogen reduction are fast enough above about 150°C to allow the dissolved hydrogen to, in fact, determine the reduction potential of the system. The nearly unoxidized UO_2 surface in Fig. 4C confirmed that this is the case.

The difference between the uranium molalities at 25°C from the flow and static systems cannot be entirely due to the dissolution kinetics since the rate constant determined from the static experiment suggests that molalities of 10^{-6} m or more should have been observed in the flow apparatus. Surface oxidation cannot be important since no high uranium molalities were observed in the flow system, even for fresh UO_2 samples. The explanation for the discrepancy very probably lies in the extreme thermodynamic stability of the U(VI) complexes, $UO_2CO_3^\bullet$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ and $(UO_2)_3(OH)_7^-$, which can form in our system if traces of oxygen and carbonate are present. For example, from Gayer and Leider's data and the other constants in Ref. 2, the room-temperature formation constant for the reaction

$$U(OH)_5^- + CO_3^{2-} + (1/2)O_2 + 3H^+ \rightleftharpoons UO_2CO_3^\bullet + 4H_2O \qquad (1)$$
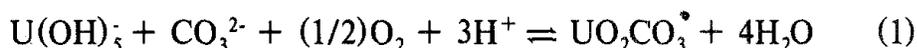
is 3×10^{55}. As a result, the aqueous uranium species in a pH 12.5 solution containing only 10^{-8} m CO_3^{2-} and purged with hydrogen containing only 10^{-5} atm O_2 have a thermodynamic ratio of $UO_2CO_3^\circ/U(OH)_5^- = 10^7$, assuming hydrogen does not react. In the flow system, however, the residual oxygen undoubtedly does react with the large excess of hydrogen at temperatures above about 150°C. At lower temperatures, the dissolved oxygen may well have been reduced in the upstream portion of the system by the reactive UO_2 and metal surfaces formed in preceding runs at high temperatures.

Gayer and Leider obtained their data in a static system using an uncharacterized phase now assumed[1-3] to have been UO_2. Their results could be high because of minute traces of dissolved oxygen and carbonate, particle size effects,[1,14] colloid formation, or simply the poorly defined nature of UO_2 prepared in alkaline solutions.[15]

We conclude that the uranium molalities in Fig. 2 above 150°C represent the solubility of UO_2 and, at lower temperatures, the solubility of either UO_2 or a higher oxide. The pH dependence (Fig. 3) must be interpreted with caution since the ^{18}F interference in the analysis is proportional to alkalinity. Nevertheless, the slope of the plot in Fig. 3, d log m(U,sat)/d log m(LiOH) = 1.2 ± 0.3 is at least consistent

with the reaction

$$UO_2 + 2H_2O + OH^- = U(OH)_5^-$$ (2)

which would correspond to a slope of unity. We therefore chose to fit the temperature-dependent data in Fig. 2 to a least-squares function based on reaction (2),

$$\log K = -5.86 + 32/T$$ (3)

where $K = m(U(OH)_5^-)/m(OH^-)$. This fitted function is based on the assumption that $\Delta C_{PR}^{\circ} = 0$ so that ΔH_R° is independent of temperature, and yields the values $\Delta G_R^{\circ}(25°C) = 32.8 \pm 1.0$ kJ-mol^{-1} and $\Delta H_R^{\circ} = -0.6 \pm 1.3$ kJ-mol^{-1} for the Gibbs energy and enthalpy changes of reaction (2). Extending Eq. (3) to include an adjustable heat capacity term did not improve the standard deviation of the fit significantly.

The treatment presented above is plausible and consistent with all the data. Uncertainties remain as to the nature of the saturating phase at low temperature and as to whether the solubility data presented here represent the true solubility or an upper limit. Again, we stress that low-temperature experimental determinations of the solubility of UO_2 are extremely sensitive to trace amounts of carbonate and oxygen.

ACKNOWLEDGMENTS

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