that they can be paired in doublets with nuclides having mass numbers 6, 4 and 3, respectively; but —much more important—no other nuclide (with the exception of ^{13}C) can be found which forms polyatomic molecular ions with as many atoms (up to 10 and more) in the molecule. Therefore, the scale $^{12}C = 12$ would allow many more direct doublet-comparisons (as a matter of fact at every multiple of 12 up to $A = 120$ and more) of masses, especially of heavy nuclides, with the reference standard than any other scale. ^{12}C has the additional advantage that it forms many more hydrides than any other nuclide (again excepting ^{13}C) so that an easy reference line for doublets can be produced at almost every mass number up to $A > 120$ Thus for physicists the scale $^{12}C = 12$ would be much better even than $^{16}O = 16$ and by far better than any other scale proposal. It seems, therefore, that from all points of view a unified scale based on $^{12}C = 12$ deserves consideration.

The author wishes to acknowledge that the proposal $^{12}C = 12$ was brought to his attention by A. O. C. Nier.

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Preparation and Thermal Stability of Lithium Titanium Fluoride[1]

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The preparation and properties of Li_2TiF_6 have been reinvestigated. After two recrystallizations and high vacuum drying at 200°, 2.57% HF and 0.75% H_2O are still retained, most likely as solvates. When heated *in vacuo* at 365°, HF and H_2O are removed with little if any decomposition of Li_2TiF_6. At higher temperatures, Li_2TiF_6 undergoes a primary decomposition to form LiF and TiF_4. Thus a sample held under high vacuum at 485° for 21 hr. was found to be 42.5% decomposed. When exposed to atmospheric moisture and heated, Li_2TiF_6 decomposes by hydrolysis, with the formation of LiF, TiO_2 and HF.

Recent investigations on the cryoscopic behavior and electrical conductance of Li_2TiF_6 in chloride melts[2] in this Laboratory stimulated an interest in the thermal properties of lithium titanium fluoride. The present communication reports an investigation of the thermal stability of Li_2TiF_6 at temperatures up to 485°. Very little information on the preparation and physical properties of this compound are found in the literature. The work of Ginsberg and Holder[3,4] on the alkali titanium fluorides is most informative qualitatively. Preliminary experiments in this Laboratory indicated that the melting point of Li_2TiF_6 was in the region of 580° rather than 480° as reported by Ginsberg[3] and that when heated in air, hydrogen fluoride rather than elemental fluorine[4a] was evolved. The need for quantitative details in the preparation and the purity of Li_2TiF_6, and an investigation of its thermal stability when heated *in vacuo* or an inert atmosphere to establish the nature of the primary dissociation process was apparent.

Experimental

Preparation of Li_2TiF_6.—The method selected was that[4a] in which the salt is formed by the addition of Li_2CO_3 to a solution of TiO_2 in HF, *i.e.*

$$TiO_2 + 6HF \xrightarrow[HF]{excess} H_2TiF_6 + 2H_2O \qquad (1)$$

and

$$H_2TiF_6 + Li_2CO_3 \longrightarrow Li_2TF_6 + H_2O + CO_2\uparrow \qquad (2)$$

The procedure and results quantitatively were as follows. TiO_2 (40 g., reagent grade), dried at 100° for 3 hr., was dissolved in concentrated HF solution (48%) using a quantity 20% in excess (150.3 g.) of that required to form H_2TiF_6. Upon complete solution, Li_2CO_3 (reagent grade) was added until evolution of CO_2 subsided. To ensure complete solution of the Li_2TiF_6, the volume was made up to approximately 300 cc. with distilled water, and the mixture filtered to remove LiF. The solution was then made slightly acidic (1–2%) by the addition of some 48% HF solution (10 cc.). Evaporation to dryness was effected in polyethylene-lined vacuum kettles under reduced pressures at 25–30°. The crude Li_2TiF_6 was twice recrystallized in the same manner, using a minimum of distilled water slightly acidified with HF in each case. The water insolubles were removed by filtration after the Li_2TiF_6 had been redissolved in each case. The product thus gained was dried to constant weight at 200° under vacuum pumping. The composition of the product was: Li_2TiF_6, 93.8 ± 0.1%; Li_2TiOF_4, 1.2 ± 0.2%; LiF, 1.6 ± 0.2%; HF, 2.57%; and H_2O, 0.75%. The yield of product calculated on the above purity of Li_2TiF_6, 71.5 g., corresponds to 76.4% of that theoretically possible. The HF and H_2O undoubtedly are held as molecules of hydration, and the above amounts correspond to 4% of $Li_2TiF_6{\cdot}2H_2O$ and 24% of $Li_2TiF_6{\cdot}HF$ still present after vacuum drying to constant weight at 200°. The oxyfluoride is accounted for as a hydrolysis product of Li_2TiF_6. The presence of LiF is attributed to the finite solubility of this compound (0.3 g./100 g. H_2O). The identity of the water insoluble oxyfluoride as Li_2TiOF_4 was confirmed by X-ray powder diffraction patterns, and titanium analysis[5] (Li_2TiOF_4: calcd. Ti, 31.1%; found Ti, 30.7%).

Melting Point.—A platinum crucible containing approximately 10 g. of Li_2TiF_6 (93.8% purity) was heated under an inert (argon) atmosphere in a Hoskins furnace. Temperatures were measured with an automatically recording platinum–platinum, 10% rhodium thermocouple. The heating rate was quite rapid, 7°/minute in range 460–550°, and 20°/minute in the range 550–600°, to minimize decomposition of the sample before reaching the melting point. The sample sintered at 530 ± 5° and was completely molten at 580 ± 25°. Vigorous gas evolution occurred once the sample was fused. No attempt was made to gain a more precise estimate of the melting point in this work.

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(1) This work, supported by the U. S. Air Force, Air Office of Scientific Research, ARDC, Contract No. AF 49(638)-50, was initiated under the sponsorship extended by the Office of Naval Research, Contract No. Nonr 591(06).

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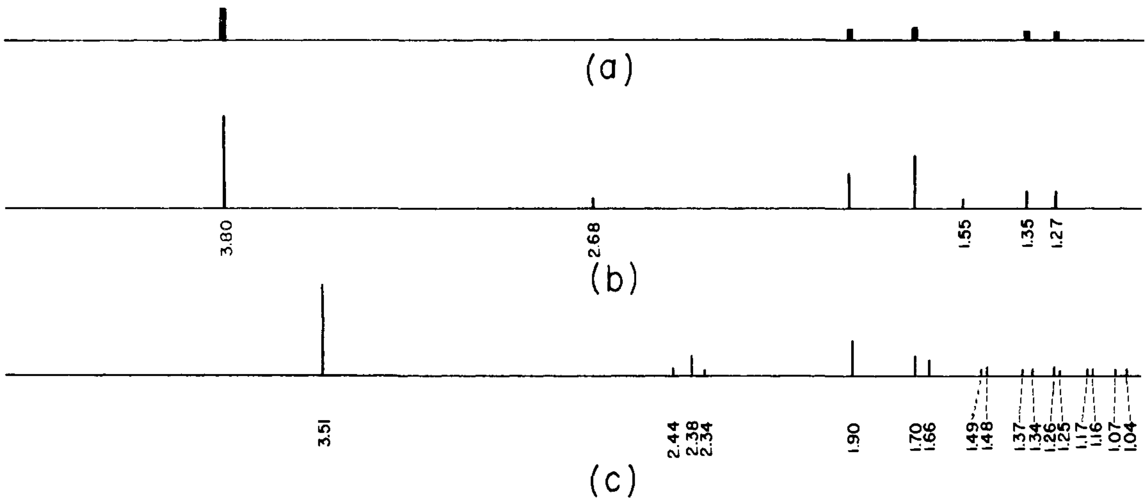

Fig. 1.—X-Ray diffraction lines and their relative intensities for the sublimation product from the thermal decomposition of Li_2TiF_6 under vacuum at 485°: (a) pattern of initial sample exposed to atmosphere; (b) pattern of sample heated to 100°; (c) pattern of sample after complete evolution of HF.

X-Ray Powder Diffraction Pattern.—The powder diffraction pattern was taken of a highly refined sample of Li_2TiF_6 (99% purity) using a General Electric XRD-3 spectrometer Cu K_α radiation for 15 hr. with a 0.02 inch collimator and a 14.32 cm. diameter camera. The results have been listed elsewhere[6] as the "d" spacings and the relative intensities as a reference standard. No data in the literature were available for comparison.

Thermal Stability.—The essential feature of the experimental assembly for the thermal stability studies was a Pyrex glass ampoule containing a tall platinum crucible with the sample in a furnace. The ampoule was connected through a short horizontal arm, which served as an air-cooled condenser for sublimation products, through a stopcock and ground glass joint to a trap at liquid nitrogen temperatures to collect gaseous volatile products. The ampoule containing the Li_2TiF_6 in the platinum crucible could be sealed by the stopcock, disconnected from the rest of the assembly and weighed as required for the material balance. A sample of Li_2TiF_6 (8.2223 g., 93.8% purity) was placed in the platinum crucible; the assembled ampoule was evacuated to 10^{-5} mm. at room temperature and weighed on an analytical balance. The assembled ampoule was heated from room temperature slowly to 300° and maintained thus for 44 hr. A weight loss of 0.2326 g. was noted and the volatiles in the liquid nitrogen trap were transferred to a 10-cm. infrared gas cell for examination. No attack or deposits were observed anywhere in the Pyrex glass ampoule or the Pyrex tubing to the cold trap; however, the low temperature trap displayed a definite attack on the glass walls. The system was reassembled, evacuated and the sample slowly heated to 365° and held at the temperature for 16 hr. The appearance of the ampoule and connecting tubing was as at 300°, *i.e.*, no solid deposits or visible attack on the glass. The additional weight loss was 0.0329 g. The volatiles were examined by infrared analysis, and the apparatus was reassembled. The temperature of the re-evacuated assembly was increased to 485°. After a period of 21 hr., the cell was cooled and weighed and the volatiles in the cold trap identified by infrared analysis. The weight loss increment was 0.1910 g. giving a total weight loss of 0.4565 g. for the experiment. After 21 hr., it was noted that the portion of the ampoule which had been at 485° showed an opaque bluish grey deposit, while the portion at room temperature to the stopcock was covered with a glassy white deposit. All solid products, *i.e.*, the material in the crucible, and the deposits on the glass, were examined by chemical and X-ray analyses.

The thermal stability of Li_2TiF_6 when heated in a platinum crucible open to the atmosphere after Ginsberg and Holder[4a] was qualitatively checked. The results confirmed LiF and TiO_2 as end products. However, tests of the escaping vapors for fluorine with potassium iodide and starch were negative, whereas tests for HF with moist litmus were positive.

Results and Discussion

The volatiles collected at 300, 365 and 485° in the cold trap all gave the same infrared spectrum. A comparison of the observed bands with the spectrum of SiF_4 reported by Bailey, Hale and Thompson[7] and Jones, Kirby Smith, Woltz and Nielsen[8] confirmed that this gaseous product was principally silicon tetrafluoride by the exact correspondence of all the bands.

The results of the X-ray powder diffraction analyses on the material remaining in the platinum crucible after completion of the thermal stability studies together with the spectra for Li_2TiF_6, LiF and TiO_2 showed that the material was unchanged lithium titanium fluoride, now containing lithium fluoride and traces of titanium dioxide (anatase). The bluish grey deposit found in the heated positions of the glass ampoule gave a diffraction pattern of pure TiO_2 (anatase).

The amorphous white sublimate on the parts of the assembly at room temperature was investigated similarly by X-ray powder diffraction methods. Titanium tetrafluoride does not give a diffraction pattern owing to its amorphous state but has been shown to hydrolyze readily with the formation of $TiOF_2$, and ultimately TiO_2. In the present case no X-ray pattern was observed initially, but on standing exposed to the atmosphere, the sample gave an X-ray pattern of 5 diffuse lines, as shown in Fig. 1a, corresponding to the spectrum for $TiOF_2$.[9] On heating gently to 100°, evolution of HF was noted, with the formation of the distinct sharp pattern for $TiOF_2$ as in Fig. 1b, indicating that the transformation to crystalline $TiOF_2$ was largely

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[6] For the detailed table supplementary to this article, order Document 5552 from American Document Institute, Washington 25, D. C., remitting $1.25 for microfilm or photocopy.

[7] C. R. Bailey, J. B. Hale and J. W. Thompson, *Proc. Roy. Soc.* (*London*), **167**, 555 (1938).

[8] E. A. Jones, J. S. Kirby Smith, P. J. H. Woltz and A. H. Nielsen, *J. Chem. Phys.*, **19**, 242 (1951).

[9] K. S. Vorres and F. B. Dutton, THIS JOURNAL, **77**, 2019 (1955).

Table I

Material Balance for the Thermal Decomposition of Li_2TiF_6 at 485°[a]

Component	Li_2TiF_6	Li_2TiOF_4	LiF	HF	H_2O	TiO_2	TiF_4
			A				
Weight (g.)	7.7125	0.1020	0.1350	0.2112	0.0616	.....	.....
G. atoms Ti	0.04388	.00066	....	....	....	.....	.....
			B(i)				
Weight (g.)	4.7373	.....	1.0476	....	....	0.1630	.....
G. atoms Ti	0.02695	.....	....	....	....	.00204	.....
			B(ii)				
Weight (g.)	.....	.....	....	....	....	0.0775	.....
G. atoms Ti	.....	.....	....	....	....	.00097	.....
			B(iii)				
Weight (g.)	.....	.....	....	....	....	.....	1.6838
G. atoms Ti	.....	.....	....	....	....	.....	0.01455

[a] A, initial composition. B, after heating 21 hr. at 485°. (i) products remaining in the platinum crucible; (ii) products on cell walls maintained at furnace temperature; (iii) products on cell walls maintained at room temperature.

complete. With more vigorous heating until HF evolution was complete, the original sublimate was transformed to TiO_2 (anatase) as confirmed by the exact correspondence of the X-ray pattern, Fig. 1c, with that for an authentic sample. These data, together with the titanium analysis and weight of the glassy white deposit (Table I, Biii), leave little doubt that the amorphous sublimate was TiF_4.

The results of the product analyses and titanium balance on completion of the studies at 485° are summarized in Table I together with the composition of the initial sample. The total g. atoms Ti accounted for after the thermal treatment is 0.04451, as compared with the initial amount of 0.04454; the agreement leaves little to be desired.

At 300 and 365°, under the conditions of this experiment, little if any decomposition of Li_2TiF_6 occurs, the volatiles being largely HF from the direct dissociation of $Li_2TiF_6 \cdot HF$ and the hydrolysis of Li_2TiF_6 by the H_2O held similarly in the present product. At 485°, Li_2TiF_6 is thermally unstable, the decomposition reaction yielding TiF_4 and LiF as primary products, *i.e.*

$$Li_2TiF_6 \longrightarrow 2LiF + TiF_4 \qquad (3)$$

The formation of TiO_2 on the walls of the glass ampoule at 485° is attributed to the secondary reaction

$$TiF_4 + SiO_2 \longrightarrow TiO_2 + SiF_4 \qquad (4)$$

once the TiF_4 has diffused out from the platinum crucible to contact the glass walls of the ampoule in the hot zone. The formation of SiF_4 will contribute to the weight loss of the ampoule owing to its extremely volatile nature. Thus from the data in Table I, the weight loss predicted would be 0.1368 g. of HF corresponding to 0.0616 g. of H_2O initially present as bound water of solvation, 0.2112 g. of HF from the direct dissociation of $Li_2TiF_6 \cdot HF$, and 0.1008 g. of SiF_4 in accord with reaction (4) above, or a total of 0.4488 g. from the ampoule. The agreement with the observed weight loss, 0.4565 g., well within the experimental accuracy of this study, is additional confirmation of the preceding conclusions.

On heating a sample of Li_2TiF_6 in a crucible open to the atmosphere the products were confirmed to be LiF, TiO_2 and HF. It appears that at 400° in air the decomposition proceeds by the hydrolysis reaction

$$Li_2TiF_6 + 2H_2O \longrightarrow 2LiF + TiO_2 + 4HF \qquad (5)$$

rather than the scheme proposed by Ginsberg and Holder,[4a] *i.e.*

$$Li_2TiF_6 \xrightarrow{\text{air}} 2LiF + TiO_2 + 2F_2 \qquad (6)$$

which postulated elemental fluorine as a product. In air, the lithium titanium fluoride was completely decomposed[4a] after 8 hr. at 400°, whereas in the present work, after 21 hr. *in vacuo* at 485°, 57.5% remained undecomposed. This difference in thermal stability may undoubtedly be attributed in part to the different processes occurring under the conditions of reaction, namely, a hydrolysis attack by atmospheric moisture in air, and a primary dissociation to LiF and TiF_4 *in vacuo* (or inert atmospheres).

The irreproducibility of the melting point (580 ± 25°) and the discrepancy between this value and that reported by Ginsberg[3] may be attributed to the varying amounts of decomposition since both in an inert atmosphere and in air these processes already occur well below the fusion temperature.

In summary, the procedure described for the preparation of lithium titanium fluoride gives a yield of 76% of Li_2TiF_6 (93.8% purity). Heated under vacuum in platinum, Li_2TiF_6 is relatively stable at temperatures up to 365°, at which temperature the dissociation of $Li_2TiF_6 \cdot HF$ is nearly complete. At higher temperatures, *e.g.*, 485°, the lithium titanium fluoride dissociates according to reaction (3), *i.e.*

$$Li_2TiF_6 \longrightarrow 2LiF + TiF_4$$

It is estimated that for a sample heated for 21 hr. at 485°, 42.5% of the Li_2TiF_6 had dissociated by the above reaction.

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