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R.163/38/March 1970

HEATS OF FORMATION OF
LIGHT ELEMENT COMPOUNDS

OUTLINE OF
FINAL SCIENTIFIC REPORT

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HEATS OF FORMATION OF LIGHT ELEMENT COMPOUNDS

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R.163/38/March 1970

I. PUBLICATION OF INVESTIGATIONS CARRIED OUT UNDER CONTRACT
   AF 61(052)-447 AND DRAFTED AND SUBMITTED UNDER CONTRACT
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   1. Heats of formation of α-beryllium chloride and α- and
      β-beryllium nitride, [P.Gross, C.Hayman, P.D.Greene
      and J.T.Bingham, Trans.Faraday Soc., 62, 2719,(1966)],
      submitted 23 May 1966.

   2. Heat of formation of boron nitride (boron fluoride).
      Halogen combustion calorimetry of refractory compounds.
      [P.Gross, C.Hayman and M.C.Stuart, Proc.of the British
      Ceramic Society, 8, 39, (1967)], submitted 26 May 1966.

II. COMPLETED WORK REPORTED IN DETAIL IN SCIENTIFIC REPORTS

   1. Heat of formation and transition temperatures of solid
      lithium hexafluoraluminate, (R.163/SR.2/March 1967).

   2. Heats of formation of the fluoborates of lithium,
      sodium and potassium, (R.163/SR.3/May 1967).

   3. Heat of formation of aluminium chloride (R.163/SR.4/
      September 1967).

   4. Heats of formation of the carbides of aluminium and
      beryllium (R.163/SR.5/July 1968).

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 ($\Delta H_{r298} = -84.0$ kcal) and auxiliary data
($\Delta H^{\circ}_{f298}, PbF_2(c) = -160.2$ kcal and $\Delta H^{\circ}_{trans}, BeF_2(gl) =$
$BeF_2(c) = 1.1$ kcal) the heat of formation of beryllium
fluoride becomes $\Delta H^{\circ}_{f298}, BeF_2(c) = -245.3$ 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 ∼500 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 O-ring.   The samples were introduced through a
port in the lid closed by a shutter consisting of a Teflon
plate sliding between small Viton O-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: ΔH°_{f298},
$Al_2O_3.3H_2O$ (gibbsite) = -618.7 kcal.   With the heat of

formation of α-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 2BeO.Li$_2$O and B$_2$O$_3$.3BeO, and in the alumina containing mixed oxides 9Al$_2$O$_3$.2B$_2$O$_3$, 2Al$_2$O$_3$.B$_2$O$_3$ and Al$_2$O$_3$.Li$_2$O

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 α-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 combination found:

$2BeO.Li_2O$	-3.9 ± 0.7	kcal
$B_2O_3.3BeO$	-9.3 ± 0.4	kcal
$Al_2O_3.Li_2O$	-25.0 ± 1.0	kcal
$2Al_2O_3.B_2O_3$	-15.1 ± 1.3	kcal
$9Al_2O_3.2B_2O_3$	-24.5 ± 5.2	kcal

4. Heat of combination in $5Al_2O_3.Li_2O$

The anhydrous mixed oxide ($5Al_2O_3.Li_2O$) is not
soluble in hot hydrofluoric acid. It is however soluble
at about 700°C in a fused salt mixture of the approximate
composition $9PbO.3CdO.4B_2O_3$.

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 symetrically 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 experi-
ments as solvent for either the double compound or a stoichio-
metric 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 $\Delta H_{comb.957},5Al_2O_3.Li_2O$ =
-31.4 ± 3 kcal has been obtained. The value is much more
consistent with that for $Li_2O.Al_2O_3$ 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.
$\Delta H^{o}_{comb.298},\alpha-Li_2BeF_4$ [from $BeF_2(gl) + 2LiF(c)$] = -3.88 ± 0.07
kcal. $\Delta H^{o}_{f298},LiBeF_3(c)$ [from $BeF_2(gl) + LiF(c)$] =
-2.28 ± 0.14 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 $Be(c) + BeCl_2(g) = 2BeCl(g)$ by least square method leads to $\log Kp = - \frac{20,480}{T} + 9.19$. 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 ΔH°_{f298}, $BeCl(g) = 5.5$ kcal, and S°_{298}, $BeCl(g) = 54$ e.u. The data obtained are in satisfactory agreement with those of Greenbaum, Arin, Wong and Farber,[3] ΔH°_{f298}, $BeCl(g) = 3.7 \pm 3.8$ kcal, S°_{298}, $BeCl(g) = 53 \pm 2.3$ e.u. It does not appear possible, however, to reconcile them with those of Hildenbrand[4] $[\Delta H^\circ_{f298}, BeCl(g) = 13.1$ kcal, S°_{298}, $BeCl(g) = 52$ e.u.$]$

7. The heat of formation of beryllium boride

A preliminary value $(\Delta H^\circ_{f348}, Be_2B \sim -20$ kcal$)$ for the heat of formation of beryllium boride, Be_2B, 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

1. The heat of formation of the fluoborates of lithium, sodium and potassium, P.Gross, C.Hayman and H.A.Joel, Trans.Faraday Soc., 64, 317, (1968).

PUBLICATION OF WORK COMPLETED (continued)

2. The heat of formation and transition temperature of
   solid lithium hexafluoaluminate, P.D.Greene, P.Gross.
   and C.Hayman, Trans.Faraday Soc., 64, 633, (1968).

3. The heat of formation of aluminium chloride,
   P.Gross and C.Hayman, Trans.Faraday Soc., 66, 565,(1970).

4. Enthalpies of formation of the carbides of aluminium
   and beryllium, R.O.G.Blachnik, P.Gross and C.Hayman,
   Trans.Faraday Soc., (in print).

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9.3.1970

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3. M.A.Greenbaum, M.L.Arin, M.Wong and M.Farber,
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    50, 5350, (1969).

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13. **Abstract**

The standard enthalpies of formation (values in kcal in brackets) of
BeF_2(c) (-245.3) and of $Al_2O_3.3H_2O$ (gibbsite) (-618.7) and the standard
enthalpies of combination (values in kcal in brackets) in the double
compounds $2BeO.Li_2O$(c) (-3.9), $B_2O_3.3BeO$(c) (-9.3), $Al_2O_3.Li_2O$(c)
(-25.0), $Al_2O_3.B_2O_3$(c) (-16.1), $9Al_2O_3.2B_2O_3$(c) (-24.5), $LiBeF_3$(c)
(-1.2) and α-Li_2BeF_4 (-2.7) have been determined calorimetrically. The
heat of combination in $5Al_2O_3.Li_2O$ has also been determined calorimetrically
at 957°K (31.4).

The enthalpies of formation of (1) $AlCl_3$(c), (2) Al_4C_3(c) and Be_2C (c)
and the heats of combination in (3) Li_3AlF_6(c) and (4) in $LiBF_4$(c),
$NaBF_4$(c) and KBF_4 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 $BeCl_2$(g) has been investigated and when formulated
as the equilibrium of the reaction Be(c) + $BeCl_2$(g) = $2BeCl$(g) one deduces
$\log Kp = \dfrac{20,480}{T} + 9.19$.

14. <u>Key Words</u>

Enthalpies of formation

Enthalpies of combination

High temperature equilibria

Light element double oxides

Light element double fluorides

$AlCl_3(c)$

$Al_2O_3 \cdot 3H_2O$ (gibbsite)

$Al_2O_3 \cdot Li_2O(c)$

$2Al_2O_3 B_2O_3(c)$

$Al_4C_3(c)$

$5Al_2O_3 \cdot Li_2O(c)$

$9Al_2O_3 \; 2B_2O_3(c)$

$KBF_4(c)$

$LiBF_4(c)$

$NaBF_4(c)$

$B_2O_3 \cdot 3BeO(c)$

$BeCl(g)$

$BeCl_2(g)$

$BeF_2(c)$

$LiBeF_3(c)$

$Li_2BeF_4(c)$

$Be_2C(c)$

$2BeO \cdot Li_2O(c)$