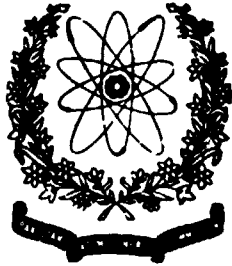


12 8200021

PINSTECH/NPD-123



**KINETICS OF HETEROGENEOUS CATALYSIS
OXIDATION OF CARBON MONOXIDE**

**Y. KHWAJA
A. SADIQ**

**NUCLEAR PHYSICS DIVISION
Pakistan Institute of Nuclear Science & Technology
P. O. Nilore, Islamabad
October, 1987**

KINETICS OF HETEROGENEOUS CATALYSIS
OXIDATION OF CARBON MONOXIDE

Y. Khwaja

A. Sadiq

Nuclear Physics Division
Pakistan Institute of Nuclear Science and Technology
P.O. Nilore, Islamabad

ABSTRACT

An irreversible kinetic surface-reaction model, based upon the reaction of carbon monoxide and oxygen on a catalyst surface is investigated by means of Monte Carlo simulation. The adsorbed molecules/atoms on the surface undergo both first and second order kinetic phase transitions. The first order transition is found to occur at $x_{CO} = x_2 = 0.5255 \pm 0.0003$, where x_{CO} is the concentration of carbon monoxide in the gas phase. The time evolution of this catalytic reaction is studied both analytically and by computer simulation. Slightly above x_2 , the oxygen coverage is found to decay exponentially, and the average relaxation time for the oxygen coverage is found to diverge as $\tau \approx \frac{1}{|x_2 - x_{CO}|^{\gamma}}$ where $\gamma = 3.54$.

CONTENTS

<u>S.No.</u>	<u>Description</u>	<u>Page</u>
1.	INTRODUCTION	1
2.	MODEL	3
3.	KINETIC PHASE TRANSITIONS	4
4.	TIME EVOLUTION OF OXYGEN COVERAGE	6
5.	ACKNOWLEDGEMENTS	10
6.	REFERENCES	11
7.	FIGURE CAPTIONS	12
8.	FIGURES	

1. INTRODUCTION

One of the aspects about solid surfaces that has the largest fundamental and technical importance is the way in which chemical reactions are affected by the presence of a surface. Many reactions proceed with rates that are orders of magnitude larger at a surface than in the gas or liquid phase. Reactions in which the surface plays the role of a catalyst are called heterogeneous catalytic reactions. The oxidation of carbon monoxide is one of the most thoroughly studied heterogeneous catalytic reactions. In recent years it has assumed added importance due to its application in automobile - emission control. In spite of these extensive studies it continues to pose difficulties and challenges for both the experimentalists and theoreticians. The reactions taking place on the surface are irreversible and show complicated behaviour. Since these systems are outside classical statistical mechanics, there is no general theory to describe them. It is therefore useful to examine specific dynamical models and study their behaviour.

An irreversible kinetic surface - reaction model, based upon the reaction of carbon monoxide and oxygen on a catalyst surface has been investigated by Ziff et al [1] by Monte Carlo simulation. They found that the adsorbed molecules/atoms on the surface undergo both first- and second-order kinetic phase transitions. The reactive steady state occurs only for $x_1 < x_{CO} < x_2$, where x_{CO} is the composition of carbon monoxide in the gas phase and $x_1 = 0.389 \pm 0.005$ and $x_2 = 0.525 \pm 0.001$ when x_{CO} is lowered below x_1 the catalyst is poisoned with oxygen. This transition is continuous and of second order. For $y_{CO} > y_2$ the only steady state is the non-reactive state in which the surface is covered with carbon monoxide. This transition is abrupt and is a first order kinetic phase transition.

More recently Kang and Redner [2] have used a scaling theory to describe the time evolution of the irreversible diffusive recombination process $A + B \rightarrow \text{inert}$. In this

reaction, the spatial distribution of the particles at time $t = 0$ is random but globally homogeneous, and for $t > 0$ one or both of the particle species move diffusively. There is no interaction between the particles of the same type, but when an A and a B particle meet they instantly and irreversibly combine to form an inert species. The mean field prediction for the decay law gives

$$x_A(t) = \frac{1}{kt} \quad [x_A(0) = x_B(0)]$$

$$x_A(t) = \exp[-k\{x_B(0) - x_A(0)\}t] \quad [x_A(0) < x_B(0)]$$

where $x_A(t)$ and $x_B(t)$ are the densities of species A and B at a time t , and k is a rate constant. As shown by Kang and Redner the spatial fluctuations alter radically the decay laws. One gets the asymptotic solutions

$$x_A(t) = \frac{1}{kt^d} \text{ for } x_A(0) = x_B(0)$$

$$\text{and } x_A(t) = \exp(-Ct) \text{ for } x_A(0) < x_B(0)$$

where $x = d/4$

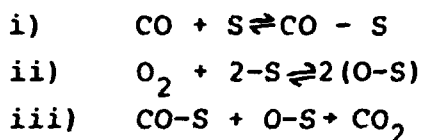
To our knowledge very little similar published literature exists for the corresponding irreversible catalytic surface reaction, in which carbon monoxide reacts with oxygen after getting adsorbed on the surface.

In this paper we present a detailed study of the heterogeneous oxidation of carbon monoxide. In particular we are interested in the time evolution of this system near the first order phase transition x_2 .

In the next section we present the salient features of the model that is used to describe the system. In section III we describe the different factors affecting the accurate determination of the critical composition x_2 . In section IV we discuss analytically and numerically the time evolution of the minority species (oxygen) near the critical composition. The conclusions are summed up in the last section.

2. MODEL

The mechanism of the heterogeneous oxidation of carbon monoxide is now well established [3.4]. It proceeds according to the following steps.



Here S denotes a free adsorption site on the surface. Step (i) represents the adsorption of carbon monoxide. The adsorption energy of carbon monoxide ranges between 120 and 170 kJ/mol. It decreases with higher coverages due to the operation of repulsive interactions. Desorption of carbon monoxide takes place in the temperature range 450 - 530 K, and can therefore be neglected. Step (ii) represents the adsorption of oxygen, this step also is irreversible at temperatures of interest. The adsorption energy is of the order of 370 K. Step (iii) represents the surface reaction given by the Langmuir Hinselwood (LH) mechanism. Carbondioxide is weakly adsorbed, the estimated adsorption energy is approximately 20 kJ/mol. This is why its life-time on the surface above room temperature is immeasurably short.

We use essentially the same simulation technique as described by Ziff et al [1]. We consider an inexhaustible supply of carbon monoxide and oxygen in a given ratio. The gas molecules impinge on a square lattice which represents the

surface of the catalyst. A carbon monoxide molecule needs a single vacant site for its adsorption, this is so since CO couples to the metal surface through the carbon atom [5] only. An oxygen molecule on the other hand needs two adjacent sites for its adsorption. The reaction of carbon monoxide with oxygen takes place only when the two are nearest neighbours. The CO_2 thus produced desorbs immediately, leaving behind two vacant sites. This model ignores various mechanisms which could take place on the surface, such as finite reaction rates, diffusion of species about the surface, multiple crystal planes, reassociation and desorption of oxygen atoms, and desorption of the unreacted CO molecules. The last two mechanisms may not be that important due to energy considerations. Because of the extremely low adsorption energy of CO_2 , its desorption is not the rate controlling step, consequently we can also ignore the finite reaction times. This model though simple, is nevertheless interesting, because of the fact that it exhibits some interesting features of this reaction.

3. KINETIC PHASE TRANSITIONS

Fig. 1 shows the range of values of x_{CO} for which the reactive state is stable. For $x_{\text{CO}} < x_1$ the steady state is a "poisoned" catalyst of pure oxygen, while for $x_{\text{CO}} > x_2$ the steady state is the state for which the catalyst is poisoned by carbon monoxide. The CO_2 production starts at x_1 and increases continuously and monotonically till x_2 . At x_2 we get a first order kinetic transition with discontinuities of the coverage fractions and activity. At x_1 the transition is continuous, and therefore it is of second order.

To obtain the steady state configuration for a given carbon monoxide concentration, we start with a blank lattice of 40×40 sites. Using periodic boundary conditions we allow the reaction to proceed for a sufficient length of time till equilibrium is achieved. For values of x_{CO} - away from x_2 the approach to the steady state is rapid and is achieved within a

few hundred Monte Carlo cycles. As we approach the transition composition x_2 the fluctuations in density start increasing, tending to infinity at the critical composition x_2 . These density fluctuations have a two fold effect upon the system. Not only does the approach to the steady poisoned state become extremely slow, the time required to achieve the steady state becomes uncertain. It can depend very critically upon the configuration evolved through the choice of a seed for the random number generator.

Starting with an initially empty lattice, the fraction of oxygen atoms on the surface (θ_o) is measured as a function of time (measured in Monte Carlo cycles) for different starting compositions of carbon monoxide (x_{CO}). θ_o is calculated by taking a time average after a certain number of Monte Carlo cycles and the final result is obtained by averaging over several runs, starting with a different seed for the random number generator. Since we are interested mostly in the time evolution of the system very near the critical composition x_2 , it is important to obtain an accurate estimate for x_2 . Near the critical composition x_2 , the time averaging is performed over 10 - 20 Monte Carlo cycles, and a final average is performed over 300 different runs.

In Fig. 2 we present results for the oxygen coverage θ_o plotted versus time for different compositions of carbon monoxide. As x_{CO} tends towards x_2 the approach towards the steady state ($\theta_o = 0$) clearly becomes slower. These results are consistent with an exponential decay for intermediate times (discussed in next section). In Fig. 3 we have plotted the same result on a semi-logarithmic scale. The inverse of the slope of these curves gives us the relaxation time.

To obtain an accurate value of the critical composition x_2 we have plotted the reciprocal of the relaxation time ζ versus the carbon monoxide composition (Fig.4). We estimate the value of x_2 for which $\zeta \rightarrow \infty$ to be 0.5255 ± 0.0003 . This value seems reasonable, since a few runs taken at $x_{CO} = 0.526$ invariably

led to a poisoned state, while at $x_{CO} = 0.525$ the steady state is a non-poisoned state.

4. TIME EVOLUTION OF OXYGEN COVERAGE

The kinetics of the irreversible diffusive recombination process $A + B \rightarrow \text{Inert}$ has been the focus of many experimental and theoretical studies [2,6]. In this reaction the spatial distribution of the particles at time $t=0$ is random but globally homogeneous, and for $t > 0$, one or both of the particle species move diffusively. There is no interaction between the particles of the same type, but when an A and a B particle meet, they instantly and irreversibly combine to form an inert species. The mean field description of such a process may be written as [7]

$$\frac{dx_A}{dt} = -kx_A(t)x_B(t) \quad (1)$$

where $x_A(t)$ and $x_B(t)$ are the densities of species A and B at time t and k is a rate constant.

At long times the solution to eqn (1) is

$$x_A(t) \approx \frac{1}{kt} \quad [x_A(0) = x_B(0)] \quad (2a)$$

$$x_A(t) \approx \exp[-k \{x_B(0) - x_A(0)\} t] \quad [x_A(0) < x_B(0)] \quad (2b)$$

However, both theoretical and experimental studies indicate slower decay laws

$$x_A(t) \propto t^{-\alpha} \quad [x_A(0) = x_B(0)] \quad (3a)$$

$$x_A(t) \propto \exp(-kt^\alpha) \quad [x_A(0) < x_B(0)] \quad (3b)$$

where α lies between 0 and 1.

The inclusion of spatial fluctuations in the particle densities resolves this discrepancy and gives the asymptotic solutions [2]

$$x_A(t) = \frac{1}{kta} \quad [x_A(0) = x_B(0)] \quad (4a)$$

and

$$x_A(t) = \exp[-C\{x_B(0)^{1/2} - x_A(0)^{1/2}\}t] \quad [x_A(0) < x_B(0)] \quad (4b)$$

where $\alpha = \frac{d}{4}$

Recently Sadiq and Khwaja [8] have carried out calculations on the catalytic irreversible recombination process of a similar type. In contrast to the diffusive recombination process where the reactants A and B are not replenished during the reaction, in this case both the reactants are constantly being replenished from the gas. They found that for $x_B > x_A$ the fraction of minority species (θ_A) decays with time as

$$\theta_A(t) \propto \exp[-(x_B - x_A)t] \quad (5)$$

for long times.

Their ideas as applied to a system of monatomic A and B atoms is equally valid for the present case, where the reservoir consists of a mixture of molecules of oxygen and carbon monoxide.

Although the carbon monoxide molecules need one site for adsorption, the oxygen molecule on adsorption dissociates into two atoms, and needs two adjacent empty sites for adsorption. This simply introduces a constant factor in the rate equation, which can be expressed as [8]

$$\frac{d\theta_o(t)}{dt} = -k(x_{CO} - x_o) \bar{b}_o(\theta) \quad (6)$$

where k is a rate constant, $\theta_o(t)$ is the fraction of adsorbed oxygen atoms and $\bar{b}_o(\theta)$ is the average number of vacancies neighbouring the adsorbed oxygen atoms.

The average cluster size of the oxygen atoms and consequently $\bar{b}_o(\theta)$ both are expected to increase with θ_o . If we assume that

$$\bar{b}_o(\theta) \propto \theta_o^{\mathfrak{S}} \quad (7)$$

then eq. (6) gives

$$\theta_o(t) \propto \exp[-(x_{CO} - x_o)t] \quad (8a)$$

for $\mathfrak{S} = 1$ and

$$\theta_o(t) \propto 1/t^{1/\mathfrak{S}-1} \quad \text{for } \mathfrak{S} \neq 1 \quad (8b)$$

To test these ideas we have plotted $\bar{b}_o(\theta)$ versus θ_o in Fig. 5. The simulation was carried out as already described in the previous section. From the slopes of these curves we find that \mathfrak{S} is very close to 1 and in fact becomes 1 for $x_2 \leq x_{CO} \leq 0.5315$. From eqn. (8a) one therefore expects an exponential decay of the minority oxygen atoms.

The simulation results for $\theta_o(t)$ as a function of time, as shown in Fig. 3 are consistent with an exponential decay for long times. The relaxation times given by the inverse of

the slope of the straight portions in Fig. 3 get larger and larger as one approaches the poisoning transition. These relaxation times (ζ_{CO}) are plotted in Fig. 6 as function of $|x_2 - x_{CO}|$. Close enough to the poisoning transition, one gets a straight line with a slope of $\gamma = 3.54$. This is consistent with a power law behaviour

$$\zeta_{CO} \propto \frac{1}{|x_2 - x_{CO}|^\gamma} \quad \text{where } \gamma = 3.54 \quad (9)$$

This is to be contrasted with the A,B system, for which $\gamma = 1.3$ [8]

5. CONCLUSIONS

The presence of the oxygen molecule, which requires two empty sites for its adsorption, alters the reaction mechanism as compared to the adsorption of a monatomic atom. For the irreversible catalytic reaction $A+B \rightarrow \text{inert}$, there is a reactive steady state only for $x_A = x_B = 0.5$. For the catalytic reaction of carbon monoxide with oxygen, the reactive steady state occurs for $x_1 < x_{CO} < x_2$ where $x_1 = 0.389$ and $x_2 = 0.5255$. Outside this interval the only steady state is a poisoned state.

For both the systems the time evolution of the minority species near the transition point follows the same exponential behaviour. The relaxation time for the minority species follows a power law behaviour expressed as

$$\zeta = \frac{1}{|x_2 - x_{\text{minority}}|^\gamma}$$

where $\gamma = 1.3$ for the A,B system

and 3.5 for the CO, O_2 system.

ACKNOWLEDGEMENTS

One of the authors (K.Y) would like to thank Prof. Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste, where most of the computational work was performed.

REFERENCES

1. R.M. Ziff, E. Gulari, Y. Barshad; Phys. Rev. Lett. 56 2553 (1986).
2. K. Kang and S. Redner; Phys. Rev. Lett. 52 955 (1984).
3. C.T. Campbell, G. Ertl, H. Knipers and J. Segner; J. Chem. Phys. 73 5862 (1980).
4. M.A. Barteau, E.I. Ko and R.J. Madix; Surf. Sc. 104 161 (1981).
5. R.J. Behm, K. Christmann, G. Ertl, M.A. Van Hove; J. Chem. Phys. 73 2984 (1980).
6. D. Toussaint and F. Wilczek; J. Chem. Phys. 78 2642 (1983).
7. A. Blumen, J. Klafter and G. Zumhofen; Phys. Rev. B27 3429 (1983).
8. A. Sadiq, Y. Khwaja; ICTP Internal Report No. IC/87/121.

FIGURE CAPTIONS

- Fig. 1: The average coverage fractions of oxygen and carbon monoxide, and the CO_2 production rate as a function of carbon monoxide concentration.
- Fig. 2: Oxygen coverage θ_o plotted as a function of time (measured in Monte Carlo cycles) for different CO concentrations in the gas phase.
- Fig. 3(a-c): Oxygen coverage θ_o plotted versus time on semi-logarithmic scale.
- Fig. 4: Relaxation time plotted versus the CO concentration. The extrapolated value of the critical composition for which $1/\tau_{\text{CO}} \rightarrow \infty$ is $x_2 \approx 0.5255 \pm 0.0003$.
- Fig. 5(a-b): Average number of vacancies neighbouring the adsorbed oxygen atoms $\bar{N}(\theta_o)$ plotted versus the oxygen coverage θ_o .
- Fig. 6: Relaxation time τ_{CO} plotted versus the difference in composition $|x_2 - x_{\text{CO}}|$. The solid line is drawn as aid to the eye.

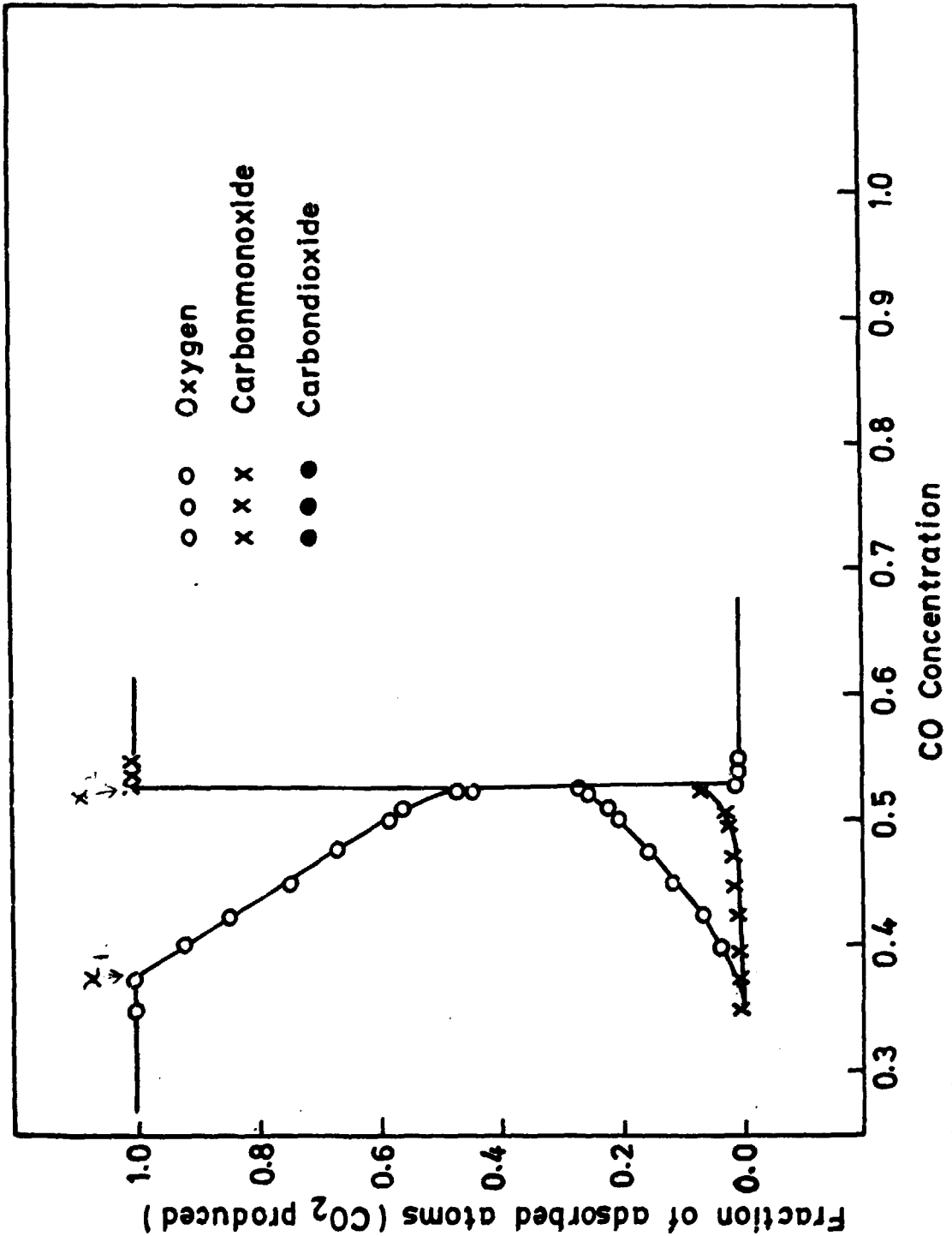


Fig.1.

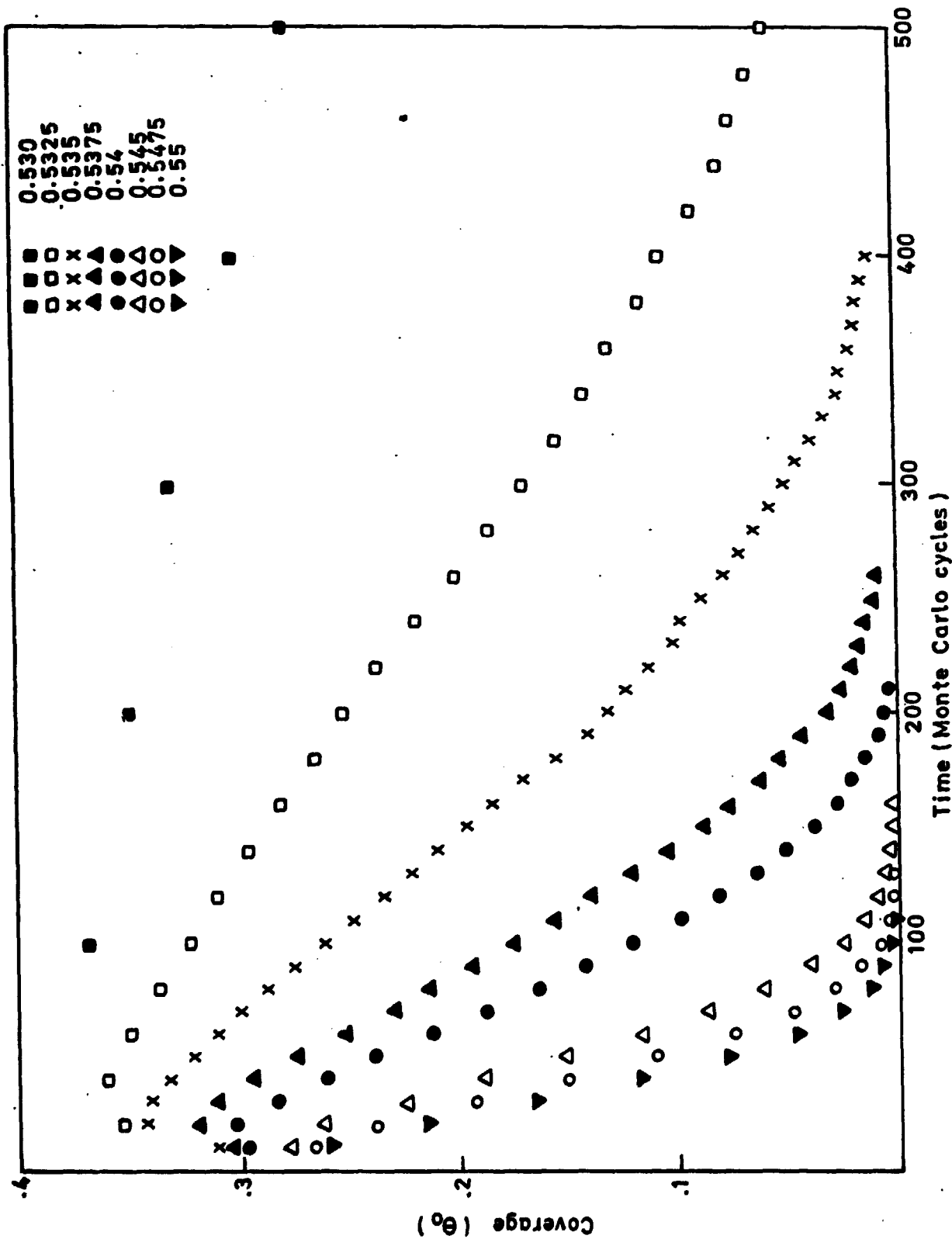


Fig. 2

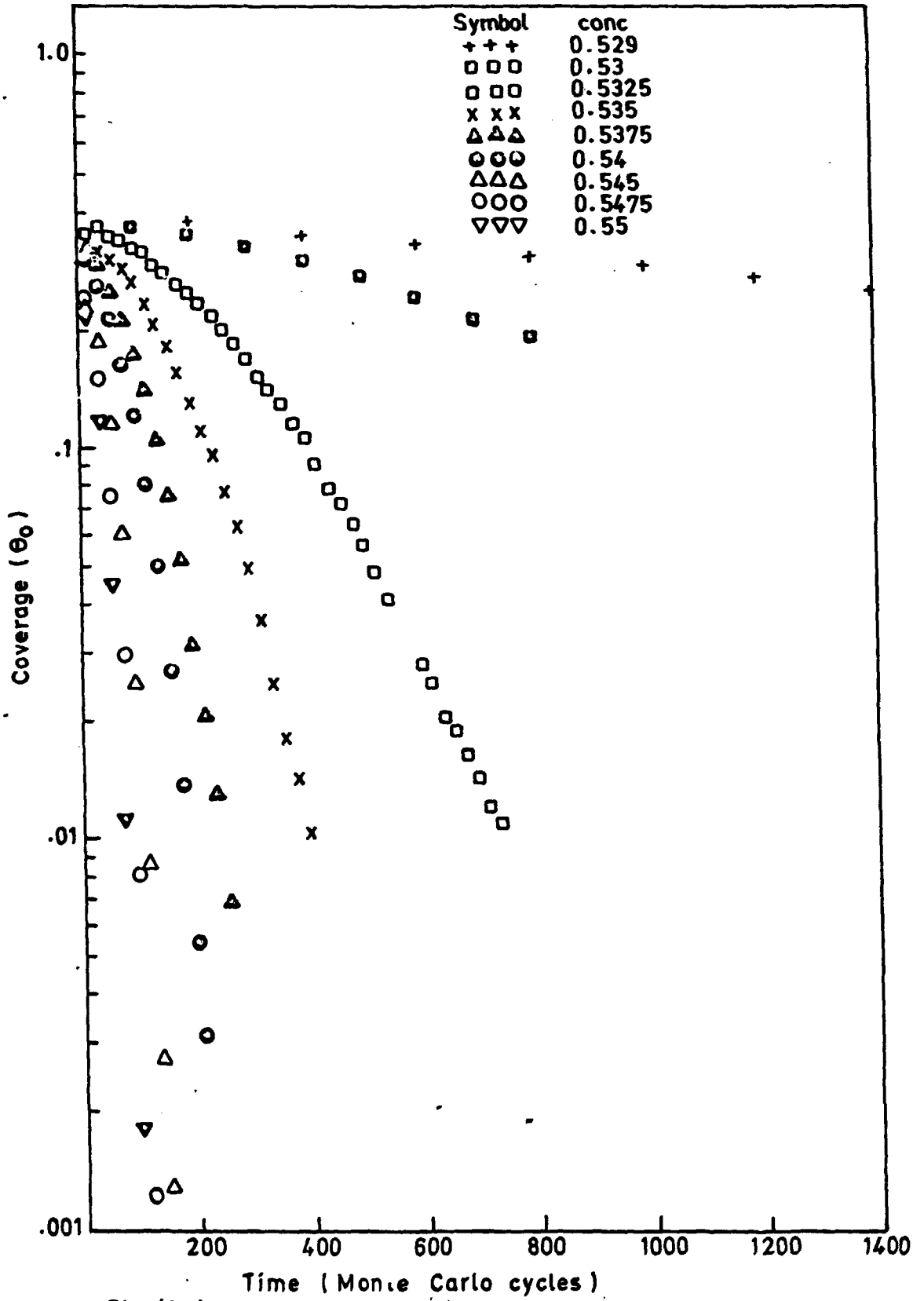


Fig. (3a).

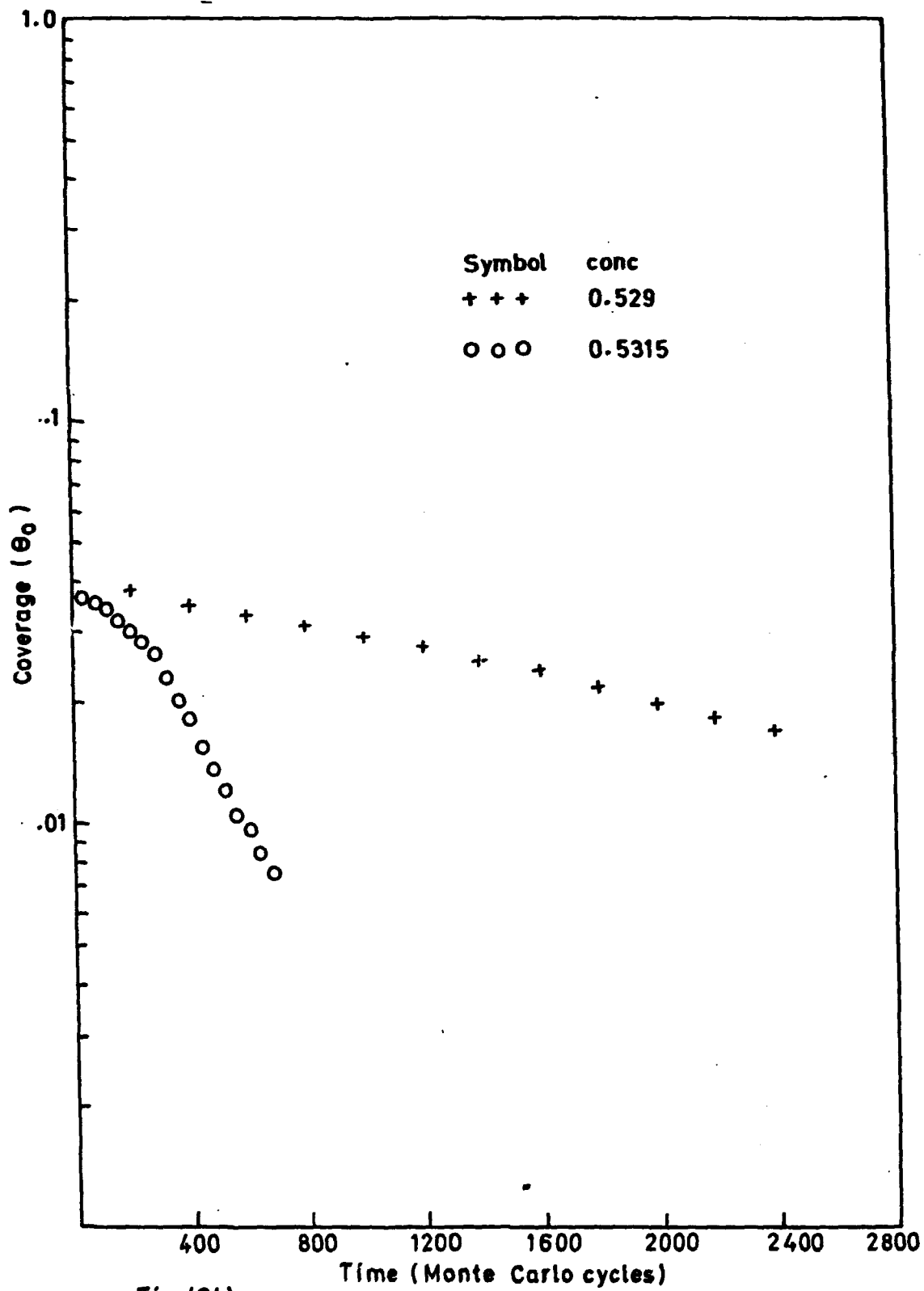


Fig. (3b).

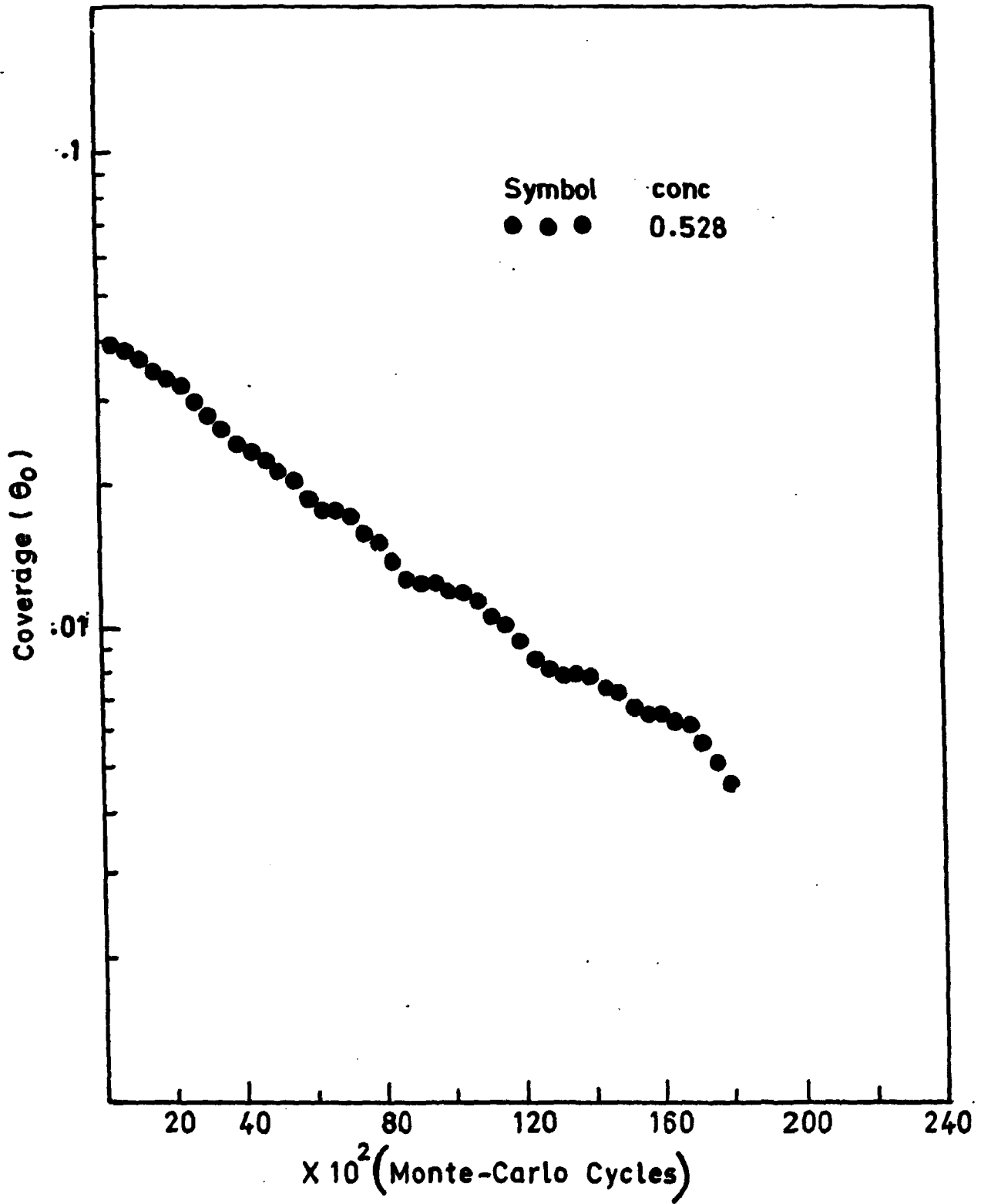


Fig. (3c).

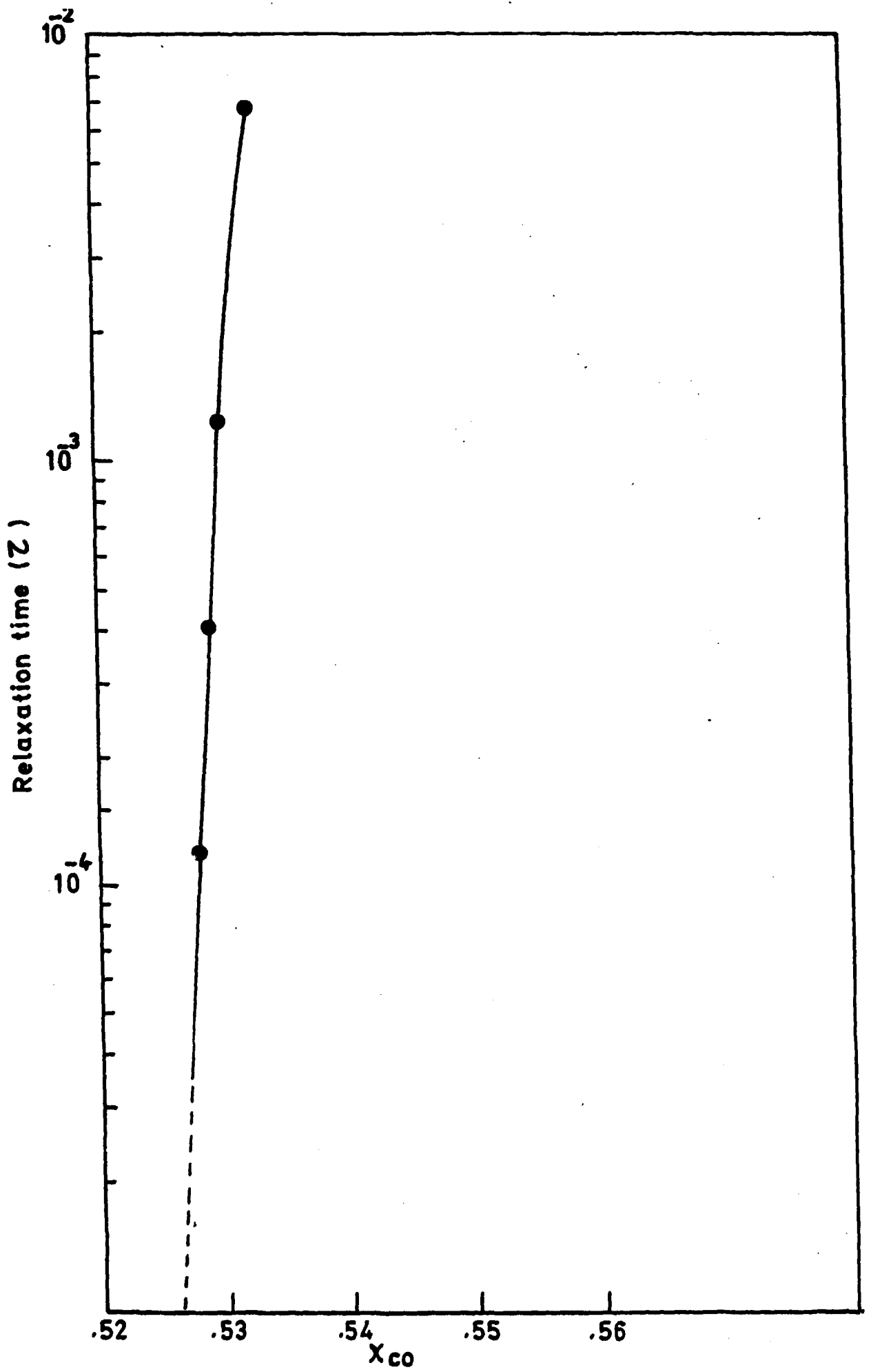


Fig. 4.

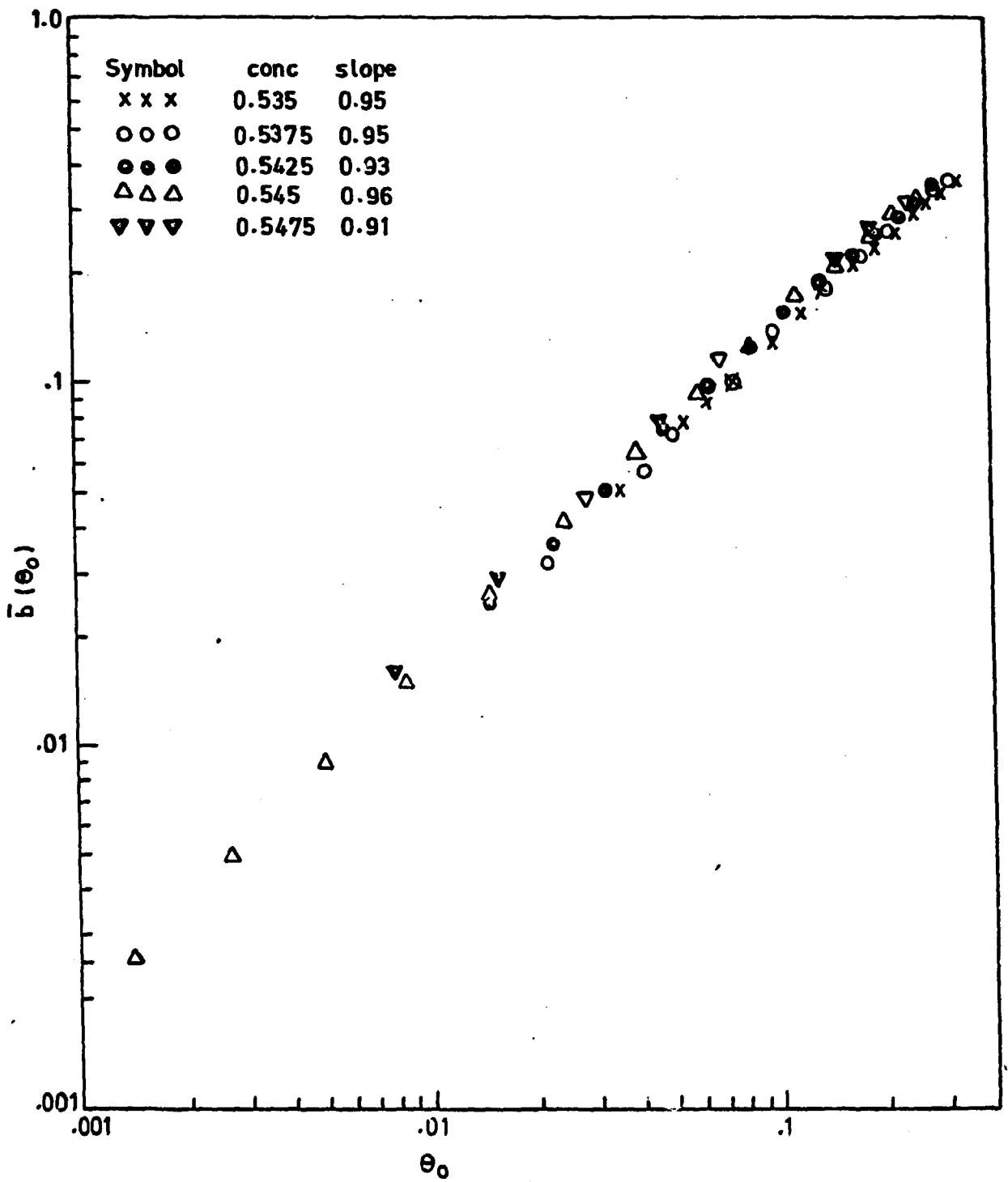


Fig. 5a.

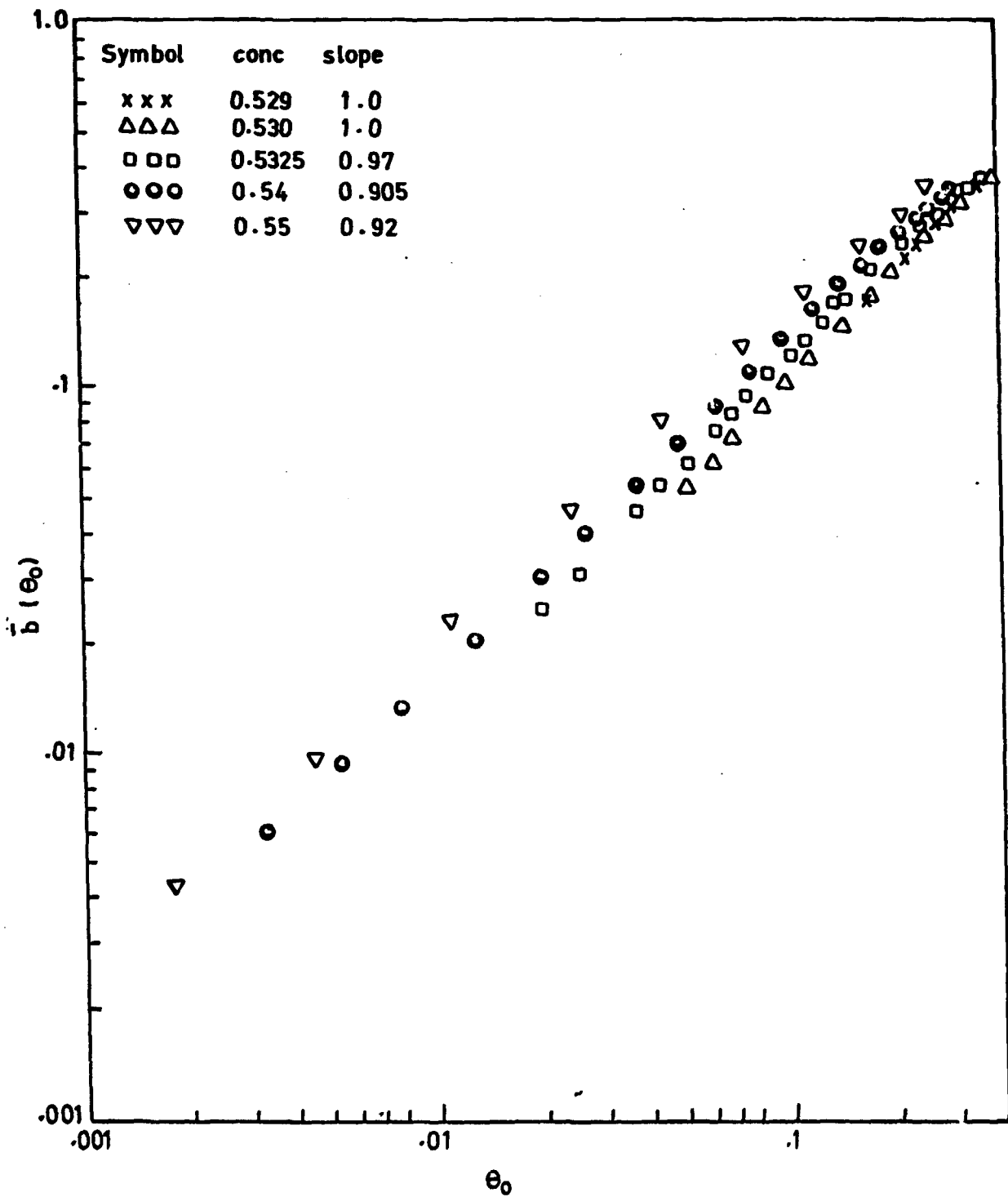


Fig. 5b.

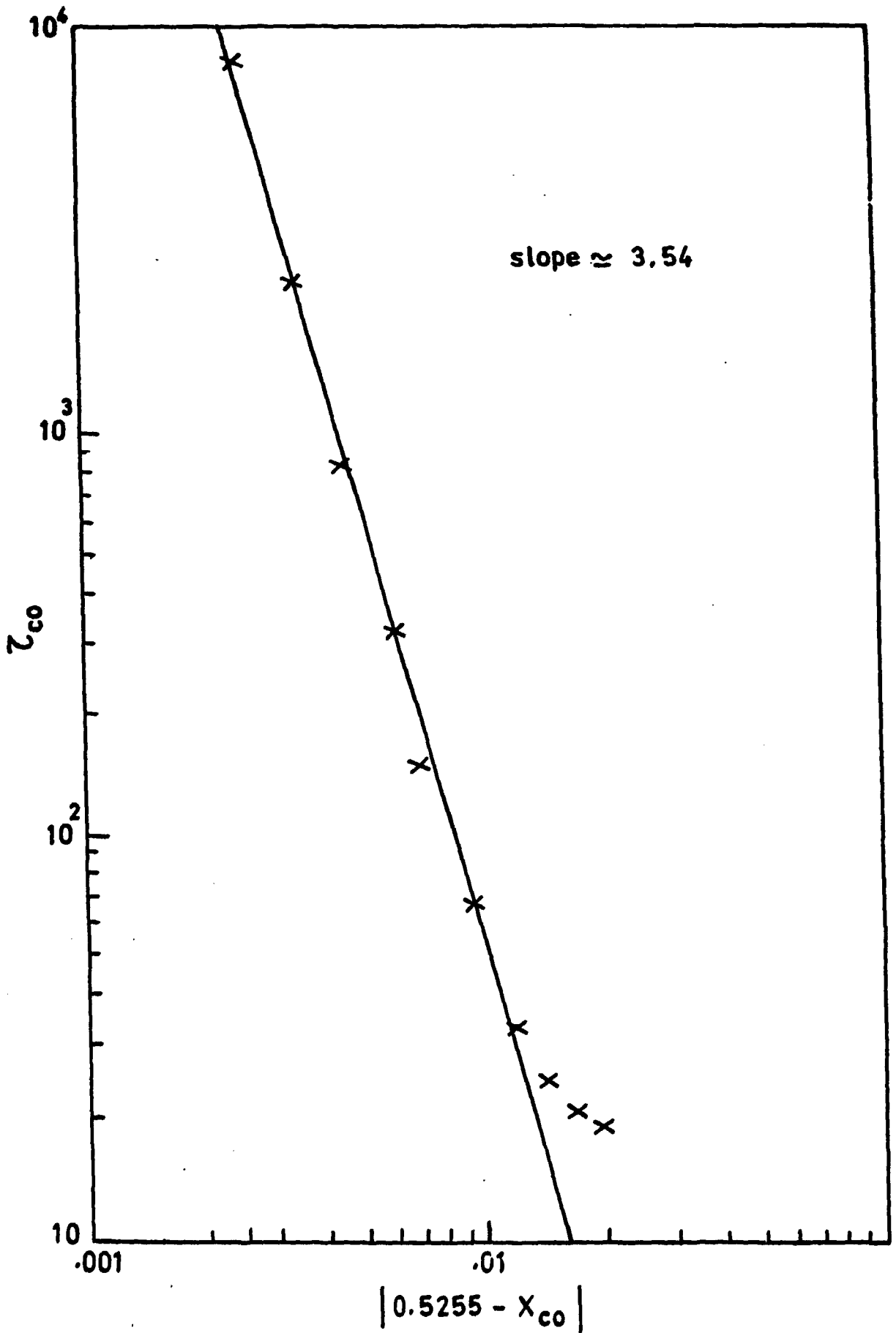


Fig. 6.

Printing Corporation of Pakistan Press, Islamabad