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HEATS OF FORMATION OF COMPOUNDS CONTAINING B, Be, Al AND Li
Title of Project

HEATS OF FORMATION OF COMPOUNDS CONTAINING B, Be, Al AND Li.

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P. CROSS
Principal Scientist
HEATS OF FORMATION OF COMPOUNDS CONTAINING B, Be, Al and Li

1. SUMMARY OF THE WORK ACCOMPLISHED

A. Beryllium Fluoride

Final evaluation of the measurements on beryllium fluoride has been deferred. Experiments on the preparation of a completely crystalline beryllium fluoride by various methods have, so far, not succeeded.

B. Double Oxides

The working of the platinum calorimeter has been simplified and the precision increased by maintaining the samples at constant temperature in a small metal block thermostat before dropping them into the calorimeter.

Solution experiments on the compound 9Al₂O₃.2B₂O₃ and on mixtures of gibbsite and boron oxide (glass) in the corresponding ratio have been made. Eight experiments on the mixture gave \( \Delta H_{\text{Sol}} = 799.3 \pm 1.0 \) kcal for the molar heat of solution. Seven experiments on the compound gave \( \Delta H_{\text{Sol}} = 900.0 \pm 1.4 \) kcal for the molar heat of solution. From these measurements and Barany's [Koehler, Barany and Kelley, Bureau of Mines Report of Investigations 5711 (1961)] heat of formation of gibbsite from α-alumina and water (\( \Delta H_{\text{hydr.}}^{298} = -7.36 \pm 0.62 \) kcal), the preliminary value \( \Delta H_{\text{Sol}}^{298} = +2.94 \pm 5.8 \) kcal is derived for the heat of combination of the oxides in 9Al₂O₃.2B₂O₃. This value is subject to corrections for small errors in the calibration of the calorimeter, in the estimate of the heat of
Several measurements on the heat of solution of the compound \( \text{Al}_2\text{O}_3\cdot\text{Li}_2\text{O} \) and corresponding mixtures of lithia and gibbsite have been made.

When, in experiments on the preparation of the compound \( 5\text{Al}_2\text{O}_3\cdot\text{Li}_2\text{O} \) in a completely anhydrous and soluble form, the constituent oxides were heated to temperatures below 900°C, reaction was incomplete. At 1,000°C or higher temperatures, the double compound became largely insoluble. Preparation of chrysoberyl, \( \text{Al}_2\text{O}_3\cdot\text{BeO} \) (according to the method briefly described by Lang, Fillmore, and Maxwell, J.Res.N.B.S. 48, 298, (1952)) gave X-ray patterns which, in addition to lines due to chrysoberyl, showed further lines possibly due to \( \text{Al}_2\text{O}_3\cdot\text{BeO} \).

C. Mixed Fluorides

X-ray powder photographs of \( \text{Li}_5\text{AlF}_6 \) in a wide temperature range have been taken. The existence of various forms of the compound designated \( \alpha, \beta, \gamma, \delta \) and \( \varepsilon \) in order of stability at increasing temperature has become evident. An extremely slow conversion of \( \alpha \) into \( \beta \) occurs when the \( \alpha \) form is heated to 225°C (± 50°C), but the direct conversion of \( \beta \) into \( \alpha \) has not been observed. The \( \beta \) form is transformed into \( \gamma \) at 475°C (± 10°C). On slow cooling the \( \gamma \) form is converted into \( \beta \) which is retained on further cooling to room temperature. If the \( \gamma \) form is rapidly cooled, the product obtained after some time at room temperature is a mixture of \( \alpha \) and \( \beta \). The \( \gamma \) form is transformed into \( \delta \) at
575°C (± 10°C) and the δ form into the ε form at 705°C (± 10°C). The conversions γ → δ and δ → ε are readily reversible. The product in the calorimetric experiments is thus a mixture of α, β and supercooled γ which slowly changes into α.

The endothermic reaction (≈0.9 kcal) obtained on re-heating the product is therefore explained by both effects mentioned in Administrative Report No. 17, L.D., i.e. retention of γ and some evaporation of LiAlF₄. The conversion α → β is probably thermochromically negligible and the most probable value for the heat of combination of the two single fluorides to form α- or β-Li₃AlF₆ is therefore ΔH²⁹⁸^0 = 5.5 (± 0.5 kcal).

The various phase changes reported here are not likely to seriously invalidate the heat opacity measurements of Li₃AlF₆ [Douglas and Neufer, N.B.S. Report 8186, Jan. 1964] so that the value for the entropy S²⁹⁸(Li₃AlF₆) = 45.04 e.u. derived from them and the heat measurements reported here cannot be significantly in error.

\[ \text{Li}_3\text{BeF}_6 \]

The heat of the reaction

\[ 2\text{LiF} \text{(crystal)} + \text{BeF}_2 \text{(glass)} = \text{Li}_3\text{BeF}_6 \text{(crystal)} \quad \text{I} \]

has been measured by heating the constituents within the small furnace in the calorimeter. Very thorough mixing of the single fluorides is necessary apparently because of the extremely high viscosity (low electrical conductivity) of molten BeF₂. From five experiments in which this precaution was taken, a value Δ_H²⁹⁸ = -5.3 ± 0.5 kcal has been derived for the heat of reaction I. The product has been identified by powder X-ray photography as the normal crystalline form [α in the designation of Novoselova, Simonov and Yarembash, Zhur.Fiz.Khim., 26, 1244, (1952)]. On
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Reheating the product after several hours at room temperature, a barely detectable endothermic heat effect is observed. This cannot be readily explained at present. This is taken care of if one assumes for the heat of formation of $\alpha$-Li$_2$BeF$_4$ from the constituents $\Delta H^\circ = -5.5 \pm 0.7$ kcal.

2. WORK IN THE NEXT PERIOD

A. Beryllium Fluoride

Further attempts to prepare BeF$_2$ in a complete crystalline state will be made with a view to determining the heat of glass - crystal transition. Addition of lithium fluoride will be made to the mixture for the Be-PbF$_2$ reaction in order to form the crystalline compound Li$_2$BeF$_4$.

B. Mixed Oxides

Measurements in the Al$_2$O$_3$ - BeO$_3$ system will be completed. Measurements in the Al$_2$O$_3$ - Li$_2$O system will continue. If a completely anhydrous and soluble 5Al$_2$O$_3$.Li$_2$O cannot be made, the previous preparation which contains about 2 weight per cent water will be used. Measurements on either the heat of formation of gibbsite or of compounds in the Al$_2$O$_3$ - BeO system, if available, will be made.

One further attempt to prepare 5Al$_2$O$_3$.Li$_2$O in a completely anhydrous and soluble form will be made. Investigations on the preparation of the compounds in the Al$_2$O$_3$ - BeO system in a well defined and hydrofluoric acid soluble state will continue.
C. Mixed Fluorides

Investigations in the BeF₂ - LiF system will continue. Of the various double compounds suggested, the existence of LiBeF₃ seems undisputed, but careful thermochemical study will be necessary to ascertain whether it is stable or metastable with respect to disproportionation into BeF₂ and Li₂BeF₄.

3. No inventions were conceived or made during the period.

4. No personnel changes or other significant administrative actions occurred during the period.

Dr. Gross visited the United States from the 13th - 30th October 1964. He discussed progress of the work with Dr. Joseph P. Wasi and Major C. J. Donovan of the Office of Scientific Research, United States Air Force; he visited several laboratories and had scientific discussions with various United States thermochemists. He attended the 19th Calorimetry Conference in Washington, D.C., and Bethesda, Md., and reported on "Heats of Formation of α'-Beryllium Chloride and α- and β-Beryllium Nitride", an investigation which had been entirely sponsored by the Air Force Office of Scientific Research.

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