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DISSOCIATION AND RELATIVE STABILITY OF

SODIUM FLUOTITANATE

BY

WALTER L. GAGE

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

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1952

Approved by _____

A. W. Schlechten, Chairman, Department of
Metallurgical Engineering and Mineral Dressing

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The author especially wishes to express his appreciation to Dr. A. W. Schlechten, Chairman of the Department of Metallurgical Engineering, for his consultation, guidance, and advice throughout the work of the thesis.

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I. INTRODUCTION

Titanium is urgently needed in the armament industry especially as a substitute for 18-8 stainless steel. There would be an almost inexhaustible supply of ores of titanium if high-purity titanium metal could be produced economically in large quantities. The use of titanium would permit much of the scarce nickel and chromium to be made available for other important uses.

It has been found by H. C. Kawecki and E. J. Bielecki[1] that

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(1) Kawecki, H. C. and Bielecki, E. J., Production of Potassium Titanium Fluoride. U. S. Pat. 2,568,341, February, 1951.

---

high-purity Na_2TiF_6, K_2TiF_6, and $(NH_4)_2TiF_6$ can be produced from iron-bearing titaniferous raw material, ilmenite ores, or a slag concentrate.

The study of the rate of evaporation and reduction of Na_2TiF_6 was undertaken as a part of a general investigation on treating the titanium compounds recovered from iron-bearing titaniferous raw materials.

The reduction of metal oxides in vacuum has been studied by Dr. Kroll and Dr. Schlechten.[2] They have been able to reduce many metals

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(2) Kroll, W. J. and Schlechten, A. W., Reactions of Carbon and Metal Oxides in a Vacuum, Journ. Electrochem. Soc., Vol. 93, No. 6, June 1948, pp. 247-258.

---

from their oxides under reduced pressures using carbon as a reducing

agent. The volatility and stability of metallic sulphides has been studied in vacuum by Dr. Hsiao and Dr. Schlechten.[3] They have been

(3) Hsiao, C. M. and Schlechten, A. W., Volatility and Stability of Metallic Sulphides, Journ. of Metals, Vol. 4, No. 1, January, 1952, pp. 65-69.

able to classify a large number of sulfides according to their relative volatility and stability.

A similar method of approach was employed in this research as described in the previously mentioned references. The first step was to make the compound (Na_2TiF_6) in the laboratory, the next step was to study this compound by the Langmuir Method, and finally an attempt was made to decompose the Na_2TiF_6 with AlF_3.

II. LITERATURE REVIEW

(A) Literature Concerning Sodium Fluotitanate

Sodium fluotitanate may be prepared in a number of different ways as described in the scientific literature.

Berzelius[4] first prepared sodium fluotitanate by adding sodium

(4) Berzelius, J. J., Svenska Akad. Handl., 2 344, 1824.

hydroxide to a solution of titanium tetrafluoride and evaporating the solution until a permanent precipitate began to form. This precipitate was reported as sodium fluotitanate.

Hunter[5] prepared sodium fluotitanate by dissolving titanium

(5) Hunter, M. A., Metallic Titanium, Journ. Chem. Soc., 13, 1910.

dioxide in hydrofluoric acid and then neutralizing the solution with a hot concentrated solution of sodium hydroxide. Sodium fluotitanate was precipitated from this solution.

Meyerhofer[6] prepared sodium fluotitanate by the interaction of

(6) Meyerhofer, A. F., Producing Complex Salts of Hydrofluoric Acid, Soc. of Chem. Ind. Journ., 44, 1925, pp. 847.

titanium tetrafluoride and silicofluoride in the presence of very dilute hydrochloric acid.

Kawecki and Bielecki[7] prepared sodium fluotitanate by digesting

(7) Kawecki, H. C. and Bielecki, E. J., op. cit.

titanium in hydrofluoric acid and then upon heating above 70°C, sodium chloride was added in the presence of free hydrofluoric acid. Sodium fluotitanate precipitates out of solution upon cooling.

(B) Literature Concerning Volatility of Fluorides

Simons[8] has compiled a list of the melting points and boiling

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(8) Simons, J. H., Fluorine Chemistry, Published by the Academic Press Inc., New York, pp. 10 & 11.

---

points of fluorides.

Hunter[9] reports that it seems that the double fluorides are

---

(9) Hunter, M. A., op. cit.

---

reduced by alkali metals in vacuo.

Kroll[10] reports that sodium fluotitanate loses titanium fluoride

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(10) Kroll, W. J., Some Aspects of Titanium Metallurgy, Metal Industry, Vol. 80, May 2, 1952.

---

when heated to 660°C.

III. PREPARATION OF SODIUM FLUOTITANATE

The sodium fluotitanate used in this work was prepared by mixing stoichiometric amounts of sodium fluoride and titanium fluoride in an aqueous solution and evaporating it to dryness to obtain sodium fluotitanate. The reaction takes place according to the equation:

$$TiF_4 + 2NaF == Na_2TiF_6$$
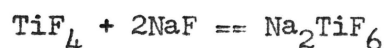
C. P. grade sodium fluoride was used and the titanium fluoride was prepared by dissolving the metallic titanium in hydrofluoric acid. The reactions that take place to form the titanium tetrafluoride as reported by Straumanis and Chen[11] are as follows:

(11) Straumanis, M. E. and Chen, P. C., The Mechanism and Rate of Dissolution of Titanium in Hydrofluoric Acid, Journ. Electrochem. Soc., Vol. 98, No. 6, June 1951, pp. 234.

$$(1)\ 2Ti + 6HF == 2TiF_3 + 3H_2$$
$$(2)\ 4TiF_3 + 4HF + O_2 == 4TiF_4 + H_2O$$
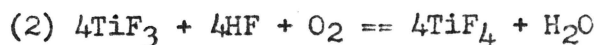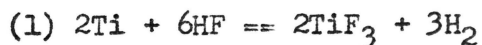
A. Procedure

1. Hydrofluoric acid (48% concentration) was weighed and placed in a plastic container.

2. Titanium metal was weighed and slowly added to the hydrofluoric acid along with water to keep the foaming during digestion to a minimum. The solution was gently heated and allowed to stand for 48 hours when the solution changed from a green color (TiF_3 state) to a light brown color (TiF_4 state).

3. Sodium fluoride was weighed and added to the warm solution

of TiF_4. The mixture was allowed to digest for 24 hours during which time the solution turned colorless.

4. The water was slowly evaporated and the sodium fluotitanate crystallized out of solution.

B. Chemical Analysis of the Product

After the sodium fluotitanate had been dried to constant weight, samples were taken for chemical analysis of the titanium. Titanium was determined quantitatively by a gravimetric method. The method consists of precipitating the titanium form an acid solution by adding the organic reagent, cupferron. The precipitate was filtered, washed with a 25% hydrochloric acid solution, ignited, and weighed as titanium dioxide. The results are given below:

Sodium fluotitanate (prepared) = 22.42% Ti

Sodium fluotitanate (theoretical) = 23.04% Ti

It can be seen from the results listed above that the sodium fluotitanate (as prepared) closely approaches the ideal results.

C. X-ray Examination of the Products

The sodium fluotitanate prepared was examined by x-ray diffraction. The x-ray diffraction method for qualitative analysis has been widely used to identify crystalline substances.[12]

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(12) Hanawalt, J. D., Rinn, H. W., Frevel, L. K., Chemical Analysis by   by X-ray Diffraction Method, Ind. Eng. Chem. Anal. Ed., Vol. 10, (1938), pp. 457-512.

In addition to being rapid and not destroying the sample, this method indicates the state of chemical combination of the elements existing

in the sample. Positive identification by the x-ray diffraction method could not be made since sodium fluotitanate has not been classified as yet. The purpose of this x-ray examination was to note if any structure changes occurred upon subsequent treatment.

The Norelco Geiger Counter X-ray Spectrometer with an automatic recorder made by the North American Phillips Co., Inc., was used in this investigation. A copper target with a nickel filter was employed for the determination. The sample was moved from a Bragg angle of forty-five to ten degrees. The 'd' values of the crystal can be calculated by the use of the Bragg Equation, $n\lambda = 2d(\sin\theta)$, where n = the order, λ = wave length of radiation, θ = Bragg angle, and d = distance between planes, since the radiation is constant (λ = 1.5374 A for copper), θ- can be measured, and n = 1. The 'd' values and the relative intensities of the respective peaks are listed in Tables II and X. Only the major peaks were recorded for identification purposes.

IV. BEHAVIOR OF SODIUM FLUOTITANATE AND ALUMINUM

FLUORIDE AT ELEVATED TEMPERATURES

A. Equipment

A schematic drawing of the apparatus used in these experiments
is shown in Figure I. The major parts are briefly described below.

(1) Electric Resistance Furnace

The furnace used in this investigation was patterned after the
one described by Dr. Hsiao and Dr. Schlechten [13] in their study of

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[13] Hsiao, C. M. and Schlechten, A. W., op. cit.

---

metallic sulphides in vacuum. The furnace consisted of a 2 1/8 inch
diameter porcelain tube 40 inches long supported in a vertical
position and with the upper closed end heated with a Smith No. 10
alloy resistance wire wound on an alundum core embedded in magnesia
cement and surrounded by crushed insulating brick.

The porcelain tube was sealed at its lower end into a metal head
with two 'O' rings. This metal head was cooled with circulating
water to ensure that these 'O' rings did not overheat. A vacuum
connection was made through the metal head which had a conical ground
joint that was vacuum tight and could be opened for the introduction
of samples into the tube.

Stainless steel tubing in sections was inserted into the porce-
lain tube. An alundum crucible containing the charge was placed on
a crucible seat between the top and middle sections. The details of
the construction of the stainless tube and the device used to hold

Figure 1

General Arrangement and Connections of the Furnace and Vacuum System
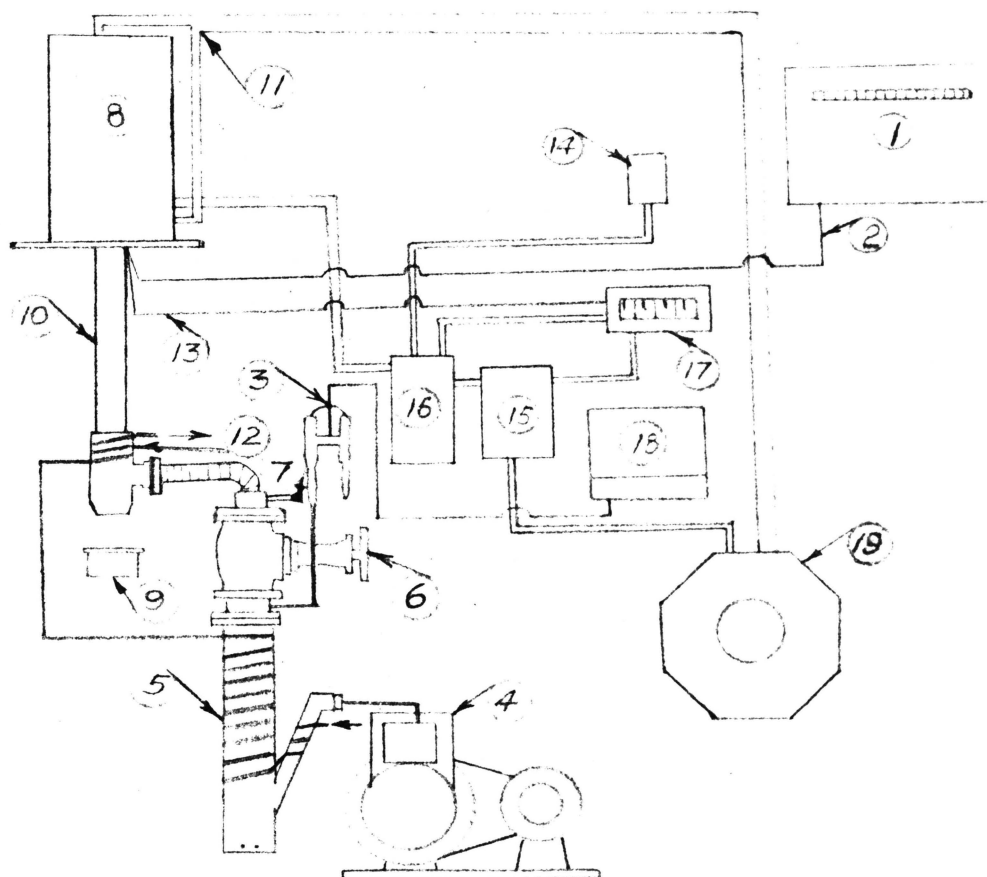
1. Brown Potentiometer (model 133RIP-53, Temperature up to 2000°F)
2. Alumel-Chromel Thermocouple (Gauge 14)
3. Pirani Tube (Distillation Products, Inc.)
4. Mechanical Vacuum Pump (W.M. Welch Scientific Co.)
5. Metal Diffusion Pump (Distillation Products, Inc.)
6. Vacuum Value
7. Rubber Stopper (for vacuum release)
8. Metal Resistance Furnace (designed by Kroll & Schlechten)
9. Furnace Cap
10. Porcelain Tube (McDanel Refractory Porcelain Co.)
11. Lead Wire to Smith No. 10 Heating Elements
12. Copper Tubing Cooling Coils
13. Pt-Pt Rh Thermocouple
14. Tork Clock (self-starting single pole type, Tork Clock Co.)
15. Safety Switch (30 amps. General Electric Co.)
16. Line Starter (single or Polyphase type, Westinghouse Elec. Co.)
17. Wheelco Control (Temperature to 1000°C)
18. Pirane Gauge (Distillation Products, Inc.)
19. Powerstat (7.5 KW. Superior Electric Co.)

Figure 2   Tube and Its Accessories
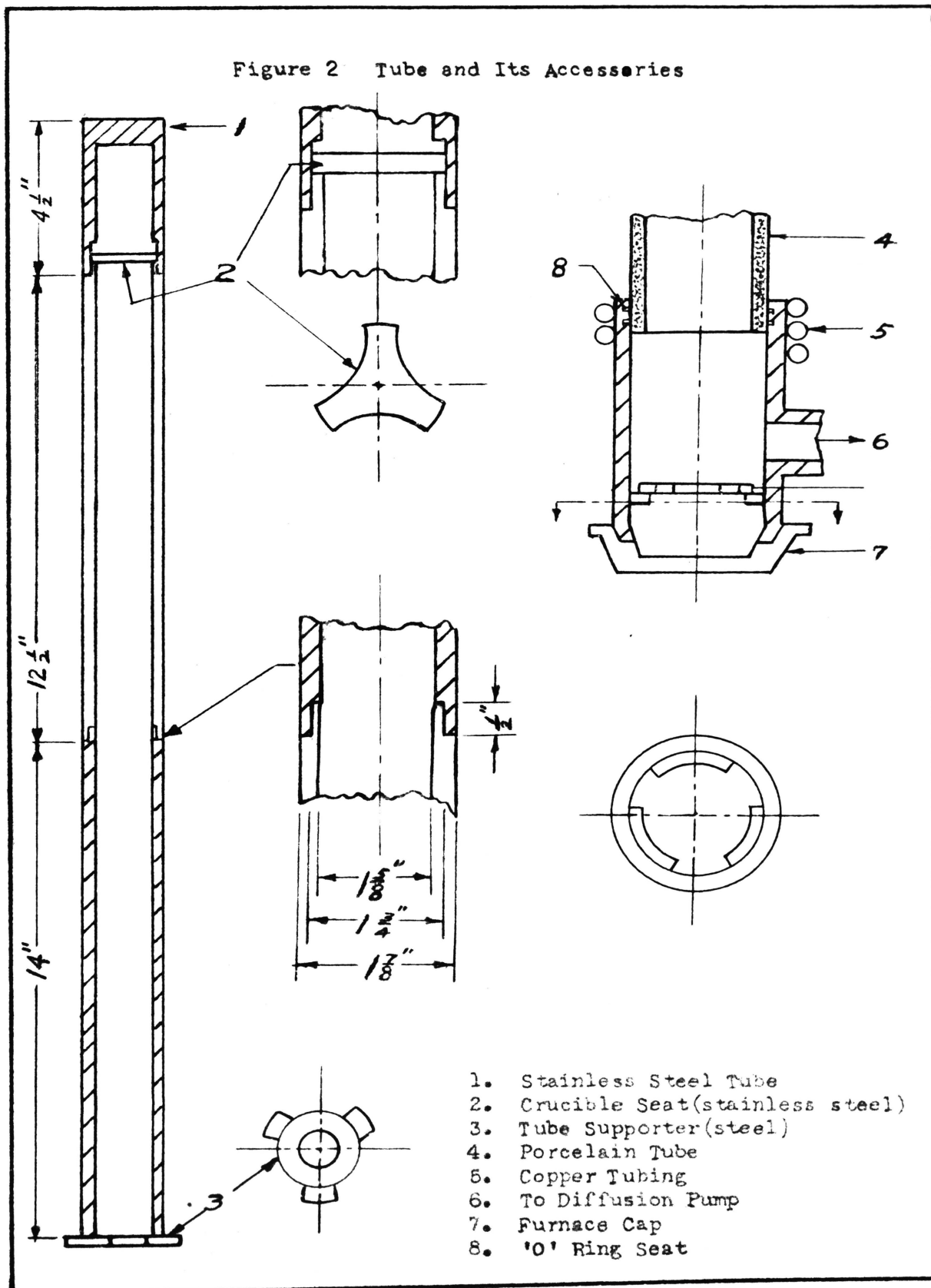
1. Stainless Steel Tube
2. Crucible Seat(stainless steel)
3. Tube Supporter(steel)
4. Porcelain Tube
5. Copper Tubing
6. To Diffusion Pump
7. Furnace Cap
8. 'O' Ring Seat

the tube in place inside the furnace are shown in Figure II.

(2) Temperature Measurement and Control

The temperature was measured at the outside wall of the porcelain tube by means of a platinum platinum-rhodium thermocouple attached to an indicating Wheelco pyrometer control.

A Tork Self-starting Clock was in the temperature controller circuit which allowed the heating time to be preset.

A powerstat, capacity 7.5 KW, was used to adjust the voltage to the furnace. The rate of heating the furnace was varied by changing the setting of the powerstat.

(3) Pressure Measurement

A Pirani gauge was used to measure the pressure. It is based on the principle that the thermal conductivity of a gas is proportional to its pressure. The gauge filament is connected to the vacuum system and as the pressure around the gauge filament changes, so does the speed at which heat is conducted away from the filament change, and this in turn changes the filament temperature and hence its resistance. The resistance change is recorded by a Wheatstone bridge circuit which is balanced with an identical evacuated compensating filament mounted in an adjacent arm of the bridge. The filament is heated at a constant rate by keeping the voltage constant. When the bridge is balanced at this temperature of the filament, a change of its temperature caused by a change in the heat conductivity of the residual gases will unbalance it. The deflection of the bridge galvanometer indicates the pressure of the residual gases.

(4) Oil Diffusion Pump

The oil diffusion pump consists of a boiler to vaporize the oil, a chimney to lead the vapor to the jets, jets to conduct the droplets of oil into the main portion of the pump, and cooling coils to condense the returning oil. The air is entrapped by the oil vapor and pulled toward the exhaust where the mechanical pump continues the exhaust process with the air that is freed as the oil is cooled and reliquified.

(B) Experimental Procedure

The operating procedure for obtaining data for the vapor pressure measurement was as follows:

1. Prepare and weight the charge.

2. Place the crucible and charge in the furnace.

3. Close the furnace by placing the cap on the metal head.

4. Switch on the mechanical pump.

5. When the system was evacuated to 100 microns, turn on the diffusion pump along with the cooling system.

6. When the diffusion pump lowered the vacuum to 25 microns, the furnace was started by setting the powerstat at a predetermined current. At the same time, the pyrometer controller was set at the desired temperature.

7. When the maximum temperature was reached, the time-clock was set for the predetermined period of time during which the furnace was to be held at this temperature.

8. Periodic vacuum gauge readings were taken to be sure that the vacuum was maintained.

9. After the heating period, the furnace was allowed to cool with

the pumps still running. The diffusion pump was turned off when the furnace temperature dropped to 100°C.

10. The vacuum valve was closed and the vacuum was released by removing the rubber stopper of the vacuum release tube.

11. The furnace cap was removed and the stainless steel tube was removed from the furnace.

12. The residue was weighed and the condensate in the stainless steel was collected.

13. The nature of the residue and the condensate was examined, chemical analyses or x-ray analyses were made when necessary.

(C) <u>Theory</u> <u>of Vapor</u> <u>Pressure</u> <u>Measurements</u>

The Langmuir method for determining the vapor pressure was employed in this investigation. The loss of weight of a substance at a specific temperature per unit area per unit of time was measured, and then the vapor pressure at the specific temperature was calculated by the Langmuir equation:[13]

$$P_{mm} = 17.15 \ G\sqrt{T/M}$$

where P_{mm} = vapor pressure in millimeters

G = loss of weight per unit area per unit time ($gms./cm^2/sec$)

T = temperature in °K

M = molecular weight

(13) Dushman, S., Vacuum Technique, Published by John Wiley & Sons, Inc., New York, pp. 20.

In the measurement of G, a weighed sample was heated in vacuum

to a certain temperature and held at that temperature for a definite length of time. The same procedure was repeated with another sample, but held at the temperature for a different length of time. The weight loss of each sample was recorded. The difference in these two weight losses is the total weight loss for the difference in time interval that the samples were held at the temperature provided that the heating and cooling of the samples were identical. The current supplied to the heating coil of the furnace was constant and therefore the samples were heated at the same rate. The furnace was allowed to air cool under constant conditions and therefore the samples were cooled at the same rate. The weight loss found in the above manner was divided by the area of the crucible and by the time interval to give the loss per unit area per unit time, which is the 'G' value in the Langmuir equation.

A substance when heated in vacuum may undergo either or both of the following changes: (1) sublimation, (2) dissociation. If the actual change is a mere physical sublimation, the above mentioned formula will give the vapor pressure correctly because in this case 'G' is solely due to the loss of the sublimed vapor. If, however, chemical dissociation takes place with the formation of a volatile product, the loss of weight will be a combined effect of sublimation and dissociation, which will yield a vapor pressure measurement that is larger than the true vapor pressure. This was the case with sodium fluotitanate since x-ray and chemical analysis proved that titanium fluoride was vaporized from the sodium fluotitanate. However, it is felt that the measured vapor pressure is a significant measurement of

the relative stability of the sodium fluotitanate and worthwhile to be reported as such.

(D) Experimental Results and Discussion

(1) Dissociation of Sodium Fluotitanate in Vacuum.

The loss of weight on heating sodium fluotitanate in vacuum at various temperatures is shown in Table I.

Sodium fluotitanate is a white colored compound which gradually changes color when heated in a vacuum. When heated to 400°C and 600°C, it changes to a gray color, and acquires a light purple tint when heated to 700°C, 800°C, and 900°C. Both chemical analysis and x-ray analysis showed that there was a chemical decomposition according to the following reaction:

$$2NaF \cdot TiF_4 + Heat = 2NaF + TiF_4$$
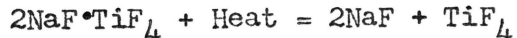
The residue analyzed 11.50% titanium when the sodium fluotitanate was heated in a vacuum to 700°C for 2 hours compared with an analysis of the charge which was 22.42% titanium. Note Table VII for the material balance of this experiment. The condensate analyzed 41.76% as compared with 38.66% titanium for the ideal percentage of titanium present in the ideal compound TiF_4.

X-ray analysis showed that TiF_4 was distilled from the charge. The residue contained sodium fluoride and an unidentified compound. Note Table II for the comparative 'd' values of the structure.

(2) Dissociation of Aluminum Fluoride in Vacuum.

The loss of weight on heating aluminum fluoride in vacuum at various temperatures is shown in Table III.

The purpose of measuring the vapor pressure of aluminum fluoride

Table I. Experimental Data Showing Loss of

Weight on Heating Na_2TiF_6 in Vacuum.

Temperature (°C)	Time (hours)	Weight of Charge (gms.)	Weight of Residue (gms.)	Loss of Weight (gms.)	Rate of Loss gms./hr.
400	3	3.0000	2.8358	0.1642	
400	2	3.0000	2.8553	0.1447	0.0195
600	3	3.0000	2.2379	0.7621	
600	2	3.0000	2.4634	0.5366	0.2255
800	3	3.0000	1.3684	1.6316	
800	2	3.0000	2.2309	0.7691	0.8625

Table II. X-ray Data for Residue From Heating Na_2TiF_6 in a Vacuum for 2 Hours at 700°C, Chemically Pure NaF, Condensate From Heating Na_2TiF_6 in a Vacuum for 2 Hours at 700°C, and TiF_4 From A.S.T.M. Standards.

Na_2TiF_6 Residue 2 hrs. at 700°C, in vacuum		NaF Chemically Pure		Na_2TiF_6 Condensate 2 hrs. at 700°C, in vacuum		TiF_4 A.S.T.M. Standards (1-0490) Low I/I_o Omitted	
d (A°)	Relative Intensity I/I_o	d (A°)	Relative Intensity I/I_o	d (A°)	Relative Intensity I/I_o	d (A°)	Relative Intensity I/I_o
2.88	20			3.81	100	3.80	100
2.43	10			3.28	20	3.22	20
2.35	100	2.36	100	2.68	20	2.68	10
2.02	20			1.90	70	1.90	40
1.65	60	1.66	80	1.70	80	1.70	40
1.63	10			1.34	60	1.35	10
1.34	10	1.35	20	1.27	20	1.27	10
1.17	10	1.17	10				

Table III. Experimental Data Showing Loss of Weight on
Heating AlF_3 in Vacuum.

Temperature (°C)	Time (hours)	Weight of Charge(gms.)	Weight of Residue(gms.)	Loss of Weight (gms.)	Rate of Loss gms./hr.
600	3	2.0000	1.3021	0.6979	
600	2	2.0000	1.3164	0.6836	0.0143
650	3	2.0000	1.0502	0.9498	
650	2	2.0000	1.1178	0.8822	0.0676
700	3	2.0000	0.7492	1.2508	
700	2	2.0000	1.0233	0.9767	0.2741

was to investigate the properties of aluminum fluoride with the thought of using it in later work to help decompose the sodium fluotitanate.

(3) Computation of Vapor Pressures of Sodium Fluotitanate and Aluminum Fluoride from Experimental Data.

The loss of weight on heating sodium fluotitanate in a vacuum at elevated temperatures has been shown in Table I. The rate of weight loss at 400°C is 0.0192 gms./hr. The crucible used, had a diameter of 2.540 cm. yielding a cross sectional area of 5.067 cm^2. Therefore the value of 'G' in the Langmuir equation is

$$G = 0.0195/3600 \text{ sec.}/5.067 cm^2$$

$$G = 0.01069 \times 10^{-5} \text{ gm./sec./} cm^2$$

Since $P_{mm} = 17.14 \ G\sqrt{T/M}$

Where M = molecular weight of Na_2TiF_6 = 207.89

T = absolute temperature = 273 + 400 = 673°K

Therefore $P_{mm} = 17.14 \times 0.01069 \times 10^{-5}\sqrt{673/207.89}$

$$P_{mm} = 0.3296 \times 10^{-4} \text{ mm Hg.}$$

Similarly, the measured vapor pressure for the other temperatures can be calculated. The results are in Table IV. By plotting the $\log P_{mm}$ versus $1/T \times 10^3$, the graph obtained is a straight line as shown in Figure III.

The loss of weight on heating aluminum fluoride in a vacuum at elevated temperatures has been shown in Table III. The rate of weight loss at 600°C is 0.0143 gms./hr. The crucible used, had a diameter of 2.540 cm. yielding a cross sectional area of 5.067 cm^2. Therefore the value of 'G' in Langmuir's equation is

Table IV. Measured Vapor Pressure Data of Na_2TiF_6.

Rate of Loss (gms./hr.)	Crucible Diameter (cm.)	G (10^5gms.)	$T(^{\circ}K)$	M	P_{mm} (10^4_{mm})	Log P_{mm}	$1/T \times 10^3$
0.0195	2.540	0.01069	673	207.89	0.3296	-4.482	1.486
0.2255	2.540	1.236	873	207.89	4.341	-3.362	1.145
0.8625	2.540	4.729	1073	207.89	18.42	-2.735	0.9320

Figure III

$\log P_{mm}$ V $1/T \times 10^3$

$$G = 0.0143/3600 \text{ sec.}/5.067 \text{cm.}^2$$

$$G = 0.07840 \times 10^{-5} \text{gms.}/\text{sec.}/\text{cm.}^2$$

Since P_{mm} = 17.14 $G\sqrt{T/M}$

Where M = molecular weight of AlF_3 = 84

T = absolute temperature = 273 + 600 = $873^{\circ}K$

Therefore P_{mm}= 17.14 x 0.07840 x $10^{-3}\sqrt{873/84}$
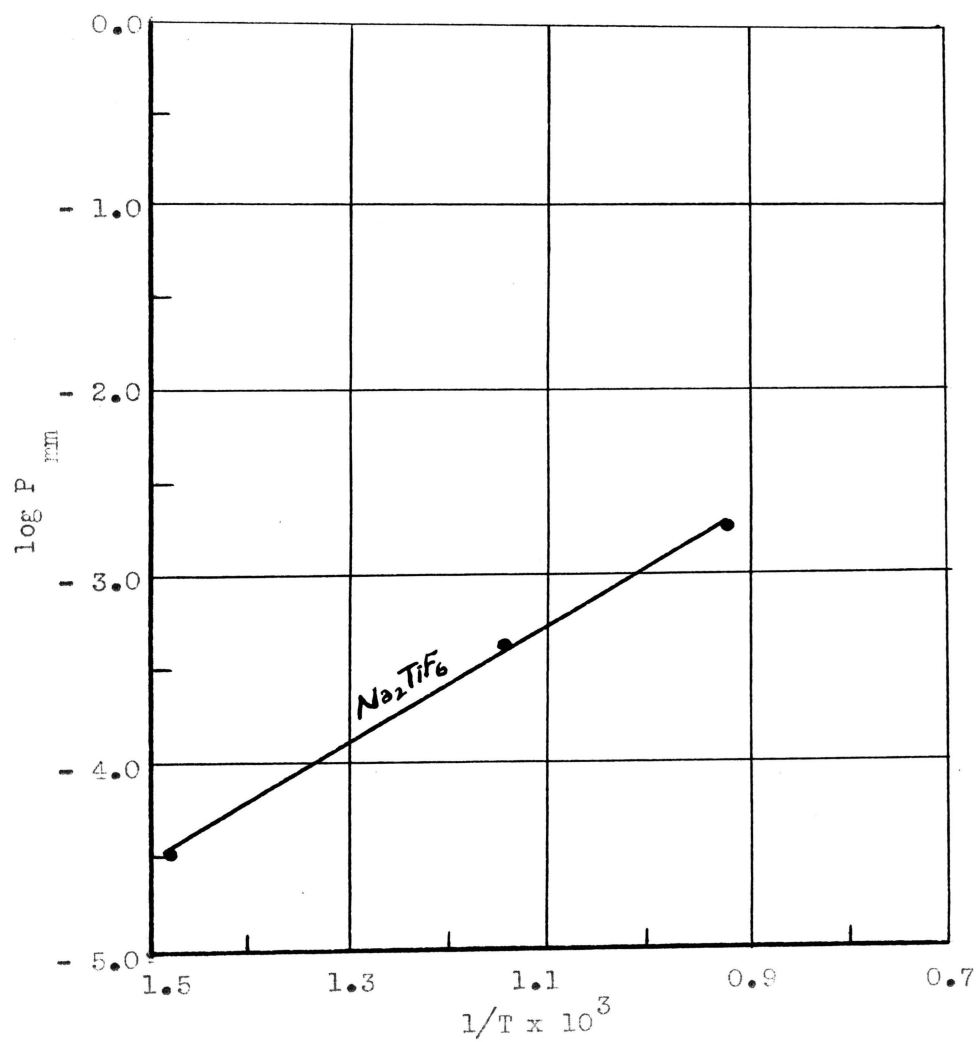
$$P_{mm} = 0.4353 \times 10^{-5} \text{mm Hg.}$$

Similarly, the measured vapor pressure for the other temperatures can be calculated. The results are in Table V. By plotting log P_{mm} versus $1/T \times 10^3$, the graph obtained is a straight line as shown in Figure IV.

It can be concluded from the results of the measured vapor pressures of both sodium fluotitanate and aluminum *fluoride* that they both have relatively high vapor pressures and are therefore relatively volatile compounds. It is interesting to note that at approximately 707°C, the measured vapor pressure of sodium fluotitanate and aluminum fluoride are equal.

Table V. Measured Vapor Pressure Data of AlF_3

Rate of Loss (gms./hr.)	Crucible Diameter (cm.)	G $(10^5 gms.)$	$T(^oK)$	M	P_{mm} (10^4)	Log P_{mm}	$1/T \times 10^3$
0.0143	2.540	0.07840	873	84	0.4353	-4.361	1.145
0.0676	2.540	0.3706	923	84	2.1057	-3.677	1.083
0.2741	2.540	1.503	973	84	8.7666	-3.057	1.028

Figure IV

log P $_{mm}$ $\not{v}$ 1/T x 10^3
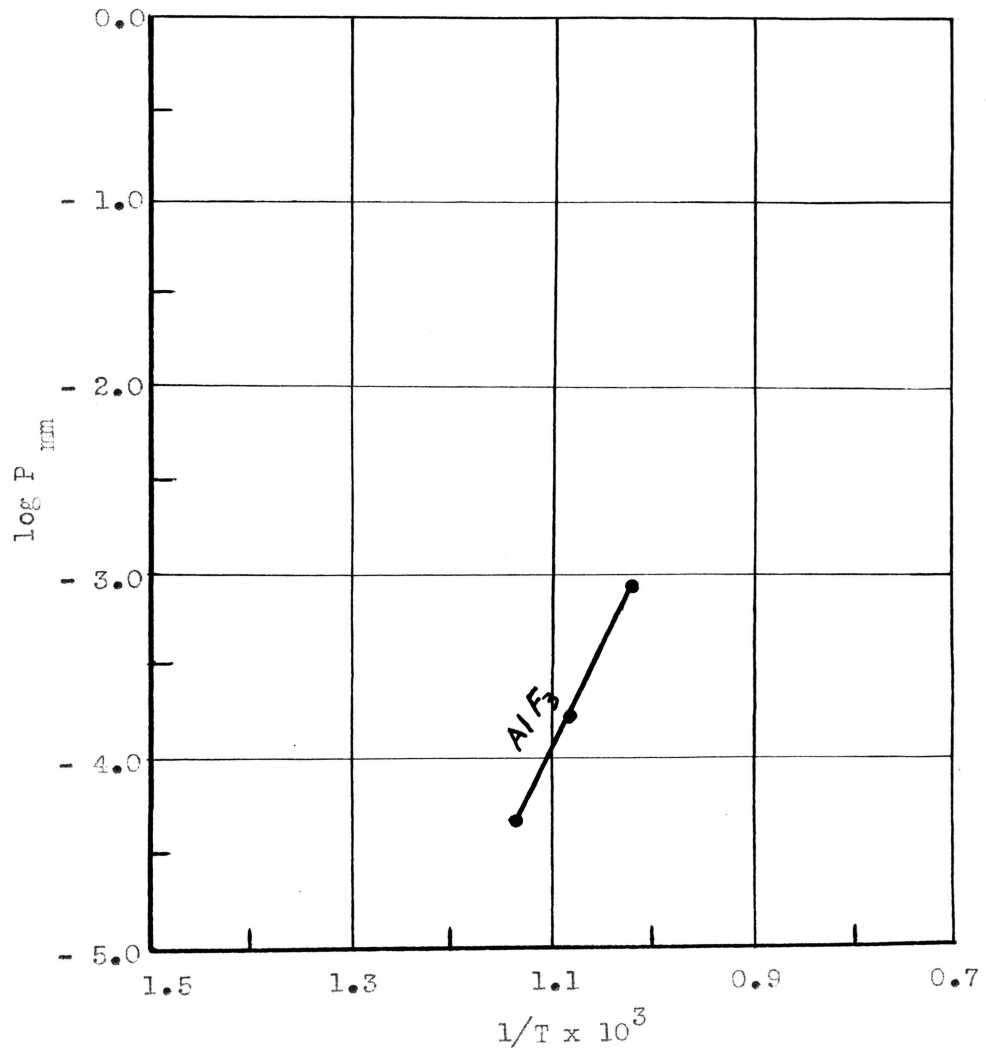
V. DISSOCIATION OF SODIUM FLUOTITANATE

(A) Theoretical Considerations

(1) Stability of Sodium Fluotitanate.

The dissociation of sodium fluotitanate may be represented by the following equation:

$$2NaF \cdot TiF_4 = 2NaF + TiF_4$$
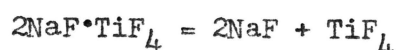
The degree of dissociation of a compound is a function of its stability. In the case of a double fluoride such as sodium fluotitanate, the stability depends on the chemical bond between the titanium fluoride and the sodium fluoride as well as on the relative volatility of both. Very little data is available concerning the sodium fluotitanate, other than that it loses titanium fluoride when heated above 660°C. Data concerning the volatility of single fluorides which has been compiled by Simons[14] is listed in Table VI. To date, the best

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(14) Simons, J. H., ob. cit.

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measurement of the stability of double fluorides is the comparison of the volatility of the single fluorides which make it up.

(2) Effect of Vacuum on Dissociation.

The effect of vacuum on the dissociation of sodium fluotitanate may be studied from a consideration of the equation:

$$2NaF \cdot TiF_4 = 2NaF + TiF_4$$
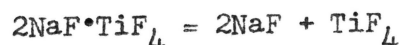
By maintaining a reduced pressure over the system, the gaseous product (TiF_4) may be removed and the dissociation will proceed to completion and no reversible reaction can take place. Of course this dissociation can only take place at an elevated temperature since sodium

Table VI. Melting and Boiling Points of Fluorides

Group I				Group II		
Compound	M.P.(°C)	B.P.(°C)	::	Compound	M.P.(°C)	B.P.(°C)
LiF	840–844	1676		BeF_2	800	
NaF	980–1040	1705		MgF_2	1225	2260
KF	850	1500–1505		CaF_2	1418	2500
RbF	775	1410		SrF_2	1300–1400	2460
CsF	684	1251		BaF_2	1280–1290	2260
CuF	908	1000		ZnF_2	734	1500
CuF_2	950(decomp.)			CdF_2	1100	1200
AgF	430	1150		Hg_2F_2	570	decomp.
AgF_2	690			HgF_2	645	decomp.

Group III				Group IV		
AlF_3	1040			TiF_4		284
GaF_2	1000	950		HfF_4		800–1000
InF_3	1170	1200		ThF_4	900	1000
TlF	298			GeF_4		-37
TlF_3	550			SnF_4		705
CeF_3	1324			PbF_2	882	1292
CeF_4	1460			PbF_4	600	
PrF_3	1370					
NdF_3	1410					

Table VI (Continued) Melting and Boiling Points of Fluorides

Group V and VI			::	Group VII and VIII		
Compound	M.P.(°C)	B.P.(°C)	::	Compound	M.P.(°C)	B.P.(°C)
VF_3	800			MnF_2	856	
VF_4		111		ReF_4	124.5	
CbF_5	73	236		ReF_6	18.8	47.6
TaF_5	97	229		FeF_2		1000
AsF_3	−8.5	63		FeF_3		1000
AsF_5	−80	−53		CoF_2	1200	
SbF_3	292	319		CoF_3	1200	
SbF_5	6	149–150		RuF_5	101	270–275
BiF_3	725–730			RhF_3		600
BiF_5		550		OsF_6	50	220–205
CrF_3	1000	1100		OsF_8	34.4	47.3
MoF_6	17.5	35		IrF_4		100
WF_6	2.3	17.5		IrF_6	44	53
UF_4	1000					
UF_6	69.2/2 atm.	56/1 atm.				

fluotitanate is stable at room temperature.

(3) Choice of a Reagent to Promote Chemical Displacement Reaction of Titanium Fluoride from Sodium Fluotitanate.

The choice of a reagent to chemical replacement of titanium fluoride from sodium fluotitanate is governed by the following factors:

(a) The replacing reagent must be relatively non-volatile, otherwise it will evaporate away and replacement would be retarded.

(b) It must have a higher affinity towards the sodium fluoride to replace the titanium fluoride from its double fluoride.

(c) It is desirable that the reagent must form a non-volatile product so as to facilitate the separation from the volatile product (TiF_4).

(d) It must not form intermetallic compounds with the titanium which would retard the dissociation or removal of the titanium fluoride from the sodium fluotitanate.

It seems impossible to choose a reagent to promote chemical displacement of titanium fluoride from sodium fluotitanate which fulfills all of the factors referred to previously. Aluminum fluoride was chosen because it is know that it forms stable double fluorides with sodium fluoride.

(B) Experimental Results and Discussions

Since it was found that aluminum fluoride was a relatively volatile compound at the temperature range where sodium fluotitanate dissociates, the attempt to promote dissociation of sodium fluotitanate was carried out at atmospheric pressure. The charge was heated in an atmosphere of helium gas so that no interferring chemical reaction could take

place with the oxygen or nitrogen in the air.

The operating procedure was as follows:

1. Attach a rubber balloon containing helium gas to the vacuum release tube in place of the rubber stopper.

2. Prepare, weigh, and charge the sample into the furnace.

3. Evacuate the system as mentioned previously.

4. When the system was evacuated to 25 microns, close the vacuum valve.

5. Introduce helium gas into the furnace by opening the connecting tube between the furnace system and the rubber balloon.

6. Heat the furnace as mentioned previously.

7. After the heating and cooling cycle, remove the stainless steel tube.

8. Weigh the residue and collect the condensate.

9. The nature of the residue and the condensate was examined, chemical analysis or x-ray analysis were made when necessary.

Aluminum fluoride forms stable compounds with sodium fluoride which are $3NaF \cdot AlF_3$ and $5NaF \cdot 3AlF_3$. An attempt was made to promote the following reaction:

$$6NaF \cdot 3TiF_4 + 2AlF_3 = 6NaF \cdot 2AlF_3 + 3TiF_4$$

Stoichiometric amounts of aluminum fluoride and sodium fluotitanate to form $3NaF \cdot AlF_3$ were mixed together and heated to 700°C for 2 hours under a helium gas atmosphere; sodium fluotitanate (prepared) was heated to 700°C for 2 hours under a helium gas atmosphere; and sodium fluotitanate (prepared) was heated to 700°C for 2 hours in a vacuum. The corresponding material balances for these experiments are

listed in Tables Ix, VIII, and VII, respectively. The x-ray analysis of these experiments may be found in Tables II and X.

The material balance shows that 82.44% of the titanium as TiF_4 was vaporized along with some sodium fluoride when sodium fluotitanate (prepared) was heated in vacuum for 2 hours at 700°C; when the sodium fluotitanate (prepared) was heated in an helium atmosphere for 2 hours at 700°C, 8.47% of the titanium as TiF_4 was vaporized; and when the stoichiometric mixture of $(Na_2TiF_6 + AlF_3)$ was heated in an helium gas atmosphere for 2 hours at 700°C, 18.98% of the titanium as TiF_4 was vaporized. Aluminum fluoride was heated in a helium gas atmosphere for 2 hours to check if there was any weight loss due to the vaporization of it alone, but there was none.

The significance of employing the vacuum treatment can be seen where 82.44% of the titanium was removed when vacuum was applied compared with 8.47% when it was not applied with all other conditions being held constant. The addition of aluminum fluoride also promoted the dissociation of sodium fluotitanate as can be seen from a comparison of 18.89% removed compared with 8.47% when it was not added.

The data from x-ray analysis in Table X, show that upon heating the sodium fluotitanate (prepared) in a helium gas atmosphere for 2 hours at 700°C, no crystal structure change took place; however when sodium fluotitanate (prepared) with a stoichiometric aluminum fluoride addition was treated similarly, a crystal structure change did take place. This new crystal structure could not be classified with the aid of the A.S.T.M. Classification System.

Table VII. Material Balance for Na$_2$TiF$_6$ Heated in Vacuum for 2 Hours at 700°C.

Material	Total Wt. (grams)	%Ti	Wt. Ti (grams)	Ti Balance (% wt.)
Charge	6.7714	22.42	1.5181	100.00
Residue	2.3186	11.50	0.2666	17.56
Condensate	4.4528	- -	1.2515	82.44

Table VIII. Material Balance for Na$_2$TiF$_6$ Heated in a Helium Atmosphere for 2 Hours at 700°C.

Material	Total Wt. (grams)	%Ti	Wt. Ti (grams)	Ti Balance (% wt.)
Charge	6.8466	22.42	1.535	100.00
Residue	6.2827	22.36	1.405	91.53
Condensate	0.5639	- -	0.130	8.47

Table IX. Material Balance for (Na$_2$TiF$_6$ + AlF$_3$) Heated in a Helium Atmosphere for 2 Hours at 700°C.

Material	Total Wt. (grams)	%Ti	Wt. Ti (grams)	Ti Balance (% wt.)
Charge	8.0185	17.67	1.417	100.00
Residue	6.0410	19.00	1.148	81.02
Condensate	1.9775	- -	0.269	18.98

Table X. X-ray Data for Na_2TiF_6 (prepared), Residue from Heating Na_2TiF_6 in a Helium Atmosphere for 2 Hours at 700°C, and Residue from Heating $(Na_2TiF_6 + AlF_3)$ in a Helium Atmosphere for 2 Hours at 700°C.

Na_2TiF_6 (prepared)		Na_2TiF_6 Residue 2 hrs. at 700°C, Helium Atmosphere		$Na_2TiF_6 + AlF_3$ Residue 2 hrs. at 700°C Helium Atmosphere	
d (A°)	Relative Intensity I/I_o	d (A°)	Relative Intensity I/I_o	d (A°)	Relative Intensity I/I_o
4.70	30	4.71	30	3.52	30
4.40	40	4.41	20	3.04	90
3.47	40	3.49	40	2.40	100
3.20	30	3.20	30	1.87	60
2.62	20	2.62	20	1.83	50
2.37	70	2.38	90	1.74	30
1.85	100	1.86	100	1.57	40
1.73	40	1.73	40	1.55	30
1.66	20	1.65	20		
1.54	30	1.54	30		
1.45	20	1.45	20		

VI. Summary and Conclusions

Sodium fluotitanate was prepared by mixing stoichiometric amounts of sodium fluoride and titanium fluoride in an aqueous solution and recovering the double fluoride upon evaporation.

When sodium fluotitanate was heated in a vacuum, it dissociated to sodium fluoride and titanium fluoride.

Both sodium fluotitanate and aluminum fluoride have relatively high vapor pressures.

Aluminum fluoride promoted the dissociation of sodium fluotitanate when heated in a helium gas atmosphere for 2 hours at 700°C.

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VITA

The author was born on February 12, 1925 in Cleveland, Ohio. He received elementary and high school training at Rocky River, Ohio. A Bachelor of Science in Metallurgical Engineering was obtained in June, 1949, from Fenn College.