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AD-A141 485

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 3	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PRESSURE-DEPENDENCE OF GLASS TRANSITION TEMPERATURE OF ELASTOMERIC GLASSES		5. TYPE OF REPORT & PERIOD COVERED Technical Report-Interim
6. AUTHOR(s) K. D. Pae, C.-L. Tang, and E.-S. Shin		7. PERFORMING ORG. REPORT NUMBER
8. PERFORMING ORGANIZATION NAME AND ADDRESS High Pressure Materials Research Laboratory Rutgers University P.O. Box 909, Piscataway, NJ 08854		9. CONTRACT OR GRANT NUMBER(s) N00014-82-K-0608
9. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 092-022X
11. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE May 1, 1984
		13. NUMBER OF PAGES 34
		14. SECURITY CLASS. (of this report) Unclassified
		15. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. Reproduction in whole or in part is permitted for any purpose of the United States Government.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) High pressure, dielectric, DTA, elastomer, α -transition, T_g , 3,3-Bis(azidomethyl) oxetane(BAMO), tetrahydrofuran(THF)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Pressure dependence of the glass transition temperature (T_g) of two elastomers, Solithane 113 and 3,3-Bis(azidomethyl)oxetane/tetrahydrofuran (BAMO/THF) has been determined, employing high pressure differential thermal analysis (HP-DTA) and dielectric techniques, up to 8.5 Kbar. The glasses of the elastomers were named the specific (or P_f -glass) or the general glass depending on how the glasses were formed. A P_f -glass was formed by lowering temperature under a constant pressure		

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20. ABSTRACT (continued)

(P_i) and the pressure dependency of the P_i - glass was determined after changing pressure only in the glassy state. The general glass consists of a series of specific glasses but the T_g is determined only at pressures under which the glass is formed. The T_g for both glasses increased with increasing pressure. However, the T_g for the P_i - glass appears to level off at very high pressures while the T_g does not level off for the general glass. Thermodynamic analysis was made to show that for many general glasses including Solithane, $n=1$ in $dT_g/dp = \alpha B / (1+n) \Delta \alpha$. It is also shown that variation in several parameters in the Gibbs and DiMarzio theory can be used effectively to predict the observed experimental results.

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 $T_g = \text{dependent on } p$



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SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

OFFICE OF NAVAL RESEARCH
Contract N00014-82-K-0608
Task No. NR 092-022X

TECHNICAL REPORT NO. 3

PRESSURE-DEPENDENCE OF GLASS TRANSITION TEMPERATURE
OF ELASTOMERIC GLASSES

by

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Prepared for Publication
in
Journal of Applied Physics

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May 1, 1984

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PRESSURE-DEPENDENCE OF GLASS TRANSITION TEMPERATURE
OF ELASTOMERIC GLASSES

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ABSTRACT

Pressure dependence of the glass transition temperature (T_g) of two elastomers, Solithane 113 and 3,3-Bis(azidomethyl)oxetane/tetrahydrofuran (BAMO/THF) has been determined, employing high pressure differential thermal analysis (HP-DTA) and dielectric techniques, up to 8.5 Kbar. The glasses of the elastomers were named the specific (or P_i - glass) or the general glass depending on how the glasses were formed. A P_i - glass was formed by lowering temperature under a constant pressure (P_i) and the pressure dependency of the P_i - glass was determined after changing pressure only in the glassy state. The general glass consists of a series of specific glasses but the T_g is determined only at pressures under which the glass is formed. The T_g for both glasses increased with increasing pressure. However, the T_g for the P_i - glass appears to level off at very high pressures while the T_g does not level off for the general glass. Thermodynamic analysis was made to show that for many general glasses including Solithane, $n = 1$ in $dT_g/dp = \Delta\beta/(1+n)\Delta\alpha$. It is also shown that variation in several parameters in the Gibbs and DiMarzio theory can be used effectively to predict the observed experimental results.

I. INTRODUCTION

Amorphous polymers may exist in the liquid (rubber) or glass state, depending on the temperature T , pressure P , and the time scale of observation t . When the t is shorter than relaxation time τ , which is the time required for the cooperative rearrangement of the segments of the polymer chains to maintain an equilibrium, the system undergoes a glass transition. When the glass is formed, the mobility of the backbone of the polymer chain is inhibited and the existing molecular configuration is essentially frozen in. Hydrostatic pressure has been shown to affect the glass transition and various theories have been developed to describe the phenomenon.⁽¹⁻⁸⁾

In this study, an investigation is made to determine the pressure dependency of the glass transition temperature (T_g) of the elastomeric glasses which were originally formed at different pressure conditions. The glass formed by lowering temperature under a constant pressure P_i is called a specific glass with a label " P_i -glass" and the glass consisted of a series of specific glassed but T_g is determined only at the pressures under which glass is formed. Previous authors, Simha⁽⁹⁾, Motosuke⁽¹⁰⁾, Goldstein⁽¹¹⁾ and others, have also distinguished the two types of glasses. The T_g of two elastomers, Solithane 113 and BAM/THF, were determined by high pressure differential thermal analysis (HP-DTA) and dielectric techniques. It was found that the T_g of P_i -glasses of both elastomers increased with increasing pressure but appears to level off at very high pressures. Moreover, the pressure, at which the leveling off occurred, depended upon how the glass was originally formed while the general glass appear not to level off. Previous studies on poly(vinyl chloride),^(12,13) poly(methyl acrylate)⁽¹²⁾, and poly(vinyl acetate)⁽¹⁴⁾ also showed the

similar result. It was also observed that, for P_f -glasses of many polymers including Solithane, $dT_g/dp = \Delta\beta/\Delta\alpha$ does not hold, but rather $dT_g/dp = \Delta\beta/2\Delta\alpha$ hold.

Analyses were made to illustrate the observed phenomena by means of thermodynamic considerations and also modifying the Gibbs and DiMarzio theory⁽⁶⁾, which is based on Statistical Mechanics.

PART I. THERMODYNAMIC CONSIDERATIONS

(1) Internal parameter - iso ξ plane

The arrangement and distribution of the molecules are formally characterized by a set of internal order parameters $\{\xi_i\}$.^(2,3) For liquids, each ξ_i is a function of T, P , i.e. $\xi_i = \bar{\xi}_i(T, P)$ when thermodynamic equilibrium is attained. It will be assumed that each ξ_i is frozen in at T_g and remains constant at normal cooling rate below T_g .

Thus one gets

$$V_L = V_L[P, T, \{\bar{\xi}_i(T, P)\}] = V_L(P, T) \quad (1)$$

$$V_G = V_G[P, T, \{\bar{\xi}_i(P, T_0)\}] = V_G(P, T, \{\xi_i\}) \quad (2)$$

where ξ_i is constant and takes the value from the function $\bar{\xi}_i(T, P)$ at pressure equal to P , under which the glass is formed at $T_g = T_0$, and temperature equal to T_0 . From Eq. (2)

$$dV_G = \left. \frac{\partial V_G}{\partial T} \right]_{P, \{\xi_i\}} dT + \left. \frac{\partial V_G}{\partial P} \right]_{T, \{\xi_i\}} dP + \left. \frac{\partial V_G}{\partial \xi_i} \right]_{P, T, \{\xi_j\}/\xi_i} d\xi_i \quad (3)$$

For simplicity, let $i = 1$. Along the transition line it becomes

$$dV_G(T, P, \xi) = dV_L(P, T) = dV \quad (4)$$

In an equi- ϵ process, $\epsilon = \text{const.}$ and thus $d\epsilon = 0$. We then obtain the differential equation of the transition line in PVT space as

$$\frac{dP}{\Delta\alpha} = \frac{dP}{\Delta\beta} = \frac{dV}{(\beta_L \alpha_G - \beta_G \alpha_L)V} \quad (5)$$

where $\Delta\alpha$ and $\Delta\beta$ are the difference thermal and compressibilities in the liquid and the glass, respectively, at the transition line and $\beta_L \alpha_G - \beta_G \alpha_L$ should always be negative.

In essence, Eq. (5) provides a family of curves, that turn out to be parallel lines in the region where β_L , β_G , α_L , α_G are constants, each curve being the intersecting line of the liquid surface with an individual glass surface. Every glass surface (G-surface) has a parameter ξ , or every G-surface is a iso- ξ surface (Fig. 1).

In the same manner, we can construct the iso- ξ planes in the SPT (entropy-pressure-temperature) space. Since along the transition line in the STP space, $dS_L = dS_G$, we can write

$$dS = -V\alpha_{p,\xi} dP = \frac{C_{p,\xi}}{T} dT = -V\alpha_L dP + \frac{C_{pL}}{T} dT$$

The equation of iso- ξ transition line is given

$$\frac{dP}{\Delta C_p} = \frac{dP}{VT\Delta\alpha} = \frac{dS}{(\alpha_L C_{pG} - \alpha_G C_{pL})V} \quad (6)$$

(2) General Glass

If, in an experiment, pressure is changed from one level (P_1) to another (P_2) in the liquid state, ξ will vary with pressure (i.e. ξ associated with P , cooling rate, etc.) as the transition line is crossed and we have

$$dV_G = V_{\alpha G} dT - V_{\beta G} dp + \left. \frac{\partial V}{\partial \xi} \right]_{P,T} d\xi \quad (7)$$

where the last term refers to the volume change due to the variation of ξ .

It can be schematically shown from Fig. 2 that

$$\Delta V = \left. \frac{\partial V}{\partial \xi} \right]_{P,T} (\xi_2 - \xi_1) \cong V_{\alpha L} \Delta T_0 - V_{\alpha G} \Delta T_0$$

An increase in the degree of order shall, by definition,⁽²⁾ be proportional to the increase of the parameter ξ (it corresponds to a decrease of entropy in statistico-mechanical treatment, as shown later), such that $d\xi = (\xi_2 - \xi_1)$ is mapped with $-dT_0 = (T_{02} - T_{01})$. Then from Eq. (7) we have

$$dV_G = V_{\alpha G} dT - V_{\beta G} dP - V_{\Delta \alpha} dT_0$$

Therefore, along the transition line, the following equation is established

$$dV = \alpha_L dT - \beta_L dP = \alpha_G dT - \beta_G dP - \Delta \alpha dT_0 \quad (8)$$

If dT_0 is considered as n multiple of dT , Eq. (8) reduces to

$$\left. \frac{dP}{dT} \right]_g = \frac{\Delta \beta}{(1+n)\Delta \alpha} \quad (9)$$

The n is thus an adjustable parameter and can be evaluated from experiments. For many polymeric materials, such as polyvinyl acetate,⁽¹⁵⁾ polyortho-methylstyrene,⁽⁹⁾ polystyrene,^(9,16) polyurethane elastomer (solithane),^(17,18) n assumes the value of 1, i.e.,

$$\frac{dT_g}{dP} = \frac{\Delta\beta}{2\Delta\alpha} \quad (10)$$

In fact, Eq. (10) is the projection of the transition line in PVT space, on T-P plane which is shown by dash-dot line in Fig. 1 of which the equation is

$$\frac{dT}{\Delta\beta} = \frac{dP}{2\Delta\alpha} = \frac{dV}{V(\beta_L\alpha_G - \alpha_L\beta_G - \Delta\alpha\beta_L)} \quad (11)$$

(3) Specific Glass

For specific glasses, or on iso- ϵ planes, the expression

$$\frac{dT_g}{dP}_\epsilon = \frac{\Delta\beta}{\Delta\alpha}$$

holds, although it may not be a true second order transition.

Isotherms can be constructed for specific glasses and these may be used conceptually to determine compressibilities. However, perturbation method⁽²⁾ is usually adopted for the determination of β in practice. When the isotherms $V(P)$ of a glass (ϵ_1) is schematically drawn in Figs. 3 and 4, the curves AOB and A'O'B' represent the isotherms of T_1 and T_2 , respectively, where $T_2 > T_1$. If a line $P = \text{const.}$ is drawn to cut these

two isotherms, it can be shown that

$$\alpha_G(\alpha\xi, p) = \lim_{\Delta T = (T_2 - T_1) \rightarrow 0} \frac{\Delta V(\overline{Q}^1\overline{Q})}{\Delta T}$$

However, when isotherms are produced with various temperature levels chosen in the liquid state (at the base of general glass), a very confusing situation may arise with respect to thermal expansivity. In such cases, the change of temperature from T_1 to T_2 is accompanied by change of ξ_1 to ξ_2 , therefore, $\Delta V(\overline{MQ})$ should be different from that obtained on a ξ_1 plane, giving rise to an increase or a decrease in thermal expansion.

For isobaric (but not iso- ξ) process (8) reduces to

$$dV_G = \alpha_G dT - \Delta\alpha dT_0 = [\alpha_G - n(\Delta\alpha)]dT$$

and the thermal expansion coefficient α_p defined in this way will be

$$\alpha_p = \frac{dV_G}{dT} = \alpha_G - n(\Delta\alpha)$$

This means that the expansion coefficient α_G obtained by direct isobaric measurement (iso- ξ process) is greater than the corresponding expansion coefficient derived by cuts through $V(P)$ -isotherms at constant pressure and was studied extensively by Rehave⁽²⁾ for polystyrene. Moreover, when n is large enough, α_p may appear to be negative, the so-called apparent negative thermal expansion is reported by O'Reilly for polyvinyl acetate.⁽¹⁵⁾

PART II. STATISTICAL MECHANICS CONSIDERATIONS

(1) Materials and Techniques

The elastomer investigated is 50/50 mol % of 3,3-Bis (azidomethyl)oxetane/tetrahydrofuran (BAMO/THF), whose glass transition temperature at atmospheric pressure is -54°C . The molecular weight is approximately 2000-4000 between and the cross-links and the density 1.18 g/cc.⁽²⁰⁾ Solithane was described in an earlier papers.^(17,18)

Dielectric measurement and High Pressure DTA and techniques were employed in determining the T_g .

(2) Determination of T_g for Specific Glasses

To form a specific glass, or P_i -glass, the elastomers were cooled at a constant pressure P_i to below the T_g at that pressure. The pressure was then applied to the P_i -glass up to the desired intensity P in the glassy state, after which the temperature was raised isobarically through the glass transition. Thus, the P_i -glass can be considered a pseudoequilibrium glass at P_i , but not at P . The general glass, as we termed, is consisted of a series of P_i (different i)-glasses.

(3) Experimental Results

In Fig. 5, the temperature of α -peak maximum (T_α) is plotted against pressure for the general glass of BAMO/THF at three different frequencies .3, 3, and 30 Hz. The T_α of the elastomer increased monotonically with increasing pressure up to 6 Kbars. The T_α was also measured for the glasses formed at three different pressures as shown in Fig. 6. The three specific glasses formed at 1 atm., 1000 atm., and 3100 atm., the T_α increased linearly up to 4000 atm., but they appear to level off at higher pressures and the leveling-off pressure increased with increasing glass formation pressure P_i . The T_α appears to be independent of the

glass formation pressure as long as the environmental pressure is below about 4000 atmospheres.

Figs. 7 and 8 show, respectively, the pressure dependence of T_g (or T_a) of Solithane 113 and BAMO/THF by HP-DTA method for the specific glass formed at atmospheric pressure. The former exhibits leveling off at about 7 Kbars which was not observed for the general glass^(18,19) and the latter shows a trend to rise again around 8.5 Kbar.

2.2 VARIATIONS OF PARAMETERS IN GIBBS AND DIMARZIO THEORY

(1) Fundamentals

The theory of Gibbs and DiMarzio^(4,6) is based on the configurational entropy of polymers by calculating its partition function. They used a lattice model in which n_x , each polymer molecules, occupy x lattice sites. The total number of lattice sites is $N_0 = xn_x + n_0$, in which n_0 is the number of unoccupied sites. Each site is associated with a unit cell of volume C . The total volume is then given by

$$V = CN_0 = (xn_x + n_0)C \quad (12)$$

When C is assumed constant, the volume of the system can vary with temperature and pressure as a result of configurational changes connected with the variations in the number of holes n_0 .

The total energy of the system is a sum of inter- and intra- molecular contributions.

$$E = \Phi + n_x \sum_i f_i E_i \quad (13)$$

The intermolecular energy $\bar{\Phi}$ is given by

$$\bar{\Phi} = z\alpha n_0 S_x / 2 \equiv E_h n_0 S_x$$

with

$$S_x = \frac{[(z-2)x+2]n_x}{[(z-2)x+2]n_x + zn_0} \quad (14)$$

where α is the energy of a segment-segment bond, z the coordination number of the lattice, and $E_h = z\alpha/2$, the hole energy.

Making use of the rotational isomer approximation, which should be the simplest case, the intramolecular energy is

$$n_x \sum_i f_i E_i = (x-3)n_x [f\epsilon_2 + (1-f)\epsilon_1]$$

where f is the fraction of flexed bonds, meaning the fraction of segments which are in a high energy conformation compared with the immediate neighbors in the chain. For the rotational isomer approximation, each segment is assumed to have only two conformational energies, namely Trans (ϵ_1) and Gauche (ϵ_2). Thus the states of the system can be characterized by specification of n_0 and f .

For the liquid state, the number of configuration of the system, $W(f, n_0)$, may be written as

$$W = \frac{N_0! z^{x n_x} \{ ([z-2]x+2]n_x + zn_0) / 2 \}! (z-1)^{n_x} (z-2)^{f(x-3)n_x} [(x-3)n_x]!}{n_0! [N_0 z / 2]! 2^{x n_x} (n_x!) [(1-f)(x-3)n_x]! [f(x-3)n_x]!} \quad (15)$$

The partition function γ and the Gibb's free energy G_1 are

$$\gamma = \sum_{f, n_0} W(f, n_0) \exp\left[-\frac{1}{kT} (PCN_0 + E\{n_0, f\})\right] \quad (16)$$

$$G_L(T, P) = -kT \ln \gamma \quad (17)$$

It can be shown⁽²¹⁾ that

$$f_{\max} = \frac{(z-2) \exp(-\Delta\epsilon/kT)}{1 + (z-2) \exp(-\Delta\epsilon/kT)} \quad (18)$$

and $(n_0)_{\max}$ is involved in an implicit equation

$$\ln[V_0^{(z/2-1)}/S_0^{z/2}] - \frac{1}{kT} E_h S_x^2 - \frac{PC}{kT} = 0 \quad (19)$$

where

$$S_0 = 1 - S_x, \quad V_0 = 1 - V_x \quad (20)$$

So far, the G_L can be computed as

$$G_L = E[f_{\max}, (n_0)_{\max}] + PV(n_0)_{\max} - kT \ln W[f_{\max}, (n_0)_{\max}] \quad (21)$$

(2) Transition Lines

The configurational entropy of the liquid state is

$$S_L = k \ln W$$

$$\begin{aligned} = & k n_x x \left\{ -\frac{V_0}{V_x} \ln S_0 + \frac{(z-2)}{2V_x} \ln \frac{V_0}{S_0} - \frac{\ln S_x}{x} + \frac{\ln([(z/2-1)x+1][z-1])}{x} \right. \\ & \left. + \left(\frac{x-3}{x}\right) (f \ln[(z-2)(1-f)/f] - \ln[1-f]) \right\} \end{aligned}$$

$$\begin{aligned}
&= kx n_x \left[\left(\frac{z-2}{2} \right) \ln \left(\frac{V_0}{S_0} \right) + \frac{n_0}{x n_x} \ln \left(\frac{V_0^{z/2-1}}{S_0^{z/2}} \right) + \frac{\ln \left\{ \left[(z-2)x + 2 + \frac{z n_0}{n_x} \right] (z-1)/2 \right\}}{x} \right] \\
&+ \left(\frac{x-3}{x} \right) \left\{ \ln \left[e^{-G/kT} + (z-2) e^{-\epsilon_2/kT} \right] + \frac{\left(\frac{G_1}{kT} \right) e^{-\epsilon_1/kT} + \left[\frac{(z-2)\epsilon_2}{kT} \right] e^{-\epsilon_2/kT}}{e^{-\epsilon_1/kT} + (z-2) e^{-\epsilon_2/kT}} \right\} \quad (22)
\end{aligned}$$

The equilibrium transition under infinitely slow cooling rate takes place when $S_L = 0$. However, S_L will take on some constant value for most experimental situations (Fig. 9).

Introducing dimensionless parameters as,

$$\frac{kT_2}{\Delta\epsilon} = T_e, \quad \frac{PC}{\Delta\epsilon} = P_e, \quad \frac{n_x}{n_0} = n, \quad \frac{\Delta\epsilon}{E_h} = E_e, \quad \frac{S_L}{kNa} = S \quad (23)$$

Using Eq. (23) Eqs. (14), (18), (19) and (22) are normalized and the curves of transition line which are now T_e vs. P_e curves, are produced. T_e vs. P_e curves for polystyrene with $z = 4$, $x = 1640$, $E_e = 0.945$,⁽⁴⁾ curves with $S_L = 0, 0.5, 1.0, 1.5, 2.0$ and 2.5 [J/K mole seg.] are plotted in Fig. 10. As can be seen T_e increases with P_e , then levels off to a plateau, but goes up again at higher pressures. Since the increase of f shifts the trans-gauche population to higher energy level on the whole, thereby raising the T_e , it can expect from Eq. (18) that $T \rightarrow \infty$ when $f \rightarrow z-2/z-1$. Moreover, it can be seen from these curves that higher the entropy, higher the T_g and dT_g/dp at lower pressure range.

Fig. 11 shows T_e vs. P_e curves with $S = 0$ but $E_e = 0.495, 0.945, 1.945$ and 9.995 . All the curves have the same shape but shift to the left as E_e decreases.

Fig. 12 shows the transition temperature T_g of polystyrene vs. pressure. Data points, ⁽²⁰⁾ converted to T_e and P_e , lie between two theoretical curves with $S = 0$, $E_e = 0.945$ and 1.945 . Allowing for a slight adjustment of flex energy $\Delta\epsilon$ for glasses formed at pressures from lower to higher, a better agreement between the experimental data and the theoretical predictions can be expected.

Fig. 13 shows the T_α of BAMO/THF vs. pressure (data of Fig. 6 converted to T_e and P_e) by using $\Delta\epsilon/k = 526^\circ\text{K}, 537^\circ\text{K}, 564^\circ\text{K}$ for glasses formed at 1 Atm, 1000 Atm and 3100 Atm respectively. Fig. 14 gives theoretical curves with $x = 5000$, $z = 3.85$ and $E_e = 1.145, 1.245, 1.365$, respectively. A good agreement is seen between Figs. 13 and 14, justifying the variation of $\Delta\epsilon$ for different pressure glasses.

ACKNOWLEDGMENTS

The authors wish to gratefully acknowledge the Propulsion and Energetics Program of Office of Naval Research (Contract N00014-82-K-0608, Task No. NR 092-576) for its financial support for this research study.

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FIGURE CAPTIONS

- Fig. 1 Schematic of PVT space.
- Fig. 2 Volume change ΔV due to the variation of ξ at constant P and T.
- Fig. 3 Projection of isothermal pressuring curves on a certain P-V plane.
- Fig. 4 Planes $T = \text{const.}$ cut the L-G surfaces on isothermal pressuring curves, $T_2 > T_1$.
- Fig. 5 Pressure vs. transition temperature (dielectric method) for 50/50 mol. % BAMO/THF. Points recorded for general glass at 0.3 Hz, 3 Hz and 30 Hz.
- Fig. 6 Pressure vs. transition temperature (dielectric method) for 50/50 mol. % BAMO/THF. Glass formed at atmospheric pressure (solid line), at 1100 atm. (broken line) and at 3100 atm. (dash-dot line).
- Fig. 7 Pressure vs. transition temperature (H.P.DTA) for Solithane 113. Glass formed at atmospheric pressure.
- Fig. 8 Pressure vs. transition temperature (H.P.DTA) for BAMO/THF (50/50). Glass formed at atmospheric pressure.
- Fig. 9 Schematic of STP space based on G.D. theory.
- Fig. 10 Theoretical curves of T_e vs. P_e for polystyrene with $S_L = 0, 0.5, 1.0, 1.5, 2.0, 2.5$ [J/K. Mole seg.].
- Fig. 11 Theoretical curves of T_e vs. P_e with $S = 0$ and $E_e = 0.495, 0.945, 1.945, 9.995$.
- Fig. 12 T_e vs. P_e for polystyrene. Solid and broken lines are theoretical curves calculated with $E_e = 0.945, 1.945$ and $S = 0$. Circles are the data according to Oels and Rehavé⁽¹⁶⁾ converted to T_e and P_e .
- Fig. 13 T_e vs. P_e for BAMO/THF (50/50), data of Fig. 6 converted to T_e and P_e .
- Fig. 14 Theoretical curves used to compare with the data of Fig. 13.

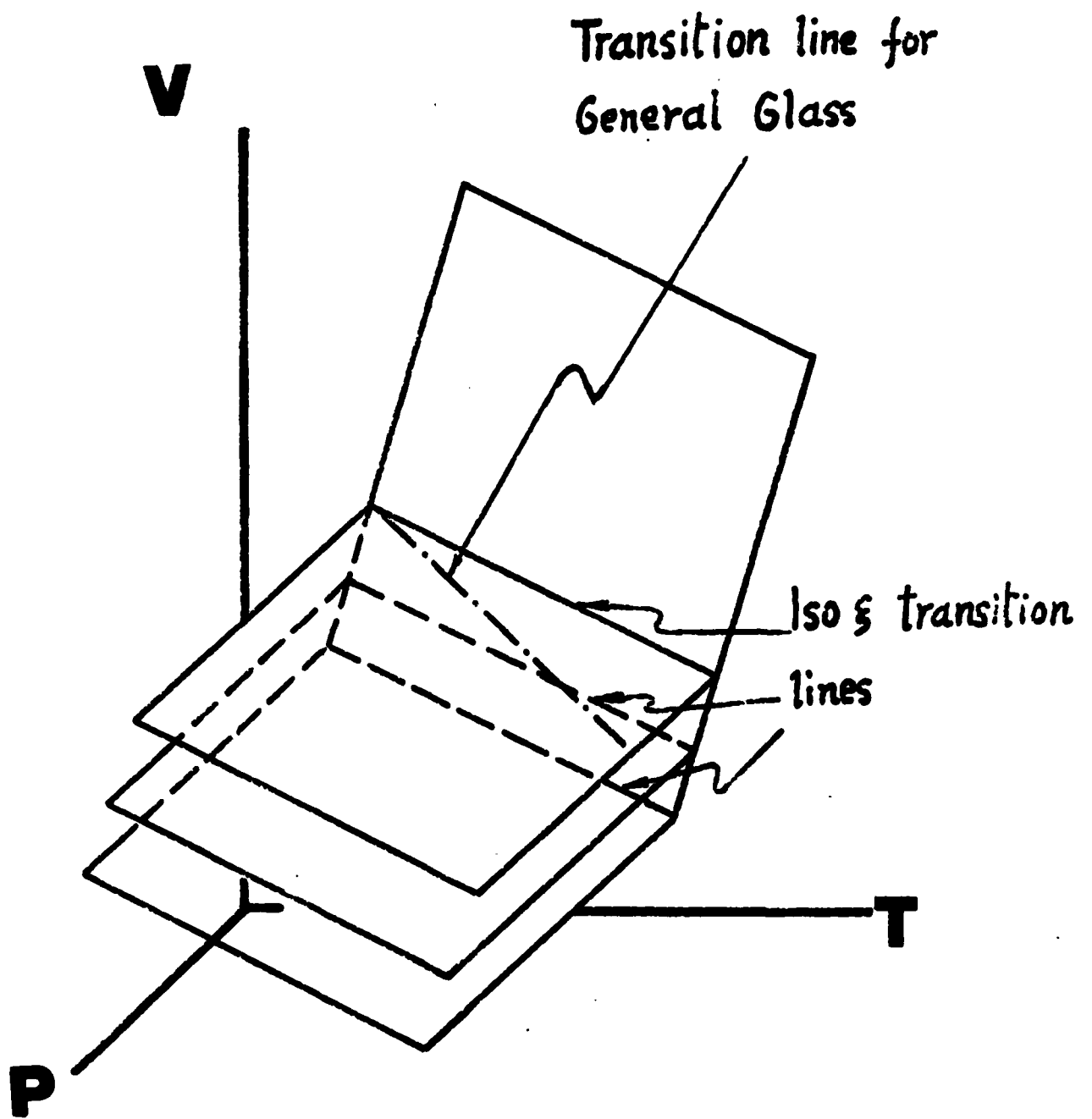


Fig. 1 Schematic of PVT space

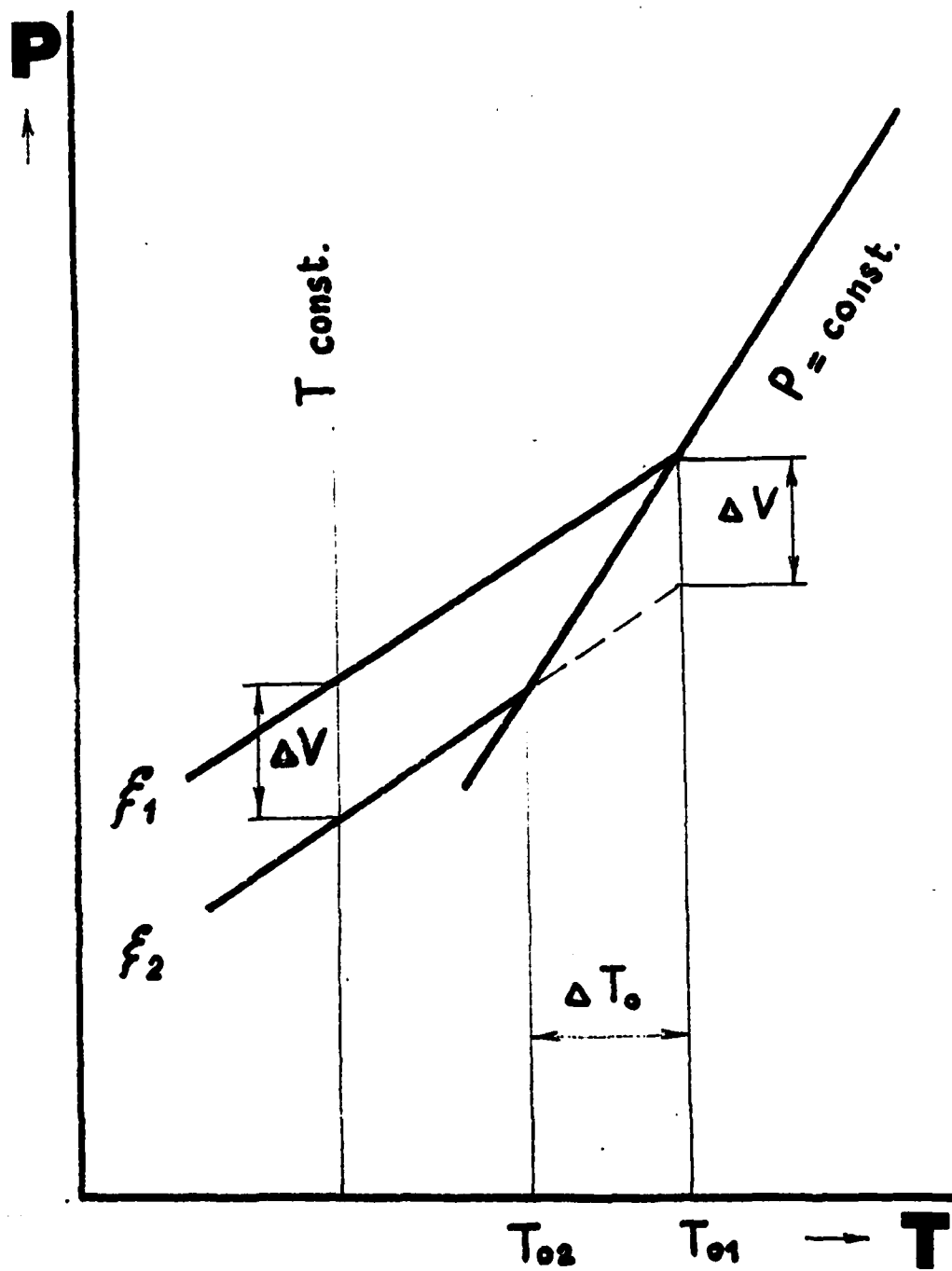


Fig. 2 Volume Change ΔV Due To The Variation Of f At Constant P and T.

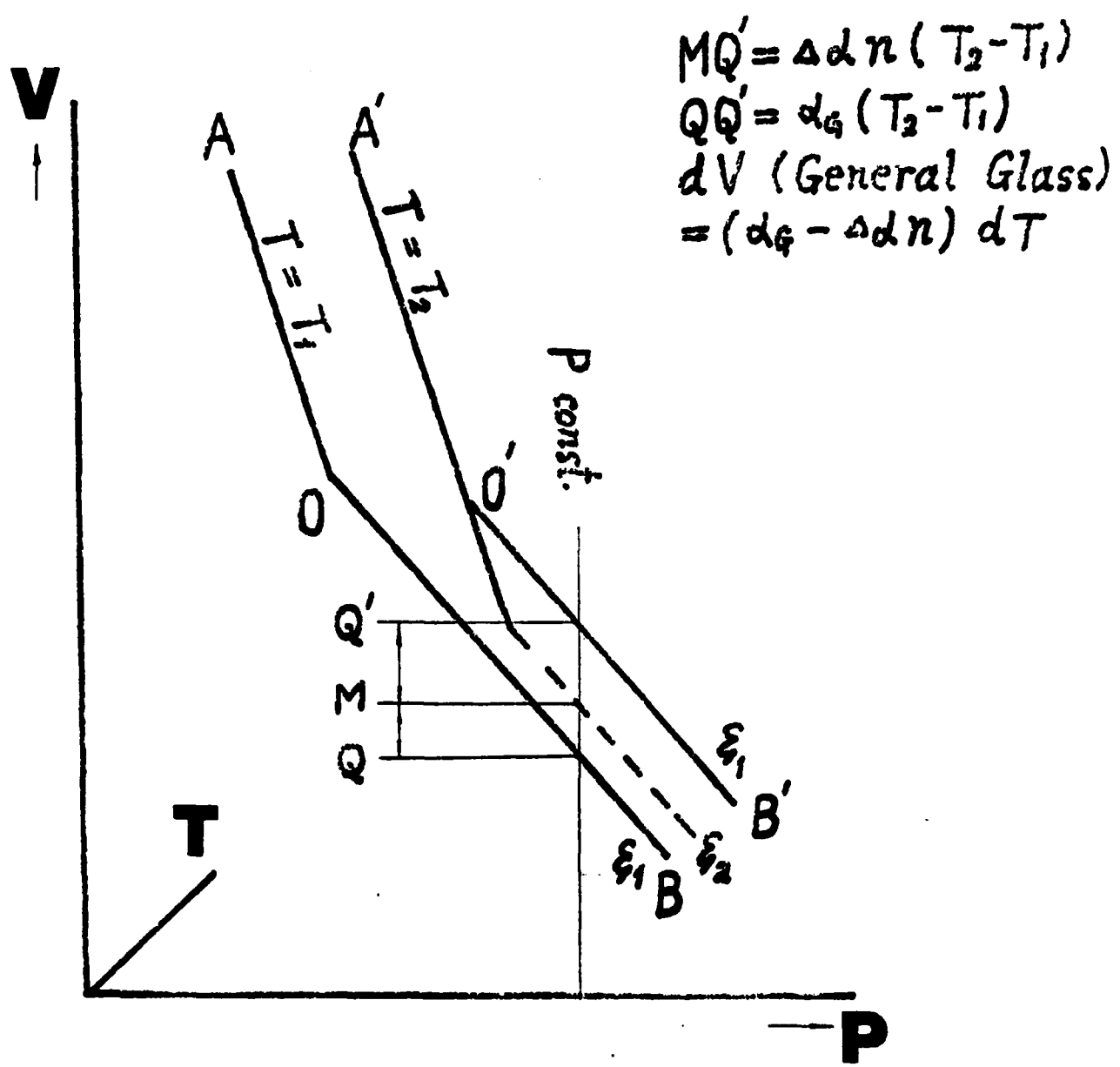


Fig. 3 Projection of isothermal
 pressuring curves on a certain
 P-V plane.

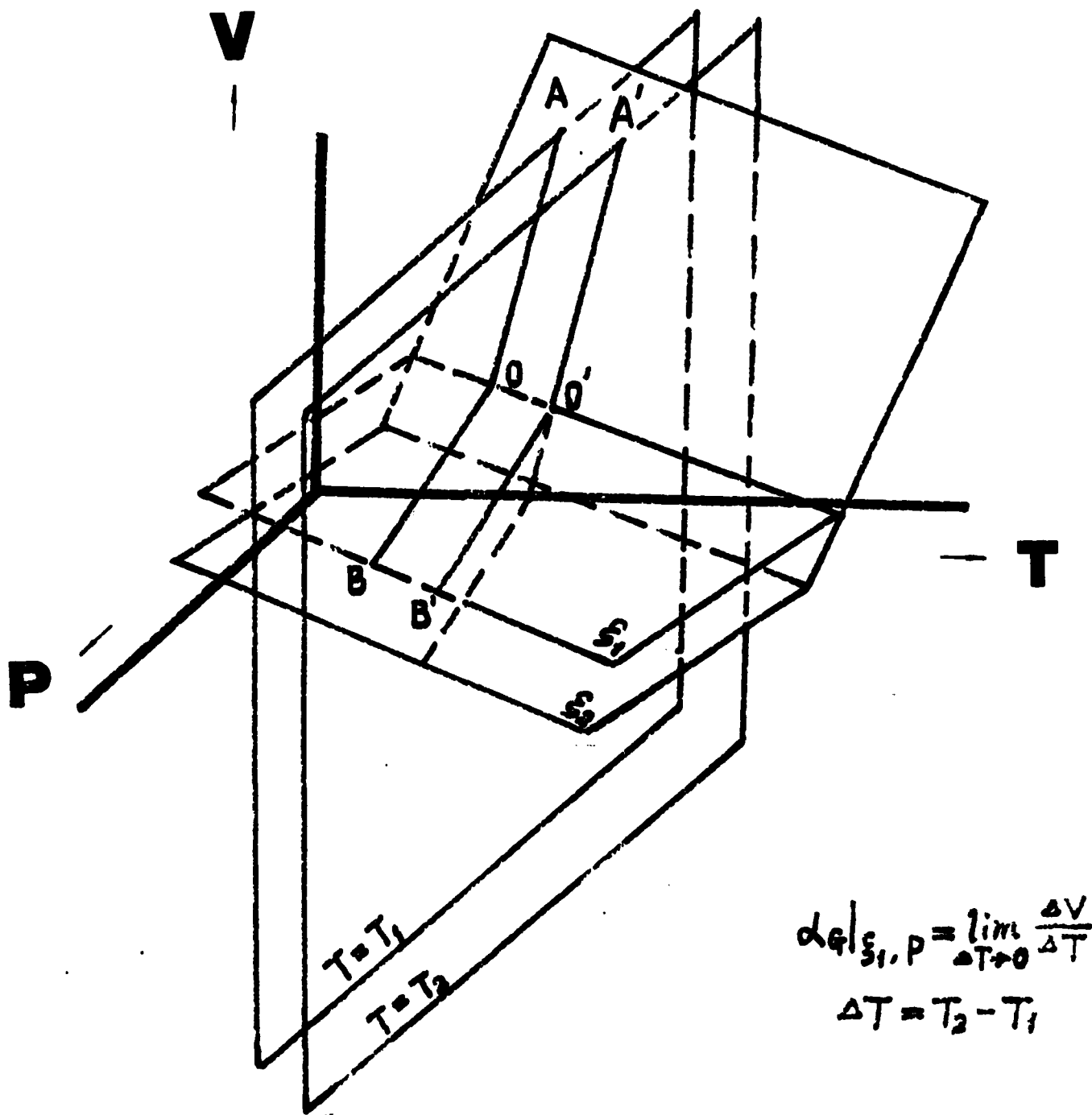


Fig. 4 Planes $T = \text{Const.}$ cut the L-G surfaces on isothermal pressuring curves, $T_2 > T_1$

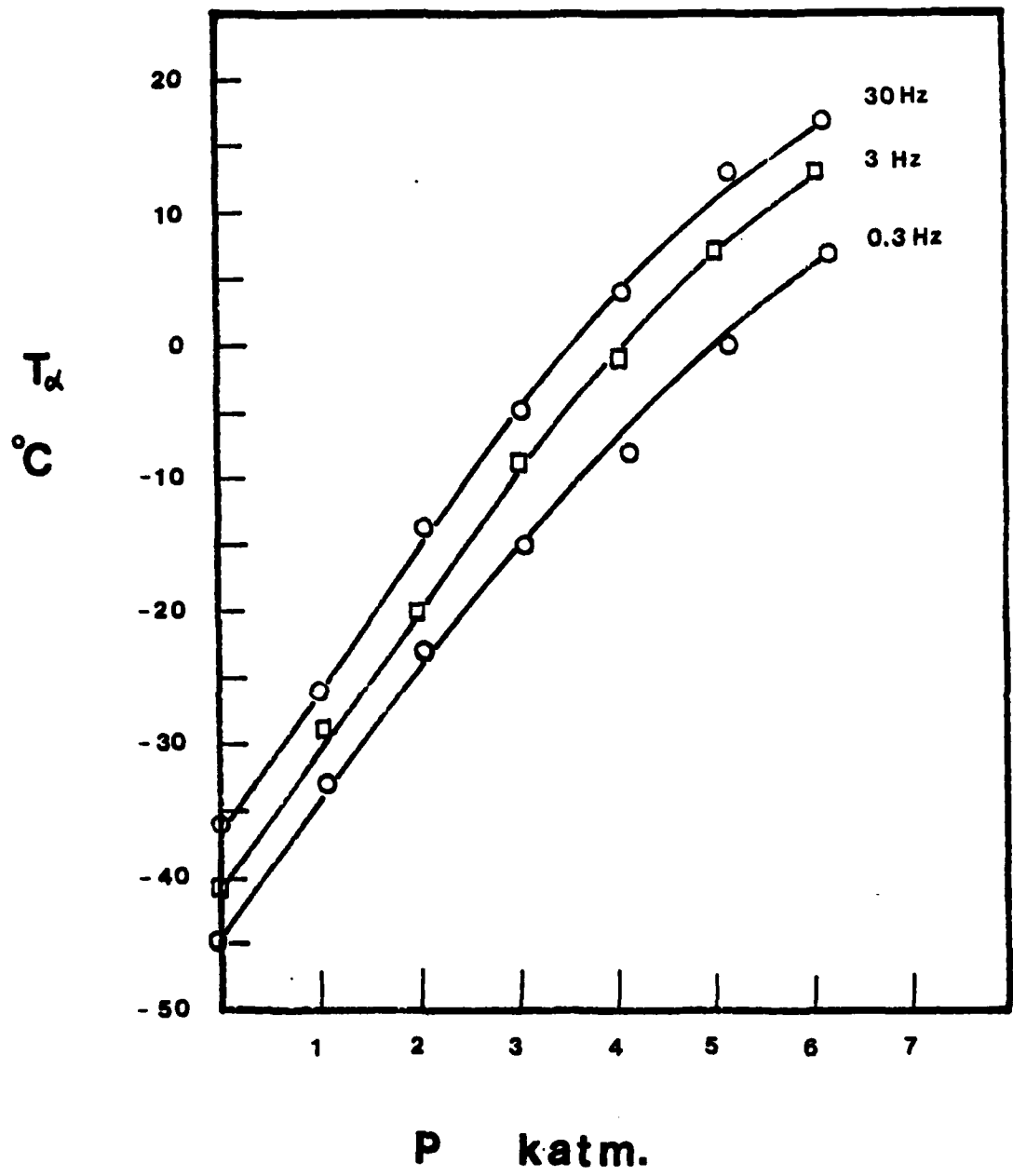


Fig. 5

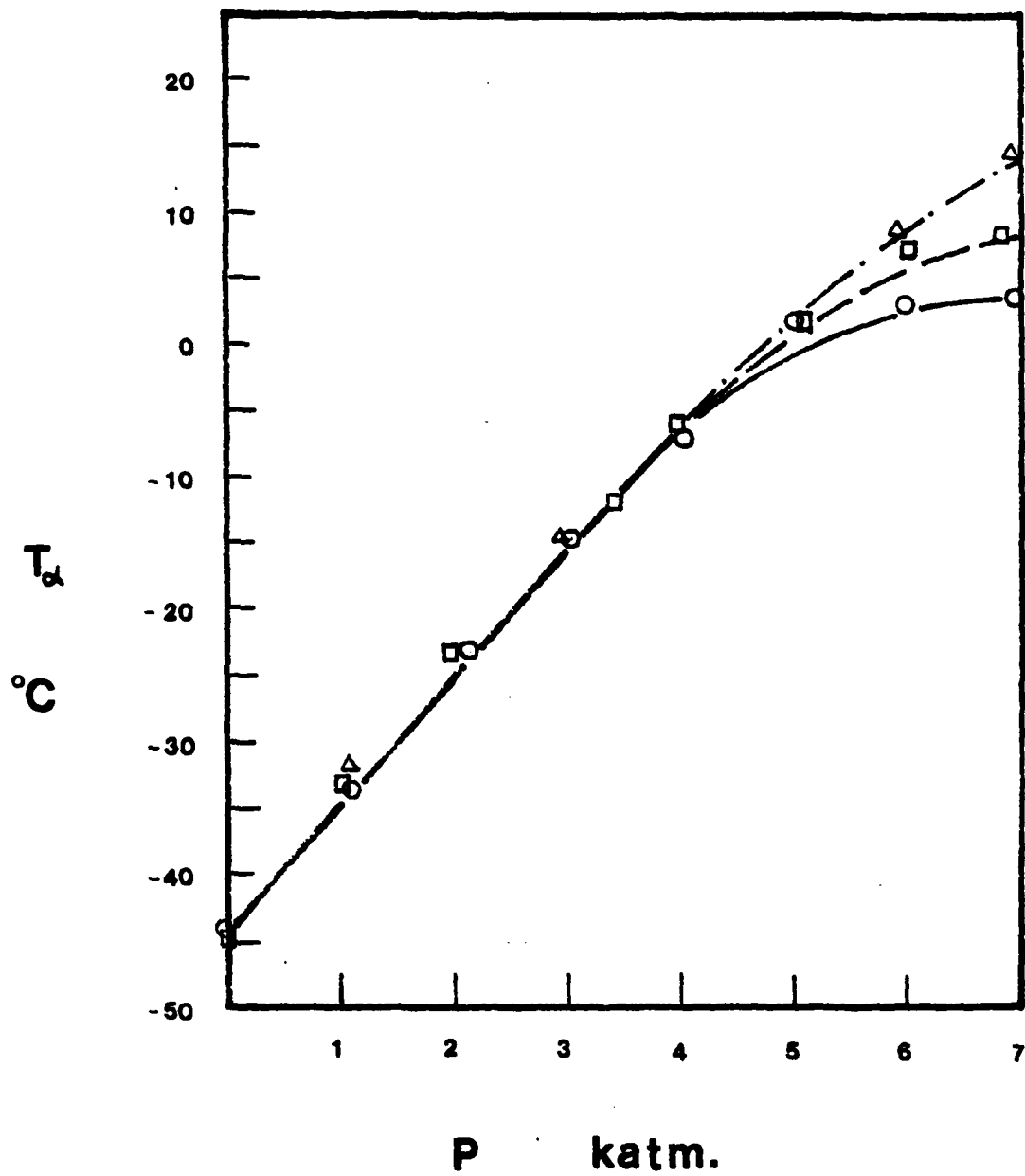


Fig. 6

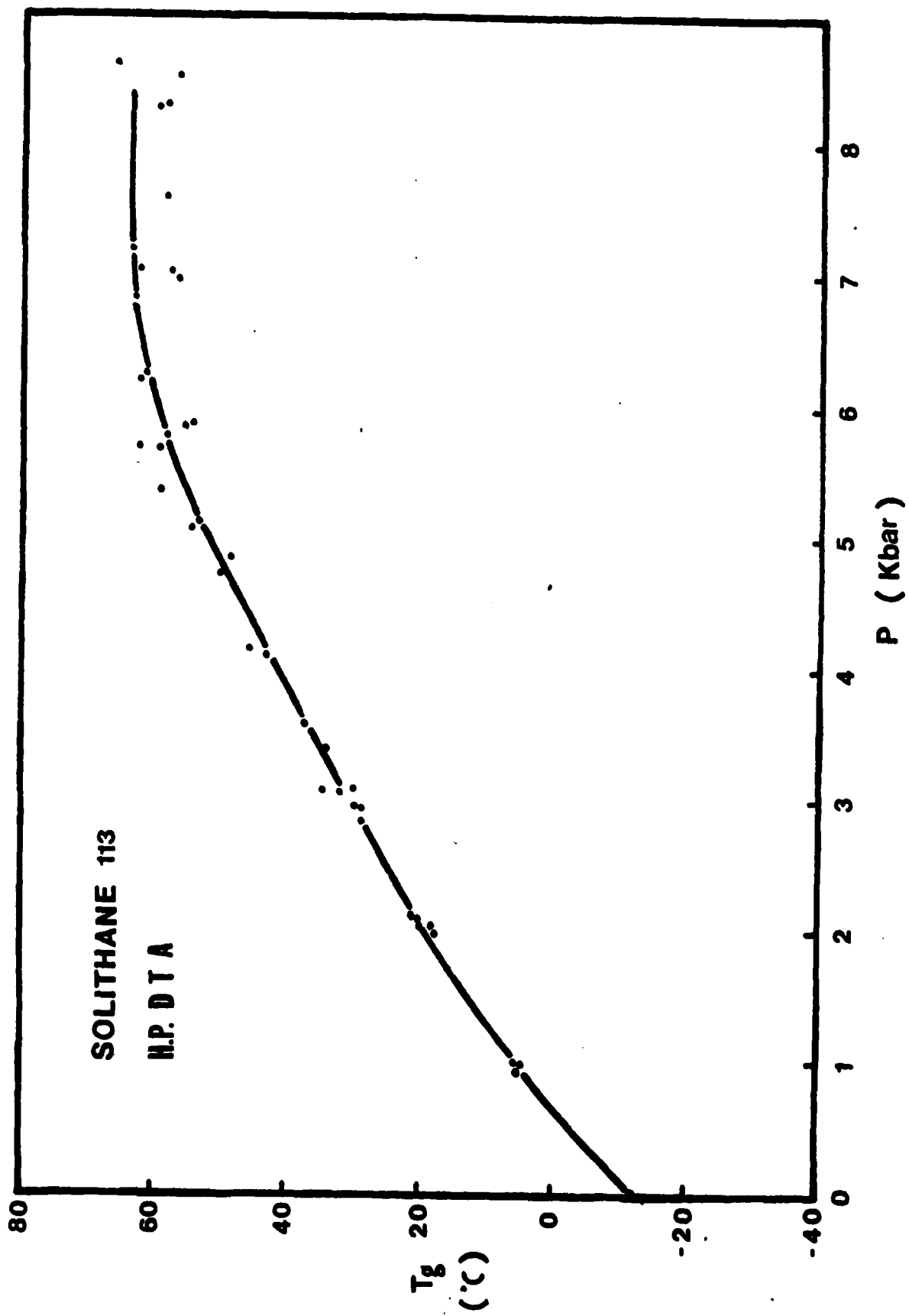


Fig. 7

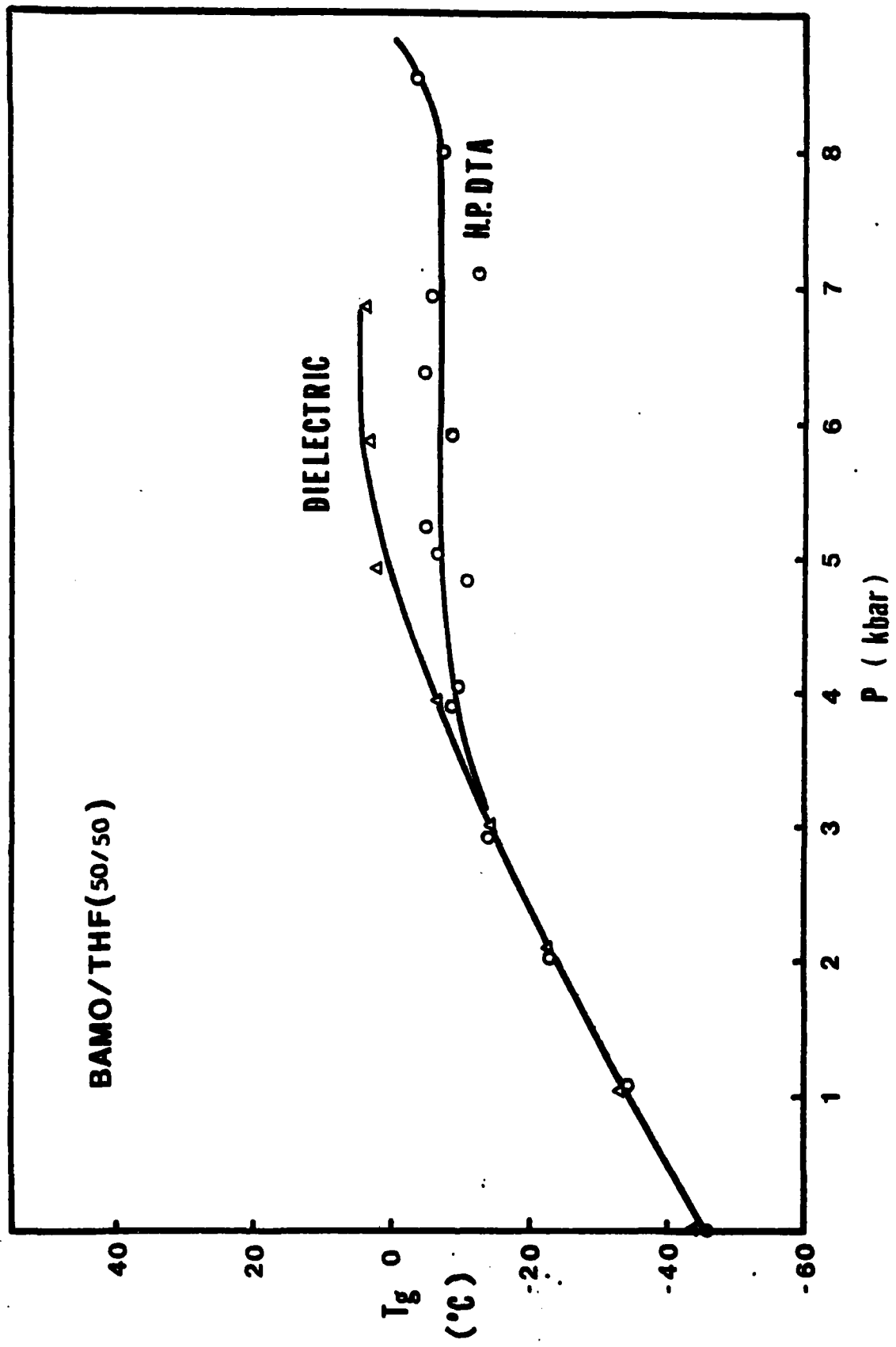


Fig. 5

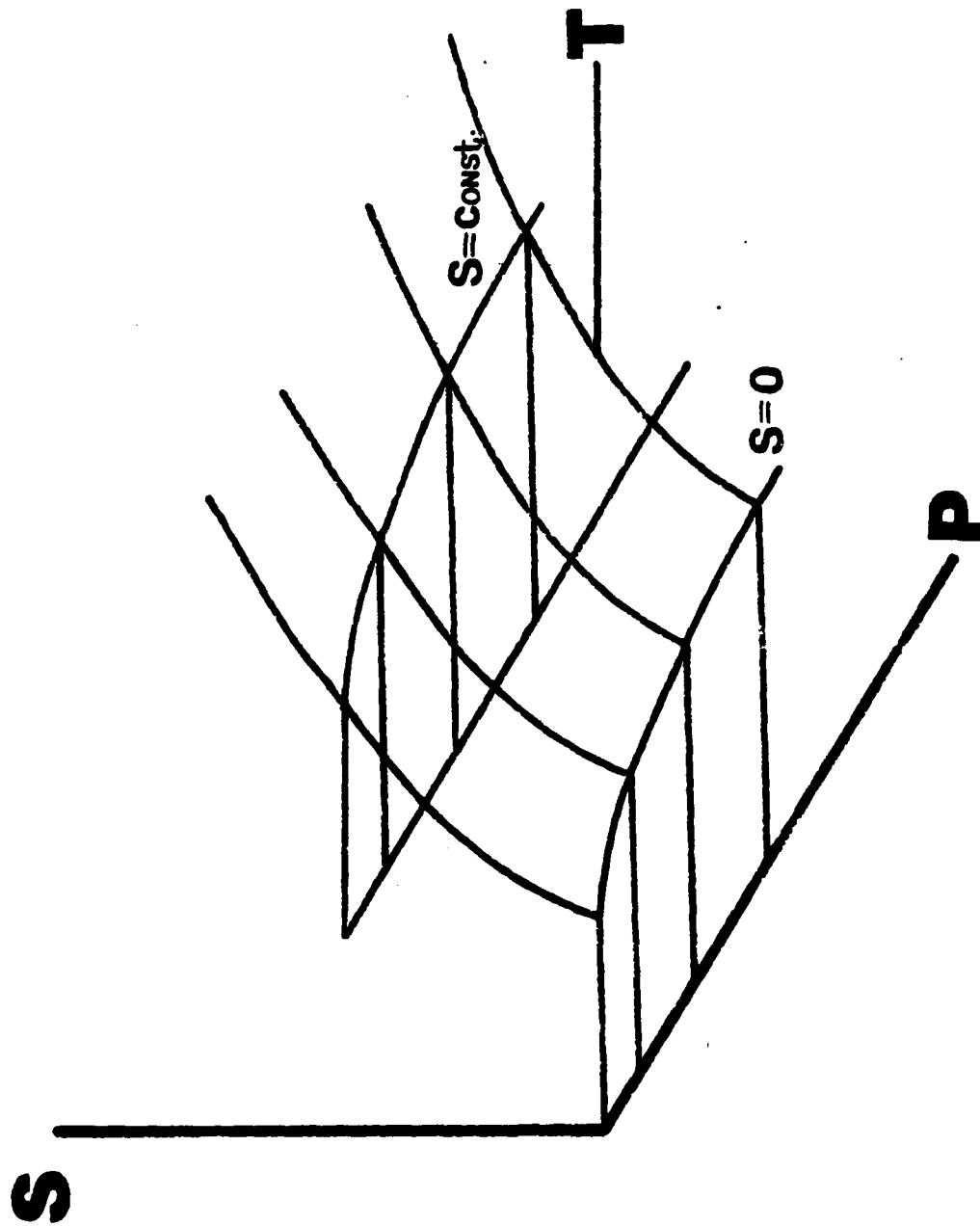


Fig. 9 Schematic of STP space
based on G.D theory

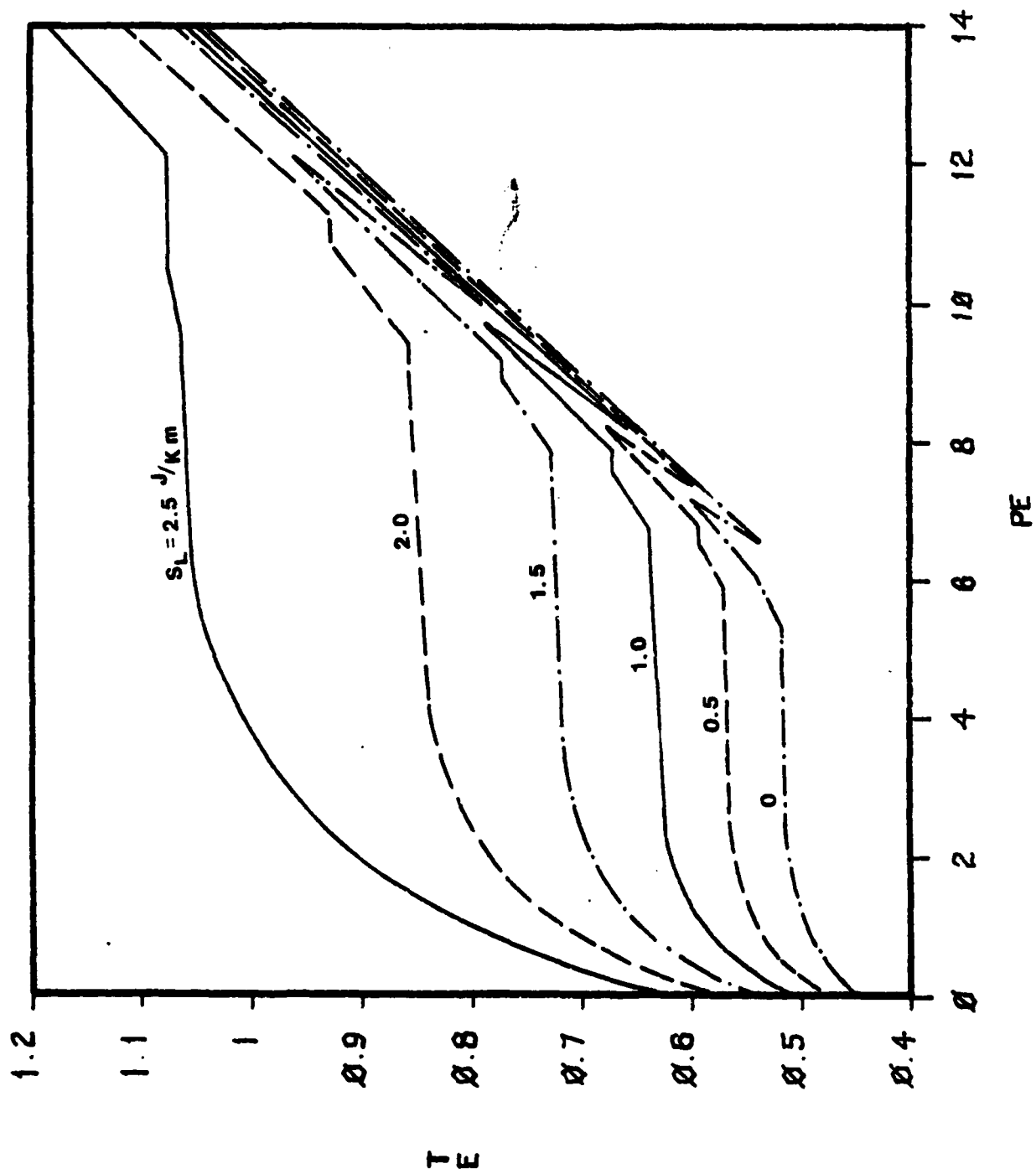


Fig. 12

Fig 11

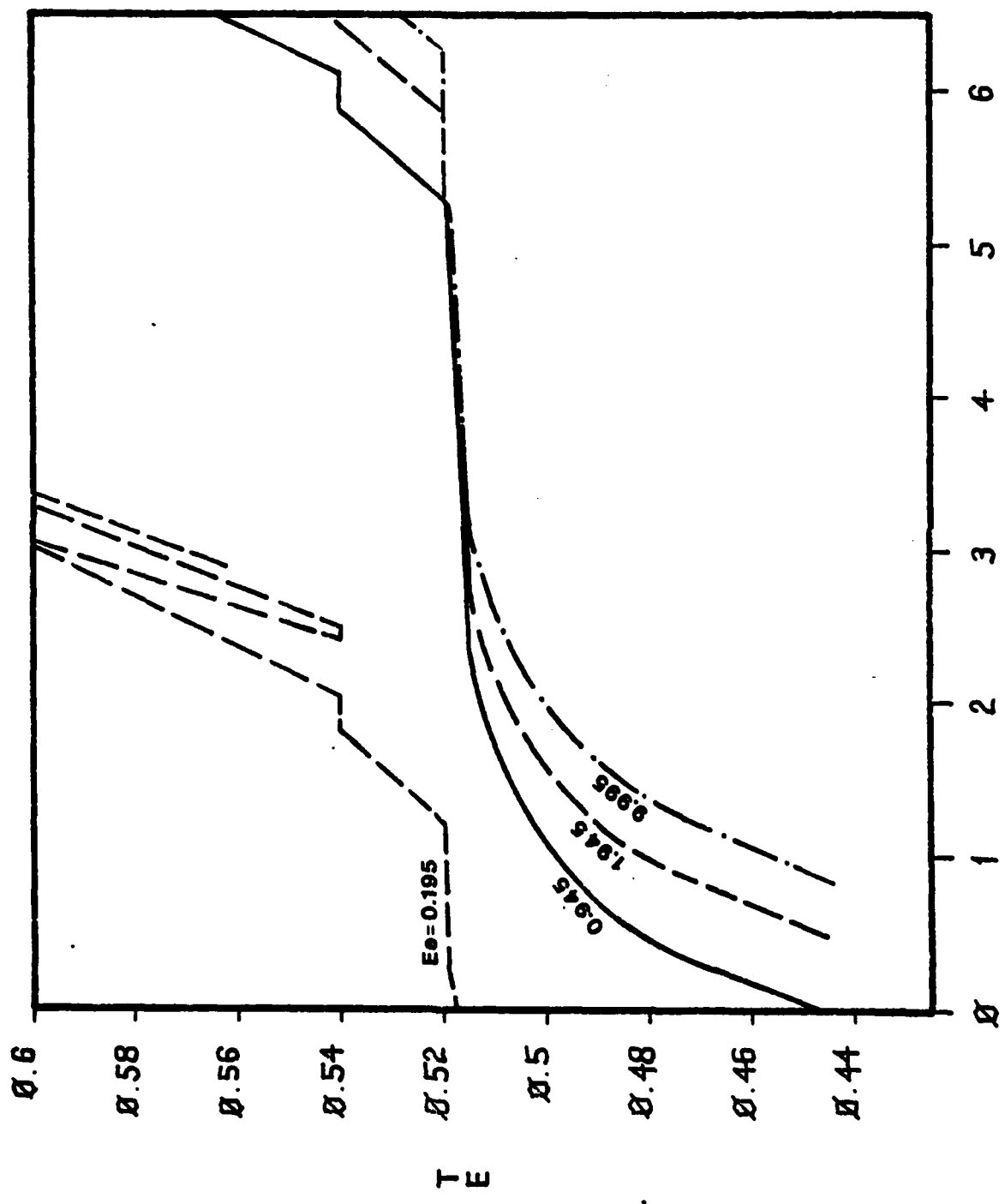


Fig 12

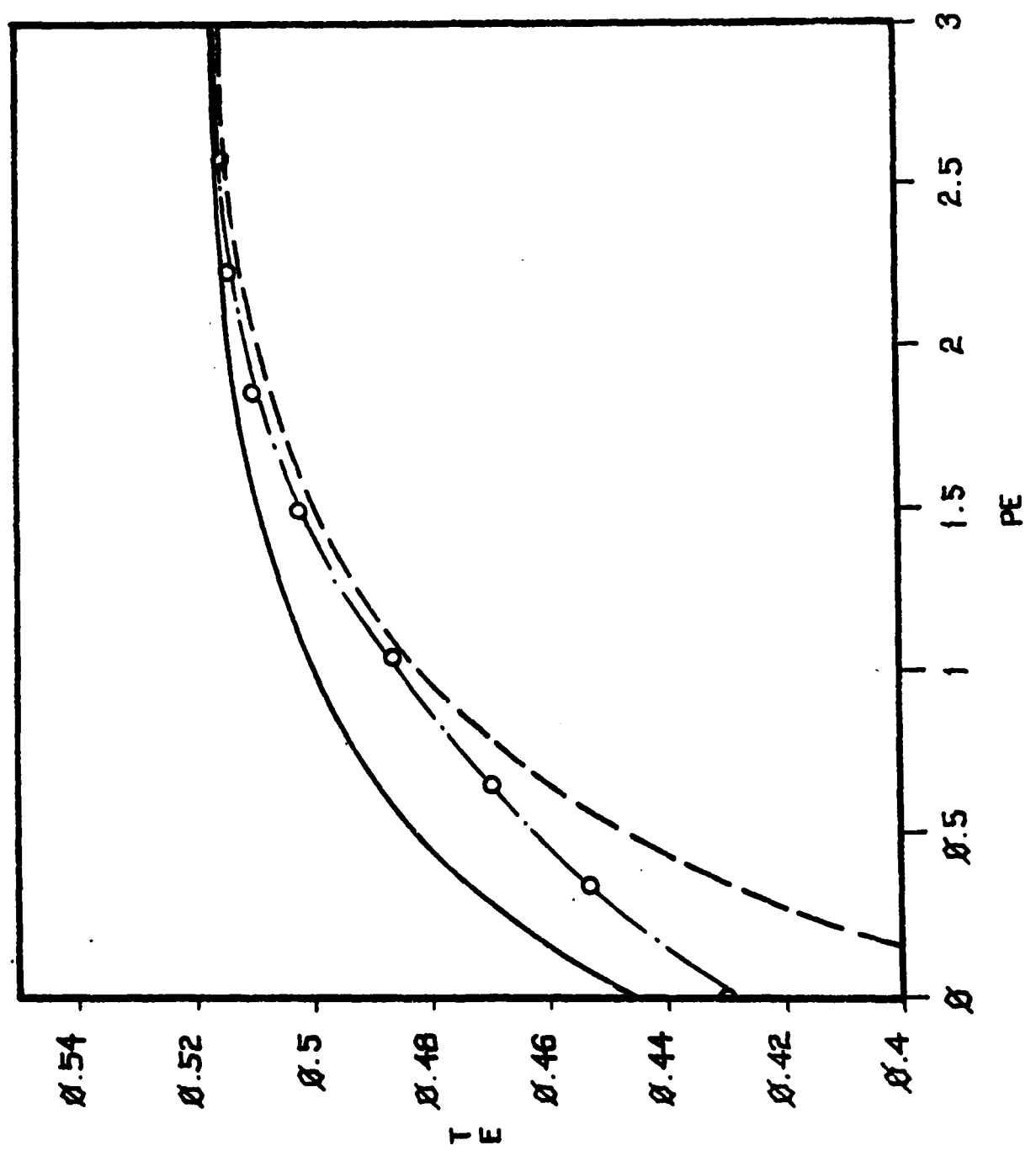


Fig. 13

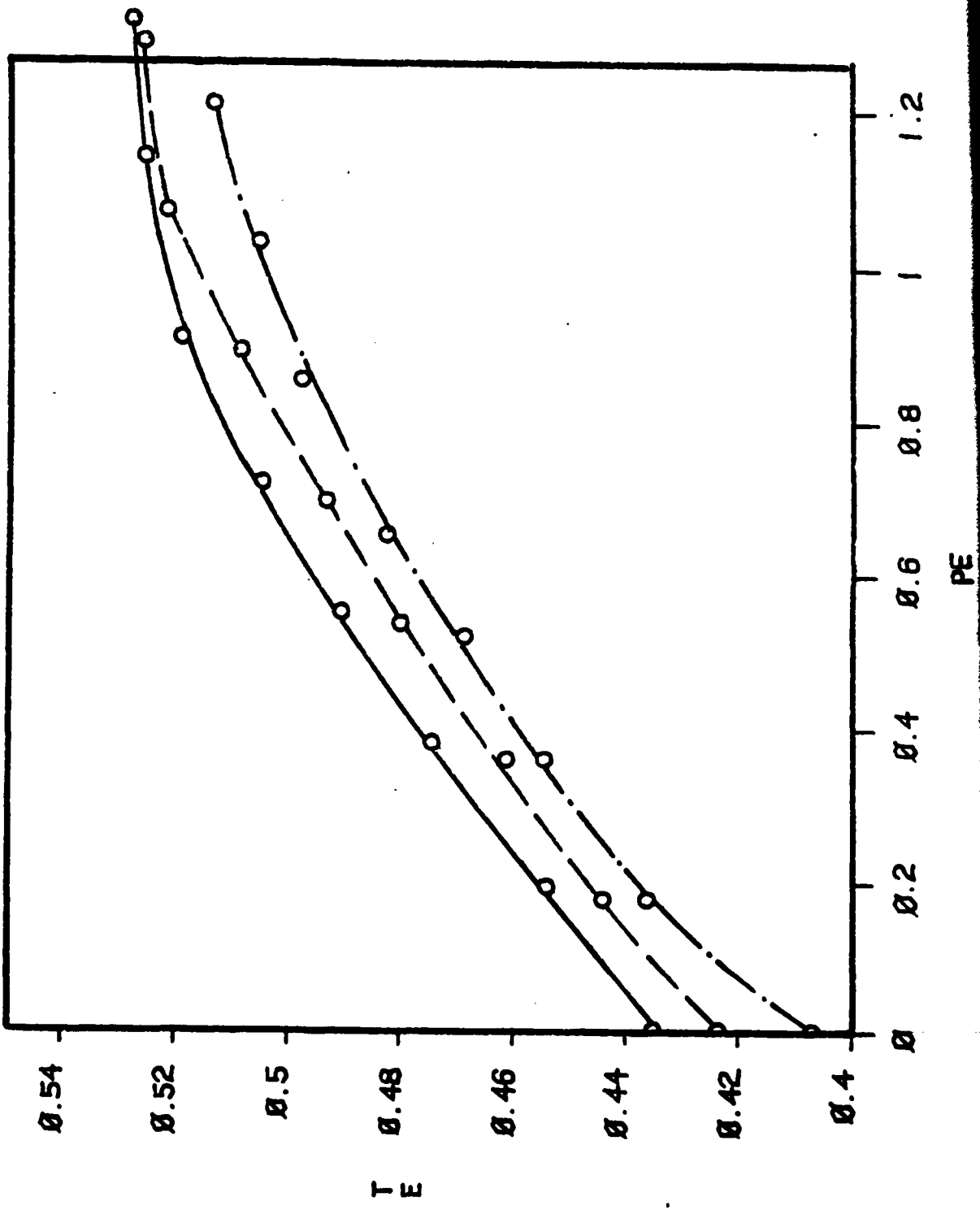
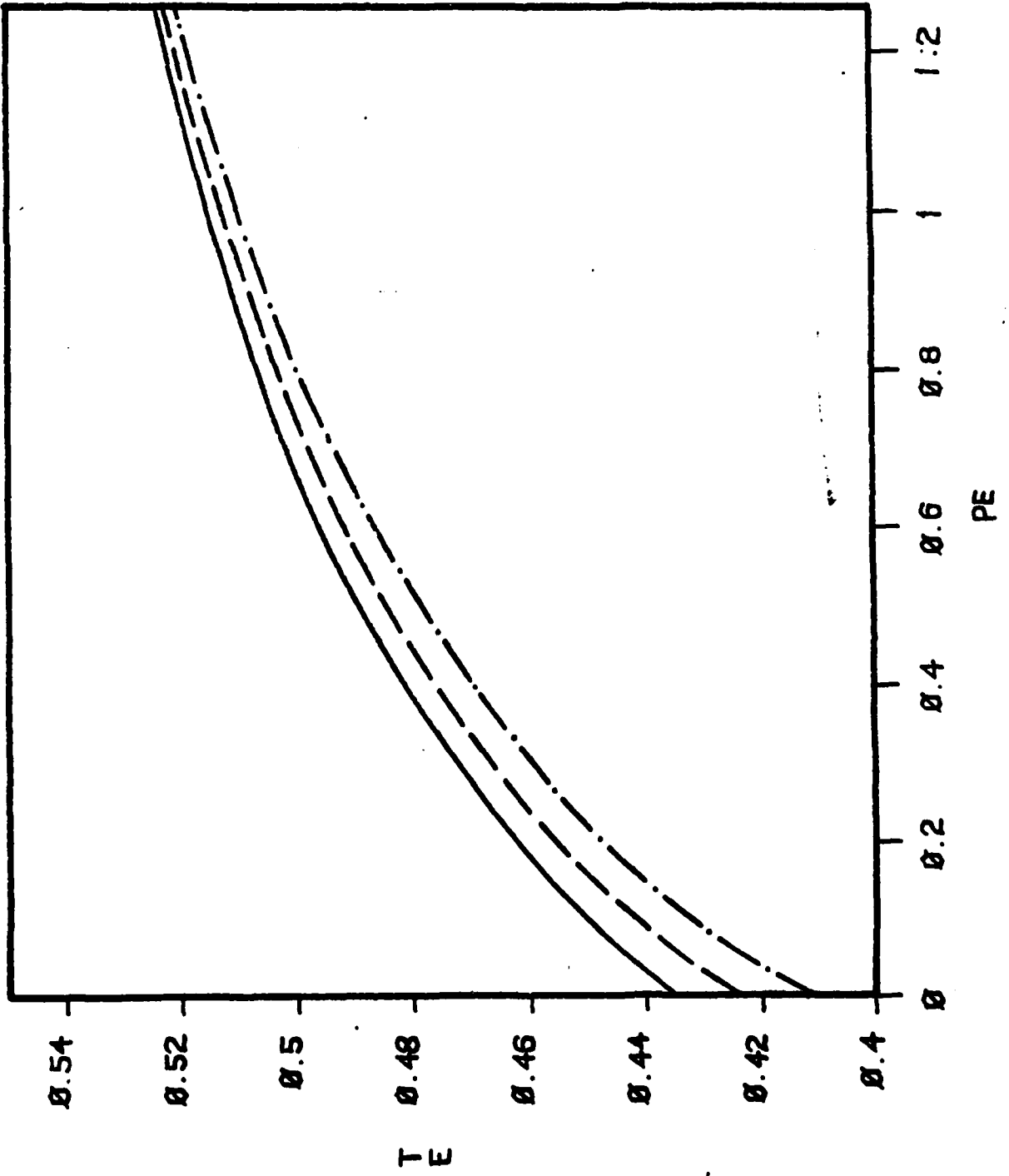


Fig. 14



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