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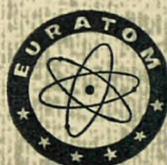
COMMISSION OF THE EUROPEAN COMMUNITIES

**THERMOGRAVIMETRIC ANALYSIS (TGA)
OF THE URANIUM OXIDE CARBOREDUCTION**

by

E. ZAMORANI, R. DE RIJK and F. TOCI

1971



Joint Nuclear Research Centre
Karlsruhe Establishment - Germany

European Institute for Transuranium Elements

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Joint Nuclear Research Centre - Karlsruhe Establishment (Germany)
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Luxembourg, March 1971 - 22 Pages - 4 Figures - B.Fr. 40.—

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- isothermally at different temperatures.

The kinetics of the carboreduction were affected by the characteristics of the starting material. The precipitation method improves the physical properties of the mixtures and can be used in the carbide preparation.

In the oxide-carbon precipitated mixtures, the reaction started already at 900 °C. The activation energy was 66 ± 4 kcal/mole. In the mechanically blended material the carboreduction started at 1 200 °C, the activation energy was 83 ± 4 kcal/mole.

The results are discussed and compared with those of previous workers.

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ABSTRACT

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KEYWORDS

URANIUM OXIDES
URANIUM DIOXIDE
CARBON
GRAPHITE

THERMOGRAVIMETRY
REACTION KINETICS
ACTIVATION ENERGY
REDUCTION

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THERMOGRAVIMETRIC ANALYSIS (TGA) OF THE URANIUM OXIDE CARBOREDUCTION

1. Introduction *)

Interest in the Uranium and Plutonium carbides and their solid solutions as possible fuel for fast breeder reactors, has encouraged considerable efforts to develop fabrication techniques. The carboreduction of oxides at high temperature and under vacuum is the main technique used in carbide preparation.

In some cases the course of UC formation can be described by the kinetic equation.

$$\frac{d\alpha}{dt} = K_1(1-\alpha)^n \quad (1)$$

where K is the rate constant. The apparent reaction order, n, may assume the values of 1 [1] [2], $3/2$ [3] or 2 [4].

In other cases [1] [2] [5] [6] [7] the experimental data fit a parabolic expression, which implies either a diffusion controlled reaction of plane geometry with the relation

$$\alpha = K_2 t^{1/2} \quad (2)$$

or of spherical symmetry [8] [9].

The probable reaction mechanism is determined by comparing the experimental data with the kinetic functions and the activation energy, E, as established by means of an Arrhenius plot.

From the experimental work of Ainsley [1] the UC formation appears to be controlled by a diffusion process, probably involving the migration of either oxygen or carbon through a UC layer. The reaction

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rate was found to be insensitive to the particle size of fused UO_2 $< 20 \mu$ and to carbon particle sizes over the range $0,1 \div 6 \mu$, but it depended upon the state of compaction of the oxide-carbon mixture. Coarse oxide particles ($> 20 \mu$) are less reactive. An activation energy of 92 kcal/mole was calculated. The values of the activation energies from the studies by Ainsley [1], Murbach et al. [3] and Smiley [4] are given in table 1a.

Table 1a

Ref.	E (kcal/mole)	Temperature range ($^{\circ}C$)	Method	order of rate law
[1]	92	1300 - 1550	UO_2 carboreduction	1°
[3]	71	1300 - 1550	U_3O_8 " "	$3/2$
[4]	73,5	1330 - 1700	UO_2 " "	2°
Pres. work	66 ± 4	900 - 1330	UO_2 carboreduction of precipitated ADU + C mixtures	$3/2$
	83 ± 4	1200 - 1450	$UO_2-U_3O_8$ carboreduction of mechanical mixtures	$3/2$

The activation energies for the diffusion of C in UC obtained by W.Chubb [10] in chemical diffusivity experiments, by A.Accary [11] in electrical resistivity measurements, and by H.M.Lee [12] using radioactive tracers, are given in table 1b.

Table 1b

Reference	E (kcal/mole)	Temperature range ($^{\circ}C$)	Method
[10]	82	1600 - 2100	Radioactive tracer UC
	64	1600 - 2100	
[11]	72	700 - 1000	Electrical resistivity
[12]	63	1266 - 1684	Radioactive tracer UC
	104	1500 - 1863	

The reaction rate could be influenced by the chemical form of the Uranium oxide. The results of Murbach [3] have shown that the reaction rate is greater for U_3O_8 than for UO_2 . The increase in K is attributed to the improved reactivity of UO_2 reduced in situ.

The reaction rate is sensitive to the build-up of carbon monoxide over pressure; therefore, during the carboreduction the gas should be rapidly removed. The relationship between the rate constant K and the experimental pressure P is approximately described by

$$K = K_0 \left[1 - \left(\frac{P}{P_e} \right) \right]^{1/n} \quad (3)$$

where K_0 is the constant rate at zero pressure, P_e the equilibrium pressure and n is an empirical factor equal to 2 ÷ 4 [1] [13].

The kinetics of UC formation are considered to be heterogeneous and controlled by

- a) the rate of the chemical reaction which occurs at the interface of the reactants;
- b) a diffusion process of the reactants through the product;
- c) a secondary chemical reaction between the forming product and the reactants;
- d) the pressure of the gas involved;
- e) the geometry of the solid starting materials.

In most cases these processes interfere with each other and the reaction rate will be determined by a combination of these. Only as a limiting case the reaction rate will follow a single rate law over the entire range of the reaction.

At present it is not possible to describe the carboreduction reaction with a single rate law for the entire course of the

reaction. The discrepancies in the activation energies according to the previous authors (see table 1a) may be due to the particular experimental procedures and the different physical characteristics of the starting materials.

In addition the mathematical fitting of the experimental data, is very often ambiguous because different equations do fit these data equally well.

The method usually employed to prepare UC, consists of firing at high temperature ($>1600^{\circ}\text{C}$) in vacuum, Uranium oxide and carbon mixture obtained by tumbling.

Previous investigations also showed that Ammonium diuranate (ADU) and carbon mixtures could be employed in the UC formation [14], [15], [16]. Heating mixtures of ADU and carbon in inert or reducing atmosphere, decomposition of ADU to U_3O_8 or UO_2 take place, followed by the UC formation at higher temperature.

Considering the previous remarks, the aim of this work is as follows:

- i) to prepare a mixture of Uranium oxide and Carbon in order to obtain a good homogeneity and to improve the reactivity of the powder;
- ii) to decrease the starting temperature for the carbo-reduction in order to limit the Plutonium losses due to the evaporation during the preparation of Uranium-Plutonium carbides;
- iii) to simplify the calculation of the kinetic parameter by analyzing one single thermogravimetric curve in which the weight is plotted versus temperature for a sample heated at a fixed rate, instead of many isothermal curves.

2. Experimental

2.1. Experimental procedure

In order to improve the physical characteristics of the powder, the Uranium and Carbon mixture was prepared as following:

- i) Carbon black (United 15) in stoichiometric amount was stirred in a $\text{UO}_2(\text{NO}_3)_2$ solution. After the precipitation of ADU performed with NH_4OH , in the range of pH $7 \div 9$, the carbon was retained in the cake.
- ii) The reduction step made at 500°C in N_2 -8% H_2 , transformed the ADU in a mixture of UO_2 and Carbon. No reaction could be observed between H_2 and C in agreement with previous results [16]. A good homogenisation between Uranium oxide and Carbon was observed. The variation in the Carbon content was about 0.1 %.
- iii) In order to compare the results obtained in UC preparation with the precipitated mixtures, U_3O_8 from UO_2 calcined in air at 600°C and UO_2 reduced at 1000°C in N_2 -8% H_2 , were dry mixed with graphite (Ringsdorff Spektralkohle RW-A) by tumbling for 24 h. The powder size was $\sim 60\mu$. In this case no good homogenisation was obtained. The variation in carbon content increased to about 2,3 %.
- iv) Before the carboreduction for all powders, the surface area was determined by the BET method. The powder obtained by the precipitation method presented a surface area of $40\text{ m}^2/\text{g}$ while the mechanical mixtures prepared according with procedure iii) presented a surface of $1 \div 4\text{ m}^2/\text{g}$. The physical characteristics of the powders and pellets employed are presented in table 2.
- v) A Mettler recording thermobalance was used in the carboreduction experiments performed with powders and pellets i), ii) or iii) contained in W crucibles. The weight loss was normally observed under a heating rate of $2^\circ\text{C}/\text{min}$ and a vacuum of 10^{-5} torr. Some data were obtained at constant temperature in the range 1120 - 1250°C .

Table 2

Ref.	Preparation method	Materials						Specif. surface of mixture (m ² /g)	Pelletising pressure (t/cm ²)	Green density (g/cc)	Vacuum (torr)
		Uranium			Carbon						
		Form	Particle size (μm)	Specific surface (m ² /g)	Form	Part. size (μm)	Spec. Surf. (m ² /g)				
[1]	Mechanical mixture	UO ₂	< 20	4	Carbon black	0.1-6	30	-	3	-	5x10 ⁻³
[3]	" "	U ₃ O ₈	< 37	-	Graphite	< 37	-	-	-	-	-
[4]	" "	UO ₂	~ 1,8	-	Graphite	2.2	-	-	8	-	-
Pre-sent work	1) Precipit. ADU+C	UO ₂ ⁺⁺	-	-	Carbon black	0,023	180	40	2-4	3,5-4	10 ⁻⁵
	2) Mechan. mixture	UO ₂	< 60	4	Graphite	< 60	2,5	2-4	2-4	"	"
	3) Mechan. mixture	U ₃ O ₈	< 60	1-5	Graphite	< 60	2,5	2-4	2-4	"	"

2.2. Mathematical approach for analysis of reaction kinetics

As remarked, a simple method to follow the course of the reaction is to obtain a simple thermogravimetric curve (TG) which is equivalent to many isothermal ones. Only a single curve is needed to calculate kinetic data and several methods have been suggested [17] [18] [19]. Three kinetic rate laws were considered in order to fit the experimental thermogravimetric data.

2.2.1. Homogeneous system

The kinetic equation

$$\frac{d\alpha}{dt} = A e^{-E/RT} (1-\alpha)^n \quad (4)$$

can be transformed into

$$y = A e^{bz} \quad (5)$$

where $y = \frac{d\alpha}{dt} / (1-\alpha)^n$

A = frequency factor

b = - E/R

Z = 1/T and

α = fraction of conversion of UO_2 to UC.

The values of A and E were calculated at a value of n for which the standard deviation of (5) is a minimum. The A, E, n values were employed to calculate α from the series resolution of the following integral

$$\int \frac{d\alpha}{(1-\alpha)^n} = A \int e^{-E/RT} dt \quad (6)$$

in order to fit the thermogravimetric curves.

2.2.2. Heterogeneous system. Plane $\sqrt{20}$ and spherical symmetry $\sqrt{8}$ $\sqrt{20}$

Similary, the following relationships were employed

$$\alpha \frac{d\alpha}{dt} = A e^{-E/RT} \quad (7)$$

and

$$\left[1 - (1-\alpha)^{-1/3} \right] \frac{d(1-\alpha)}{dt} = A e^{-E/RT} \quad (8)$$

All calculations were accomplished by means of a IBM 1130 digital computer.

3. Results

3.1. Constant heating rate (TGA curves)

The fraction of conversion α , obtained under variable temperature conditions ($2^{\circ}\text{C}/\text{min}$) for the precipitated ADU-carbon black mixtures, is shown in fig.1. Powders have a starting temperature of reaction of 900°C (line A). An increase in starting temperature (1050°C , line B) was observed when the material was compacted at $2 \div 4 \text{ tons}/\text{cm}^2$.

The experimental data are fitted best by the eq.(6) in section 2.2.1. for $n = 3/2$. The circles on the lines represented the calculated values. A plot of $\log K$, obtained by the thermogravimetric curves A and B, versus $1/T$ is shown in fig.2 (line 1 and 2). An activation energy of $66 \pm 4 \text{ kcal}/\text{mole}$ was calculated. The results are given in table 1a with those of the previous workers.

The investigations on the mechanical mixtures of UO_2 or U_3O_8 and graphite show a starting reaction temperature in the range of $1200 - 1350^{\circ}\text{C}$ and an activation energy of $83 \pm 4 \text{ kcal}/\text{mole}$ (Fig.2 line 3).

3.2. Constant temperature experiments

Pellets from precipitated powders prepared by procedure i) of section 2.1., were examined under isothermal conditions at temperatures of 1100 - 1125 - 1150 - 1200 and 1250°C. The weight loss curves could be fitted by the parabolic equation 2) and the results are given in fig.3. Using the linear part, extending to about 65 % of the reaction, and the integrated eq. 4), 7), 8) in section 2.2.1. and 2.2.2., the values of K were calculated. An activation energy of 66 ± 4 kcal/mole was obtained by the Arrhenius plot of fig.4.

3.3. Gram scale preparations

The methos i) and ii) were used for gram scale preparations (~ 50 g) of UC. The analyses, effectuated on the end product sintered at 1600°C in vacuum, gave the following results:

C %	N ₂ %	O ₂ %	XR UC - phase
4,89	0,05	0,26	4,9606 \pm 0,0005

No other phases were detected.

4. Discussion

The thermograms obtained under variable temperature conditions (2°C/min) were fitted best by the equation for homogeneous system. All the other equations considered, did not give a good result. The thermograms in Fig.(1) are representative of the experiments effectuated on the powder (line A) and pellets (line B)

obtained by precipitated mixtures. The circles on the lines were calculated by the eq. (6) in sect. 2.2.1. An Arrhenius plot in Fig.(2) (line 1 and 2) of the reaction rate K versus $1/T$ allows one to calculate an activation energy of 66 ± 4 kcal/mole, unaffected by the powder compaction.

The precipitated ADU-Carbon black mixtures prepared by procedure i) of section 2.1. have a starting temperature of the reaction in the range $900 - 1100^{\circ}\text{C}$. This limit is lower than that which is obtained with the mechanical mixtures (see table 1a). In the carboreduction reaction of Uranium and Plutonium oxides, a low temperature is an advantage because of the Plutonium carbide volatilisation at high temperature.

As shown in fig.(2) line 1 and 2, a decrease in K was observed when the material was compacted at $2 \div 4$ tons/cm² (see table 2).

The results seem to agree with those of Ainsley, who attributes the decrease of the reaction rate to a CO overpressure in the pellets' matrix. In contrast, Smiley's results show a slight increase in K for pellets, but the agreement between the experiments is too poor to be significant.

When coarse oxide UO_2 or U_3O_8 and graphite particles were employed to prepare mechanical mixtures, different results from those of the precipitation were obtained. The starting reaction temperature was higher ($1200 - 1350^{\circ}\text{C}$) and comparable with that of the previous works on the same mixtures (see table 1a ref. [1][3][4]). A decrease in K and an increase in E (83 ± 4 kcal/mole), calculated by the plot of fig.(2) line 3, was observed.

The influence of the particle size in the reaction rate was studied by Jander [5] on the $\text{BaCO}_3/\text{SiO}_2$ system. The experimental data showed that K is affected by the particle radius r (table 3).

Table 3

r in mm	K (min ⁻¹)
0,153	5,7 10 ⁻⁶
0,086	16,2
0,053	42,3
0,036	96,0
0,033	125,0

Rate constant for BaCO₃/SiO₂ - 860°C

The experimental results of Ainsley on the UO₂ carboreduction showed that for particle size > 20 μ, the decrease in the reaction rate is very marked and the increase in particle size above about 100 μ has little further effect on the reaction rate for powders or pellets.

In the present work the reaction rate K was not affected by the compaction state or by the chemical form of the starting material. This fact can be attributed to the great particle size and low reactivity of the powders which eliminate any influence of these parameters. The differences in the particle size between the precipitated materials and mechanical mixtures result in the different values of the specific surfaces. These surfaces were found to differ by a factor of ten (see table 2). Microscopic investigation on the precipitated powders revealed sub-micron size particles.

The isothermal kinetic of UC formation, was observed on the same pelleted powders, previously employed in the variable temperature experiments. The weight loss curves at the temperature of 1100 - 1125 - 1150 - 1200 and 1250 °C could be fitted by the parabolic equation (2), indicating a diffusion-controlled reaction (see fig.3). The non-linear part of the plot, more evident at low temperature, was also observed by previous authors. These non-linear parts of α versus

\sqrt{t} plot imply two effects: a vacuum decrease when the reaction starts, due to the formation of CO ($10^{-5} \div 10^{-3}$); and a reaction other than the diffusion controlled one (nucleation).

At the moment, it is not possible to separate and evaluate these effects.

After the linear part, which extends to about 65 % of the reaction, a decrease in α was observed. Smiley attributes the spontaneous decrease, occurring above 1400°C and at 90 % completion of the carboreduction, to a difference in the course of the reaction, i.e. U_2C_3 reacting with UO to form UC . This picture is in contrast with the results of Ainsley who found that over the range of reaction from 33 to 100 % the only intermediate product was the monocarbide. The decrease in α occurred at lower temperature and at about 70 % completion of the reaction.

An explanation for this decrease in the reaction rate has been sought in a sintering effect [21].

By the integrated equations (4), (7), (8) of the sections 2.2.1. and 2.2.2., the values of K were calculated and an activation energy of 66 ± 4 kcal/mole was obtained by the Arrhenius plot of fig.(4). The lines A, B, C correspond to the homogeneous system in which $n = 3/2$, to a diffusional controlled rate in plane, and in spherical symmetry, respectively. The activation energies were unaffected by the different equations considered.

The same value of the activation energy obtained in the variable temperature and isothermal experiments, permit the use of the equation (4) for the homogeneous system with a formal order of reaction of $3/2$ to describe the kinetic of UC formation. This is only a mathematical approach and does not contradict the point that the process is heterogeneous and controlled by diffusion.

5. Conclusions

It appears from these experiments, that the wet Uranium oxide-C preparation method, can be usefully employed in the carbide fabrication.

The improved characteristics of the powders as particle size, reactivity and homogeneity, affect the starting reaction temperature and the activation energy of the process.

The thermogravimetric analysis, effectuated at the constant heating rate, revealed the difference of the two Carbon-Uranium oxide mixtures employed.

A starting reaction temperature as low as $900 - 1100^{\circ}\text{C}$ was observed on the wet preparation with an activation energy of 66 ± 4 kcal/mole. The reaction rate was affected by the compaction of the powders.

Higher starting temperatures ($1200 - 1350^{\circ}\text{C}$) and $E = 83 \pm 4$ kcal/mole were observed when coarse particles were employed in the mechanical mixtures. In this case the reaction rate was unaffected by the chemical form of the Uranium oxides (UO_2 or U_3O_8) or by the compaction of the powders.

For the carboreduction of U-Pu-oxides, the precipitation method looks promising because the ammonia precipitation of ADU and $\text{Pu}(\text{OH})_4$ facilitates the formation of a solid solution between Uranium and Plutonium [22] which is necessary to improve the U-Pu Carbide fabrication.

In the mechanical mixtures, Plutonium sesquicarbide tends to appear and single-phase material is difficult to obtain [1][23]. The low starting reaction temperature, presented by the precipitated mixtures, could be an advantage for U-Pu Carbide fabrication because of the Pu carbide volatility at high temperature.

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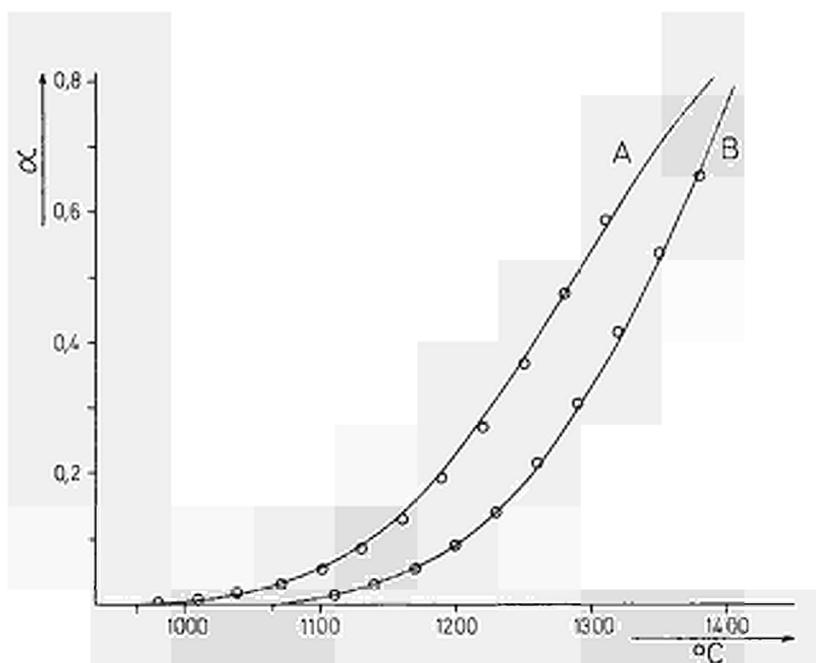


Fig. 1 Carboreduction at constant heating rate (2°C/min) of precipitated C-UO₂ mixtures versus T °C.
 A = powders
 B = pellets
 O = calculated values

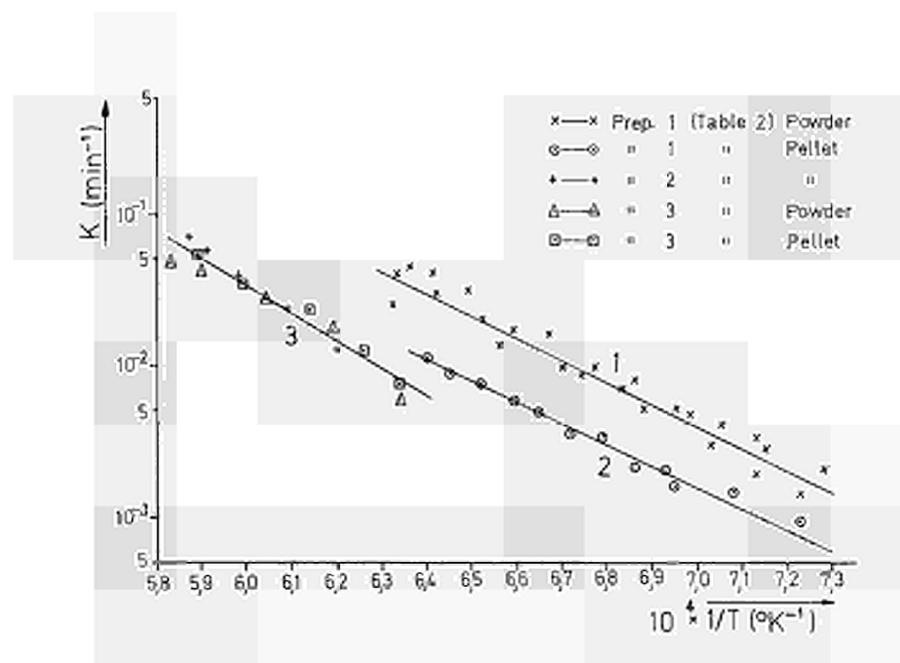


Fig. 2 Carboreduction at constant heating rate (2°C/min) Arrhenius plot of log K, calculated by eq. (4) for $n = 3/2$, versus $1/T$.

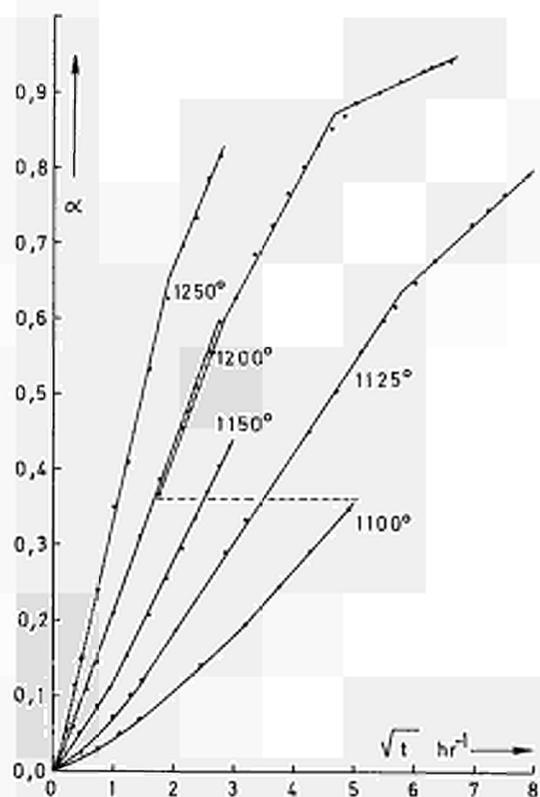


Fig. 3 Isothermal carboreduction. α versus $t^{1/2}$. Pellets of preparation 1 (table 2).

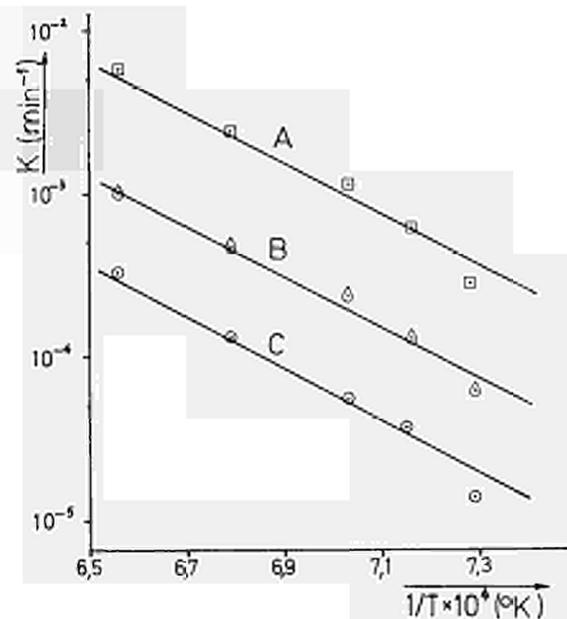


Fig. 4 Isothermal carboreduction. Arrhenius plot of $\log K$ versus $1/T$. Pellets of preparation 1 (table 2)
 A = homogeneous system (Eq. 4 for $n = 3/2$)
 B = diffusional phase system (Eq. 7)
 C = diffusional sphere system (Eq. 8)

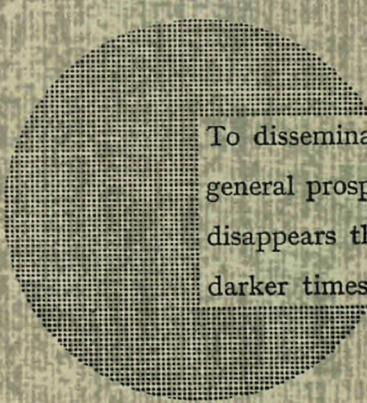
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Alfred Nobel

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