Letters to Editor

KINETIC STUDY OF CdS OXIDATION PROCESS IN NON-ISOTHERMAL CONDITIONS

N. Moldovanska[1]*, R. Dimitrov[2] and L. Radev[2]

[1]University of Plovdiv, Department of Inorganic Chemical Technology,
24 Tsar Assen Str., 4000 Plovdiv, Bulgaria
[2]University of Chemical Technology and Metallurgy, Department - Fundamentals of Chemical Technlogy, 8 Kl.Ohridski Blvd., 1756 Sofia, Bulgaria

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Abstract

The paper presents results of kinetic studies of the oxidation of synthetic pulverous CdS in non-isothermal conditions

The oxidation in non-isothermal conditions was carried out by DTA-DTG-TG-analyses at heating rates of 5, 10 and 20 C.min^{-1}. The apparent activation energy was calculated for some basic reactions in CdS oxidation by using Kissinger's and Ozawa's methods.

Results of the X-ray analysis of initial samples of CdS and calcine obtained at 600, 800 and 1000°C are presented. A chemical scheme of the oxidation process is proposed.

Keywords: Activation energy, CdS oxidation, non-isothermal kinetic DTA-TG-DTG, X-diffraction

* Corresponding author

1. Introduction

MeS oxidation is a typical heterogeneous, multistage, exothermic process [1,2]. The thermodynamics, kinetics and mechanism of MeS oxidation have been dealt with in references [3-8]. A main point of argument in the experimental data is the mechanism of oxidation. According to the supporters of the oxide theory [9] CdO is the first product in the process of CdS oxidation, and $CdSO_4$ is obtained due to the interaction between the obtained oxides and the formed SO_2. According to the sulfate theory [5, 10] $CdSO_4$ is an intermediate product in the CdS-$CdSO_4$-CdO scheme.

Some authors [11] point at the origin and crystallographic characteristics of CdS as to factors determining whether the oxidation follows the first or the second theory. The authors of the present study have made a thermodynamic analysis of the Cd-S-O system [12] and have found out that with the increase of temperature the stability of phases in the temperature interval 600 - 1000°C changes as follows: CdS-$CdSO_4$-$(CdO)_2$.$CdSO_4$-CdO

The data for the kinetics and mechanism of CdS oxidation are quite controversial. There is no systematic comparison between the kinetic characteristics of oxidation carried out in different conditions. Therefore the present study aims at determining the apparent activation energy of CdS oxidation roasting in isothermal and non-isothermal conditions at characteristic temperature intervals; determining a limiting stage, and proposing a chemical scheme of the process.

2. Experimental

The experiments were carried out with pulverous (<1 μm) synthetic CdS specimen with semiconductor purity.

DTA-TG-DTG-analyses was carried out using Q Derivatograph (Hungary) under the following conditions: DTA sensitivity 0.5mV; DTG sensitivity 1.0 mV; TG sensitivity 100 mg; heating rates of 5, 10, and 20 $C.min^{-1}$; sample mass of 100 mg; platinum crucible and air environment.

The X-ray analysis of the initial sample of CdS and the obtained calcine was made using Philips equipment provided with Cu tube and Fe filter.

3. Results and discussion

Fig.1 presents DTA-TG-DTG curves of CdS oxidation at a heating rate of 5 C·min^{-1}.

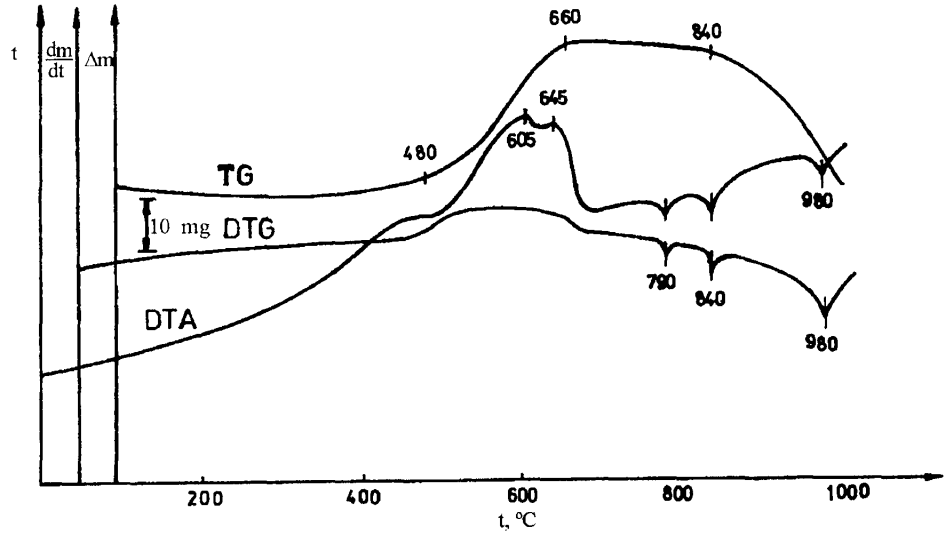

Fig.1. DTA-TG-DTG curves of CdS at a heating rate of 5°C.min^{-1}.

Sulfatization of the sample begins at 470°C (the mass increases). Initial sulfatization is most intensive at Tm = 605°C when most probably $CdSO_4$ is formed. The second exoeffect is at Tm = 645°C and is probably due also to the formation of $(CdO)_2.CdSO_4$. The TG curve shows that up to the point T = 660°C not all of the CdS sulfatizes (Δm = +24,5%), and probably along with the sulfatization, desulfatization of some of the obtained sulfates also takes place. The two endoeffects (at temperatures Tm=790°C and Tm=840°C), as well as the invariable mass in the temperature interval 660 - 840°C point to the following transitions taking place: $\alpha CdSO_4 \rightarrow \beta CdSO_4$ and $\beta CdSO_4 \rightarrow \gamma CdSO_4$.

At temperatures over 850°C the intensive decrease in mass is most probably due to CdS sublimation and to thermal dissociation of the major part of the initially formed sulfates. CdO is formed most intensively at a temperature of about 980°C.

On the basis of the obtained results, the following chemical scheme of CdS roasting in non-isothermal conditions is proposed:

T>470°C $CdS + 2O_2 \rightarrow CdSO_4$

600 ÷ 770°C $CdS + 2O_2 \rightarrow CdSO_4$ (1)

$3CdS + 4O_2 \rightarrow (CdSO)_2.CdSO_4 + SO_2$ (2)

probable secondary reactions:

$CdS + 1{,}5O_2 \rightarrow CdO + SO_2$

$CdSO_4 \rightarrow CdO + SO_2 + 0{,}5O_2$

770 ÷ 800°C $\alpha CdSO_4 \rightarrow \beta CdSO_4$ (3)

800 ÷ 840°C $\beta CdSO_4 \rightarrow \gamma CdSO_4$ (4)

840 ÷ 1000°C $CdSO_4 \rightarrow CdO + SO_2 + 0.5O_2$

$(CdO)_2.CdSO_4 \rightarrow 3CdO + SO_2 + 0{,}5O_2)$ (5)

$CdS_{(s)} \rightarrow CdS_{(g)}$

probable secondary reactions:

$CdS_{(g)} \rightarrow Cd + S \;\; S_2$

$Cd + 0{,}5O_2 \rightarrow CdO$

$CdS + 1{,}5O_2 \rightarrow CdO + SO_2$

The kinetic analysis was carried out by Kissinger's [13] and Ozawa's [14] methods. Heating rates of 5, 10 and 20 $C.min^{-1}$ were used.

Due to the complex nature and the simultaneity of several chemical reactions apparent activation energy of the main reactions was calculated in certain temperature intervals.

Fig 2 presents the dependence between the maximums in the DTA-curves and the heating rate. Fig.3 presents the dependencies $\ln(\phi/T^2_m) = f(1/T_m)$ and $\ln\phi = f(1/T_m)$ for the main reactions (1) - (5) where is the heating rate and Tm is the temperature at the maximum of the thermal effect in the DTA or DTG curves.

Table 1 presents the calculated values of Ea and the integrating constants C and C_1 for reactions (1) - (5).

Fig.4 presents X-ray diagrams of initial samples of CdS and calcines obtained at 600, 800 and 1000°C for roasting time of 1 h. This X-ray diagrams confirm the initial formation of $CdSO_4$, after which the end product, CdO, is formed. Even at a temperature of 1000°C and time of heating 1 hour

there is still $(CdO)_2.CdSO_4$ present in the calcine. This fact confirms the results for the final degree of desufurisation ($\alpha_{max} \leq 85\%$).

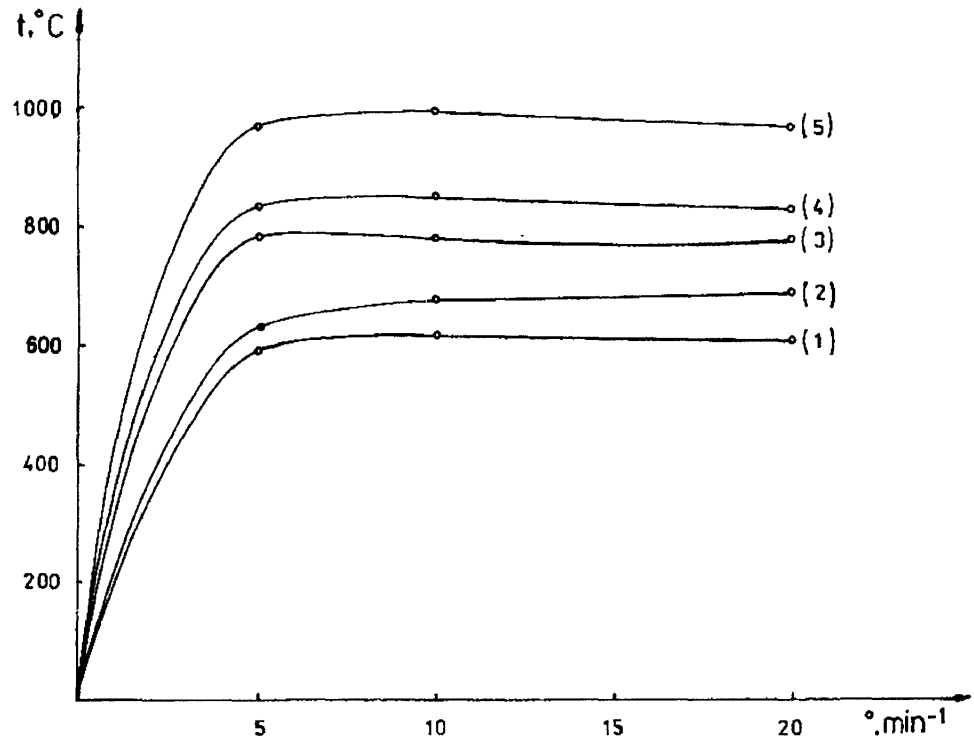

Fig. 2. Dependence of Tm upon the rate of heating for processes (1) - (5) when CdS is oxidised in non-isothermal conditions.

Table 1. Calculated values for the activation energy and integration constants for the cadmium sulphide oxidation process in non-isothermal conditions.

Temperature interval	Process	Method			
		Kissinger		Ozawa	
°C		C	Ea, kJ/mol	C_1	Ea, kJ/mol
600-630	1	111	4,18	120	$1,31.10^8$
630-770	2,1	162	1,99	160	$7,65.10^9$
770-800	3	75	$4,59.10^{-2}$	83	$1,33.10^5$
800-840	4	142	$3,89.10^1$	163	$4,68.10^8$
840-1000	5	165	$4,47.10^1$	166	$8,30.10^7$

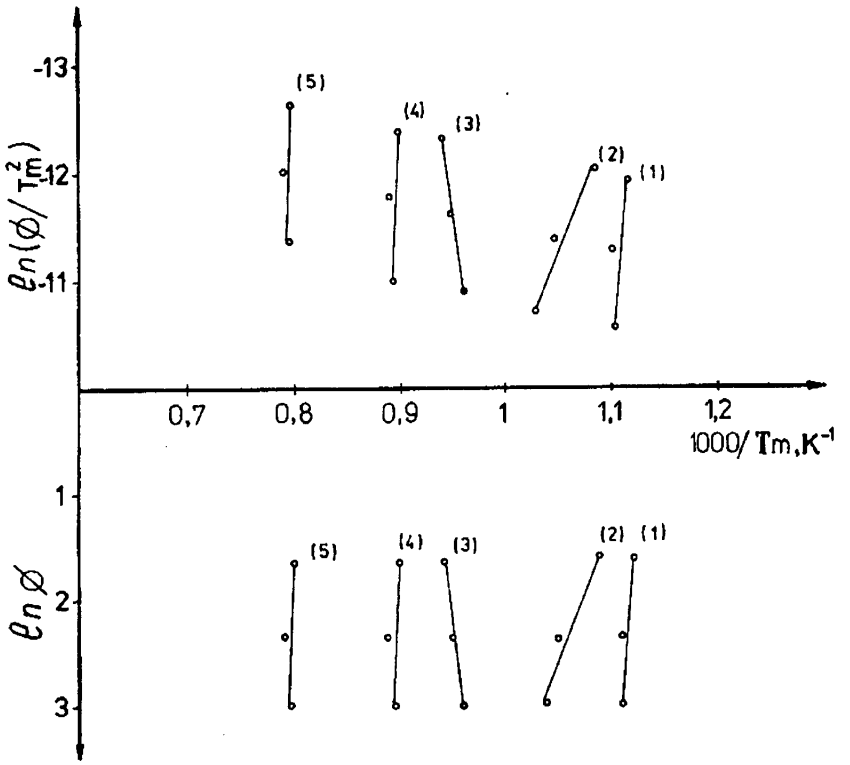

Fig.3. Dependencies ln (ϕ/T^2_m) = f(1/Tm) and ln ϕ = f(1/Tm) for CdS oxidation in non-isothermal conditions.

4. Conclusion

The experiments carried out and the results obtained prove the complex nature of the process of CdS roasting. This is a multistage, heterogeneous, exothermic process which depends on a number of elementary adsorption, diffusion, chemical and desorption stages.

The conditions of carrying out the roasting, the origin and granulometric characteristics of the sample also affect the kinetics and mechanism of the roasting processes taking place.

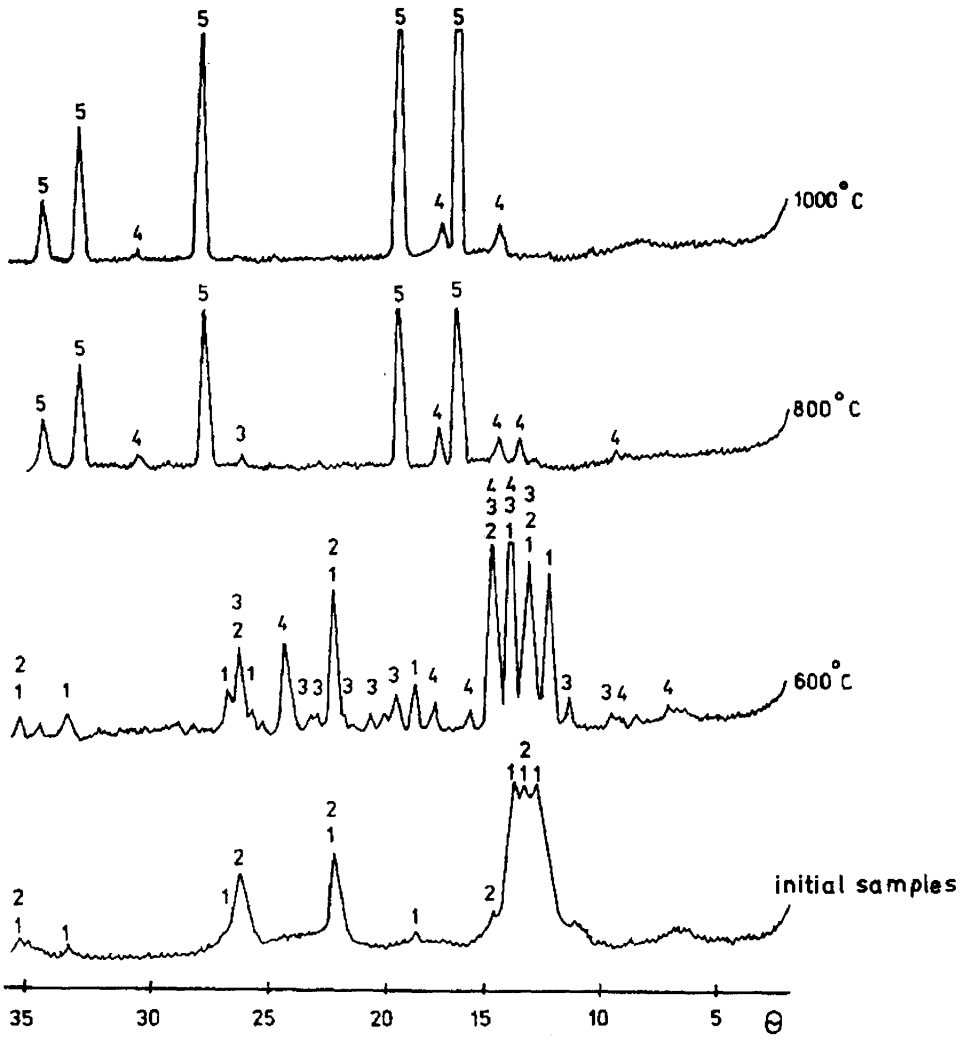

Fig. 4. X-ray analysis of the CdS oxidation products at different temperatures.

The results obtained through DTA-TG-DTG and X-ray analyses confirmed the sulfate theory of oxidation of pulverous, synthetic CdS of semiconductor purity in non isothermal conditions.

In non-isothermal conditions the main reactions of two-stage sulfatization, polymorphic transformation, desulfatization, sublimation and oxidation take place in the kinetic zone.

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