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A STUDY OF THE DECOMPOSITION OF HIGHER COBALT ARSENIDES BY THERMAL ANALYSIS

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ABSTRACT

The thermal behaviour of the higher cobalt arsenides $CoAs_3$ and $CoAs_2$ has been studied by thermogravimetry. Differential thermal analysis and X-ray diffraction were used as supplementary techniques. Arsenide minerals are often found in ore deposits used as feed materials in some Canadian metallurgical industries. The two compounds were prepared using elaborate experimental procedures to ensure their purity and homogeneity. The triarsenide was found to decompose in two distinct steps; the diarsenide decomposes directly to the monoarsenide CoAs, with the release of arsenic vapour. The verification of existing phases was done at different stages of the decomposition. The influence of heating rate on decomposition was found to be noticeable. An attempt was made to determine the kinetics of the decomposition using non-isothermal thermogravimetric data.

INTRODUCTION

Cobalt arsenide minerals like skutterudite (Co, Fe, Ni)As_3 and safflorite (Co, Fe, Ni)As_2 occur, together with other metal arsenides, in Canadian ore deposits [1] that may be used as feed material for metallurgical industries. Such arsenides are the main source of the arsenic that often appears in the final product and in the flue gases. Arsenic and its compounds are known for their adverse environmental effects, and more understanding of their thermal behaviour is required. The decomposition and oxidation reactions of nickel arsenide NiAs (niccolite) were examined in a recent study by Wilson and Mikhail [2], but very few studies have been published on the thermal behaviour of the higher cobalt arsenides $CoAs_3$ and $CoAs_2$. These two compounds, which are isostructural with skutterudite and safflorite, respectively, are unstable at high temperatures, and earlier studies of the solid–liquid phase relations in the system Co–As have been limited to compounds with arsenic/cobalt ratios of up to 1 [3].

Kochnev [4,5] studied the dissociation of $CoAs_2$ and other lower arsenides, and reported that the compound decomposes to Co_2As_3 and arsenic vapour, with the dissociation pressure reaching 1 atm. at 875 ° C. Ventriglia [6] examined the behaviour of synthetic $CoAs_3$ when heated in vacuum, and reported that the compound loses arsenic to form Co_2As_3 in the temperature range 400–450 ° C, and CoAs at temperatures above 450 ° C. In a recent study by Celmer and Toguri [7], the decomposition pressures of higher cobalt arsenides were determined using a carrier gas transportation method. At high temperatures, the decomposition of $CoAs_3$ was found to take place with the formation of $CoAs_2$ and arsenic vapour, predominantly in the form of the tetramer As_4. The diarsenide was found to decompose to CoAs and arsenic vapour in the form of a mixture of As_4 and As_2. The sublimation pressure of pure arsenic was found to reach 1 atm. around 630 ° C.

There is particular concern about the behaviour of arsenic during roasting, because of strict restraints on arsenic emissions for the protection of the environment. In the present work, the behaviour of $CoAs_3$ and $CoAs_2$ when heated in an inert atmosphere at high temperatures was examined by thermal analysis. This investigation is part of a study of the behaviour of arsenide minerals under conditions that pertain to the roasting of ores and concentrates.

EXPERIMENTAL

High purity cobalt (99.8%) and arsenic (99.5%) were used in the synthesis of the arsenides. Both materials were ground to fine powders and reduced at high temperatures in a hydrogen flow (1.5 h at 800 ° C for the cobalt, and 0.5 h at 450 ° C for the arsenic) to remove any oxides they might have contained. The arsenic powder was further reduced at 500 ° C for a short period of time just before use. For each of the two compounds $CoAs_3$ and $CoAs_2$, stoichiometric amounts of the materials (with 0.5 mass % excess As) were mixed and loaded into a quartz ampoule which was later sealed under high vacuum. Each sample ampoule was also sealed under argon inside another quartz ampoule. The ampoules were then heated slowly (for 24 h) to 700 ° C in a tube furnace and were maintained at that temperature for 15 days, before being air quenched to room temperature. During that period of time, the ampoules were turned around and rotated several times, to promote homogeneous mixing and prevent segregation of the reactants. The purity and homogeneity of the arsenides produced were verified by X-ray diffraction (XRD), microscopic examination and electron microprobe analysis.

Thermal analyses were conducted using a DuPont 9900TA system with a 951TGA thermobalance and high-temperature DTA modules. The thermocouples were coated with a very thin layer of alumina paste for protection against the severe corrosive action of arsenic vapour. This measure may have resulted in a lag in the thermocouple reading of 3–5 ° C. The effect of gas flow rates of between 35 and 65 ml min^{-1} on the decomposition of the arsenides was examined, and the results indicated no significant influence at rates above 40 ml min^{-1}. The experiments were carried out using samples of 20–30 mg in a flow (50 ml min^{-1}) of high-purity oxygen-free nitrogen gas. A number of experiments were terminated at different temperatures, and samples at different stages of decomposition were examined by XRD.

RESULTS AND DISCUSSION

The decomposition trend of cobalt triarsenide $CoAs_3$ in an inert atmosphere was determined in terms of the change in the sample weight with temperature. Figure 1 shows TG diagrams of the process carried out at four different heating rates. It can be seen that under the experimental conditions used in this work, the decomposition occurred in two distinct stages. The first stage consisted of a weight loss of about 26%, which commenced gradually at around 500 °C and ended at 733, 756, 777 and 797 °C for heating rates of 5, 10, 20 and 40 °C min^{-1}, respectively. A theoretical weight loss of 26.4% is associated with the decomposition of $CoAs_3$ according to the reaction

$$CoAs_3 = CoAs_2 + \tfrac{1}{4}As_4 \quad (1)$$

The second stage of weight loss followed immediately and proceeded

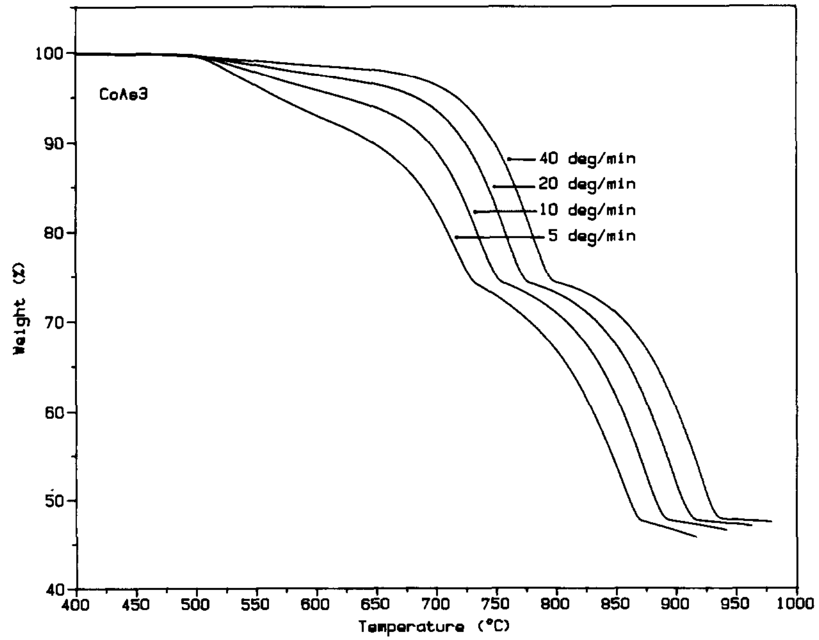

Fig. 1. TG diagrams for the decomposition of $CoAs_3$ in an inert atmosphere.

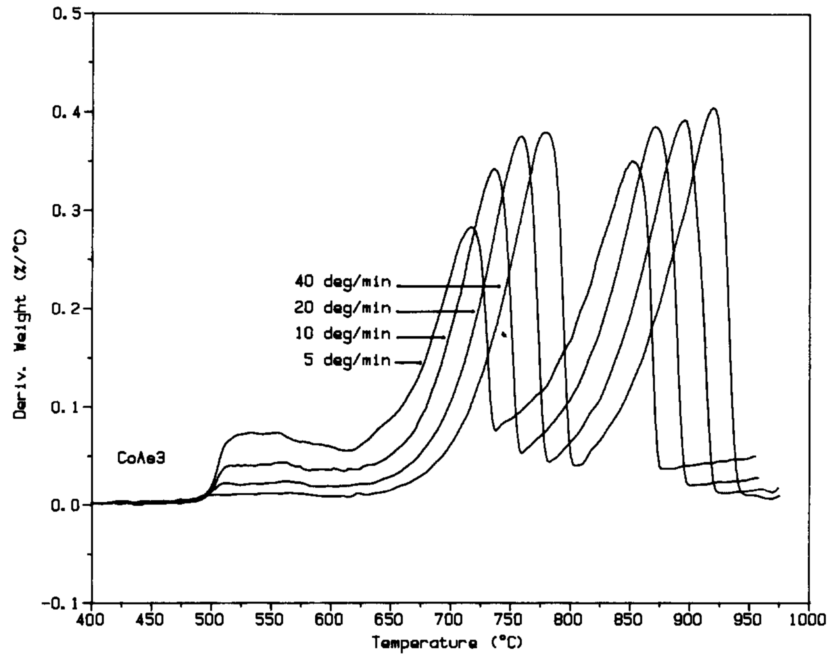

Fig. 2. DTG diagrams for the decomposition of $CoAs_3$ in an inert atmosphere.

smoothly, ending at 871, 894, 918 and 936 °C for the same four heating rates, respectively, with a further weight loss of about 35.8% (relative to the weight of the product of the first stage). This is compared to a theoretical weight loss of 35.9% associated with the decomposition of $CoAs_2$ according to the reaction

$$CoAs_2 = CoAs + \tfrac{1}{4}As_4 \qquad (2)$$

During the decomposition reactions, arsenic vapour condensed on the colder parts of the reaction tube.

It is noticeable in Fig. 2 that in the temperature range 520–630 °C there are small peaks (more apparent at lower heating rates) in the rate of weight loss, which occur slightly below the sublimation temperature of arsenic. This unexpected behaviour can be tentatively explained in terms of a solid state disproportionation of $CoAs_3$ to arsenic-deficient $CoAs_{3-x}$ and arsenic, followed by the volatilization of the latter product. During this process, a build up of arsenic partial pressure in the system would result in a decrease in the rate of decomposition below the sublimation temperature of 630 °C. At lower heating rates, more disproportionation would take place within a given temperature range, leading to higher rates of weight loss as observed on the DTG diagrams. The two major peaks at higher temperatures represent the rates of weight loss during the decomposition of the triarsenide and the diarsenide.

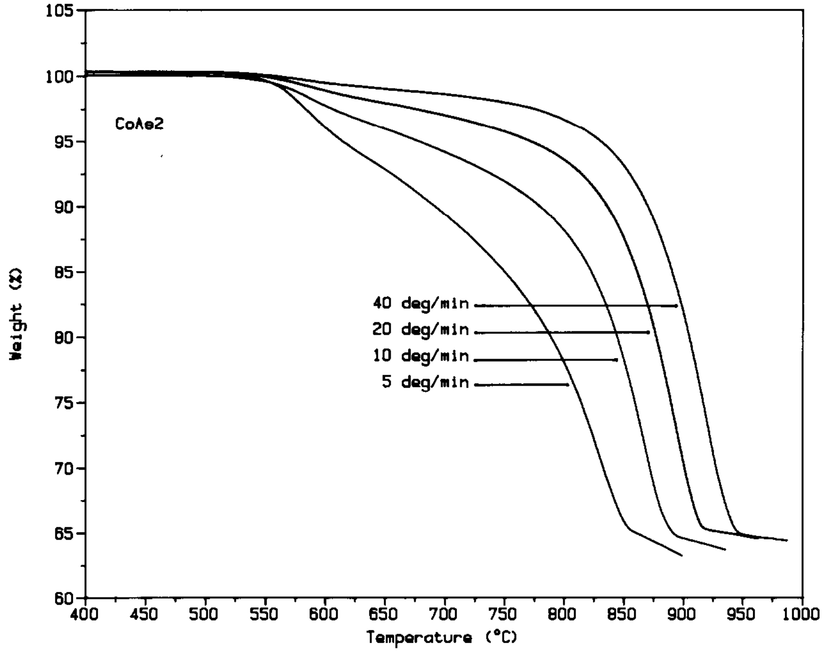

Fig. 3. TG diagrams for the decomposition of $CoAs_2$ in an inert atmosphere.

Figure 3 shows TG diagrams for the decomposition of $CoAs_2$, again for the four different heating rates. The decomposition started gradually at around 550 °C and terminated at 850, 895, 915 and 945 °C for heating rates of 5, 10, 20 and 40 °C min^{-1}, respectively, with a total weight loss of about 35.2%. The slight difference in weight loss between the synthesized $CoAs_2$ and that generated by the decomposition of $CoAs_3$ indicates that the former may have developed traces of surface oxides, despite all the precautions, before examination by thermal analysis. A temporary change in the rate of weight loss in the early stages of decomposition similar to that which occurred during the decomposition of $CoAs_3$ was observed, particularly at lower heating rates. This can be seen clearly on the derivative curves in Fig. 4.

The decomposition of the two compounds was also examined by DTA using a heating rate of 20 °C min^{-1}, and the results are presented in Fig. 5. The DTA diagram for the decomposition of $CoAs_3$ includes two distinct endothermic peaks corresponding to the two stages of decomposition, to $CoAs_2$ and to CoAs. Very little overlap between the two stages is observed. The second diagram, with one endothermic peak, represents the decomposition of $CoAs_2$ in one step to CoAs. The agreement between the decomposition peak of $CoAs_2$ on the two diagrams is obvious.

A number of TG experiments were interrupted at different temperatures during heating of $CoAs_3$ at 5 °C min^{-1}, and the samples examined by XRD.

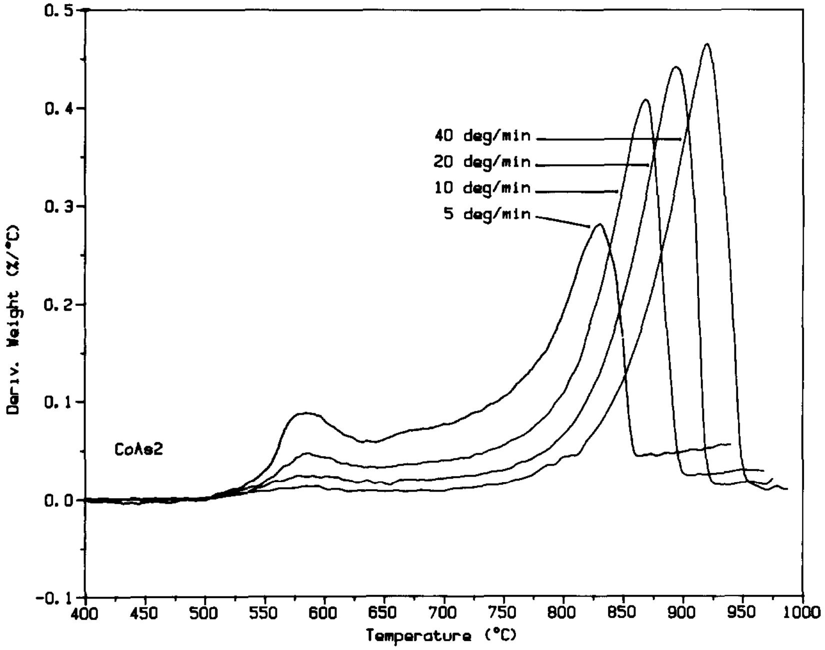

Fig. 4. DTG diagrams for the decomposition of $CoAs_2$ in an inert atmosphere.

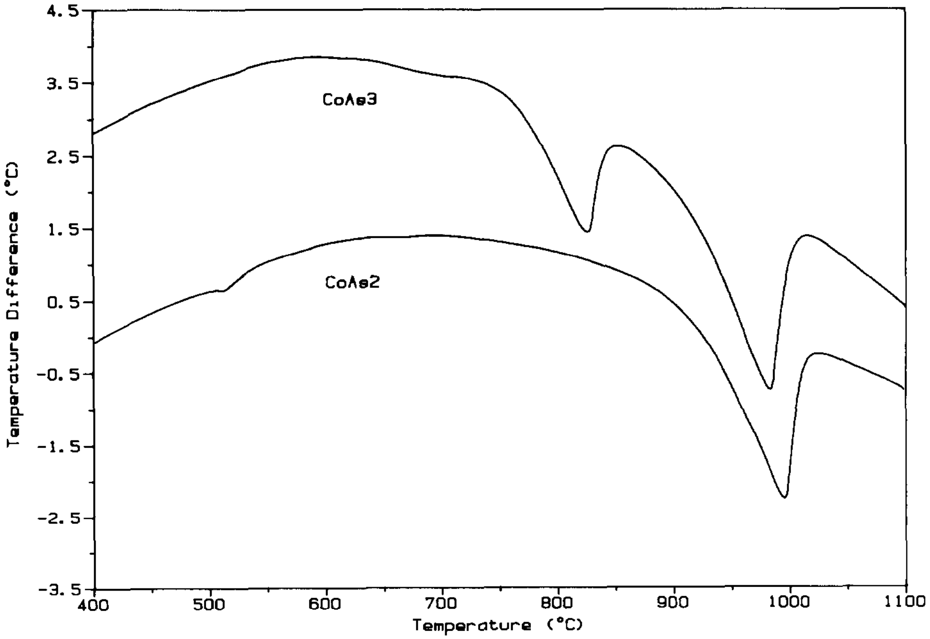

Fig. 5. DTA diagrams for the decomposition of $CoAs_3$ and $CoAs_2$ in an inert atmosphere.

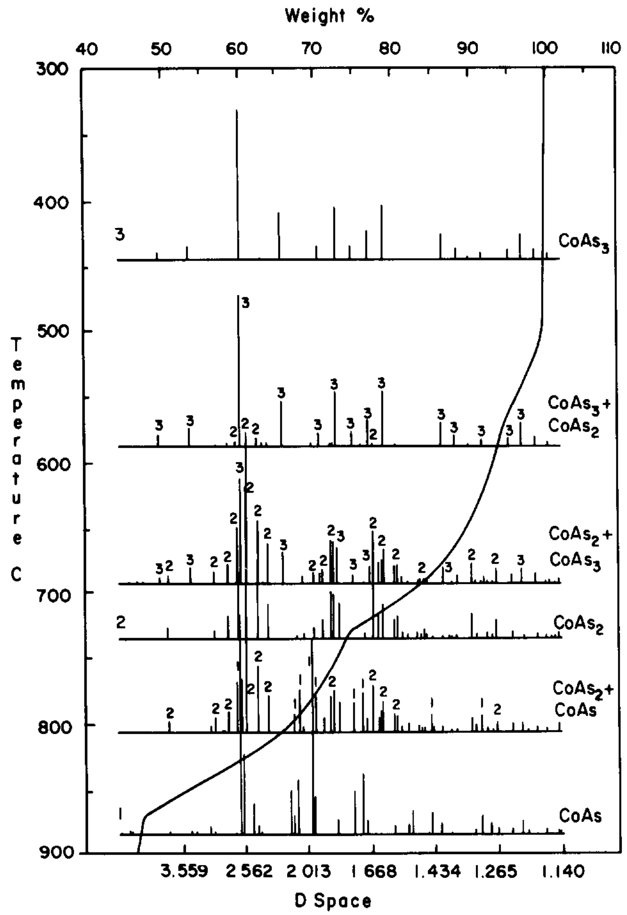

Fig. 6. XRD patterns of $CoAs_3$ and the decomposition products at different temperatures, superimposed on the corresponding TG diagram.

Selected XRD patterns of the starting material at 450 °C and of the decomposition products at 590, 700, 730, 810 and 878 °C are shown in Fig. 6, superimposed upon the corresponding TG diagram. It is apparent that there is no evidence of the existence of phases other than $CoAs_2$ between $CoAs_3$ and CoAs, which is in agreement with the findings of Celmer and Toguri [7]. The XRD pattern at 878 °C indicates the presence of a trace amount of Co_2As, which is an expected decomposition product of CoAs at temperatures below 940 °C, the lower limit of stability of Co_3As_2 [8].

Kinetics

An attempt was made to determine the decomposition kinetics of $CoAs_3$ and $CoAs_2$ from the non-isothermal TG data obtained in the $CoAs_3$ diagrams, using methods previously used for the decomposition of inorganic

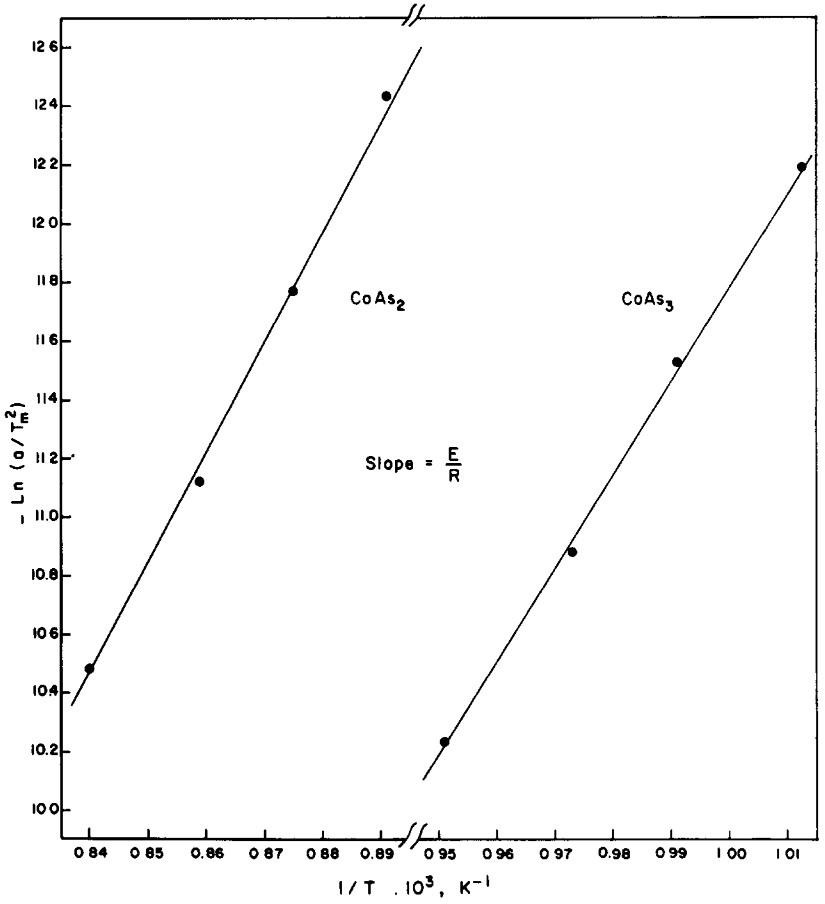

Fig. 7. Decomposition kinetics for $CoAs_3$ and $CoAs_2$ according to eqn. (3).

materials. The two methods were developed by Kissinger [9] and by Ozawa [10], on the basis of the following mathematical models, respectively

$$d\left[\ln\left(a/T_m^2\right)\right]/d(1/T_m) = -E/R \tag{3}$$

$$-\log a_1 - 0.4567\frac{E}{RT_1} = -\log a_2 - 0.4567\frac{E}{RT_2} \text{ (for a given mass)} \tag{4}$$

where a is the heating rate, T_m is the temperature at the maximum rate of reaction, E is the activation energy, R is the gas-law constant and T is the absolute temperature. In the first method, T_m was determined from the DTG diagrams at the different heating rates in Fig. 2. On the basis of eqn. (3), $\ln(a/T_m^2)$ was plotted vs. $1/T_m$ for the two decomposition reactions, resulting in straight lines (Fig. 7) with a slope of E/R. The apparent activation energies for the decomposition of $CoAs_3$ and $CoAs_2$ were found to be 260.4 and 314.0 kJ mol^{-1}, respectively. The second method was applied by plotting log a vs. $1/T$ for constant mass fractions according to

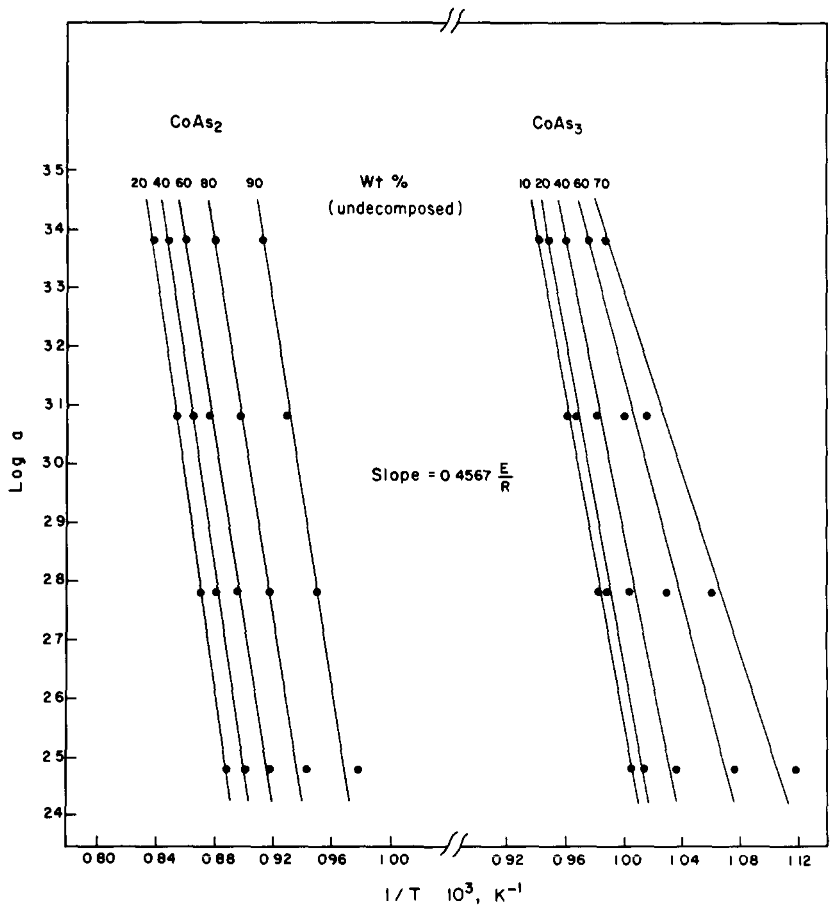

Fig. 8. Decomposition kinetics for $CoAs_3$ and $CoAs_2$ according to eqn. (4).

eqn. (4) (Fig. 8). From the slopes of the lines (= 0.4567 E/R), the apparent activation energies for the decomposition of $CoAs_3$ and $CoAs_2$ were determined as 150.7–275.5 and 305.6–324.5 kJ mol^{-1}, respectively. The large variations in the value of the activation energy of the $CoAs_3$ decomposition obtained by the second method were especially noticeable for the earlier stages of the decomposition. This may be due to anomalous behaviour observed at the beginning of the decomposition reaction. It is quite possible that the higher range given for the activation energy for the decomposition of $CoAs_3$ is more reliable. The agreement between the two methods in the value of the activation energy for the decomposition of $CoAs_2$ is excellent.

CONCLUSIONS

If, under conditions of roasting As-bearing ores and concentrates, oxygen-deficient conditions exist locally in part of the charge in a roaster, a knowledge of the conditions under which metal arsenides dissociate to form arsenic vapour becomes important. The present investigation indicates that skutterudite ($CoAs_3$) and safflorite ($CoAs_2$) dissociate to the lower arsenides and elemental arsenic vapour under non-oxidizing conditions above about 550 and 600 ° C, respectively.

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