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CONSTRUCTION AND APPLICATION OF A NEW TYPE OF THERMOBALANCE

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Norman, Oklahoma

CONSTRUCTION AND APPLICATION OF A NEW TYPE OF THERMOBALANCE

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APPROVED BY nes ender/ 9 Iruce . BA-27 ٨ DISSERTATION COMMITTEE

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MOTHER AND DAD

whose love, encouragement,

and self-sacrifice

made this possible

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CONSTRUCTION AND APPLICATION OF A NEW TYPE OF THERMOBALANCE

CHAPTER I

INTRODUCTION

The thermobalance is a device for continuously weighing a material either heated from ambient to an elevated temperature at a constant rate or maintained at a specific, known temperature. The data obtained are presented as a plot of sample weight against time or increasing temperature called a pyrolysis or thermolysis curve. The technique of production, study, and interpretation of thermolysis curves is known as thermogravimetry.

Credit for developing the first thermobalance is given to Honda (19). He and his students using the balance and some modifications of it pyrolysed some 300 precipitates such as manganese carbonate and calcium carbonate (7). Added impetus to thermogravimetry and modification of equipment was provided by Guichard and his pupils beginning in 1925. However, the most important development in thermogravimetry was the automatic photographically recording Chevenard thermobalance, which was developed primarily for the study of the oxidation of alloys (5). Duval and his co-workers have found the Chevenard thermobalance, with or without modification, to be a creditable instrument

and have used it for the study and evaluation of about 1000 precipitates recommended for gravimetric analysis and many of the analytical primary standards (7, 8, 9, 10, 11).

Since the work by Duval's group, which has been said to put gravimetric analysis on a sound, reliable, and documented basis, numerous reports have been made of new types of thermobalances and uses for them (1, 2, 4, 6, 14, 15, 16, 17, 21, 23, 24, 25, 29). Instruments have even been constructed for producing differential thermogravimetric curves; some simultaneously trace the usual thermolysis curve with the differential curve (12, 26, 27). These are indicative of the importance and some of the enthusiasm for thermogravimetry among analytical chemists in recent years. The reports are also indicative of a desire and need for new and better equipment.

The enthusiasm for thermogravimetry has been generated principally in gravimetric analysis, for now a precipitate and its decomposition products may be evaluated relative to purity, effectiveness of washing procedures, stability, and composition. The thermolysis curve allows the establishment of drying or ignition times and temperatures unambiguously and without the unnecessary procedures often employed (7, 8). The continuous curve provided by automatic recording has helped to dispel the suspicions of the chemist for the uncertainties between "taken" and "found" in an analysis (20). Thermogravimetry has also been used to study solid state reactions, the roasting and calcination of minerals, coal, petroleum, and wood, absorption and adsorption properties of materials, rates of evaporation and sublimation, thermal degradation of polymers, reactions in such special atmospheres as

hydrogen, argon, nitrogen, and carbon dioxide. Direct analyses and the discovery and the preparation of new compounds have been accomplished with the thermobalance (1, 7, 8, 18).

As the result of having been the first relatively rugged and dependable recording thermobalance incorporating certain desirable features available to Duval, the Chevenard thermobalance in its two present forms has been used more than any other type for the studies described. The photographic instrument preceded the present penrecording device and will be described first. The balance is a beam in the form of a rod bifunicularly torsion suspended from tungsten wire. On one end of the beam is a mirror which reflects a ray of light to a photographic plate. The other end of the beam supports a vertical oildamped silica rod in such a fashion that the rod holds the crucibles or metallic samples above the balance. A bell-shaped furnace lowers over the top of the rod where the sample is held. Change in weight of the sample produces movement by the beam and the tracing of a curve by the light ray on a photographic plate. The pen-recording Chevenard balance replaces the mirror on the beam by a contact wire, Contact between the wire and a movable plate actuates a reversible synchronous motor which moves the recorder pen and the plate so that the contact is broken. The motor then reverses until contact is made. A fine wavy line is drawn as the chart paper moves, producing a trace of weight change of the sample. Both models of the Chevenard balance use a "program" guide for furnace control consisting of a cylinder with a raised cardboard bead. A pointer, connected to the furnace switch, follows the bead on the rotating cylinder in such a way as to provide

either a constant temperature or a constant rate of temperature increase during an experiment (7).

The Chevenard balances are reported to give an accuracy of from 0.1 to 0.4 per cent with an equal reproducibility for the amount taken. The sensitivity has been given as 2.04 mg. per mm. of pen travel. The temperature range is from room temperature to 1050° C with almost any type of heating program being allowed. Special equipment allows a temperature maximum of 1300° C. The temperatures are stated to be accurate to 1° C at heating rates of 1.5° to 15° C per minute. The cost of the photographic recording balance is given as \$2,835 and the pen-recording as \$4,130 (7, 13, 25).

Other commercial thermobalances are in about the same price range when equipped with recorder and furnace. The Stanton thermobalance is operated by an intermittent capacitance plate sensitization of a servo-mechanism. The Sartorius-Werke balance uses an electromagnetic field acting on a core suspended from the balance into a solenoid (2). Neither balance seems to have been used to any great extent.

The only other commercial thermobalance is one that has recently been placed on the market. This is the American Instrument Company's "Thermo-Grav" which is priced at \$12,000. The "Thermo-Grav" utilizes a transducer or a linear variable differential transformer with the appropriate electronic equipment to follow the displacement of a spring caused by change in sample weight. This exceptional piece of equipment allows temperatures from liquid air to 1000°C and heating rates from 5°C to 1000°C per hour. Also included is an arrangement for

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experimenting in a vacuum or special atmospheres. The instrument has temperature scale expansions, can be weight calibrated at any time, and gives 2 mg. accuracy for 50 mg. to 200 mg. changes in sample weight (1).

The transducer used with the "Thermo-Grav" to modify the Chevenard, and on many non-commercial instruments is a movable iron core that is suspended from the balance beam into a transformer coil. The two secondary windings of the coil are connected 180° out of phase. Displacement of the iron core from the center of the coil produces an AC signal that may be demodulated and amplified or fed to a sensitive recorder (1, 14, 15, 24). Some transducer actuated thermobalances are reported to give and accuracy of 0.25 per cent for a weight range of 200 mg. (1).

Besides the transducer actuated balances, others have been reported using a mechanism controlled by photocells. One type used a single photocell which is placed behind a black flag attached to the pointer of an analytical balance (17). The signal from the photocell is amplified to bring the balance back to a null position by the use of a magnet suspended from the beam into a coil. The change in current through the coil is proportional to the weight change. Sensitivity of 0.3 mg. and an accuracy of 0.8 mg. are reported. The furnace is placed above the balance case and is requlated by a Wheelco controller driven by a clock motor.

Another photocell operated thermobalance is that of Wendlandt (29). His equipment utilizes 2 photocells and a commercial torsion balance. A mirror on the beam of the torsion balance reflects light on one photocell or the other when displaced from null position. The output

of the photocell is amplified to actuate a reversible, synchronous motor which brings the torsion balance back to the null position. Coupled between the motor and balance is a cylinder which acts as the drum of a recorder. Another synchronous motor drives a pen along the cylinder to produce a thermolysis curve. A third synchronous motor drives a powerstat furnishing power to a furnace constructed by winding resistance wire over a vycor tube. The apparatus reportedly cost \$400 excluding labor and gives an accuracy of 0.5 per cent for a weight change of 102 mg. The temperature range was from ambient to 850°C at a rate of 5°C per minute.

Still another type of thermobalance uses a strain gauge wire to control an analytical balance converted to a thermobalance (2). The strain gauge wire, a length of 0.9 mil 800 ohm per cmf alloy wire, was used to restrict movement of the balance beam. Change in weight of sample produces a change in resistance of the wire as measured by a Wheatstone Bridge. The signal from the bridge is fed to a recorder. This type of thermobalance is reported to give greater weight ranges and a more rapid following of the weight change than others.

The thermobalances in present use possess one or more disadvantages. All excepting the Wendlandt balance are somewhat expensive. The Chevenard photographically recording balance is far more inconvenient than the pen-recording balance and requires more manipulation and adjustment. The bifunicular, torsion suspension used in the Chevenard allows displacement of the sample in the furnace and, in the case of the pen-recording balance, displacement of the actuating contact.

All of the balances that were built from analytical balances possess the disadvantages inherent in knife-eages as found in the experiments at the Acieries d'Imphy (Nievre) (7, page 11). These experiments show bifunicular suspension to be superior. The knife-edges dull and are displaced by vibration. The hole to the furnace causes convection currents or restricts free movement of the support rod (8). Also most of the balances require a more complicated electrical circuit than is desired for easy construction.

While some attempts have been made to modify the instruments available, the research reported here has been aimed at developing an inexpensive instrument of simple design that could be easily constructed by chemists in laboratories of quite modest means. The thermobalance was also to be relatively free of the other disadvantages already mentioned. Extreme versatility was another objective kept in mind during the designing and the construction of the thermobalance described in the following chapter.

CHAPTER II

LQUIPMENT

Silica Balance

A silica torsion balance was constructed from silica tubing and rod. A rectangular frame, 2.6 cm. by 17.5 cm., to hold the balance was made from tubing. The rest of the balance was constructed from 2mm. and 3mm. rod. One upright 1.3 cm. in length was placed on the center of each long side of the base. The 45 cm. by 3 mm. beam of the balance was attached to the uprights by extremely fine silica fibers drawn from the rods. A 1.25 inch cylindrical Alnico V magnet was fixed perpendicularly to the center of the beam.

A fine pointer was drawn out on one end of the balance beam and blackened with ink for observation through a cathetometer. On the same end with the pointer was attached a hook made from 1 mm. silica rod. The platinum sample bucket was suspended about 18 cm. from the beam by a 10 cm. platinum wire supported from a 5 cm. length of 1 mm. silica rod connected to a 3 cm. platinum wire which hung from the hook.

The platinum bucket was made by rolling platinum foil around the end of a wooden pencil and cutting away the excess foil. A bail was made by attaching a platinum wire to two holes punched in the edge

of the bucket. The bucket and bail weighed 0.626 gram.

Balancing Circuit

(See Figure 1) A copper wire is clamped to the arm of the beam opposite the pointer. Near the torsion suspension, the copper wire is soldered to a platinum wire that dips into a mercury pool "A". The other end of the copper wire is soldered to a platinum wire that extends beyond the beam to a point between two closely spaced platinum contacts held in place by a piece of polyethylene wedged into the balance case. If the balance arm moves the platinum wire from null position, the wire touches one of the contacts and an electrical circuit is completed through one of the SPST relay switches.

Each relay switch has a resistance of 200 ohms and is actuated by 10 ma. of current. The two switches are wired in a manner that permits the DC motor "C" to be operated either clockwise or counterclockwise, depending upon the direction of imbalance from null position.

The ten-turn, 200 ohm potentiometer "E" is driven by the motor "C" through the speed reduction gear-train "D". Rotation of the potentiometer shaft varies the current through the field coil "G" as read from ammeter "B". The magnet "H" on the balance beam is deflected by the field coil, causing the balance arm and platinum point to return to null position. An increase in weight at bucket "I" causes an increase in current through the field coil. The change in potential drop across the field coil is followed by the recorded "F" connected through a potential divider.

The DC motor was an inexpensive battery operated toy motor with a spur gear on the shaft. The gear-train driven by the spur was

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FIGURE 1.

fashioned from the parts of an old alarm clock. The potentiometer was driven by a shaft from the gear-train rotating against a rubber friction wheel. The field coil was made by wrapping number 25 magnet wire on the pyrex tube forming the balance case until the wire was 6 layers deep for a length of 13 cm. The coil had a resistance of 30 ohms when completed.

Balance Case

(See Figure 2) The balance case was a 63 cm. pyrex tube, 4.5 cm. in diameter, closed at one end with a flat window. An 1.8 cm. diameter side arm 10 cm. in length, terminating in a female 24/40joint, was attached perpendicularly to the large tube for connecting the furnace. Another side arm was placed 52.5 cm. from the closed end of the tube. The second side arm was 6 cm. long and terminated in a female 14/35 S joint. The center of the field coil was 27.5 cm. from the closed end. The open end of the balance case was a female 45/50 S joint.

The male $\frac{15}{50}$ $\frac{5}{5}$ joint for closing the balance case was joined to a 7/25 $\frac{5}{5}$ female joint which could be either closed or connected to a gas supply. Three tungsten wires were sealed into the male $\frac{14}{35}$ $\frac{5}{5}$ joint fitting the small side arm. Electrical connections to the platinum contacts and the mercury pool were made through the tungsten wires when an isolated system was desired.

The glass balance case is supported from rubber-tipped threefinger clamps bolted above a box constructed from asbestos board. The central section of the box contains the batteries, motor, gears, wiring, and ammeter. A partition separates the central section from the furnace

FIGURE 2



THERMOBALANCE CASE

section which is open on the end. The furnace section is lined with sheet aluminum and shields the glass balance case and center of the box from the heat of the furnace.

About 6 cm. of the 24/40 S joint from the balance case protruded through the asbestos and aluminum furnace section of the box. A constriction in the furnace side arm was fabricated by wrapping a short section of 9 mm. glass tubing with asbestos tape to fit the inside of the side arm. The asbestos was covered with aluminum foil and forced into the side arm to restrict heat transfer from the furnace into the tube containing the balance.

Furnace

The furnace is similar to that described by Wendlandt (28). A 25 cm. piece of 2.5 cm. diameter vycor tubing was attached to a male $2\frac{1}{40}$ ycor joint. A small constriction was blown between the joint and the body of the tube.

A heating coil was made by bending 18 feet of number 18 B & S gauge Hoskins Chromel A (0.95 ohms per foot) around a mandrel 0.3 cm. in diameter to form a helix 85 cm. long. The helix was then wound around the vycor tube over a thin sheet of asbestos at 0.6 cm. spacings. The heating coil was then covered with two layers of asbestos tape for insulation. Figure 3 shows the furnace and controlling powerstats.

The free ends of the heating coil were connected to a powerstat which was rotated by a synchronous, 1/4 turn per hour motor. The motor driven powerstat was plugged into another powerstat set to give the desired rate of temperature increase. The motor driven powerstat was designed to be reset to the same starting position for each new

FIGURE 3



FURNACE AND POWERSTATS

experiment. This was accomplished by mounting the synchronous motor on a plate which was held by springs so that the pin drive on the motor shaft meshed with slots on the shaft of the powerstat.

The bottom of the vycor furnace tube was sealed and a side arm attached just 1.5 cm. from the closed end. The side arm was a 10 cm. length of small bore tubing ending in a 12/2 male ball joint. The side arm provided an exit for gases introduced into the balance case, for gases produced by pyrolysis of samples, or for evacuating the case.

Vacuum Apparatus

The vacuum apparatus consisted of an Eimer and Amend vacuum pump, a manometer, heavy rubber tubing for connections, a three-way stopcock, and a 1.3 cubic foot capacity metal reservoir. The stopcock was placed so that the reservoir could be pumped out while the balance case was open or the balance case could be pumped out without opening the reservoir. When the balance case and reservoir were pumped to the desired pressure, the balance case manometer, and reservoir could be connected and isolated from the pump.

Recorder

The first recorder used with the thermobalance was a 10 mv. range Varian G-11. The chart speed of this recorder was much greater than desired and the width of the chart paper a little narrow.

The recorder used for the work reported here was a Brown 'Electronik' Model 153ClOPS-21-20. This recorder was primarily designed for temperature recording from the input of an iron-constantan thermocouple. The internal temperature compensation and exceptionally slow

chart speed were the only disadvantages to the use of this recorder. However, the chart speed was only slightly slower than desired for the most definitive curve production.

CHAPTER III

EXPERIMENTAL

Procedure

The heating rate of the furnace was determined by placing a glass insulated 30 gauge, iron-constantan thermocouple into the furnace cavity through the gas exit tube. The thermocouple was connected to a Brown temperature recorder calibrated for measurements to 500°C. With the furnace in place on the balance case and a slow current of air flowing, the starting position of the contact on the motor driven powerstat and the input potential to the motor driven powerstat were varied until a linear temperature increase from room temperature was obtained. Starting the motor driven powerstat at a point designated as 23 on the 0 to 130 face scale gave no initial boost or lag in the heating, found to be linear at a rate of 5.2 centigrade degrees per minute from room temperature to 500°C, when the input potential was 61 volts. Excellent reproducibility was obtained.

After the 5.2 degrees per minute rate was established to 500°C, the limit of the brown recorder, the thermocouple was connected to a Sargent Laboratory Recorder using another iron-constantan thermocouple in a 0°C ice bath as the reference. The 50 millivolt span of the Sargent instrument was used and the readings obtained were converted

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to degrees centigrade. A plot of temperature versus time showed the heating rate to be linear to about 700° C. Between 700° C and the apparent limit of 660° C, the heating rate decreased. Accuracy of the temperature measurements over 600° C seemed to be poor because of the deterioration of the fine thermocouple wires and some extraneous signals.

After establishment of the temperature-time curve to 860°C, the balance was adjusted by counter-weighting the beam until a direct current of about 10 milliamps through the field coil was necessary to balance the platinum sample bucket containing a 50 milligram weight. This arrangement allowed use of 100 milligram samples and provided a means of weight calibration. Calibration was made during a weighing by adding approximately 50 milligram sof sample after starting the recorder, removing the 50 milligram weight, and then increasing the sample to 100 milligrams. The almost full-scale deflection of the recorder pen after removal of the 50 milligram weight gives an accurate calibration.

For experiments in which a sample smaller than 100 milligrams must be used, a platinum wire of appropriate weight was placed on the hook supporting the platinum bucket. The sample was then placed in the bucket to obtain maximum pen deflection of the recorder. Adding and then removing a small weight such as a 10 milligram rider, before introducing the sample, provided weight calibration for the experiment.

When the sample was in place, the furnace was raised into position around the bucket. The ground-glass fitting was graphite lubricated to prevent sticking. For vacuum experiments a silicon

vacuum grease was used over the graphite. Non-vacuum experiments were made with a slow current of the desired gas passing into the balance case and out the furnace exit tube. Air flow at the rate of 150 milliliters per minute was used for most experiments. A similar flow of tank nitrogen was used for a few experiments.

A timing clock taken from an electric stove was used to control the time period of an experiment by the simultaneous starting and stopping of all the AC-operated equipment. Since imbalance at the end of an experiment is unlikely and since the field coil uses only a very small amount of current, no timing device was used for the control of DC equipment. The timing device was a convenience, not a necessity.

Most of the experiments were timed to run three hours to reach maximum temperature. After the three hour curve for some substances having only early weight changes was made, the experimental time was often shortened.

At the termination of an experiment, the chart was marked, the powerstat reset, DC equipment turned off, and the furnace removed. The platinum bucket was cleaned by boiling in dilute hydrochloric acid, rinsing with distilled water, and flaming over a Bunsen burner. Occasionally the platinum wire supporting the bucket was flamed to remove any deposits accumulating there.

Results

The results obtained with the thermobalance are best presented by representative curves coupled with a brief description and interpretation of the salient parts of each curve. A tabulation of some of the experiments follows the curves. The temperatures used are

to be considered accurate to $\pm 5^{\circ}C_{\circ}$. This seemingly large variation is of little consequence for the majority of studies made. Duval notes that an analyst is interested only in finding a horizontal and uses a temperature taken from the middle of the temperature range of a horizontal (7). Notice of the variation of decomposition temperatures is made by Wendlandt who has made a correlation between decomposition temperature and rate of heating (30). Sample size also affects the decomposition temperature (28).

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An experiment was made using a 50 milligram sample of CuO to discover any apparent weight changes due to convection currents in the furnace, gas flow, or instability of weighing apparatus. A flat line horizontal to the temperature axis was obtained. However, a small apparent weight change was obtained when the room temperature changed during an experiment as a result of the temperature compensation built into the Brown recorder.

Most of the thermolysis curves presented in this work were begun at a room temperature within 3 degrees of $28^{\circ}C$. All of the curves shown are 2/3 the actual size obtained on the Brown recorder.

AgNO₃

Pyrolysis of samples of Baker & Adamson Reagent Grade AgNO₃ gives the curve shown in Figure 4. A small, steady weight increase is observed until decomposition begins at 410°C. Weight loss is rapid until only metallic silver remains at 580°C. Duval, Wadier, and Servigne also noted a weight increase by AgNO₃ believed to be due to absorption of oxygen (11). The curve reported by Duval and co-workers shows slightly higher temperatures and a slower decomposition than reported here.



TEMPERATURE

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NaHCO3

The thermolysis curve for Fisher Certified Reagent NaHCO₃ (Figure 5) shows loss of H₂O and CO₂ beginning at 115° C. Conversion to Na₂CO₃ is complete at 230°C with no further decomposition occuring below 850°C. Duval reports 4 milligrams of 256 milligram weight loss occuring by 113° C (9). His curve also shows decomposition to be complete at 186°C, followed by loss of CO₂ again at 840°C.

Ignition of samples of NaHCO3 under 10 millimeters of mercury pressure produced similar curves. The decomposition did seem to begin closer to 110°C than 115°C.

Na3P01 •12H20

Figure 6 indicates that analytical grade $Na_3PO_{l_4}$ ·12H₂O begins losing weight at 50°C with the stable anhydrous material present above 270°C. No sample ignited was found to yield the theoretical amount of water. Duval confirms this finding by reporting the composition to vary between 10 to 12 water molecules for each $Na_3PO_{l_4}$ (9). No explanation has been offered for the step-like portion of the curve below 270°C which also appears in Duval's curve. The temperatures given by Duval are 30°C and 230°C.

KC103

Curve I of Figure 7 indicates that the decomposition of $KClo_{3}$ to KCl begins at 385°C and is complete by 545°C. Sublimation of the KCl is observed above 765°C. Some of the samples of Fisher Certified Reagent KClo₃ seemed to contain an impurity which gave a 2.5% loss of weight at 320°C. Duval, Wadier, and Servigne give 495°C as the beginning of weight loss with completion at 552°C.





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KClO_l

The pyrolysis curve for $KClO_4$ (curve II of Figure 7) is quite similar to that of $KClO_3$. Oxygen loss starts at 575°C and is complete by 680°C. The weight loss for all of the samples of Fisher Certified Reagent $KClO_4$ was about 5% greater than the theoretical oxygen content.

"Chromium Sulfate"

The two curves in Figure 8 were obtained by ignition of samples of 'Chromium Sulphate C. P. Quality Scales packaged by J. D. Riedel-E. de Haëns A.-G. E. de Haën Works, Seelze/Hanover (Germany) for W. M. Welch Scientific Co.' The 'Chromium Sulphate' is believed to be $\downarrow0$ or 50 years old. Curve I represents the original material; curve II, some of the material that had been heated with the hope of having dried the material. As illustrated by these curves, some compounds yield no plateau below elevated temperatures. Calculation of weight losses gives little insight into the composition of the material except that insufficient SO₃ is lost to give $Cr_2(SO_{1})_3$. The material is most likely a chromic basic sulfate. The familiar Cr_2O_3 was present above $815^{\circ}C$.

CoCl2•6H20

Samples of CoCl2•6H2O ignited in the thermobalance produced curves such as the one shown in Figure 9. Water of hydration is lost from 50°C to 225°C in two unequal portions. The compound remaining at 130°C can be calculated to be the dihydrate. The small loss of weight from 225°C to 285°C may be due to loss of impurities of the water deep inside some large crystals. The anhydrous CoCl₂ is stable



"CHROMIUM SULFATE"







to 485°C above which chlorine is replaced by oxygen leaving a black residue of Co₂O₃ above 735°C. Sample containing only very small crystals lost much less than the theoretical amount of water.

Co(NH3) LC12:C1

A series of experiments were made upon some $Co(NH_3)_{l_1}Cl_2:Cl$ obtained from Dr. Norman Fogel of the University of Oklahoma. The results of the experiments are shown by the four curves in Figure 10. Curve I results from heating some material containing some sulfate ion as impurity as shown by a loss of weight between $725^{\circ}C$ and $830^{\circ}C$. Curve II represents the purified material as ignited in a current of air; curves III and IV represent ignition of the purified material in nitrogen and under reduced pressure, respectively.

Only the reduced pressure curve IV fails to show the initial weight loss as proceeding in two steps. The first step in curves I, II, and III from about 200°C to 335°C represents loss of one ammonia and one chlorine. The second step corresponds to a loss of the remaining three molecules of ammonia (although the order may be the reverse). CoCl₂ not CoCl₃ is left at 405°C. In air, the CoCl₂ begins losing weight at about 465°C, as has already been shown, until Co_{2O3} remains after about 720°C. The CoCl₂ appears to be somewhat more stable in nitrogen since significant weight is not lost below 595°C. The weight loss between 595°C and 830°C is almost equivalent to the loss of the two chlorine atoms. A small amount of oxygen in the nitrogen prevents the theoretical weight loss from being obtained. The metallic cobalt and small amounts of oxide are obtained as a brown powder.



 $C_0(NH_3)_4Cl_2:Cl$





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TEMPERATURE

The reduced pressure or vacuum experiments were made between 10 and 15 millimeters of mercury pressure. The decomposition temperature of the complex was lowered about 40 degrees. No explanation has been developed for the sequence of weight changes after $CoCl_2$ is obtained at $340^{\circ}C_{\bullet}$

$Cu(C_3H_6O_2S)$

The precipitate formed by the reaction of cupric ion with 3-mercapto 1,2-propanediol as described by Bishop (3) is found to produce curves similar to that in Figure 11. In accordance with Duval's finding that the method of preparation of a precipitate often affects its thermolysis curve (7), the shape of the $Cu(C_3H_6O_2S)$ curve was altered by different pre-drying procedures. All of the curves had the same general shape as the one shown but differed in the size of the weight changes occuring above $225^{\circ}C_{\bullet}$

The initial weight loss represents drying of the precipitate to give the anhydrous stable compound between $145^{\circ}C$ and $225^{\circ}C_{\circ}$. From $225^{\circ}C$ to $380^{\circ}C$, the sample melts and loses weight giving a frothy meltthat tends to splatter out of the platinum bucket. At $380^{\circ}C$ the weight loss is complete and a black solid is present that can be approximated to be CuS. The CuS is partially oxidized to CuSO₄ which is present from $600^{\circ}C$ to $710^{\circ}C_{\circ}$. The CuSO₄ loses SO₃ above $710^{\circ}C$ leaving CuO at $870^{\circ}C_{\circ}$.

Fe(C5H5N)LCl2

The pyrolysis of $Fe(C_5H_5N)_4Cl_2$ in air is represented by curve I of Figure 12 while curve II is obtained when a nitrogen atmosphere



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TEMPERATURE

is used. Two molecules of pyridine are lost between 50° C and 122° (. in air ignition, but no compound between the dipyridyl compound and ferric oxide (450°C) appears to be stable in the hot sir.

In the nitrogen atmosphere, the loss of the first two pyridine molecules occurs at slightly higher temperatures than in air. The dipyridyl complex decomposes to give a monopyridyl complex at 200° C, both seeming to be rather stable. The monopyridyl complex loses the remaining pyridine in two steps that are in a 1:2 ratio. The FeCl₂, remaining at 360° C, loses chlorine until 780° C giving metallic iron and a little Fe₂O₃.

The samples of $Fe(C_{5H_5N})_{\mu}Cl_2$ were obtained from a student in an inorganic preparations course. The material was in the form of bright yellow needles possessing the odor of pyridine.

Na2C20),

Powdered samples of Na₂C₂O₄ lose CO above 170° C forming Na₂CO₃ which is stable from 645° C to 850° C as can be seen from Figure 13. These values agree reasonably well with those of Duval, Wadier, and Servigne who report decomposition beginning at 500° C and completing around 590° C. They were also able to reach the decomposition temperature of the Na₂CO₃ at 870° C (10).

. К₂С₂0₄•Н₂0

Ignition of $K_2C_2O_{l_1} \cdot H_2O$ was carried out in a current of air (curve I, Figure 14) and at reduced pressure (curve II). Water is lost at 80°C at 10 millimeters of mercury pressure and at 95°C in air. The anhydrous material is stable to about 500°C, forming the carbonate by



TEMPERATURE



K2C204 • H20





TEMPERATURE

loss of CO. Under reduced pressure the K_2CO_3 loses weight while it is stable to $850^{\circ}C$ in air.

Student prepared samples of the bright green $K_3Fe(C_2O_{\downarrow})_3 \cdot 3H_2O$ were ignited to produce curve I shown in Figure 15. The freshly prepared crystals were wet with a mixture of alcohol and water which gives the downward taper at the beginning of the curve. The weight loss to $165^{\circ}C$ also includes water of hydration. The anhydrous compound loses CO above 290°C to give the carbonates of iron and potassium. The $Fe_2(CO_3)_3$ loses CO_2 from $360^{\circ}C$ to $420^{\circ}C$. The weight loss from $420^{\circ}C$ to $710^{\circ}C$ represents about 5% by weight of the anhydrous material and has not been explained.

Curve II is the pyrolysis curve of a sample containing $Fe_2(C_2O_{ij})_3$. Since this material was dry, a plateau was obtained before water of hydration is lost at 210°C. The portion of curve I from 285°C after decomposition of the $Fe_2(C_2O_{ij})_3$ is the same as curve II from 290°C.

$K_3Cr(C_2O_1)_3 \bullet 3H_2O$

Large, black crystals of $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ obtained from students in an inorganic preparations course, were treated in the same fashion as the analagous iron compound. The results are given in Figure 16. Curves I and II represent ignition in slow currents of air and nitrogen, respectively.

On each curve the first loss is water of hydration; the second loss is a mixture of CO and CO_2 . The products remaining above 530°C in





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FIGURE 16

the air environment are K_2CO_3 and K_2CrO_4 . In nitrogen, K_2CO_3 and Cr_2O_3 . containing small amounts of K_2CrO_4 remain after ignition.

A greenish-blue powder thought to be $K_3Co(C_2O_{12})_3 \cdot 3H_2O$ was obtained from students in the inorganic preparations course. Ignition of the powder in the thermobalance produced the curve in Figure 17. No plateau representing a stable compound is obtained between $50^{\circ}C$ and $280^{\circ}C$. From the calculated weight losses and the material present after ignition, the reaction is believed to be the formation of K_2CO_3 and $Co_2(CO_3)_3$ by loss of water of hydration and CO between $50^{\circ}C$ and $280^{\circ}C$ followed by loss of CO_2 from $Go_2(CO_3)_3$ leaving K_2CO_3 and black Co_2O_3 above $410^{\circ}C_{\bullet}$

 $K_{3}A1(C_{2}O_{4})_{3} \cdot 3H_{2}O$

Close examination of a material supposed to be the aluminum compound analogous to the preceeding three oxalate complexes revealed two different types of crystals. The opaque, white plates and the transparent rectangular crystals are easily distinguished and can be separated by hand. Curve I in Figure 18 results from ignition of the white plates while the clear, rectangular crystals decomposed as shown by curve II. Curve I resembles the curves of the analagous iron and chromium compounds, but curve II resembles the curve of the cobalt compound.

No identification of either of the two materials was attempted, but some similarites were noted. Both curves show a decomposition step beginning around 415°C and also at 535°C. Curve I yields a calculated weight loss closer to the theoretical for the complex compound than does curve II which gives a value over 10% too large.





K₃A1(C₂O₄)₃•3H₂O

FIGURE 18

Tables

Table 1 is a series of 17 approximately 100 milligram samples of NaHCO₃ in which the weight loss is presented as weight per cent. The error is the difference between the theoretical weight loss in per cent and the calculated value in the table. The error is also given as error in weighing, shown to the nearest 0.1 milligram. The weighing error is less than 1 milligram for all but one sample. The error in weighing for samples run in a vacuum (not listed) is about 3 milligrams.

Table 2 shows the weight losses calculated for the six samples of $K_2C_2O_{l_1}$ ·H₂O ignited in air. The per cent loss of CO from anhydrous $K_2C_2O_{l_1}$ is presented with the per cent weight loss of water from the hydrate. The variation in the water content of the hydrated material shows the necessity of calculation of carbon monoxide loss on the basis of the anhydrous material. The error in weighing, the difference between theoretical and calculated values for CO loss, is given to the nearest 0.1 milligram.

Table 3 presents the values representing deflection of the recorder pen in arbitrary units (about 0.5 millimeter) caused by adding and removing some 10 milligram weights to the platinum sample bucket one at a time. The greatest error that could be realized from this data would be 6 arbitrary units or 0.86 milligram. This is about the same value obtained in Tables 1 and 2 for maximum error.

| TABLE | 1 |
|-------|---|
|-------|---|

A SERIES OF 100 MG. SAMPLES OF NaHCO3 IGNITED IN AIR

| Percent Loss (H ₂ 0, ∞_2) | Error in Percent | Error in Mg. |
|--|------------------|--------------|
| 36.49 | 0.43 | 0.3 |
| 37.60 | 0.68 | 0•7 |
| 37.25 | 0.33 | 0.3 |
| 37.69 | 0.77 | 0.7 |
| 37.05 | 0.13 | 0.2 |
| 36.38 | 0.54 | 0.5 |
| 36.86 | 0.06 | 0.1 |
| 36.25 | 0.57 | 0.6 |
| 37.48 | 0.56 | 0•5 |
| 37.85 | 0•93 | 0.8 |
| 37•34 | 0.42 | 0.4 |
| 36.95 | 0.03 | - |
| 38.25 | 1.33 | 1.2 |
| 37•55 | 0.63 | 0.6 |
| 37.00 | 0.08 | 0.1 |
| 38.08 | 1.16 | 1.0 |
| 37.06 | 0 .1 4 | 0.1 |
| | | |

TABLE 2

Percent CO (Based on $K_2C_2O_4$) Percent H_20 CO Error

DATA OBTAINED FROM PYROLYSIS OF K2C204+H20

| (10.35 Theoretical) | (16.85 Theoretical) | (in mg.) |
|---------------------|---------------------|----------|
| 11.24 | 16,89 | - |
| 10.73 | 16.84 | - |
| 10.88 | 16.94 | 0.1 |
| 10.87 | 17.09 | 0.2 |
| 10.44 | 17.28 | 0.4 |
| 10.70 | 16.96 | 0.1 |
| | | |



•

PEN TRAVEL IN ARBITRARY UNITS PER 10 MG. WEIGHT CHANGE

| 73 | 74 | |
|----|------------|-------------------------|
| 76 | 76 | Maximum Error = 76 - 70 |
| 74 | 73 | = 6 units |
| 71 | 71 | or |
| 76 | 70 | = 0.86 mg. |
| 72 | 7 5 | |
| 72 | 73 | |
| 74 | 70 | |

CHAPTER IV

CONCLUSIONS

The main purpose of this work was to develop a simple, inexpensive, and practical thermobalance, the results given in Chapter III show this new thermobalance to be practical and relatively simple while achieving the sensitivity of some of the more expensive commercial instruments. The cost of the equipment described, omitting labor and the recorder, is less than \$200. A commercial recorder may be obtained for \$400 or a satisfactory recorder may be built for about \$100.

While the accuracy of the balance as used may not be great, notice should be called to the fact that the accuracy obtained was sufficient in most cases and can be increased by using larger samples. Larger samples will produce larger weight changes without appreciably changing the error of weighing (0.8 milligram). The capacity of the silica balance will allow the use of samples of at least 5 grams with no difficulty. The accuracy may be expected to increase from 2% of a weight change to 0.2%.

The construction of the silica balance is reasonably easy, after a little practice. A good glassblower can do the job in less than an hour. The balance is amazingly rugged and possesses a high capacity and sensitivity in spite of its seemingly delicate construction.

The electrical system is very dependable and requires a knowledge of only Ohm's Law for complete underatanding since no amplification is involved. Wiring involves only connections to the binding posts of batteries and a faw solder connections to the terminals of the relays and potentiometers.

As had been anticipated the ability to isolate the sample in special atmospheres or in vaccum has been a very practical aid in the study of the decomposition of certain compounds. This rather unique feature greatly expands the capabilities and usefulness of the thermobalance. Considerable industrial interest has been expressed recently in the ability to study such materials as catalysts, construction metals, and solid reactants in the presence of gases at conditions existent or desired in commercial processes.

The secondary purpose of this research has been to use the new type of thermobalance to examine a few compounds heretofore not studied thermogravimetrically. The 3-mercapto 1,2-propanediol precipitate of copper was pyrolysed and found to give two stable and reproducible compounds. The conditions for obtaining the compounds are obvious from the curve and substantiate the previous treatment of the precipitate for analytical use (3).

Corroborative evidence for the composition of some complex inorganic compounds has been obtained, as well as indications of their purity and stability. Some of the curves could and should be studied further to provide explanations for all phenomena observed, but even Duval has had to leave some portions of a few curves unexplained (8). In all fairness to the reader, attention must be called to

the fact that while the equipment has been found simple, rugged, inexpensive, and practical, it also has zome disadvantages. First, the apparatus is extremely sensitive to vibration, requiring careful mounting and isolation for reliable working. Secondly, faster chart speed is necessary for more accurate observation of temperatures. Third, the platinum contacts should be made more rigid to minimize the frequency of adjustment. Finally, the apparatus should be modified for the use of larger samples so greater accuracy can be obtained when desired.

In spite of a few disadvantages, the thermobalance described in this work is a satisfactory and practical instrumental addition to any chemical laboratory not already possessing similar equipment. Anyone with a minimum of mechanical ability, having access to the materials described or reasonable substitutes, can build such an instrument. A serviceable thermobalance is certainly within reach of laboratories operating on the most modest budgets.

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