THERMAL STUDIES OF SOME METAL THIOCARBONATES AND SULPHIDES.

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D E D I C A T I O N

This study is dedicated to my wife, Sadiya and my children, Aminatu and Abdurahman.

P R E F A C E

The Research work embodied in this thesis has been carried out in the laboratories of Ahmadu Bello University, Zaria, Nigeria, under the guidance and supervision of Dr. K. Singh and Dr. B. Basak. The extent of work derived from the existing literature has been listed at the end of each chapter with reference at appropriate places in the text. The work is original and has not been submitted in part or full for any other diploma or degree of any University.

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Muhammad A. Bappa

A B S T R A C T

Hydrogen sulphide has boon playing a commendable role in the sulphide reactions in analytical field for over a hundred years. However, Hydrogen sulphide gas suffers from a number of serious drawbacks-high toxicity hazards, contamination of laboratory atmosphere and low solubility in water.

potassium thiocarbonate (PTC) is a substitute for hydrogen sulphide in chemical analysis. PTC is Inorganic in nature and as a good cation precipita; it is capable of furnishing a high degree of thiocorbonate ions in neutral or alkaline medium and of sulphide ions in regulated acidified conditions. It affords greater simplicity, efficiency and economy in pursuing chemical analysis both at semi-micro and micro scales affording clean precipitation of sulphides from homogenous solution.

The study intends to investigate convenient method of preparation of PTC and establish a convenient method of precipitating its metal thiocarbonates and metal sulphides. Also investigate the ranges of temperatures for different stages of transformation and the conditions of their quantitative estimation as thiocarbonotes, sulphides, sulphates, or oxides by weighing. Similarly, the study enables one to detect any

deviations from the stoichiometric compositions of the metal thiocarbonates or sulphides.

The stability and purity of the thiocarbonates and sulphides are studied and their transition energy and transition rate calculated.

In order to study the purity, stability, staichiometry and general behaviour of various metal thiocarbonates and sulphides, three thermal methods of study are used.

(a) Differential Scanning calorimatry (DSC) Method. The following metal thiocarbonates are studied by this method. Ag(I), Pb(II), Sn(Il), Fe(II), Ni(II), Tl(I), Co(n) and Bi(III), Metal sulphides studied by this method are Fe(n), Mn(II), Aa(III), Co(Il), Cu(Il), Sn(lV), W(IV), Sb(III), Pd(lV), Ag(I), Pb(II), Ni(II) and TL(I).

(b) Thermogravimetric (TG) Method. The thermogravimetric behaviour of Ag(I) and Mn(n) thiocarbonates; and sulphides of Zn(H), l\li(II), Pb(ll), Fe(ll), and Tl(I) are also investigated using the TG method.

(c) Differential Thermal Analysis (DTA) Method. The metal thiocarbonates studied by this method are zn(II), Mn(II), and Pb(II). Metal sulphides of Fe(I), Tl(IV), Bi(IV), Pt(IV), pd(IV) end Sb(III) are also studied using DTA method.

These three thermal methods of analysis jointly reveal the chemical reactions and physical changes that take place during heating or cooling of the precipitated metal thiocarbonates and sulphides. The results have been both qualitative and quantitative.

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INTRODUCTION

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C H A P T E R I

INTRODUCTION

1 - 1 POTASSIUM THIOCARBONATE REAGENT - A SUBSTITUTE FOR GASEOUS HYDROGEN SULPHIDE

Potassium thiocarbonate[1] (K_2CS_3) is increasingly being used as a sulphide precipitant replacing the use of hydrogen sulphide (H_2S). Potassium thiocarbonate has proved to be the most efficient and economical alternative to the conventional uses of gaseous hydrogen sulphide in chemical analysis affording clean laboratory atmosphere. The stinking of laboratories and toxicity hazards due to hydrogen sulphide are becoming increasingly features of the past with the advent of thiocarbonate reagent.

Fresenius, an inorganic chemist[2] formulated a scheme of qualitative analysis in which hydrogen sulphide played an important roll almost 136 years ago. There were several modifications to make it efficient and more illustrative in chemical principles hence its use in precipitating sulphides of most metals in systematic qualitative analysis.[3]

It is due to tremendous importance and extensive applications of sulphide reactions in all fields of chemical study and analytical study in particular that the roll of hydrogen sulphide gas as a fundamental reagent has been commendable.

During the last two decades various studies have been made with non-gaseous reagents with a view to replacing gaseous hydrogen sulphide since it is toxic and contaminates the laboratory atmosphere.

Most of these non-gaseous reagents are organic in nature and hence there would be possibilities of contaminations. However, potassium trithiocarbonate (PTC) being an inorganic reagent affords better efficiency and economy than other substitutes. A lot of work has been done by John[1] on PTC and has proved that it is possible to replace gaseous hydrogen sulphide with the PTC in all qualitative inorganic analysis studies.

1 - 2 OTHER SUBSTITUTES REPLACING HYDROGEN SULPHIDE GAS

Owing to the toxicity hazards and other disadvantages of hydrogen sulphide, successive attempts have been made in the past to find convenient substitutes which are non-toxic.

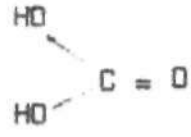
Various sulphur containing compounds have been studied[4] e.g. thiourea, thiosulphates ammonia sulphide, sodium sulphide, thioacetate, thioglycollates, thiosalicyllates, thioformamide and thiocarbonates, to determine their applicability as parent compounds for the generation of hydrogen sulphide gas in solution. Barber and Grzeskomiate[5] have done an extensive work on thioacetamide, since its first application as a cation precipitant in qualitative analysis of metal ions and has proved to be useful in analytical procedures. It was proved that out of all these substitutes the most widely used is the thioacetamide. It generates hydrogen sulphide on hydrolysis (at $80^{o}C$) but acetate ions also accumulate in solution acting as buffer and causing Coprecipitation of some unwanted metal ions. It is also very costly and hence uneconomical to use.

Potassium thiocarbonate being an inorganic reagent does not suffer these drawbacks and can be used as efficient sulphide precipitant in qualitative and quatitative analysis of metal ions.

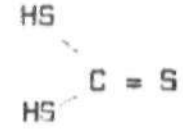
1 - 3 THE CHEMICAL CHARACTERISTICS OF POTASSIUM THIOCARBONATE K_2CS_3(PTC)

Unlike organic substitute[6,7] suggested from time to time thiocarbonate reagent being inorganic in character as sulphur anologue of potassium carbonate does not creat complications in the systematic precipitation of cations for their separation into analytical groups.

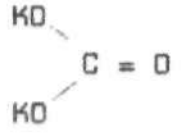
It is a normal salt of tri-thiocarbonic acid. It can be seen that thiocarbonic acid H_2CS_3 and potassium thiocarbonate K_2CS_3 are analogue to carbonic acid and potassium carbonate but with sulphur taking place of oxygen.



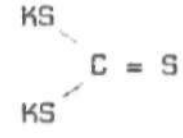
Carbonic acid



Thiocarbonic acid



Potassium Carbonate



Potassium thiocarbonate

It can be seen that as carbondioxide is an anhydride of carbonic acid, so is carbon disulphide be looked upon as the anhydride of the thiocarbonic acid.

Because of the physical state of the anhydrides, thiocarbonic acid is appreciably more stable than carbonic acid.

(i) Precipitation from Neutral or Alkaline Medium

In its moderate concentrations in aqueous solution, thiocarbonic acid has an orange - red colour which changes yellow on dilution. Similarly potassium thiocarbonate has this same colour. The aqueous solution of potassium thiocarbonate is alkaline (pH 8.5 - 9.0) due to partial hydrolysis:-

$$K_2CS_3 + 2H{\cdot}OH \rightleftharpoons 2KOH + H_2CS_3$$

So long non of the products of hydrolysis is used or removed, the equilibrium is always maintained.

Since potassium thiocarbonate is soluble it ionizes in solution so as to interact with metal ions resulting in the precipitation of the metal thiocarbonates at room temperature according to the equations.[8]

$$K_2CS_3 \longrightarrow 2K^+ + CS_3^{2-}$$
$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$

$$K_2CS_3 + CuSO_4 \longrightarrow CuCS_3\downarrow + K_2SO_4$$

The precipitation of the metal depends on the availability of concentrations of the thiocarbonate in solution. The thiocarbonate is generally precipitated at room temperature whilst sulphide needs warmer temperatures.

Some metals like cobalt, nickel and iron are known to form soluble complex thiocarbonate anions[4] with excess of potassium thiocarbonate reagent, while metals like aluminium titamin and zirconium would precipitate their hydroxide with PTC because of the hydrolysis shown above. However, the hydroxides could be prevented from precipitating in alkaline solutions with the use of masking agent like the cyanide, or tarteric acid or disodium EDTA.

(ii) Precipitation from Acidic Medium

PTC liberates gradually a corresponding amount of thiocarbonic acid, in the presence of a non-oxidising acid.

With the controlled increase in acidity and temperature, the thioacid[9] gets transformed gradually to hydrogen sulphide:-

$$K_2CS_3 + 2HCl \xrightarrow[(\ pH.1)]{} 2KCl + H_2CS_3 \quad .. \quad .. \quad (i)$$

$$H_2CS_3 + 2H.OH \xrightarrow[(\ pH.1)]{} 3H_2S + CO_2 \quad .. \quad .. \quad (ii)$$

To utilize the three moles of hydrogen sulphide produced per mole of thiocarbonic acid, control of its concentration and addition of PTC would be required.

Almost 2.5 - 2.7 moles of hydrogen sulphide generated per mole of PTC are invariable concentration is added dropwise to solutions with optimum pH.

Generally, in the acidic medium PTC reacts with certain metals resulting in their initial precipitation as thiocarbonates and finally transformed to sulphides depending on the concentration and the prevention temperature of the medium[9]

For example copper,

Thiocarbonate precipitation:-

$$K_2CS_3 + 2HCl \longrightarrow 2KCl + H_2CS_3 \quad \ldots \quad (i)$$

$$CuSO_4 + H_2CS_3 \longrightarrow CuCS_3 + H_2SO_4 \quad \ldots \quad (ii)$$

Sulphide precipitation:-

$$H_2CS_3 + 2HOH \longrightarrow 3H_2S + CO_2 \quad \ldots \quad (iii)$$

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4 \quad \ldots \quad (iv)$$

$$CuCS_3 + 2H.OH \xrightarrow{60^oC} CuS + 2H_2S + CO_2 \quad \ldots \quad (v)$$

If mixtures of thiocarbonate and sulphide are heated to 60^oC, the mixture will transform to metal sulphides. This is normally done by leaving the precipitated solution on a water bath for about 20 minutes

1 - 4 ADVANTAGES OF POTASSIUM THIOCARBONATE REAGENT OVER H_2S AND ITS ANALYTICAL IMPORTANCE

The name "Stinks" is normally associated with Hydrogen sulphide in chemical laboratories. Experiments will have to be performed in fume chambers or in an extremely secluded areas in the laboratory.

A part from the offensive odour of rotten eggs, hydrogen sulphide suffers a series of drawbacks:

(i) Precipitated sulphides are generally collaidal, difficult to filter and to wash and above heterogerous.

(ii) Precipitation action is slow and apt to be in complete. A lot of gas will have to be passed for a long time for visible reaction.

(iii) For a solution of practical importance to be prepared, it has to be used in gaseous form, since it is almost insoluble in water. The saturated solution contains only 0.1M at $25^{o}C$.

(iv) It corrodes metal equipments of the laboratory and being toxic is hazardous.[4]

The drawbacks listed above have made it necessary to sought for other chemical reagents that guarantee efficiency in analysis and economy of chemicals.

Potassium thiocarbonate (K_2CS_3), however, does not suffer most of these shortcomings experienced with other substitutes. The work done by K. N. Johri and K. Singh has proved beyond reasonable doubt the ability of this reagent to be substituted for hydrogen sulphide gas in qualitative and quantitative analysis of metal ions.

Unlike other sulphide precipitant it can be used both in hot and cold solutions. Being inorganic in nature it is used as a good cation precipitant capable of furnishing a high degree of thiocarbonate ions in neutral or alkaline medium and of sulphide ions in regulated acidified conditions.

The reagent when freshly prepared is kept in a stoppered bottle and remains stable for a length of time. To proclaim further, the importance of potassium thiocarbonates and its universal acceptance Johri and Co-workers did an extensive work on estimation of thiocarbonate sulphur and its role in various analytical procedures. Johri and Co-workers, after establishing methods of these analytical procedures using K_2CS_3 went further to validate its roll by studying the thermal stability of some precipitated thiocarbonate compounds using thermogranimetric method of analysis (TGA) (see under past work).

1 - 5 PAST WORK ON POTASSIUM THIOCARBONATE REAGENT

Although early inorganic chemists like Fresenius[2] have recognised the use of trithiocarbonic acid, H_2CS_3 and its salts, the knowledge regarding their Chemistry remained undeveloped till recently. One of the most important reasons for not having proper record and sufficient literature on the subject could be traced to the easy decomposibility of solid thiocarbonates on exposure to atmosphere or in aqueous medium affecting their stability and purity.

However, Mellor[6] did some studies on preparation and properties of various metal thiocarbonates which helped various workers in expending and establishing the reaction mechanism of the thiocarbonates ions and their various physico - chemical aspects as well.

Although the studies done by Berzelius,[6] Tarugi and Magri were found to be isolated in scope, later studies made by Ingram and Tons,[6] Gattow,[7] Johri and others are found more systematic and wider in scope. For example Pilz's work relates the quantitative precipitation of metal sulphides like Copper,[8] zinc[9] Molybdeum,[10] Amtimony,[11] Manganese[12] and their conversion into oxides to constant weight for their gravimetric evaluation.

Analytical applications of potassium thiocarbonate reagent replacing hydrogen sulphide in cation analysis, as earlier reported, has necessitated evaluation of thiocarbonate contents of the reagent of various strengths for ensuring its purity.

Standisation of concentrated aqueous solutions of potassium thiocarbonate employing titrimetric and gravimetric methods were described by Singh and Johr.[13]

Oxidimetric methods for determing the strength of aqueous potassium thiocarbonate solution by the use of iodine, potassium iodate and iodic acid were also investigated by Singh and Johri.[14] Other oxidimetric methods were employed by Johri and Kaushik[15] making use of chloramine T, potassium ferricyanide and potassium permanganate. A simple vanadometric estimation[16] also carried out using ammonium metavanadate as oxidant.

As pointed out earlier, analytical separations of different metal ions with PTC in the presence of such masking agents[17] as EDTA, potassium cyanide, tartaric acid, and excess of PTC have been worked out.

To show a wide spectrum usage of PTC, its application in the Ring Oven Technique in inorganic micro-analysis have been studied.[18]

Ring Oven method[18] has also been used for semi quantitative determination of metal ions in mixtures using PTC as a fixing agent. Some work has been done with PTC using thin layer

chromatography[21] in the separation of metals like Copper[(11)], Nickel[(11)], and Cobalt[(11)].

Thin layer chromatography method has also been used in conjuction with ring-oven Calorimetry.[22] Qualitative separation and determination of various metals has also been reported using PTC.[19,20]

Thermogranimetric[11](TG) Studies have also been carried out to study the stoichiometry of various metal products precipitated with PTC at different temperatures with a view to determine purity of the products, mods of decomposition with increasing temperature and to determine conditions of their gravimetric analysis.

1 - 6 SCOPE OF PRESENT WORK

The developments of sulphides and thiocarbonates studies have increasingly become interesting and so it should be realised that without further study in the systematic sequences of these studies, the utility of PTC as an analytical reagent would remain limited in scope.

This study is therefore intended to investigate the following:

(i) to find convenient methods and optimum conditions for the preparation of metal thiocarbonates and sulphides,

(ii) the ranges of temperature for the different stages of transformation of the metal thio-compounds affording standardization of the conditions of their quantitative estimation as thiocarbonates, sulphides, sulphates or oxides by weighing,

(iii) any deviations from the stoichiometric compositions of the precipitated products, thereby establishing the extent of purity of the metal thiocarbonates or sulphides,

(iv) to measure simultaneously the temperature within the sample, determine the weight changes and energy changes in the sample,

(v) to calculate the transition energy and transition rate of various metal thiocarbonates and sulphides during phase changes on heating.

To achieve the above stated objectives, studies have been carried out on metal thiocarbonates and metal sulphides using Differential Scanning Calorimetry (DSC) method, thermogravimetry (TG) method, and Differential Thermal Analysis (DTA) method.

REFERENCES

1. Johri, K. N., Chemical Analysis without H_2S using Potassium Trithiocarbonate.
   Asia Publishing House, Bombay, 1968.

2. Johri, K. N., J. Sc. Industrial Research, 1959, 18B, 430.

3. Johri, K. N., Ind. J. Appl. Chem., 1963, 28, 114.

4. Singh, K., Ph.D. Thesis, University of Delhi, 1967.

5. Barber, H., and Grzeskowiak, E., Anal. Chem., 1947, 21.

6. Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, Green & Co. London, 1961, Vol. VI, pp. 119.

7. Gattow, G. and Krebs, B., Angew. Chem., 1962, 74, 29.
   C. A., 1962, 57, 12081 i.

8. Gagliardi, E. and Pilz, W. Monatsh, 1952, 82, 54.
   C. A., 1952, 46, 6991 d.

9. Pilz, W., Monatsh, 1952, 83, 471.
   C. A., 1952, 46, 7932 a.

10. Gagliardi, E. and Pilz, W., Z. Anal. Chem., 1952, 136, 344.

11. Singh, K., Kaushik, N. K., and Johri, K. N., Journal of Thermal Analysis, 1970, 2, 37.

12. Pilz, W., Monatsh, 1952, 83, 1291,
    C. A. 1952, 47, 4243 a.

13. Johri, K. N. and Singh, K., Indian J. Chem. 1965, 3, 158.

14. Johri, K. N. and Singh, K., Analyst, 1965, 90, 745.

15. Johri, K. N. and Kaushik, N. K., Analyst, 1968, 93, 792.

16. Johri, K. N. and Kaushik, N. K., Indian J. Chem. 1969, 7, 14.

17. Johri, K. N. and Singh, K., Bull. Chem. Soc. Japan, 1967, 40, 4.

18. Johri, K. N. and Singh, K., Mikrochim. Acta, 1970, 1.

19. Johri, K. N. and Singh, K., Indian J. Appl. Chem. 1965, 28, 90.

20. Johri, K. N. and Singh, K. Indian J. Appl. Chem. 1968, 31, 94.

21. Johri, K. N. and Kaushik, N. K., Chromatographia, 1976, 9(5), 233.

22. Johri, K. N., Kaushik, N. K. and Sakshi, K., Chromatographia, 1972, 5(12) 326.

C H A P T E R II

PREPARATION OF POTASSIUM THIOCARBONATE REAGENT AND METAL THIOCARBONATES AND SULPHIDES

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C H A P T E R II

PREPARATION OF POTASSIUM THIOCARBONATE REAGENT AND METAL THIOCARBONATES AND SULPHIDES

II - 1 PREPARATION OF POTASSIUM THIOCARBONATE (PTC)

In the past, organic reagents were used to prepare thiocarbthiocarbonates[1], and the emphasis was on separation and isolation of solid product. However, under the conditions, it was found that organic thiocompounds and some polysulphides were also formed and hence the products obtained were impure.[2]

The usual method of preparing potassium thiocarbonate reagent is by the addition of pure carbon disulphide to a solution of known concentration of potassium hydroxide. The hydrolytic reaction:-

$$6KOH + 3CS_2 \longrightarrow 2K_2CS_3 + K_2CO_3 + 3H_2O$$

From the above equation, it could be seen that

(i) $\frac{1}{3}$ of the potassium hydroxide used was wastage as the rest was used in the formation of K_2CO_3.

(ii) The K_2CO_3 might intereere with the metal thiocarbonate in the process of precipitation of the required metal thiocarbonate.

These can be considered as the shortcoming of this method.

Johri[3] used shaken carbon disulphide with elemental sulphur but yielded to no avail as the products also contain polysulphide sulphur.

In order to eliminate this contamination by potassium carbonate and polysulphide sulphur, Singh[2] observed that startin with freshly prepared potassium monosulphide and reacting it with rectified carbon disulphide converts it to thiocarbonate quantitatively. This ensures high concentration and purity of the reagent and has been employed here for all preparations.

EXPERIMENTAL

Reagents

Potassium Hydroxide Solution 4M: Pellets of potassium hydroxide of analytical grade were accurately weighed and standardised against a standard solution of hydrochloric acid.

Carbon Disulphide: Prepared from B.D.H. Analytical grade.

Procedure

4M potassium hydroxide was saturated with hydrogen sulphide and an equal volume of the 4M potassium hydroxide added to it.

The resulting solution, potassium monosulphide was transfered into a 500 ml. flask and set on a magnetic stirrer-cum-hot plate with a separatory funnel containing carbon disulphide allowing it to drop at a rate of 1 - 2 Cm^3 per minute into the flask. The resulting mixture was kept at 40^0 to 41^0C and with constant stiring for an hour till the completion of the reaction which was marked by the appearance of the dark-red colour due to high concentration of PTC in solution and some excess of unreacted carbon disulphide.

It was allowed to cool overnight in the refrigerator. It was then removed and the excess carbon disulphide filtered off leaving clear dark-red solution of PTC (colour of the solution depends on the concentrations of chemicals used).

The reaction course follows:-

(i) $KOH + H_2S \longrightarrow KHS + H_2O$

(ii) $KHS + KOH \longrightarrow K_2S + H_2O$

(iii) $K_2S + CS_2 \xrightarrow{41^0C} K_2CS_3$

The last stage, being the most important of the three, so for any pure method of preparing potassium thiocarbonate (PTC) the temperature will have to be controlled and contents kept stirring for uniformity through out the experiment.

II - 2 PREPARATION OF METAL THIOCARBONATES

The following metal thiocarbonates have been prepared: Bi(III), Tl(I), Ag(I), Fe(II), Cu(II), Pb(II), Cd(II), Hg(II), Mn(II), Ni(II), Co(II) and Zn(II).

Precipitation of the precipitated metal thiocarbonates fall under two conditions of media of preparation. They are generally precipitated from aqueous or neutral medium or from alkaline (complexation with masking agents) medium.

(i) Preparation of Bi(III), Tl(I) and Ag(I) Thiocarbonates

EXPERIMENTAL

Reagent

PTC reagent: An aqueous solution of PTC(IM) prepared by the modified direct method[4] was used as a stock solution and its working solutions were obtained by suitable dilutions.

Metal ion solutions: Aqueous solutions of Bismuth nitrate, thalium nitrate and silver nitrate were prepared by dissolving their analytical grade salts (B.D.H, Analar) in distilled water All other chemicals used were of Analytical grade unless otherwise stated.

Procedure

For pure thiocarbonates,[5] PTC was introduced dropwise into the metal ion solution using a pipette and with continous shaking till dense precipitate of the compound was formed. After complete precipitation, as marked by the appearance of colourless supernatant liquid above the precipitate, the product was then washed with distilled water several times till the last washings were free from nitrate ions. This was tested and confirmed by using a drop of potassium iodide which showed absence of turbidity. The products were filtered off using whatman filter paper No. 40; and dried in a vacum desiccator for 36 hours.

(ii) Preparation of Ni(II), Co(II) and Zn(II) Thiocarbonates

EXPERIMENTAL

Reagents

PTC reagent - prepared by the rectified direct method.

Ammomin Hydroxide - 1:1 Ammomin hydroxide prepared from Analytical grade.

Metal ion solutions: Alkaline metal ion complexes of Ni(II), Co(II), and Zn(II) were prepared from their Analytical grade salts.

Procedure

The thiocarbonates of these metal ions were prepared by adding PTC to metal amine complexes till the precipitation was complete and the supernatant liquid was clear. It was then allowed to settle down steadily. The products were filtered and washed with distilled water several times, transferred to a clear open container and dried in a vacuum desiccator. It was removed, finely ground and put in labelled sample bottles. (See Table I below).

(iii) Preparation of Cu(II), Pb(II), Cd(II), Hg(II), and Mn(II) Thiocarbonates

EXPERIMENTAL

Reagents

PTC reagent - Prepared by the direct method.[4]
And appropriate dilutions made as required.

Disodium EDTA: A1:1 disodium EDTA freshly prepared.

20% Alcohol: V/V freshly prepared from the absolute analar bottle.

Tartaric Acid: 1M of acid prepared fresh from Analytical grade reagent.

Procedure

PTC was added to the metal EDTA complex in alkaline medium of Cu(II), Pb(II), Cd(II), Hg(II) and Mn(II) salts of Analytical grade. The process was continued till the dense metal thiocarbonate precipitate settle down steadily on addition of slight excess of PTC. The product was filtered and washed with water and then with 20% alcohol.

In order to obtain ferrous thiocarbonate, PTC was added dropwise to the iron tartrate complex in ammonical medium till the precipitate was complete. The product was similarly washed and dried in a vacuum desiccator for 36 hours.

The prepared thiocarbonates[6] were then finely ground and put in labelled bottles ready for analysis. (See table I above for general thiocarbonate preparation).

TABLE I

PREPARATORY METHODS FOR METAL THIOCARBONATES

No.	Compound	Colour	Salt of Metal taken	Condition for Preparation
1.	Thalium thiocarbonate ($TlCS_3$)	red	$TlNO_3$	Precipitated from aqueous solution.
2.	Silver thiocarbonate (Ag_2CS_3)	black	$AgNO_3$	-do-
3.	Bismuth thiocarbonate ($Bi(CS_3)_3$	black	$Bi(NO_3)_3 \cdot 5H_2O$	-do-
4.	Nickel thiocarbonate ($NiCS_3$)	red	$Ni(NO_3)_2 \cdot 6H_2O$	PTC added to metal ammine complex till
5.	Cobalt thiocarbonate ($CoCS_3$)	greenish black	$Co(NO_3)_2 \cdot 6H_2O$	Precipitation was complete
6.	Zinc thiocarbonate ($ZnCS_3$)	Cream white	$Zn(NO_3)_2 \cdot 6H_2O$	-do-
7.	Copper thiocarbonate ($CuCS_3$)	brown	$CuSO_4 \cdot 5H_2O$	PTC added to metal EDTA complex in alkaline medium.
8.	Lead thiocarbonate ($PbCS_3$)	red	$Pb(NO_3)_2$	-do-
9.	Cadmium thiocarbonate ($CdCS_3$)	yellow	$Cd(NO_3)_2$	-do-
10.	Mercuric thiocarbonate ($HgCS_3$)	black	$HgCl_2$	-do-
11.	Manganese thiocarbonate ($MnCS_3$)	brown	$MnCl_2 \cdot 4H_2O$	-do-
12.	Iron thiocarbonate ($FeCS_3$)	bromish black	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2$	PTC added to metal tartrate complex in ammonical medium

II - 3 PREPARATION OF METAL SULPHIDES

Metal sulphides[7] can be prepared by two different ways: those that can be precipitated from aqueous medium as thiocarbonates and then digested to transfer into sulphides and those that can be directly prepared from acidic medium and digested to obtain the metal sulphides.

Sulphides of the fomer are Tl(I), Pb(II), Co(II), Ni(II), Mo(IV), Pt(IV), Pd(II), Au(III), V(V), Te(IV), As(III) and Sb(III).

EXPERIMENTAL

Reagent

PTC reagent: Aqueous solution of the PTC((IM) prepared by direct method was used.

Metal ion solutions: Analytical grade reagents of the salt solution were used in all the preparations unless otherwise stated.

Hydrochloric Acid: Various concentrations of the acid were prepared from the stock solution. It was also prepared from the analytical bottle of the reagent.

Procedure

The first set of metal ions were prepared as described under the thiocarbonate method of preparation. The thiocarbonates

precipitates were then transferred to a water bath for digestion for 30 minutes. It was cooled and filtered and products kept dried in a vacum desiccator.

For the second set of metals, PTC was gradually added to their metal solutions till the precipitation was complete. The solution was then transferred into a sizeable flask and heated over a water bath at $60^{0}C$ for 30 minutes. After the digestion, it was then removed, cooled and filtered off with similar washings with distilled water.

The products[8] were removed, dried in a vacum desiccator for 36 hours.

TABLE II

PREPARATORY METHODS FOR METAL SULPHIDES

No.	Compound	Colour	Salt of Metal Taken	Condition for precipitate
1.	Thallous sulphide Tl_2S	Vermilion	$TlNO_3$	Precipitated from aqueous media as thi thiocarbonates and digested to transform to sulphide
2.	Lead sulphide PbS	red	$PbNO_3$	
3.	Cobalt sulphide CoS	black	$Co(NO_3)_2 \cdot 6H_2O$	
4.	Nickel sulphide NiS	red	$Ni(NO_3)_2$	-do-
5.	Zinc sulphide ZnS	cream white	$Zn(NO_3)_2$	-do-
6.	Iron sulphide FeS	brown	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	-do-
7.	Silver sulphide	black	$AgNO_3$	-do-
8.	Copper sulphide CuS	black	$CuSO_4 \cdot 5H_2O$	Made acidic (pH 0.7-1.0) for complete precipitation and digesting on steam bath for half an hour
9.	Cadmium sulphide CdS	yellow	$Cd(NO_3)_2$	
10.	Mercury sulphide HgS_2	black	$HgCl_2$	
11.	Bismuth sulphide Bi_2S_3	black	$BiONO_3$	
12.	Molybdenum sulphide MoS_2	black	$(NH_4)_2MoO_4 \cdot 12H_2O$	-do-
13.	Platimum sulphide PtC_2	black	H_2PtCl_6	PTC added to acid solution and digesting on water bath for 30 minutes
14.	Palladim sulphide PdS_2	black	$PdCl_2$	
15.	Gold sulphide Au_2S_3	brown	$HAuCl_4$	

No.	Compound	Colour	Salt of Metal Taken	Condition for precipitate
16.	Vanadim sulphide V_2S_5	dark brown	NH_4VO_3	PTC added to acid solution and digesting on water bath for 30 minutes
17.	Tellurium sulphide TeS_2	brown	K_2TeO_3	
18.	Arsemic sulphide AS_2S_3	yellow	AS_2O_3	PTC added to hot acid solution
19.	Antimony sulphide Sb_2S_3	orange	KSb tartrate	-do-

In all cases the precipitate was collected by filtration through whatman filter paper No. 40, washed thoroughly with distilled water and then with 20% alcohol. They were then dried as described and ready for subsequent analysis.

REFERENCES

1. Mellor, J. W., Comprehensive Treatise on Inorganic and Theoretical Chemistry. Longmans. Green & Co. 1961, Vol. VI. pp.119.

2. Singh, K., Ph.D. Thesis, University of Delhi, 1967.

3. Johri, K. N., Analyst. 1961, 86, 487.

4. Johri, K. N., Kanshik, N. K., and Singh, K. Curr. Sci. 1967, 36, 458.

5. Mellor, J. W., A Comprehensive on Inorganic and Theoretical Chemistry. Longmans, Green & Co. London, 1961 Vol. VI pp. 129.

6. Gordon, L., Salutsky, M. L., and Willi[illegible]rd, H. H. precipitation from Hamogeneous solution. John Wiley & Sons, Inc. N.Y. 1959.

7. Johri, K. N., Kanshik, N. K., and Singh, K., Journal of Thermal Analysis. 1970, 2, 37.

8. Kaushik, N. K., Ph.D. Thesis University of Delhi, India, 1969.

C H A P T E R III

DIFFERENTIAL SCANNING CALORIMETRIC (DSC) STUDIES OF METAL THIOCARBONATES AND SULPHIDES

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C H A P T E R III

DIFFERENTIAL SCANNING CALORIMETRIC (DSC) STUDIES OF METAL THIOCARBONATES AND METAL SULPHIDES

The DSC-2 Differential Scanning Calorimeter is a sophisticated instrument for the measurement and characterization of the thermal properties of materials. It detects and record transition such as melting, boiling, dehydration or crystallization in the sample material.

Generally the operator, using front panel controls, brings the average temperature of sample holders to a desired initial temperature, selects a program rate and programs the desired change in average temperature of the sample holders to a desired final temperature.

The Instrument has been used to study metal thiocarbonates and sulphides phase transitions and heat energy involued when heated from 323°K to 880°K.

EXPERIMENTAL

Apparatus

Differential Scanning Calorimeter, Model DSC-2 made by Perlim Elmer was used. Gold and Alumium plates (pans) were used to contain samples for the DSC analysis. High sensitive electric balance was also used for weighing samples. Unless other wise stated chart speed was 20mm/min. and heating rate 20^{o}/min.

III - 1 SAMPLE PREPARATION

Model DSC-2 is suitable for analysing both solid and liquid samples. Solid samples can be in film, powder, crystal or granular form.

Although quantitative accuracy will remain the same regardless of sample shape, the qualitative appearance of a run will however be affected by the sample configuration. Therefore, for maximum peak sharpness and resolution, a configuration which maximizes the contact surface between the pan and sample is desirable.[1] Thin discs or films of sample or fine granules spread in a thin layer on the pan bottom are the best shapes for optimum performance.

The samples were dried and finely powdered and then weighed to fourth decimal place on a sensitive balance. For the purpose of comparison a contant weight of 5.00 milligrames of each metal thiocarbonate or metal sulphide were taken. The sample was securely covered and corked with lids using a crimper-press and finally sealed with set of forceps ready for running. In all cases aluminium or gold sample pans were used. Samples analysed with gold pans were FeS, Ag_2CS_3, $PbCS_3$, MnS, $NiCS_3$, CuS, Tl_2CS_3, SnS and PbS white the remaining ones were analysed using aluminium. Temperature ranges were set as the same for both sample pans used.

Procedure Followed

With the DSC-2 model, as with every thermal analyser, there is always a "trade-off"[2] between sample size and scanning rate when trying to obtain high sensitivity and peak resolution in a particular analysis. This "trade-off" is necessary because sensitivity is imposed by using small samples scanned at low programme rates.

After taking care of the above drawback, the sample was weighed carefully and sealed in an aluminium or gold plate and ready for use. The Sample pellet was now introduced into to the machine after making necessary adjustments. Heating rates, voltage, control nobs were all observed and recorded on the chart paper for each sample. Since each sample pan, which contained the substance itself has a range of temperature within which the transition temperatures occur, it was then possible to see and know when all reactions must have been completed. The machine was switched off and allowed to cool to attain the environment temperature.

The chart which contained the various peaks and lines were then removed for analysis and interpretations.

III - 2 ANALYSIS AND INTERPRETATION OF DATA

Heating rate of $20^{\circ}C$/min was stable throughout for a regulated range of the instrument. The range was 10 mcal/sec. set for a programmer.

The programmer is completely digital, with 30 digital steps per degree.[3] The temperatures were also set to a tenth of a degree on the chart.

When a transition such as melting, boiling, hydration or crystalization occurs in the sample material, an endothermic or exothermic reaction takes place. The change in power required to maintain the sample holder at the same temperature as the reference holder (i.e. its programmed temperature) during transition was recorded as a peak. The following could be computed for from the chart:-

(i) Area of Peaks: This was traced with similar chart paper and cut out nicely to represent the area enclosed within the peak. A one square inch was cut out from the same chart paper and weighed easily and then weight-area proportions worked out.

For example one square inch weighed 0.0377 gm, therefore areas of other peaks could be related and calculated for each peak or resolution curve of all the substances scanned.

(ii) Transition Temperature: It is the temperature which the sample undergoes change in state. This can be easily determined by drawing a base line to connect the edges (bottom) of the peak enclosed therein. For sharper peak, a central line dividing the peak into two was taken as the transition temperature and for fairly broad based peaks, interpolation of the base and peak was done to get the transition temperature point.

(iii) Transition Energy: There always exist an amount of heat evolued or absorbed, during the cause of scanning, in this change is called Transition energy.

The energy of the first transition is directly proportional to the area under the transition peak. The general formula connecting these relationships is:-

$$H = \frac{K \times R \times A}{W \times S} \quad .. \quad .. \quad .. \quad (1)$$

where:-

H = Transition energy in Cals/gm.

K = Calibrated instrument constant.

R = Range Sensitivity in millicals/sec-inch.

A = Peak area in square inch.

W = Weight of Sample in milligrams.

S = Recorder chart speed in inch/sec.

Heat transition of indium was taken as standard and used as reference in all the experiments carried out. It was also used for determining the instrument constant K. K was found = 1.04 for all DSC-2 experiments.

(iv) Transition Rate: The instantaneous rate of a transition as a function of time (isothermal Scan) or temperature (dynamic Scan) is calculated from the equation:-

$$\text{Transition rate (Tr)} = \frac{K \times R \times D}{W} \quad .. \quad .. \quad (2)$$

where:-

Tr = is transition rate in Cal/g-sec.

K = Instrument Calibration constant

R = Range sensitivity in mCal/Sec-in.

D = Ordinate displacement in inches.

W = Weight of Sample in milligrams.

The instrument constant K was best determined with the sapphire standard, in the range required (i.e. $273^{o}K$ - $773^{o}K$). The K factor was also calibrated within the range and was found to be const. $(K = 1.04)^{4}$.

The instrument range was 10mV.

Chart speed was 20mn./min. = 0.0131 inch/sec.

Heating rate was 20^{o}/min.

Since the whole width of the paper was 9 inches. The range

R was therefore $\frac{20}{9}$ = 2.22 mCal/sec-in. It was reported (see III-1) that all weights used was each 5 milligrams of samples. Therefore, using equations (1) and (2) above and with the following constants K, W, R and S all known, the Transition energy and transition rate[5] could be calculated for each sample.

The constants have the following values:-

K = 1.04

W = 5.00 milligrams

R = 2.22 mCal/sec-in

S = 0.0131 inch/sec.

The values of Transition energy (H) in Cal/gram. and Transition rate in Cal/g-sec. were computed for and entered into the table as shown.

Duval and Co-workers[6-9] have reported similar energy values of sulphide compounds before and most of the reported energy values were in close agreement with those studied here. Those were sulphides precipitated with hydrogen sulphide and sodium sulphide. A critical review of the thermal behaviour of metal sulphides precipitated by different thio-reagents has been given by Duval[10] as well.

TABLE I

PEAK AREAS AND WEIGHTS OF METAL THIOCARBONATES AND SULPHIDES STUDIED BY DSC ANALYSER

Sample	Peak Weights (g)	Ordinate (D) (inch.)	Area (A) (Sq. in.)
FeS	0.0377	2.01	2.0584
$SnCS_3$	0.1625	5.71	4.3104
Ag_2CS_3	0.0771	4.50	2.0451
$PbCS_3$	0.0494	0.98	1.3104
MnS	0.0651	0.98	1.7268
$NiCS_3$	0.0426	1.10	1.3000
AS_2S_3	0.0214	0.47	0.5676
CoS	0.0549	1.22	1.4562
CuS	0.0313	0.91	0.8302
SnS	0.0554	0.71	1.6495
NiS	0.0456	0.51	1.2096
Tl_2CS_3	0.0189	1.30	0.5013
WS_2	0.0740	0.95	1.9629
Sb_2S_3	0.0108	0.39	0.2865
PdS_2	0.0087	0.39	0.2308
$CoCS_3$	0.0585	1.06	1.5517
Ag_2S	0.0207	2.76	0.5491
PbS	0.0461	1.02	1.2228
$Bi_2(CS_3)_3$	0.0217	0.95	0.5756
Au_2S_3	0.0243	0.71	0.6446
Tl_2S	0.0147	2.21	0.3899

TABLE II

ENERGY CHARACTERISTICS OF METAL THIOCARBONATES AND SULPHIDES

Sample	Transition Temperature (°K)	Transition Rate (Tr.)	Transition Energy (ΔH)
FeS	564	0.93	72.56
$SnCS_3$	430, 700	2.64	151.94
Ag_2CS_3	452	2.07	72.90
$PbCS_3$	460	0.45	46.20
MnS	415, 480	0.45	60.87
$FeCS_3$	544, 490	0.51	45.82
AS_2S_3	710	0.20	20.00
CoS	388	0.56	51.33
CuS	590, 702	0.42	29.26
SnS	405	0.33	58.14
$NiCS_3$	644, 490	0.55	24.96
Tl_2CS_3	505, 705	0.60	17.67
WS_2	385	0.44	69.19
Sb_2S_3	505	0.18	10.10
PdS_2	710	0.18	68.14
$CoCS_3$	435	0.49	54.70
Ag_2S	453	1.28	19.36
PbS	460	0.47	43.10
$Bi_2(CS_3)_3$	446	0.44	20.29
Au_2S_3	496	0.33	22.72
NiS	522	0.24	42.64
Tl_2S	494, 718	1.02	13.75

III - 3 DISCUSSION OF RESULTS

A sharp, first order transition, such as the melting of a pure material is an isothermal behaviour.[11] Hence since the temperature of the sample does not increase during the transition, the temperature of transition is that temperature at which the transition is first detected. From values it was not influenced by variations in sample size as would be the peak temperature.

From table II it is also apparent that the larger the peak area, the greater the energy of transition for example $SnCS_3$ with a peak area of 4.3104 square inches has a transition energy of 151.94 Calories whereas Ag_2CS_3 with a peak area of 2.0451 square inches has a transition energy of only 72.90 calories.

It can be deduced generally that the metal sulphides needed greater energy of transition than metal thiocarbonates. For example Tl_2CS_3 decomposed to Tl_2S at 505°K and the Tl_2S decomposed to its oxide at 705°K. PdS decomposed to its oxide and finally to sulphate at 710°K; clearly showing that heavy metal sulphides needed higher energy to decompose than sulphides of lighter metals (see table II).

In table II, colum 2, some of the metal thiocarbonate and sulphide have two transition temperatures e.g. $NiCS_3$ 490K and 644K for the decomposition of thiocarbonate to sulphide

and finally to the oxide respectively. Other metal thiocarbonates have only one decomposition temperature because the second sulphide transition temperature was higher than the maximum temperature attainable by the sample pan during analysis;[12] and hence only that of the thiocarbonate decomposition was observed.

REFERENCES

1. Perkin-Elmer DSC-2 Model Reference Hand Book No. 1, 1976, U.S.A.

2. Hannevijk, R., and Haighton, E. DSC Studies on Polymeric Materials and Soaps, 1958.

3. Wendlant, W. W., Thermal Methods of Analysis. Interscience, New York, 1964.

4. Perkin-Elmer, DSC-2 Issue No. 2, Standard Handout using Indium Standard, 1978.

5. Wendlant, W. W., A Chemist Analyst, 1957, 26, 78.

6. Duval, C., Anal. Chim. Acta, 1955, 13, 427.

7. Moser, L., and Beer, M., Z. Anorg. Chem., 1924, 134, 67.

8. Taimni, I. K., and Tandon, S. N., Anal. Chim. Acta, 1960, 22, 34.

9. Duval, C. and Wadier, C., Anal. Chim. Acta, 1959, 20, 3 263.

10. Duval, C., Inorganic Thermogravimetric Analysis, Elsevier Publishing Co., Amsterdam, 1963, 463.

11. Urzendowski, R. and Guenther, A. H., Thermal Analysis. Academic Press, New York, London, 1969.

12. Martens, P. H., Bull Inst. Agron et start., Recherches Gembloux, 1953, 21, 134.

C H A P T E R IV

THERMOGRAVIMETRIC (TG) STUDIES OF METAL THIOCARBONATES AND SULPHIDES

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C H A P T E R IV

TGA STUDIES OF METAL THIOCARBONATES AND SULPHIDES

IV - 1 TGA METHOD OF ANALYSIS

Thermogranimetric Analysis (TGA). Thermogranimetry is the science and art of weighing substances while they are being heated. In the analysis, these changes in weights are measured as a function of increasing temperature.[1]

Thermogranimetry, like other thermal methods that encorporate this definition, provide information relating to certain physical and chemical phenomena thus:-

Physical phenomena	Chemical phenomena
Crystalline transition	Chemisorption
Fusion	Desolvation
Vaporation	Decomposition
Sublimation	Oxidation/reduction
Absorption	
Desorption.	

The basic instrumental requirements for thermogravimetric analysis are a precision balance and a furnace that is programmed for a linear rise of temperature with time.[2]

Although information can be obtained by carrying out the weighing operations manually, nowadays automatic recording of the weight and temperature are usual. This ensures that no features of the weight loss-temperature curve are overlooked.

The results from a thermogravimetric run may be presented by:-

(i) Weight (corrected weight) versus temperature (or time) curve referred to as thermogranimetric curve.

(ii) Rate of loss of weight versus temperature curve, referred to as the differential thermogravimetric curve.

IV - 2 FACTORS AFFECTING THERMOGRAVIMETRIC ANALYSES

TGA curves may be influenced by two groups of factors. These are the instrumental factors and the sample characteristics factors.[3]

(i) Instrumental factors:- These include the furnace geometry, heating rate, its atmosphere type and conditions. Also the effect of sample holder, geometry, size and compositions. Under this factor, others like sample holders thermal characteristics and whether the holder is open or loosely covered also affect the analysis. To an extent random fluctrations in balance and recording mechanisms affect the general procedure of experiments.

(ii) Sample Characteristics:- These include its form, nature, size, volume particle size and distribution. Similarly its packing density, thermal conductivity, heat capacity and the solubility of gas in sample will have to be taken into consideration. Also heat of reactions and speed of the reactions in general affect the values.

"Stanton" Thermobalance is one of the TGA machines recently made to overcome all these short comings listed above.

Stanton thermobalance is located in the M.Sc. laboratory of Chemistry Department, Ahmadu Bello University, Zaria.

IV - 3 (a) THE SAMPLE

The actual sample weight selected for a particular thermobalance depends to some extent upon the actual figures loss to be expected. The following figures are given for guidance where a weight loss of between 25 and 100% is expected:[4,5]

For a milligram model thermobalance a sample weight of 500 - 1000 mg. is usual.

For a fifth milligram model thermobalance a sample weight of 50 - 100 mg. is usual.

"Stanton" Thermobalance is suitable for a fifth milligram model type. i.e. 100 - 200 mg. accomodative for all experiments. The sample should be firmely ground (200 mesh) and completely dried for clearer resolutions.

Present Studies

Johri and Co-workers[6] carried out thermal studies of some metal thiocarbonates and sulphides precipitated with PTC by thermogravimetric method.

Taimni and Co-workers[7-9] earlier studied thermal behavior of sulphides precipitated with alkali sulphides.

In the present study, attempt has been made to study the remaining thiocarbonates and sulphides by the TGA Method.[10]

The following compounds have been studied: Thallium sulphide, Ferrous sulphide, lead sulphide, silver thiocarbonate, zinc sulphide, Manganese thiocarbonate and Nickel sulphide.

The widest application of thermogravimetric analysis lies in investigating analytical procedures for determining suitable and stable weighing compound forms of elements within specified limits of temperature. The main aim of undertaking such study is to obtain information relating to the decomposition with respect to sample weight as it is subjected to heat. The curve should be constructed as plot of weight against temperature.

With the present study, the data would determine the ranges of different temperatures for the different stages, deviations from stoichiometric compositions, and mode of transformation of metal sulphides or thiocarbonates to sulphide, sulphate and oxide form with rise in temperature.[11]

IV - 4 (b) TGA STUDIES OF Tl_2S, FeS, PbS, Ag_2CS_3 ZnS, $MnCS_3$ and NiS

EXPERIMENTAL

Reagents

4M Potassium thiocarbonate reagent prepared by the modified direct method[12] was used as a stock solution and its working solutions obtained by suitable dilutions.

Metal Solutions: All the metal ion solutions were prepared from the salts of Analytical grade reagents.

Apparatus: Stanton's Model - 1 thermobalance installed at the Department of Chemistry, Ahmadu Bello University, Zaria was used in running all the samples.

Procedure

The precipitate of metal thiocarbonates and sulphides were prepared in accordance with the procedure[13] described in tables 1 and 2 in Chapter II.

The metal thiocarbonates and sulphides were used for the investigations on the "Stanton's" thermobalance. The thermal analyser uses thermocomples of Pt - Pt/Rh, and platinum crucible was used for holding sample. All investigations were carried out in air atmosphere.

The platinum crucible was heated to 100^{o}C and cooled before putting the sample in it. The crucible was weighed before and after transfering the sample. The samples should be finely ground, and should be able to pass a 100 mesh (i.e. smaller than 150μ).

The sample was then added to the crucible and then lightly tapped to ensure even settling and reweighed within specified limits. It was then transferred and placed securely in the heating chamber of the TGA machine.

All necessary adjustments made and the heating started till when all the expected reactions must have taken place. Thermogravimetric curves showing the changes in weight against temperatures were simultaneously recorded.

IV - 5 RESULTS AND DISCUSSION

(a) The Thermogravimetric data were then collected and corresponding change in weight for short temperature intervals of 100°C were recorded for each experiment. A graph of change in weights versus temperature was plotted to show the general behaviour of the sample when subjected to continuous heating in the furnace of the TG machine.

(b) Thermogravimetric behaviour.[6]

Thalium sulphide (Tl_2S): There was no appreciable change in weight between 50 - 150°C. At 150°C there was a sharp decrease in weight due to oxidation of the sulphide to its oxide. At 360°C, a combination of mixed oxides of thalium started to gain weight steadily till 690°C where all the mixed compounds remained stable.[14]

Ferrous sulphide (FeS): No sign of loss of moisture and weight up to 250°C. It decomposed and lost weight steadily till at 450°C. At 450°C the hot iron starting being oxidised to its various forms of oxides and hence a steady increase in weight till at 650°C where it remained stable. (see fig. I.)

Silver thiocarbonate (Ag_2CS_3): Showed a conspicuous stability to heat from 50 - 330°C. The thiocarbonate lost carbondisulphide at 330°C and decomposed gradually to various oxides of silver. These mixed oxides remained stable between temperatures of 400°C

and 600°C. There was further oxidation to sulphate and other forms of oxides upto 700 showing appreciable increase in weight.

Zinc Sulphide (ZnS): There was also a gradual loss in weight due to decomposition of the sulphide at 300°C. There was an increase in weight due to the oxidation of the zinc to its sulphate and other forms of oxides which represented the steady rise of the curve from 300°C to 700°C.

Manganese thiocarbonate ($MnCS_3$): Like all other thiocarbonates, manganese thiocarbonate lost weight gradually up to 100°C due to adherent moisture. The thiocarbonate also lost carbondisulphide due to its decomposition at 400°C.

The manganese sulphide then started being oxidized at 400°C to manganese sulphate and other oxides of manganese. These contributed to the sharp rise in the curve from 550°C to 620°C as claimed by Terem and Aklam.[15]

Nickel Sulphide (NiS): It was very stable up to 50°C but started decomposing at 50°C to nickel oxide at 150°C. The sharp decrease in gradient could also be attributed to loss of moisture before real decomposition temperature. The compound continued losing weight after remaining stable within the region of 150 - 350°C and ultimately the oxides gained weight due to their conversion to sulphate at 650°C and hence steady increase in weight from 500°C to 650°C. Similar studies reported by Domassieux and Malard.[16]

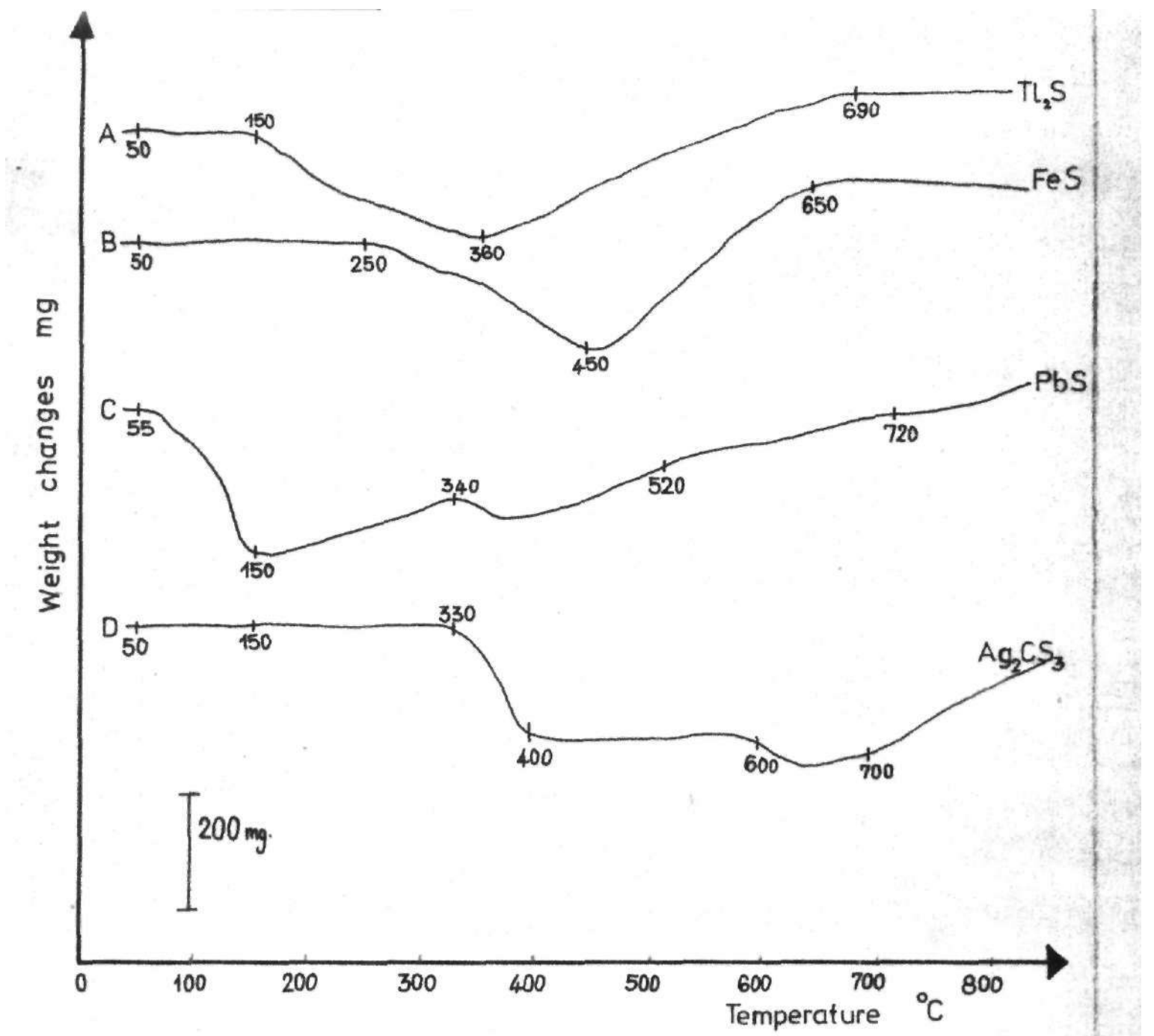


Fig 1. TG curves

A : Thalium Sulphide [Tl_2S]

B : Ferrous Sulphide [FeS]

C : Lead Sulphide [PbS]

D : Silver Thiocarbonate [Ag_2CS_3]

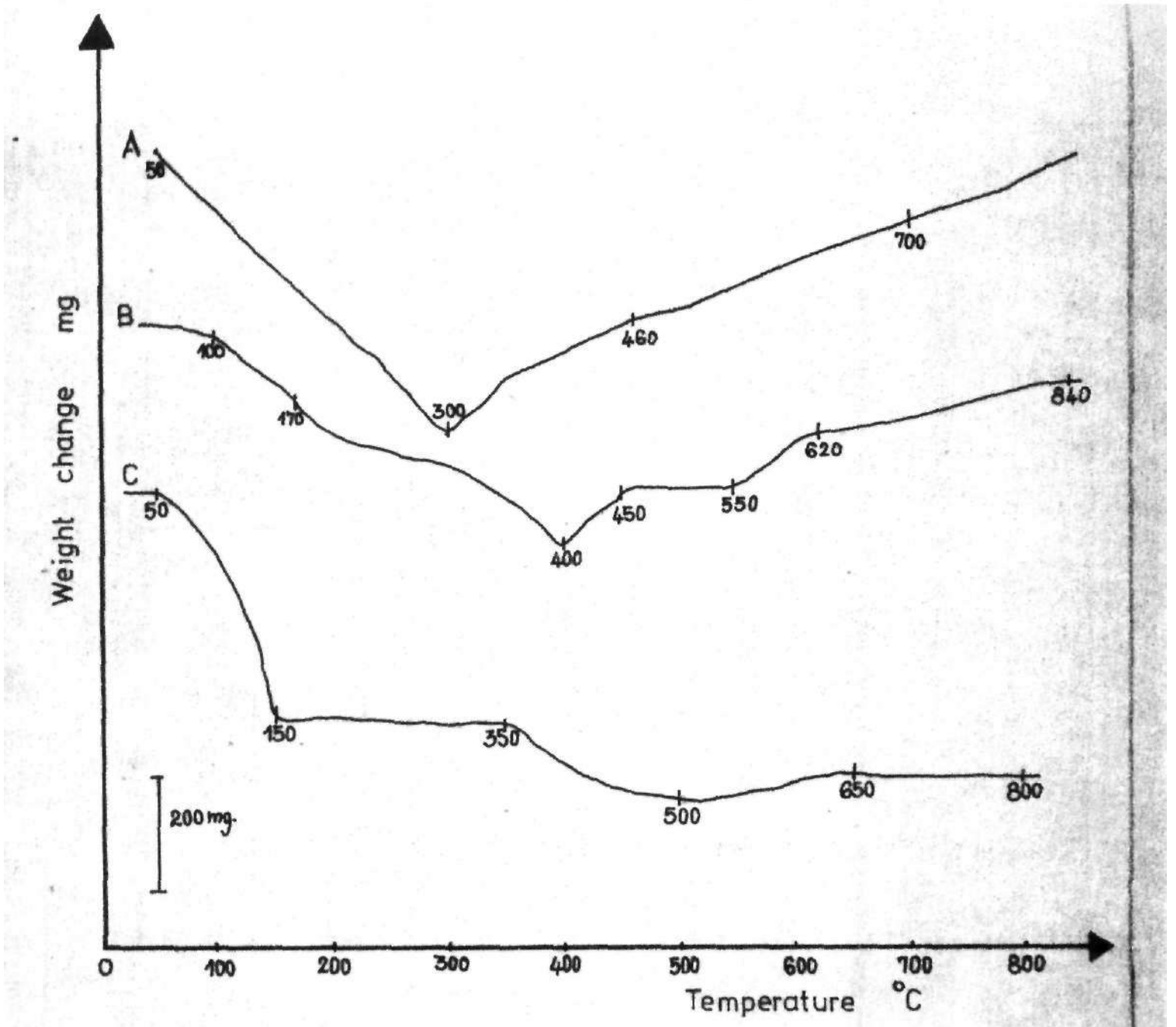


Fig 11 TG curves of

A Zinc Sulphide (ZnS)

B Manganese Thiocarbonate ($MnCS_3$)

C Nickel Sulphide (NiS)

C H A P T E R V

DTA STUDIES OF METAL THIOCARBONATES AND SULPHIDES

V - I DTA METHOD OF ANALYSIS

Differential thermal analysis (commonly abbreviated to DTA) is a technique of recording the difference in temperature between a substance and a reference material as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controled rate.[1-2]

Like all thermal methods, DTA gives a veriation of different peaks on the curves and it is these peaks that are the primary value of the method. It has been observed that a symetical peak yields shape ratio of unity whereas lower or higher values indicate increasing assymetry in either direction.[3]

Throughout this study great care was taken both with the apparatus and with the experimental techique employed so as to select conditions leading to a baseline with $T = 0$. It has to be clear too that the amount of heat supplied by the source to the sample is greater than that supplied to the reference in

endothermic reaction. And conversely the amount of heat supp supplied to the sample from the source is less than that supplied to the reference material over the whole range of an endothermic peak.

Reflections of transformations in any DTA curve are broadly of fine classes.[4,5] These are phase transition, solid state reaction, decomposition, reaction with an active gas (surface reaction) and second order transitions (a change in entropy without a change in enthalpy).

In all forms of classes, peak areas are characteristic of each and is independent of heating rate, the rate at which the reaction takes place, and the specific heat of the sample. It however, depends on heat of reaction per unit volume of the sample, conductivities of the materials in the furnace and sample and heat transfer coefficient between holder and furnace wall.[6]

Present Studies

In the past majority of the DTA investigations have been carried out in static air atmosphere.[6] This technique is now considered very important especially in phase study of chemical substances.

There has been no reported work on DTA studies on thio-carbonates and sulphides precipitated with PTC; whereas studies

on sulphides precipitated with reagents other than thiocarbonates have been reported earlier.[7-9]

DTA study on sulphides was also reported by Hiller[10] and Probathain. They reproduced curves of the sulphide compounds using an inert atmosphere.

Similar studies by Brownell,[11] Kopp[12] and Kerr[12], and Erdg[13] et al. on sulphides of iron, nickel, cobalt and zinc were undertaken.

Owing to tremendous analytical importance of PTC,[14,15,16] attempt has therefore been made to carry out Differential thermal studies of various metal thiocarbonates and sulphides precipitated with PTC reagent.

V - 2 DTA STUDIES OF $ZnCS_3$, $MnCS_3$, $PbCS_3$, FeS, PtS_2, TeS_2, Bi_2S_3, PdS_2 and Sb_2S_3

EXPERIMENTAL

Reagents:- Aqueous solution of potassium thiocarbonate prepared by the modified direct method was used as a stock solution and its working solutions were obtained by suitable dilutions. The metal ion solutions were prepared by dissolving analytical grade salts (Analar) in distilled water. Similarly all other chemicals used were of analytical grade. (see Table I and II).

Apparatus:- A derivatograph made by MOM Budapest, Hungary in the Department of Geology, Ahmadu Bello University, Zaria was used at a regulated speed of $10^{o}C$/~~sec~~ Min. and a chart speed of 2 Cm/minute at a regulated voltage of 10 mV.

Procedure

A weighed sample of dried metal thiocarbonate/sulphide (200-500)mg (2·0c-5·0c) was transferred to a crucible freshly tared after heating and subsequently stored in a dessicator. The sample was then subjected to a heating rate of $10^{o}C$ per ~~second~~ Minute in an atmosphere of air. The data were collected for a range of temperatures up to $1000^{o}C$. The data collected, values corrected for buoyancy, were used for plotting different points of the original graph on X and Y axes. That is change in temperature ΔT versus temperature T. (see Fig. I - III).

V - 3 RESULTS AND DISCUSSION

The Data collected from this analysis were plotted as shown in fig. I - III. The curves characteristics can be summarized as shown in the table below.

TABLE I

DTA RESULTS FOR METAL THIOCARBONATES AND SULPHIDES

Curve	Formula	Phase Transition ^{o}C	Dissociation ^{o}C	Melting ^{o}C
A	$ZnCS_3$	175	285	625
B	$MnCS_3$	140	600	750
C	FeS		750	775
D	PtS_2	100	225	750
E	$PbCS_3$	300	530	915
F	TeS_2		530	750
G	Bi_2S_3	370		825
H	PdS_2			840
I	Sb_2S_3	300	375	835

Zinc Thiocarbonate ($ZnCS_3$). Showed a phase[1] transition at 175^{o}C after loosing some adherent moisture. It dissociated at 285 °C and maintained a steady temperature up to 640^{o}C where it started melting.

Manganese Thiocarbonate ($MnCS_3$): Lost moisture and ~~volat~~ volatile material between 30 and 150°C. It decomposed to give the metal sulphide which was stable up to 600°C. The mixture of manganese oxide, manganese sulphide and sulphate steadily decomposed and melted at 750°C.

Lead Thiocarbonate ($PbCS_3$): Showed a stable characteristics till the thiocarbonate decomposed to give the sulphide at 450°C giving an endothermic broad peak. The second peak at 900°C showed different phase transition which is characteristic of most thiocarbonates at higher heating rates to show metastable compounds of unknown stoichiometry.

Iron Sulphide (FeS): Showed a stable behaviour up to 770°C where it decomposed to iron oxide. The endothermic peak at 770°C served as both the dissociation and melting temperature. There was a possibility of presence of heavier iron oxide which had helped to raise the melting point temperature higher and a partial increase in weight.

Platinum Sulphide (PtS_2): The endothermic peak at 150 °C was due to loss of adherent moisture and there was no further appreciable change in composition till it finally melted at about 750°C.

Tellurium Sulphide (TeS_2): It lost moisture and volatile products upto 220°C. The little endothermic peak at 525°C shows decomposition of the compound which apparently became mixed with tellurium oxide and melted at 750°C. Bismuth sulphide (Bi_2S_3)[1] little work appears to have been done on the DTA of bismuth compounds. But decomposition studies of its salts like the carbonates have been undertaken by Shargorodskii and Shor (1954).

The large endothermic peak exhibited by its sulphide at 360°C showed bismuth has a wide variable decomposition points when part of the water of hydration was removed. The temperature of the second peak nearly corresponded with the sulphide prepared from its thiocarbonate and consequently melting point of the sulphide 825°C also coincided with the literature value.

Palladium Sulphide (PdS_2): It showed little or no water of hydration upto 750°C where it finally melted and maintained a constant stable temperature. A

Amtimony Sulphide (Sb_2S_3): It lost moisture and volatile material at 195°C to give an endothermic peak at 300°C which was due to the sulphide decomposition. This also maintained a constant temperature due to formation of its other allotropes and oxides till at 830°C the mixture decomposed and melted.

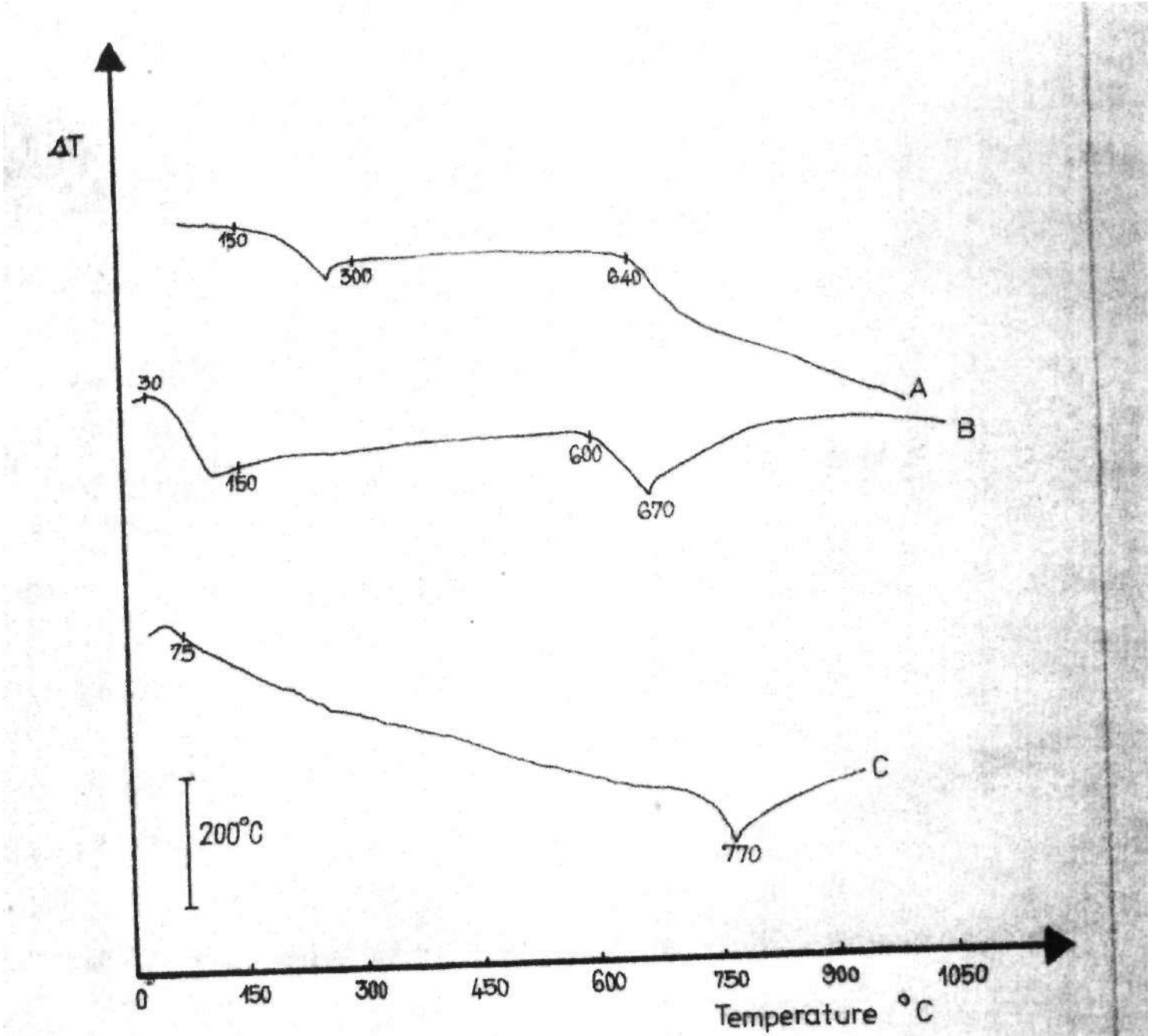


Fig 1 DTA curves of

A Zinc Thiocarbonate ($ZnCS_3$)

B Manganese Thiocarbonate ($MnCS_3$)

C Ferrous Sulphide (FeS)

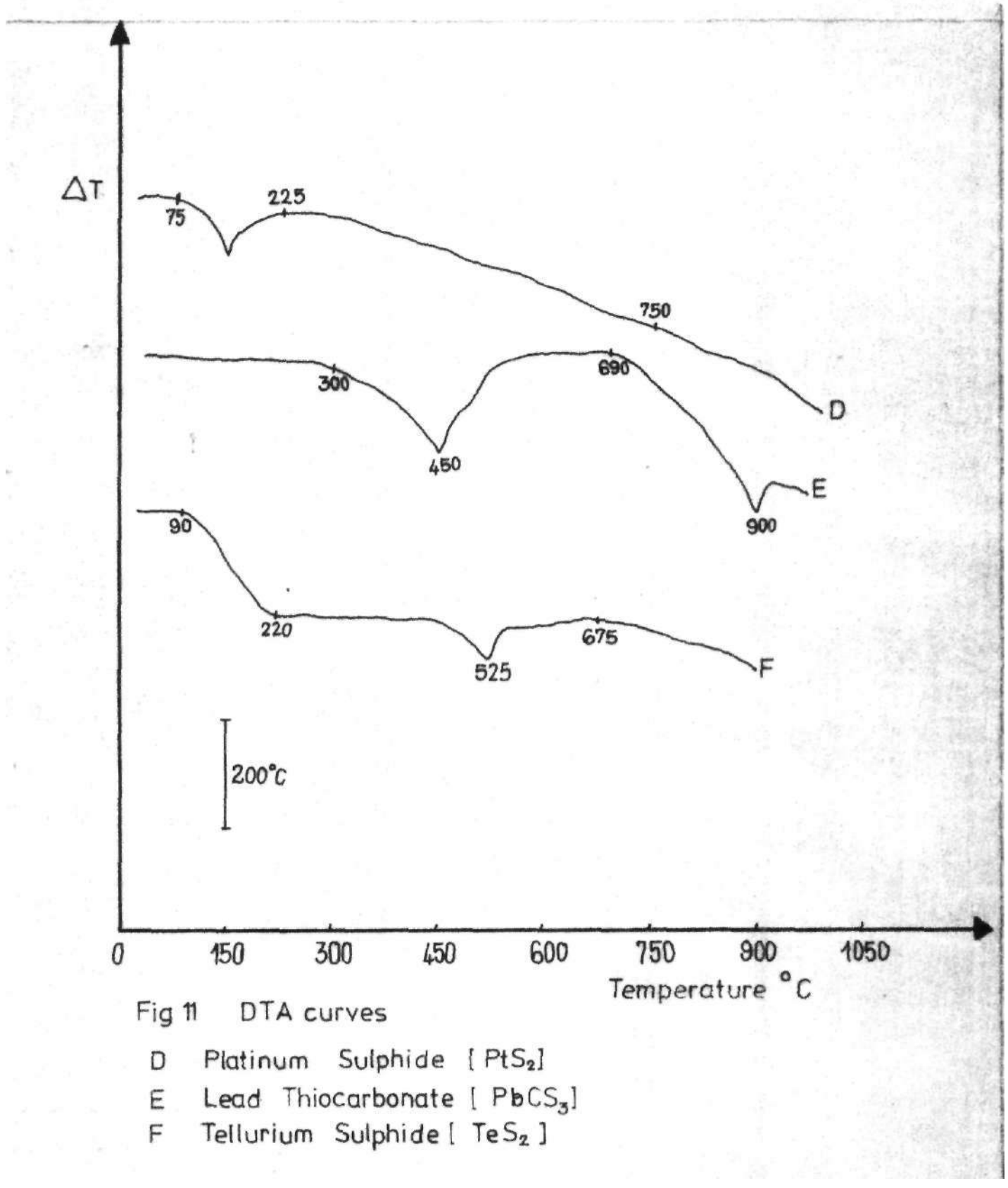


Fig 11 DTA curves

D Platinum Sulphide [PtS_2]

E Lead Thiocarbonate [$PbCS_3$]

F Tellurium Sulphide [TeS_2]

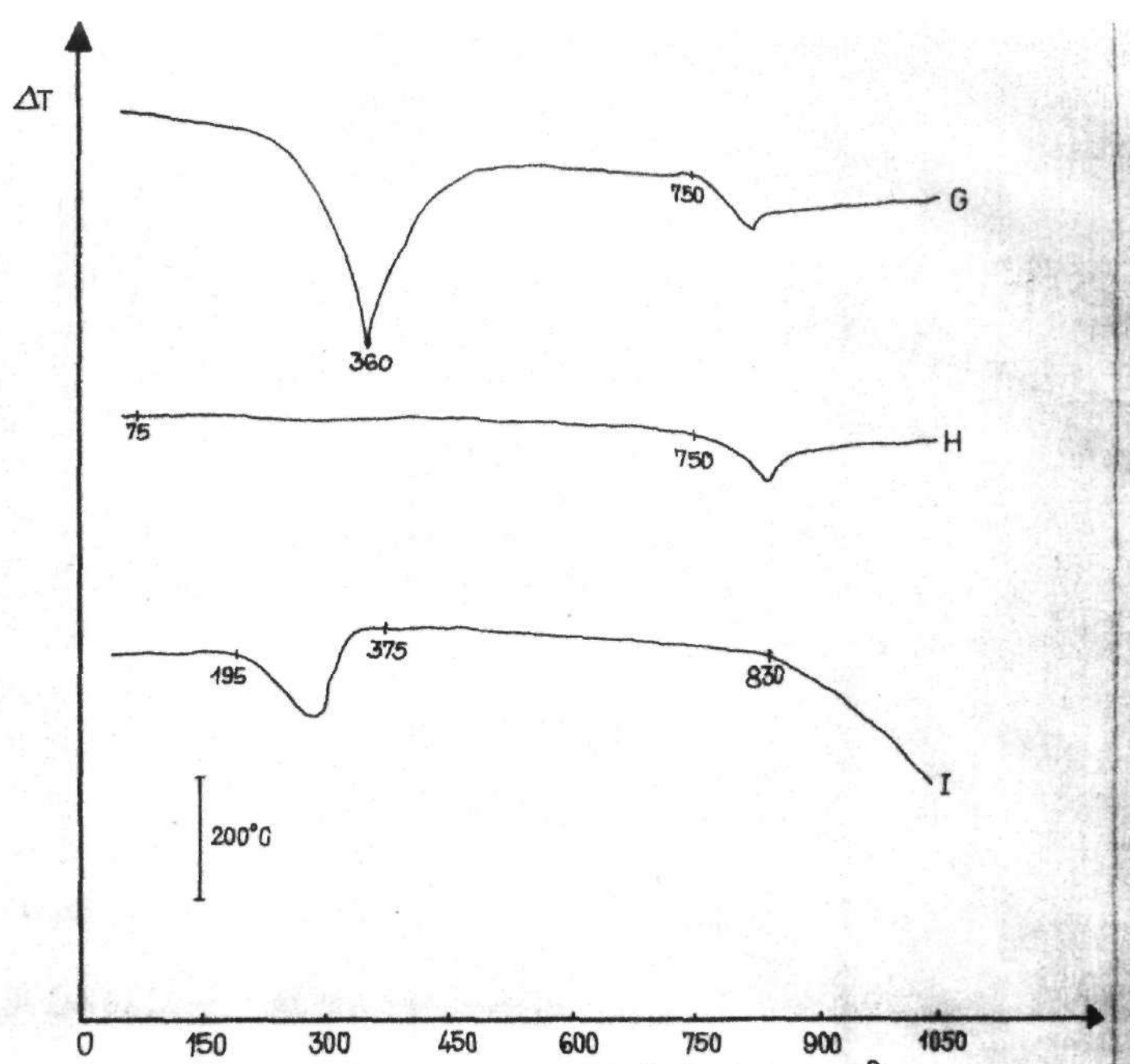


Fig 111 DTA curves

G : Bismuth Sulphide [Bi_2S_3]

H : Palladium Sulphide [PdS]

I Antimony Sulphide [Sb_2S_3]

REFERENCES

1. Barrall, E. M. and Rogers, L. B., Analyt. Chem., 1962, 34, 1106.

2. Mackenzie, R. C., Differential Thermal Analysis, Academic Press, London and New York, 1970.

3. Mackenzie, R. C., and Mitchell, B. D. Analyst, London, 1962, 87, 420.

4. Mackenzie, R. C. Complier, Scifax, Differential Thermal Analysis Data, Index, Clever-Hume, London, 1962.

5. Murphy, C. B., Analyst. Chem., 1966, 38, 443.

6. Garn, P. D., Thermoanalytical Methods of Investigation, Academic Press, New York, 1965.

7. Dural, C., Inorganic Thermogravimetric Analysis, Elsevier Publishing Co., Amsterdam, 1963.

8. Taimni, I. K., and Salaria, G. B. S., Anal. Chim. Acta, 1954, 11, 54.

9. Taimni, I. K. and Tandon, S. N., Anal. Chim. Acta, 1960, 22, 34.

10. Hiller, J. E. and Probsthain, K. Geologie, 1965, 5, 607.

11. Brownell, W. E., J. Am. Ceram. Soc., 1958, 41, 261.

12. Kopp, O. C. and Kerr, P. F. Am. Miner., 1957, 42, 445.

13. Erdey, L., Liptay, G. Svehla G. and Paulik, F. Talanta 1962, 9, 489.

14. Johri, K. N. and Singh, K., Analyst, 1965, 90, 745.

15. Johri, K. N. and Singh, K., Bull. Chem. Soc. Japan, 1967, 40, 990.

16. Johri, K. N., Kaushik, N. K. and Singh, K., J. of Thermal Analysis, 1970, 2, 37.