Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

METAL AND ANION CONTENT OF SOME INORGANIC MATERIALS VIA TGA IN ACTIVE ATMOSPHERES*

HENRY W. WILLIAMS

Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898 (U. S. A.)

(Received December 29th, 1969)

ABSTRACT

Thermogravimetric analysis (TGA) yields valuable information for inorganic chemists and for scientists working with solid-state materials especially when only very small amounts of sample are available. TGA on many inorganic compounds in appropriate atmospheres offers an elegant method for analysis, for example determining metal content, oxygen from oxides and sulfur from sulfides.

The purity of single crystals of Fe, Co, and Ni disulfides was determined. Rare earth sesquisulfides were transformed to rare earth oxysulfides. An analytical method is given for the determination of the ratio of Fe^{0}: Fe^{II}: Fe^{III} when present as a mixture of iron and iron oxides supported on an inert material.

Purity and thermal stability of prospective standards for X-ray fluorescence, atomic absorption and wet chemistry analyses have been checked by TGA.

INTRODUCTION

Most work in thermal analysis today utilizes instrumentation improvements and techniques evolved during the past few years. Anderson[1] has described some basic instrumentation and applications of thermogravimetry. A TGA–mass spectrometric method[2] has been applied to organic structure elucidations and determination of volatile products. The thermal degradation spectra of polymers and the rate of weight loss[3] have been studied.

The purpose of this paper is to demonstrate the value and versatility of modern TGA as an analytical tool when applied to problems of *inorganic* compounds and materials. The technique can be particularly valuable when the sample of interest is in the form of single crystals too small to be analyzed by conventional analytical techniques. Such samples are quite commmon in research laboratories where they can result from various low-yield syntheses (such as certain chemical transport reactions) or are part of a low-volume, multiphase product and are separated physically from the mixture.

All of the results reported here were obtained in atmospheres of either oxygen–

*Contribution No. 1612.

argon or hydrogen–argon. Inert argon is used for reasons of safety. It was possible to determine both metal and sulfur content of single crystals[4] using ~10-mg samples. The compounds[5] $SrCrO_3$ was oxidized to $SrCrO_4$ and $CrVO_4$ (ortho) was reduced to $CrVO_3$ thereby yielding their oxygen values. The oxygen contents (*e.g.*, see Fig. 1

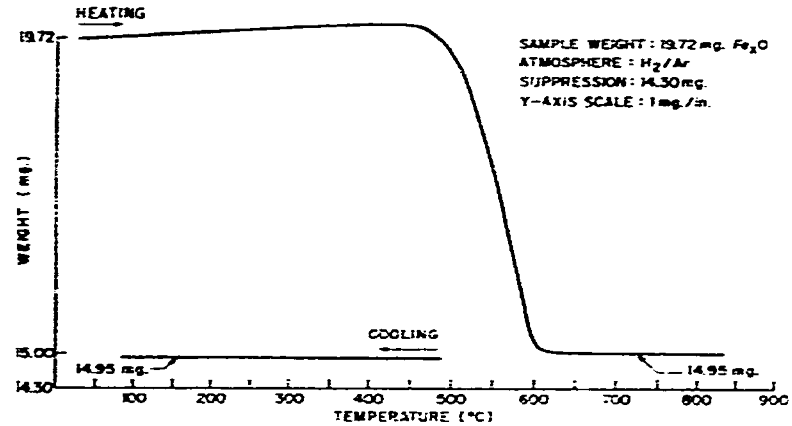

Fig. 1. Reduction of Fe_xO; 14.95 mg Fe = 0.268 mole, 4.77 mg O_2 = 0.298 mole, 0.268/0.298 = 0.90 or $F_{0.90}$ O, 100 × (4.77/19.72) = 24.19% loss of O_2 (lit.[6] = 24.17%).

for $Fe_{0.90}$ O) for various compositions within the Wüstite field gave excellent agreement with the work of others[6]. Rare earth sesquisulfides were converted to rare earth oxysulfides with a "wet" hydrogen–argon atmosphere. A wet chemistry–TGA method permits determination of Fe°, Fe^{II}, and Fe^{III} when each is present in small amounts as a mixture of Fe° and iron oxides supported on an inert material.

EXPERIMENTAL

Instrument

A DuPont 950 Thermogravimetric Analyzer and a DuPont 900 Thermal Analyzer were used for all measurements. The 950 TGA is a semi-micro balance designed to measure the weight of a material as a function of a linearly increasing temperature. The instrument is capable of attaining temperatures up to 1200°C with any linear heating rate between 0.5 and 30°C/min. A 10°C/min heating rate was employed for most of this work.

Weight suppression is continuously variable from 0 to 10 mg using the fine control and in steps of 10 to 100 mg using the coarse control. Suppression enables the operator to observe small weight *changes* in a sample at very sensitive instrument settings.

Atmosphere control equipment

Fig. 2 shows the atmosphere control arrangement. Bench-top-size cylinders of H_2, O_2, and Ar gases are employed. Other gases are centrally piped. Each cylinder is equipped with an Airco Pressure Regulator. In addition, the hydrogen system has

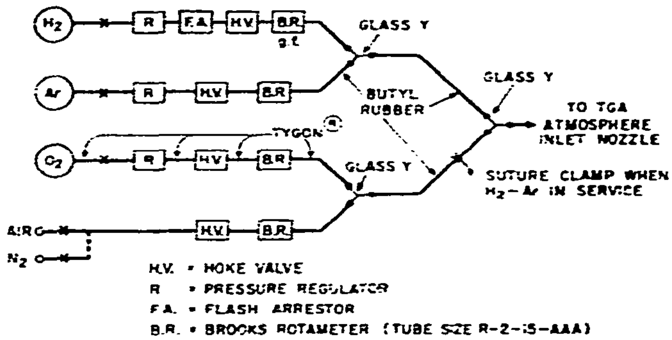

Fig. 2. Atmosphere control system.

a flash arrestor located downstream from the pressure regulator. The hydrogen and oxygen are diluted with inert argon to keep the atmospheres below known explosive composition limits. The regulator outlet pressure is maintained at a few p.s.i. to permit better control of the flow rate through the respective flowmeters (Brooks). Control of flow rate is further aided by use of Hoke valves up-stream from the flowmeters. Butyl rubber tubing (1/4" I.D. × 1/8" wall) is utilized for all lines except the oxygen line which is Tygon^R.

The oxygen, hydrogen, and argon lines are interconnected in a manner that permits either oxygen–argon or hydrogen–argon use simply by placing a suture clamp on the line not in service. This quick interchange provision is especially useful when, for example, a metal oxide is heated in a reducing atmosphere. An immediate switch to an oxidizing atmosphere can be made to permit following the cooling curve to determine the temperature at which the metal reacts with oxygen and finally the total amount of O_2 reacted.

The final outlet of the butyl rubber line is connected to the threaded 1/8" plastic male fitting provided on the DuPont 950 TGA. For safety reasons, the argon atmosphere is always turned on first, prior to a TGA run and turned off last at the conclusion of a run. All tests employ either platinum or quartz sample pans.

RESULTS AND DISCUSSION

Single crystals purity

Fig. 3 shows the oxidation of 10.41 mg of NiS_2 to NiO at 10°/min heating rate in argon–oxygen atmosphere to 950°C. The sulfur was removed in two temperature regions (390–490 and 690–785°C.) After the system was cooled to ~100°C, a hydrogen–argon atmosphere was introduced and the 6.36 mg of NiO was heated. The NiO was reduced to the metal (4.99 mg) mainly between 350–400°C. Total sulfur loss was 52.1% [(10.41–4.99)/10.41]100. Theory is 52.2%. Direct reduction of sulfides to H_2S is avoided by this procedure, thus eliminating toxicity and corrosion problems.

The oxidation loss of 8.75 mg of CoS_2 occurred mainly in two steps (510–580 and 760–850°C). For the second-stage loss, it was found advantageous to slow the heating rate to 5°/min to decrease the rate of reaction. The reaction rate could have

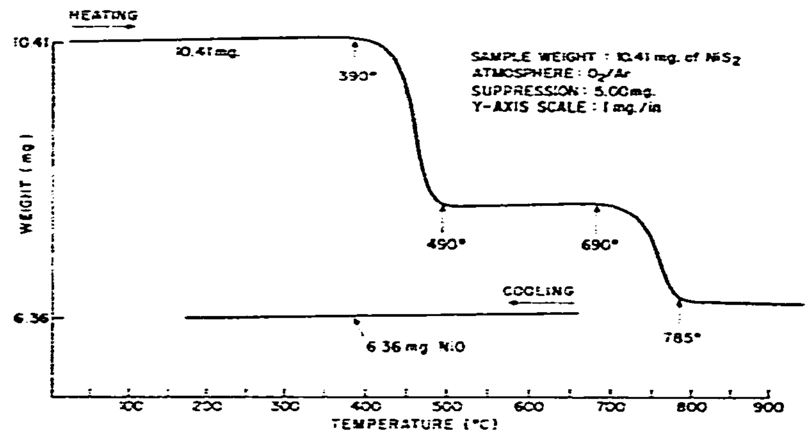

Fig. 3. Conversion of NiS_2 to NiO: 10.41 mg NiS_2 at start, 6.36 mg NiO after oxidation.

been further decreased by reducing the O_2 flow rate. The Co_3O_4 was then reduced to 4.20 mg of Co with the major weight loss occurring between 350 and 395 °C. The % sulfur observed was 52.0 (theory = 52.1%).

The oxidation to completion of 3.86 mg of FeS_2 single crystals gave 2.58 mg of Fe_2O_3. Reduction of this oxide yielded 1.80 mg of Fe (46.6%). The theroretical yield of Fe is 46.65% for pure FeS_2.

Table I summarizes the results of some additional experiments. The precision of this method of analysis was determined by reduction of powdered ruthenium oxide. A standard deviation of 0.11% was obtained from 10 measurements. Sample size ranged from 9–22 mg.

TABLE I

SUMMARY OF ADDITIONAL OXIDATION–REDUCTION DATA

Starting compound	*Atmosphere*	*Result* (%)	*Calc.* (%)	*Reaction temperature* (°C)
$CrVO_4$ (ortho)	H_2–Ar	9.5 O_2 loss	9.6	515–630
Cr_2O_5	H_2–Ar	17.3 O_2 loss	17.4	340–430
Fe_3O_4	H_2–Ar	27.7 O_2 loss	27.6	320–520
$SrCrO_3$	O_2–Ar	8.3 O_2 gain	8.5	375–750

Rare earth oxysulfides

We have found that nearly all the rare earth sesquisulfides prepared by Sleight[7] may be transformed to the rare earth oxysulfide. A mixture of H_2 and Ar in a 1:2 ratio was bubbled through water and then passed over a sample of a rare earth sesquisulfide. The hydrogen prevents sulfate formation. The moisture supplies oxygen to gain the oxysulfide form. The sample was heated in the thermogravimetric analyzer, employing 10°/min heating rate to the start of weight loss and 7°/min rate during the remainder of the test. The reaction (Eqn. 1) began at about 500°C and the M_2O_2S plateau was generally reached before 800°C.

$$M_2S_3 + 2H_2O \underset{\Delta}{\overset{H_2}{\rightarrow}} M_2O_2S + 2H_2S \quad (1)$$

Fig. 4 on α-dysprosium sulfide illustrates the type of weight-loss pattern obtained and shows sample calculations. Table II summarizes data from eleven rare earth

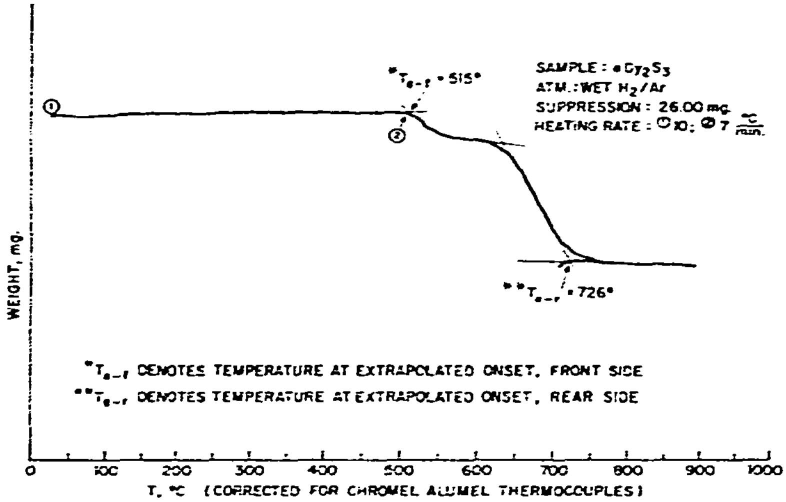

Fig. 4. Transformation of α-Dy_2S_3 to Dy_2O_2S; 31.36 mg α-Dy_2S_3, 29.02 mg Dy_2O_2S at T_{e-r}.

sesquisulfides that were converted to metal oxysulfides. Excellent agreement with calculated values was obtained for several samples, indicating high purity. The products still appeared to be single crystals.

TABLE II

TRANSFORMATION OF RARE EARTH SESQUISULFIDES TO OXYSULFIDES BY TGA

Starting material	*Product*	*Net % wt. loss*[a]	
		Calc.	*Found*
Nd_2S_3	Nd_2O_2S	8.4	8.3
α-Dy_2S_3	Dy_2O_2S	7.6	7.5
Er_2S_3	Er_2O_2S	7.5	7.3
Yb_2S_3	Yb_2O_2S	7.3	6.9
Pr_2S_3	Pr_2O_2S	8.5	8.5
Ho_2S_3	Ho_2O_2S	7.5	7.1
Dy_2S_3	Dy_2O_2S	7.6	7.4
Ce_2S_3	Ce_2O_2S	8.5	8.5
Y_2S_3	Y_2O_2S	11.7	11.3
La_2S_3	La_2O_2S	8.6	8.4
Tm_2S_3	Tm_2O_2S	7.4	6.9

[a]Loses 2 sulfurs, gains 2 oxygens.

Wet chemistry + TGA method for iron states

An analytical method was needed to determine the ratio of Fe^{0}: Fe^{II}: Fe^{III} when present as a mixture of Fe^{0} and iron oxides supported on an inert material.

A requisite for the thermal analysis portion of this method is the ability to provide accurate weighing throughout the temperature range of each experiment. Via the TGA record one is assured of the completion of the oxidation and reduction. Reaction temperature information is also obtained.

The following method was developed and used.

Steps. — (1) EDTA titration yielded total iron (% Fe_T).

(2) By TGA reduction the % wt. loss of O_2 was determined which was then calculated as (Fe^{II} + Fe^{III}).

$$Fe_3O_4 + 4H_2 \xrightarrow[\Delta]{Ar} 3Fe^0 + 4H_2O$$

where Fe_3O_4 is $Fe^{2+}\ Fe_2^{3+}\ O_4$

(3) By difference between (1) and (2), elemental iron was calculated $Fe^0 = Fe_T - (Fe^{II} + Fe^{III})$.

(4) By TGA oxidation of the original mixture the total % wt. gain (% O_2) was determined.

$$4Fe^0 + 3O_2 \xrightarrow[\Delta]{} 2Fe_2O_3$$

$$2(Fe^{2+}\ Fe_2^{3+})O_4 + 1/2\ O_2 \xrightarrow[\Delta]{Ar} 3Fe_2O_3$$

(*a*) Knowing from (3) the amount of Fe^0 present, the amount of O_2 required to oxidize it completely to Fe_2O_3 (X% oxygen) was calculated.

The % oxygen gained −X% oxygen = Y% oxygen where Y is amount of oxygen gained by Fe^{II} during oxidation.

(*b*) Thus, Y g of oxygen × (Fe_3O_4/O_4) × ($3Fe/Fe_3O_4$) × 100 = % Fe^{II}.

TABLE III

RESULTS OF COMBINED METHOD FOR IRON STATES

Step	*Description*	*Results (%)*	
		Actual	*Theory*
1	Fe_T by EDTA	10.6	10.5
2	TGA reduction (O_2 loss)	2.5	2.5
	$Fe^{II} + Fe^{III}$ equivalent	6.6	6.6
3	$Fe^0 = 1 - 2$	4.0	3.9
4	TGA oxidation to Fe_2O_3	2.1	2.0
	(*a*) O_2 gain in oxidizing Fe^0	1.7	1.7
	O_2 difference (gain by Fe^{II})	0.4	0.3
	(*b*) Fe^{II} equivalent	0.9	0.8
5	$Fe^{III} = Fe_T - Fe^0 - Fe^{II}$	5.7	5.8

(5) By difference the % Fe^{III} was obtained.

$$Fe^{III} = Fe_T - Fe^{\circ} - Fe^{II}$$

Example: A standard synthetic mixture containing 1.02201 g of inert material + 0.04525 g Fe° + 0.10786 g Fe_3O_4, whose purity was ascertained by TGA, yielded the results in Table III.

ACKNOWLEDGMENT

The author is grateful to Donald D. Bly for many helpful discussions, to E. A. Abrahamson for suggesting the iron states method, and to Joan D. Hogan for collaboration on the method.

REFERENCES

1 H. C. ANDERSON, in P. E. SLADE, JR., AND S. T. JENKINS (Eds.), *Techniques and Applications of TGA*, Vol. 1, Marcel Dekker, New York, 1966, p. 87.
2 F. ZITOMER, *Anal. Chem.*, 40 (1968) 1091.
3 O. VOGL, V. IVANSONS, H. MILLER, AND H. WILLIAMS, *J. Makromol. Chem. A2*, 1 (1968) 175.
4 R. J. BOUCHARD, *J. Cryst. Growth*, 2 (1968) 40.
5 B. L. CHAMBERLAND, *Solid State Commun.*, 5 (1967) 663
6 R. L. LEVIN AND J. B. WAGNER, *Trans AIME*, 236 (1965) 516.
7 A. W. SLEIGHT AND C. T. PREWITT, *Inorg. Chem.*, 7 (1968) 2282.