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KINETICS OF INITIAL STAGE SINTERING
OF STOICHIOMETRIC AND NONSTOICHIOMETRIC ACTINIDE
OXIDES

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Abstract :

The kinetics of initial stage sintering of UO_2 powder were reinvestigated, using Ar-10 % H_2 atmosphere. The effect of the addition of neodymium oxide was studied. The results revealed that grain boundary diffusion mechanisms predominate. The values of activation energies were found to be 48.48 ± 3.51 Kcal/mole in the temperature range 870 - 942°C and 89.88 ± 9.87 Kcal/mole in the temperature range of 942 - 1030°C for UO_2 , and 115.61 ± 7.77 Kcal/mole in the temperature range 1030 - 1150°C for $\text{UO}_2 + \text{Nd}_2\text{O}_3$. A remarkable decrease in the calculated diffusion coefficient occurs by the addition of Nd_2O_3 .

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INTRODUCTION

Non stoichiometry in oxides might affect the rate and the mechanism of material transport during sintering, according to the characteristics of the defect structure which it creates. This was investigated thermodynamically for uranium oxides (1).

Mixing with higher oxides, control of sintering atmosphere and doping with soluble additions of materials with different valencies (5) are some of the techniques used for producing non stoichiometry in UO_2 .

The early stage of sintering of both stoichiometric and hyperstoichiometric UO_2 was the subject of several investigations (2-4, 6-13), which show large discrepancies from single mass transport mechanism, volume diffusion (2, 3, 6) or grain boundary diffusion (4, 7, 11, 12), to more than one operating mechanism (8-10, 13).

Measured values of process activation energies - initial sintering - varies in a wide range from 20 Kcal/mole (19) to 107 Kcal/mole (6). However, for most authors, one can observe some positive agreement concerning the activation energies, 90-110 Kcal/mole (7, 11, 12, 6) for the stoichiometric oxide and 50-65 Kcal/mole for the hyperstoichiometric oxide. Unfortunately they end with contradicting interpretations of the controlling mechanism, grain boundary (7, 11, 12) or volume diffusion (2, 3, 6, 10).

By the use of a method of analysis - of shrinkage data - insensitive to error in the zero point of shrinkage and time, then applying simultaneous grain boundary and volume diffusion model (14), one can distinguish confidently between the two mechanisms.

In this work, the above methods of analysis were applied for the initial sintering of both UO_2 and $UO_2 + 2.12$ mole % Nd_2O_3 in $Ar-H_2$ atmosphere (used in practice).

EXPERIMENTAL

UO_2 powder of BET surface area of $2.4 \text{ m}^2/\text{g}$ was obtained by the reduction of UO_3 with argon - 10 % hydrogen at 700°C for 5 h. Some of the UO_2 powder was mechanically mixed with 3.11 % by weight of neodymium oxide. Spectrographic analyses for impurities in each powder are given in tables I and II.

TABLE I

Principal impurities in UO_2 powder
(in 10^{-6} g/g of uranium)

Ag	Al	B	Co	Cr	Cu	Fe
<1.3	<50	<0.7	<20	12	<5	41
M	Mo	Ni	Pb	Si	Sn	
<8	10	15	13	65	<10	

TABLE II

Principal impurities in Nd_2O_3
powders (in 10^{-6} g/g of Nd_2O_3)

Ag	Al	As	B	Ba	Be	Bi	Cd
3	30	10	10	30	1	1	3
Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni
3	10	10	25	10	3	30	10
Pb	Si	Sn	Ti	U			
3	30	10	10	10			

Cylindrical pellets were prepared by pressing the powders in a double acting hydraulic press, under a pressure of 5 t/cm^2 .

The pellets dimensions were of the order of 6 millimeters in diameter and 10 millimeters in height, and with green densities of the order of 63 % of theoretical density.

Differential dilatometer DHT 60 of S.A. Instruments (15) was used for shrinkage measurements (with readability of 2×10^{-4} cm).

A heating rate of 300°C/h was used till the sintering temperature. The temperature was measured by Pt-Pt 10 % Rh thermocouples above the middle of the pellet. The sintering atmosphere was Ar-10 % H_2 , purified by passing through Ti-Zr gas purifier. It had a water content of less than 50×10^{-6} . A vacuum of 2×10^{-5} torr was used in this investigation.

Thermogravimetric analysis was made in Ar-10 % H₂ as a reducing atmosphere with 0.08 l/min flow at a heating rate of 300°C/h, using a microbalance of accuracy ≈ 0.2 μg (16) ; these conditions are similar to those used in dilatometric investigation. The result is shown in figure 1 which is in fair agreement with previous investigations (6, 10, 17). The major weight loss was observed between 300°C & 600°C, while from 600 to 900°C a weight loss with much smaller rate was observed and even continued after 900°C, which indicates that complete reduction to UO_{2,00} was not yet attained, in agreement with the literature (6, 10, 17, 18). Adsorbed H₂ (19) and adsorbed water make the determination of the exact stoichiometry difficult to perform.

Similar analysis - as shown in fig. 2 - was made for neodymium oxide. A weight loss of about 15 % - mostly due to dehydration - was reached at a temperature of 900°C, which is quite below the sintering temperature. This value of weight loss agrees with published values (20).

The above mentioned value of 3.11 % by weight should be corrected to 2.12 mole %.

RESULTS AND DISCUSSION

Shrinkage data could generally be represented by the equation :

$$y = \left(\frac{A \gamma \Omega D t}{K T r^P} \right)^n \quad (1)$$

where : y is the fractional shrinkage, γ is the surface energy, Ω the vacancy volume, D is the diffusion coefficient, r is the particle radius, and A , n , P are constants depending on the model which could fit the shrinkage data as given in table III.

TABLE III

Values of constants for eqn. (1)
for various diffusion models

Diffusion path	A	n	p	Ref.
Bulk	$\frac{3l}{\Pi^2}$	0.46	3	(21)
	4.2	0.48	3	(22)
	$\frac{20}{\sqrt{2}}$	0.40	3	(23)
	2	0.50	3	(24)
Grain boundary	$\frac{50b^*}{7 \Pi}$	0.31	4	(20)
	1.55b	0.32	4	(22)
	15a*	0.33	4	(24)

*b, a, grain boundary width

Plots of log shrinkage vs. time suffer from errors in the zero of time and shrinkage which necessitate making corrections (21). One can obtain-by differentiating and rearranging equation (1) - two linear equations giving the experimental shrinkage y as a function of $\dot{y}^{(n/n-1)}$ and the experimental time t as a function of $\dot{y}^{(1/n-1)}$ where \dot{y} is the shrinkage rate. These equations - which are similar to those obtained by JOHNSON (25) - are insensitive to both errors in the zero of time and shrinkage.

Shrinkage rate was obtained from a polynomial fitting of the experimental data, and shrinkage and time corrections y_0 , t_0 could be readily obtained from a plot of $\dot{y}^{n/n-1}$ vs. y , and a plot of $\dot{y}^{1/n-1}$ vs. t respectively.

Figures 3, 4 show the corrected data for UO_2 and $UO_2-Nd_2O_3$ respectively, plotted according to the grain boundary diffusion model proposed by JOHNSON and CLARK (22). Straight lines passing by the origin were obtained, which suggests the validity of the proposed mechanism.

Sintering model based on simultaneous grain boundary and volume diffusion leads to the following equation :

$$f(D_V, D_B) = (Y)^{2.1} \times (\dot{Y}) = \frac{2D_V \gamma \Omega}{r^3 kT} Y + \frac{D_B b \gamma \Omega}{2 r^4 kT} \quad (2)$$

Replotting of the corrected data according to this equation - fig. 5, 6 - shows nearly horizontal lines indicating that volume diffusion was negligible in the sintering of both UO_2 and $(UO_2-Nd_2O_3)$. JOHNSON (14) stated that volume diffusion can be neglected if $rD_V/2\pi b D_B < 0.1$. If we take r calculated from specific surface area as 0.114μ and $b = 5 \text{ \AA}$ and the ALCOCK (26) value D_B/D_V of 10^5 , one can find that the above mentioned value - $rD_V/2 b \pi D_B$ - is 3.68×10^{-4} which is far smaller than 0.1. This, once again, suggests that grain boundary diffusion could be predominant.

Taking the parameters in equation (1) to be $\gamma = 600 \text{ erg/cm}^2$ (27), $\Omega = 4.02 \times 10^{-23}$, $r = 0.114 \mu$ and $b = 5 \text{ Angstrom}$, grain boundary diffusion coefficients could be calculated. The results are shown in fig. 7, which shows for UO_2 , two straight lines with quite different slopes, i.e. two activation energies of $48.48 \pm 3.51 \text{ Kcal/mole}$ in the temperature range of $870 - 942^\circ\text{C}$ and $89.88 \pm 9.87 \text{ Kcal/mole}$ in the temperature range $942 - 1038^\circ\text{C}$; hence the diffusion coefficient could be represented by the following equations :

$$D = (4.5 \pm 0.09) 10^{-8} \text{ Exp} - \left(\frac{48.48 \pm 3.55}{RT} \right) \quad 870 \leq T \leq 942^\circ\text{C}$$

$$D = (1.33 \pm 0.13) 10^{-8} \text{ Exp} - \left(\frac{89.88 \pm 9.87}{RT} \right) \quad 942 \leq T \leq 1038^\circ\text{C}$$

KEY

(a) UO_2

ref(11) (f) 110

ref(20)

The small activation energy obtained in the lower temperature range could be attributed to the presence of a small amount of oxygen in excess. This is supported by the thermogravimetric results mentioned before and agree with the thermodynamic analysis of MATZKE (1). It is also in agreement with most of the published values obtained from sintering kinetics of UO_{2+x} (2, 3, 4, 10) and agree with estimated activation energies 45 ± 17 Kcal/mole for grain boundary diffusion (28), and with the value obtained for self-diffusion during argon annealing (29).

As the temperature is increased, the oxygen in excess will be removed gradually till stoichiometric composition is reached ; then, a higher activation energy will be obtained. This agrees with the above mentioned thermodynamic analysis (1).

This value of activation energy - 89.88 Kcal/mole - as compared with those obtained from the sintering data for grain boundary diffusion in stoichiometric UO_2 (7, 11, 12) was in good agreement, as shown in fig. 8. The calculated diffusion coefficients - if extrapolated to high temperature - are in better agreement with those obtained for grain boundary diffusion obtained by ALCOCK (26) than those obtained for volume diffusion (26, 29-31).

For $UO_2+Nd_2O_3$ the sintering was retarded for about $200^\circ C$ and the diffusion coefficients calculated from the sintering data were smaller by more than two orders of magnitude than those calculated for stoichiometric UO_2 (fig. 7) and the activation energy of 115.61 ± 7.77 Kcal/mole was obtained which is somewhat higher than that obtained for UO_2 ; these decreases in the diffusion coefficient are in agreement with similar investigations in UO_2 doped with Y_2O_3 (5). A solid solution of $UO_2-Nd_2O_3$ formed on the surface of UO_2 particles (probably by surface diffusion) has a lower concentration of uranium vacancies than stoichiometric UO_2 which may explain the observed

decrease in diffusion coefficients.

X-ray diffraction patterns showed - from line displacement - a slight increase and a slight decrease in the lattice parameter - with respect to UO_2 - for a pellet treated at 1150°C and for the same pellet after being equilibrated under $\text{H}_2/\text{H}_2\text{O}$ at 900°C respectively. This agrees with the reported behaviour for $(\text{U,Nd})\text{O}_{2-x}$ and $(\text{U,Nd})\text{O}_{2.00}$ (32). This may suggest the presence of solid solution with slight substoichiometry during the isothermal treatment.

From the values of activation energies and the calculated diffusion coefficients for UO_2 and $\text{UO}_2+\text{Nd}_2\text{O}_3$ mentioned above, uranium vacancy mechanism could be suggested to control the initial stage of sintering both for stoichiometric, slightly hyper and sub-stoichiometric oxide.

In a vacuum of (2×10^{-5}) torr) sintering starts at a temperature quite lower than in Ar-10 % H_2 , by about 200°C . The results are difficult to analyse because of unexpected variations of shrinkage rate during the isothermal treatment. This could be a result of gas desorption (19), and/or oxidation.

Results concerning PuO_2 and its mixture with UO_2 could not be given here and should be treated separately.

CONCLUSION

1) The initial sintering of UO_2 in Ar - 10 % H_2 showed activation energies of 48.48 ± 3.51 Kcal/mole in the temperature range of $870 - 942^\circ\text{C}$ and 89.88 ± 9.87 Kcal/mole in the temperature range $942 - 1030^\circ\text{C}$, with grain boundary diffusion as the predominant mechanism.

2) The addition of Nd_2O_3 decreases the diffusion coefficient and the grain boundary diffusion mechanism remains predominant.

3) Uranium vacancies control the sintering process (in the initial stage) both for stoichiometric and slightly hyper and (Nd-induced) sub-stoichiometric uranium oxide.

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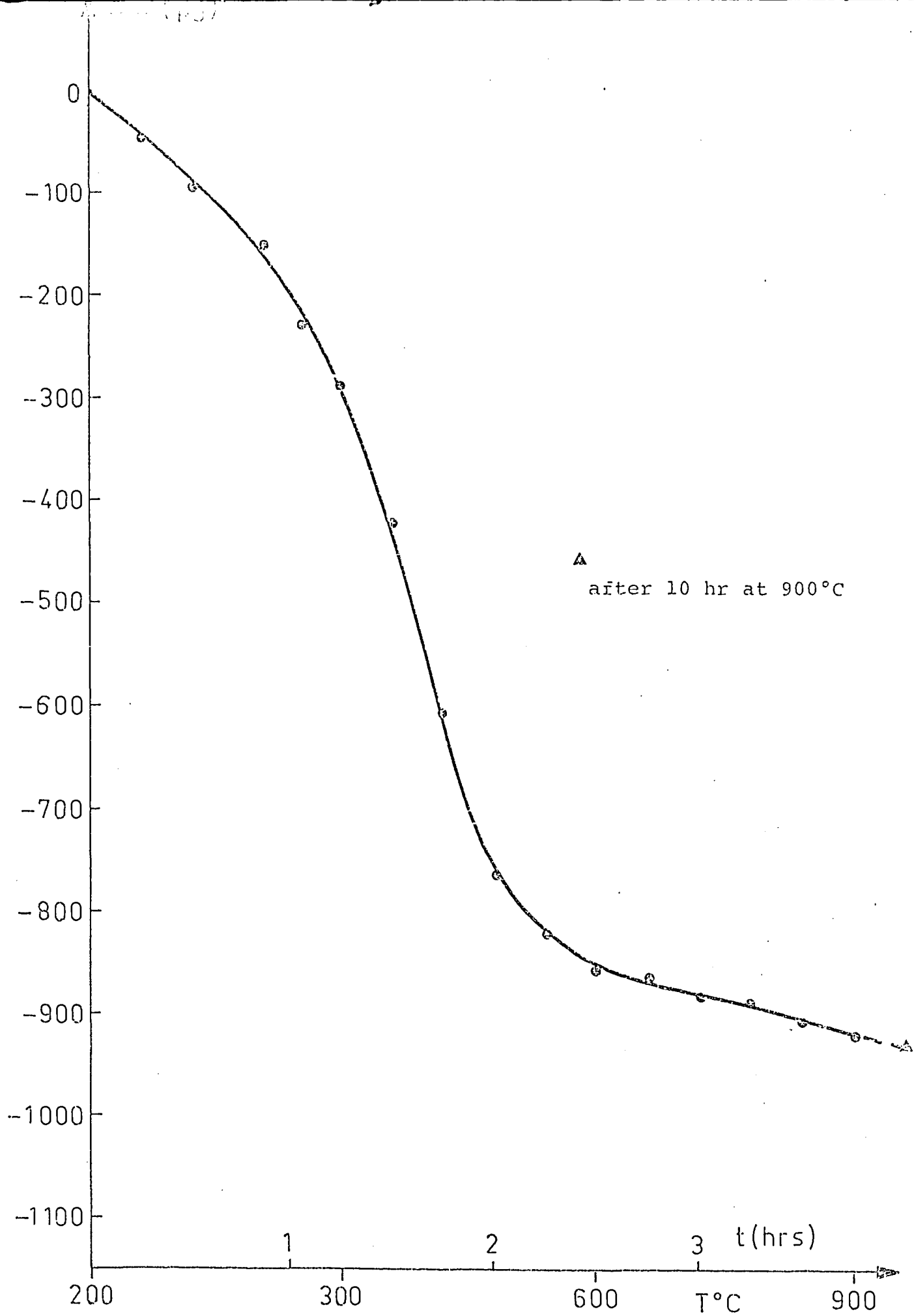


Fig.(1) Weight loss in Ar-H₂ of UO₂ compact

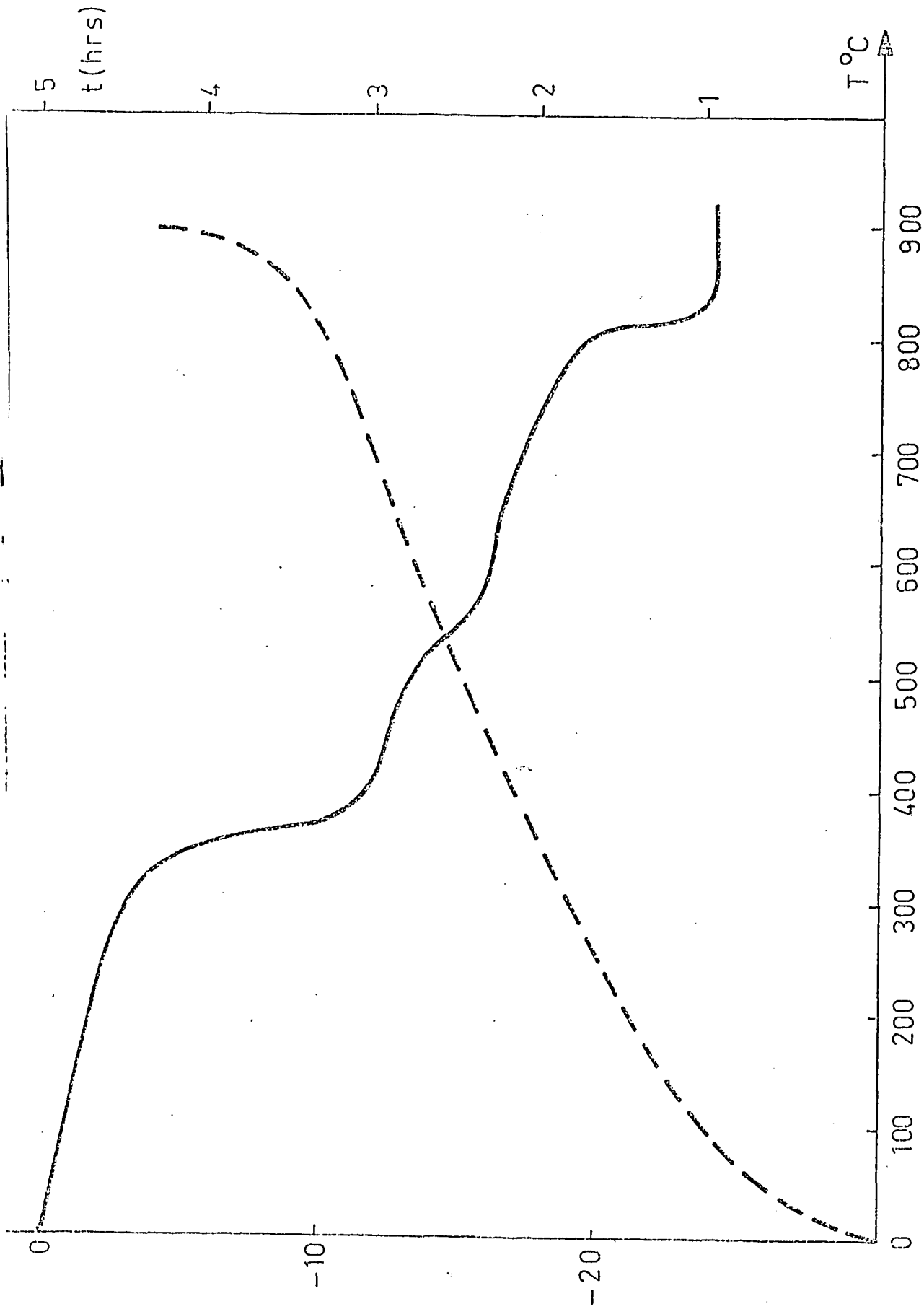


Fig.(2) Weight loss in Ar-H₂ of Nd₂O₃

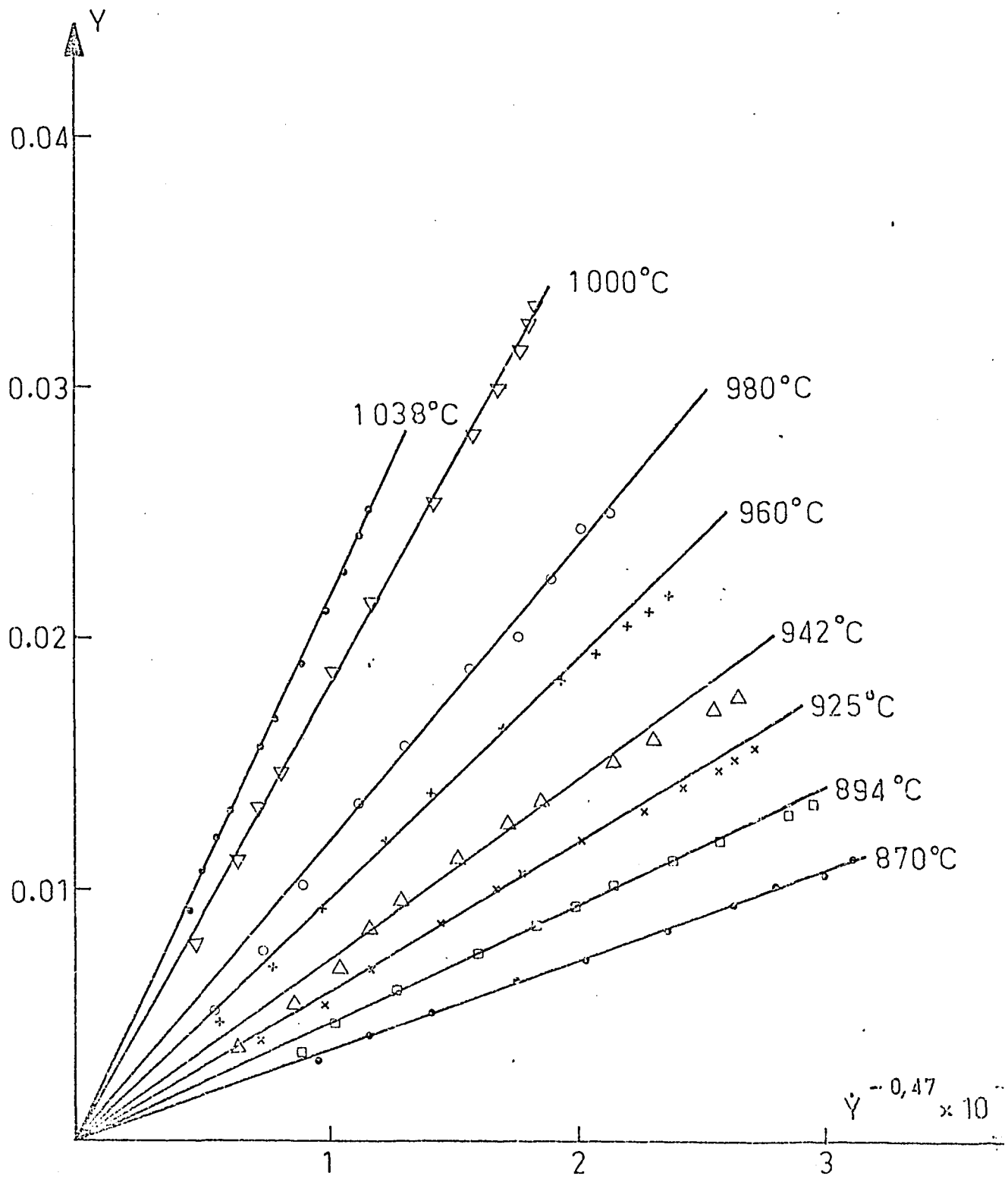


Fig.(3) Shrinkage isotherms for uranium oxide

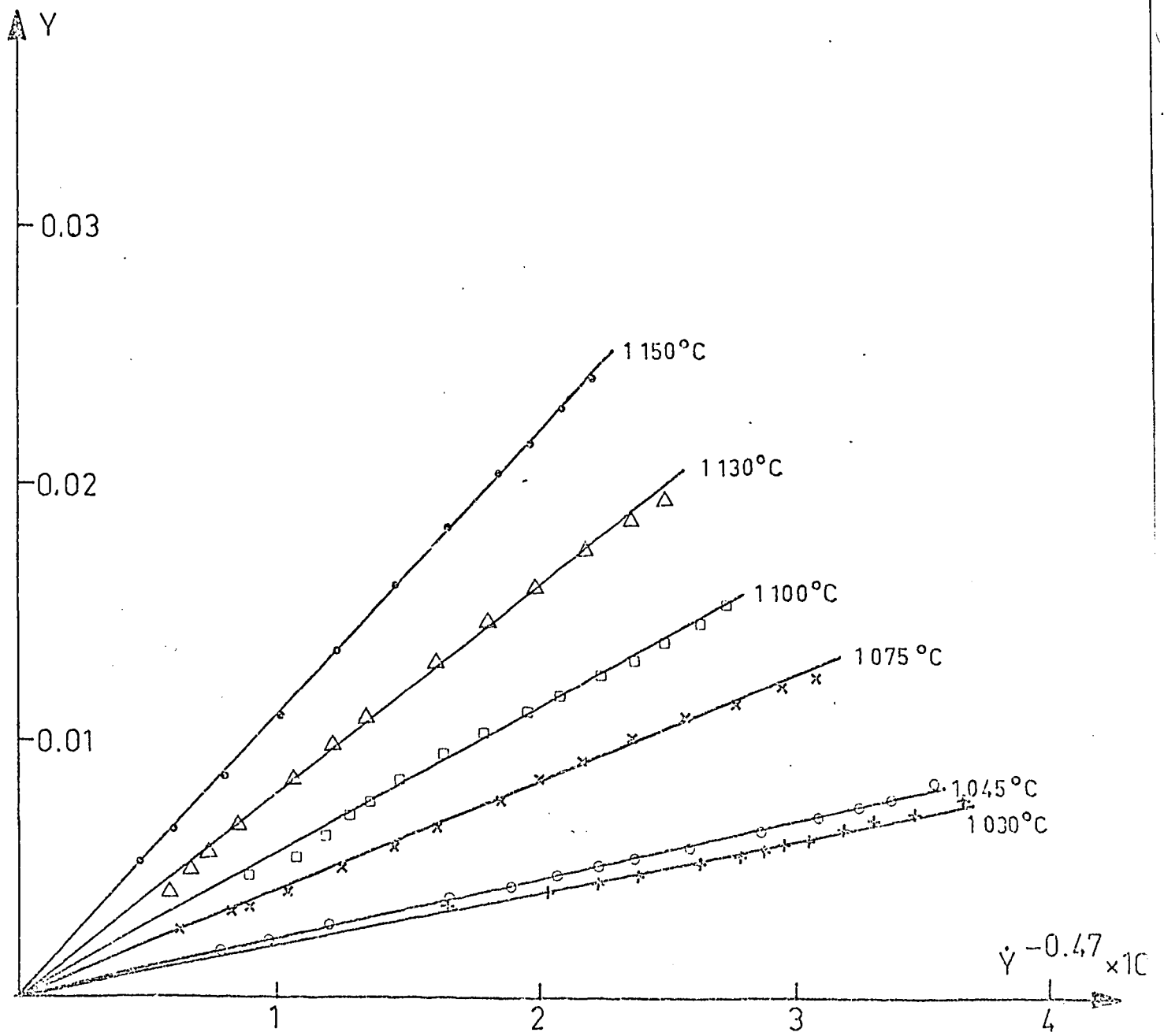


Fig. (4) Shrinkage isotherms for $(UO_2+Nd_2O_3)$

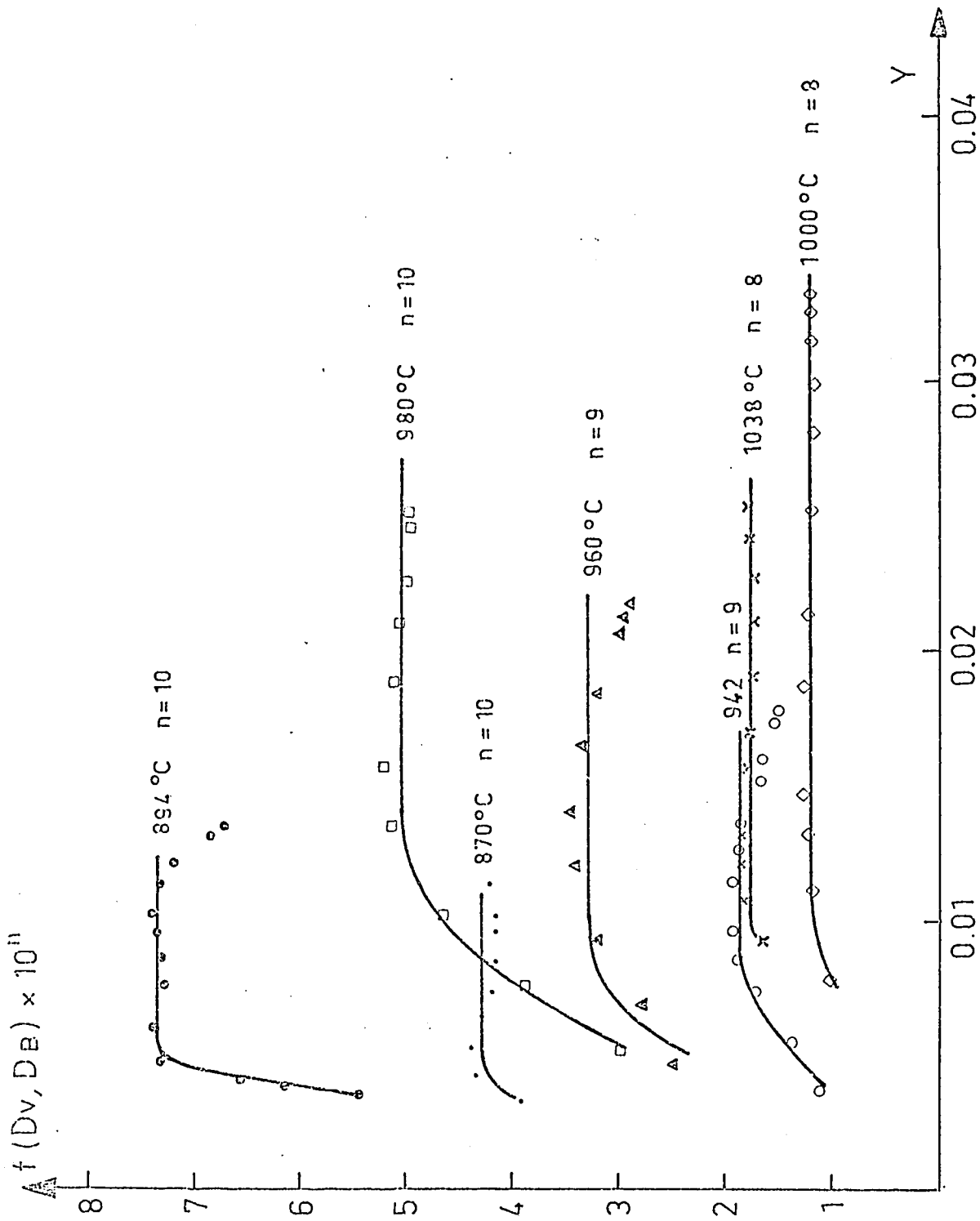


Fig.(5) Shrinkage isotherms for UO_2 plotted as in eqn (2)

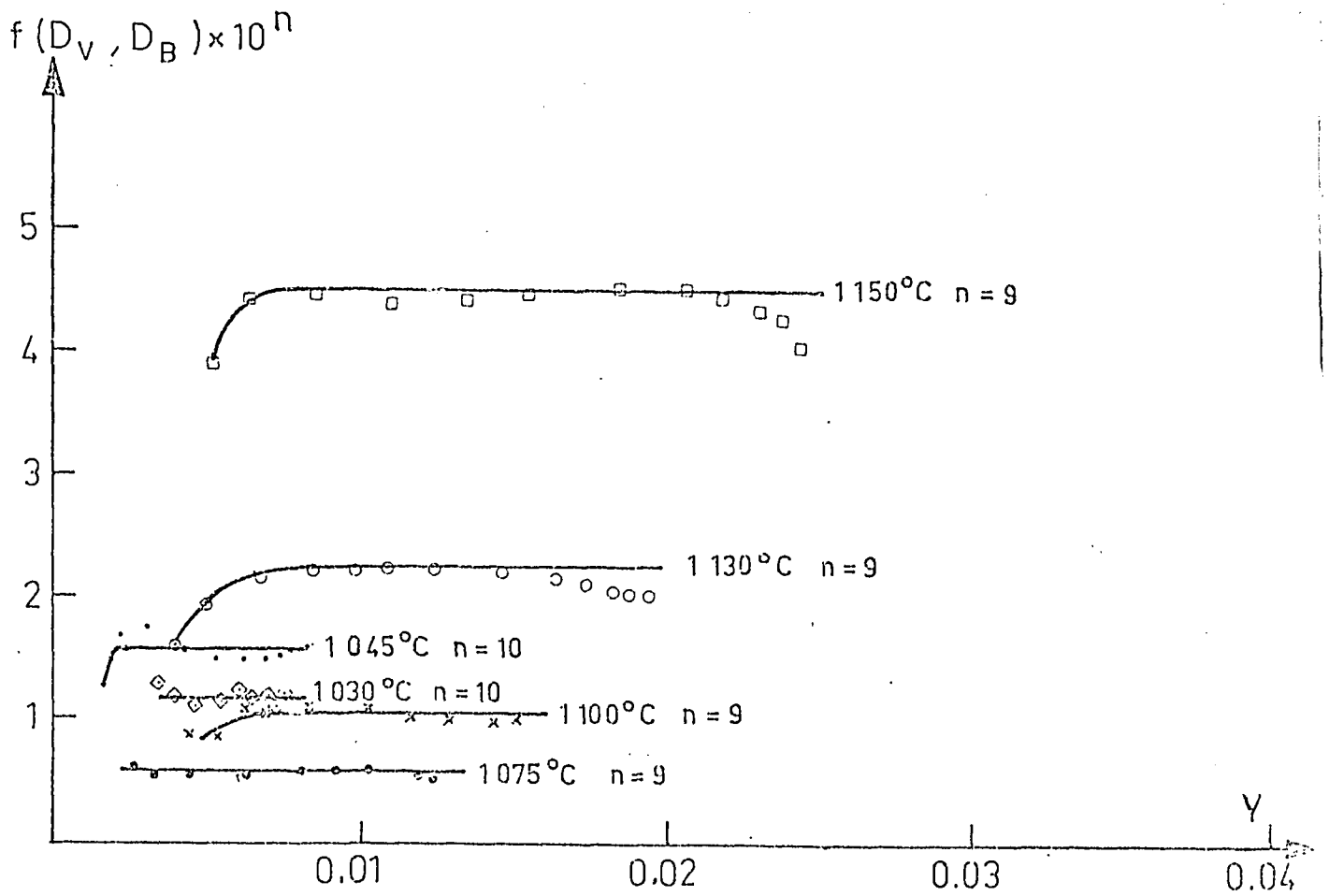


Fig. (6) shrinkage isotherms for $(\text{UC}_2 + \text{Nd}_2\text{O}_3)$, plotted as in eqn (2)

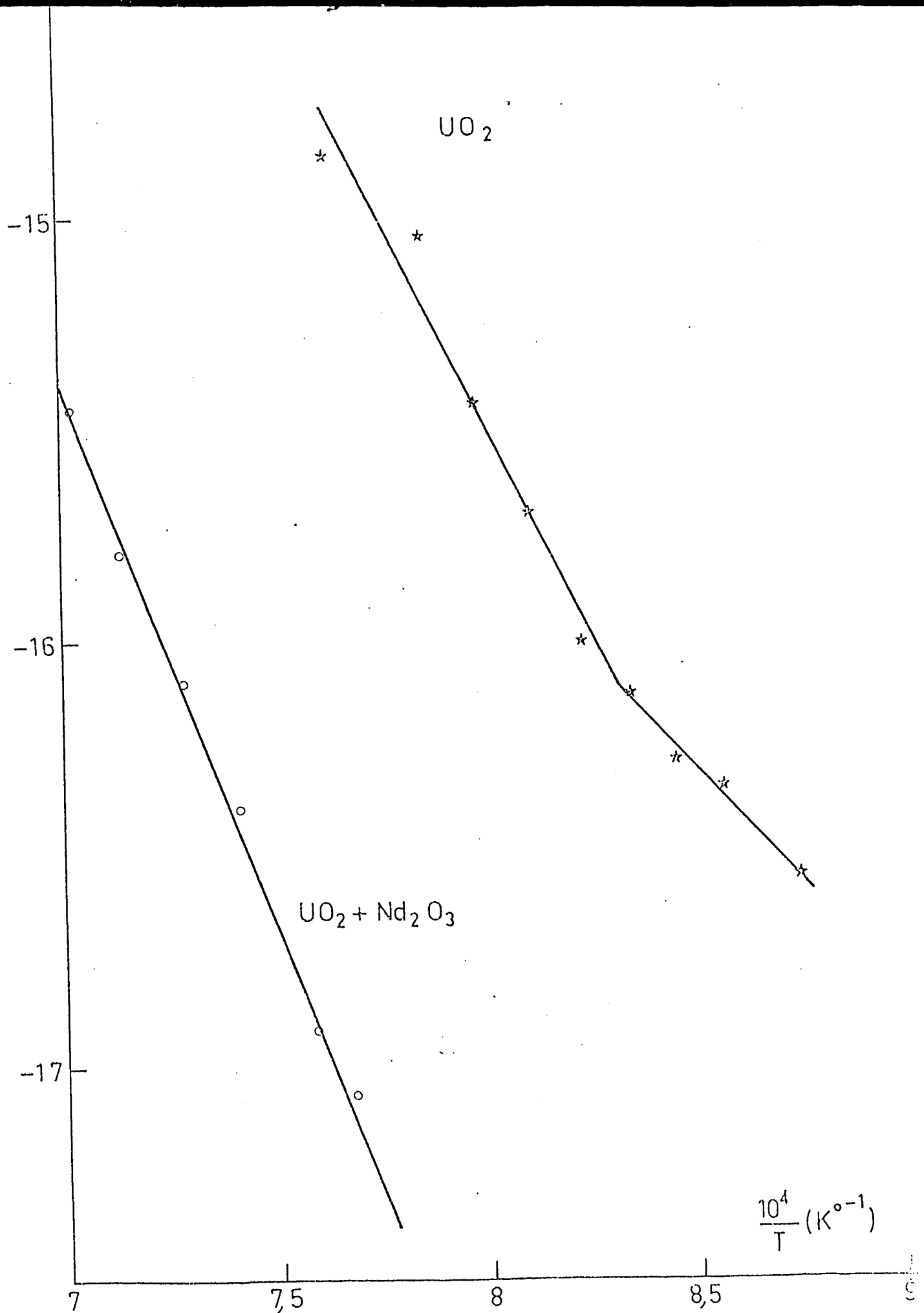


Fig. (7)

(a) UO_2	ref.(11)	(f) UO_2	ref.(29)
(b) UO_2 (powder p)	ref.(7)	(g) UO_2	ref.(26)
(c)	present results	(h) UO_2	ref.(30)
(d) $UO_2 + x$	ref.(10)	(i) UO_2	ref(31)
(e) $UO_2 + x$	ref.(2)		

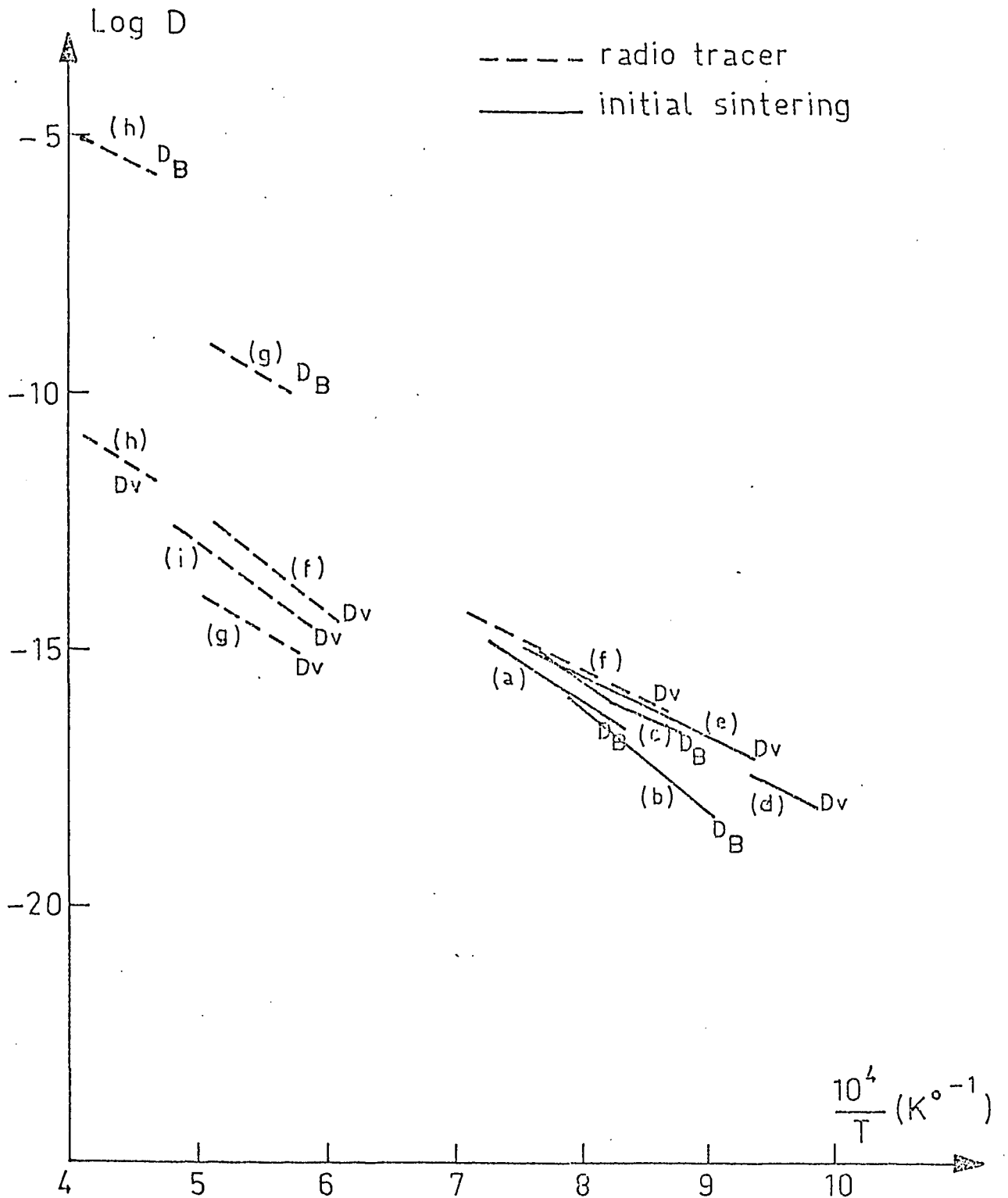


Fig. (8) D_v & D_B from initial sintering & tracer measurement

