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HEATS OF FORMATION OF LIGHT ELEMENT COMPOUNDS

OUTLINE OF FINAL SCIENTIFIC REPORT
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STATES AIR FORCE, UNDER CONTRACTS AF 61(052)-447 AND
AF 61(052)-863
I. PUBLICATION OF INVESTIGATIONS CARRIED OUT UNDER CONTRACT AF 61(052)--47 AND DRAFTED AND SUBMITTED UNDER CONTRACT AF 61(052)--863


II. COMPLETED WORK REPORTED IN DETAIL IN SCIENTIFIC REPORTS


III. WORK ON WHICH EXPERIMENTS HAVE BEEN COMPLETED BUT WHICH HAVE NOT YET BEEN FULLY EVALUATED AND REPORTED.

1. Heat of formation of beryllium fluoride

The heat of formation of beryllium fluoride has been measured by reacting beryllium with lead fluoride. Weighed quantities of the purified reactants in the form of powders were mixed and a short length of fine tungsten wire was embedded in the mixture. Reaction was started by heating the tungsten wire momentarily with a battery of about 12 volts. The ignition energy was measured by a ballistic galvanometer [the procedure has been used and
described before in detail[1]. From the measured heat of reaction \( \Delta H^\circ_{298} = -84.0 \text{ kcal} \) and auxiliary data 
\( \Delta H^\circ_{298}, \text{PbF}_2(c) = -160.2 \text{ kcal} \) and 
\( \Delta H^\circ_{\text{trans}, \text{BeF}_2(gl)} = \text{BeF}_2(c) = 1.1 \text{ kcal} \) the heat of formation of beryllium fluoride becomes 
\( \Delta H^\circ_{298}, \text{BeF}_2(c) = -245.3 \text{ kcal} \).

2. Heat of formation of gibbsite

For the determination of the heat of formation of gibbsite and the heats of combination in the mixed oxides enumerated below in (3), a platinum calorimeter for use with 40 weight per cent hydrofluoric acid at 75°C was built. The calorimeter (volume \( \sim 500 \text{ cc} \)) was stirred by a PTFE (teflon) enclosed magnet moved by a magnet underneath the calorimeter. The lid of the calorimeter was secured by two metal rings and made gas-tight by a Viton 0-ring. The samples were introduced through a port in the lid closed by a shutter consisting of a Teflon plate sliding between small Viton 0-rings. The samples were in general contained in gelatine capsules, but for hygroscopic substances or aqueous solutions, glass capsules were used. Before their introduction into the calorimeter they were held in a block above the calorimeter maintained at 25°C.

The heat of formation of gibbsite is based on the comparison of the heat of solution of anhydrous aluminium chloride and water, introduced in separate glass capsules, with that of gibbsite and diluted hydrochloric acid, also in separate capsules. From these experiments the heat of formation of gibbsite was found: 
\( \Delta H^\circ_{298}, \text{Al}_2\text{O}_3.3\text{H}_2\text{O} \text{(gibbsite)} = -618.7 \text{ kcal} \). With the heat of
formation of $\alpha$-alumina ($-400.4$ kcal) and that of water
($-68.32$ kcal) the heat of hydration of alumina to gibbsite
was found to be $-13.3 \pm 0.6$ kcal. This is a significantly
more negative value than the older but currently accepted
(2) value of $-7.4$ kcal.

3. The heats of combination in the mixed oxides $2$BeO$\cdot$LiqO
and $B_2$O$_3$.3BeO, and in the alumina containing mixed
oxides $9$Al$_2$O$_3$.2B$_2$O$_3$, $2$Al$_2$O$_3$.B$_2$O$_3$ and $Al_2$O$_3$.LiqO

The first of these mixed oxides (2BeO.Li$_2$O) has
been found in this investigation by thermal analysis of the
beryllium oxide-lithium oxide system. The X-ray pattern
for the compound has been established.

In general, the mixed oxides were made by heating
together powder mixtures of the single oxides, or their
hydrates or carbonates; the products were usually reground
between periods of heating. Careful chemical analysis of
the mixed oxides was made; they were characterised by
their X-rays.

The heats of combination in the compounds not
containing alumina were determined by comparing their heats
of solution in hydrofluoric acid with stoichiometric mixtures
of the single oxides. Since $\alpha$-alumina is not soluble in
hot hydrofluoric acid gibbsite was used for the comparison
experiments in the alumina containing compounds. For the
solution experiments the calorimeter briefly described
under (2) above was used and the following heats of com-
bination found:
2BeO.Li₂O  \quad -3.9 \pm 0.7 \text{ kcal}
B₂O₃.3BeO  \quad -9.3 \pm 0.4 \text{ kcal}
Al₂O₃.Li₂O  \quad -25.0 \pm 1.0 \text{ kcal}
2Al₂O₃.B₂O₃  \quad -15.1 \pm 1.3 \text{ kcal}
9Al₂O₃.2B₂O₃  \quad -24.5 \pm 5.2 \text{ kcal}

4. **Heat of combination in 5Al₂O₃.Li₂O**

The anhydrous mixed oxide (5Al₂O₃.Li₂O) is not soluble in hot hydrofluoric acid. It is however soluble at about 700°C in a fused salt mixture of the approximate composition 9PbO.3CdO.4B₂O₃.

For the solution measurements with this solvent at 700°C a Calvet-type calorimeter was built. It consists briefly of a stainless steel block heated electrically to and controlled at 700°C. The block is surrounded by an insulating brick inside a large water cooled steel vessel. The block contains two symmetrically arranged wells into each of which is fitted an assembly consisting of thin walled silica tubes surrounded by thin walled stainless steel tubes which are thermally joined to the block by an array of 120 thermocouples in series measuring the temperature difference between the block and the inner steel tube. The currents from the two series of thermocouples are opposed to each other and the difference amplified and recorded. This difference is proportional to the temperature difference between the two thin steel tubes. In the bottom of the silica tubes are two gold crucibles, one of them containing the molten borate glass which serves in consecutive experiments as solvent for either the double compound or a stoichiometric mixture of the single oxides. The assembly was
calibrated by supplying known amounts of electrical energy to one of the wells. The difference between the heat of solution of the compound and the oxide mixture is the heat of combination of the double oxide at 700°C.

In this apparatus a value of \( \Delta H_{\text{comb.957,5Al}_2\text{O}_3.\text{Li}_2\text{O}} = -31.4 \pm 3 \text{ kcal} \) has been obtained. The value is much more consistent with that for \( \text{Li}_2\text{O}.\text{Al}_2\text{O}_3 \) than a previous value obtained by the solution of a non-anhydrous sample in hydrofluoric acid.

5. The heats of combination of mixed beryllium-lithium fluorides

The heats of combination of the solid mixed lithium-beryllium fluorides have been determined in the apparatus and by the method described in detail in R.163/SR.2/March 1967.

\[
\Delta H^\circ_{\text{comb.298,\alpha-Li}_2\text{BeF}_4} [\text{from BeF}_2(\text{gl}) + 2\text{LiF}(c)] = -3.88 \pm 0.07 \text{ kcal.}
\]

\[
\Delta H^\circ_{\text{298,\text{LiBeF}_3(c)}} [\text{from BeF}_2(\text{gl}) + \text{LiF}(c)] = -2.28 \pm 0.14 \text{ kcal.}
\]

6. Transport of beryllium in beryllium dichloride gas

Experiments on the determination of the equilibrium between beryllium (c), beryllium dichloride (g), and a lower beryllium chloride gas have been made in the temperature range from 980 to 1235°C. Beryllium chloride vapour has been led over beryllium contained in a Knudsen cell. The beryllium chloride evaporator and the Knudsen cell were combined in one alumina tube, the two parts separated by an alumina capillary. The beryllium dichloride pressure has been determined by the weight loss of the beryllium dichloride from the evaporator. The extent of formation of beryllium monochloride has been determined by reversal of the reaction on a platinum absorber and quantitative
emission spectroscopic analysis for the beryllium content of the absorber.

Evaluation of the results for the reaction

\[ \text{Be}(c) + \text{BeCl}_2(g) = 2\text{BeCl}(g) \]

by least square method leads to

\[ \log K_p = - \frac{20,480}{T} + 9.19. \]

The results are in as good agreement with each other as can be expected considering the corrections for the evaporation of beryllium metal and for the absorption of beryllium from dichloride vapour which have to be made. Of these the former are the more important at the higher temperatures and the latter at the lower temperatures. From the equation for the equilibrium constant one derives with auxiliary data \( \Delta H_{298}^{o}, \text{BeCl}(g) = 5.5 \text{ kcal} \) and \( S_{298}^{o}, \text{BeCl}(g) = 54 \text{ e.u.} \). The data obtained are in satisfactory agreement with those of Greenbaum, Arin, Wong and Farber,\( ^3 \Delta H_{298}^{o}, \text{BeCl}(g) = 3.7 \pm 3.8 \text{ kcal} \), \( S_{298}^{o}, \text{BeCl}(g) = 53 \pm 2.3 \text{ e.u.} \). It does not appear possible, however, to reconcile them with those of Hildenbrand\( ^4 \) \( [\Delta H_{298}^{o}, \text{BeCl}(g) = 13.1 \text{ kcal}, S_{298}^{o}, \text{BeCl}(g) = 52 \text{ e.u.}] \).

7. **The heat of formation of beryllium boride**

A preliminary value \( (\Delta H_{298}^{o}, \text{Be}_2\text{B} \sim -20 \text{ kcal}) \) for the heat of formation of beryllium boride, \( \text{Be}_2\text{B} \), has been obtained by comparing the heat of solution of the compound with a stoichiometric mixture of beryllium metal and anhydrous beryllium oxide in hot hydrochloric acid in closed glass vessels.

**IV. PUBLICATION OF WORK COMPLETED**


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9.3.1970
REFERENCES


The standard enthalpies of formation (values in kcal in brackets) of BeF₂(c) (-245.3) and of Al₂O₃·3H₂O (gibbsite) (-618.7) and the standard enthalpies of combination (values in kcal in brackets) in the double compounds 2BeO·Li₂O(c) (-3.9), B₂O₃·3BeO(c) (-9.3), Al₂O₃·Li₂O(c) (-25.0), Al₂O₃·3BeO(c) (-16.1), 9Al₂O₃·2B₂O₃(c) (-24.5), Li₂BeF₄(c) (-1.2) and 2·Li₂BeF₄ (-2.7) have been determined calorimetrically. The heat of combination in 5Al₂O₃·Li₂O has also been determined calorimetrically at 957ºK (314).

The enthalpies of formation of (1) AlCl₃(c), (2) Al₃C₃(c) and Be₂C (c) and the heats of combination in (3) Li₃AlF₁₂(c) and (4) in LiBF₄(c), NaBF₄(c) and KBF₄ have also been determined and all details given in Fulmer Research Institute Scientific Reports (1) R.163/SR.4, (2) R.163/SR.5 (3) R.163/SR.2 and (4) R.163/SR.3.

The transport of Be(c) in BeCl₂(g) has been investigated and when formulated as the equilibrium of the reaction Be(c) + BeCl₂(g) = 2BeCl(g) one deduces log Kp = 20.490 + 9.19.

The standard enthalpies of formation (values in kcal in brackets) of BeF₂(c) (-245.3) and of Al₂O₃·3H₂O (gibbsite) (-618.7) and the standard enthalpies of combination (values in kcal in brackets) in the double compounds 2BeO·Li₂O(c) (-3.9), B₂O₃·3BeO(c) (-9.3), Al₂O₃·Li₂O(c) (-25.0), Al₂O₃·3BeO(c) (-16.1), 9Al₂O₃·2B₂O₃(c) (-24.5), Li₂BeF₄(c) (-1.2) and 2·Li₂BeF₄ (-2.7) have been determined calorimetrically. The heat of combination in 5Al₂O₃·Li₂O has also been determined calorimetrically at 957ºK (314).

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The transport of Be(c) in BeCl₂(g) has been investigated and when formulated as the equilibrium of the reaction Be(c) + BeCl₂(g) = 2BeCl(g) one deduces log Kp = 20.490 + 9.19.
14. **Key Words**

- Enthalpies of formation
- Enthalpies of combination
- High temperature equilibria
- Light element double oxides
- Light element double fluorides

AlCl₃(c)
Al₂O₃·3H₂O (gibbsite)
Al₂O₃·Li₂O(c)
2Al₂O₃·B₂O₃(c)
Al₄C₃(c)
5Al₂O₃·Li₂O(c)
9Al₂O₃·2B₂O₃(c)
KBF₄(c)
LiBF₄(c)
NaBF₄(c)
B₂O₃·3BeO(c)
BeCl(g)
BeCl₂(g)
BeF₂(c)
LiBeF₃(c)
Li₂BeF₄(c)
Be₂C(c)
2BeO·Li₂O(c)