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# THE ESTIMATION OF HEATS OF FORMATION.

by

Leo Brewer



February 2, 1948

(Addition to Report CC-3585)

Berkeley, California

Chemistry-General

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## ABSTRACT

The procedure for estimation of heats of formation of compounds is illustrated by discussion of compounds of several of the elements of the actinide series. The procedure is particularly suited for lanthanide and actinide elements because of the similarity of the ionic radii and types of bonding.

University of California
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THE ESTIMATION OF HEATS OF FORMATION

By Leo Brewer

February 2, 1948
(Addition to Report CC-3585

For Research, development, or manufacturing work.

It is often possible to estimate values for the heats of formation of compounds from related thermodynamic data. Although such estimates can not usually be made with high accuracy, data of considerable value can often be obtained. Brewer, Bromley, Lofgren, and Gilles[1, 2, 3, 4] have used such estimations in their compilations of the thermodynamic properties of molybdenum, tungsten, uranium, neptunium, plutonium, and they[5] have also used the method to some extent in their more extensive compilation of the thermodynamic properties of the elements in general.

As an illustration of this method, the heats of formation of some compounds of Th, Np, and Am will be estimated.

Westrum and Eyring[6] have determined the heats of solution of Th metal, $ThCl_4$, and $Th_2S_3$ in 6 moles per liter HCl. These determinations give one $\Delta H_{298}$ = -285.2 kilocals. for $ThCl_4(s)$, $\Delta H_{298} = -306.8 \pm 2$ for $Th_2S_3$, and $\Delta H_{298} = -185.5$ kilocals. for $Th^{4+}$(1M HCl). These experimental values may now be used to estimate heats of formation of the other tetravalent and trivalent compounds of thorium.

Brewer, Bromley, Lofgren, and Gilles[2] give the best available data for the heats of formation of $UF_4$, $UCl_4$, $UBr_4$, and $UI_4$. With these data, one could estimate the heats of formation of $ThF_4$, $ThBr_4$, $ThI_4$ from the value for $ThCl_4$ by assuming the differences between the heats of formation of the above compounds and that of $ThCl_4$ are the same as the differences between the corresponding uranium compounds and $UCl_4$. Normally one could not make such a simple assumption and one would have to consider the variation in such differences as a function of the ionic radius of the cation. Thus the heat difference $MCl_4 - MI_4$ should increase as the size of $M^{4+}$ decreases due to increasing anion repulsion. However, the ionic radii of $Th^{4+}$ and $U^{4+}$ are close enough; so that within the general uncertainty of such estimations, one can neglect this variation. This is especially necessary since data are lacking for the effect of the size of the tetravalent ion on the heats of formation for ions of the size of $Th^{4+}$.

Thus the heat difference $UF_4$-$UCl_4$ is 192 kilocals. The difference $UCl_4$-$UBr_4$ is 40 kilocals. The difference $UCl_4$-$UI_4$ is 94 kilocals. Applying these differences to the heat of formation of $ThCl_4$ given above, one estimates the following heats of formation: $ThF_4$, $\Delta H_{298}$=-477 kilocals; $ThBr_4$, $\Delta H_{298}$=-245 kilocals; $ThI_4$, $\Delta H_{298}$ = -191 kilocals. Future data on the effect of the difference in ionic radius of $Th^{4+}$ and $U^{4+}$ will probably move these values closer together by one to two kilocalories. By a similar process of comparison of $UO_2$ and $UCl_4$, we estimate the heat of formation of $ThO_2$ to be $\Delta H_{298} = -304 \pm 5$ kilocalories. Bichowsky and Rossini[7] report three different values -327, 330, and -293 kilocalories, all obtained from the heat of combustion of thorium metal. Oxide impurities could cause low results while hydrogen impurity could cause high results. The best one can do is to take about $\Delta H_{298}$=$-310 \pm 20$ kilocalories as the heat of formation of $ThO_2$.

From the heat of formation of $Th_2S_3$, one may make estimates of the heats of formation of other trivalent compounds of thorium. The most similar trivalent sulfide for which the heat of formation is known is $Ce_2S_3$. The heat of formation of $Ce_2S_3$ as tabulated by Brewer, Bromley, and Gilles[8] is 40.3 kilocalories more negative than the heat for $Th_2S_3$. If one assumed that $Ce_2S_3$ and $Th_2S_3$ were compounds of similar structure, one would then assume that the heat of formation of $2CeCl_3$ would be more negative by 40.3 kilocalories than the heat of formation of $2ThCl_3$. Such an assumption gives $\Delta H_{298} = -240$ kilocalories for $ThCl_3$. Actually, all one can say is that this value gives an upper limit to the stability of $ThCl_3$. Whereas in the case of comparison of tetravalent thorium with tetravalent uranium, we were comparing compounds with similar crystal structure and similar bonding, in the case of $Th_2S_3$ and $Ce_2S_3$, the compounds have different crystal structures and $Th_2S_3$ definitely appears to have more metallic-type bonding than $Ce_2S_3$[9]. This type of bonding should give a more stable sulfide than one bonded like $Ce_2S_3$. If $ThCl_3$, on the other hand, has bonding very similar to that of $CeCl_3$, which would be expected, than we should make our estimated heat of formation for $ThCl_3$ less negative. We do not know how far the true value is from the limit given above. The effect of different crystal structures can not be large; since it is believed that $Ce_2S_3$ exists in the $Th_2S_3$ crystal structure type when a small amount of oxide impurity is present.[10] This indicates the difference in crystal structures does not involve a large energy difference. It appears very difficult to estimate the effect of metallic bonding, and the best one can do at this time is to give the limiting value. Having fixed the limit of stability of $ThCl_3$, one can by a process similar to that used for the tetravalent state calculate the upper limits of stability of $ThF_3$, $ThBr_3$, and $ThI_3$ by comparison with Ce and U trivalent halides.

This procedure gives as limiting values the following: $ThF_3$, $\Delta H_{298}$ = -383 kilocals.; $ThBr_3$, $\Delta H_{298}$ = -207 kilocals.; $ThI_3$, $\Delta H_{298}$ = -163 kilocals.

The very surprising thing about these figures is that they indicate that $ThI_3$, $ThBr_3$, and $ThCl_3$ should all be stable compounds with respect to the reactions of the type $4ThCl_3(s) = 3ThCl_4(s) + Th(s)$ if the trivalent heats are near the limiting value and therefore should be preparable. Warf[11] appears to have demonstrated that $ThF_3$ is not stable which would require $\Delta H_{298} \doteq -358$ kilocals. This would make $ThBr_3$ and $ThI_3$ unstable, but $ThCl_3$ could still be stable. The only other data which might be used to check these predictions are some vapor density measurements on $ThCl_4$ gas by Kruss and Nilson[12] which show that $ThCl_4$ vapor is undissociated below 1000°C. Above 1000°C., the $CO_2$ they used reacts with $ThCl_4$, and their data do not give any evidence on whether $ThCl_4$ is dissociated, in spite of the fact that their data are widely quoted to indicate dissociation of $ThCl_4$. Using the value of $\Delta H_{298}$ = -240 kilocals. for $ThCl_3(s)$ which gives the highest possible stability to the trivalent state, we calculate for the reaction $ThCl_4(g) = ThCl_3(g) + Cl\ (g)$ at 1100°K. that $K = 10^{-12}$ by using the vapor pressures given by Brewer[(5)]. This calculation indicates that $ThCl_4$ vapor would not be appreciably dissociated even at very high temperatures although $ThCl_3(s)$ could be quite stable. It would require a strong reducing agent to obtain $ThCl_3$ from $ThCl_4$. A similar calculation indicates that $ThCl_3$ should vaporize without appreciable disproportionation if $\Delta H_{298}$ = -240 kilocalories is taken for $ThCl_3(s)$.

It should be rather simple to check the above predictions by heating $ThCl_4$ with thorium metal. If the calculations given above are reliable, one should obtain a reaction giving $ThCl_3$. Experiments of this type are in progress.

Brewer, Bromley, Gilles, and Lofgren[(3)] have given values for the heats of formation of the neptunium ions and halides. The oxide system will be taken here as an example. By comparing the heat of formation of $UO_2$ with $UCl_4$ or aqueous $U^{4+}$, and applying the differences to the heat of formation of $NpCl_4$ or $Np^{4+}$, one calculates $\Delta H_{298} = -289 \pm 7$ kilocalories for $NpO_2$. In a similar manner, one can estimate $\Delta H_{298} = -618 \pm 15$ kilocalories for $Np_2O_5$ and $\Delta H_{298} = -298 \pm 7$ kilocalories for $NpO_3$. Using these values, one calculates that $NpO_2$ and $Np_2O_5$ are both stable with respect to disproportionation or decomposition. For example at 1000°K., one calculates that the oxygen partial pressure over a mixture of $NpO_2$ and $Np_2O_5$ would be only about $10^{-8}$ atmospheres. However, one calculates that $NpO_3$ would be unstable at all temperatures. In view of the uncertainties of the values given above, it is difficult to calculate how much $NpO_3$ might dissolve in $Np_2O_5$, but it does not seem likely that one could obtain an oxide phase above $NpO_{2.51}$. Thus one would predict, that although $Np_2O_5$ could be prepared, one would not be able to prepare any solid solutions above $Np_2O_5$, e.g. $Np_3O_8$. Gruin and Katz(13) have reported the preparation of $Np_3O_8$ or $Np_6O_{17}$. Details of the work are not available yet. It would be interesting to know if actual analyses were performed. $Np_2O_5$, $Np_3O_8$, and $Np_6O_{17}$ would all give virtually the same X-ray pattern so they could be distinguished only by very careful and precise analyses. Although it is not possible to eliminate $Np_3O_8$ and $Np_6O_{17}$ in view of the uncertainties of the estimated values, one would suggest that the preparation may have been $Np_2O_5$ instead of the reported compositions.

In addition to the oxides discussed above, NpO also probably exists, but not enough data are available to allow one to estimate its heat of formation.

In the cases of the estimates made above, we had in every case a heat of formation of some species at the desired oxidation state as a starting point for the calculations.

If no heats are known for any species at a given oxidation state, it is usually not possible to make any reasonable estimates of heats of formation. However, sometimes one can estimate the stability of one oxidation state relative to another even when absolute values of the heats of formation can not be estimated. Thus if the stability of $Am^{4+}$ relative to $Am^{3+}$ were known, one could calculate the stability of the tetravalent halides and oxides relative to the trivalent compounds. Unfortunately no oxidation-reduction potentials or other data are available for the $Am^{3+}$-$Am^{4+}$ couple. However, in order to provide a very rough idea of the possible compounds of Am, one can extrapolate the potential for the 3-4 couple for the series U, Np, and Pu to a very rough value for Am. This gives us $\Delta H_{298}$ = 31 kilocalories for $Am^{3+} + H^+ = Am^{4+} + 1/2\ H_2(g)$. A similar procedure may be carried out for the other oxidation states. Such a procedure allows one to predict that the trivalent chloride, bromide, iodide, and sulfide will be the highest oxidation state preparable in those systems. In the oxide system, one would predict that $AmO_2$ would be preparable in addition to $Am_2O_3$. In the fluoride system, $AmF_4$ and $AmF_3$ should be preparable, but no higher states should exist. The stability of the tetravalent oxide and fluoride relative to the trivalent state may be judged qualitatively by comparison with cerium, which has a potential for the $Ce^{3+}$ - $Ce^{4+}$ couple which is close to that predicted for the Americium couple.

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