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THEORIES AND MEASUREMENTS ON
NON-ISOTHERMAL REACTION KINETICS

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ABSTRACT

In connection with the thermal decomposition of calcium carbonate and calcium oxalate, we investigated the validity of equations derived from different non-isothermal reaction kinetics theories based upon the analysis of DTA and TG as well as of TG and DTG plots. The obtained activation energies and reaction orders are in good agreement with the data found in the literature.

АННОТАЦИЯ

Была исследована справедливость уравнений полученных по неизотермическим реактивно-кинетическим теориям, основывающимся на анализе различных кривых ДТА, ТГ и ТГ, ДТГ в связи с термическим распадом карбоната и оксалата кальция. Полученные значения активационной энергии и порядок реакций соответствуют значениям, приведенным в литературе.

KIVONAT

Különböző, a DTA, TG, valamint a TG és DTG görbék analizésére épülő nem izoterm reakciókinetikai elméletek szolgáltatotta egyenletek érvényességét vizsgáltuk a kalcium-karbonát és kalcium-oxalát termikus bomlása kapcsán. A kapott aktiválási energia-értékek, valamint a reakciórendüések jól egyeznek az irodalomban található értékekkel.

1. INTRODUCTION

Differential thermal analysis /DTA/, thermal gravimetry /TG/ and differential thermogravimetry /DTG/ plots obtained from derivatographic measurements permit also non-isothermal reaction kinetics to be analysed [1], [2], [3]. In the present report some theories on non-isothermal reaction kinetics are reviewed in the light of data obtained in our measurements. A derivatograph made by MOM, Hungary and a Mettler thermoanalyser were used in the measurements. The reactions under investigation were chosen to be the dehydration and the thermal decomposition according to the third step in calcium oxalate monohydrate and the thermal decomposition of the original calcium carbonate.

2.1 ANALYSIS OF THE DTA-PEAK

2.1.1 Kissinger's theory [4] is based on the observation that the temperature T_m [K] associated with the peak maximum shifts to higher values as the heating rate ϕ increases. It can be shown that the associated ϕ and T_m values are related to the activation energy E [$\frac{\text{cal}}{\text{mole}}$] as

$$\frac{d \ln\left(\frac{\phi}{T_m^2}\right)}{d\left(\frac{1}{T}\right)} = - \frac{E}{R} , \quad /1/$$

where R [$\frac{\text{cal}}{\text{mole K}}$] is the gas constant.

If relation /1/ holds, the plot for $\ln \frac{\phi}{T_m^2} \rightarrow \frac{1}{T_m}$ yields a straight line with a slope from which the activation energy can be evaluated. The so-called pre-exponential factor $k \left[\frac{1}{\text{time}} \right]$ is then given by the expression [5]

$$\frac{E\phi}{RT_m^2} = ke^{-\frac{E}{RT_m}} \quad /2/$$

The reaction order n can also be evaluated by using the a and b values as interpreted from Fig. 1 and eq. [4]

$$S = \frac{a}{b} = 0,63 n^2 \quad /3/$$

Figure 2 represents, in terms of eq. /1/, the thermal decomposition of calcium oxalate monohydrate in the form $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ according to the third step. The slope of this straight line gives for the activation energy $E = 39.5$ kcal/mole which lies in the range of the reported values of 35 to 48.7 kcal/mole [6].

By the use of the pertinent equations, we get 0.43 for the reaction order and $1.8 \times 10^5 \text{ sec}^{-1}$ for the pre-exponential factor.

Considerably different values of E and of k were obtained on the two types of equipment in the measurements on the original calcium carbonate. However, the different values correspond to the law of the effect of kinetic compensation [12] since the plot for $\lg k \rightarrow E$ gives a straight line, as can also be seen from Fig. 3.

Although, it is now already well known that the maximum reaction rate is not associated with the maximum of the DTA peak, as assumed in the derivation of /1/ [7], [8], Kissinger's theory can still furnish useful data in the cases under investigation.

2.1.2 Another theory based on the analysis of the DTA peak is that of Pilojan and Novikova [6] who have shown that in the transformation degree range of $0.5 > \alpha > 0.4$ we can write

$$\ln \Delta t = C - \frac{E}{RT} \quad /4/$$

where Δt is the temperature difference between the base line and the given point of the DTA peak, $T[K]$ is the temperature and C is a constant.

If /4/ holds, the plot for $\Delta t \rightarrow \frac{1}{T}$ will give a straight line with a slope which determines the activation energy E . Figure 4 shows, in terms of /4/, the data obtained from the measurement on the thermal decomposition of calcium carbonate. The thus calculated value $E = 40.0$ kcal/mole again lies in the reported range of 35 to 48.7 kcal/mole [6].

The advantage of this theory is that it greatly simplifies the calculation; however, it has the drawback that neither the order of the reaction nor the pre-exponential factor are obtainable from this formulation.

2.2 ANALYSIS OF THE TG CURVE

2.2.1 Coats and Redfern's theory [9]. The considerations of these authors led to the equation

$$\lg \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \lg \frac{kR}{\phi E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2,3RT} \quad /5/$$

where α is the degree of transformation.

If the reaction order is properly chosen from the usual values such as 0, 1/2, 2/3 or 1, the plot for

$$\lg \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \quad \frac{1}{T}$$

will yield a straight line with a slope and an intersection with the axis which determine the values of E and k , respectively.

Figure 5 shows the linearization /5/ for the dehydration of calcium oxalate monohydrate as described by the equation $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} = \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$. Similarly to Coats and Redfern's result the reaction order was found to be 2/3. The activation energy, obtained as $E = 17.6$ kcal/mole is in good agreement with the reported 20 to 22 kcal/mole [11]. The pre-exponential factor was obtained as $k = 4.0 \times 10^4 \text{ sec}^{-1}$

It can be noted that the above linearization is now extensively used [12] in thermoanalytical reaction kinetics.

2.2.2 TG data are utilized also in Pilojan and Novikova's theory [6]. These authors formulated an equation of the form

$$\ln \alpha = 2 \ln T = A' - \frac{E}{RT} \quad /6/$$

/where A' is a constant/ which holds in the range of transformation degrees $\alpha = 0.4$ to 0.5 .

If the thermal decomposition is truly described by /6/, the plot for $\ln \alpha - 2 \ln T \rightarrow \frac{1}{T}$ will give a straight line with a slope determining the activation energy E. The validity of /6/ is confirmed for the thermal decomposition of calcium carbonate, as can be seen in Fig. 6. The activation energy evaluated as $E = 37.6$ kcal/mole from the slope again lies in the reported range of 35 to 48.7 kcal/mole [6].

2.2.3 The DTG and TG curves were analysed by Freeman and Carroll [10]. Their theory led to the formulation of the equation

$$\frac{\Delta \ln \left(- \frac{dX}{dt} \right)}{\Delta \ln X} = n - \frac{E}{R} \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \ln X} , \quad /7/$$

where X is the number of not yet dissociated molecules in the starting material at time t.

If /7/ holds, the plot for

$$\frac{\Delta \ln \left(- \frac{dX}{dt} \right)}{\Delta \ln X} \rightarrow \frac{1}{T}$$

will give a straight line with a slope and an intersection with the axis which determine the values of E and n, respectively.

Figure 7 shows in terms of /7/ the straight line for the dehydration of calcium oxalate monohydrate. The activation energy,

evaluated as $E = 22.0$ kcal/mole from the slope is in good agreement with the reported 20 to 22 kcal/mole [11]. The order of reaction was evaluated as $n = 0$.

3. Summarizing, it can be stated that the equations, though formulated using different assumptions, yield reasonable values when calculated from the data of our present measurements.

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FIGURE CAPTIONS

1. Determination of the shape index S [4]
2. Experimental verification of Kissinger's theory for the thermal decomposition of calcium carbonate
3. The kinetic compensation effect for the thermal decomposition of calcium carbonate
4. Experimental verification of Pilojan and Novikova's theory for the dehydration of calcium oxalate monohydrate
5. Experimental verification of Coats and Redfern's theory for the dehydration of calcium oxalate monohydrate
6. Experimental verification of Pilojan and Novikova's theory for the thermal decomposition of calcium carbonate
7. Experimental verification of Freeman and Carroll's theory for the dehydration of calcium oxalate monohydrate

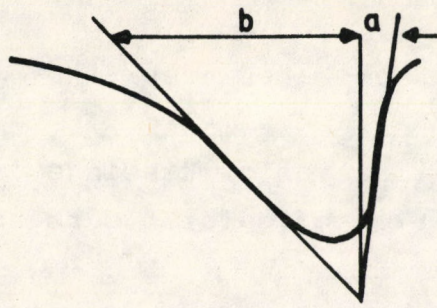


Fig. 1

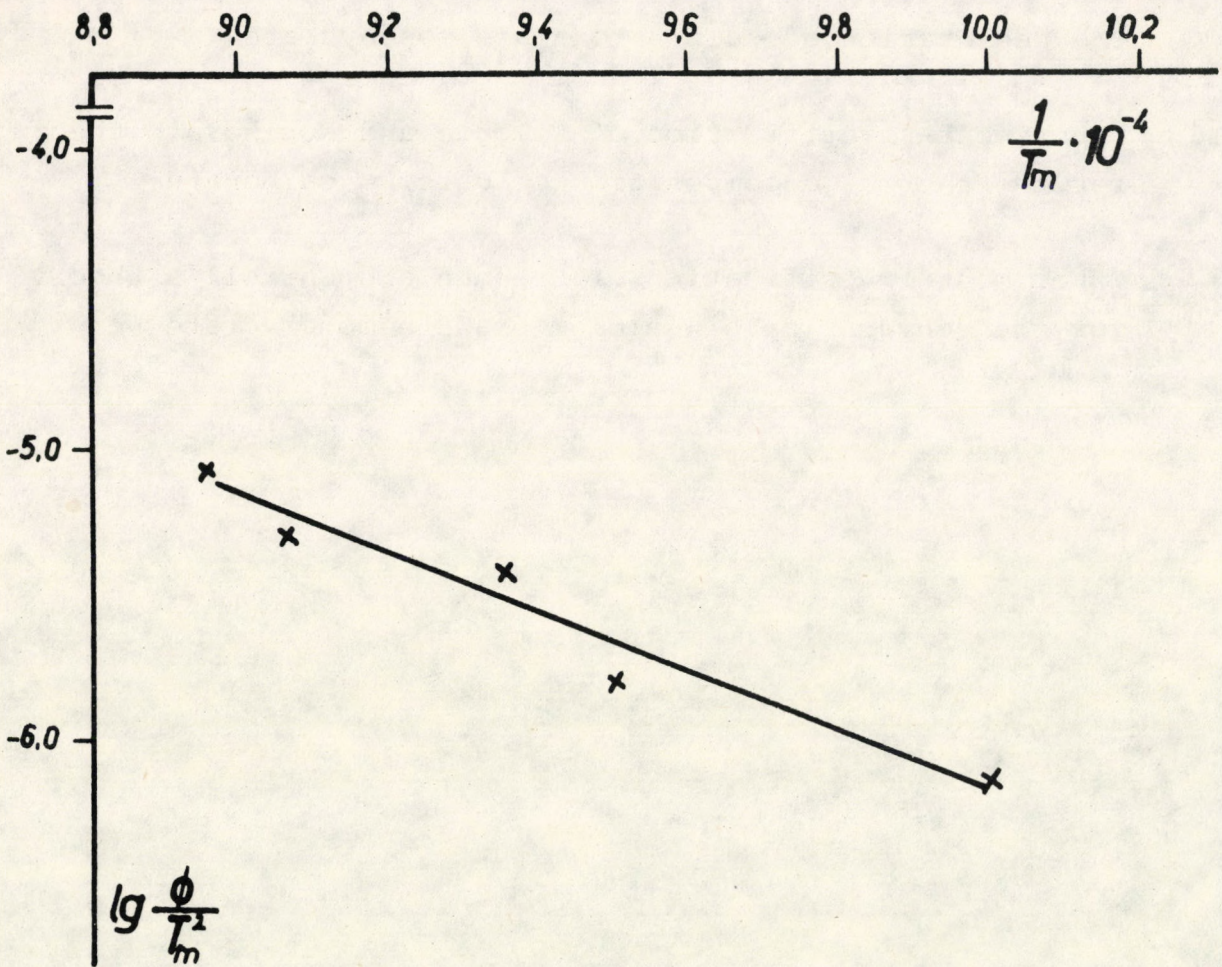


Fig. 2

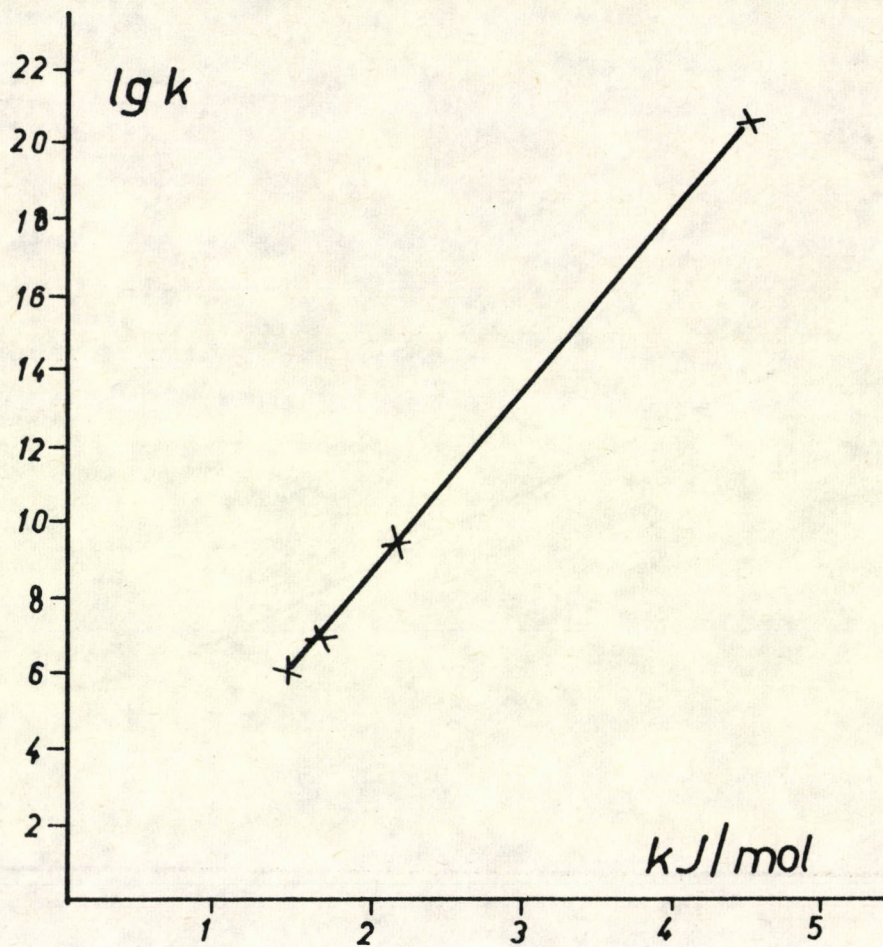


Fig. 3

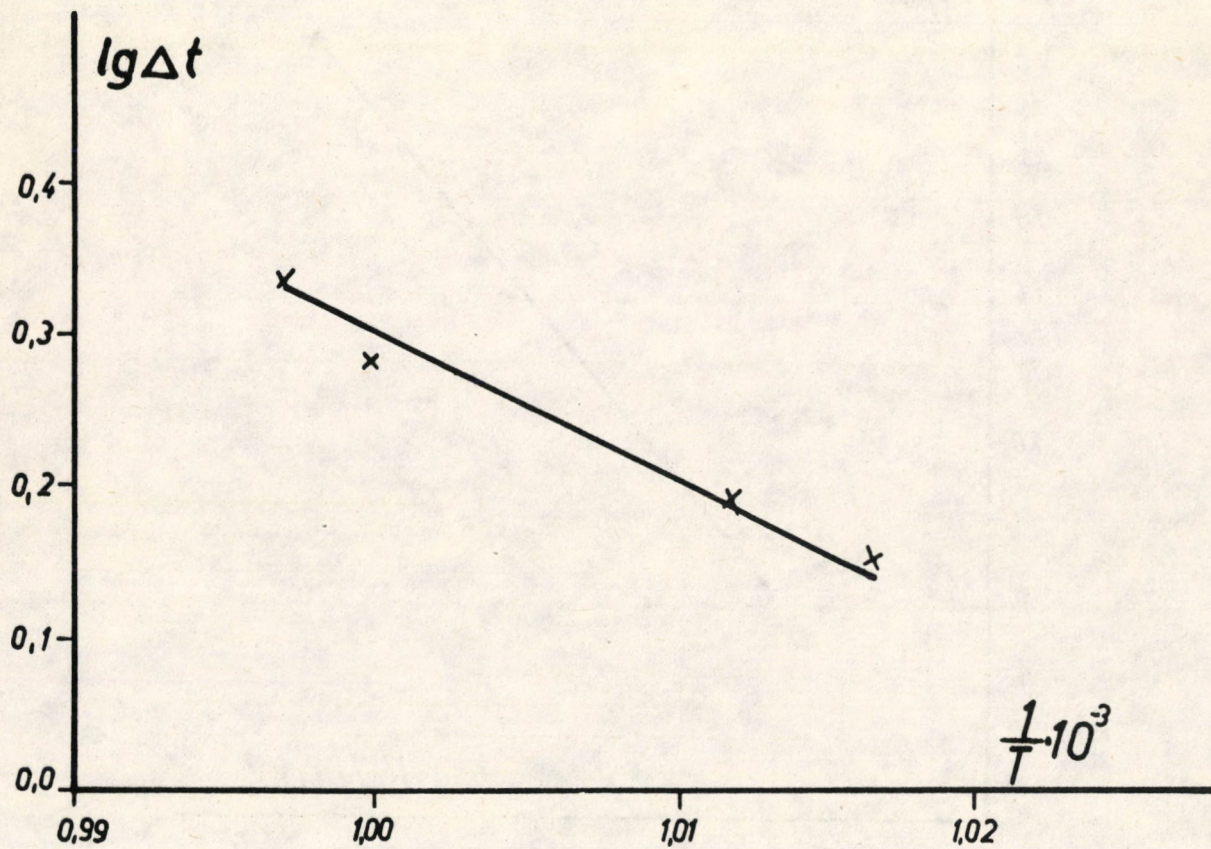


Fig. 4

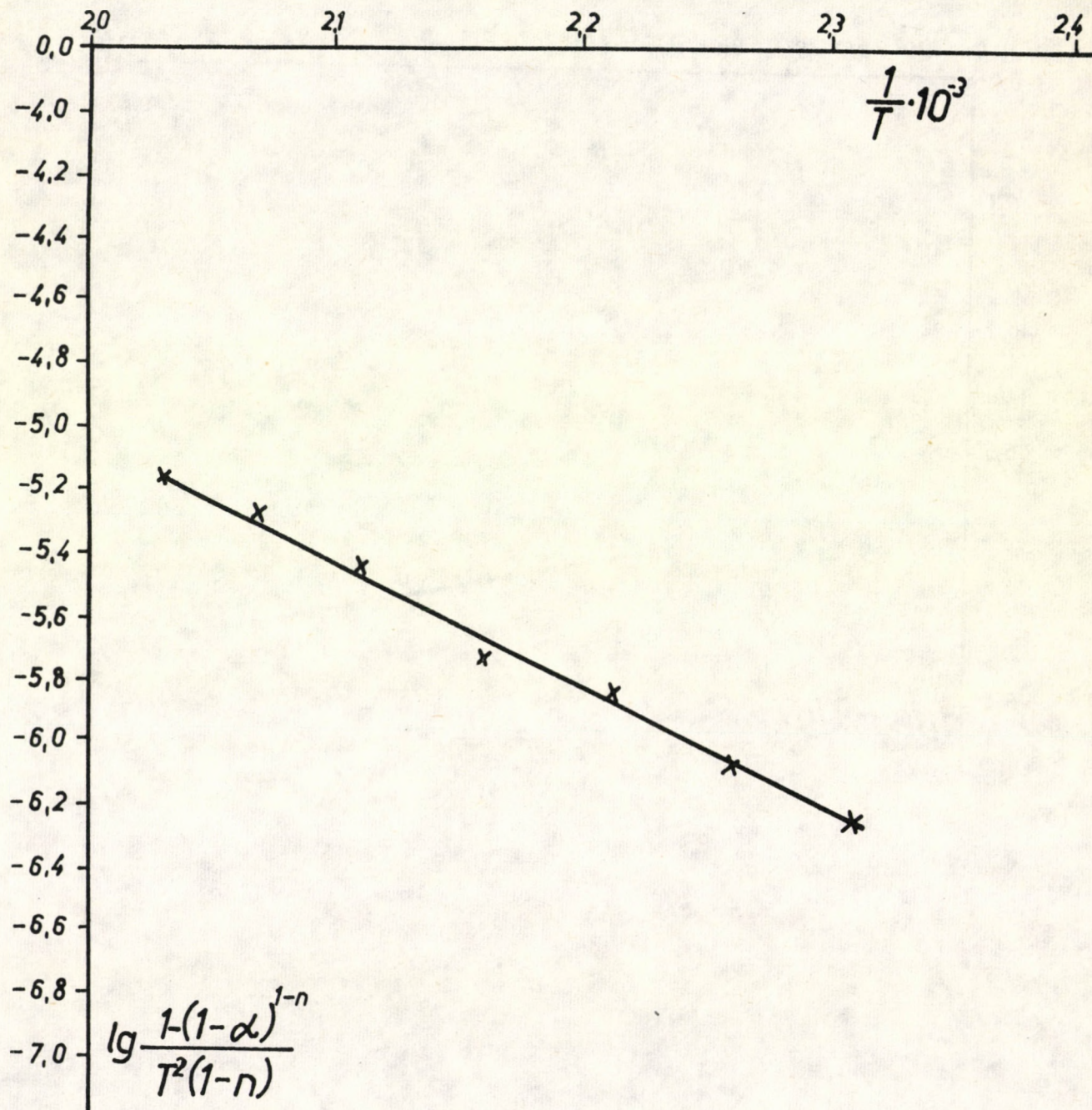


Fig. 5

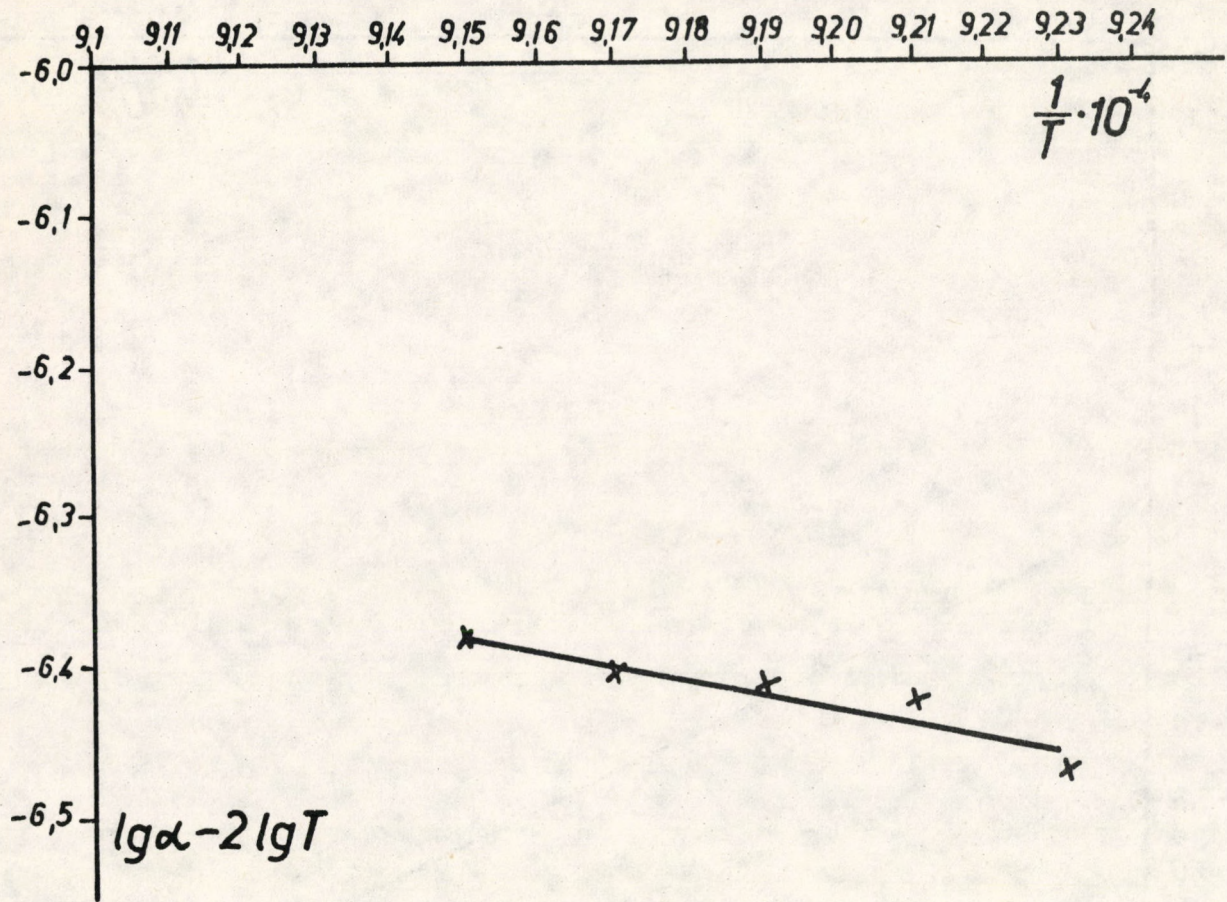


Fig. 6

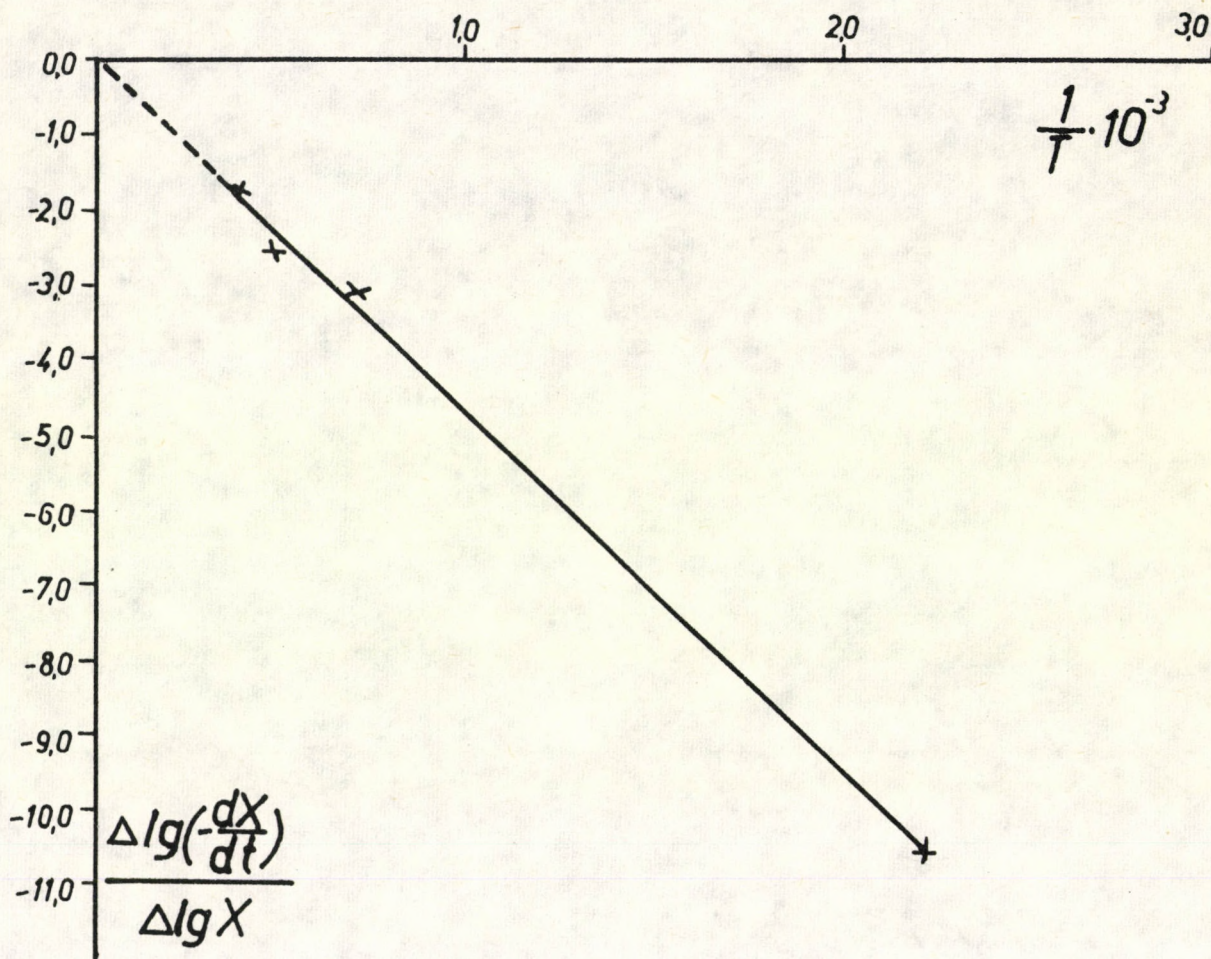
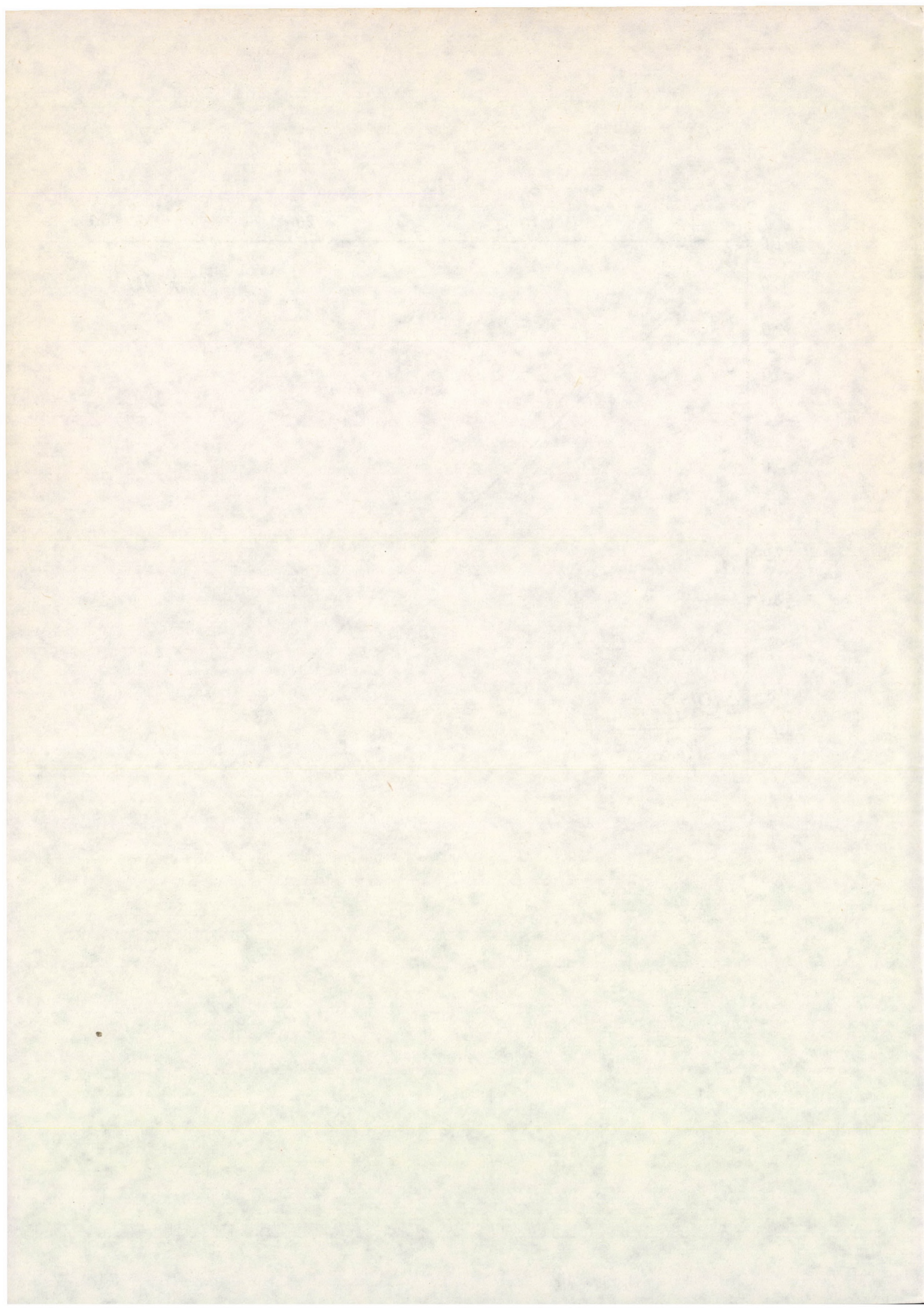
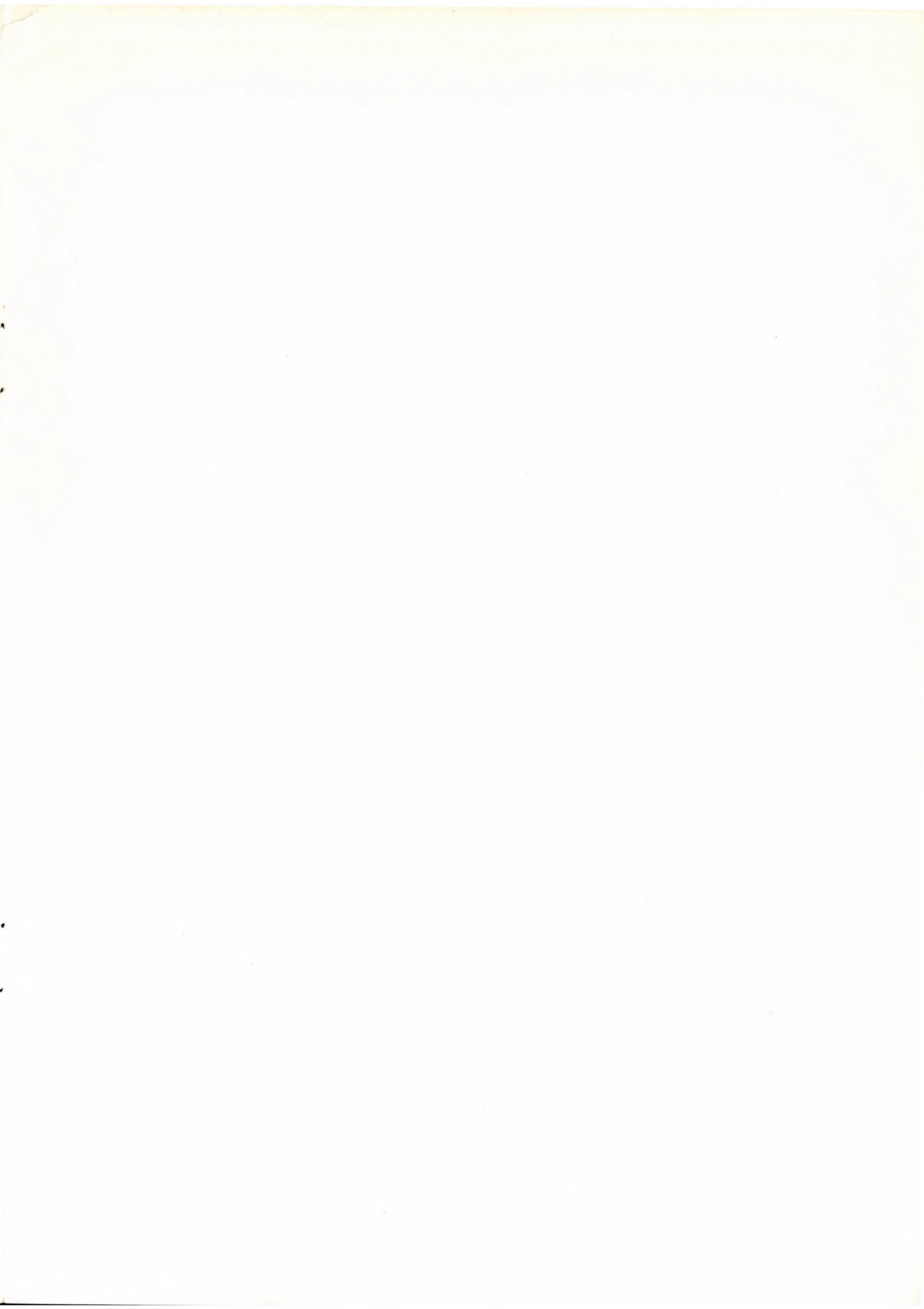


Fig. 7







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