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**THE THERMAL RELEASE OF KRYPTON
FROM THIN LAYERS OF UO₂**

by

O. GAUTSCH, C. MUSTACCHI, A. SCHÜRENKÄMPER and H. WAHL

1967



**Joint Nuclear Research Center
Ispra Establishment - Italy**

Engineering Department - Metallurgy and Ceramics - Physical Chemistry

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In both cases large fractions of gas were released below 900°C within 2 hours. Between 300°C — 900°C gas emission from bombarded pellets was found to be mainly controlled by activation energies in the range of 50 — 70 Kcal/mole. For UO_2 films, condensed from the vapour phase no gas release could be observed up to 300°C. Between 300°C — 500°C the emission of Kr occurred with activation energies ranging from 40 — 90 Kcal/mole roughly. The dominating values of activation energies could not be established.

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SUMMARY

The release of Kr from thin UO_2 layers was investigated. One type of experiments consisted in annealing sintered UO_2 pellets which were previously bombarded with Kr-ions of a few KeV. In a second type of experiments layers of recondensed UO_2 , containing between 0.04 and 0.1 Kr-atoms per atom of U, were annealed.

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C o n t e n t s

- 1.) Introduction
- 2.) Release of Kr trapped by ion bombardment
in sintered UO_2
- 3.) Release of Kr trapped in recondensed UO_2
- 4.) Conclusions

1. Introduction (*)

1.1 The scope of the present experiments was to obtain release data for Kr which was embedded in thin layers of UO_2 . Such data would show whether inert gases which are "attached" (1) (2) (3) to the surface, or buried just below the surface, are released from polycrystalline UO_2 with an essentially single activation energy or over a wide range of activation energies. A single activation energy was observed for the release of Kr from UO_2 monocrystals (4). A range was found for the release of fission Xe buried just below the surface of UC (3).

Two types of samples were used:

- a) sintered UO_2 wafers, bombarded to saturation with Kr-ions of a few KeV(5),
- b) thin layers of recondensed UO_2 , produced by sputtering a UO_2 wafer with Kr-ions (5).

The release data were analyzed by a method describing annealing processes distributed in activation energies.

(*) Manuscript received on November 21, 1966

2. Release of Kr trapped in sintered UO₂

2.1 UO₂ wafers were bombarded with known amounts of (Kr + Kr⁸⁵)-ions of 1, 5, and 8 KeV. After bombardment the initial beta activity of trapped Kr⁸⁵ was measured in a vacuum of about 10⁻⁵ mm Hg, the target being mounted in the release assembly (Fig. 2.1.1). Each target was then annealed in successive temperature steps.

The vacuum during heating was better than 10⁻⁴ mm Hg. The preset temperatures were attained within a few minutes. The Kr⁸⁵ activity in the target was recorded as a function of time and temperature. The fraction of the gas which remained in the sample was plotted vs time. When the slopes of the release curves became very small, the following annealing step was started at a higher temperature. Some typical curves are shown in Fig. 2.1.2. A significant release was observed already at about 335°C.

2.2 To obtain the activation energy E from the kinetic curves, the relation of Overhauser (6) was used, which is applicable for 2 successive stages of step-annealing, if the processes occur with a single activation energy. If the processes are distributed in activation energy, the above relation will give approximate values for E when the temperature steps are small.

If T_1 and T_2 are the temperatures of 2 successive annealing steps ($^{\circ}\text{K}$), then

$$(1) \quad E = \frac{2.3 R T_1 T_2 \log V}{T_1 - T_2} \text{ cal/mole.}$$

R is 2 cal/mole degree and $V = (dF/dt)_1 / (dF/dt)_2$. The values for dF/dt (F = fraction of gas left in the sample, t = annealing time) were obtained from the slopes of the F vs t curves at the beginning of the successive stage 2, where the value of F is the same. In all annealing experiments only a few with small temperature steps of about 50°C were performed which could be used to calculate E from eq. (1). The values obtained are shown in Table 2.2.1.

Table 2.2.1

	Activation Energy E [Kcal / mole]		
Bombardment energy T-step, $^{\circ}\text{C}$	1 KeV	5 KeV	8 KeV
600-650	31		
707-750		46	
800-848	83		
853-902		74	
900-951			60

The results obtained do not confirm the assumption that a process with a discrete activation energy controls the gas release. There is some indication for a distribution spectrum of activation energies. A similar behavior was found by A. Auskern (3) for the release of fission Xe from UC powders.

2.3 In order to get more information about the spectrum of activation energies, a method outlined by W. Primak (7) was used. The characteristic activation energy E_0 is defined by

$$(2) \quad E_0 = RT \ln (Bt)$$

where B is a frequency factor. B is assumed to be a constant in first approximation, since E is not particularly sensitive to changes in B .

If $p_0 (E_0)$ is the initial activation energy distribution as function of the characteristic activation energy the gas release can be described by the following equation (7)

$$(3) \quad \frac{dF}{dt} = - p_0 (E_0) \frac{d E_0}{dt} = - p_0 (E_0) \frac{RT}{t}$$

Setting $p_0(E_0) = K$ eq. (3) can be written:

$$(4) \quad K = \frac{dF}{d(\ln t)} \quad \frac{1}{RT}$$

Eq. (2) - (4) require that $p_0(E_0)$ be the same for all samples from which the single points of the distribution curve are to be determined. Therefore release curves obtained by successive step annealing cannot be analyzed by means of eq. (2) - (4), because after the first annealing step the distribution curve has another shape than before. However, the application of the above equations seems to be justified as an approximation for sufficient large temperature steps and sufficient long annealing times where the influence of the preceding step is assumed to be small. This means that the slopes dF/dt or $dF/d(\ln t)$ have about the same value after a long annealing time, regardless if the sample was brought to a given temperature instantly or if it was already annealed before.

Fig. 2.3.1. shows typical curves, obtained by re-plotting the data of Fig. 2.1.2. as F vs $\log t$. The slopes of the curves for a given temperature are within experimental errors constant between 10 and 200 min. Values of K were obtained from the slopes of the curves and are shown as a function of temperature in Fig. 2.3.2. The highest K -values were found at about 600°C for the 1 KeV-samples, 800°C for 5 KeV, and 850°C for 8 KeV.

For the calculation of the characteristic activation energy E_0 for each temperature by eq. (2), B must be known. The frequency factor B may be estimated using the relation $B = D_0/l^2$ where D_0 is obtained from diffusion measurements, and the penetration depth l from an independent experiment. For sintered UO_2 $D_0 = 6.6 \cdot 10^{-6}$ cm²/sec (8) and $l = 2 \cdot 10^{-8}$ cm \pm 50 % per KeV (5). Taking $\log B = 10$, and $t = 600-12000$ sec, E_0 can be calculated. For the temperatures which correspond to the maxima of K in Fig. 2.3.2. the results are shown in Table 2.3.1.

Table 2.3.1.

Bombardment energy, KeV	1	5	8
temperature of maximum K, °K	880	1070	1140
Activation energies corresponding to the maximum of the initial distribution, Kcal/mole	52-57	63-69	67-74

The results are in reasonable agreement with those obtained by using the relation (1) outlined by Overhauser. Release of Kr from UO_2 saturated by ion bombardment is therefore controlled mainly by an activation energy of about 50 - 70 Kcal/mole.

3. Release of Kr trapped in recondensed UO_2

3.1 Thin UO_2 layers, containing between 0.04 and 0.1 Kr-atoms per atom of U were deposited on Al-collectors in an ion getter assembly (5). Heat treatment of the collectors was performed as described in Section 2. Typical release curves are shown in Fig. 3.1.1. and 3.1.2. Up to $300^\circ C$ no gas release was observed at all (see also ref.9). If we assume also for these experiments that the gas release is proportional to the annealing of structural defects, an attempt can be made to analyze the release curves by the method of Overhauser (6).

The results obtained for experiments with small temperature steps are given in Table 3.1.1.:

Table 3.1.1.

Activation Energy E in Kcal/mole

T-step, $^\circ C$	E
312-352	62
340-362	87
381-341	42
395-450	46
400-451	56
445-490	89

The activation energies for the release seem to be comparable to the values obtained for the release of Kr injected into sintered UO_2 .

3.2 The logarithmic plot of the release curves shows that after about 40 minutes the slopes of some release curves change abruptly. This behavior would indicate changes of the structure of UO_2 to which gas release may be related. In fact, electron diffraction micrographs showed that the deposited UO_2 was initially amorphous. Only during heating by an electron beam rings characteristic for the crystalline structure of UO_2 appeared. This is shown in Fig. 3.2.1. The values given in Table 3.1.1. can therefore be considered to be indicative. A more detailed analysis (e.g. by Primak's method) would not be justified.

4. Conclusions

4.1 Large fractions of surface trapped Kr are released from UO_2 at temperatures below 900°C within 2 hours. Similar release behavior was found by A. Auskern (3) for the release of fission Xe from UC powders.

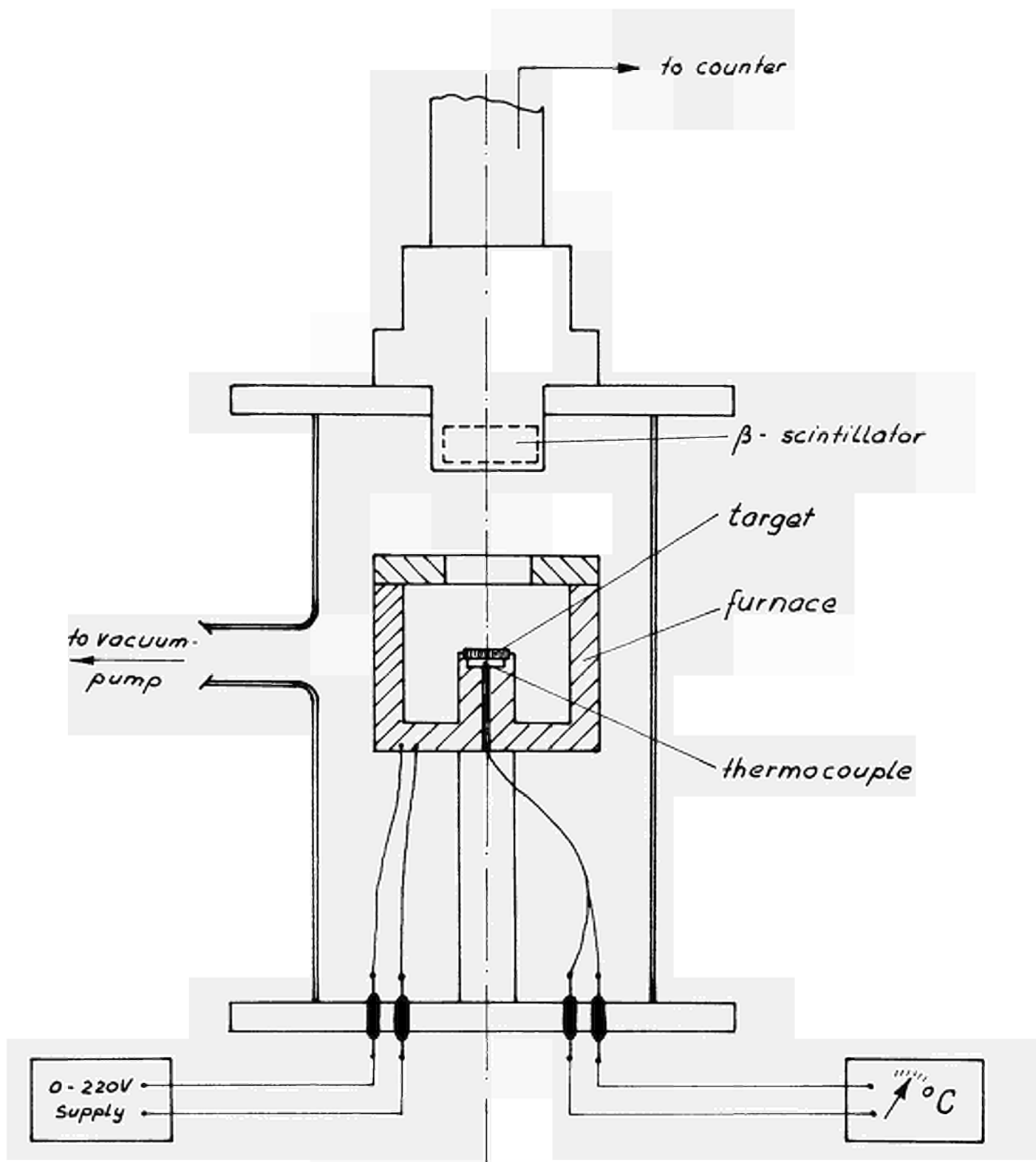
4.2 An attempt was made to analyze the obtained results by the methods of Overhauser and Primak. Both methods gave evidence of an activation energy distribution with a maximum at 50 - 70 Kcal/mole in case of Kr-bombarded UO_2 wafers.

4.3 The release of Kr from recondensed UO_2 gave some indication of structural changes during annealing at temperatures between $300^{\circ}C$ and $500^{\circ}C$. Indicative values for the activation energies involved are 40 - 90 Kcal/mole. The dominating values of the activation energies could not be determined.

4.4 The results lead to the conclusion that the kinetic of gas release at low temperature is different from the kinetic of bulk diffusion. Apparent bursts observed in diffusion measurements may be of the same kind as the release observed in the described experiments.

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Release assembly.

Fig. 2.1.1

Release of Kr from UO₂ (1KeV)

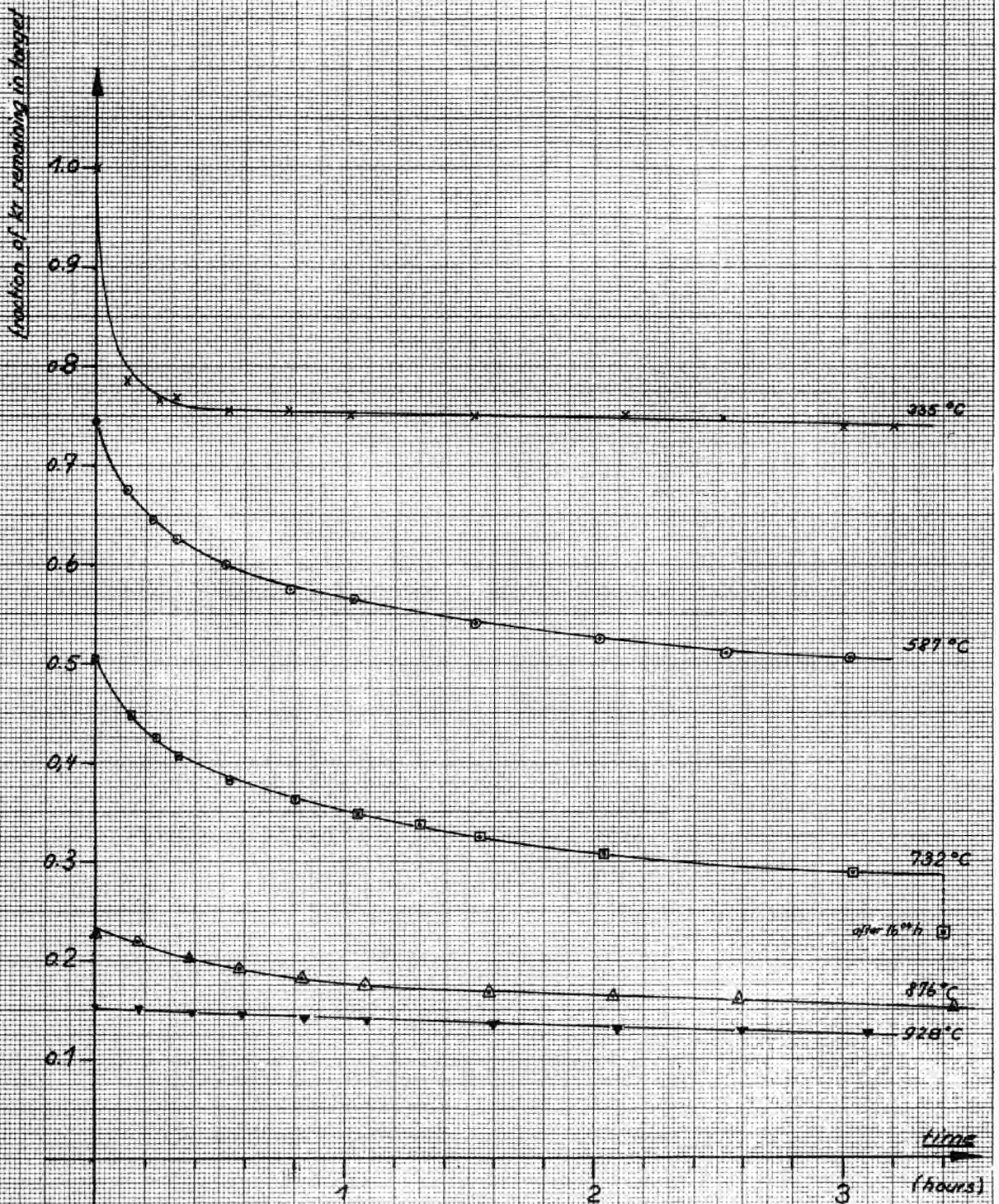
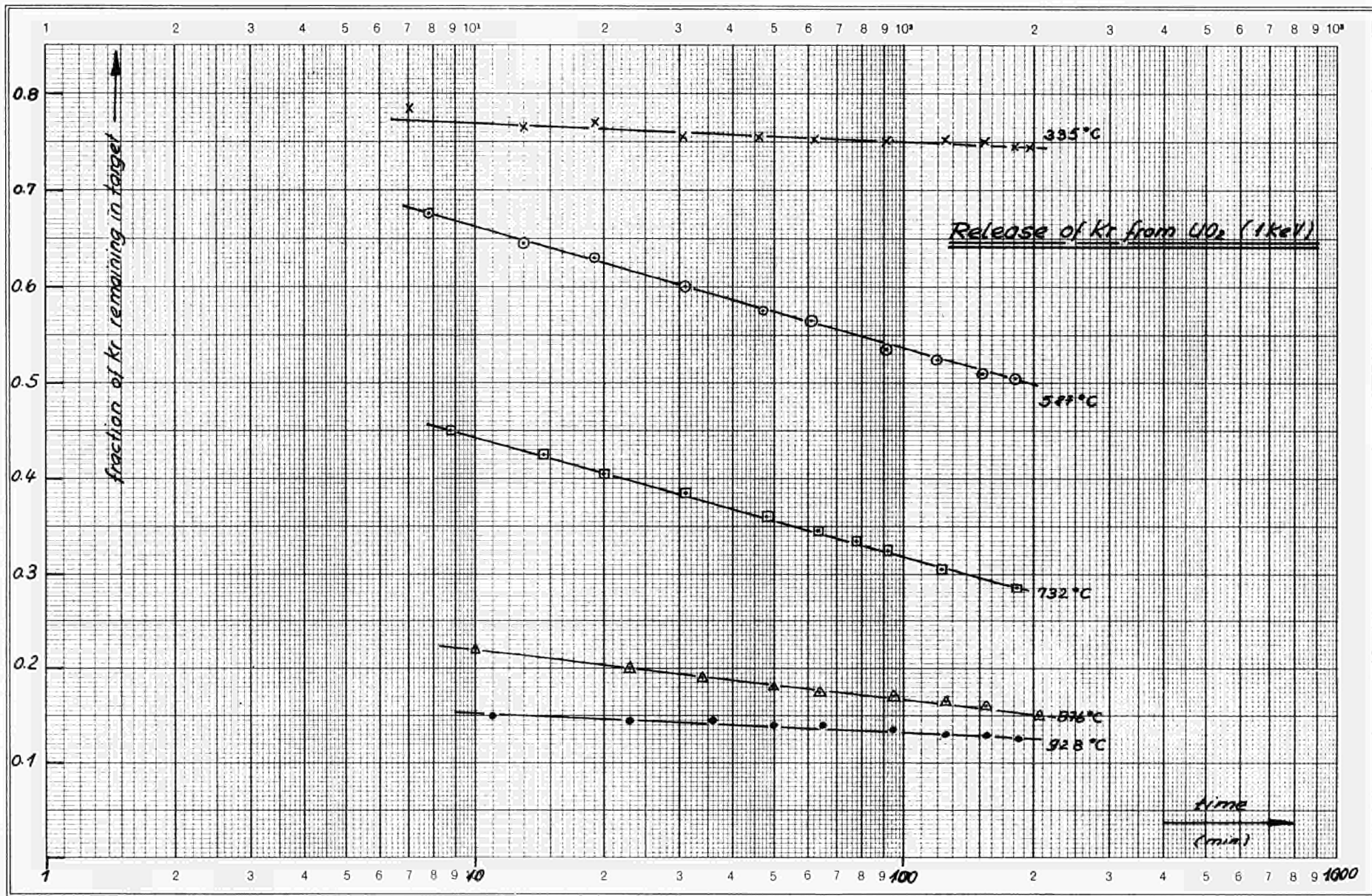
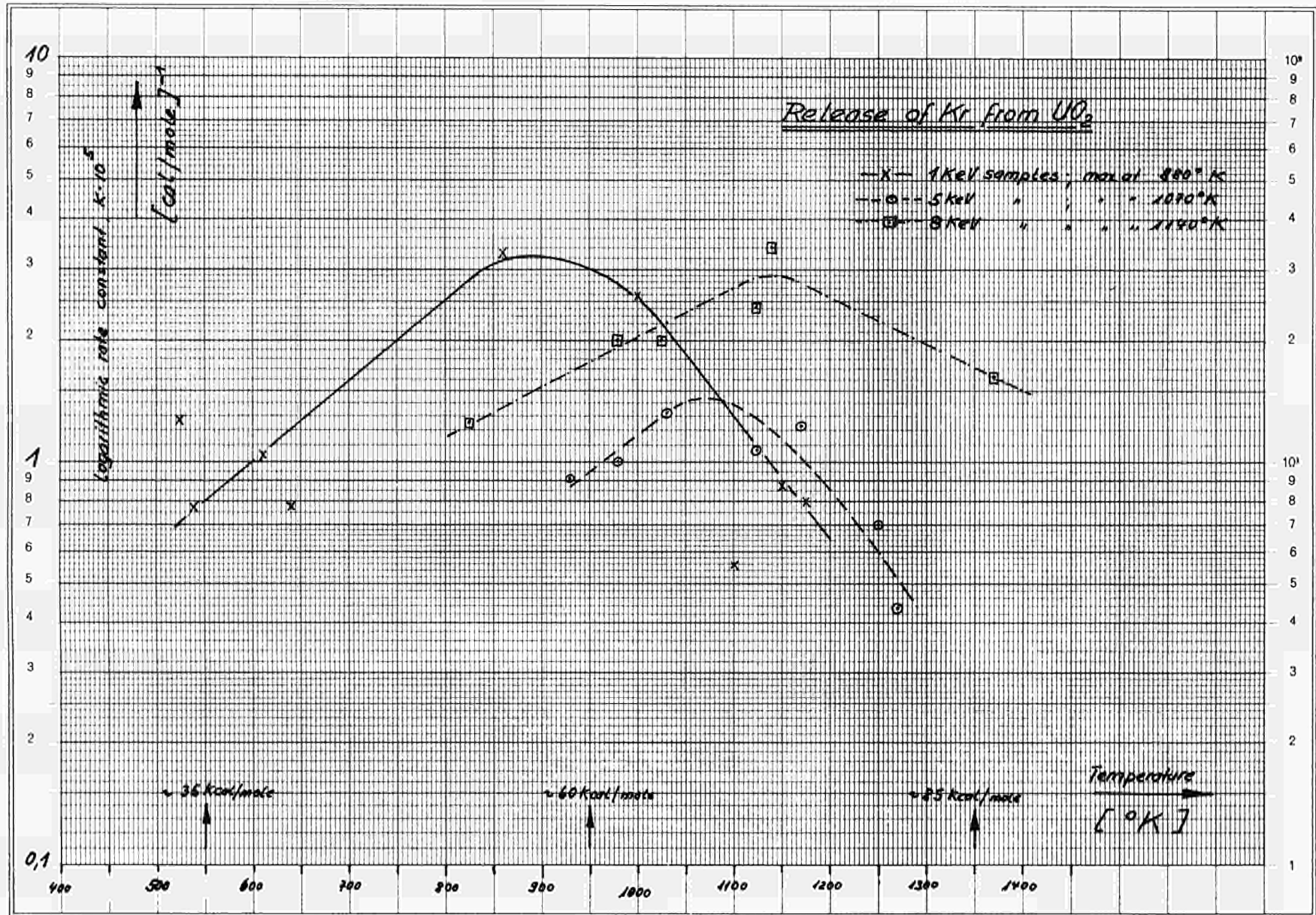


Fig. 2.1.2



Logar. Teilung } 1 - 1000 Einheit } 90 mm
 Division } Unité }

Fig. 2.3.1



Logar. Teilung } 1 - 100, Einheit } 83,33 mm
 Division } Unité }

Fig. 2.3.2

Release of Kr from recondensed UO₂

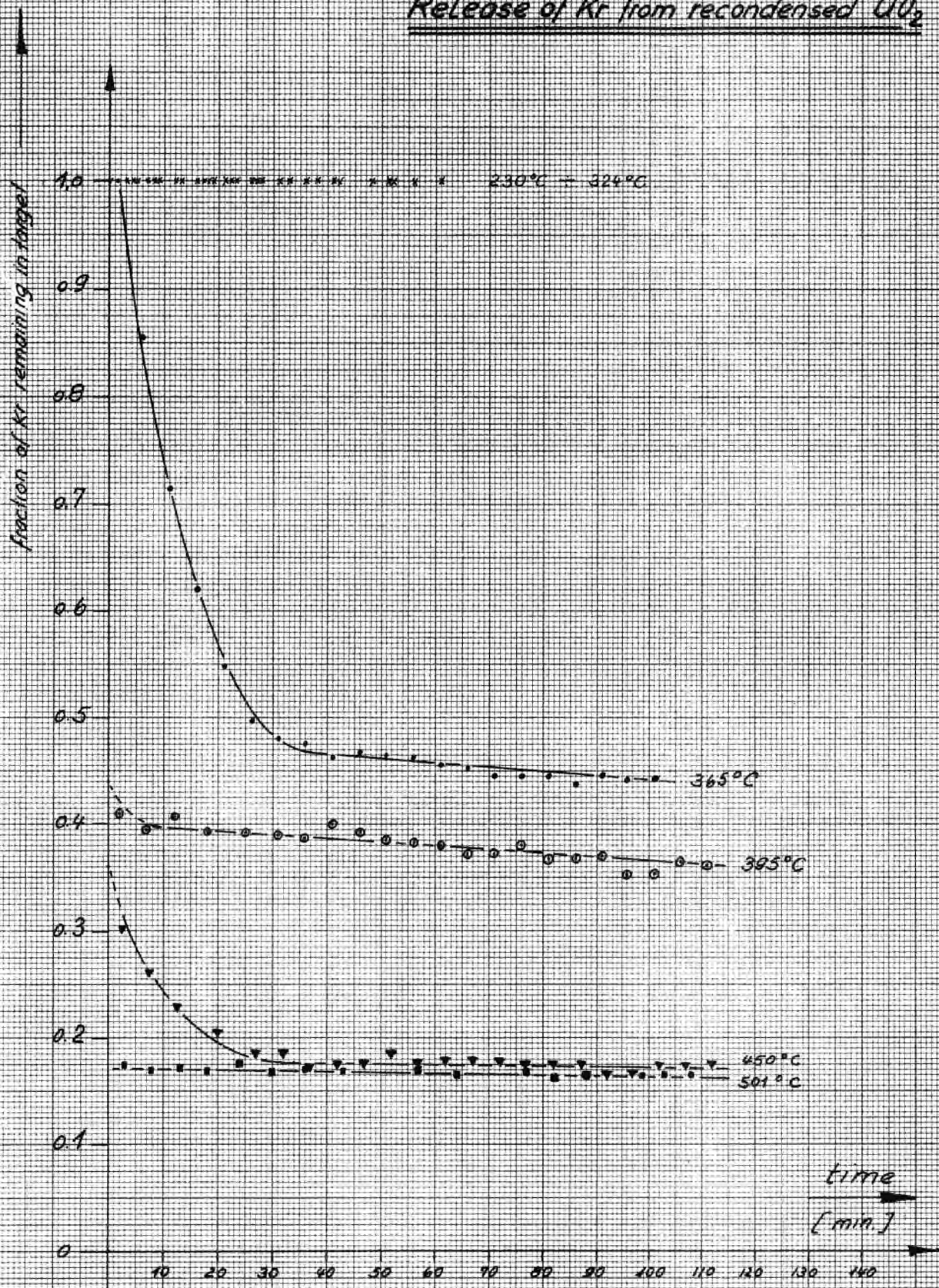


Fig. 3.1.1

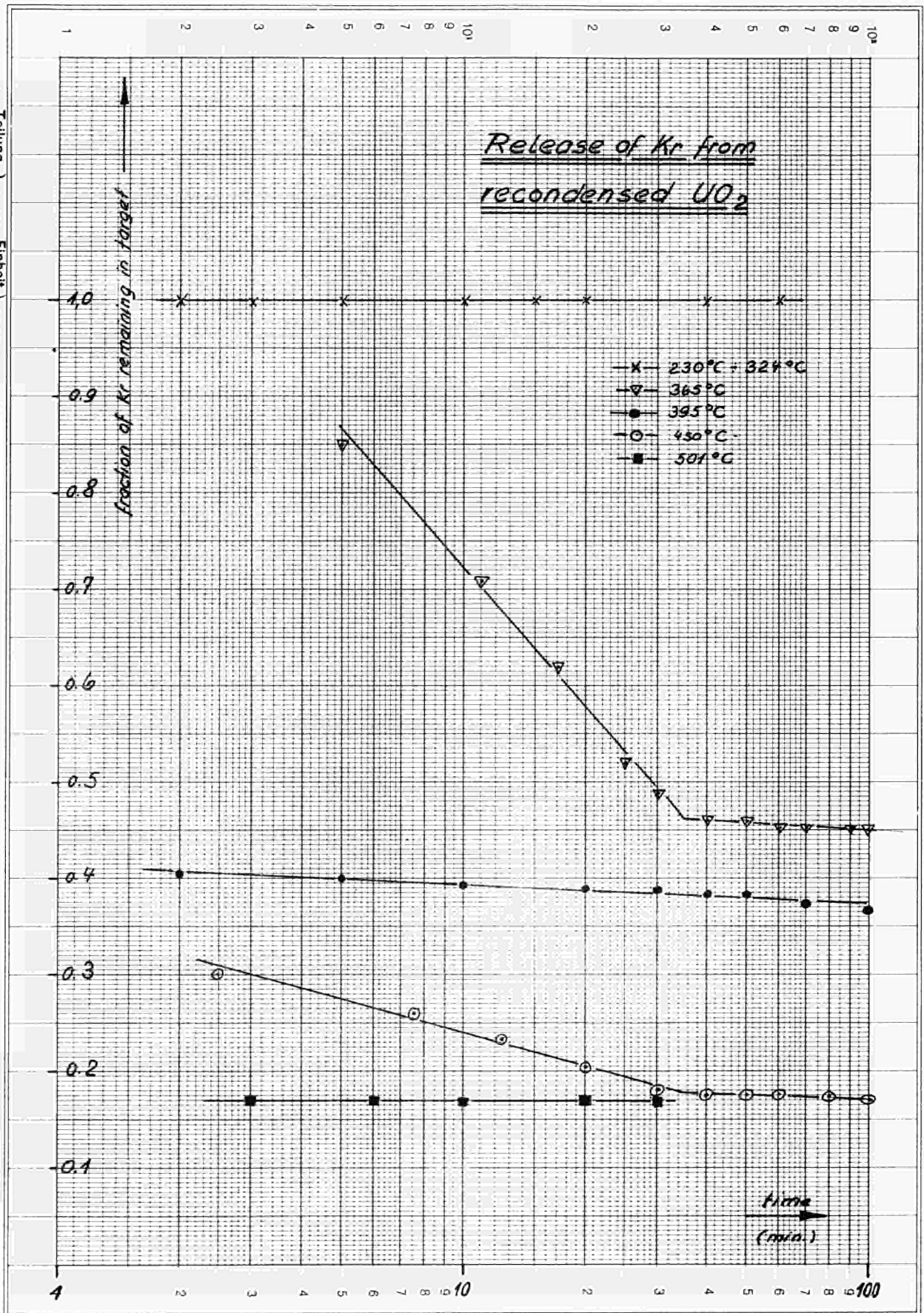
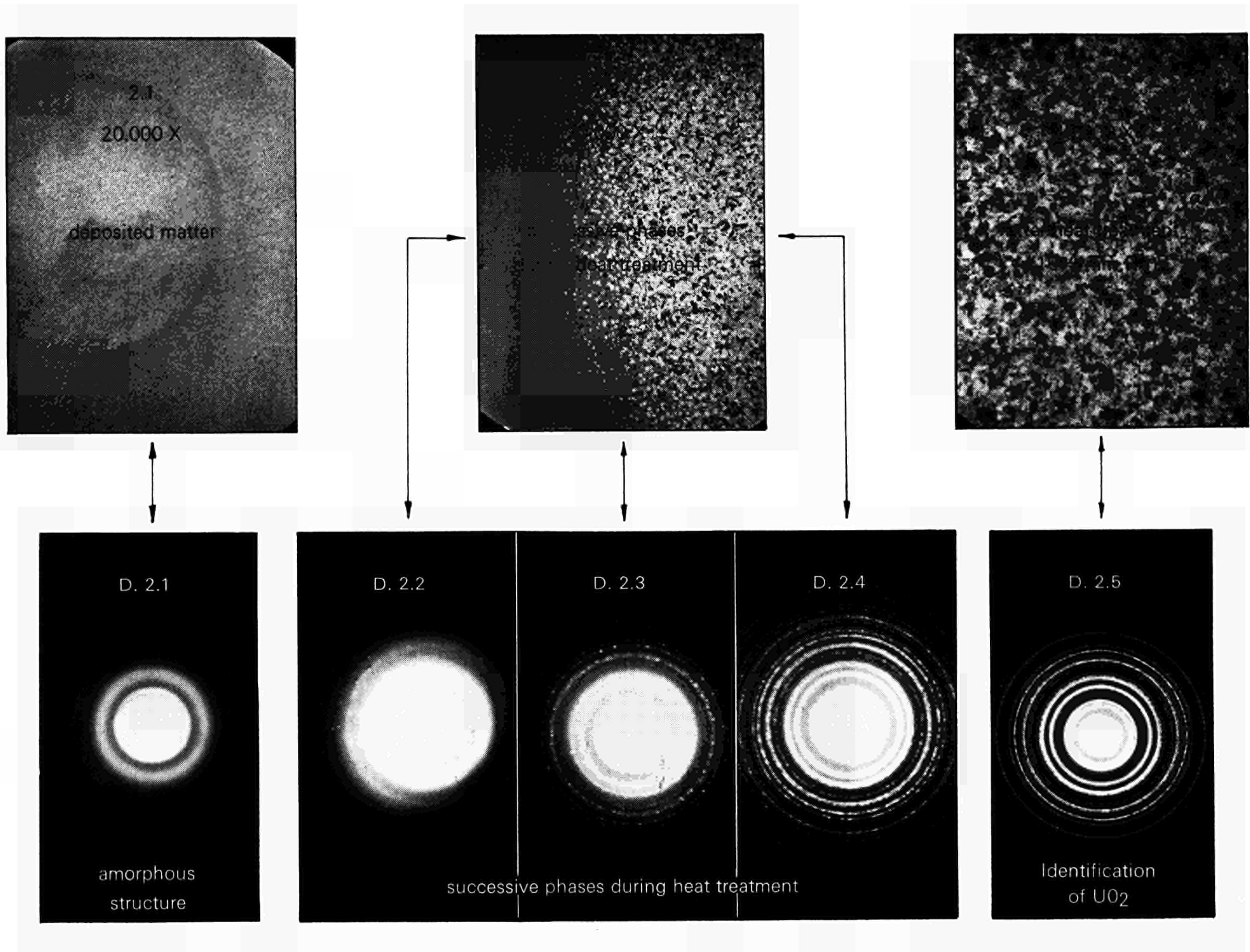


Fig. 3.1.2

Fig. 3.2.1



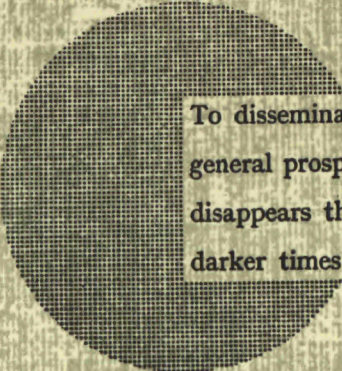
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To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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