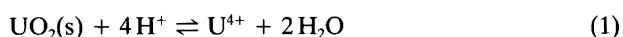Short Communication

A Reinterpretation of the Solubility Product of Solid Uranium(IV) Dioxide

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In two previous publications[1,2] we have investigated the solubility product K_{s0} for the reaction:

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

for both crystalline and amorphous materials.

The value we obtained for K_{s0} for the crystalline material was found to be in disagreement with the value calculated for reaction (1) employing a thermodynamic cycle (log K_{s0} = −4.6). We believed this discrepancy to be the result of either surface oxidation or differences in the degree of crystallinity of the solid phases considered. Shoesmith et al.[3] have made a careful study of the dependence of the degree of oxidation in the UO_2 surface as a function of the redox potential of the solutions in contact. They applied XPS spectroscopy and found that the formation of UO_{2+x} surface phases occurs for redox potential values above −200 mV. The conditions under which the solubility experiments were performed, viz. $H_2(g)$ bubbling in the presence of a Pd catalyst, prevented the oxidation of the surface. Consequently, we have devoted our attention to possible particle size effects on the solubility product of $UO_2(s)$.

We have now made a determination of the BET specific surface area of the amorphous and crystalline UO_2 solids used in our experiments. The results of these measurements and the corresponding log K_{s0} values are reported in Table 1.

The free energy of a solid in a given solvent is dependent on the surface area and the solid/liquid interfacial tension according to the expression:

$$\delta G(\text{surface}) = \gamma \delta S \tag{2}$$

where γ is the interfacial tension and δS is the change in molar surface. According to Schindler,[4] the variations in the solubility product can be correlated to changes in the molar surface area by the expression:

$$\log K_{s0}(S) = \log K_{s0}(S=0) + \gamma_{LS}(S/2.3\,RT) \tag{3}$$

where S is the molar surface area, R is the gas constant (8.314 J Mol^{-1} K^{-1}) and T is the temperature in degrees Kelvin. By using eqn. (3) we should find a linear correlation between the logarithms of the solubility products of the three different phases, i.e. the amorphous and crystalline solids and the one derived from calorimetric measurements, and their molar surfaces. The data suggest a rapid increase in log K_{s0} at low values of S and a more gradual increase at higher values of S. Nevertheless, if the three data points are fitted to a straight line from the slope, we obtain a value for the mean interfacial tension, γ_{LS}, of $UO_2(s)$ of 2.1 ± 0.2 J m^{-2}. This is to be compared to the value obtained by contact angle measurements,[5] viz. γ_{LS} = 1.72 J m^{-2}.

The fair agreement between the calculated and the experimentally determined interfacial tension indicates that variations in the surface area of the UO_2 solids considered could explain the differences in log K_{s0} values. Uranium(IV) oxide has a relatively large interfacial tension compared to the normal values for other metal oxides (0.2–1.5 J m^{-2}). Hence, surface area effects are particularly important and should be considered when comparing and applying thermodynamic data for the solubility of $UO_2(s)$. There does not seem to be discrepancy between the solubility products obtained by direct solubility measurements and that derived from calorimetric data. Finally, an empirical linear relationship between the solubility product for different UO_2 solid phases of varying crystallinity and their molar surface can be expressed by:

$$\log K_{s0}(S) = 1.385 \log S \tag{4}$$

Table 1. Log K_{s0} and BET specific surface area for $UO_2(s)$.

Solid phase	log K_{s0}	Molar surface area/m² mol⁻¹
Crystalline	−1.6±0.2	54.2±0.4
Amorphous	0.6±0.2	7954±19

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