

4
15 52

科學記錄

SCIENCE RECORD

New Series: Vol. III, No. 1

January, 1959

SCIENCE PRESS
PEKING, CHINA

SCIENCE RECORD

New Ser. Vol. III, No. 1, 1959

CONTENTS

MATHEMATICS

- Sur quelques classes de fonctions méromorphes quasi exceptionnelles.....
..... Fan Wui-kwok (范会国) 1
- On Dirichlet's Divisor Problem Yin Wen-lin (尹文霖) 6

CHEMISTRY

- Mechanism of Hydrogen-ion Catalysis in Esterification
IV. A Study on the Kinetics of Esterification Reactions
between Sebacic Acid and Normal-or Iso-octyl Alcohol.....
..... Tang Au-chin (唐敖庆), Yuo Kuo-sui (岳国粹),
Zheng Rhen-kun (郑仁坤) and Gin Yung-da (金荣达) 9
- Studies on the Polyesterification of Dibasic Acids and Glycols
II. On the Relationships between the Velocity Constants of Poly-
esterification and the Molecular Structures of Dibasic Acids and
Glycols Tang Au-chin (唐敖庆), Yuo Kuo-sui (岳国粹),
Su Chu-pi (许川璧) and Liu Chin-po (刘金波) 16

PHYSICS

- Configurational Partition Function of Solid Solutions
..... T. S. Chang (张宗燧) 27
- The Angular Distribution of the Decay Products of Hyperons
..... J. M. Chen (陈中谟), T. H. Ho (何祚麻),
D. C. Sen (洗鼎昌) and H. Y. Tzu (朱洪元) 31
- The Mean Life Time Ratio of K^+ -Meson and Hyperons and Their Branching
Ratios of Different Decay Modes..... W. T. Lee (李文鏞),
D. C. Sen (洗鼎昌), T. H. Ho (何祚麻),
J. M. Chen (陈中谟) and H. Y. Tzu (朱洪元) 35

BIOPHYSICS

- Cosmic Radiation and Tuberculosis
II. Action of Cosmic Radiation on Tubercle Bacilli.....
..... S. G. Ong (王善源) 40

GEOLOGY

- Some Palaeomagnetic Investigations on Chinese Rocks
..... Chang Wen-you (张文佑) and A. E. M. Nairn 46

SUR QUELQUES CLASSES DE FONCTIONS MÉROMORPHES QUASI EXCEPTIONNELLES*

FAN WUI-KWOK (范会国)

(L'université normale de Pékin)

Nous avons appelé *fonction méromorphe quasi exceptionnelle*^[1], toute fonction méromorphe $f(z)$ telle que la famille des fonctions

$$f_n(z) = f(2^n z).$$

Soit quasi normale dans la couronne (Γ) définie par $\frac{1}{2} \leq |z| \leq 2$. Si l'ordre total de la famille $f_n(z)$ est fini, nous avons dit que la fonction $f(z)$ est une *fonction méromorphe quasi exceptionnelle d'ordre total fini*. Dans ce petit mémoire, nous allons étudier quelques classes de ces fonctions.

1. D'après un critère bien connu de quasi normalité de famille de fonctions méromorphes, nous avons immédiatement la proposition suivante:

Toute fonction méromorphe $f(z)$ qui ne prend pas plus de p fois la valeur 1, ni la valeur 0, ni la valeur infinie dans chaque couronne (Γ_n) définie par $2^{n-1} \leq |z| \leq 2^{n+1}$, est une fonction méromorphe quasi exceptionnelle d'ordre total fini.

Toute fonction méromorphe vérifiant ces conditions sera dite désormais pour abrégé, fonction vérifiant les conditions C_{p+p+p} .

Nous remarquerons qu'une fonction méromorphe vérifiant les conditions C_{p+p+p} peut être exceptionnelle dans des cas particuliers, si l'on ne lui ajoute aucune autre condition (par exemple, si l'on suppose que $f(z)$ vérifie les conditions C_{p+p+p} et admette une valeur exceptionnelle, elle sera nécessairement quasi exceptionnelle).

Cherchons maintenant la forme sous laquelle la fonction $f(z)$ vérifiant les conditions C_{p+p+p} doit se mettre. Nous avons^[2] en effet

$$f(z) = \frac{\varphi(z)}{\psi(z)} e^{H(z)}, \quad (1)$$

*Received Oct. 31, 1958.



et

$$1 - f(z) = \frac{\theta(z)}{\psi(z)} e^{K(z)}, \quad (2)$$

$\varphi(z)$, $\psi(z)$ et $\theta(z)$ étant des fonctions entières de genre nul et d'ordre nul; $H(z)$ et $K(z)$, des polynomes ou des fonctions entières.

De (1) et (2), on déduit

$$\varphi(z)e^{H(z)} + \theta(z)e^{K(z)} = \psi(z).$$

Comme d'après Borel, cette identité n'est possible que si $H(z)$ et $K(z)$ sont des constantes, la fonction $f(z)$ sera donc de la forme

$$f(z) = \frac{\varphi(z)}{\psi(z)}.$$

Proposons nous enfin de chercher une limite supérieure de $|f(z)|$ dans le plan dont nous excluons toutes les couronnes circulaires obtenues de la manière suivante: Soit β_μ le module d'un pôle b_μ , nous tracerons de l'origine comme centre les deux cercles de rayons $\beta_\mu - 1$, $\beta_\mu + 1$ et nous excluons la couronne (C_μ) comprise entre ces deux cercles.

Comme la fonction entière $\psi(z)$ est d'ordre nul, il résulte que d'après un théorème de M. Hadamard on a dans le plan dont on a exclu les couronnes (C_μ)

$$|\psi(z)| > e^{-r^\epsilon} (|z| = r). \quad (3)$$

D'autre part, la fonction entière $\varphi(z)$ étant d'ordre nul et le nombre de ses zéros dans chaque couronne (Γ_n) étant borné, nous avons à l'aide d'un théorème de Valiron^[3]

$$M(r) < e^{A(\log r)^2}, \quad (4)$$

$M(r)$ désignant le module maximum de $\varphi(z)$ pour $|z| = r$, A étant une constante.

Il résulte de (3) et (4) que l'on a dans le plan dont on a exclu les couronnes (C_μ)

$$|f(z)| < e^{r^\epsilon + A(\log r)^2}. \quad (5)$$

Ce qu'il importe d'observer ici, c'est que la région exclue du plan est infiniment petite par rapport à celle que l'on conserve. Il en résulte que l'inégalité (5) est valable dans la plupart du plan.

En terminant ce paragraphe, nous énonçons la proposition suivante dont la démonstration n'est pas difficile:

Pour qu'une fonction méromorphe $f(z)$ soit quasi exceptionnelle, il est nécessaire que les rapports de deux suites au moins de racines des équations $f(z) = a$, $f(z) = b$, $f(z) = c$ admettent l'unité pour limite, a , b , c étant des constantes.

2. Dans la dernière proposition du paragraphe précédent, nous avons fait intervenir 3 suites de valeurs de z donnant à $f(z)$ des valeurs fixes; mais nous pouvons aussi ne faire intervenir que deux suites de valeurs seulement, par exemple, la suite de ses zéros et la suite de ses pôles, et déterminer ainsi une classe de fonctions méromorphes quasi exceptionnelles. À ce propos, nous allons démontrer la proposition suivante:

Etant donnée une fonction méromorphe de la forme

$$f(z) = z^m \frac{\prod \left(1 - \frac{z}{a_\lambda}\right)}{\prod \left(1 - \frac{z}{b_\mu}\right)},$$

si les zéros a_λ et les pôles b_μ satisfont aux conditions suivantes:

I. La différence entre le nombre des zéros et le nombre des pôles contenus dans le cercle $|z| \leq r$ a un module borné, quel que soit r ;

II. Le nombre des zéros et le nombre des pôles contenus dans la couronne définie par $2^n \leq |z| \leq 2^{n+1}$ sont bornés, quel que soit n ;

III. Les nombres

$$|a_p|^m \frac{\prod_{|a_\lambda| < |a_p|} \left| \frac{a_p}{a_\lambda} \right|}{\prod_{|b_\mu| < |a_p|} \left| \frac{a_p}{b_\mu} \right|} \quad \text{et} \quad |b_q|^{-m} \frac{\prod_{|b_\mu| < |b_q|} \left| \frac{b_q}{b_\mu} \right|}{\prod_{|a_\lambda| < |b_q|} \left| \frac{b_q}{a_\lambda} \right|}$$

sont bornés, quel que soient p et q ;

IV. Une au moins des valeurs limites des rapports $\frac{a_\lambda}{b_\mu}$ est égale à l'unité; cette fonction est méromorphe quasi exceptionnelle d'ordre total fini.

En effet, considérons la famille des fonctions

$$f_n(z) = f(2^n z) = (2^n z)^m \frac{\prod \left(1 - \frac{2^n z}{a_\lambda}\right)}{\prod \left(1 - \frac{2^n z}{b_\mu}\right)},$$

et posons

$$f_n(z) = \varphi_n(z)\psi_n(z)\theta_n(z)$$

avec

$$\varphi_n(z) = \frac{\prod \left(1 - \frac{2^n z}{a_\lambda}\right)}{\prod \left(1 - \frac{2^n z}{b_\mu}\right)}, \quad \text{pour } |a_\lambda| \geq 2^{n+1}, \quad |b_\mu| \geq 2^{n+1},$$

$$\psi_n(z) = (2^n z)^m \frac{\prod \left(1 - \frac{2^n z}{a_\lambda}\right)}{\prod \left(1 - \frac{2^n z}{b_\mu}\right)}, \quad \text{pour } |a_\lambda| \leq 2^{n-1}, \quad |b_\mu| \leq 2^{n-1},$$

$$\theta_n(z) = \frac{\prod \left(1 - \frac{2^n z}{a_\lambda}\right)}{\prod \left(1 - \frac{2^n z}{b_\mu}\right)}, \quad \text{pour } 2^{n-1} < |a_\lambda| < 2^{n+1}, \quad 2^{n-1} < |b_\mu| < 2^{n+1};$$

alors en faisant un raisonnement comme celui qu'a fait M. Montel^[4], nous pourrons voir que de toute suite infinie

$$f_{n_1}(z), f_{n_2}(z), \dots, f_{n_k}(z), \dots$$

de fonctions $f_n(z)$, on peut extraire une suite partielle

$$f_{n'_1}(z), f_{n'_2}(z), \dots, f_{n'_k}(z), \dots$$

convergeant uniformément dans le domaine (Γ) sauf peut-être en points qui annulent à la fois les polynômes $P(z)$ et $Q(z)$, et qui sont évidemment en nombre fini, $P(z)$ désignant la limite des polynômes $P_{n'_k}(z)$, $Q(z)$, celle des polynômes $Q_{n'_k}(z)$ avec

$$\theta_{n'_k}(z) = \frac{P_{n'_k}(z)}{Q_{n'_k}(z)}.$$

Or d'après un théorème de M. Ostrowski, la famille $f_n(z)$ ne peut être normale dans la couronne (Γ) , elle y est donc quasi normale.

De plus, l'ordre de chaque point irrégulier est évidemment fini, le nombre des zéros et le nombre des pôles de $f(z)$ voisins de ce point étant bornés, l'ordre total est donc aussi fini.

Par conséquent la fonction $f(z)$ est une fonction méromorphe quasi exceptionnelle d'ordre total fini.

Remarque. Comme toute fonction méromorphe quasi exceptionnelle ne peut admettre plus d'une valeur exceptionnelle P , nous avons ici l'avantage de pouvoir affirmer que pour une fonction quelconque de la classe que nous venons de déterminer, le cas d'exception de Picard ne peut se présenter que pour une valeur au plus. Il serait intéressant d'étudier s'il en sera de même pour valeur exceptionnelle B .

INDEX BIBLIOGRAPHIQUE

- [1] Fan, W. K. 1937 *Bull. des sc. math.* **2**, LXI, 369—379.
- [2] Fan, W. K. 1936 *Bull. des sc. math.* **2**, LX, 102—111.
- [3] Valiron, G. 1914 *Ann. Fac. sc. univ. Toulouse* **3**, 5, 117—257.
- [4] Montel, P. 1927 *Leçons sur les familles normales*, Paris.

ON DIRICHLET'S DIVISOR PROBLEM*

YIN WEN-LIN (尹文霖)

(Peking University)

Let $d(n)$ denote the number of divisors of n and $D(x) = \sum_{n \leq x} d(n)$. It is well known that as $x \rightarrow \infty$, Dirichlet proved that

$$\Delta(x) \equiv D(x) - x \log x - (2\gamma - 1)x = O(x^{\frac{1}{2}}),$$

where γ is the Euler constant. Geometrically $D(x)$ is the number of lattice points under the hyperbola $UV = x$ in the first quadrant of the UV -plane, containing those on the curve but not those on the coordinate axes.

Let θ be the lower bound of the values of α satisfying $\Delta(x) = O(x^\alpha)$. With regard to θ , on the one hand, Hardy^[1] proved in 1915 that $\theta \geq \frac{1}{4}$ and on the other hand, adopting Professor S. H. Min's^[2] method, T. T. Chin^[3] proved in 1950 that $\theta \leq \frac{15}{46}$. The same result was published in 1953 by Richert^[4]. In conclusion, the improvements of the upper bound of θ are

$$\theta \leq \frac{1}{3}, \quad \frac{33}{100}, \quad \frac{27}{82}, \quad \frac{15}{46}.$$

These results belong respectively to Voronoi^[5], van der Corput^[6], van der Corput^[7] and T. T. Chin.

It is well known that the divisor problem is harder than, but similar to, the circle problem. And the result on the last problem was improved to $\frac{13}{40}$ in 1942 by Professor L. K. Hua^[8]. Now, under the supervision of Professor S. H. Min, the author has proved that

$$\theta \leq \frac{13}{40},$$

just like the circle problem.

*Received Nov. 15, 1958.

The method used here is still the two-dimensional Van der Corput's method. But, instead of approximating a double sum by a double integral, we twice used a modified one-dimensional inversion formula, as stated in the following lemma.

Lemma. Let $f(x)$ be an algebraic function defined in the interval (a, b) . Let

$$0 < \frac{A}{R} \leq |f''(x)| \leq \frac{A}{R}, \quad |f'''(x)| \leq \frac{A}{RU}.$$

Let (α, β) be the image of (a, b) under the transformation $y = f'(x)$, then

$$\sum_{a \leq n \leq b} e^{2\pi i f(n)} = e^{\pi i/4} \sum_{\alpha \leq v \leq \beta} \frac{e^{2\pi i \{f(n_v) - v n_v\}}}{\sqrt{f''(n_v)}} + O(\log(\beta - \alpha + 2) + O((b - a + R)U^{-1} + R^{\frac{1}{2}})),$$

where n_v is the solution of $f'(n_v) = v$.

The proof of this paper is based on the speciality of the problem. For example, corresponding to the non-vanishing property of the Hessian in [8], we get easily that the number of "zero lines" of this paper does not exceed 3 (in other words, let $u = x'/y'$, the number of positive roots of u is less than or equal to 3).

It should be noticed that, first, the method used in this paper is a simplification of the method of approximation by double integral, and may be used either to simplify Professor S. H. Min's proof on the order of $\zeta\left(\frac{1}{2} + it\right)$ or to improve on his result; secondly, the method used in this paper is a refinement of approximation by double integral. If we use the original method, even neglecting the difficulty of the vanishing of the Hessian (which is the main difficulty), we can only obtain

$$S \ll t^{\frac{1}{32}} R^{\frac{13}{16}} N^{\frac{15}{16}} \log^4 t,$$

but the corresponding estimation of this paper is that

$$S \ll t^{\frac{1}{32}} (RN)^{\frac{7}{8}} \log^{\frac{3}{8}} t,$$

where

$$S = \sum_{x=R}^{R'} \sum_{y=N}^{N'} e^{2\pi i \sqrt{xy}}, \quad R < R' \leq 2R, \quad N < N' \leq 2N, \quad t^{\frac{3}{20} + \epsilon} \leq x \leq y \leq \frac{t^{\frac{7}{20}}}{x}.$$

Evidently, it is impossible to derive $\theta \leq \frac{13}{40}$ by the original method.

Finally, it seems very possible that, by this method with some modifications, we can even get a still better result, i.e. $\theta \leq \frac{12}{37}$. At the same time we can improve on the result concerning the circle problem to $\frac{12}{37}$. These have been expected for a long time.

The author wishes to express his thanks to Prof. S. H. Min for his help.

REFERENCES

- [1] Hardy, G. H. 1916 *Proc. Lond. Math. Soc.*, **2**, 15, 1—25.
- [2] Min, S. H. 1949 *Trans. Amer. Math. Soc.* **65**, 448—472.
- [3] Chin, T. T. 1950 *The Science Report of Tsing Hua University*, **5**, 4, 402—427.
- [4] Richert, H. E. 1953 *Math. Zeit.* **58**, 204—218.
- [5] Voronoi 1903 *Jour. für die reine und angewandte Math.* **126**, 241—282.
- [6] Van der Corput 1922 *Math. Ann.* **87**, 39—65.
- [7] Van der Corput 1927—28 *Math. Ann.* **98**, 697—716.
- [8] Hua, L. K. 1942 *Quart. Jour. Math. (Oxf.)* **13**, 18—29.
- [9] Titchmarsh, E. C. 1951 *The Theory of the Reimann Zeta-Function*, Oxford.
- [10] Виноградов, И. М. 1952 *Избранные Труды*, 119—127, Москва.

MECHANISM OF HYDROGEN-ION CATALYSIS IN ESTERIFICATION*

IV. A STUDY ON THE KINETICS OF ESTERIFICATION REACTIONS BETWEEN SEBACIC ACID AND NORMAL- OR ISO-OCTYL ALCOHOL

TANG AU-CHIN** (唐敖庆), YUO KUO-SUI (岳国粹), ZHENG RHEN-KUN (郑仁坤)
AND GIN YUNG-DA (金荣达)

(Institute of Applied Chemistry, Academia Sinica, Changchun)

Normal-octyl sebacate and iso-octyl sebacate are two important plasticizers in the modern plastic industry. The purpose of this report is to indicate the probably best conditions for preparations of the above-mentioned two important plasticizers from the viewpoint of kinetic studies, and is also to examine the mechanism of hydrogen ion catalysis in esterification suggested by two members of the authors^[1].

The experimental procedures of this report are the same as those of our first report^[2]. When sebacic acid and normal octyl alcohol or iso-octyl alcohol in equivalent quantity ratio react at different temperatures in the presence or absence of the foreign acid, the experimental results of the esterification reactions are treated respectively according to the following kinetic equations:

$$(1/1-p)^{3/2} - 1 = 3/2KC_0^{3/2}t, \quad (1)$$

$$1/1-p - 1 = K_2 C_A C_0 t, \quad (2)$$

where p is the extent of the reaction, $K = \frac{K_{s/2}}{1+K'}$; C_0 , the initial concentration of the carboxyl group of sebacic acid in equivalents per kilogram; and C_A , a constant, represents the concentration of hydrogen ion derived from the foreign acid.

EXPERIMENTAL RESULTS

The results of the esterification reactions between an equivalent quantity ratio of sebacic acid and normal-octyl alcohol, and between an equivalent

*Received Nov. 3, 1958.

**Member of Academia Sinica.

quantity ratio of sebacic acid and iso-octyl alcohol at 140, 150, 160 and 170°C in the absence of foreign acid, are plotted in Figs. 1 and 2 and shown in

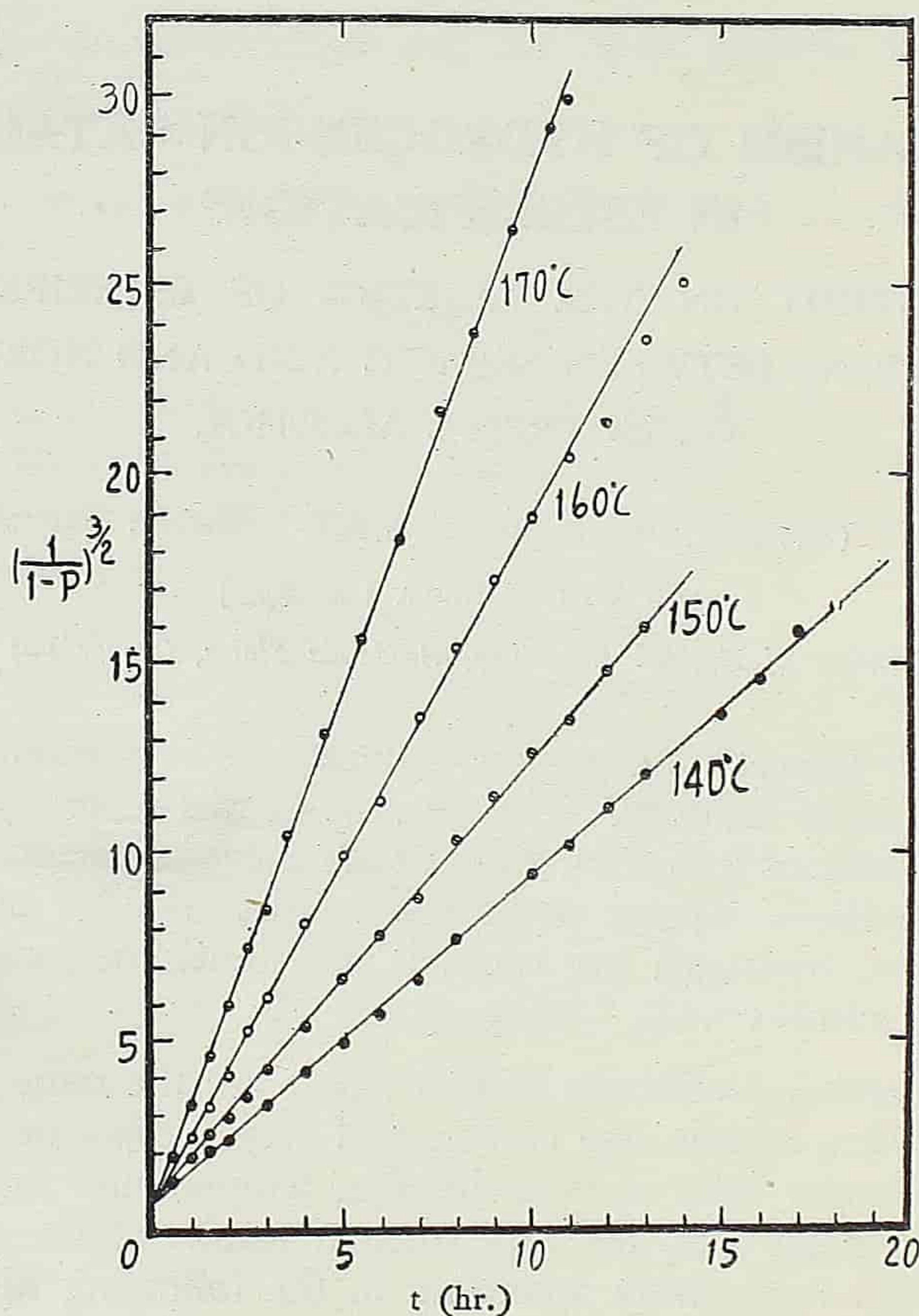
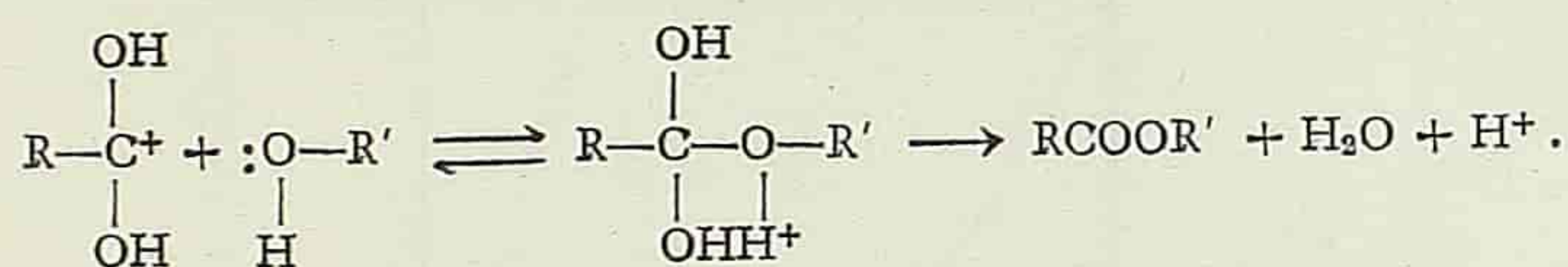


Fig. 1 Reactions of equivalent quantity ratio of sebacic acid with normal-octyl alcohol at different temperatures.

Table 1 and 2 according to equation (1). All the results are in conformity with a $2\frac{1}{2}$ order reaction. The relationships between temperatures and specific velocity constants in the reactions of sebacic acid with normal-octyl alcohol and that with iso-octyl alcohol are shown in Fig. 3, from which the activation energy is found to be 14 Kcal. for the former reaction, and 16 Kcal. for the latter. Tables 1 and 2 further show that the velocity constant for the reaction of sebacic acid and normal-octyl alcohol is about five times greater than that for the reaction of sebacic acid and iso-octyl alcohol at the same temperature. This phenomenon may be explained by the theory of molecular structure. Since the normal-octyl alcohol $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{OH}$ is different from the iso-octyl alcohol $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHOH-CH}_3$ by one hydrogen atom on the carbon atom of the latter molecule being substituted by the methyl group, and since the methyl group can form hyperconjugation with the lone pair of electrons of the oxygen

atom, the oxygen atom in the molecule of iso-octyl alcohol thus carries less negative charge than that in the molecule of normal octyl alcohol. Again we consider the more important step in hydrogen ion catalysis in esterification:



It is clearly shown that the more negative charge the oxygen atom carries, the easier the esterification reaction proceeds. This explains why the velocity constant for the reaction of sebacic acid with normal-octyl alcohol is rather greater than that of sebacic acid with iso-octyl alcohol.

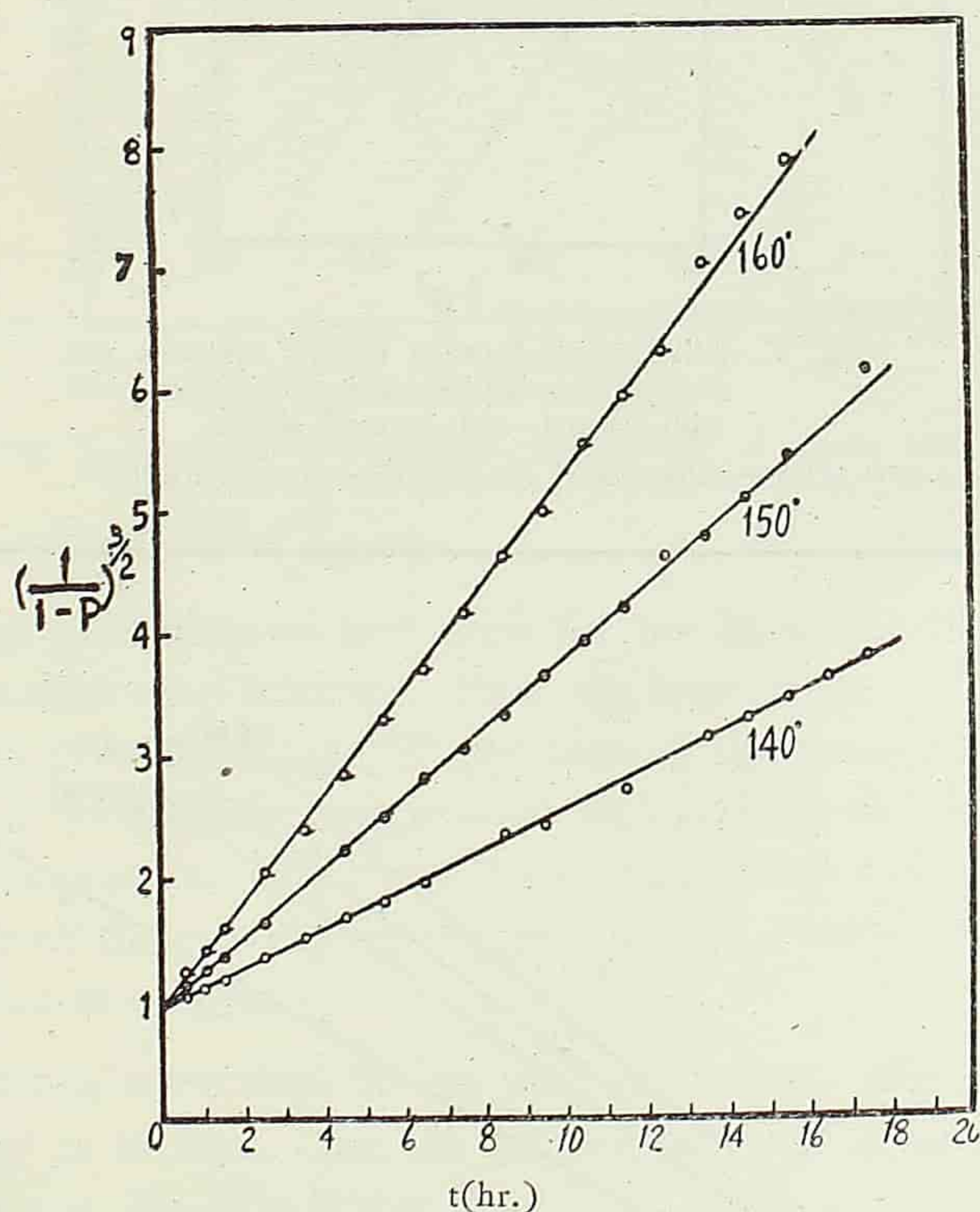


Fig. 2 Reactions of equivalent quantity ratio of sebacic acid with iso-octyl alcohol at different temperatures.

The results of the esterification reaction between an equivalent quantity ratio of sebacic acid and normal-octyl alcohol at 160°C, or between an equivalent quantity ratio of sebacic acid and iso-octyl alcohol at 150°C in the presence of sulfuric acid as catalyst, treated by means of equation (2), are plotted in Figs. 4 and 5, and shown in Tables 3 and 4. All the results are in conformity with the second order reaction. Tables 3 and 4 show obviously that by increasing the concentration of hydrogen ion derived from the sulfuric acid, the rate of esterification is greatly increased. Though the time of esterification is shortened as the rate of reaction increases, yet the products have a

deep colour, probably due to the occurrence of side reactions. Therefore, the quantity of sulfuric acid added must be proper.

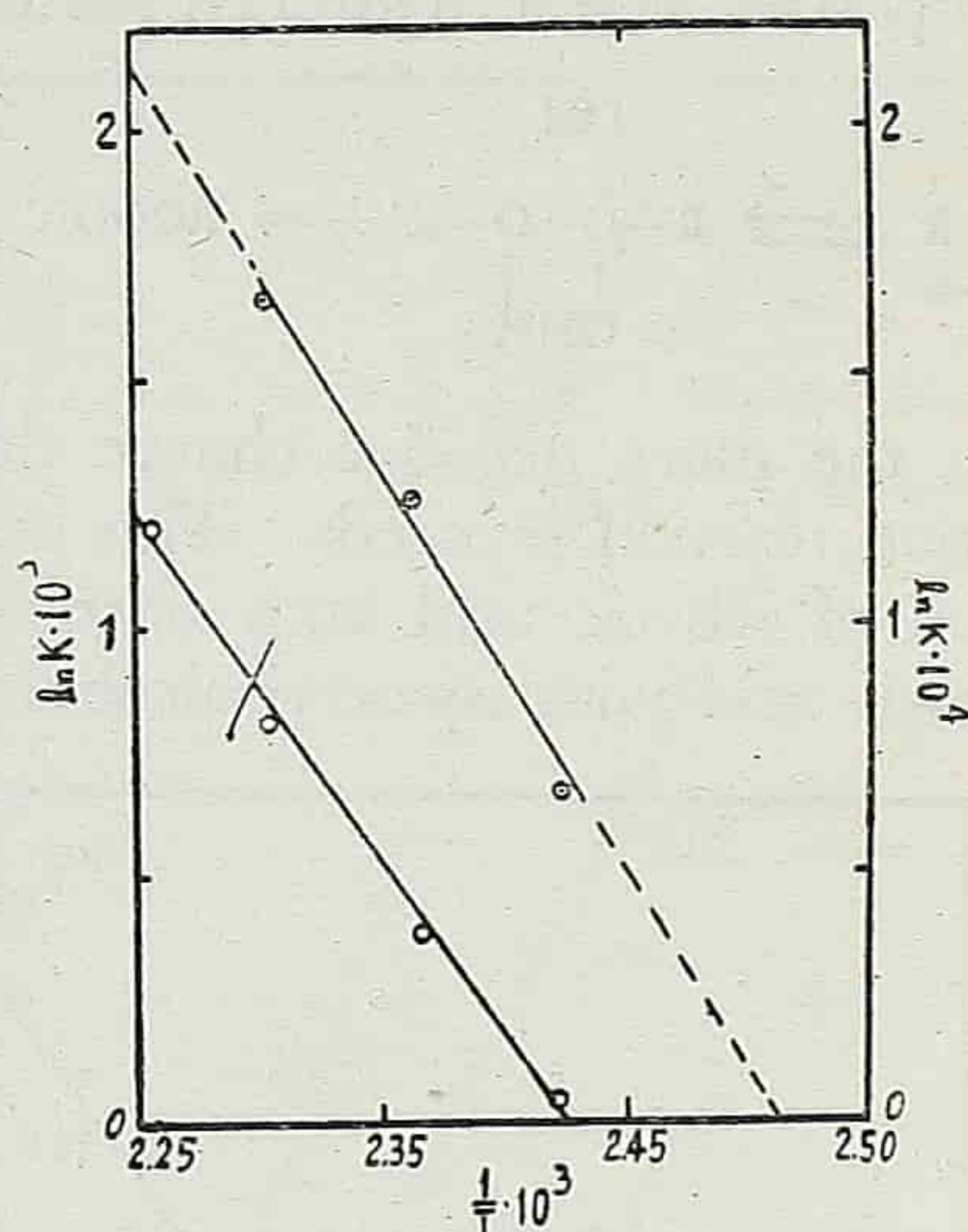


Fig. 3 Relationships between velocity constants and temperatures in the reactions of sebacic acid with normal- and iso-octyl alcohol.

○—normal-octyl alcohol, ○—iso-octyl alcohol.

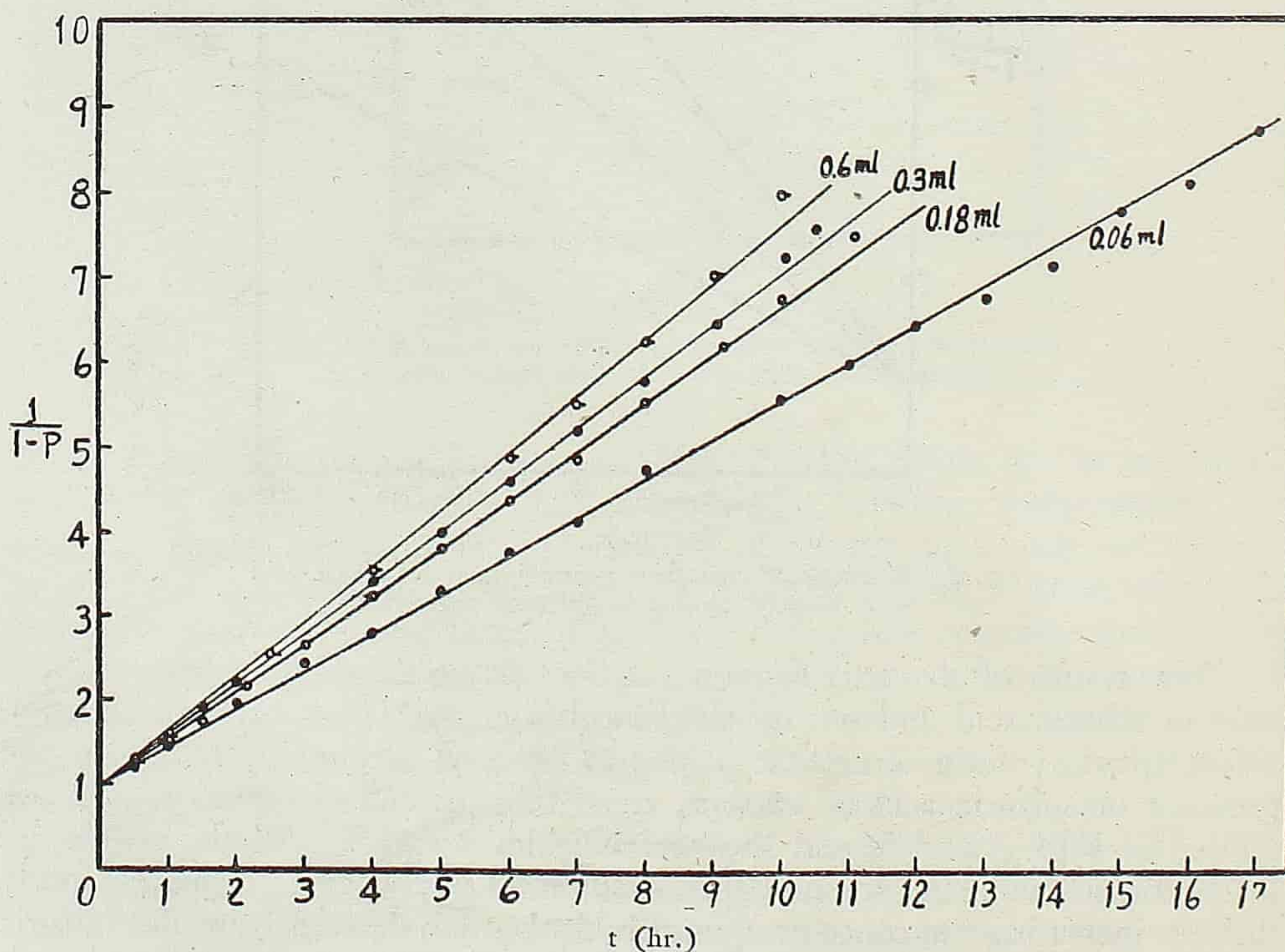


Fig. 4 Reactions of equivalent quantity ratio of sebacic acid with normal-octyl alcohol at 140°C catalyzed by 2.142 N sulfuric acid.

According to the experimental data in Tables 1, 2, 3 and 4, we may point out:

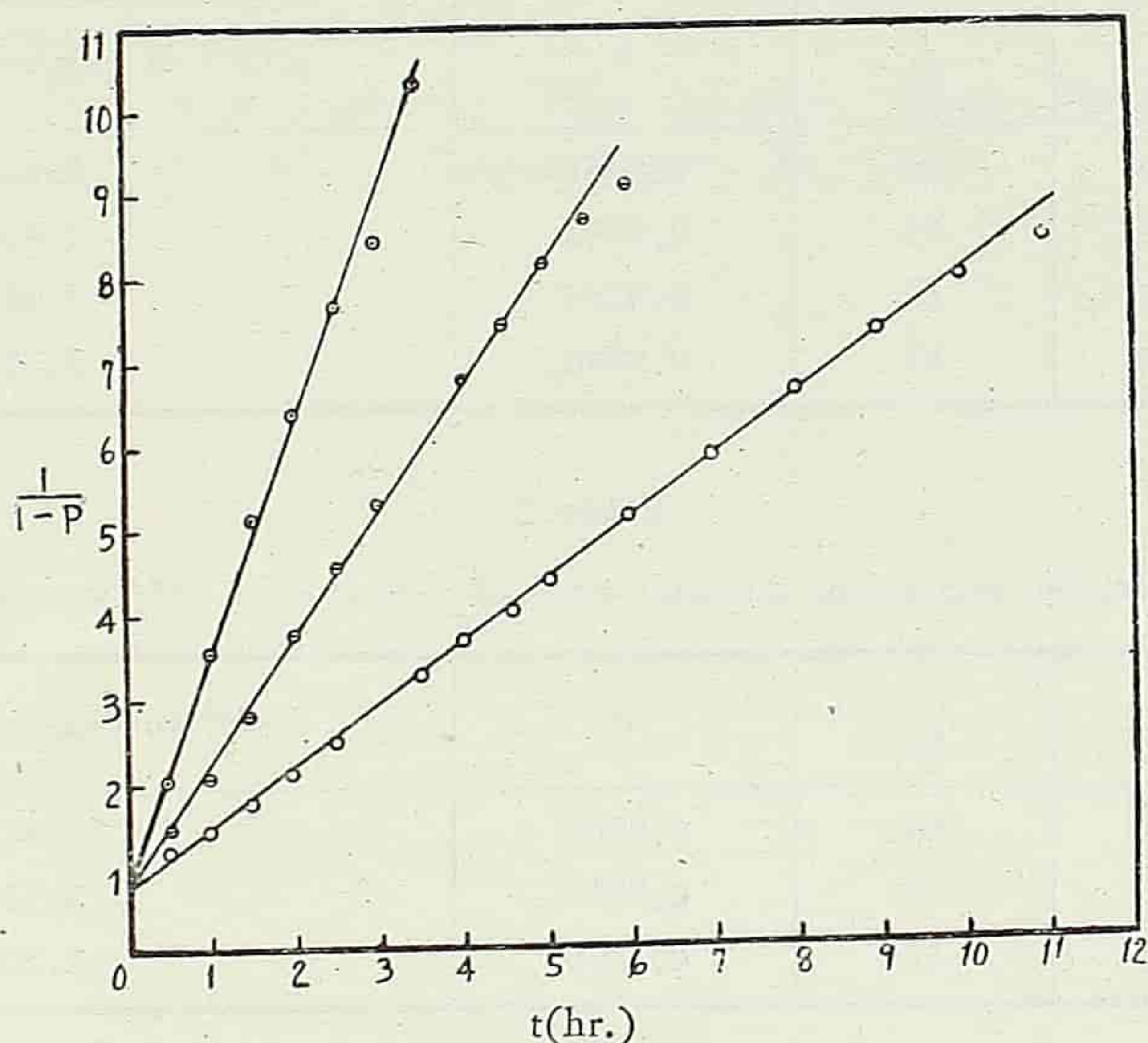


Fig. 5 Reactions of equivalent quantity ratio of sebacic acid with iso-octyl alcohol at 160°C catalyzed by 6.4275 N sulfuric acid.

I. There are probably two best ways for obtaining the highest yield for preparation of normal octyl sebacate. First, the experimental No. 3 in Table 1 is an example to give more than 90 per cent of the product in the absence of foreign acid, if we raise the temperature and prolong the time of reaction; Secondly, the experimentals No. 1 and 2 are two examples of producing more than 95 per cent of the product in the presence of a very small quantity of sulfuric acid added as catalyst.

II. For gaining more than 90 per cent of iso-octyl sebacate we have to add sulfuric acid as catalyst, raise the temperature and prolong the time of reaction, such as exp. No. 3 in Table 4.

CONCLUSIONS

We have studied the kinetics of esterification between sebacic acid with normal-octyl alcohol and that with iso-octyl alcohol at different temperatures in the presence or absence of sulfuric acid as catalyst. According to our experimental results, we have pointed out the best conditions for preparation of normal-octyl and iso-octyl sebacates. Furthermore, our experimental results confirm once more the mechanism of hydrogen ion catalysis in esterification as suggested by us.

Table 1

Reaction between equivalent quantity ratio of sebacic acid and normal-octyl alcohol

Exp. No.	T °C	t hr	P	$K \cdot 10^3$ in (kg/equiv) ^{3/2} /min
1	140	18	0.8461	1.06
2	150	13	0.8442	1.45
3	160	13	0.8780	2.23
4	170	11	0.9000	3.35

Table 2

Reaction between equivalent quantity ratio of sebacic acid and iso-octyl alcohol

Exp. No.	T °C	t hr	P	$K \cdot 10^4$ in (kg/equiv) ^{3/2} /min
1	140	18	0.5902	1.92
2	150	18	0.7013	3.53
3	160	17	0.7570	5.20

Table 3

Reaction between equivalent quantity ratio of sebacic acid and normal-octyl alcohol at 150°C in the presence of 2.142 N sulfuric acid as catalyst

Exp. No.	Sulfuric acid added ml	t hr.	P
1	0.015	4.0	0.9524
2	0.025	2.25	0.9538
3	0.035	2.0	0.9511

Table 4

Reaction between equivalent quantity ratio of sebacic acid and iso-octyl alcohol at 160°C in the presence of 6.4275 N sulfuric acid as catalyst

Exp. No.	Sulfuric acid added ml	t hr.	P
1	0.005	10	0.8739
2	0.010	6	0.8900
3	0.020	3.5	0.9032

The velocity constant of sebacic acid and normal-octyl alcohol as compared with that of sebacic acid and iso-octyl alcohol is about five times greater; this phenomenon has been explained by the theory of molecular structure. The activity energies for the reactions of sebacic acid with normal alcohol and for that with iso-octyl alcohol are 14 and 16 Kcal, respectively.

REFERENCES

- [1] Tang Au-chin, Yao Kuo-sui, Lin Te-hou, Li Yu-wei and Li Shin-wei 1957
Science Record, New Ser. **1**, 49.
- [2] Tang Au-chin, Yao Kuo-sui, Ting Kai-sha, Lang Pei-chen and Chao
Cheng-ta 1958 *Acta Chimica Sinica*, **24**, (6).

STUDIES ON THE POLYESTERIFICATION OF DIBASIC ACIDS AND GLYCOLS**II. ON THE RELATIONSHIPS BETWEEN THE VELOCITY CONSTANTS OF POLYESTERIFICATION AND THE MOLECULAR STRUCTURES OF DIBASIC ACIDS AND GLYCOLS***

TANG AU-CHIN** (唐敖庆), YUO KUO-SUI (岳国粹), SU CHU-PI (許川璧)
AND LIU CHIN-PO (刘金波)

(*Institute of Applied Chemistry, Academia Sinica*)

On the basis of our own many experimental results and a great number of foreign authors' data we have suggested a new mechanism of hydrogen ion catalysis in esterification, polyesterification and three dimensional polyesterification reactions and clarified the long disputed question of the order of the esterification and polyesterification reaction^[1, 2].

A fundamental assumption of the kinetics of polycondensation reactions is that all similar functional groups have the same reactivity and hence the same velocity constant K is independent of the chain-length of the molecules themselves. Flory^[3] has attempted to confirm this assumption with studies on the kinetics of polyesterification reactions between three pairs of dibasic acids and glycols, but due to the mechanism and the order of polyesterification reaction remaining unclarified, of course, the velocity constants calculated by him according to the kinetic equation of third order reaction are meaningless. The present report is chiefly concerned with the relationships between velocity constants and molecular structures of dibasic acids and glycols. Hence, in order to prove the fundamental assumption we have studied the kinetics of polyesterification reactions between thirty five pairs of dibasic acids and glycols.

According to the theoretical analysis of our first report^[1], when dibasic acids and glycols react in equivalent quantity ratio in the absence of foreign acid, the results of polyesterification reactions satisfy the following kinetic equation:

$$\left(\frac{1}{1-P}\right)^{3/2} - 1 = \frac{3}{2} K C_0^{3/2} t, \quad (1)$$

*Received Nov. 19, 1958.

**Member of Academia Sinica.

where P is the extent of reaction, $K = \frac{K_{5/2}}{1+K}$, and C_0 , the initial concentration of the carboxyl group of dibasic acid in equivalent per kilogram.

The experimental procedures of this paper are the same as those in our first report. The results of the polyesterification reactions between equivalent quantity ratios of succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid with ethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, diethylene glycol and 1,6-hexamethylene glycol at 150°C in the absence of foreign acid respectively are shown in Table 1 and Figs. 1, 2, 3, 4 and 5 according to eq. (1). All the results are in conformity with a $2\frac{1}{2}$ order reaction. The mechanism of hydrogen ion catalysis in polyesterification reactions suggested by us is further examined here by a large amount of experimental data. The relationships between velocity constants and molecular structures of dibasic acids and glycols are plotted in Figs. 6 and 7. In Fig. 7 the coordinate axes are so selected that in the ordinate axis the original point for succinic acid, glutaric acid, adipic acid, etc., corresponds to zero, 1, 2, . . . respectively; while in the abscissa axis we regard propylene glycol and hexamethylene glycol as having three and five carbon atoms of glycols respectively.

Table 1

The velocity constants of the polyesterification reactions between dibasic acids and glycols, $K \cdot 10^3$ in (kg/equi.)^{3/2}/min.

Dibasic acids	Ethylene glycol	1, 2-Propylene glycol	Diethylene glycol	1, 4-Butylene glycol	1, 4-Hexamethylene glycol
Succinic acid	0.68	0.37	0.80	1.65	2.24
Glutaric acid	0.64	0.34	0.75	1.44	1.96
Adipic acid	0.57	0.29	0.65	1.27	1.48
Pimelic acid	0.48	0.28	0.64	1.07	1.67
Suberic acid	0.57	0.30	0.61	1.17	1.49
Azelaic acid	0.61	0.30	0.63	1.12	1.49
Sebacic acid	0.70	0.36	0.69	1.39	1.77

From Table 1 and Fig. 6 it is clearly shown that the velocity constants of the polyesterification reactions between a same glycol with dissimilar dibasic acids almost have no difference, their average values all varying in the range of $\pm 20\%$. This explains that two carboxyl groups at the end of the molecule have the same velocity constant independent of the number of carbon atoms in the midst of the chain for the dibasic acid.

From Table 1 and Fig. 7 it is also obviously seen that the relationships of the velocity constants of the polyesterification reactions between a same dibasic acid with different glycols are essentially the same independent of the chain-length of the molecules themselves. This explains that the effects between two hydroxyl groups at the end of the molecule with each other may be

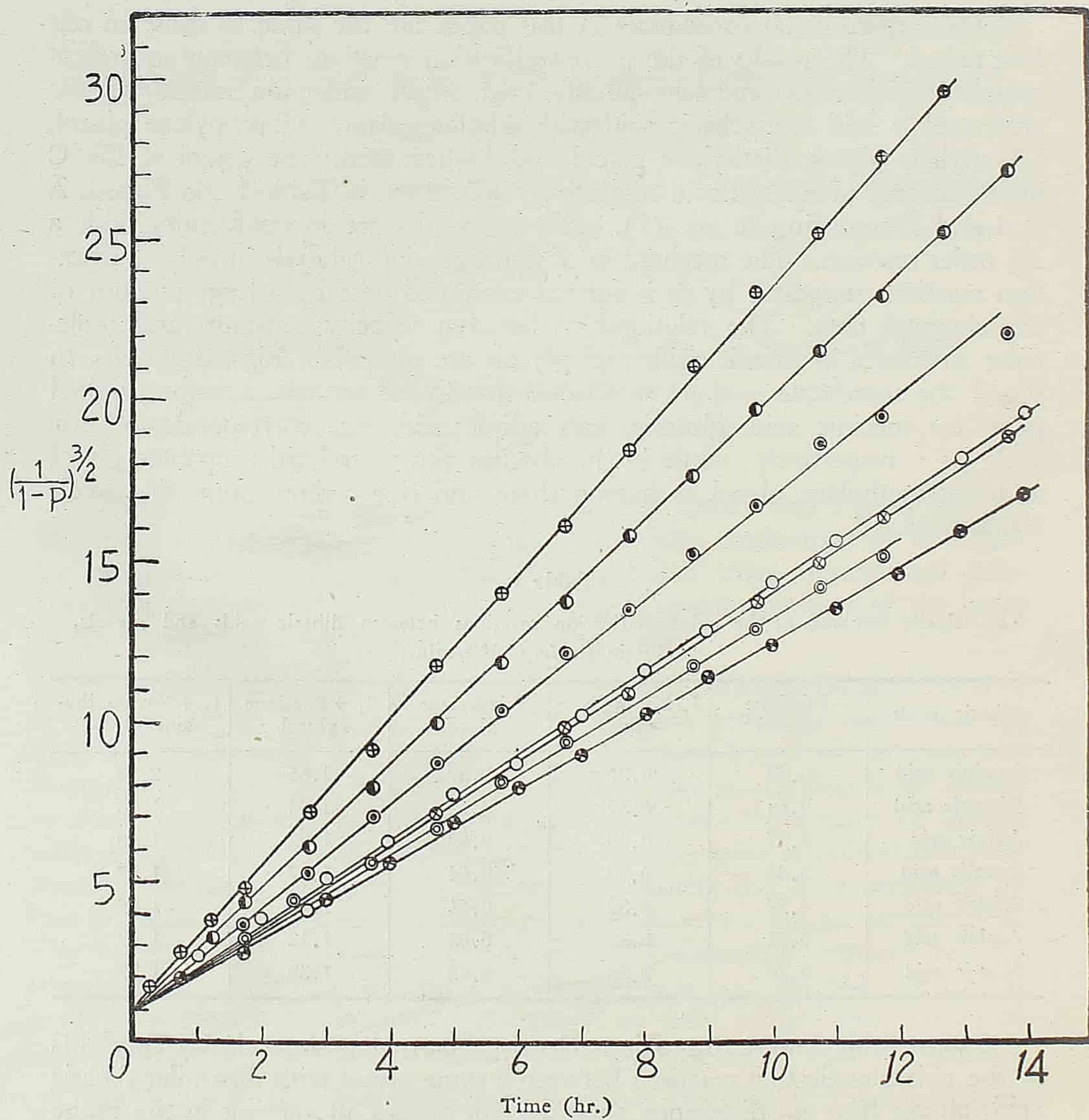


Fig. 1 Reactions of equivalent quantity ratio of dibasic acids and ethylene glycol at 150°C.

⊕ — succinic acid; ⊙ — glutaric acid; ⊙ — adipic acid; ⊗ — pimelic acid;
 ⊗ — suberic acid; ⊙ — azelaic acid; ○ — sebacic acid.

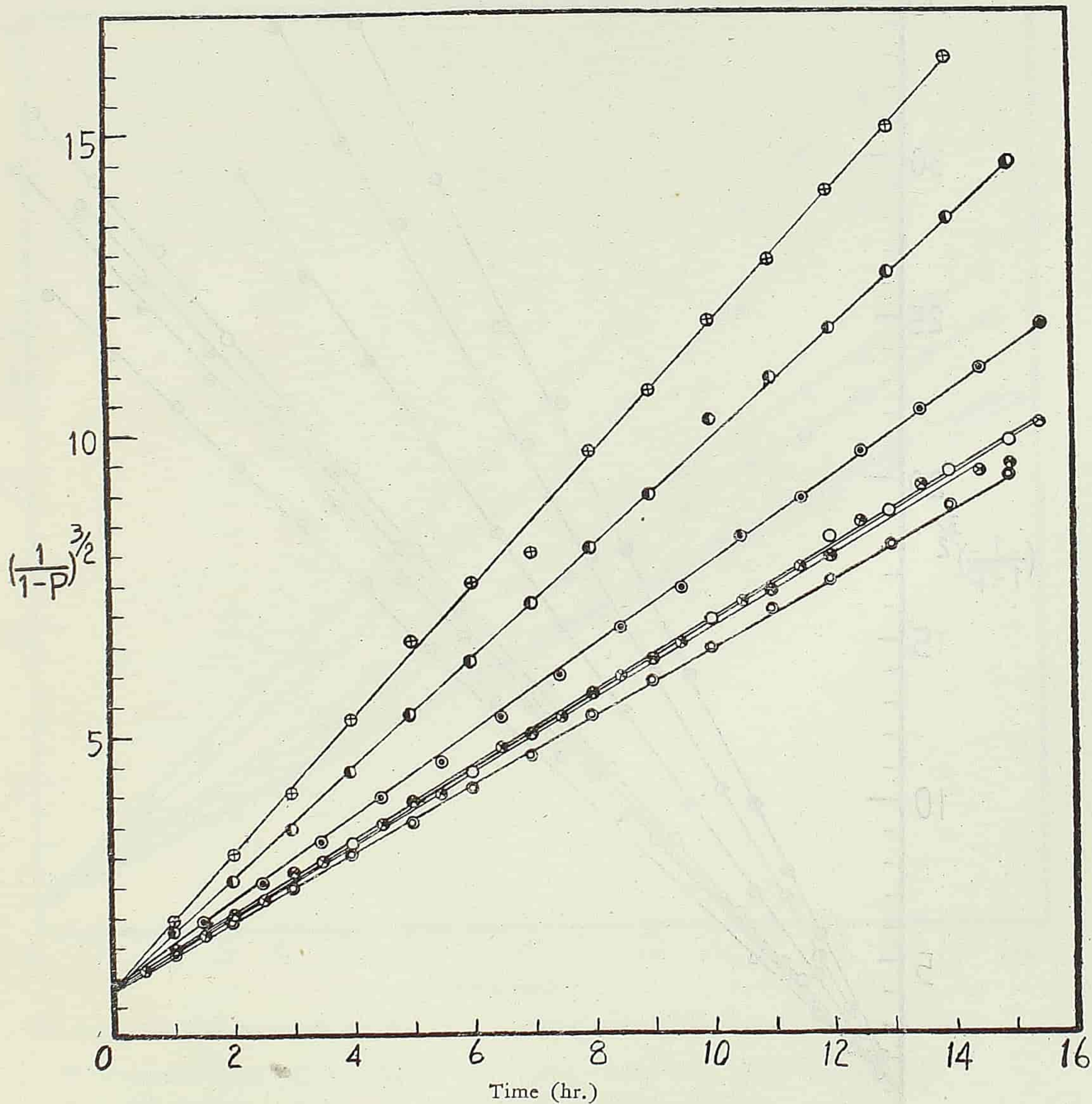


Fig. 2 Reactions of equivalent quantity ratio of dibasic acids and 1,2-propylene glycol at 150°C.

- ⊕ — succinic acid; ● — glutaric acid; ⊙ — adipic acid; ⊗ — pimelic acid;
 ⊗ — suberic acid; ⊙ — azelaic acid; ○ — sebacic acid.

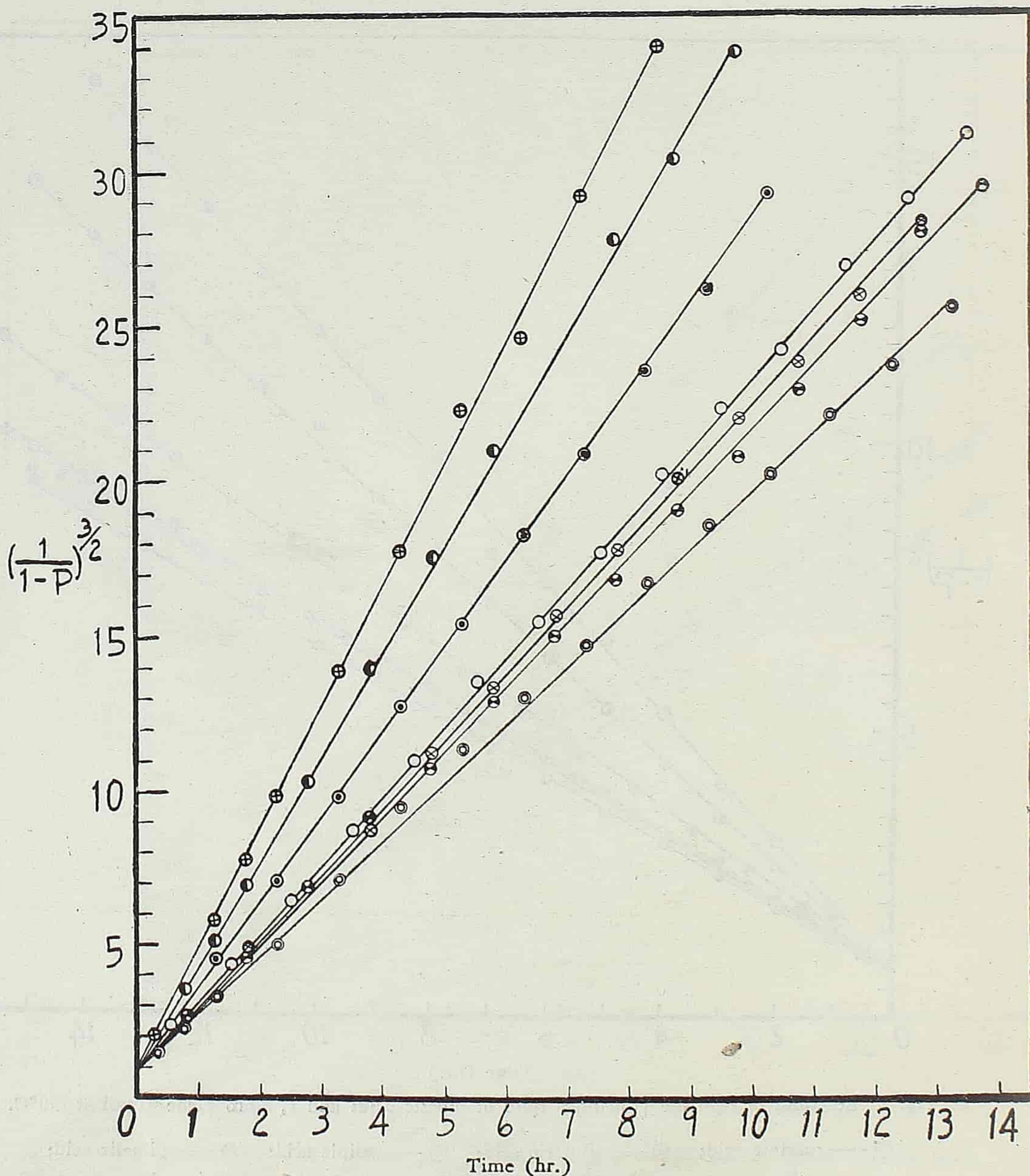


Fig. 3 Reactions of equivalent quantity ratio of dibasic acids and 1, 4-butylene glycol at 150°C.

- ⊕ — succinic acid; ● — glutaric acid; ⊙ — adipic acid; ⊗ — pimelic acid;
 ⊗ — suberic acid; ⊙ — azelaic acid; ○ — sebacic acid.

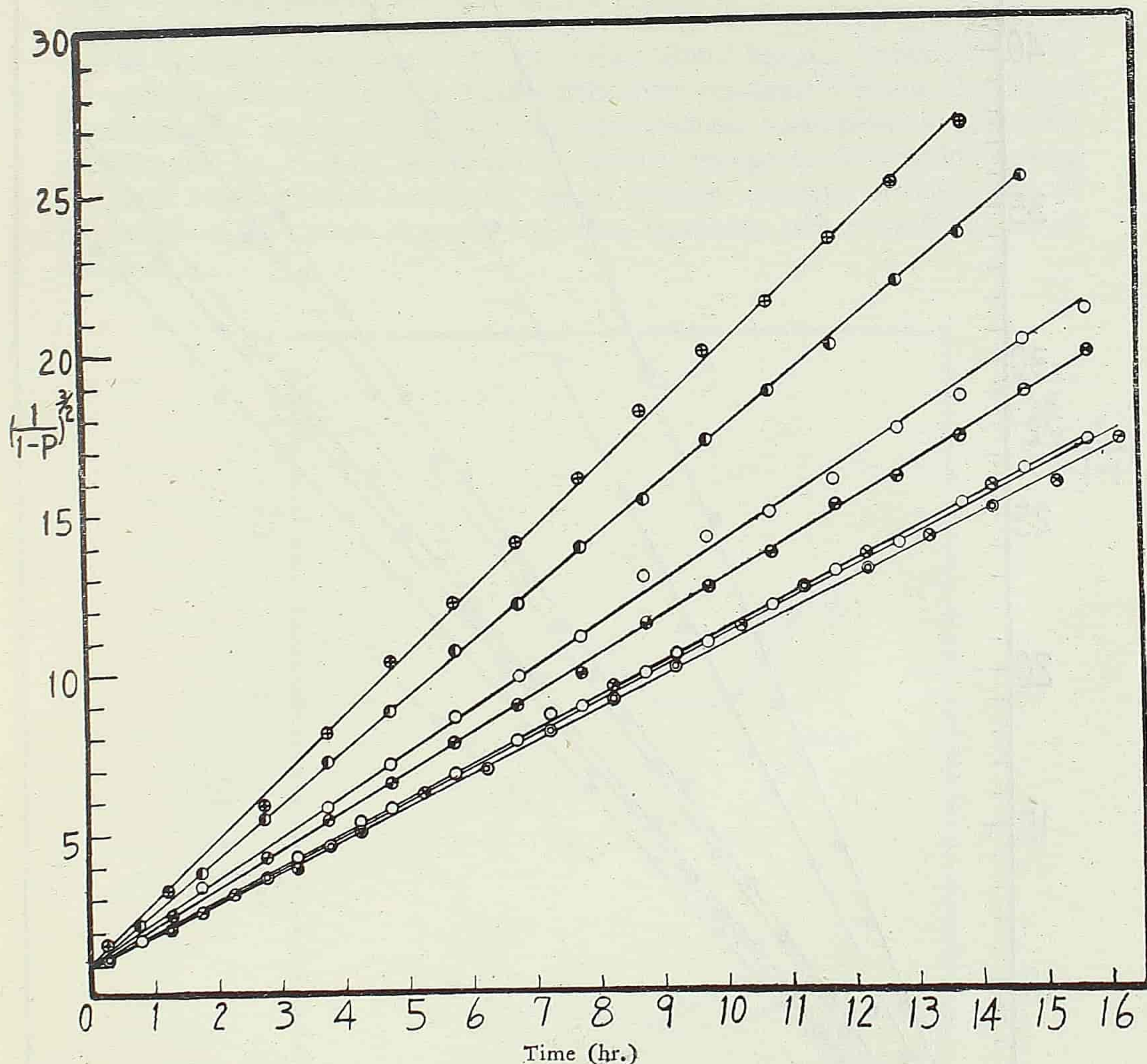


Fig. 4 Reactions of equivalent quantity ratio of dibasic acids and diethylene glycol at 150°C.

⊕ — succinic acid; ● — glutaric acid; ⊙ — — adipic acid; ⊗ — pimelic acid;
 ⊗ — suberic acid; ⊙ — azelaic acid; ○ — sebacic acid.

N.B.:—The points for the third line from the top should have dots in the circles, being inadvertently obliterated during electro-plating.—The Editorial Office.

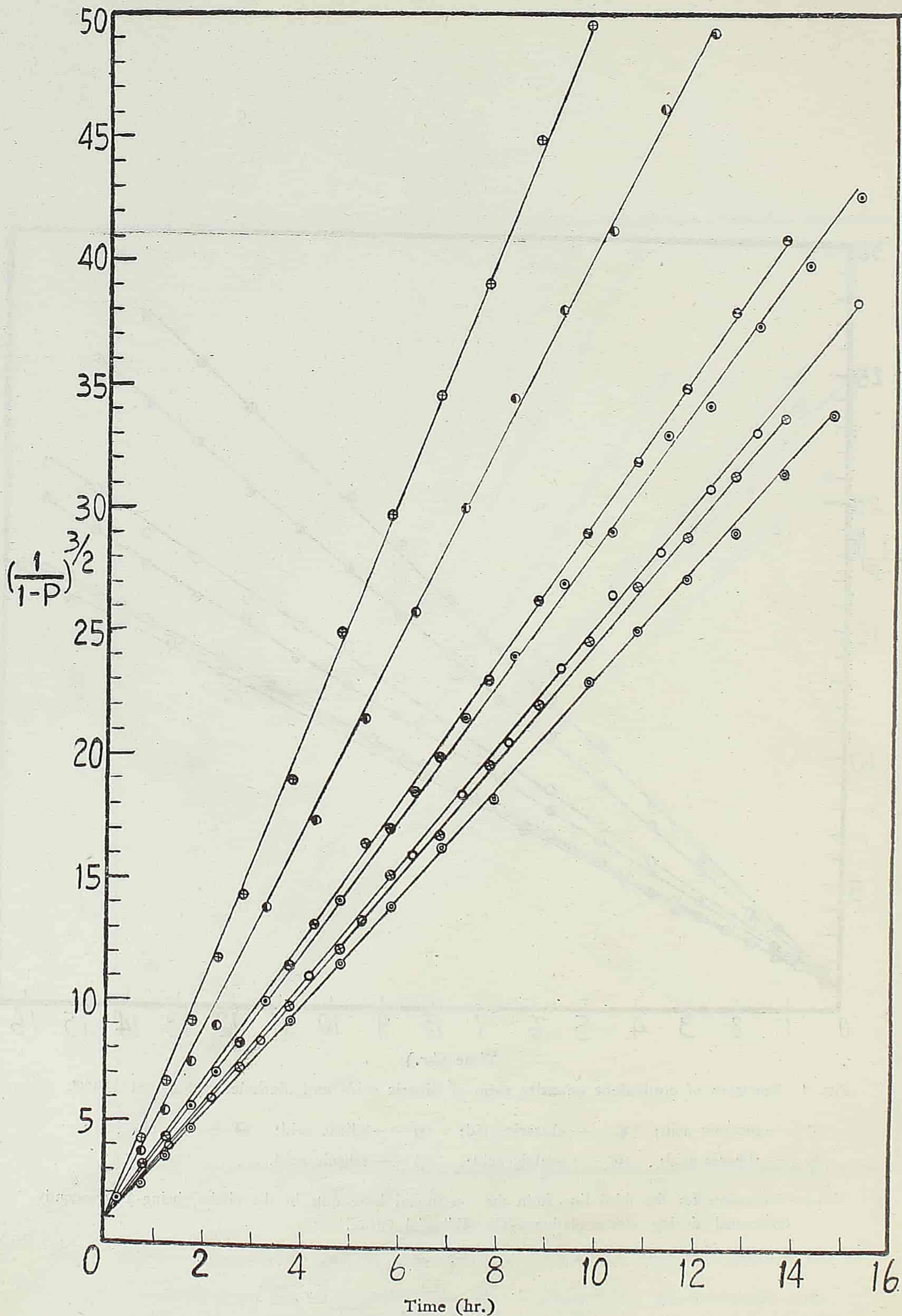


Fig. 5 Reactions of equivalent quantity ratio of dibasic acids and 1, 6-hexamethylene glycol at 150°C.

neglected if the glycol contains more than five carbon atoms in the chain (in the diethylene glycol there are four carbon atoms and one oxygen atom). Hence, we may predict that the velocity constants of polyesterification reactions between dibasic acids and glycols in which two hydroxyl groups at the end of the chain have more than six carbon atoms reach a limiting value of the velocity constants of the polyesterification reactions. From the above discussions we may conclude that the fundamental assumption in the polyesterification, i.e., that all the similar functional groups in the reaction having the same reactivity and hence the same velocity constant independent of the length of the carbon atoms in the chain, represents rather truly the actual condition.

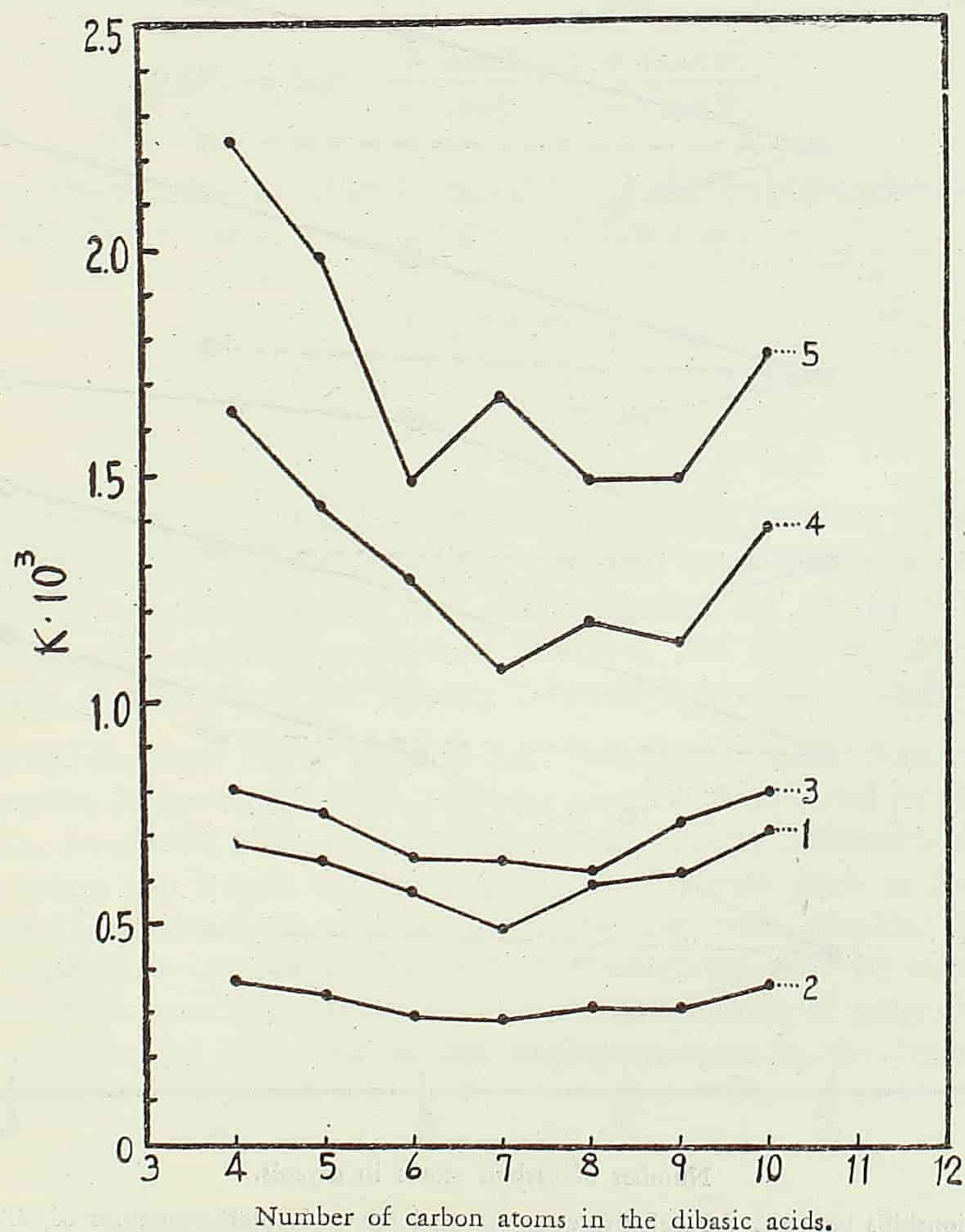


Fig. 6 Relationships between the velocity constants and the molecular structures of dibasic acids and glycols.

1 — ethylene glycol; 2 — 1, 2-propylene glycol; 3 — diethylene glycol;
4 — 1, 4-butylene glycol; 5 — 1, 6-hexamethylene glycol.

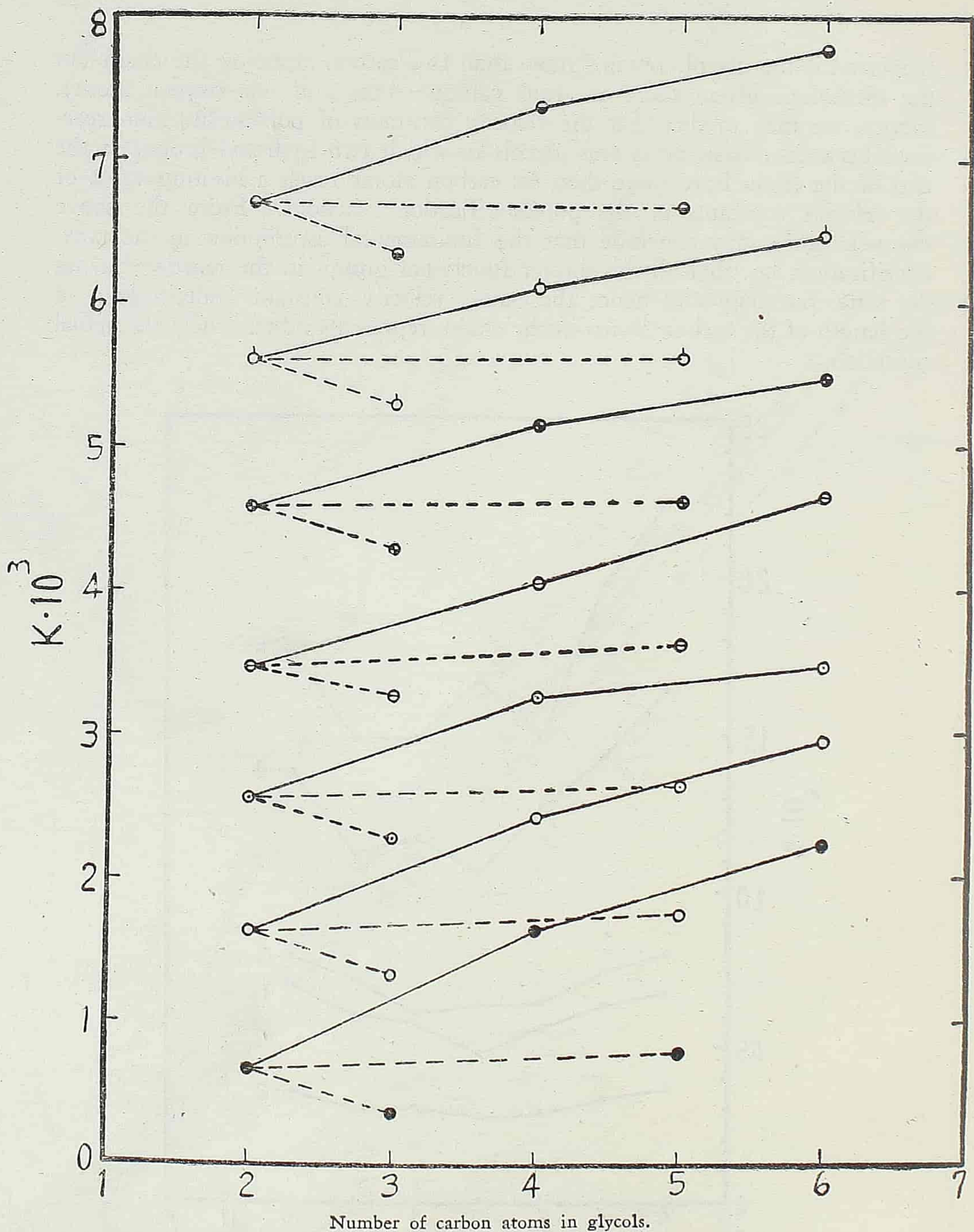


Fig. 7 Relationships between the velocity constants and the molecular structures of dibasic acids and glycols.

● — succinic acid; ○ — glutaric acid; ⊙ — adipic acid; ⊖ — pimelic acid;
 ⊗ — suberic acid; ⊘ — azelaic acid; ⊚ — sebacic acid.

However, we may furthermore make a detailed analysis of the experimental data; it is spontaneously found that the curves in Fig. 6 show somewhat a saddle tendency. This phenomenon may be explained as follows: Because the length of the chain in the succinic acid or in the glutaric acid is rather short, the carboxyl groups at the two ends of the chain slightly interact with each other, and therefore, their velocity constants are a little greater than those of the adipic acid, pimelic acid, suberic acid and azelaic acid. As the length of the chain is further increased, due to its flexibility, the carboxyl groups at the end of the chain may interact again, so the velocity constant is also slightly increased. But the velocity constant will not vary too much as the length of the chain increases indefinitely, because the average distance $\langle l^2 \rangle$ between the two end carbon atoms for long molecules obeys the following formula:

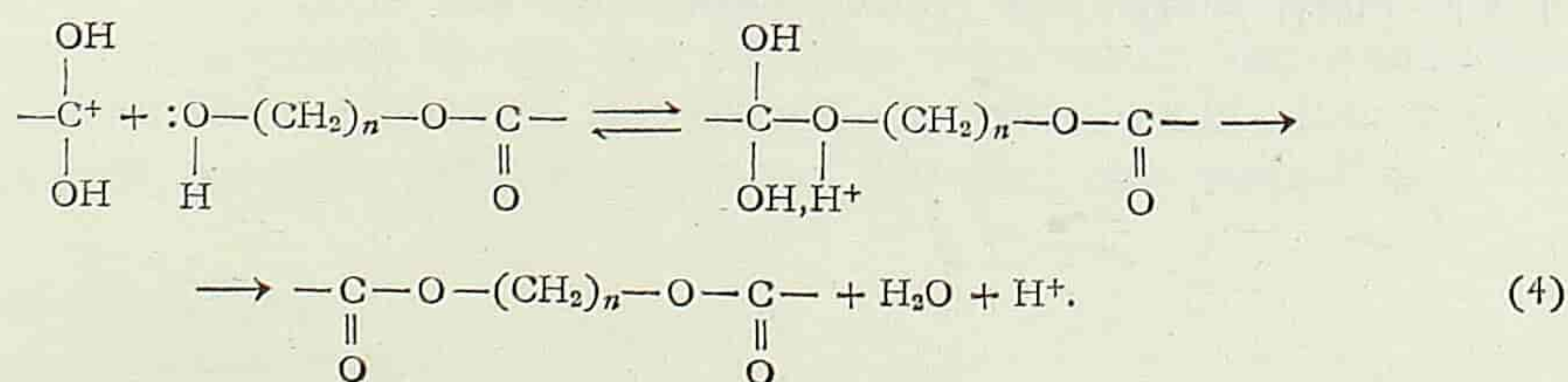
$$\langle l^2 \rangle = Nb^2 \frac{1 + \cos \beta}{1 - \cos \beta} \cdot \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle}, \quad (2)$$

where N is the number of links in the chain, b the carbon-carbon bond distance, β the valence angle, and $\langle \cos \phi \rangle$ is defined as

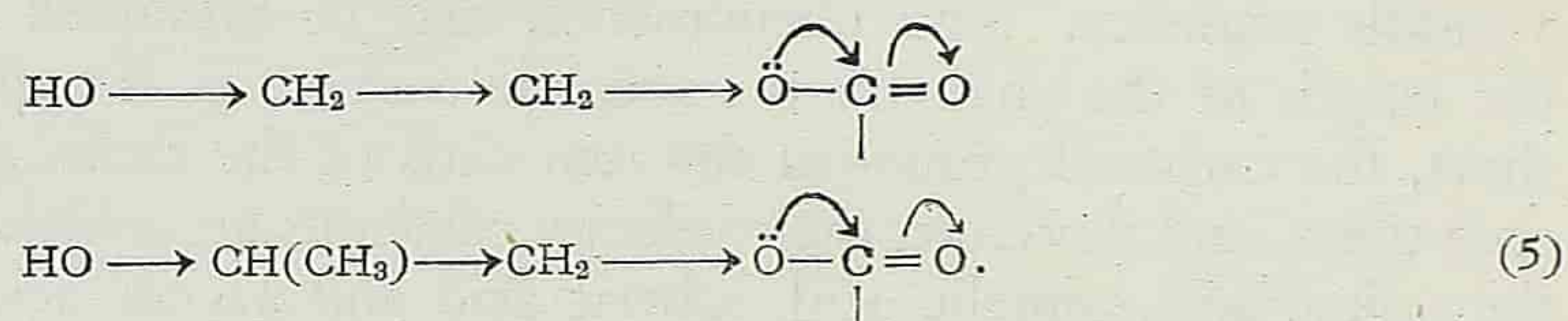
$$\langle \cos \phi \rangle = \frac{\int_0^{2\pi} e^{-V(\phi)/KT} \cos \phi \, d\phi}{\int_0^{2\pi} e^{-V(\phi)/KT} \, d\phi}, \quad (3)$$

here $V(\phi)$ being the potential function of the internal rotation. The average distance between two carboxyl groups is obviously proportional to the square root of $\langle l^2 \rangle$, i.e. proportional to $\sqrt{N} b$. Hence, when the length of the chain is rather long, the interaction between the two end carboxyl groups tends toward zero, and therefore the velocity constant approaches a definite value.

From Table 1 and Fig. 7 we may find two phenomena: First, when one hydrogen atom in the chain of the ethylene glycol is substituted by the methyl group in the formation of 1,2-propylene glycol, its velocity constant is decreased; secondly, when the length of the chain becomes longer such as 1,4-butylene glycol and 1,6-hexamethylene glycol in comparison with ethylene glycol, the velocity constant is increased. These two phenomena may be explained by the theory of the molecular structures and the mechanism of polyesterification reaction supposed by us. One of the important steps in the hydrogen ion catalysis in polyesterification is



In the polyesterification reaction between ethylene glycol and 1,2-propylene glycol with dibasic acid, their electrons are transferred as follows:



Because the methyl group can form hyperconjugation with the lone pair of electrons of oxygen atom, the oxygen atom in the 1,2-propylene glycol thus carries less negative charge than that in the ethylene glycol, and therefore the reaction in the former proceeds more easily than that in the latter. This explains why the first phenomenon occurs. For the second phenomenon we may explain in a similar manner as for the first. When the length of the chain along the two hydroxyl groups of the glycol is increased, the effect of the electronic transference becomes small in formula (5), the reaction in eq. (4) proceeds easily, and therefore, the velocity constants are increased as the length of the chain becomes longer. Of course, the velocity constant will tend toward a definite value as the length of the chain becomes sufficiently long so that the interaction between the two hydroxyl groups can be neglected.

In conclusion, from the large amount of experimental data which we have obtained by our kinetic studies on the polyesterification reactions among the thirty five pairs of dibasic acids and glycols, we have confirmed once again the newly suggested mechanism of hydrogen ion catalysis in polyesterification reaction, and furthermore, we have verified that the fundamental assumption in the kinetics of the polycondensation reaction, i.e., that all similar functional groups have the same reactivity and hence the same velocity constant no matter whatever the chain-length of the molecules may be, is essentially correct. We have also made a detailed analysis of the relationships between the velocity constants of polyesterification reactions and the molecular structures of the dibasic acids and the glycols, and explained those phenomena theoretically.

REFERENCES

- [1] Tang, Au-chin, Yao, Kuo-sui, Lin, Te-hou, Li, Yu-wei and L. Shin-wei 1957 *Science Record*, New Ser. **1**, 243.
- [2] Tang, Au-chin, Yao, Kuo-sui and Co-workers 1958 *Acta Chimica Sinica*, **24**, (6).
- [3] Flory, P. J. 1939 *J. Am. Chem. Soc.* **61**, 3334.

CONFIGURATIONAL PARTITION FUNCTION OF SOLID SOLUTIONS*

T. S. CHANG (张宗燧)**

(Institute of Mathematics, Academia Sinica)

In an earlier paper^[1], it is proved that the configurational free energy F of regular solid solutions is linear in certain coordination numbers defined through the so-called neighbour matrices. To be precise, we let $\lambda_{cc'}$, $\mu_{cc'}$, \dots , be defined as functions of the sites c, c' as follows:

$$\begin{aligned} \lambda_{cc'} &= 1 && \text{if } c, c' \text{ are nearest neighbours,} \\ &= 0 && \text{if otherwise,} \\ \mu_{cc'} &= 1 && \text{if } c, c' \text{ are next nearest neighbours,} \\ &= 0 && \text{if otherwise, } \dots \end{aligned}$$

The coordination numbers are then

$$\begin{aligned} N^{-1} \sum \lambda_{cc'}, \\ N^{-1} \sum \lambda_{cc'} \lambda_{cc''} \mu_{c'c''}, \\ N^{-1} \sum \lambda_{cc'} \lambda_{cc''} \lambda_{c'c''}, \\ N^{-1} \sum \lambda_{cc'} \lambda_{cc''} \lambda_{c'''c'} \lambda_{c'''c''}, \end{aligned} \tag{1}$$

etc., where N denotes the total number of sites and the summation is taken over all positions of c, c', \dots , with the understanding that they are never "equal". If we wish to study the long-distance order, we divide sites among various sublattices and denote points on them by $a, a', \dots, b, b', \dots$, and then the relevant coordination numbers are

$$(2N)^{-1} \sum \lambda_{ab}, \quad (2N)^{-1} \sum \lambda_{ab} \lambda_{a'b} \mu_{aa'}, \tag{2}$$

etc., a, a', \dots being again always unequal, \dots . The right hand sides of (1), (2) are characterized by the fact that the term under the summation sign is an irreducible product in the suffices, i.e. not divisible into two or more parts with one or no suffix in common. Thus we may write F as

*Received Nov. 21, 1958.

**Member of Academia Sinica.

$$F_0 + Z_1 F_1 + Z_2 F_2 + \dots, \quad (3)$$

where the Z 's denote the coordination numbers and the F 's are to be determined. From this it is obvious that F_0 is the free energy when all interaction energies vanish and thus may be written down immediately. To find F_1, F_2, \dots , it is also pointed out in the said paper that all we have to do is to find the free energy F for certain pseudo-lattices for which all Z except a few vanish.

Such a calculation is now envisaged. It is easily seen that the coefficients F for those Z in (1), (2) are closed forms of the Boltzmann factors, and to get their explicit expressions, the only troublesome work is to solve for an algebraic equation of the 3rd or 4th degree. Such expressions will not be written out here^[2], as they are all cumbersome. By using suitable combination of the F 's, we get configurational free energy of binary solid solutions of the type AB , with or without next nearest neighbour interactions, with or without long-distance order, of solid solutions on a face-centred lattice, etc.

One may also discuss quasi-chemical formulas based on the above method. We point out first that if we neglect all the coordination numbers except the lowest (i.e. the average number of nearest neighbours of a site), we obtain the quasi-chemical formula for the different number X of pairs of nearest neighbours, quite independently of the number of components present in the solution. Thus for $i, j = 1, 2, \dots (i \neq j)$, we get

$$\frac{X_{ij}^2}{X_{ii}X_{jj}} = 4 \exp \{(-2V_{ij} + V_{ii} + V_{jj})/kT\} \quad (4)$$

with obvious meanings for the notations. Next, we include higher coordination numbers and obtain in this way natural extensions of the quasi-chemical formulas. Thus after including the next coordination number, the new quasi-chemical formula for a binary solid solution on a face-centred lattice becomes

$$\begin{aligned} X_{AA} &= X'_{AA} + 3X'' \begin{pmatrix} A \\ A A \end{pmatrix} + 3X'' \begin{pmatrix} A \\ A B \end{pmatrix}, \\ X_{AB} &= 2X'_{AB} + 6X'' \begin{pmatrix} A \\ A B \end{pmatrix} + 6X'' \begin{pmatrix} A \\ B B \end{pmatrix}, \\ X_{BB} &= X'_{BB} + 3X'' \begin{pmatrix} B \\ B B \end{pmatrix} + 3X'' \begin{pmatrix} A \\ B B \end{pmatrix}, \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{(X'_{AB})^2}{X'_{AA} X'_{BB}} &= \frac{\left[X'' \begin{pmatrix} A \\ A B \end{pmatrix} \right]^2}{X'' \begin{pmatrix} A \\ A A \end{pmatrix} X'' \begin{pmatrix} A \\ B B \end{pmatrix}} = \frac{\left[X'' \begin{pmatrix} A \\ B B \end{pmatrix} \right]^2}{X'' \begin{pmatrix} B \\ B B \end{pmatrix} X'' \begin{pmatrix} A \\ A B \end{pmatrix}} \\ &= \exp \{(-2V_{AB} + V_{AA} + V_{BB})/kT\}, \end{aligned} \quad (6)$$

$$\begin{aligned} 2(X'_{AA} + X'_{AB}) &= -36N\theta_A, \\ 2(X'_{AB} + X'_{BB}) &= -36N\theta_B, \end{aligned} \quad (7)$$

$$\begin{aligned}
3X'' \binom{A}{A A} + 6X'' \binom{A}{A B} + 3X'' \binom{A}{B B} &= 24N\theta_A, \\
3X'' \binom{B}{B B} + 6X'' \binom{A}{B B} + 3X'' \binom{A}{A B} &= 24N\theta_B.
\end{aligned} \tag{8}$$

In the above, $N\theta_A$, $N\theta_B$ denote the numbers of A , B atoms; X' , X'' are numbers determined by (6), (7), (8), and their substitution into the right hand side of (5) gives the numbers X_{AA} , X_{AB} , X_{BB} of AA , AB , BB pairs of nearest neighbours.

In this connection it may be pointed out that if we call three atoms forming mutually nearest neighbours as a triplet and denote by $X \binom{A}{AA}$, $X \binom{A}{AB}$, \dots the various numbers of the different types of triplets, then for a solid solution on a face-centred lattice, we may guess (by analogy to (4))

$$\frac{\left[X \binom{A}{A B} \right]^2}{X \binom{A}{A A} X \binom{A}{B B}} = \frac{\left[X \binom{A}{B B} \right]^2}{X \binom{B}{B B} X \binom{A}{A B}} = 3 \exp \left\{ - \frac{2V_{AB} - V_{AA} - V_{BB}}{kT} \right\}. \tag{9}$$

These X 's will satisfy

$$\begin{aligned}
3X \binom{A}{A A} + 2X \binom{A}{A B} + X \binom{A}{B B} &= 24N\theta_A, \\
3X \binom{B}{B B} + 2X \binom{A}{B B} + X \binom{A}{A B} &= 24N\theta_B,
\end{aligned} \tag{10}$$

and the numbers X_{AA} , X_{AB} , X_{BB} of pairs of nearest neighbours will be connected to them by

$$\begin{aligned}
X_{AA} &= \frac{1}{4} \left\{ 3X \binom{A}{A A} + X \binom{A}{A B} \right\}, \\
X_{AB} &= \frac{1}{4} \left\{ 2X \binom{A}{A B} + 2X \binom{A}{B B} \right\}, \dots
\end{aligned} \tag{11}$$

It may be worthwhile to add that the difference between (5)—(8) and (9)—(11) is actually small in spite of their appearances.

Combinatory formulas corresponding to (4) and (9) are easily derived. In fact, from (4) (which holds for multi-component solutions), we get

$$\begin{aligned}
\log g &= N(z-1) \sum \theta_i \log \theta_i + \frac{1}{2} Nz \log \frac{1}{2} Nz - \\
&- \sum_i X_{ii} \log X_{ii} - \sum_{i>j} X_{ij} \log \frac{1}{2} X_{ij}, \quad (i, j = 1, 2, \dots)
\end{aligned} \tag{12}$$

where $z \equiv N^{-1} \sum \lambda_{cc'}$, and from (9), (10) and their extended forms for multi-component solid solutions, we get

$$\begin{aligned} \log g = & 8N \log 8N + 23N \sum \theta_i \log \theta_i - \sum X \binom{i}{i \ i} \log X \binom{i}{i \ i} \\ & - \sum_{i>j} \left[X \binom{i}{i \ j} \log \frac{1}{3} X \binom{i}{i \ j} + X \binom{i}{j \ j} \log \frac{1}{3} X \binom{i}{j \ j} \right] - \\ & - \sum_{i>j>k} X \binom{i}{j \ k} \log \frac{1}{6} X \binom{i}{j \ k}. \quad (i, j, k = 1, 2, \dots). \end{aligned} \quad (13)$$

REFERENCES

- [1] Wang, T. M., Hsu, H. C., and Chang, T. S. 1957 *Chinese Journal of Physics*, **13**, 525.
- [2] A paper to be published shortly in *Chinese Journal of Physics*. There calculations of the F 's are given.

**THE ANGULAR DISTRIBUTION OF THE DECAY
PRODUCTS OF HYPERONS***

J. M. CHEN (陳中謨), T. H. HO (何祚庥), D. C. SEN (洗鼎昌)
AND H. Y. TZU (朱洪元)

(*Institute of Atomic Energy Research, Academia Sinica*)

Experimental facts^[1] revealed a large asymmetry of the angular distribution of the decay products of polarized Λ particles. If the angular distribution of completely polarized Λ particles in its rest system is proportional to

$$1 + \alpha \cos \theta, \quad (1)$$

then the experimental value^[2] of the asymmetry parameter is

$$|\alpha| \geq 0.73 \pm 0.14, \quad (2)$$

where θ is the angle between the spin of the Λ particle and the momentum of the emitted proton. Lee and Yang^[3] pointed out that the large value of $|\alpha|$ strongly suggests the spin of Λ particle being $\frac{1}{2}$. It is very difficult to reconcile the theoretical result with the experimental value of α , if the spin of the Λ particle is larger than $\frac{1}{2}$.

Assuming various forms of interaction Hamiltonian, we calculate in this note the angular distribution of hyperon decay products. The value of α is not only sensitive to the magnitude of the spin of Λ , but also valuable in determining the type of interaction Hamiltonian inducing the decay process. It depends on the relative values of interaction constants. Hence, the accurate determination of the value of α is useful to the determination of the effect of renormalization.

The angular distribution of hyperon decay is discussed phenomenologically first. The hyperon may decay into nucleon and π -meson directly or indirectly through the medium of other fields by way of a series of intermediate states. It is convenient for the study of hyperon decay process to eliminate all other fields except those of hyperons, nucleons and π -mesons and to

*Received Dec. 10, 1958.

express the effect of eliminated fields by equivalent direct interactions between hyperons, nucleons and π -mesons. These equivalent interactions, usually of the non-local type, may depend on the higher derivatives of the field quantities. As a first step, let us examine the simplest direct equivalent interaction which does not depend on the derivatives of the field quantities.

It is assumed that the interaction Hamiltonian which leads to the decay process

$$\Lambda^0 \longrightarrow p^+ + \pi^- \quad (3)$$

is of the following form:

$$H_i^{(1)} = g\bar{\psi}_p(\xi_1 + \gamma_5)\psi_\Lambda \cdot \varphi + g\bar{\psi}_\Lambda(\xi_1 - \gamma_5)\psi_p \varphi^*, \quad (4)$$

where ψ_Λ , ψ_p and φ represent the field operators of Λ , p and π respectively. It is assumed here that the Λ particle is a spin $1/2$ particle and obeys the Dirac equation. g and ξ_1 are real numbers. If we are not interested in the spin of the proton in the final state, then we obtain the following matrix which determines the angular distribution of protons:

$$\Theta_1 = 1 + \alpha_1(\vec{\sigma} \cdot \vec{e}), \quad (5)$$

where $\vec{\sigma}$ is the Pauli matrices, \vec{e} the unit vector in the direction of the momentum of the proton and α_1 the asymmetry parametre,

$$\alpha_1 = \frac{2\xi_1 p}{m(\xi_1^2 - 1) + E_n(\xi_1^2 + 1)}, \quad (6)$$

where m represents the mass of the proton, E_n the energy of the proton and p the absolute value of the momentum of the proton. If α_1 is to be made equal to 1, then the value of ξ_1 must be taken equal to 0.05. Thus the coupling constant of the parity non-conserving term must be very much smaller than that of the parity conserving term, if it is assumed that the Λ particle and the nucleon are of the same parity.

We assume next that the interaction Hamiltonian density contains the first derivative of the π -meson field quantity, i.e.,

$$\begin{aligned} H_i^{(2)} = & f\bar{\psi}_p \gamma_\mu (\xi_2 + \gamma_5) \psi_\Lambda \frac{\partial \varphi}{\partial x_\mu} - f\bar{\psi}_\Lambda \gamma_\mu (\xi_2 + \gamma_5) \psi_p \frac{\partial \varphi^*}{\partial x_\mu} \\ & - \frac{f^2}{2} \bar{\psi}_p \hat{n} (\xi_2 + \gamma_5) \psi_\Lambda \bar{\psi}_\Lambda \hat{n} (\xi_2 + \gamma_5) \psi_p, \end{aligned} \quad (7)$$

where n_μ represents the unit vector in the direction of the normal of the space-like curved surface. From the Hamiltonian $H_i^{(2)}$, we obtain the following matrix which determines the angular distribution:

$$\Theta_2 = 1 + \alpha_2(\vec{\sigma} \cdot \vec{e})$$

$$\alpha_2 = \frac{-2\xi_2 p(2E_n E_\pi + E_\pi^2 + p^2)}{(\xi_2^2 + 1)(E_n E_\pi^2 + E_n p^2 + 2p^2 E_\pi) + (\xi_2^2 - 1)mm_\pi^2}, \quad (8)$$

where E_π and m_π represent the energy and the mass of the π -meson respectively. If we let $\xi_2 = 1$ and substitute the experimental value of E_n , E_π into (8), then we obtain $\alpha_2 = -0.89$, which agrees well with the experimental results¹⁾. But this value is already quite near the upper limit of the experimental value.

We assume further that the decay is induced by the universal Fermi interaction of the $V-A$ type^[4] and strong interactions involving π -mesons. If the renormalization effect is neglected, then the matrix determining the angular distribution has the same form as (8) with $\xi_2 = 1$. The asymmetry parameter α is then equal to -0.89 . However, if $\xi_2 \neq 1$ due to the renormalization effect, α will change correspondingly. If $g_A^2/g_V^2 = 1.55$, which is the ratio of that the spin of g_A^2 to g_V^2 in β -decay phenomena, then

$$\alpha = -0.97 - 0.97. \quad (9)$$

Hence, the accurate determination of the value of α will be helpful to the investigation of the effect of the renormalization. Some experiments show that the spin of Λ particles might be $3/2$. It is thus interesting to study the angular distribution of the decay products of a spin $3/2$ particle. It is assumed that the Λ particle obeys the Rarita-Schwinger equation with a spin $3/2$. The following interaction Hamiltonian is introduced.

$$H_i^{(R)} = \frac{F}{\sqrt{2}} \{ \bar{\psi}_\mu (1 + \gamma_5) \psi_p \bar{\psi}_p \gamma_\mu (1 + \gamma_5) \psi_N$$

$$+ \bar{\psi}_N \gamma_\mu (1 + \gamma_5) \bar{\psi}_p \bar{\psi}_p (\gamma_5 - 1) \psi_\mu \} + O(F^2), \quad (10)$$

where ψ_μ is a hyperon field which obeys the following equation and supplementary conditions:

$$\left(\gamma_\nu \frac{\partial}{\partial x_\nu} + M \right) \psi_\mu = 0,$$

$$\gamma_\mu \psi_\mu = 0,$$

$$\frac{\partial}{\partial x_\mu} \psi_\mu = 0,$$

$$\mu = 1, 2, 3, 4. \quad (11)$$

¹⁾ It came to the authors' notice after the completion of this note that the same result has been pointed out by Marshak and Sudarshan,

$O(F^2)$ is additional terms ensuring that the Schrödinger equation is integrable. Since the various terms in $O(F^2)$ are proportional to F^n with $n \geq 2$, their contributions are negligible.

It is found that the maximum average value of $\cos \theta$ is $1/5$, which agrees with the general conclusion of Lee and Yang^[3]. When the mean value of $\cos^3 \theta$ takes the maximum value, there then appear simultaneously terms proportional to $\cos^2 \theta$ and $\cos^3 \theta$ with quite large coefficients. The experimental average value of $\cos \theta$ for the partially polarized Λ particle^[3] is 0.17, but appreciable terms proportional to $\cos^2 \theta$ and $\cos^3 \theta$ do not exist. Hence, it is very unlikely that the Λ particle is a particle of spin $3/2$ obeying the Rarita-Schwinger wave equation.

The details of the investigation will be published elsewhere.

REFERENCES

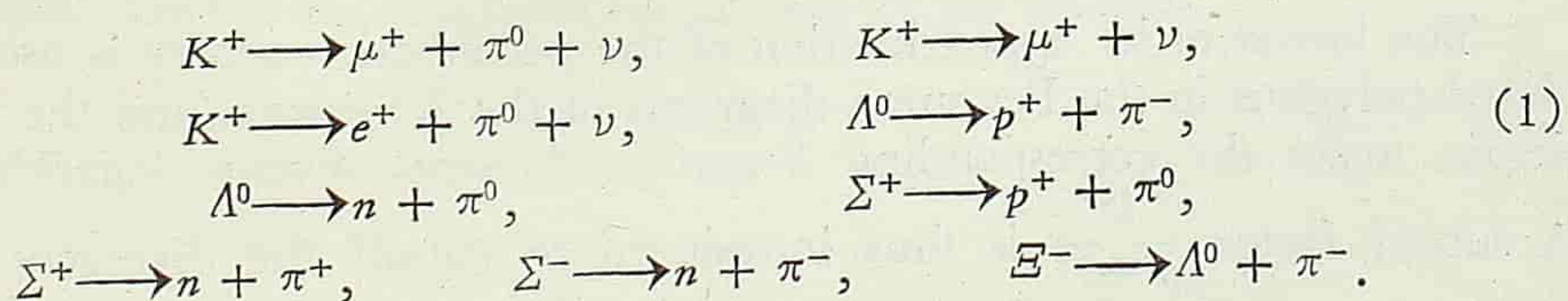
- [1] Eisler, F. et al 1957 *Phys. Rev.* **108**, 1353.
- [2] Glaser, D. A. 1958 *Annual International Conference on High Energy Physics at Cern*, 265.
- [3] Lee, T. D. and Yang, C. N. 1958 *Phys. Rev.* **109**, 1755.
- [4] Feynman, R. P. and Gell-Mann, M. 1958 *Phys. Rev.* **109**, 193.
- [5] Sudarshan, G. and Marshak, R. E. 1958 *Phys. Rev.* **109**, 1860.
- [6] Rarita, W. and Schwinger 1941 *J. Phys. Rev.* **60**, 69.

THE MEAN LIFE TIME RATIO OF K^+ -MESON AND HYPERONS AND THEIR BRANCHING RATIOS OF DIFFERENT DECAY MODES*

W. T. LEE** (李文鏞), D. C. SEN (洗鼎昌), T. H. HO (何祚庥)
J. M. CHEN (陈中謨), AND H. Y. TZU (朱洪元)
(Institute of Atomic Energy Research, Academia Sinica)

The theory of the universal Fermi interaction proposed independently by Feynman and Gell-Mann^[1] on the one hand and Sudarshan and Marshak^[2] on the other has been successfully applied to explain the β -decay and many other phenomena caused by weak interactions. It will be interesting to apply the theory to the discussion of other phenomena involving weak interactions.

In this note, the mean life time ratio of K^+ -meson and hyperons and the branching ratios of some of the different decay modes of K^+ -meson and hyperons are calculated by using the Feynman—Gell-Mann universal interaction. These decay processes are the following:



The universal Fermi weak interaction has the following form:

$$H_w = \frac{G}{\sqrt{2}} (\bar{A} \gamma_\mu (1 + \gamma_5) B) (\bar{C} \gamma_\mu (1 + \gamma_5) D), \tag{2}$$

where A, B, C, D represent the field operators of various Fermi particles, which can be $N, \Lambda, \Sigma, \Xi, \mu, \nu, e$ etc. in this note. \hbar and c are each chosen as unit and equal to 1. G is a universal constant, whose value is given by the following equation:

$$G m_N^2 = (1.01 \pm 0.01) \times 10^{-5}, \tag{3}$$

m_N being the mass of the nucleon.

*Received Dec. 10, 1958.

**Now at the Chekiang University,

All the decay processes given in (1) are the results of the joint effect of the strong as well as the weak interaction. The strong interaction chosen in this note is the isotopic invariant Hamiltonian suggested by Salam *et al.*^[3, 4] The forms of the Hamiltonian are

$$H_s = \sum_{n=1}^8 g_n H_n,$$

$$\begin{aligned} H_1 &= \bar{N} i \gamma_5 \boldsymbol{\tau} \cdot \boldsymbol{\pi} N, \\ H_2 &= \bar{\Lambda}^0 i \gamma_5 \boldsymbol{\pi} \cdot \boldsymbol{\Sigma} + \bar{\boldsymbol{\Sigma}} \cdot \boldsymbol{\pi} i \gamma_5 \Lambda^0, \\ H_3 &= i[\bar{\boldsymbol{\Sigma}} \times \boldsymbol{\pi}] i \gamma_5 \boldsymbol{\Sigma}, \\ H_4 &= \bar{\boldsymbol{\Xi}} i \gamma_5 \boldsymbol{\tau} \cdot \boldsymbol{\pi} \boldsymbol{\Xi}, \\ H_5 &= \bar{N} i \gamma_5 K \Lambda^0 + \Lambda^0 i \gamma_5 K^* N, \\ H_6 &= \bar{N} i \gamma_5 \boldsymbol{\tau} \cdot \boldsymbol{\Sigma} K + K^* \bar{\boldsymbol{\Sigma}} \cdot \boldsymbol{\tau} i \gamma_5 N, \\ H_7 &= \bar{\Lambda}^0 i \gamma_5 K i \tau_2 \boldsymbol{\Xi} - \bar{\boldsymbol{\Xi}} i \tau_2 K^* i \gamma_5 \Lambda^0, \\ H_8 &= \bar{\boldsymbol{\Xi}} i \gamma_5 \boldsymbol{\tau} \cdot i \tau_2 K^* \boldsymbol{\Sigma} - \bar{\boldsymbol{\Sigma}} i \gamma_5 K i \tau_2 \cdot \boldsymbol{\tau} \boldsymbol{\Xi}. \end{aligned} \quad (4)$$

The above Hamiltonian is slightly different from that proposed by Salam. In our case, the coupling of K -meson to nucleon and hyperons involves γ_5 , which is different from the corresponding expression in Salam's Hamiltonian. H_7 and H_8 are also slightly modified in order to guarantee the invariance under time reversal.

The lowest order approximation of the perturbation theory is used. The closed polygons in the Feynman diagrams of the K^+ -meson and the hyperon decays make the corresponding S -matrix elements diverge logarithmically. A cut-off factor $\frac{\lambda^2}{p^2 + \lambda^2}$ is thus introduced to cut-off the divergent part of the integral. The absolute life times obtained can hardly be trusted, as in our calculation the perturbation theory with a cut-off is used. The mean life time ratio and the branching ratios of different decay modes are thus discussed and compared with the experimental results.

The Feynman diagrams of K^+ -meson decay can be easily written down. However, two points need to be considered while discussing the hyperon decay, as the weak interactions involved are those between two pairs of heavy particles.

1. Experiments show that in the decay of strange particles, the change of the strangeness quantum number can be ± 1 only. In order to exclude the possibility of the strangeness quantum number changing by two units in the decay processes, the pair of charged particles and neutral particles must be chosen in such a way that $\Delta Q = \Delta S$. The pairs of baryons satisfying this condition are the following:

$$\begin{array}{ll}
(\bar{P}, \Lambda) & (\Lambda, P) \\
(\bar{P}, \Sigma^0) & (\bar{\Sigma}^0, P) \\
(\bar{N}, \Sigma^-) & (\bar{\Sigma}^-, N) \\
(\bar{\Lambda}, \Xi^-) & (\bar{\Xi}^-, \Lambda) \\
(\bar{\Sigma}^+, \Xi^0) & (\bar{\Xi}^0, \Sigma^+) \\
(\bar{\Sigma}^0, \Xi^-) & (\bar{\Xi}^-, \Sigma^0)
\end{array} \tag{5}$$

2. The following problems appear while dealing with the weak interaction involving two pairs of baryons. To illustrate the problem, we choose the following example: The universal weak interaction between baryons may contain the following two terms:

$$\begin{aligned}
& \frac{G}{\sqrt{2}} (\bar{\psi}_{\Sigma^-} \gamma_{\mu} (1 + \gamma_5) \psi_{\Sigma^0}) (\bar{\psi}_P \gamma_{\mu} (1 + \gamma_5) \psi_{\Lambda}), \\
& \frac{G}{\sqrt{2}} (\bar{\psi}_{\Sigma^-} \gamma_{\mu} (1 + \gamma_5) \psi_{\Lambda}) (\bar{\psi}_P \gamma_{\mu} (1 + \gamma_5) \psi_{\Sigma^0}).
\end{aligned} \tag{6}$$

Although representing two different combinations of baryon pairs formally, they are completely equivalent to each other mathematically. Thus the following question arises: Should the contributions of both terms be included in the calculation? In this paper, it is assumed that only the contribution of one of the terms of (6) should be counted.

There is another related question, which can be illustrated by the following example. One of the diagrams which lead to the process:

$$\Sigma^- \longrightarrow N + \pi^- \tag{7}$$

is the following:

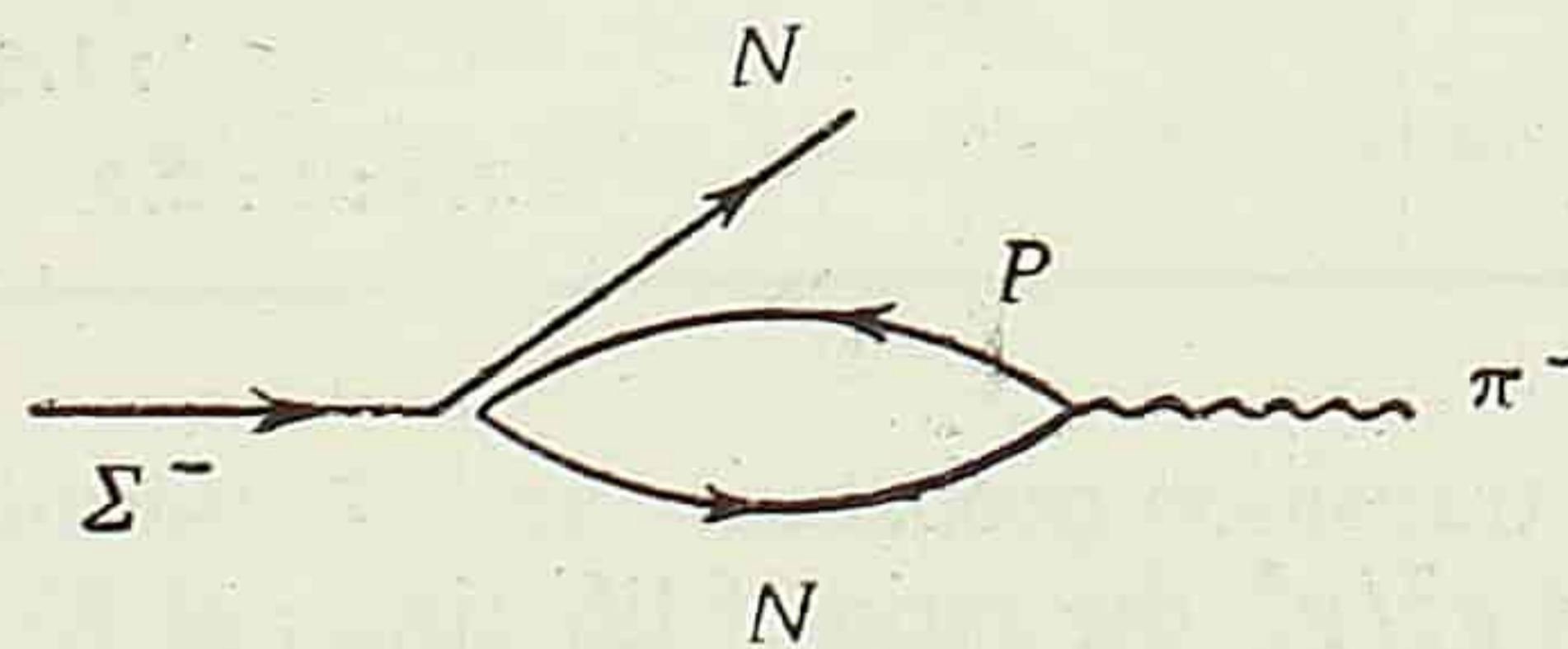


Fig. 1

The weak interaction represented by the vertex on the left hand side is:

$$\frac{G}{\sqrt{2}} (\bar{\psi}_N \gamma_{\mu} (1 + \gamma_5) \psi_P) (\bar{\psi}_N \gamma_{\mu} (1 + \gamma_5) \psi_{\Sigma^-}). \tag{8}$$

There are two operators $\bar{\psi}_N$ in the expression (8), both of which can represent the external neutron line in Fig. 1. Hence, the following question arises:

Shall the contribution of Fig. 1 be counted once or twice? In this paper it is assumed that the contribution of diagrams of this type should be counted only once.

The following assumptions about the strong interaction constants g_1, g_2, \dots, g_8 , are assumed:

$$\begin{aligned} -g_1 &= g_2 = g_3 = g_4 = g_\pi, \\ g_5 &= g_6 = g_7 = g_8 = g_K. \end{aligned} \quad (9)$$

With the help of the experimental data of the transition probability of $K^+ \rightarrow \mu^+ + \nu$ and $\pi^+ \rightarrow \mu^+ + \nu$, the ratio between g_π and g_K can be derived. The Feynman diagrams describing these two processes are very very similar to each other. It is easily found that

$$\frac{g_\pi^2}{g_K^2} = 1.8 \left(\frac{m_\pi}{m_K} \right)^2 \left(\frac{m_K^2 - m_\mu^2}{m_\pi^2 - m_\mu^2} \right)^2, \quad (10)$$

m_K, m_π, m_μ being the masses of K, π, μ mesons respectively.

By using the above assumptions the following results are obtained:

Table 1

	Theor. value	Exp. value ^[5]
$\frac{W_{\Sigma^+ \rightarrow P + \pi^0}}{W_{\Sigma^+ \rightarrow N + \pi^+}}$	1.0	$0.46 \pm 0.06 : 0.54 \pm 0.06 \cong 1$
$\frac{W_{\Lambda \rightarrow P + \pi^-}}{W_{\Lambda \rightarrow N + \pi^0}}$	1.5	$65 \pm 5 : 35 \pm 5$
$\tau_\Lambda : \tau_{\Sigma^+} : \tau_{\Sigma^-}$	4.0 : 1 : 1.2	$2.77 \pm 0.15 : 0.78 \pm 0.07$ $: 1.58 \pm 0.17$ $= 3.6 : 1 : 2.3$

Here W represents the transition probability and τ the mean life time. From the value of the ratio of g_π^2/g_K^2 , the ratio of life times of K -meson and hyperons can be calculated. The result is

$$\frac{\tau_{K^+}}{\tau_{\Sigma^-}} = 66, \quad (11)$$

while the experimental result is $(1.22 \pm 0.013) \times 10^{-8} : (1.58 \pm 0.17) \times 10^{-10} \cong 78$. The branching ratio of the K^+ -meson decay calculated is:

$$W_{K^+ \rightarrow \nu^+ + \nu} : W_{K^+ \rightarrow e^+ + \pi^0 + \nu} : W_{K^+ \rightarrow \mu^+ + \pi^0 + \nu} = 16 : 1 : 0.67. \quad (12)$$

The corresponding experimental value is ^[5]:

$$58.8 \pm 2.0 : 4.19 \pm 0.42 : 4.0 \pm 0.79 \cong 14 : 1 : 0.95. \quad (13)$$

If the following assumption about the coupling constants of strong interaction

$$\begin{aligned} g_1 = g_2 = g_3 = g_4 = g_\pi, \\ g_5 = g_6 = g_7 = g_8 = g_K, \end{aligned} \quad (14)$$

is made instead of (9), then the branching ratio of the K^+ -meson decay obtained is:

$$W_{K^+ \rightarrow \mu^+ + \nu} : W_{K^+ \rightarrow e^+ + \pi^0 + \nu} : W_{K^+ \rightarrow \mu^+ + \pi^0 + \nu} = 12 : 1.5 : 1$$

which agrees quite well with (13), but not as good as (12). However, the calculated branching ratio of the Λ -decay then differs widely from the experimental data.

As a whole the calculated results of this note differ from the experimental values at most by a factor 2. Some of the calculated results are in quite good agreement with experiment. As the method of calculation used is rather crude, the over-all degree of agreement with the experiments may be regarded as fairly good. Thus the results of this note give support to the theory of universal weak Fermi interaction proposed by Feynman and Gell-Mann. The detailed calculation of this note will be published elsewhere.

REFERENCES

- [1] Feynman, R. P. and Gell-Mann, M. 1958 *Phys. Rev.* **109**, 1755.
- [2] Sudarshan, G. and Marshak, R. E. 1958 *Phys. Rev.* **109**, 1860.
- [3] Salam, A. 1956 *Nucl. Phys.* **2**, 173.
- [4] Gell-Mann, M. 1957 *Phys. Rev.* **106**, 1296.
- [5] Gell-Mann, M. and Rosenfeld, A. H. 1957 *Annu. Rev. Nucl. Sci.* **7**, 409.

SCIENCE RECORD

New Ser. Vol. III, No. 1, 1959

BIOPHYSICS

COSMIC RADIATION AND TUBERCULOSIS

II. ACTION OF COSMIC RADIATION ON TUBERCLE BACILLI*

S. G. ONG (王善源)**

(*Institute of Epidemiology, Academy of Medical Sciences, Peking*)

1. In a preliminary experiment it has been shown that tubercle bacilli exposed to cosmic radiation at Jungfrauoch (3,457 m) with or without screen showed a significant difference in virulence when injected into mice^[1]. In fact, the virulence decreased in the following order of treatments:

Treatments	Mean times of survival in days
Under 30 m of rock	20.5
Under 2 cm of lead	79.9
Direct cosmic radiation	116.0
Under 10 cm of lead	(Tubercle bacilli killed)

The objection to this experiment and to all other experiments on the biological action of cosmic radiation is that the action of radio-active radiation from the environment is not eliminated.

2. We repeated the above experiment by enclosing the tubercle bacilli in a lead box of 1 cm thickness so that most of the radio-active rays were eliminated. Fig. 1 shows the dimensions of the box. By inserting lead plates of approximately 1 cm thickness between the tubes, numbered 1—20, different thicknesses of lead can be obtained. The box was placed in an incubator maintained at 37°C on the roof of the laboratory (63 m above sea-level). On the top of the box were placed two unscreened control tubes with tubercle bacilli being thus exposed to the direct action of cosmic radiation. After 53 days the tubercle bacilli from the various tubes were injected into mice. For each pair of tubes 20 mice were injected intravenously with 0.4 mg of tubercle bacilli. However, in groups 3, 4 and 5 the quantity of tubercle bacilli was not sufficient, therefore 15, 19 and 19 mice were used respectively.

*Received Nov. 22, 1958.

**Member of Academia Sinica.

Table 1

Frequency of times of survival of mice after intravenous injection with 0.4 mg of tubercle bacilli exposed to cosmic radiation.

Group	1a	1b	1c	2	3	4	5	6	7	8	9	10
T	Screen cm Pb.											
	0	0	0	1.1	2.1	3.2	4.2	5.3	6.3	7.4	9.5	10.5
	Control											
12		3		2			1					
13	1		2									
14	2		2	2					1			
15	3	1	2	1								
16	1	3		2		1						2
17	5	4	2	3			2	4	3			2
18	2	3	9	2		1	5	6	1			3
19	3	3	2	2		3			4			6
20	2	2	1	5		7	7	6	3			3
21		1		1		4	2	2	1			2
22						2	1		4			1
23						1	1					
24	1							1	1			
25									1			1
26								1				
34									1	2		
35										1		
36										2		
41											1	
43					2							
44										1		
69										1		
Total	344	339	338	345		382	363	388	411			383
Means	17.2	17.0	16.9	17.3		20.1	19.1	19.4	20.6			19.2

T, times of survival in days after infection.

Table 2

Analysis of variance of groups 1a, 1b, 1c, 2, 4, 5, 6, 7 and 10.

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Total	1 470.50	177		
Treatments	327.89	6	54.65	8.18
Error	1 142.61	171	6.68	

Mean of pooled controls = 17.0 days. Significant difference between two means = 1.7 days, $P = 0.01$ and 2.2 days for $P = 0.001$. Groups 4, 5, 6, 7 and 10 all show a highly significant difference when compared with the control.

Table 1 shows the times of survival in days after infection with tubercle bacilli. It is seen that the tubercle bacilli screened with 2.1, 7.4 and 9.5 cm

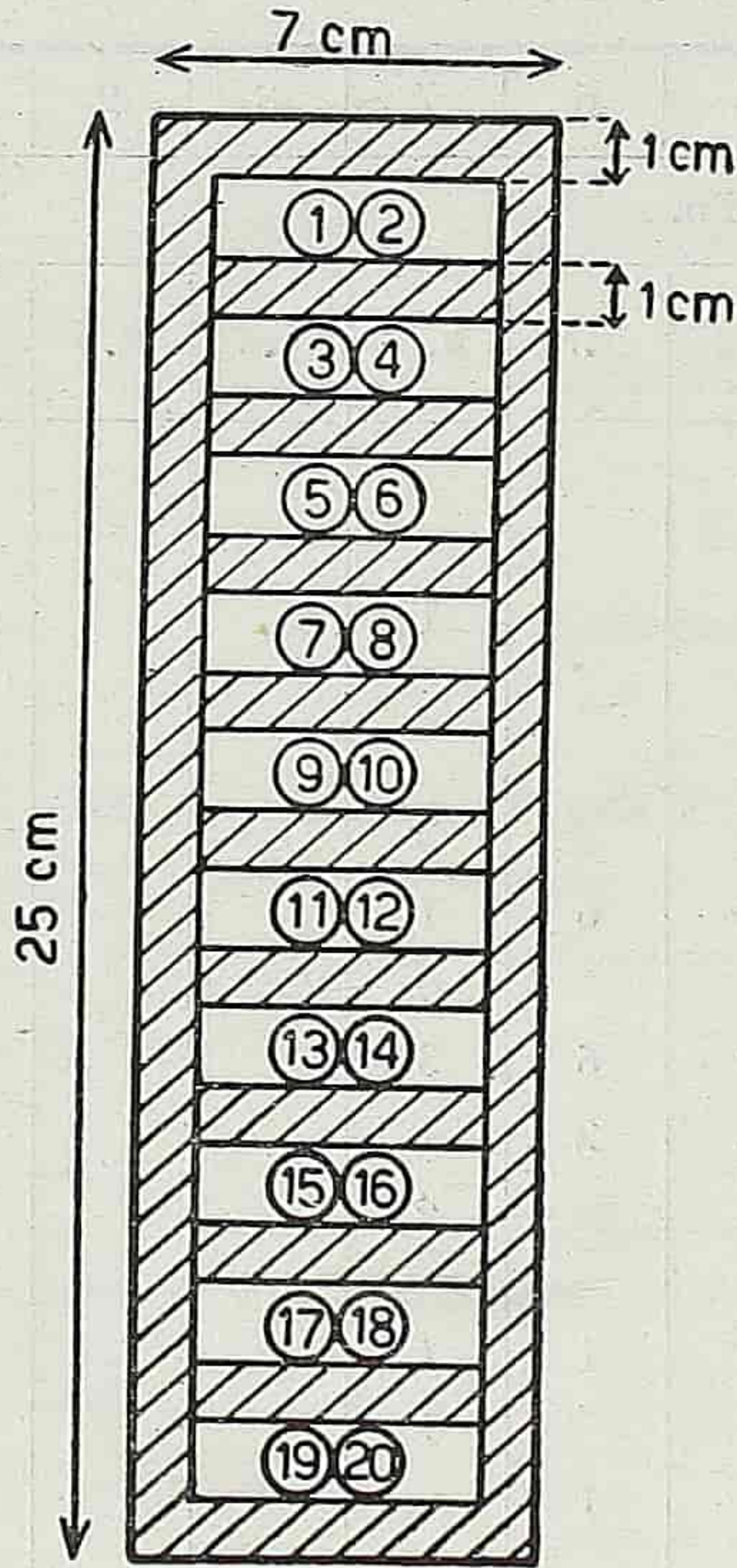


Fig. 1 Lead box for exposing the tubercle bacilli to cosmic radiation under various thickness of lead screen and for screening it from radioactive rays.

of lead showed a great decrease in virulence as only 2, 7 and 1 mice died 43, 34-69 and 41 days after infection respectively. The remaining 45 mice are still living 80 days after infection. The analysis of variance of the other groups of mice (Table 2) shows that the difference between the mean times of survival of mice injected with tubercle bacilli screened with 3.2, 4.2, 5.3, 6.3 and 10.5 cm of lead and that of the control mice is highly significant. There is no significant difference between the means of the three control groups, i.e. the control mice were random samples from the same population.

In Fig. 2 the mean times of survival of the various groups of mice are plotted against the thickness of lead screen. It is seen that there is a sharp maximum at approximately 2 cm of lead corresponding to a maximum number of showers and a second broad maximum between 7 and 10.5 cm of lead.

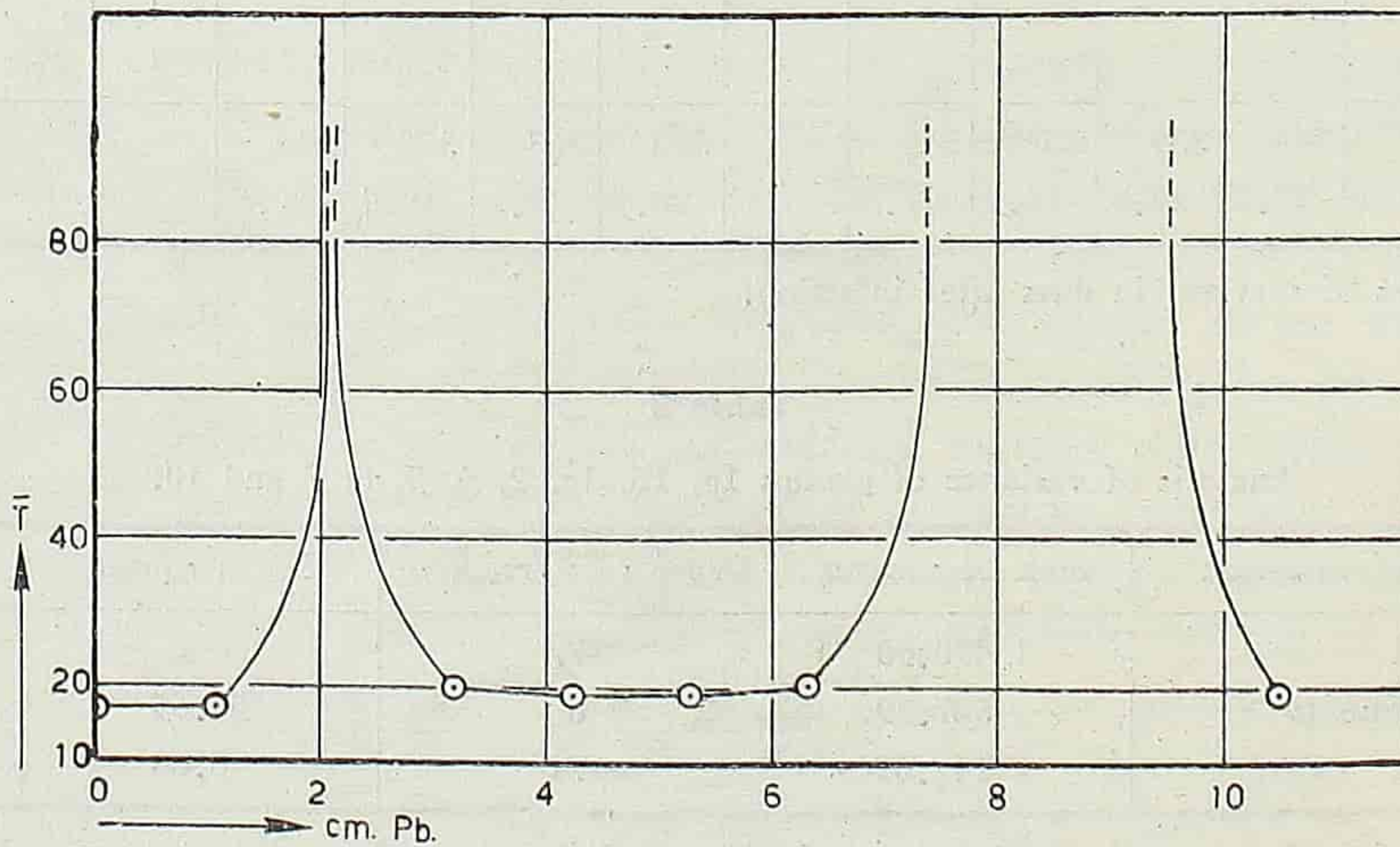


Fig. 2 Mean times of survival of mice injected with 0.4 mg of tubercle bacilli exposed to cosmic radiation plotted against the thickness of lead screen. \bar{T} , mean time of survival in days.

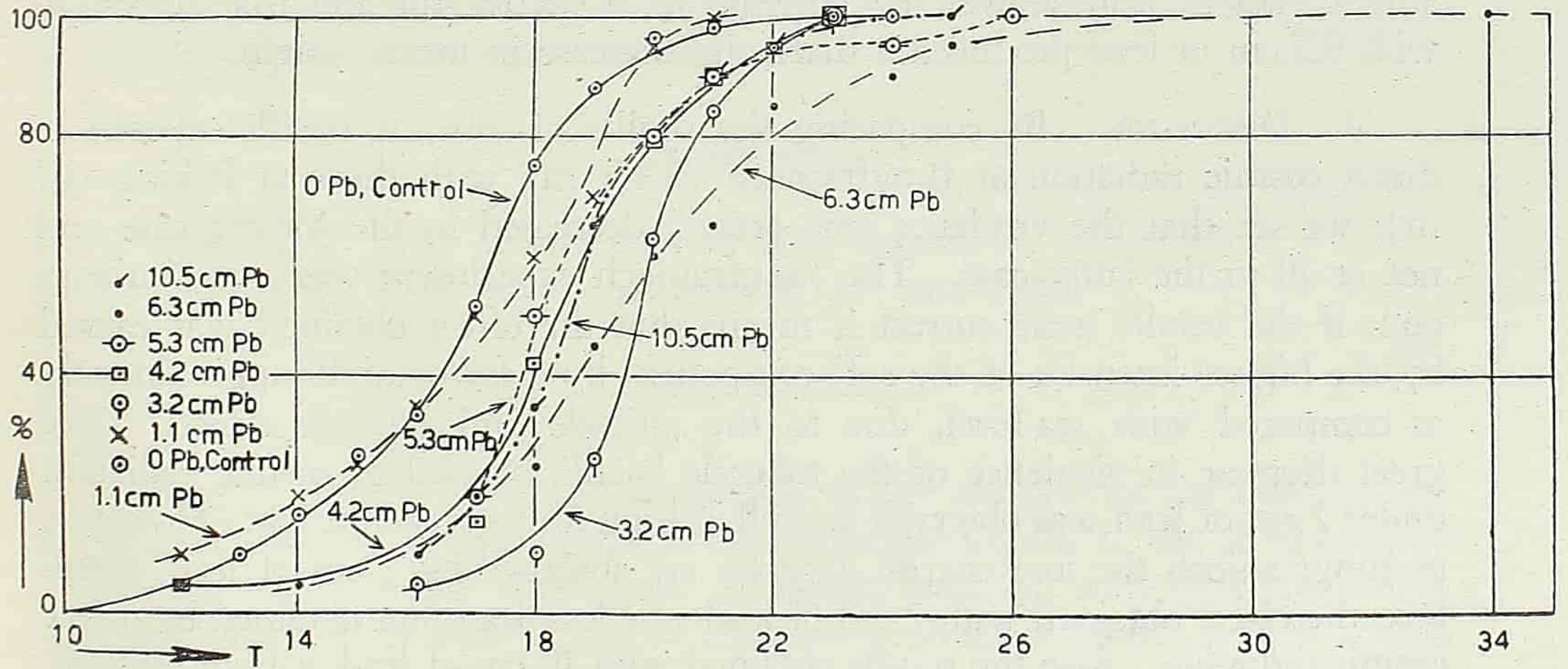
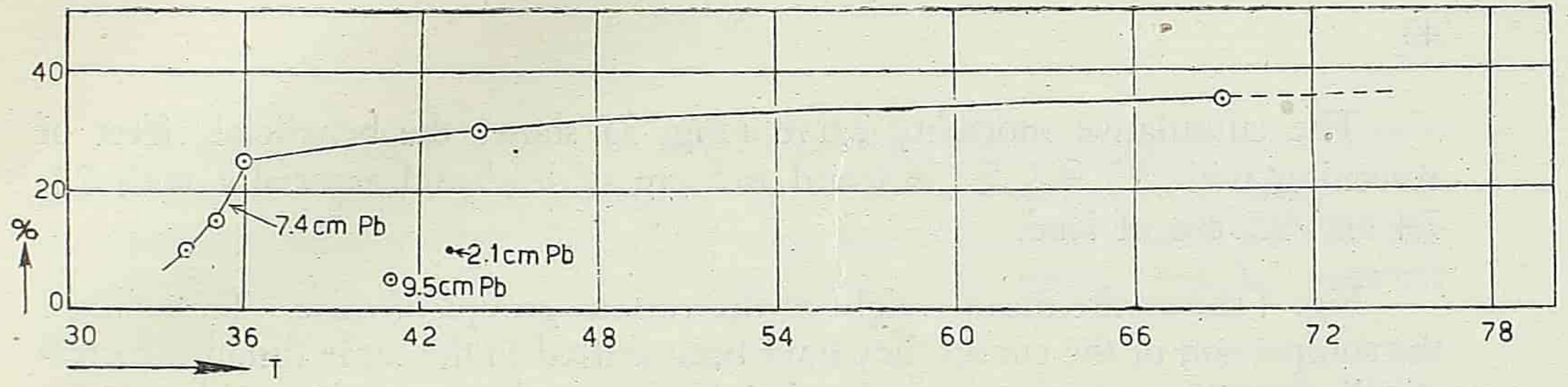


Fig. 3 Cumulative mortality curves of mice injected with 0.4 mg of tubercle bacilli exposed to cosmic radiation. T, time of survival in days.

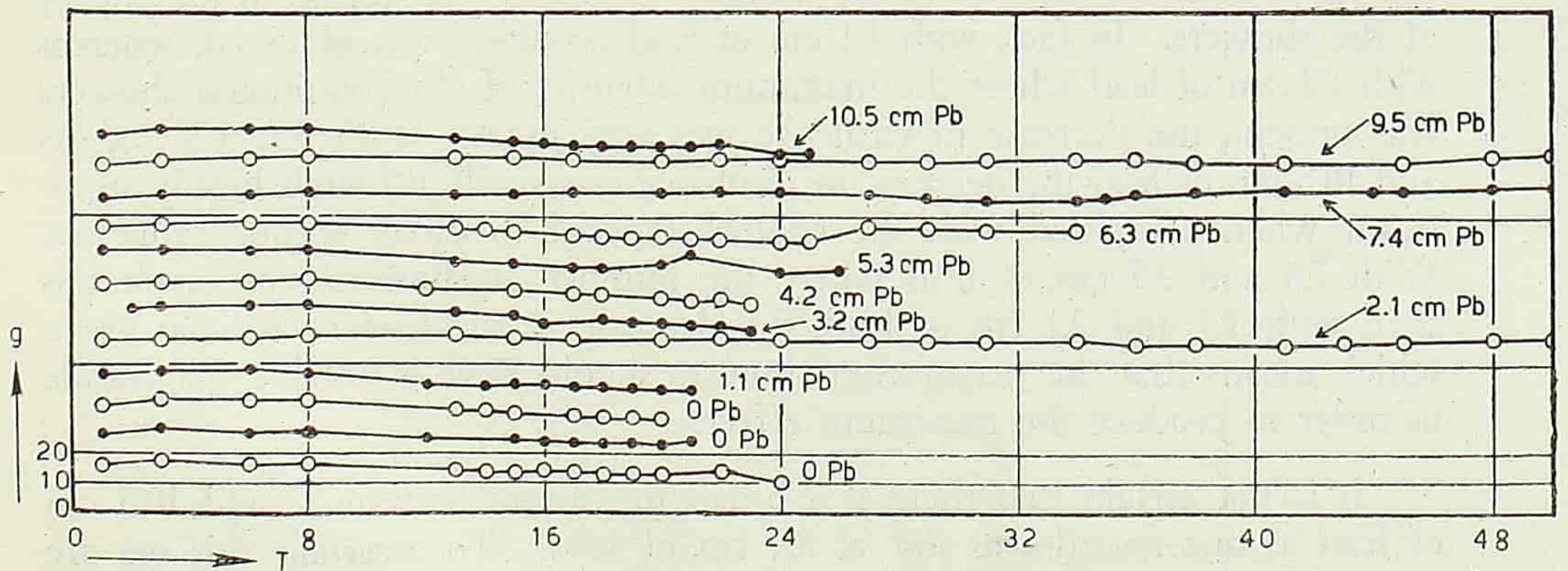
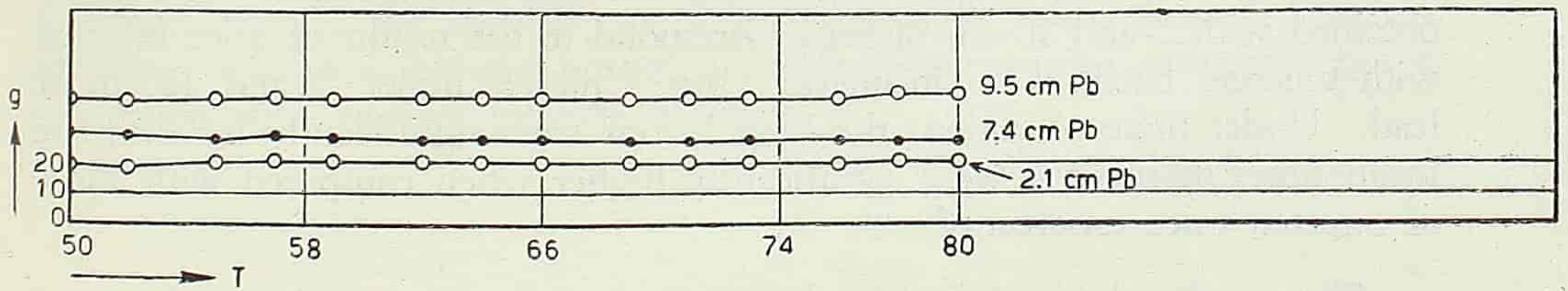


Fig. 4 Mean weight curves of mice injected with 0.4 mg of tubercle bacilli exposed to cosmic radiation. T, time in days, g, grams. To facilitate comparison the curves have been shifted to the same distance corresponding to 10 g on the vertical axis.

The cumulative mortality curve (Fig. 3) shows the beneficial effect of screening with 3.2, 4.2, 5.3, 6.3 and 10.5 cm of lead and especially with 2.1, 7.4 and 9.5 cm of lead.

Fig. 4 shows the mean weight of the various groups of mice. To facilitate the comparison of the curves they have been shifted to the same distance corresponding to 10 g on the vertical axis. It is seen that screening with 2.1, 7.4 and 9.5 cm of lead showed no decrease in mean weight and that screening with 9.5 cm of lead produced a markedly increase in mean weight.

3. DISCUSSION. By comparing the results of tubercle bacilli exposed to direct cosmic radiation at Jungfraujoch (3,457 m) with those at Peking (63 m), we see that the virulence was greatly decreased in the former case and not at all in the latter case. The Jungfraujoch experiment was a preliminary one; if the results were correct it means that the effect obtained was caused by the higher intensity of the soft component by a factor of 10 approximately as compared with sea-level, due to the altitude and latitude effects. The great decrease in virulence of the tubercle bacilli exposed to cosmic radiation under 2 cm of lead was observed as well at high altitude as at 63 m. However, at Jungfraujoch the low energy particles are absorbed by 2 cm of lead, therefore the effect obtained with 2 cm of lead was less than that obtained by direct cosmic radiation. Also the results obtained with 10 cm of lead at high altitude, where the tubercle bacilli were killed, correspond to the results obtained with 9.5 cm of lead at 63 m, where the virulence was decreased the most. The results obtained with 2 and 10 cm of lead correspond to the results of mice infected with tubercle bacilli^[1] or influenza virus^[2] placed under 2 and 10 cm of lead. Under these conditions the lung lesions were significantly less and the mean times of survival were significantly higher when compared with those of infected mice unscreened.

The results obtained in Fig. 2 suggest that the decrease in virulence of the tubercle bacilli was due to the number (intensity) as well as to the energy of the showers. In fact, with 1.1 cm of lead no effect was obtained, whereas with 2.1 cm of lead where the maximum intensity of electron-photon showers was present, the decrease in virulence was very great. With 3.2, 4.2, 5.3, 6.3 and 10.5 cm of lead the decrease in virulence was small although highly significant when compared with the control exposed to direct cosmic radiation. With 7.4 and 9.5 cm of lead where the number of showers was much less than with 1.1 and 2.1 cm of lead, the decrease in virulence was very great, which means that the penetrating showers should have a suitable magnitude in order to produce the maximum effect.

It is not certain that there is a broad maximum between 7 and 10.5 cm of lead as one record was lost at 8.4 cm of lead. To ascertain this we are now repeating the experiment with 4.8, 5.8, 6.9, 7.9, 9.0, 10.0, 11.1 and 12.1 cm of lead.

As stated above 45 mice out of 55 mice infected from groups 3, 8 and 9 are still alive 80 days after infection. In order to know if these mice show an immunity against tuberculosis, they were injected intravenously with 0.4 mg of tubercle bacilli together with 60 new mice. The results will be reported in a separate communication.

I am indebted to Professor W. Y. Chang for discussions on cosmic radiation. Also to Mrs. C. S. Fang, Messrs. Y. M. Liu and P. S. Yen for assistance in the cosmic radiation experiments.

REFERENCES

- [1] Ong, S. G. 1958 *Science Record*, New Ser. **II**, 9, 289—296.
- [2] Ong, S. G. 1958 *ibid.*, New Ser. **II**, 11, 364—372.

Added in proof: Since the submission of the manuscript for publication, i.e. 48 days after the injection with virulent tubercle bacilli, 51 out of 60 control mice were killed, while with those previously injected with tubercle bacilli screened with 3.2, 7.4 and 9.5 cm of lead, the number of deaths was 4, 5 and 1 respectively.

Thus it becomes obvious that the tubercle bacilli exposed to cosmic radiation with 3.2, 7.4 and 9.5 cm of lead screen not only showed a strong attenuated virulence, but also possessed a strong immunizing property against reinfection with virulent tubercle bacilli.

The author

SCIENCE RECORD

New Ser. Vol. III, No. 1, 1959

GEOLOGY

SOME PALAEOMAGNETIC INVESTIGATIONS ON CHINESE ROCKS*

CHANG WEN-YOU (张文佑)**

(Institute of Geology, Academia Sinica)

A. E. M. NAIRN†

(Department of Physics, King's College,
University, Durham, England)

Previous palaeomagnetic investigations^[1] on European and North American rocks agree in suggesting that those areas were so positioned that the pole appeared to lie on or near the Chinese mainland from Palaeozoic to late Mesozoic times. If the geology of China is examined for those same periods the climate indicated is more equatorial than polar^[2]. These two apparently contradictory facts make the palaeomagnetic study of Chinese rocks particularly interesting, and account for the publication of the results of the first collection from China despite the small sample size.

The collection was comprised of some eleven samples, of which eight were of the Tertiary Kansu Series collected at three sites in Kansu, while the remaining three were of red Middle Silurian siltstones from the southern part of Yümen, Kansu Province. The Tertiary rocks unfortunately were magnetically unstable, being characterised by low intensities of magnetization and scattered results. The measurements on the Silurian rocks yielded a more consistent pattern (Fig. 1).

The mean declination was N 66.4°W, mean inclination +55.3° with a circle of confidence of 8.5° calculated from 17 measured discs. The mean intensity of magnetization was $(8.8 \pm 3.8) \times 10^{-6}$ e.m.u./cm.³

The position of the ancient pole was 168°W, 49°S or 22°E, 49°N which compares with the Silurian pole from North America of 138°E, 19°N and by extrapolation an estimated position of a European pole in 165°E, 22°N. If this Chinese result is confirmed by further collections the following implication, first suggested by Nairn^[3] as a result of comparing Permian palaeoclimatic and palaeomagnetic data would seem to be valid, namely, that differential movement occurred between Europe and North America and Eastern Asia. This is a significant addition to the Continental Drift theory, for it implies that at the time when Gondwanaland was a single unit, China at least was not part of the Laurasian continent. Further investigation of this possibility is at present in progress.

*Received Dec. 3, 1958.

**Member of Academia Sinica.

†Field work was done by Chang Wen-you and laboratory work by A. E. M. Nairn.

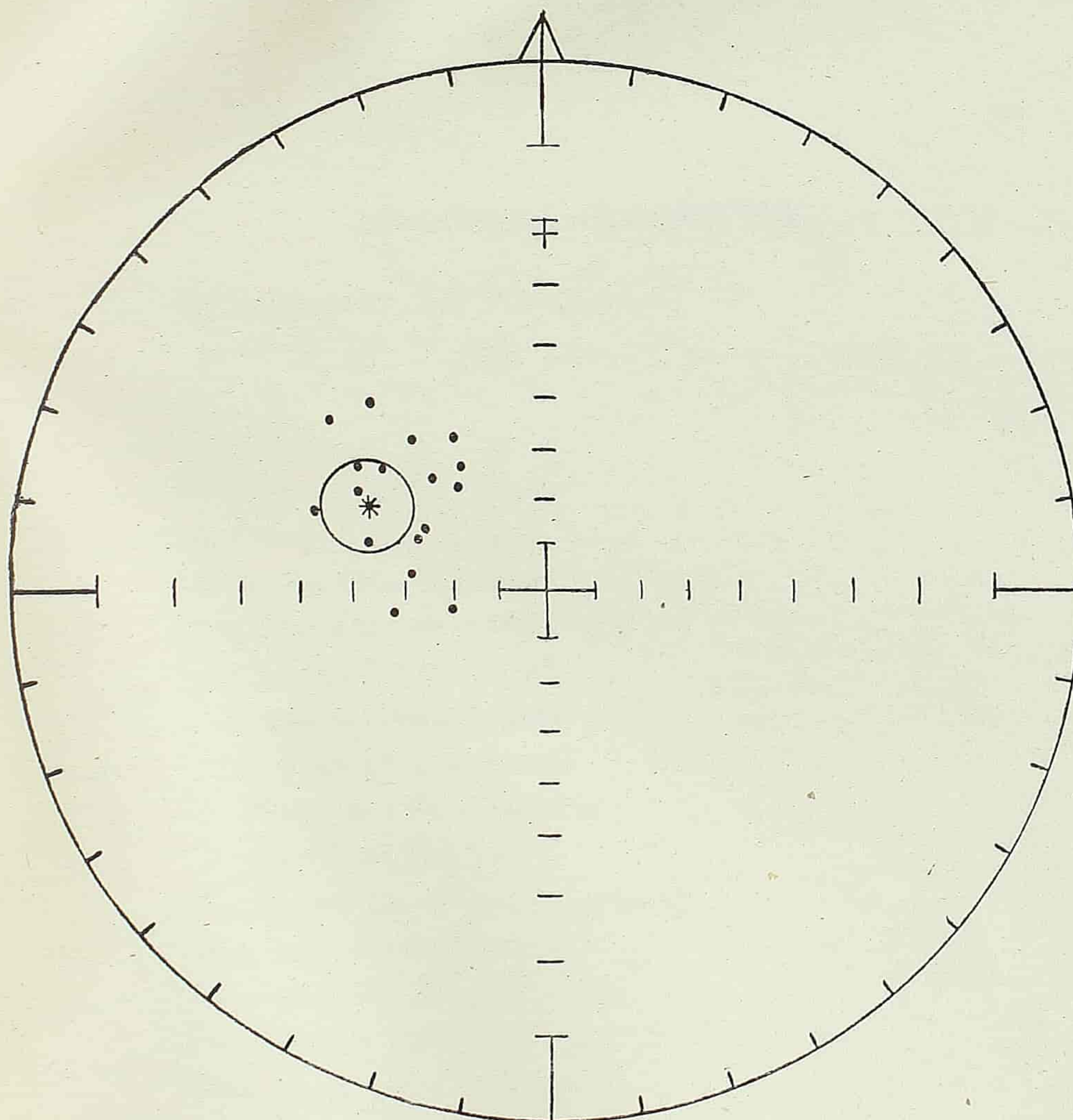


Fig. 1

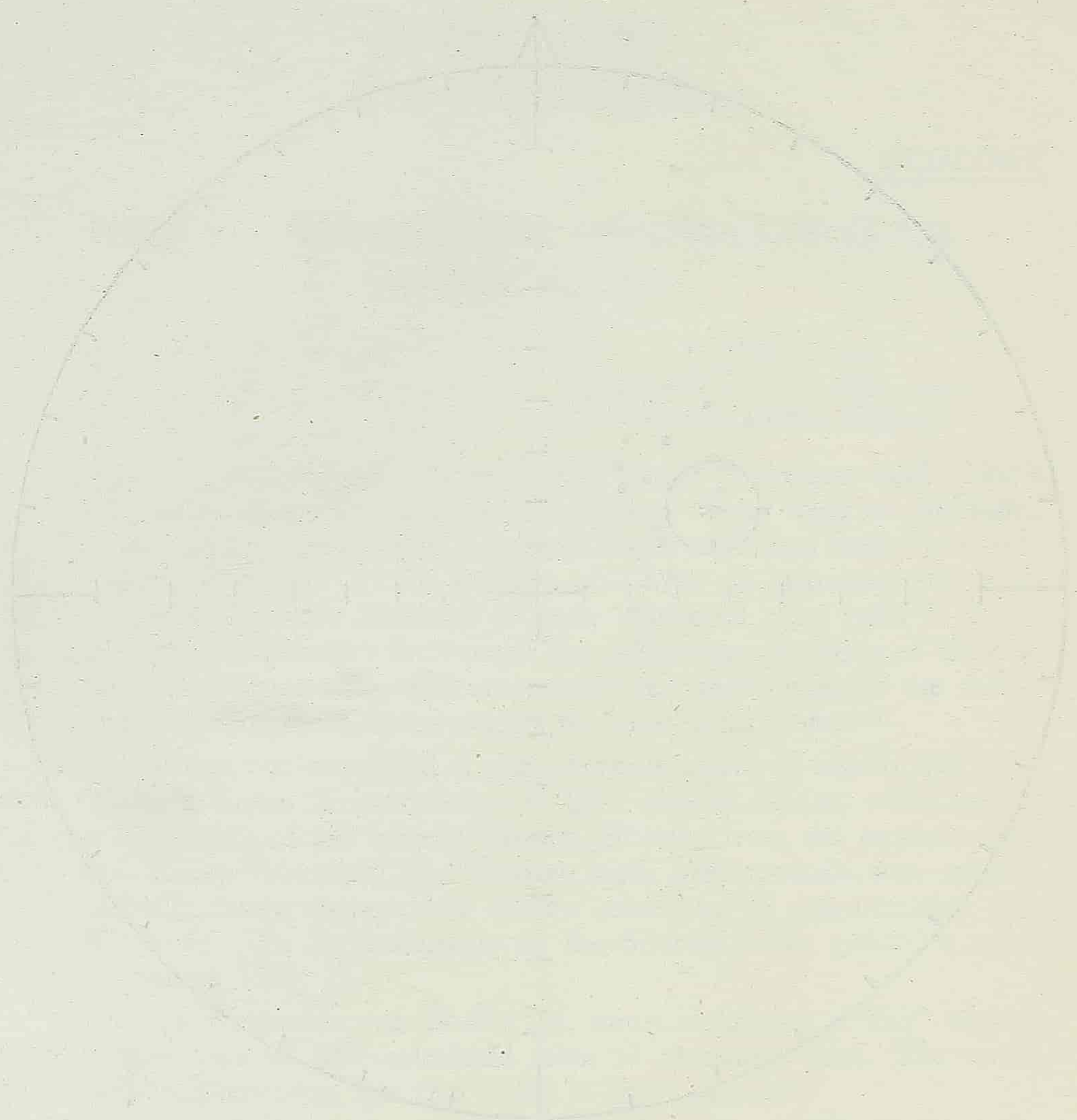
Stereographic projection

- N pole pointing down.
- ⊥ Theoretical dipole field of the site.
- * Mean direction of magnetization with the circle of confidence also drawn.

REFERENCES

- [1] Creer, K. M., Irving, E. and Runcorn, S. K. 1957 *Phil. Trans. Roy. Soc. A.*, **250**, 144.
- [2] Lee, J. S. 1939 *The Geology of China*, Murby, London.
- [3] Nairn, A. E. M. 1957 *Bull. Soc. Geol. France*, **7**, 721.





Faint, illegible text located below the circular diagram, possibly a title or descriptive notes.

EDITORIAL COMMITTEE

Bei Shi-zhang (S. Pai, Vice-Chairman)
Fu Cheng-yi (C. Y. Fu)
Fu Ying (Ying Fu)
Guo Yong-huai (Yung-huai Kuo)
Huang Wen-xi (Huang Wen-hsi)
Liu Chong-le (Liu Chung-lo)
Ma Da-you (Maa Dah-you)
Meng Xian-min (Meng Hsien-min)
Qian Xue-sen (H. S. Tsien)
Wang Zhu-xi (Wang Jwu-shi)
Wu Wen-jun (Wu Wen-tsün)
Wu Zhong-hua (Wu Chung-hua)
Ye Du-pei (Chu-thay Yap)
Yun Zi-qiang (T. C. Yun, Chairman)
Zhang Jing-yue (C. Y. Chang)
Zhang Qing-lian (Chang Tsing-lien)
Zhang Wen-yu (Wen Yu Chang, Vice-Chairman)
Zhang Xi-jun (H. C. Chang)

SCIENCE RECORD

New Series: Vol. III, No. 1

Published by Science Press

國外發行者： 國際書店

Sales Agent:

Guozi Shudian, 38 Suchou Hutung, Peking.

Гөцзй Шудянь, КНР, Пекин, Сучжоухутун 38.

Printers: Academia Sinica Printers, Peking, China.

January, 1959 Price: ¥ 1.40

本刊代號： 2—517