

proved by Evans.¹⁴⁻¹⁶ In the crystals, these similar ions are both thick hexagonal discs, approximating oblate spheroids. From the crystallographic data, the effective minor radius (half-thickness) of each may be estimated as 2.7-3.0 Å. and the effective major radius averages about 6.0 Å. The volume of each of these two disc anions is about 600 Å.³. In arriving at these estimates, the possible closeness of approach of water molecules to the irregular surface of the polyanion was considered. While the nickelate and tellurate complexes each contain twenty-four oxygen atoms, the 6-molybdocobaltate(III) anion and its Cr, Fe and Al isomorphs might contain as few as twenty-one oxygen atoms apiece (their proportion of "constitutional water" being uncertain at present).^{7,8,12} The discrepancy between the effective hydrodynamic volume determined above and the probable range of the total crystallographic volume of the anion is easily understood in view of the size and probable disc shape of the anion. The size is below that for which good applicability of the Einstein equation should be assumed for polyions. Factors involving the fit of solvent molecules to the irregular surface of the solute particle are proportionately more important the smaller a polyanion becomes. These 6-molybdo ions are presumably far from spherical; and, if they have the probable disc-like structure, it is likely that their planes would become oriented parallel to the direction of liquid flow. In view of the dimensions cited, it is most reasonable that such anions would have an apparent hydrodynamic volume close to that observed. The results also indicate that the degree of solvation of the anion is negligible. This is consistent with the low charge density on the surface of heteropoly anions and with the negligible solvation observed for 12-tungstosilicate ion.³

An attempt to measure the viscosity of solutions of the free acid of 6-molybdiodate(VII), which is presumably isomorphous with the 6-molybdotellurate(VI),¹⁶ was unsuccessful owing, apparently, to decomposition of the acid in concentrated solution. For the same reason, analogous measurements could not be made upon the heteropoly 6-molybdo anions of Cr(III), Fe(III) or Al(III).

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THE PYROLYSIS OF ACETYLACETONE

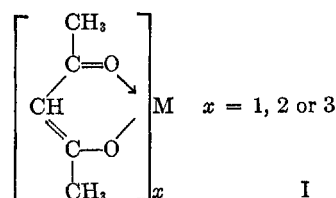
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In previous work concerning the pyrolysis of the metal acetylacetonates (I), acetylacetonone itself was observed in several instances as one of the major

degradation products.¹ These results suggested that acetylacetonone may be more heat stable than



the metal chelates derived from it. The present work on the pyrolysis of acetylacetonone permits a more direct comparison of the heat stabilities and also permits a comparison of the degradation products from acetylacetonone with those of the metal acetylacetonates. There appears to have been no previous comparison of the pyrolysis of a chelating agent with the pyrolyses of the metal chelates derived from it.

Table I gives the gaseous products obtained by heating acetylacetonone in sealed evacuated glass tubes for 4 hours at the temperatures indicated. At the lowest temperature employed, 266°, little decomposition has occurred. This is in contrast to the Cu(II), Ni(II), Co(II), Co(III), Al(III), Cr(III), Fe(III) and Mn(III) acetylacetonates, all of which decompose to a significant extent at this temperature.¹ The introduction of a metal atom into the acetylacetonone molecule results, therefore, in a decrease of thermal stability, at least for these metals.²

TABLE I
THERMAL DEGRADATION OF ACETYLACETONE
Samples heated 4.0 hours at the temperature indicated

Components of gas	Moles gas per mole of acetylacetonone taken		
	266°	346°	462°
Acetylacetonone	0.99	0.78	0.00
Acetic acid	.01	.08	.08
Acetone	.00	.12	.88
CO ₂	.00	.01	.34
CO	.00	.00	.39
CH ₄	.00	.00	.28

The principal gaseous products of pyrolysis for acetylacetonone given in Table I are also major decomposition products for the metal acetylacetonates.¹ This fact suggests that at least one possible route for the decomposition of the metal acetylacetonates involves first the formation of acetylacetonone followed by decomposition of the latter to the products given in Table I. That acetylacetonone is actually found as nearly the sole decomposition product, at the lower temperatures, for the Mn(III) and Cu(II) chelates supports this view.¹ The fact that only small amounts of acetylacetonone were found among the decomposition products of the other metal acetylacetonates studied may indicate that, in these instances, the decomposition of the initially formed acetylacetonone is catalyzed by the

(1) J. von Hoene, R. G. Charles and W. M. Hickam, *THIS JOURNAL*, **62**, 1098 (1958).

(2) On the basis of volatile decomposition products, sodium acetylacetonate appears to be more stable than acetylacetonone. The decomposition of the former compound may, however, involve non-volatile pyrolysis products which cannot be detected by the mass spectrometer (ref. 1).

presence of undecomposed metal acetylacetonate or by metal-containing decomposition products.

The principal pyrolysis products of acetylacetonate at 346° are acetic acid and acetone. At 462° appreciable quantities of CO₂, CO and methane are also present. The latter products may very well result from the pyrolysis of the initially formed acetone or acetic acid rather than from acetylacetonate directly.

The only previous study of the pyrolysis of acetylacetonate is that of Hurd and Tallyn.^{3,4} These workers determined the formation of ketene from acetylacetonate, using a flow system and much higher temperatures than those employed here. The production of ketene is not inconsistent with the present results since ketene is, under the proper experimental conditions, a product of the pyrolysis of acetone.⁵

Experimental

A Consolidated mass spectrometer was used to identify and to determine the pyrolysis products. The apparatus and procedure were essentially the same as those previously employed.¹ Ten-mg. samples of high purity acetylacetonate⁶ were weighed into Pyrex glass tubes having break-tips and the tubes were evacuated and sealed. The acetylacetonate was cooled with liquid nitrogen during the evacuation and sealing procedures. The tubes were heated for 4 hours in a constant temperature tube furnace with the sealed portions entirely within the hot zone. The heated tubes were cooled to room temperature, sealed to the inlet system of the mass spectrometer and the gas expanded, before analysis to 3000 ml. by breaking the break-tip with a magnetic bar.

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(4) C. D. Hurd, "The Pyrolysis of Carbon Compounds," A.C.S. Monograph No. 50 (Chemical Catalog Co.), Reinhold Publ. Corp., New York, N. Y., 1929, p. 264.

(5) C. D. Hurd, *ref. 4*, p. 248.

(6) R. G. Charles and S. Barnartt, *THIS JOURNAL*, **62**, 315 (1958).

THE SYSTEM GALLIUM TRIOXIDE— SILICA (Ga₂O₃—SiO₂)

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Although no previous studies have been reported, the system Ga₂O₃—SiO₂ is of interest. The ionic radius of Ga⁺³ (0.62 Å.)² is intermediate between that of Al⁺³ (0.57 Å.) and Fe⁺³ (0.67 Å.). The structure of the stable (β) modification of Ga₂O₃ is related to that of α-Al₂O₃ and α-Fe₂O₃. It is of interest, therefore, to examine the melting relations of Ga₂O₃ with other common oxides and compare the behavior of Ga₂O₃ with that of Al₂O₃ and Fe₂O₃. For this purpose, phase relations in the system Ga₂O₃—SiO₂ have been determined.

Experimental

Starting materials were prepared by blending Ga₂O₃ and SiO₂. One gram batches were prepared from electronic grade Ga₂O₃ (Eagle Pitcher Co.), and ignited SiO₂ gel

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(2) Goldschmidt radii are used throughout.

(Baker Analyzed Reagent Grade). The calculated proportions of Ga₂O₃ and SiO₂ were weighed out and ground under alcohol in an agate mortar. The alcohol was evaporated off and the dried powder blended thoroughly. It was returned to the mortar, moistened with alcohol, reground and redried. This resulted in a starting material of satisfactory homogeneity, as later proved by replicate runs on small portions of the original preparation.

Equilibrium determinations were made as follows. A small portion of the starting preparation was wrapped in platinum foil and suspended in a controlled temperature furnace. At the conclusion of the equilibration, the sample was quenched by dropping it into a dish of mercury. The phases present at the high temperature were determined by petrographic examination and powder X-ray diffraction techniques.

Furnaces were of a vertical tube model suited for quenching work. They were heated by a platinum-20% rhodium resistance element and the temperature regulated by a Weston-Tagliabue "Celectray" controller. The furnace temperature could be regulated to ±2°. Temperatures inside the furnace were read by a platinum-platinum 10% rhodium thermoelement suspended next to the sample. The thermoelement was calibrated frequently at the melting point of CaMg(SiO₃)₂ (1391.5°) and CaSiO₃ (1544°). The thermocouple error was of the order of ±2°, making the temperatures reported here accurate to about ±4°.

Results

The experimental results are shown diagrammatically in Fig. 1. From the melting point of SiO₂ at 1723°, liquidus temperatures fall to a eutectic at about 7 mole % Ga₂O₃ and 1642°. Phases in equilibrium at this eutectic are β-Ga₂O₃, liquid and silica (cristobalite). Liquidus temperatures rise slightly from this eutectic to a point located at about 8 mole % Ga₂O₃ and 1652°, marking one end of an extensive region of liquid immiscibility. The range of compositions melting to two liquids extends to ~65 mole % Ga₂O₃. From 65–100 mole % Ga₂O₃ liquidus temperatures rise from 1652° to the melting point of Ga₂O₃ (1725°).³ This is shown as a dashed line in Fig. 1, as no runs were made on compositions between 70 mole % Ga₂O₃ and Ga₂O₃.

Discussion of Results

Recognition of the high temperature liquid immiscibility in the system Ga₂O₃—SiO₂ is comparatively simple. Quenched charges of appropriate compositions heated above 1652° contain two glassy phases. One is a clear isotropic glass, having *N* = 1.504 (sodium light). The other is a partly devitrified brownish glass of high index. The index of this gallium oxide-rich liquid could not be determined, on account of its partial devitrification upon quenching. The relative proportions of the two glasses varies with the bulk composition of the mixture. The liquids have a relatively low viscosity, and separate fairly well in runs of a few minutes' duration: however, the high silica liquid frequently traps droplets of the Ga₂O₃-rich liquid.

Although gallium oxide is essentially non-volatile,³ possible losses of Ga₂O₃ from the mixtures were checked by duplicating runs on the 10 mole % and 70 mole % Ga₂O₃ compositions using samples sealed in platinum tubes. The tubes were welded shut at one end, a sample inserted and the open end welded shut. Using a micro-welder, it was possible to weld tubes shut without sensible heating of the

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