

[PUBLICATION NO. 68 OF THE RESEARCH LABORATORIES, MUTUAL CHEMICAL COMPANY OF AMERICA]

## Calcium Dichromate

BY WINSLOW H. HARTFORD, KEITH A. LANE AND WILLIAM A. MEYER, JR.

Calcium dichromate was first prepared by Vauquelin<sup>1</sup> and the trihydrate later described by Bahr,<sup>2</sup> as deliquescent red crystals which melted on heating and became yellowish-brown on drying. Mylius and von Wrochem<sup>3</sup> report the existence of the tetrahydrate, but give no supporting data. Uses of the compound or its solution as a catalyst,<sup>4</sup> in the manufacture of chromyl chloride<sup>5</sup> and chromium trioxide,<sup>6</sup> and as a corrosion inhibitor<sup>7</sup> are cited, but details of preparation of the salt are not given. A solution of calcium dichromate is also reported to result from treatment with carbon dioxide under pressure<sup>8</sup> of an aqueous suspension of the product obtained by calcining chrome ore and calcium oxide in an oxidizing atmosphere. The further investigation of the physical properties of calcium dichromate appeared to be desirable in view of the numerous references to it, and also as a continuation of a program of investigation of the properties of the dichromates.<sup>9</sup>

### Experimental

**Preparation of Calcium Dichromate Solution.**—A solution of 3 kg. of technical chromium trioxide in 3.8 liters of water was treated slowly with 1.5 kg. of precipitated calcium carbonate or the equivalent quantity of finely-divided calcium oxide or hydroxide and warmed until the reaction was complete. The resulting solution was diluted with water to adjust the density to not over 1.45, the maximum concentration permissible for satisfactory electrolysis. The solution was electrolyzed, to oxidize trivalent chromium, as previously described,<sup>9d,9e</sup> and filtered through an inert filter medium such as glass cloth. It was then concentrated to a density of 1.86 for crystallization, after adjusting the pH to 0.7 with chromic acid to minimize precipitation of calcium chromate through hydrolysis, again filtered as described above, and allowed to crystallize by cooling with agitation.

**Crystallization of  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ .**—On cooling the solution to not less than 42.1°, brilliant orange-red crystals separated. From a solution concentrated as above (saturated at about 70°) the yield was about 25%, or 1160 g. from the procedure given above. The crystals are characteristically striated bipyramids<sup>10</sup> (Fig. 1) and are stable

in air. They were readily separated by centrifuging, washing lightly with warm water, and drying in a current of warm air in a rotary dryer.

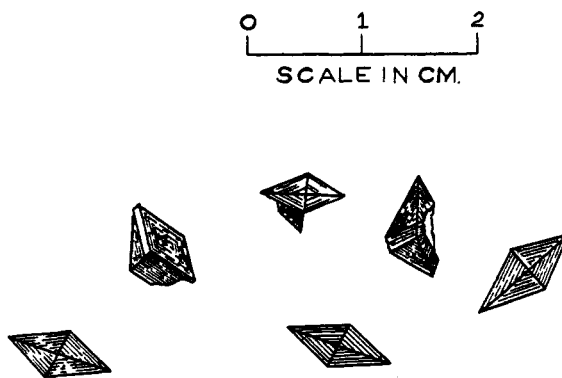


Fig. 1.—Crystals of  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ .

Their bright red-orange color is characteristic of pure dichromates; the reddish-brown color of a recent technical preparation<sup>11</sup> was undoubtedly due to the presence of trivalent chromium. *Anal.* Calcd. for  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ : CaO, 18.09;  $\text{Cr}_2\text{O}_3$ , 64.50;  $\text{H}_2\text{O}$ , 17.41. Found: CaO, 18.05;  $\text{Cr}_2\text{O}_3$ , 64.66;  $\text{H}_2\text{O}$ , 17.43. In this and subsequent analyses, calcium was determined gravimetrically as oxide after precipitation as oxalate, chromium was determined by potentiometric titration with ferrous sulfate solution standardized against C. P. potassium dichromate, and water by drying for sixteen hours at 105–110°. The density of the crystals,  $d_{20}^{20}$  2.370, was determined in a pycnometer with toluene as the immersion liquid.

**Crystallization of  $\text{CaCr}_2\text{O}_7 \cdot 4.5\text{H}_2\text{O}$ .**—Cooling of mother liquors from the above crystallization usually produced additional trihydrate, which characteristically underwent transition to another crystalline form at about 25°, with rise in temperature to nearly 40°. Cooling of this solu-

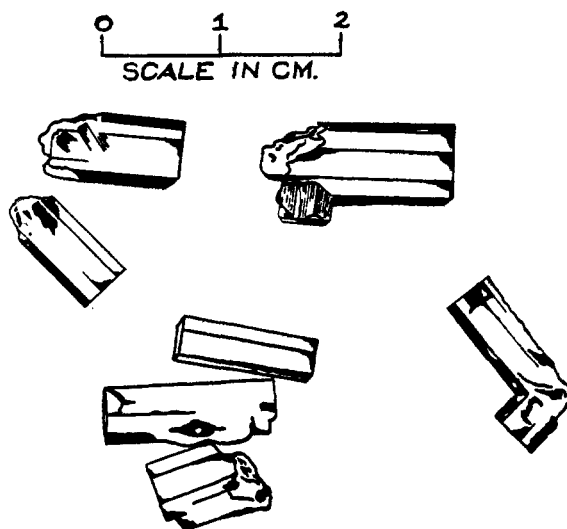


Fig. 2.—Crystals of  $\text{CaCr}_2\text{O}_7 \cdot 4.5\text{H}_2\text{O}$ .

(1) L. N. Vauquelin, *Ann. chim. phys.*, [1] **70**, 89 (1809).

(2) J. F. Bahr, *Oefvers. Akad. Förh.*, **9**, 155 (1852); *J. prakt. Chem.*, [1] **60**, 60–61 (1853).

(3) F. Mylius and J. von Wrochem, *Ber.*, **33**, 3690 (1900).

(4) M. Pier, U. S. Patent 1,921,478, August 8, 1933.

(5) I. G. Farbenindustrie, British Patent 472,089.

(6) A. R. Fraser (to Chromium Mining and Smelting Corp.), U. S. Patent 2,520,532, May 13, 1947.

(7) A. Quartaroli, *Ann. chim. applicata*, **32**, 199 (1942); K. W. Brighton and R. H. Lueck, *Ind. Eng. Chem.*, **36**, 532 (1944).

(8) G. F. Alexander, British Patent 496,890.

(9) (a) H. J. Kaufmann, W. B. Lauder and R. K. Kepner, *Ind. Eng. Chem.*, **32**, 423 (1940); (b) W. H. Hartford, *THIS JOURNAL*, **63**, 1473 (1941); (c) D. F. Altimier, *ibid.*, **64**, 175 (1942); (d) W. H. Hartford, *ibid.*, **68**, 2192 (1946); (e) W. H. Hartford and K. A. Lane, *ibid.*, **70**, 647 (1948); (f) W. H. Hartford, *Ind. Eng. Chem.*, **41**, 1933 (1949).

(10) Although these crystals were unsatisfactory for contact goniometric measurements, they show a definite inclination of the axes. They are therefore either monoclinic or triclinic in symmetry.

(11) City Chemical Co., *Chemical Industries*, **65**, 581 (1949).

tion produced a crop of red-orange crystals of considerably less brilliance than the trihydrate and evidently of lower refractive index. These crystals were characteristically stout prismatic, and octagonal in cross-section. They were separated by centrifuging, washed lightly with cold water and dried in a current of dry air in a rotary drier, keeping the temperature below 40°. The yield of 1300 g. on cooling to 25° was about 25% additional on the basis of the original batch.

The first crystals prepared were small, and difficult to dry. Analyses showed compositions varying from a pentahydrate to approximately a tetrahydrate; the latter material, however, showed obvious surface efflorescence. Crystals over 1 cm. long (Fig. 2) were prepared by slow evaporation of liquors, or by cooling under conditions giving smaller yields, and carefully dried at relative humidities of about 40%. (It was found that deliquescence occurred above about 50% relative humidity, and efflorescence, forming the trihydrate, on drying in a desiccator over calcium chloride.) Because the first analysis indicated the presence of an unusual, previously unreported 4.5-hydrate, analyses of three batches of crystal were performed to confirm these findings. Results were

	I	II	III	Av.	Calcd. for CaCr <sub>2</sub> O <sub>7</sub> ·4.5H <sub>2</sub> O
CaO, %	16.50	16.80	16.64	16.65	16.64
CrO <sub>3</sub> , %	59.17	59.25	59.54	59.32	59.34
H <sub>2</sub> O, %	24.54	23.99	23.95	24.15	24.02

The density of the crystals,  $d^{20}_4$ , 2.136.

No evidence was obtained in this work or in the subsequent phase studies of the tetrahydrate of Mylius and von Wrochem.<sup>3</sup> The ease with which the 4.5-hydrate is overdried suggests that their "tetrahydrate" was the over-dried 4.5-hydrate.

A subsequent preparation of the 4.5-hydrate gave crystals with perfect faces, 3 cm. in length, permitting measurements with a contact goniometer. The pinacoid faces were found to be at 90° to each other; the external symmetry of the crystals is therefore orthorhombic. Since no dome or pyramid faces were present on the crystals obtained, estimation of axial ratios was impossible.

### The System CaCr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>O

**Transition Point.**—The transition point between the trihydrate and 4.5-hydrate was recognized by the well-defined thermal breaks (60–140 minutes) resulting when 500 ml. of an agitated thick slurry of 4.5-hydrate was heated or cooled at a rate not exceeding 0.03° per minute. Results, using a calibrated 0.1° thermometer, were

Type of cycle	Transition point, °C.
Heating	42.0
Heating	42.2
Heating	42.2
Cooling	42.0
Average value	42.1

**Solubility.**—Linari<sup>12</sup> has reported values for the solubility of "calcium dichromate" in sodium chlorate solutions obtained by electrolysis in concrete cells, but it is apparent from his results that calcium chromate was the material in question.

In the present work solubility was determined as in previous experiments.<sup>9e</sup> Because of the slow rate of reaching equilibrium, each run was allowed to agitate twenty-four hours before re-

moving samples for analysis. The solutions were analyzed for both calcium and hexavalent chromium in order to check for congruent solubility, although the results were calculated on the basis of the chromium determination alone because of the greater precision and accuracy of the method, the average deviation from the mean being only 0.03% CrO<sub>3</sub>. Duplicate analyses were made of at least two samples taken at each temperature. The average results are

Temp., °C.	Wt. % CaO	Wt. % CrO <sub>3</sub>	Mol. ratio CaO:CrO <sub>3</sub>	Wt. % CaCr <sub>2</sub> O <sub>7</sub> based on Cr	Solid phase
-12.2	11.12	39.28	0.505	50.29	CaCr <sub>2</sub> O <sub>7</sub> ·4.5H <sub>2</sub> O
0.4	11.65	41.40	.502	53.01	CaCr <sub>2</sub> O <sub>7</sub> ·4.5H <sub>2</sub> O
20.0	12.49	44.62	.499	57.13	CaCr <sub>2</sub> O <sub>7</sub> ·4.5H <sub>2</sub> O
30.0	13.08	46.52	.501	59.56	CaCr <sub>2</sub> O <sub>7</sub> ·4.5H <sub>2</sub> O
35.0	13.48	47.64	.505	61.00	CaCr <sub>2</sub> O <sub>7</sub> ·4.5H <sub>2</sub> O
40.0	13.63	48.79	.498	62.47	CaCr <sub>2</sub> O <sub>7</sub> ·4.5H <sub>2</sub> O
45.0	14.02	49.52	.505	63.40	CaCr <sub>2</sub> O <sub>7</sub> ·3H <sub>2</sub> O
50.0	13.98	50.15	.497	64.21	CaCr <sub>2</sub> O <sub>7</sub> ·3H <sub>2</sub> O
60.0	14.38	51.34	.499	65.74	CaCr <sub>2</sub> O <sub>7</sub> ·3H <sub>2</sub> O

Above 60°, congruent solubility no longer exists, as evidenced by the precipitation of calcium chromate in the solutions. It is probable that under equilibrium conditions, the maximum temperature of congruent solubility is lower, but that the above measurements are possible because of the strong tendency of calcium chromate to supersaturate and to precipitate slowly.

The above solubility data, when plotted, show a distinct break in the curve between 40 and 45°. The point of intersection was graphically determined as 41.8°, a reasonable check on the transition temperature determined above. Accepting the determined temperature of 42.1° as correct, extrapolation of the two curves gives for the transition composition:

From the 4.5H <sub>2</sub> O curve,	62.99% wt. CaCr <sub>2</sub> O <sub>7</sub>
From the 3H <sub>2</sub> O curve,	63.05% wt. CaCr <sub>2</sub> O <sub>7</sub>
Average	63.02% wt. CaCr <sub>2</sub> O <sub>7</sub>

**Freezing Point.**—Freezing points of solutions were determined by measuring the thermal break points obtained on slowly cooling and heating an agitated solution of known analysis, temperature being measured with a calibrated thermometer. Results were

CaCr <sub>2</sub> O <sub>7</sub> , wt. %	F. p., °C.	Solid phase
0.00	0.0	Ice
8.00	-1.2	Ice
18.55	-3.1	Ice
26.25	-6.1	Ice
33.69	-11.0	Ice
40.59	-17.2	Ice
46.74	-26.2	Ice
47.50	-27.1	Ice
48.90	-29.9	Ice

The eutectic temperature was observed by further cooling of the solution as -31.3°. Graphical

(12) A. Linari, *Chim. e ind. (Italy)*, **18**, 171 (1936).

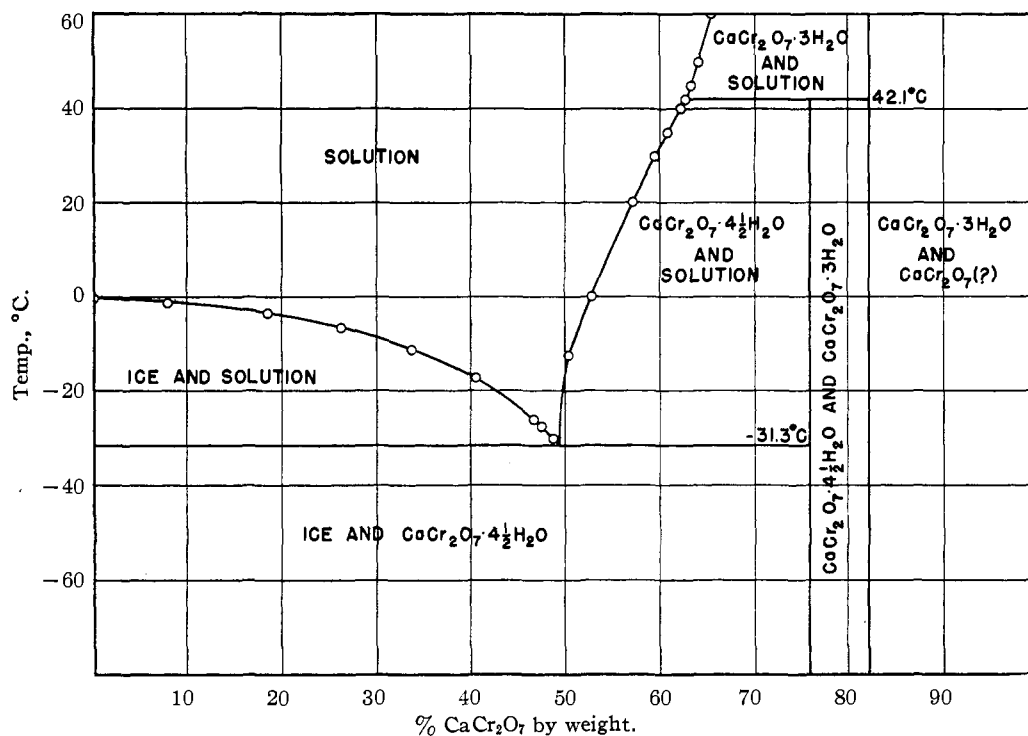


Fig. 3.—The system  $\text{CaCr}_2\text{O}_7\text{-H}_2\text{O}$ .

interpolation establishes the eutectic composition as 49.3%  $\text{CaCr}_2\text{O}_7$  by weight.

The entire phase relationship for the system calcium dichromate–water is shown in Fig. 3.

**Density of Solutions.**—Density of the solution was measured in a pycnometer at 30°. The results fit the empirical equation

$$d^{30}_4 = 0.9957 + 8.127 \times 10^{-3} C + 2.132 \times 10^{-5} C^2 + 8.869 \times 10^{-7} C^3$$

where  $C$  is concentration in weight per cent. of  $\text{CaCr}_2\text{O}_7$ , with an average deviation of 0.0004 in the density from the experimental results.

$\text{CaCr}_2\text{O}_7$ , wt. %	$d^{30}_4$ , obsd.	$d^{30}_4$ , calcd.	Diff.
0.00	0.9957	0.9957	0.0000
4.53	1.0330	1.0331	-.0001
10.07	1.0798	1.0806	-.0008
19.07	1.1646	1.1646	.0000
27.76	1.2568	1.2567	.0001
34.15	1.3348	1.3334	.0014
39.70	1.4074	1.4074	.0000
48.90	1.5469	1.5478	-.0009
54.58	1.6469	1.6469	.0000
59.56 (satn.)	.....	1.7434	.....

**Behavior on Heating.**—When either of the hydrates of calcium dichromate is dried at 105–125°, the salts hydrolyze in their water of crystallization, yielding largely a mixture of chromium trioxide and calcium chromate. This mixture redissolves in water at room temperature to form a solution of calcium dichromate. No reduction of hexavalent chromium to trivalent

takes place under these conditions, and no evidence was obtained of the existence of anhydrous  $\text{CaCr}_2\text{O}_7$  as a definite crystalline phase. A further study of the material was made by heating a sample of dried  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  in air in an electric muffle for two-hour periods at progressively increasing temperature and measuring the weight loss due to oxygen evolution.

Temp., °C.	% wt. loss, (cumulative)	% wt. loss, (individual heating)	Atoms O evolved/mole $\text{CaCr}_2\text{O}_7$	Appear. of material
200	0.50	0.50	"	Red-brown
300	0.89	0.39	"	Red-brown
400	1.29	0.40	0.065	Brown
500	9.64	8.35	1.401	Green
600	10.18	0.54	1.488	Green
700	10.22	.04	1.495	Green
800	10.27	.05	1.502	Green
900	10.29	.02	1.506	Green
1000	10.32	.03	1.510	Green
1100	16.80	6.48	2.547	Black
1200	18.93	2.13	2.887	Violet-black cryst.
1300	19.06	0.13	2.909	Violet-black cryst.
1400	19.22	.16	2.935	Violet-black cryst.
1500	19.38	.16	2.961	Violet-black cryst.

<sup>a</sup> Weight loss due to moisture only.

Examination of the data and the products of decomposition reveals that the reaction  $2\text{CaCr}_2\text{O}_7$  (or  $\text{CaCrO}_4 + \text{CrO}_3$ )  $\rightarrow$   $2\text{CaCrO}_4 + \text{Cr}_2\text{O}_3 + \frac{3}{2}\text{O}_2$  starts at 400° and becomes rapid and substantially complete at 500°. At 1100–1200° the further reaction  $2\text{CaCrO}_4 + \text{Cr}_2\text{O}_3 \rightarrow 2\text{CaCr}_2\text{O}_4 +$

$3/2\text{O}_2$  occurs with formation of violet-black crystals of calcium chromite, which are green when finely ground. Vasenin,<sup>13</sup> in a study of thermal decomposition of calcium chromates, cites a decomposition of  $\text{CaCr}_2\text{O}_7$  to form  $\text{CaCr}_2\text{O}_4$  at  $1112^\circ$  following evolution of hydrate water at  $150^\circ$ , but the intermediate decomposition at  $500^\circ$  is not described. The failure of the data to show exactly 3 atoms of O evolved per mole of  $\text{CaCr}_2\text{O}_7$  is probably due to slight reoxidation of  $\text{CaCr}_2\text{O}_4$  on cooling in air.

**Solubility in Organic Liquids.**—Solubility characteristics of both hydrates are similar. They are insoluble in ether, carbon tetrachloride and hydrocarbon solvents, dissolve in alcohol with immediate reduction of the dichromate and precipitation of brown hydrous chromic chromate, and dissolve in acetone, with subsequent precipitation of calcium chromate. In this respect, the calcium dichromates resemble lithium dichromate dihydrate.<sup>9c</sup>

#### Summary

1. A procedure has been outlined for the

(13) F. I. Vasenin, *Zhur. Priklad Khim.*, **21**, 429-436 (1948).

preparation of calcium dichromate solutions.

2. Two crystalline hydrates of the salt  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  and the previously unknown  $\text{CaCr}_2\text{O}_7 \cdot 4.5\text{H}_2\text{O}$ , have been prepared. The latter is orthorhombic in external symmetry.

3. The system  $\text{CaCr}_2\text{O}_7\text{-H}_2\text{O}$  has been investigated. Two invariant points exist at atmospheric pressures:  $\text{CaCr}_2\text{O}_7 \cdot 4.5\text{H}_2\text{O}\text{-CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}\text{-solution}$  at 63.02%  $\text{CaCr}_2\text{O}_7$  and  $42.1^\circ$ ; ice- $\text{CaCr}_2\text{O}_7 \cdot 4.5\text{H}_2\text{O}\text{-solution}$  at 49.3%  $\text{CaCr}_2\text{O}_7$  and  $-31.3^\circ$ .

4. The density of calcium dichromate solutions has been determined at  $30^\circ$  for concentrations up to saturation.

5. On heating the hydrates, partial decomposition to  $\text{CaCrO}_4$  and  $\text{CrO}_3$ , due to hydrolysis, occurs. There is no evidence of the existence of anhydrous  $\text{CaCr}_2\text{O}_7$  as a pure crystalline phase. Further heating results in the loss of oxygen at  $500^\circ$  to give a mixture of  $\text{Cr}_2\text{O}_3$  and  $\text{CaCrO}_4$ , which loses oxygen at  $1100\text{-}1200^\circ$  to form  $\text{CaCr}_2\text{O}_4$ .

6. The qualitative solubility in common organic solvents has been reported.

BALTIMORE, MD.

RECEIVED DECEMBER 23, 1949

[CONTRIBUTION FROM THE DIVISIONS OF CHEMISTRY AND VITICULTURE, COLLEGE OF AGRICULTURE, AND THE RADIATION LABORATORY, DEPARTMENT OF PHYSICS, UNIVERSITY OF CALIFORNIA]

## The Reaction of Wolfram Dioxide with Dichlorodifluoromethane<sup>1</sup>

BY A. DINSMOOR WEBB AND HERBERT A. YOUNG

It has been known for several years that carbon tetrachloride could be used as a chlorinating agent for several of the heavy metal oxides, including those of wolfram and uranium.<sup>2</sup> Only recently, however, has the use of a simple freon type compound been reported for the halogenation of a metallic oxide.<sup>3</sup> Booth and co-workers found that dichlorodifluoromethane would reduce and fluorinate uranium trioxide to produce uranium tetrafluoride in nearly quantitative yields.

Because of recent interest in the comparison of the chemical properties of wolfram and uranium, it was thought to be of some interest to study the reaction between wolfram dioxide and freon, particularly since such a reaction might produce the unknown wolfram tetrafluoride.<sup>4</sup>

(1) Scheduled but not presented because of illness at the meeting of the American Chemical Society in Atlantic City, September, 1949. Taken in part from report BC-70 revised to the Radiation Laboratory, University of California, and based on the dissertation submitted by A. Dinsmoor Webb to the Faculty of the Graduate Division of the University of California in partial fulfillment of the requirements for the degree, Doctor of Philosophy.

(2) A. Michael and A. Murphy, *Amer. Chem. Jour.*, **44**, 382 (1910).

(3) H. S. Booth, W. Krasny-Ergen and R. E. Heath, *THIS JOURNAL*, **68**, 1969 (1946).

(4) The preparation and characterization of wolfram tetrafluoride was reported by H. F. Priest and W. C. Schumb, *ibid.*, **70**, 3378 (1948), during the course of this investigation.

The experimental procedure developed was the simple one of leading the pure gaseous freon over the heated metallic oxide, held at temperatures up to  $525^\circ$ , and collecting and analyzing the products. A condensing unit, as shown in Fig. 1, was constructed with several separately removable collecting units which could be maintained at successively lower temperatures. In operation, this allowed for the separate collection of samples with differing volatilities.

#### Experimental

Since dichlorodifluoromethane is extremely corrosive at temperatures near  $500^\circ$ , it was necessary to use nickel vessels<sup>5</sup> for all equipment that came in contact with the freon at high temperatures and the reaction products at all temperatures. The reaction chamber was constructed from a piece of two inch i. p. s. nickel pipe three feet long with flanges and removable cover plates at each end. The pipe was heated for a distance of eighteen inches from one end by an electrical resistance tube furnace, the power being regulated by a thermocouple mounted within a thin walled nickel tube so located that the thermocouple was about one-half inch above the surface of the reacting wolfram dioxide. A large variable autotransformer and potentiometer type off-on controller completed the power regulating assembly. The unheated portion of the nickel pipe reactor was wrapped with asbestos cloth to help maintain a constant temperature gradient. The cooler end of the nickel pipe reactor was wrapped with a copper tubing

(5) R. Landau and R. Rosen, *Ind. Eng. Chem.*, **39**, 281 (1947), show nickel metal to be most resistant to action of fluorine.