following the reactor tube. The purpose of the soda lime was to remove any fluorine which may have passed through the reactor. Furthermore, these traps served to aid the control of the rate of supply of fluorine gas, since development of heat within them was taken as an indication of the presence of free fluorine, the progress of which through the system could thus be followed, and hence controlled by regulation of the needle valve on the fluorine cylinder. The reactor for use with cobalt trifluoride was simply a monel tube which was placed in a furnace set for the desired temperature. An exit line led to the soda lime traps. In either system the line continued through a Housekeeper seal to a liquid nitrogen trap, with sulfuric acid and sodium hydroxide bubblers at various points to remove unwanted by-products.

Most of the runs with elementary fluorine were initiated at room temperature by means of a fuse of elementary silicon (about 0.1 g.). From 5 to 10 g. of the carbide was placed with the fuse in the reactor and reaction induced by passing fluorine into the system. Nitrogen was used as a diluting gas and to aid in the control of the reaction. Runs generally lasted approximately 90 minutes. For the runs with cobalt trifluoride, a few grams of the carbide were rapidly mixed with cobalt trifluoride and placed in the reactor, which then was heated to 440° to start the reaction. Runs lasted approximately 9 hr.

The products were identified by means of infrared spectroscopy, as reference spectra were available.[5] The mixtures were analyzed using the Beer–Lambert law in a standard manner and separated when necessary by gas chromatography, using an activated alumina column 6 feet in length, at room temperature and 184°, with helium as the eluting gas. It was found that room temperature was quite satisfactory for the separation of the first two members of the fluorocarbon series, and 184° proved to be an optimum temperature for the separation of the higher members (C_3F_8 and *i*- and *n*-C_4F_{10}).

Results

All of the carbides gave quite similar fluorination products. CF_4, C_2F_6, C_3F_8, *n*-C_4F_{10} and probably some *i*-C_4F_{10} were present in comparable mixtures in every case. SF_6, SO_2F_2 and OF_2 were found in some cases as the result of impurities in the carbides. Typical results of runs, using elementary fluorine as the fluorinating agent, are as tabulated.

Carbide	Mole % of product fluorocarbons				
	CF_4	C_2F_6	C_3F_8	*n*-C_4F_{10}	*i*-C_4F_{10}
SiC	68	16	14	2.2	Trace
B_4C	88	9.2	2.4	0.5	Trace
TiC	86	11	2.9	.4	Trace
WC	67	26	7.0	.6	Trace
Fe_3C	86	9.5	3.5	.7	Trace
Cr_3C_2	91	6.4	2.4	.5	Trace
Al_4C_3	88	9.2	2.9	..	Trace
CaC_2	75	19	5.5	0.6	Trace

The results of the different runs were all qualitatively quite similar and the variations that were present were felt to be due to slight differences in flow rates or in the reaction temperatures prevailing at the site. It was observed that in general higher temperatures gave greater percentages of CF_4. The cobalt trifluoride runs gave similar mixtures of products also.

The findings indicate that the use of elementary fluorine and cobalt trifluoride result in experimental conditions too drastic for any structural correlations to be observed between composition of the carbide and nature of the product fluorocarbons. Some type of polymerization mechanism must be postulated to explain the mixtures of products that were obtained. Some sort of abstraction of the carbon atoms or ions from the carbides as fluorinated fragments appears necessary, but whether the combination of these fragments occurs on the surface of the carbide or in the gas phase is not known. Further, the possibility of the formation of an intermediate such as $(CF)_x$ should be pointed out. It is known that this substance decomposes on heating to give fluorocarbons.[6]

A similar study of the fluorination of various types of nitrides has been completed recently and will be reported in a future issue.

The authors are indebted to the Office of Naval Research Contract No. Nonr-1841(07) and to a grant provided by Owens-Illinois Glass Co. for assistance in this investigation.

CAMBRIDGE, MASS.

---

[5] D. G. Weiblen, "Fluorine Chemistry," J. H. Simons, Editor, Vol. II, Academic Press, Inc., New York, N. Y., 1954, pp. 469–503.

[6] L. A. Bigelow, ref. 5, Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 379.

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES CORPORATION]

Heterogeneous Equilibria in the System K_2CO_3–Na_2CO_3

BY ARNOLD REISMAN

RECEIVED AUGUST 21, 1958

The heterogeneous equilibria in the system K_2CO_3–Na_2CO_3 have been investigated in the range room temperature to their melting points, using differential thermal analysis and X-ray techniques. Data obtained for the melting and freezing curves are in good agreement with previously reported values and indicate the formation of a minimum melting composition at 710 ± 2° somewhere between 55 and 58 mole % Na_2CO_3. In the subsolidus range the results were found to be in marked disagreement with the literature concerning the number of homogeneous and heterogeneous regions and their temperature and compositional intervals of stability. X-Ray examination of the room temperature diagram indicated the formation of an intermediate solid solution in the range 30–45 mole % Na_2CO_3.

Introduction

In 1894, Le Chatelier[1] described the solidus curve for the system Na_2CO_3–K_2CO_3. The carbonates were found to be completely miscible, exhibiting a melting point minimum at approximately 58 mole % Na_2CO_3 and 690°. Makarov and Shulgina[2] reexamined the fusion characteristics of the system and reported that the minimum occurred "at about 40 mole % K_2CO_3 and 706°." In addition, these

---

[1] H. Le Chatelier, *Compt. rend.*, **118**, 350 (1894).

[2] S. Makarov and M. P. Shulgina, *Bull. Acad. Sci. U.R.S.S.*, **5**, 691 (1940).

authors studied the polymorphic behavior and solid phase interactions of the end members (Fig. 1). On the basis of differential thermal analysis, each compound was said to exist in four polymorphic states "with conversion points at 618, 486 and 356° for Na_2CO_3, and 622, 428 and 250° for K_2CO_3."

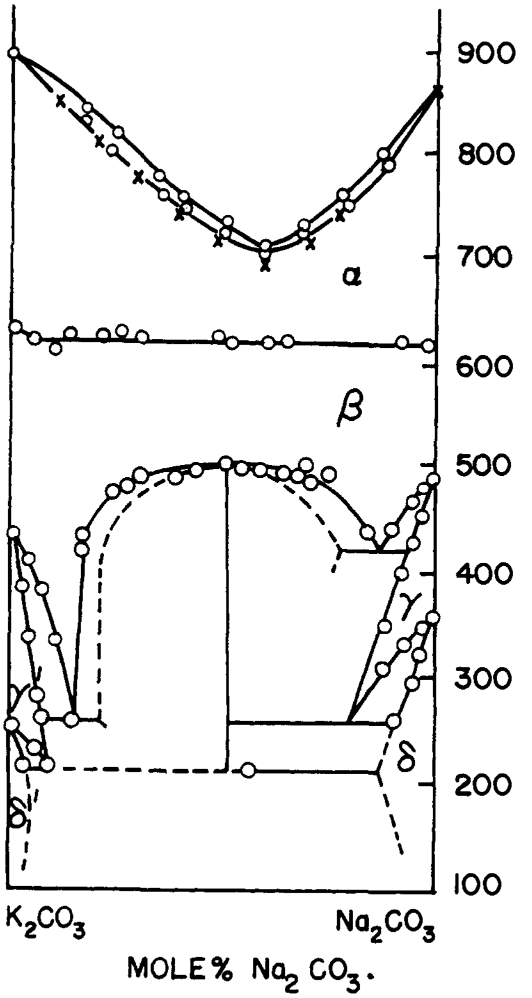

Fig. 1.—The system Na_2CO_3–K_2CO_3 after reference 2.

Recently, Reisman, *et al.*,[3] in conjunction with other work, re-examined the thermal behavior of Na_2CO_3 and found transitions at 485 and 355°. Since spurious heat effects were detected if the carbonate was not examined in a CO_2 atmosphere, it was concluded that the previous results were obtained with contaminated material. This prompted an investigation of the polymorphic behavior and fusion characteristics of other alkali carbonates.[4] K_2CO_3 exhibited only one specific heat anomaly, at 422°. If, however, the analysis was conducted in air, additional effects appeared at 367 and 253° but never in the neighborhood of 600°.

Because the earlier data appeared to be in error, the diagram for the polyphase interactions proposed by Makarov and Shulgina is at least partially negated, and a reinvestigation of the system appeared worthwhile.

Experimental Procedure

1. **Reagents.**—Analytical reagent grades of Na_2CO_3 and K_2CO_3 dried at 285° in gold–20% palladium under a CO_2 atmosphere and stored over Drierite were used for all experiments.

2. **Preparation of Samples.** (a) **DTA.**—The dried components were weighed and mixed in glass vials and then transferred to 15-cc. gold–20% palladium crucibles. These were placed in a furnace at 910° until the samples melted, whereupon they were removed and the melts poured into liquid nitrogen. The "quenched" beads obtained in this manner were ground in a dry box and loaded into 1-cc. gold–20% palladium crucibles. In order to make certain that the liquid nitrogen quench had no unexpected effects, several samples prepared by quenching on a platinum foil were also examined and gave identical results within the limits of experimental error.

(b) **X-Ray.**—The samples prepared as described above were placed in 8-cc. gold–20% palladium crucibles and heat treated in CO_2 at 675° for 24 hr. to increase their crystallinity. They were then cooled to 150° at 25°/hr. and placed in a desiccator containing Drierite, in order to prevent reaction with moisture in the air.

3. **Differential Thermal Analysis.**—All analyses were performed in a CO_2 atmosphere using the low heat capacity furnace previously described.[5] Solid state phenomena were studied at a gain of 5 μv./inch, while fusion data were gathered at 15 μv./inch. Heating and cooling rates of 0.5–2°/minute were used in all experiments.

4. **X-Ray Analyses.**—The samples prepared for X-ray analyses were slightly pulverized and loaded into capillaries in the dry box. A plastic putty was used to seal the open end of each capillary to protect the samples from moisture. X-Ray examinations of the room temperature specimens were made with a 57.3 mm. radius Debye–Scherrer camera, using nickel filtered copper radiation generated at 40 kv. and 20 ma. and an exposure time of 1 hr.

Discussion of Experimental Results

The problem of establishing the structure of a complex solid solution diagram is generally a serious one because of the difficulty in achieving sample equilibrium at given temperatures. In the present study X-ray examinations could not be performed at elevated temperatures because of the great reactivity of the samples with X-ray transparent containers. Furthermore, since the earlier studies[3,4] indicated that the phase transformations of the pure components resulted in strained end products, it appeared that heating curves would not provide quantitative data in low temperature regions. The solution appeared therefore to depend on cooling curve analyses starting with homogeneous mixtures, in which case only the temperatures of first deviation from the differential curve could be relied upon,[6] assuming exsolution and transformation phenomena were not suspended. Preliminary experiments conducted at cooling rates of 0.5–2°/minute showed the temperatures for heat effects to be spontaneous and reproducible to within ±2° for transformations and ±5–7° for exsolutions. Furthermore the very large and reproducible heat effects coincident with exsolutions indicated that diffusion in the solid state was rapid and that X-ray studies at room temperature might be rewarding.

The following sequence of experiments was devised in order to obtain exsolution and/or transformation, solidus and liquidus data from a single

---

(3) A. Reisman, F. Holtzberg and E. Banks, THIS JOURNAL, **80**, 37 (1958).

(4) A. Reisman, *ibid.*, **80**, 3558 (1958).

(5) F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *ibid.*, **79**, 2039 (1957).

(6) The temperatures of heat effects were chosen by extrapolating the maximum peak inflection to the intersection with the base line. The point of intersection was chosen as the temperature of the anomaly.

specimen. A sample was heated to 700° and held at this temperature for 3 hr. It was then heated at 0.5°/minute and the course of the heating curve was monitored at a gain of 5 μv./inch. When the differential trace began to deviate from the base line, indicating that solidus melting had commenced, the temperature was immediately lowered 20–25°, and when thermal equilibrium was attained, the sample was cooled at 1–2°/minute to room temperature. Based on the size of the melting peak obtained later, the melting that occurred during the heating cycle could not have represented more than 0.1–0.2% of the sample, and the treatment served to increase the crystallinity of the sample as well as to alleviate most of the strain created during the sample preparation. Specimens equilibrated for 24 hr. at 700° in the DTA apparatus prior to the cooling analysis, but not partially melted first, gave results which agreed within the limits of experimental error.

After the sample had cooled to room temperature, the furnace was heated at 1–2°/minute through the solidus melting. The sample was permitted to melt and was then cooled at 1–2°/minute through the liquidus crystallization. Supercooling was apparently not a problem since seeding of the melts did not affect the results. Each experimental cycle required two days, and in most cases two analyses were performed at each of 51 compositions, at 2.5 mole % intervals, to check the reproducibilities of the temperatures and magnitudes of heat effects.

X-Ray studies were performed on 21 different compositions at 5 mole % intervals. It is evident that since no other method was available for establishing that the room temperature samples were a good approximation to the equilibrium state at this temperature, the X-ray data might be questioned. However, the powder photographs themselves at least provide a means for evaluating the self-consistency of the method.

In each single phase region a progressive line shifting was observed and in each two phase region a progressive line intensity decrease for one solid solution and accompanying line intensity increase for the coexisting solid solution was observed. Furthermore no line shifting was seen in the two phase powder photographs and no inconsistencies were observed over the entire compositional range. On the Na_2CO_3 rich side of the diagram some supporting evidence for the X-ray data was obtained because of the depression of the Na_2CO_3 s.s. transition. Consequently, it would appear that the samples examined with X-rays represented the equilibrium states fairly well. Unfortunately none of the powder data was readily indexable.

The thermal and X-ray data are listed in Table I and the proposed diagram based on these data is shown in Fig. 2. Since the slopes of both the liquidus and solidus curves are zero at the minimum the experimental uncertainty of ±2° prevents its precise location. The minimum appears to be between 55 and 58 mole % Na_2CO_3 at 710 ± 2°, in good agreement with the values reported by Makarov and Shulgina. The 422° transition in K_2CO_3 is depressed approximately 12°/mole % Na_2CO_3, and accompanying this decrease a diminution of the latent heat of transformation was observed. It is difficult to assess the cause of the apparent variation of latent heat as a function of composition. Thus, it would appear that the transformation becomes second order. On the other hand it can be argued that the separation of the upper and lower boundaries of the α-β transformation increases with increasing addition of Na_2CO_3, making it more difficult to approach equilibrium during the non-static experiments. If the latter is the cause of the variation and the transformation is not spontaneous and if the latent heat subsequently evolved per unit time is below the sensitivity of the apparatus, one will observe the decrease in latent heat of transformation. Resolution of this question will have to wait until a technique for studying the transitions with X-rays is forthcoming.

TABLE I

THERMAL AND X-RAY DATA FOR THE SYSTEM Na_2CO_3–K_2CO_3

Na_2CO_3, mole %	Liquidus	Solidus	Transition	Exsolution	Phase(s) identified with X-rays at 25°
0	901	. .	422	. .	β
2.5	. .	. .	401	. .	. .
5	. .	866	378	. .	β
7.5	875	845	354	. .	. .
10	. .	829	324	. .	β + trace γ
12.5	. .	824	291	. .	. .
15	842	810	252	. .	$\beta + \gamma$
17.5	834	794	210	. .	. .
20	822	787	174	474	$\beta + \gamma$
22.5	818	774	159	. .	. .
25	805	764	147	574	$\beta + \gamma$
27.5	792	752	146	610	. .
30	783	750	145	620	γ + trace β
32.5	774	740	142	618	. .
35	766	734	. . .	608	γ
37.5	756	729	. . .	606	. .
40	746	720	. . .	613	γ
42.5	739	718	. . .	609	. .
45	731	716	. . .	611	γ + trace δ
47.5	725	. .	. . .	614	. .
50	719	713	. . .	612	$\gamma + \delta$
52.5	713	709	. . .	604	. .
55	709	709	. . .	613	δ + trace γ
57.5	711	711	. . .	609	. .
60	711	708	. . .	610	δ
62.5	712	710	. . .	612	. .
65	717	710	. . .	610	δ
67.5	722	712	365	600	. .
70	731	714	378	604	δ
72.5	740	717	390	600	. .
75	751	721	400	590	δ + trace ϵ
77.5	758	724	408	561	. .
80	765	730	410	. .	$\delta + \epsilon$
82.5	784	737	421	. .	. .
85	788	742	430	. .	ϵ + trace δ
87.5	797	752	434	. .	. .
90	810	766	449	. .	ϵ
92.5	822	791	451, 276	. .	. .
95	839	809	463, 312	. .	ϵ
97.5	. .	834	478, 336	. .	. .
100	854	. .	489, 361	. .	ϵ

At 20 mole % Na_2CO_3, the first small heat effect due to exsolution is observed and the temperature

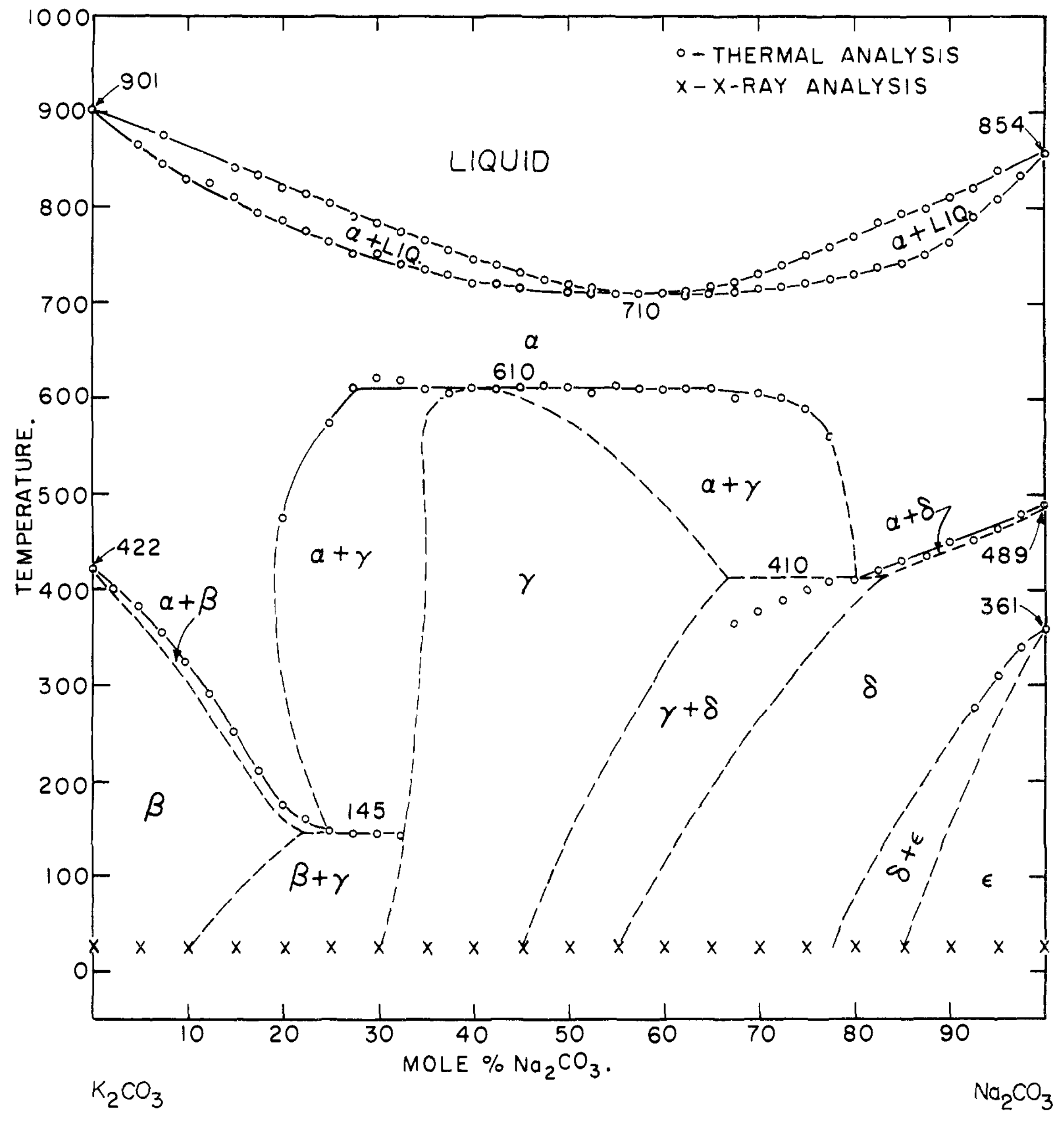

Fig. 2.—Proposed construction for the system Na_2CO_3–K_2CO_3.

of the α–β transformation levels off at approximately 145°. The leveling off, which indicates intersection of the transformation curve with the exsolution curve, also implies that the transformation $\alpha \rightarrow \beta + \gamma$ is spontaneous and that a reasonably good approximation to thermal equilibrium is maintained during the exsolution process.

At approximately 32.5 mole % the 145° transition terminates. The temperature of exsolution increases to a value of 610 ± 5° at approximately 27.5 mole % Na_2CO_3 with an accompanying increase in the size of the heat anomaly to a maximum value at 40 ± 2.5 mole % Na_2CO_3. Since no exsolution discontinuity was detected, the possibility that two separate but proximate gaps exist is precluded. X-ray examination of room temperature samples showed disappearance of the homogeneous β-phase at approximately 10 mole % Na_2CO_3. A two phase region containing β and a new phase γ then persists to approximately 30 mole % Na_2CO_3 and from 30–45 mole % the γ-phase is present as a homogeneous solid solution. The presence of the γ-phase in this state suggests that a compound of Na_2CO_3 and K_2CO_3 occurs somewhere between 30 and 45 mole % Na_2CO_3, and correlating this information with the magnitude of the exsolution anomalies establishes the compound stoichiometry at approximately $2Na_2CO_3 \cdot 3K_2CO_3$. From the shape of the exsolution curves it is evident that the "compound" is very dissociated. Considering that this discussion is being applied to a solid state phenomenon and that even in the solid state the "compound's" stability is tenuous, it would appear that the use of the word compound is semantic. For this reason the isopleth showing the 2:3 stoichiometry has been omitted in the construction of Fig. 2.

The 489° transformation in Na_2CO_3 makes its first appearance at 67.5 mole %. No level range is observed indicating that this transformation is not quite as spontaneous as its opposite member. The 361° transition in Na_2CO_3 is not detectable until approximately 92.5 mole % from which point its latent heat increases continuously. The X-ray data indicate that the upper and lower curves have approximately a 10 mole % separation at room temperature which explains the rapid decrease in the magnitude of the spontaneous latent heat. The consistency of the patterns in the δ–ϵ two phase region indicates that the X-ray sample preparation resulted in a fairly good approach to equilibrium and this also lends support to the validity of the entire diagram as constructed.

NOTE ADDED IN PROOF.—The author has hitherto been unable to offer any explanation for the heat effects at *ca.* 620° reported in ref. 2. Subsequent to the compilation of this manuscript, a probable explanation for the "anomalous heat effects" was forthcoming in a private communication from Drs. F. W. Wilburn, C. V. Thomasson and J. D. Mullen of Pilkington Brothers, Ltd., St. Helens, England which is abstracted herewith.

In the course of differential thermal analysis studies in the sodium carbonate–silica system we also have been unable to observe this peak (at *ca.* 600°) when using analytical reagent sodium carbonate. However, when using commercial sodium carbonate, which is known to contain up to 0.5% sodium chloride, a small peak at about 620° is observed. D. T. A. curves of sodium carbonate–sodium chloride mixtures (both of analytical reagent quality) show a small peak at about 620° which increases in area with increasing chloride content. Moreover Mellor[7] states that eutectic melting occurs between sodium carbonate–sodium chloride mixtures at 636°. Analytical reagent quality potassium carbonate shows no peak at about 620°, but a peak appears when analytical reagent quality potassium chloride is added as an impurity. Mellor again gives the eutectic melting temperature of these two substances at 636°.

Acknowledgments.—The author wishes to thank Miss J. Karlack for assisting with the experiments and Miss C. Linde for taking the powder photographs.

NEW YORK, NEW YORK

(7) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," (1927) p. 769.

[CONTRIBUTION FROM MELLON INSTITUTE]

The Crystal Structure of Antimony Pentachloride at −30°

BY STANLEY M. OHLBERG[1]

RECEIVED AUGUST 15, 1958

Antimony pentachloride belongs to the hexagonal system with a = 7.49 Å. and c = 8.01 Å. The space group is D^4_{6h}–$P6_3/mmc$ with two molecules to the unit cell. It forms a molecular crystal and the trigonal bipyramidal structure observed for the gaseous molecule is retained in the solid state. The bond distances between antimony and the three basal chlorine atoms is 2.29 Å. and that between antimony and the two apical chlorines is 2.34 Å.

Introduction

The crystal structures of a number of inorganic compounds in which a 1:5 stoichiometric ratio exists have been determined. Klug, Kummer and Alexander[2] have cited five different structural methods by which the 1:5 ratio is achieved in crystals, and none of them involves fivefold coördination. Byström and Wilhelmi[3] did observe fivefold coördination in K_2SbF_5. They describe a configuration of $SbF_5^{=}$ as an octahedron with a stereochemically active pair of s-electrons occupying the sixth corner. Another, and perhaps more obvious, method for achieving fivefold coördination would involve the formation of trigonal bipyramids. Although PCl_5[4] has a trigonal bipyramidal configuration in the gaseous state, it forms ionic crystals involving PCl_4^+ tetrahedra and PCl_6^- octahedra.[5] Antimony pentachloride also has a trigonal bipyramidal configuration in the gaseous state,[6] and moreover the low dielectric constant, 3.3, measured by Lowry and Jessop[7] at 0° suggests that $SbCl_5$ forms a molecular type crystal. In addition, examination of the Raman spectra[8,9] points to the retention of the trigonal bipyramidal configuration in both the liquid and the solid state. In view of these facts the structure determination of solid $SbCl_5$ was undertaken in order to demonstrate its method for achieving a 1:5 stoichiometric ratio.

Experimental

The $SbCl_5$ was distilled under reduced pressure into thin-walled glass tubes of approximately 0.3 mm. in diameter. The samples were frozen with a Dry Ice slush and the tubes sealed off. Single crystals were grown by conventional low temperature techniques.[10,11] Both precession and Weissenberg photographs were taken at −30 ±2° with Zr-filtered MoK and Ni-filtered CuK radiation, respectively. Zero and first level photographs were taken about the [00·1], [10·0] and [11·0] axes. The hexagonal cell parameters determined from precession photographs are a = 7.49 Å. and c = 8.01 Å. The density calculated on the basis of 2 molecules per unit cell is 2.55 g./cm.^{3}, in line with the density reported for the liquid, 2.378 g./cm.^{3} at 2.6°.[12]

The symmetry and systematic extinctions, $hh2\bar{h}l$ with l odd, limited the possible space groups to D^4_{6h}-$P6_3/mmc$. D^4_{3h}–$P\bar{6}2c$, and C^4_{6v}–$P6_3mc$. Subsequent interpretation

---

(1) Pittsburgh Plate Glass Research Center, P. O. Box 11472, Pittsburgh 38, Pa.

(2) H. P. Klug, E. Kummer and L. E. Alexander, THIS JOURNAL, **70**, 3064 (1948).

(3) A. Byström and K. Wilhelmi, *Arkiv för Kemi*, **3**, 461 (1951).

(4) M. Roualt, *C. R. Acad. Sci. Paris*, **206**, 51 (1938).

(5) H. M. Powell, D. Clark and A. F. Wells, *J. Chem. Soc.*, 642 (1942).

(6) M. Roualt, *Ann. Phys., Lpz.*, **14**, 78 (1940).

(7) T. M. Lowry and G. Jessop, *J. Chem. Soc.*, 782 (1930)

(8) H. Moureau, M. Magat and G. Wetroff, *Proc. Ind. Acad. Sci.*, *Raman Jubilee Vol.*, 361 (1938).

(9) K. A. Jensen, *Z. anorg. Chem.*, **250**, 264 (1943).

(10) H. Kaufman and I. Fankuchen, *Rev. Sci. Instr.*, **20**, 735 (1949).

(11) S. C. Abrahams, R. L. Collins, W. N. Lipscomb and T. B. Reed, *ibid.*, **21**, 396 (1950).

(12) J. H. Simons and G. Jessop, THIS JOURNAL, **53**, 1265 (1931).