

Studies on Metal Carbonate Equilibria.

9. Calorimetric Determination of the Enthalpy and Entropy Changes for the Formation of Uranium(IV and VI) Carbonate Complexes at 25 °C in a 3 M (Na,H)ClO₄ Ionic Medium

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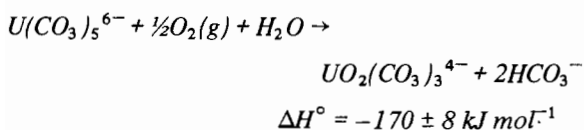
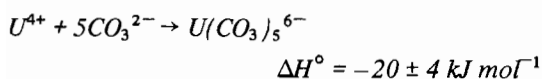
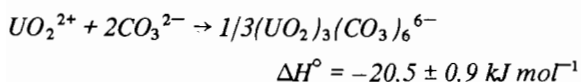
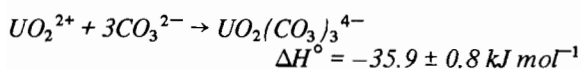
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The enthalpy changes for the reactions



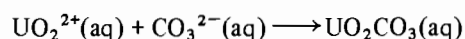
in 3 M (Na,H)ClO₄ have been derived from calorimetric results at 25 °C obtained by the use of a reaction-solution rotating bomb calorimeter. The entropy changes for the reactions were calculated by using the calorimetric data and equilibrium constants determined previously. All complexes are strongly entropy stabilized and thus conform to the behaviour expected for reactions between hard donors and acceptors.

The polymerization reaction $\text{UO}_2(\text{CO}_3)_2^{2-} \rightarrow 1/3(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ results in an increase in the number of coordinated carbonate oxygens from four to six per uranium atom. This change is followed by a large enthalpy change, $\Delta H^\circ = -35.1 \text{ kJ mol}^{-1}$, while the corresponding entropy change is negative, $\Delta S^\circ = -69.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

Introduction

Thermodynamic data for uranium species in solution, for minerals and other solid uranium com-

pounds have been evaluated by Fuger and Oetting [1], Langmuir [2], and Lemire and Tremaine [3]. These authors also review the earlier literature on the subject. There is a noticeable lack of precise thermochemical information about the uranium (IV, V and VI)–H₂O–carbonate systems. The enthalpy data presented are with one exception (reaction (13), cf. Fig. 1. Devina *et al.*, [4]) obtained from the temperature dependence of equilibrium constants, cf. Langmuir, [2], Table II. The derived enthalpy values may be fairly uncertain, even though precise data over a wide temperature range have been obtained. This is demonstrated by the investigations of Sergeyeva *et al.* [5] and by Pirozhkov and Nikolayeva [6]. These authors determined enthalpy changes for the reaction



and obtained at 25 °C values which were equal to 4.6 and –10.9 kJ mol^{–1}, respectively. Both sets of investigations were based on measurements of the temperature dependence of an equilibrium constant in approximately the same temperature range.

In previous parts of this series (Ciavatta *et al.* [7, 8] and Ferri *et al.* [9]), we reported equilibrium constants for several equilibria in the uranium(IV, V and VI)–H₂O–carbonate system. These data refer to 25 °C and a 3 M NaClO₄ ionic medium. The medium of constant and high ionic strength is necessary for the correct interpretation of the complicated redox and complex formation equilibria in the uranium–carbonate system. In this communication, we will present calorimetric enthalpy data for some of the previously studied reactions. These data will provide an addition to, and to some extent and independent check of, the present thermochemical data base for the uranium–carbonate system. However, our data refer to a 3 M (Na,H)ClO₄ solvent,

while the existing data use the pure water reference state.

Experimental

Materials and Analysis

Uranyl perchlorate and other stock solutions, as well as the CO₂-N₂ gas mixtures were obtained and analyzed as described before [7].

Solutions of UO₂(CO₃)₃⁴⁻ of known composition were prepared from the appropriate stock solutions. The exact concentrations of the various species present in solution were calculated from the known total concentrations, the known equilibrium constants and the measured free hydrogen-ion concentration.

Solutions containing approximately 75% of uranium(VI) as (UO₂)₃(CO₃)₆⁶⁻, were prepared and analyzed as described above.

Solutions of U(CO₃)₅⁶⁻ were prepared by cathodic reduction of a UO₂(CO₃)₃⁴⁻ solution [8]. The solutions are very easily oxidized and had to be contained in closed calorimeter ampoules. In order to avoid oxidation during filling the following procedure was used: The ampoules were fitted with a long thin glass neck. They were flushed with nitrogen by inserting a thin teflon tube through the neck. After flushing, the tubing was raised into the neck. Then the U(IV) carbonate solution was transferred from the hermetically closed titration cell to the ampoule using a gas-tight syringe. The flushing continued during the filling and sealing operations. By using this procedure the amount of uranium(IV) oxidized was always less than 0.3%.

Solutions of the various uranium carbonate complexes could not be made as concentrated as was wished due to the formation of the solid phases UO₂CO₃(s), Na₄UO₂(CO₃)₃(s) and UO₂(s).

Calorimetric Measurements

An LKB 8721-4 reaction-solution rotating bomb calorimeter (Olofsson *et al.*, [10]) was used for the calorimetric measurements. The internal volume of the hermetically sealed stainless steel reaction vessel was 75.9 cm³. The original plug and socket unit on top of the calorimeter lid has been modified, thus reducing the equilibration time to about 6 min for this vessel. This modification also improved the precision of the measurements. The booster heater was replaced by a vent, making it possible to purge the calorimeter liquid by bubbling through N₂(g) or to equilibrate the solution with the CO₂-N₂ gas mixture. In the oxidation experiments oxygen was introduced into the gas phase through the gas inlet microvalve after assembling the calorimeter. Samples to be reacted were placed in spheroidal glass ampoules of 1.8 ml volume. Ampoules larger than

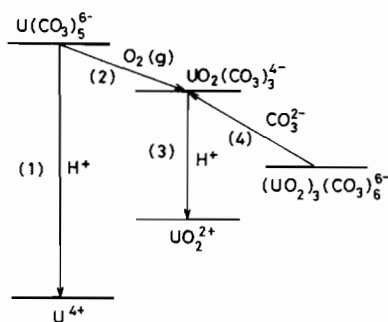


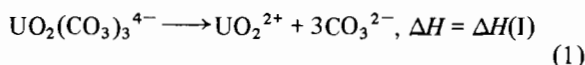
Fig. 1. The figure illustrates the uranium carbonate systems studied calorimetrically. The arrow indicates the direction of the various reactions (1)–(4) and the horizontal bars the initial and final states for the uranium containing species. The other reactants are indicated at the arrows.

1.8 ml cannot be used in this calorimeter. The reactions were fast, giving reaction periods ranging from about 6 min (which is the time the calorimeter takes to equilibrate) in the oxidation experiments, to about 12 min in the experiments of the neutralisation of Na₂CO₃ solutions in 3 M HClO₄.

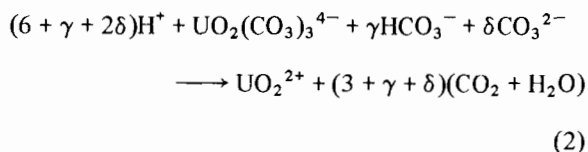
The quantity of heat evolved by the electromagnet when breaking the ampoules (about 5 J) was determined from separate experiments. This quantity is reproducible within ± 0.02 J. The method used to evaluate the corrected temperature rise and to correct for heat exchange *etc.* is described elsewhere [10].

Dissociation of UO₂(CO₃)₃⁴⁻

The enthalpy of dissociation of UO₂(CO₃)₃⁴⁻ in 3 M NaClO₄ was determined from the difference



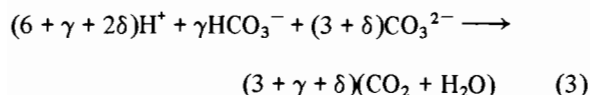
between the enthalpy changes observed upon addition of an excess of HClO₄ to solutions Ia and Ib, respectively. Solution Ia had the following composition: 3.00 mM UO₂(CO₃)₃⁴⁻, 0.99 mM HCO₃⁻, 0.55 mM CO₃²⁻, 0.014 mM OH⁻ and 14.10 mM Na⁺ in 3 M NaClO₄. In the calorimetric experiments 2.4 × 10⁻³ mol HClO₄ in the form of 0.79 ml 3 M HClO₄ was added to 65.11 ml of solution Ia. This gives an acidic final solution of UO₂²⁺, where all (HCO₃⁻ + CO₃²⁻) has been transformed to (H₂CO₃ + CO₂) and the acidity is high enough to suppress the hydrolysis of UO₂²⁺. The reaction in the calorimeter may be written



The observed enthalpy change was $h_2 = -191$ J, $s(h_2) = 0.05$ J ($n = 5$). In the following the results of individual series of measurements will be given as the mean, h , the estimated standard deviation of the mean, s , and the number of experiments, n .

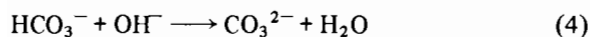
In the second series of measurements the same amount of HClO₄ was added to 65.11 ml of solution Ib of the following composition: 1.18 mM HCO₃⁻, 9.36 mM CO₃²⁻, 0.205 mM OH⁻ and 20.14 mM Na⁺ in 3 M NaClO₄.

The reaction in the calorimeter is



The resulting enthalpy change was $h_3 = -9.42$ J, $s(h_3) = 0.06$ J ($n = 4$). Subtraction of (3) from (2) gives (1).

However, the difference between the compositions of solutions Ia and Ib due to hydrolysis of CO₃²⁻ gave a small difference between the δ and γ in reactions (2) and (3). The correction was evaluated taking into account the following process:



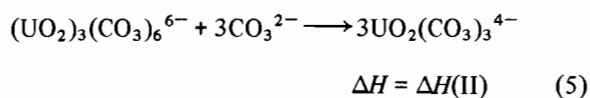
The molar enthalpy change for reaction (4) is estimated to be $\Delta H_4 = -40.0$ kJ mol⁻¹ with an uncertainty of ± 1 kJ mol⁻¹ in 3 M NaClO₄ (Arnek and Kakolowicz, [11] Berg and Vanderzee, [12]), thus for the molar enthalpy of dissociation we have

$$\Delta H(I)/kJ \text{ mol}^{-1} = (h_2 - h_3)/0.1953 + 0.064 \cdot \Delta H_4$$

which gives $\Delta H(I) = 35.9$ kJ mol⁻¹. The uncertainty expressed as $2 \cdot s(\Delta H(I))$ is estimated to be ± 0.8 kJ mol⁻¹. The random errors in the calorimetric experiments are considered to give the major contribution to the overall uncertainty of the molar reaction enthalpies.

Transformation of (UO₂)₃(CO₃)₆⁶⁻ to UO₂(CO₃)₃⁴⁻

The enthalpy change for the process



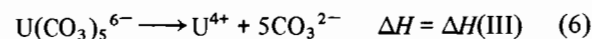
in 3 M NaClO₄ was determined from measurements of the enthalpy change when adding an excess of Na₂CO₃ (in solution) to solution IIIa containing (UO₂)₃(CO₃)₆⁶⁻. Solution IIIa had the following composition: 5.00 mM (UO₂)₃(CO₃)₆⁶⁻, 5.00 mM UO₂(CO₃)₃⁴⁻, 4.67 mM HCO₃⁻, 2.04 mM (H₂CO₃ + CO₂) and 54.67 mM Na⁺ in 3 M NaClO₄. This solution was saturated with a 10% CO₂-N₂ gas mixture.

To ensure that the solution had the given composition, the CO₂-N₂ gas mixture was also bubbled through the calorimeter vessel for ½ h after the transfer of solution IIIa. In the calorimetric experiments 1.67 ml of 0.70 M Na₂CO₃ in 3 M NaClO₄ was added to 67.0 ml of solution IIIa. All of the trinuclear complex reacts to give the mononuclear complex. The [H⁺] of the final solution was measured ([H⁺] = 10^{-7.34}) and was found to agree with the value calculated assuming reaction (5). The observed enthalpy change was $h_5 = -17.55$ J, $s(h_5) = 0.06$ J ($n = 5$).

Blank experiments were carried out in order to correct for the sum of the enthalpy of solution of gaseous CO₂, the enthalpy of the reaction (H₂CO₃ + CO₂(aq) + H₂O) + 2CO₃²⁻ → 4HCO₃⁻ and the enthalpy of dilution of Na₂CO₃ in 3 M NaClO₄. In these experiments the same amount of Na₂CO₃ solution as above was added to 67.0 ml of solution IIIb. Solution IIIb was prepared by bubbling the CO₂-N₂ gas mixture through a solution containing a relatively high concentration of HCO₃⁻ ions in order to suppress the hydrolysis of CO₃²⁻ during the calorimeter reaction. The same procedure as with solution IIIa was used when filling and equilibrating solution IIIb. The conditions were chosen so that solution IIIb contains the same amount of (CO₂(aq) + H₂CO₃) as solution IIIa, the same amount of CO₂(g) in the free space of the calorimeter vessel, approximately the same pH as solution IIIa and enough bicarbonate to suppress the hydrolysis of the excess CO₃²⁻ after the reaction. The blank experiment gave as a result $h_6 = -2.07$ J, $s(h_6) = 0.04$ J ($n = 3$). The molar enthalpy change $\Delta H(II)$ for reaction (5) is then calculated as $\Delta H(II)/kJ \text{ mol}^{-1} = (-17.55 + 2.07)/0.335$ $\Delta H(II) = -46.21$ kJ mol⁻¹ with an estimated uncertainty $2s[\Delta H(II)] = 0.44$ kJ mol⁻¹.

Dissociation of U(CO₃)₅⁶⁻

The enthalpy change for the dissociation of U(CO₃)₅⁶⁻ in 3 M HClO₄ was determined from the

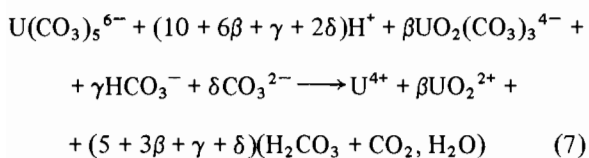


difference between the enthalpy changes observed when adding solutions IIIa and IIIb respectively, to a large excess of 3 M HClO₄. From the known equilibrium constants (Kraus and Nelson, [13]) for the hydrolysis of U(IV) we find that 99.7% of the uranium is present as U⁴⁺ and 0.3% as UOH³⁺.

The composition of solution IIIa was the following: 19.05 mM U(CO₃)₅⁶⁻, 0.96 mM UO₂(CO₃)₃⁴⁻, 139.8 mM HCO₃⁻, 9.22 mM CO₃²⁻, 1.7×10^{-3} mM OH⁻ and 276.4 mM Na⁺ in 3 M NaClO₄.

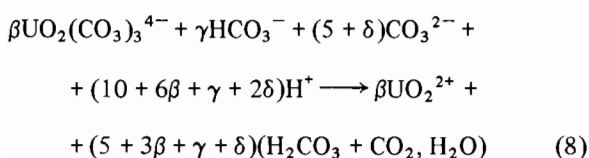
In the calorimetric experiments 1.7 ml of solution IIIa was added to 67.0 ml 3 M HClO₄. Nitrogen was bubbled through the perchloric acid before use and for some minutes after transfer to the calorimeter

vessel even though simulation of the reaction in an open vessel showed no appreciable oxidation of U(IV) in this acidic medium. In the reaction all $\text{U}(\text{CO}_3)_5^{6-}$ reacts to give U^{4+} (and a small amount UOH^{3+}), all HCO_3^- and CO_3^{2-} give $(\text{H}_2\text{CO}_3-\text{CO}_2)$:



The observed enthalpy change was $h_7 = -2.38$ J, $s(h_7) = 0.04$ J, ($n = 4$). The composition of solution IIIb used for the blank experiments was: 0.96 mM $\text{UO}_2(\text{CO}_3)_3^{4-}$, 139.8 mM HCO_3^- , 104.5 mM CO_3^{2-} , 1.9×10^{-3} mM OH^- and 352.6 mM Na in 3 M NaClO_4 .

In the calorimetric experiments 1.7 ml of solution IIIb was added to 67 ml 3 M HClO_4 :



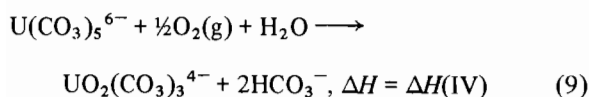
The observed enthalpy change was $h_8 = -3.04$ J, $s(h_8) = 0.04$ J, ($n = 4$). Subtraction of (8) from (7) gives (6) and after correction for the enthalpy of hydrolysis (Kraus and Nelson, [14]) the molar enthalpy of dissociation was calculated as

$$\begin{aligned} \Delta H(\text{III})/\text{kJ mol}^{-1} = \\ = (h_7 - h_8)/32.39 \times 10^{-3} - 0.03 \cdot 46 \end{aligned}$$

which gives $\Delta H(\text{III}) = 20$ kJ mol $^{-1}$ with an estimated uncertainty $2s[\Delta H(\text{iii})] = 4$ kJ mol $^{-1}$.

Oxidation of $\text{U}(\text{CO}_3)_5^{6-}$ to $\text{UO}_2(\text{CO}_3)_3^{4-}$

The enthalpy of oxidation of $\text{U}(\text{CO}_3)_5^{6-}$ in 3 M NaClO_4 was determined from experiments in which



ampoules containing the $\text{U}(\text{CO}_3)_5^{6-}$ ion were broken in the calorimeter containing solution IVb plus gaseous O_2 . The solution IVa containing the $\text{U}(\text{CO}_3)_5^{6-}$ ion had the following composition (compare solution IIIa): 19.72 mM $\text{U}(\text{CO}_3)_5^{6-}$, 0.29 mM $\text{UO}_2(\text{CO}_3)_3^{4-}$, 134.1 mM HCO_3^- , 8.42 mM CO_3^{2-} , 0.016 mM OH^- and 270.4 mM Na^+ in 3 M NaClO_4 .

The solution IVb used as calorimeter liquid had the composition 20.01 mM $\text{UO}_2(\text{CO}_3)_3^{4-}$, 133.1 mM HCO_3^- , 8.38 mM CO_3^{2-} , 0.016 mM OH^- and

229.9 mM Na^+ in 3 M NaClO_4 . Thus with the exception of the uranium complex ions, solutions IVa and IVb have nearly the same composition. The ampoules contained 1.7 ml of solution IVa. The volume of the calorimeter liquid was 59.1 ml, leaving a gas phase of 15 ml containing O_2 at 2.5 atm. The partial pressure of oxygen can be considered constant, since only 1.7×10^{-6} mol O_2 is consumed during the reaction. The measured energy change which refers to reaction (9) was $u_9 = -5.66$ J, $s(u_9) = 0.14$ J, ($n = 4$). The molar enthalpy change equals $\Delta U(\text{IV}) - \frac{1}{2}RT$ which leads to $\Delta H(\text{IV}) = -170$ kJ mol $^{-1}$, with an estimated uncertainty $2s[\Delta H(\text{IV})]$ equal to 8 kJ mol $^{-1}$.

Results and Discussion

Thermochemical data are usually referred to the infinite dilution reference state, while our data refer to a 3 M (Na, H) ClO_4 solvent. This choice was made because of experimental considerations. It is difficult or impossible to determine precise equilibrium constants for reactions involving ions of high charge in solutions of low ionic strength. An obvious example is offered by the uranium(IV) reactions, where the $\text{U}^{4+}(\text{aq})$ ion exists only at fairly high concentrations of acid. The redox- and complex-formation equilibria in the uranium systems are so complicated that precise equilibrium data are needed to calculate the chemical composition of the solutions used in the calorimetric experiments.

A summary of experimental enthalpy values and free energy and entropy data for the uranium-carbonate system is given in Table I. This table also contains experimental data obtained by other authors.

Some of the calorimetric measurements, particularly those involving reaction (6) have fairly large errors. This is due to the small amounts of uranium reacting, which in turn are determined by the chemical properties of the system, and the physical characteristics of the calorimeter as discussed previously.

All uranium carbonate complexes are strongly entropy stabilized and the enthalpy changes decrease from $\text{UO}_2\text{CO}_3(\text{aq})$ to $\text{UO}_2(\text{CO}_3)_3^{4-}(\text{aq})$. These features are typical for interactions of hard acceptors with hard donors (e.g. Åhrland [15]).

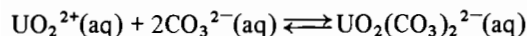
The mononuclear complex $\text{UO}_2(\text{CO}_3)_2^{2-}$ is formed only at very low total concentrations of uranium(VI), 10^{-4} M and less (Grenthe *et al.* [17]). At higher total concentrations $\text{UO}_2(\text{CO}_3)_2^{2-}$ forms a trimer, $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, the structure of which has been determined by Åberg *et al.* [16]. The polymerization results in an increase in the number of coordinated carbonate oxygens from four to six per uranium atom. This change is followed by a large enthalpy change, $\Delta H^\circ = -35.1$ kJ mol $^{-1}$, while the

TABLE I. Free Energy, Enthalpy and Entropy Data for the Uranium Carbonate System. The data in the present study refer to a 3 M NaClO₄ reference state, while all other data correspond to the infinite dilution standard state.

Reaction	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \longrightarrow \text{UO}_2(\text{CO}_3)_3^{4-}$			
This work	-129.0	-35.9 ± 0.8	312
Devina <i>et al.</i> [4]		-40.3	
Langmuir [2]		-37.2	
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_3^{2-} \longrightarrow 3\text{UO}_2(\text{CO}_3)_3$			
This work	-66.4	-46.2 ± 0.4	67.7
$\text{U}^{4+} + 5\text{CO}_3^{2-} \longrightarrow \text{U}(\text{CO}_3)_5^{6-}$			
This work	-220.3	-20 ± 4	672
$\text{U}(\text{CO}_3)_5^{6-} + \frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O} \longrightarrow \text{UO}_2(\text{CO}_3)_3^{4-} + 2\text{HCO}_3^-$		-170 ± 8	
This work			
$\text{UO}_2^{2+} + \text{CO}_3^{2-} \longrightarrow \text{UO}_2\text{CO}_3(\text{aq})$			
Sergeyeva <i>et al.</i> [5]	-56.3	4.6 ± 1.7	204
Pirozhkov and Nikolayeva [6]		-10.9	
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \longrightarrow \text{UO}_2(\text{CO}_3)_2^{2-}$			
Langmuir [2]	-97.0	14.6	374
<i>Derived quantities</i>			
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \longrightarrow \frac{1}{3}(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$			
This work	-106.9	-20.5	290
$\text{UO}_2(\text{CO}_3)_2^{2-} \longrightarrow \frac{1}{3}(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$			
This work	-14.4*	-35.1	-69.4
$\text{U}^{4+} + \frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O} \longrightarrow \text{UO}_2^{2+} + 2\text{H}^+$			
This work	-125 ± 9		
Fuger and Oetting [1]	-141.8 ± 4		

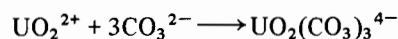
*This value has been calculated by using the equilibrium constants of Grenthe *et al.*

corresponding entropy change is negative, $\Delta S^\circ = -69.4 \text{ J K}^{-1} \text{ mol}^{-1}$. These data are based on the equilibrium constant for the reaction



given by Grenthe *et al.* The ΔH° value for the reaction above was calculated from the enthalpies of formation of reactants and products given by Langmuir [2]. The enthalpy of formation of $\text{UO}_2(\text{CO}_3)_2^{2-}$ is based on an *estimated* temperature function, *cf.* Langmuir page 552.

Our value for the enthalpy change for the reaction

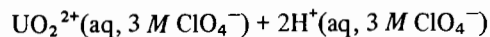
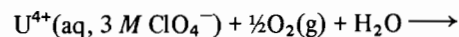


agrees fairly well both with the previous calorimetric determination of Devina *et al.* [4] and with the value reported by Langmuir. However, these values refer to solutions of lower ionic strength

0.1–0.2 M and the infinite dilution reference state, respectively.

No previous enthalpy information is available for the formation of $\text{U}(\text{CO}_3)_5^{6-}(\text{aq})$. The degree of entropy stabilization of this ion is higher than for $\text{UO}_2(\text{CO}_3)_3^{4-}(\text{aq})$, as expected for hard–hard interactions (Ahrland [14]).

By combining the measured enthalpy values for reactions (1), (6) and (9) with the enthalpies of ionization of H_2O and HCO_3^- (Arnek and Kukulowicz [11], Berg and Vanderzee [12]) we obtain the enthalpy change for the reaction



This value is $\Delta H^\circ = -125 \pm 9 \text{ kJ mol}^{-1}$, as compared to $\Delta H^\circ = -141.8 \pm 4 \text{ kJ mol}^{-1}$, calculated from the data of enthalpies of formation of $\text{UO}_2^{2+}(\text{aq})$ and $\text{U}^{4+}(\text{aq})$ given by Fuger and Oetting,

[1]. The agreement is fairly good considering that two different reference states are used, *i.e.* 3 M (Na, H)ClO₄ and pure water, respectively.

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