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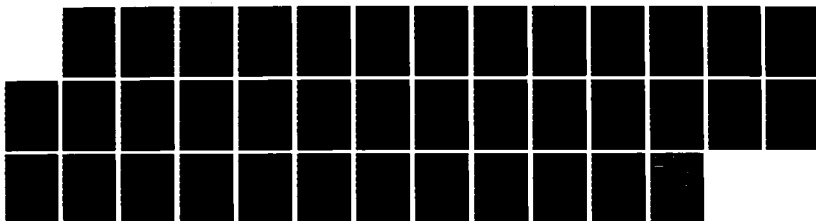
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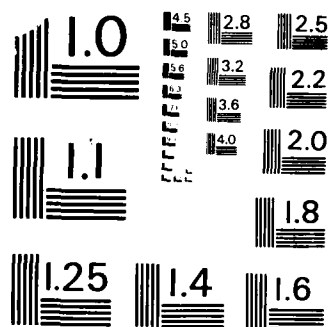
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of aging time. When all the experimental data, obtained at various (P,T) states for a specific path, were replotted in a form of $\log E$ vs $1/P$ for isothermic glass and $\log E$ vs $1/T$ for isobaric glass, all curves appear to converge to a specific value of E . The value was chosen as E_{∞} , the equilibrium modulus. The relaxation behavior was analyzed by a parameter:

$$\delta^E = \frac{E_{\infty} - E(P,T,t)}{E_{\infty}}$$

When $\delta^E = 1$ is used to define the glass transition, the pressure dependent glass transition lines for isobaric glasses are found to be entirely different than isothermic glasses. The nonequilibrium behavior of E of the glass was analyzed by an equation, analogous to Kovac's equation for the kinetics of relaxation, namely

$$\frac{-d\delta^E(P,T,t)}{dt} = \frac{\delta^E(P,T,t)}{\tau(P,T,\delta^E)}$$

where $\delta^E(P,T)$ is the relative departure of $E(P,T,t)$ from the equilibrium value E_{∞} . In general, the isobaric glasses at a specific state (P,T) relaxed faster, relatively, than isothermic glasses for the experimental conditions of heating rate or pressurization rate.

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EFFECT OF PHYSICAL AGING ON MECHANICAL BEHAVIOR
OF AN ELASTOMERIC GLASS
UNDER COMBINED PRESSURE AND TEMPERATURE

by

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EFFECT OF PHYSICAL AGING ON MECHANICAL BEHAVIOR
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UNDER COMBINED PRESSURE AND TEMPERATURE

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ABSTRACT

The relaxation or physical aging behavior of a polyurethane elastomeric glass (Solithane 113, $T_g = -20^\circ\text{C}$ at atm.) has been studied at various states of pressure and temperature, near and far away from the glass transition. Those (P, T) states were reached via either isobaric or isothermal paths. Relaxation behavior of these glasses has been found to be a function of P, T and paths. The Young's modulus (E) has been determined as a function of aging time. When all the experimental data, obtained at various (P,T) states for a specific path, were replotted in a form of $\log E$ vs $1/P$ for isothermic glass and $\log E$ vs $1/T$ for isobaric glass, all curves appear to converge to a specific value of E. The value was chosen as E_∞ , the equilibrium modulus. The relaxation behavior was analyzed by a parameter:

$$\delta^E = \frac{E_\infty - E(P,T,t)}{E_\infty}$$

When $\delta^E = 1$ is used to define the glass transition, the pressure dependent glass transition lines for isobaric glasses are found to be entirely different than isothermic glasses. The nonequilibrium behavior of E of the glass was analyzed by an equation, analogous to Kovac's equation for the kinetics of relaxation, namely

$$\frac{-d\delta^E(P,T,t)}{dt} = \frac{\delta^E(P,T,t)}{\tau(P,T,\delta^E)}$$

where $\delta^E(P,T)$ is the relative departure of $E(P,T,t)$ from the equilibrium value E_∞ . In general, the isobaric glasses at a specific state (P,T) relaxed faster, relatively, than isothermic glasses for the experimental conditions of heating rate or pressurization rate.

1. Introduction

Attention has been focused recently on the properties of glasses which have been prepared from the melt under elevated pressure [1-11]. Because of the strong dependence of T_g on pressure, glasses made in this manner actually have been vitrified at different temperatures. These glasses are characterized by reduced volume and increased population of high energy bonds [3-7]. The studies of pressure-densified glasses were carried out by most of the workers at atmospheric pressure after pressure was released. Those glasses are highly unstable and undergo "memory behavior" of structural relaxation in time [12]. Theoretical equations of state have been developed to describe the Pressure-Volume-Temperature relations of polymers [13-15]. The theories are mostly applicable to the liquid state since there is a true thermodynamic state characterized by a single surface in PVT space. The same is not true for the glassy state where the volume depends on the glass formation pressure as well as ambient pressure, temperature and the rate at which the glass is formed [14,16-19].

Pressure increases T_g anywhere from 10 to 35°C per kilobar [20,21]. Thermodynamic theories are developed on the assumption that T_g is or reflects a true second-order thermodynamic transition. Hence, the DiMarzio theory [22] predicts the Ehrenfest relations [23] to hold ($dT_g/dP = \Delta\beta/\Delta\alpha = TV\Delta\alpha/\Delta C_p$). Pressure dependence of the T_g of Solithane 113 elastomer has been studied and it was found that $\Delta\beta/\Delta\alpha > dT_g/dP$ but $\Delta\beta/\Delta\alpha \approx dT_g^*/dP$ where T_g^* is the glass-transition temperature of the glass formed at atmospheric pressure [24]. Indeed, the expression dT_g/dP derived from the Adam-Gibbs theory is shown to be variant with Ehrenfest relation [25]. It was observed that the properties of glass depend upon the manner in which it is formed [24]. Thermodynamic analysis was made to show that for many general glasses $dT_g/dP = \frac{\Delta\beta}{(1+n)\Delta\alpha}$ holds, in

which $n = 1$ for Solithane and some other glasses [26]. An extension of the DiMarzio theory has been proposed to account for the effect of applied stress on the glass transition temperature of glass forming polymers [27].

The nonlinear dependence of relaxation time on the structural change of glass has been approached phenomenologically by Moynihan and coworkers [28,29]. Moynihan's model is modified to include hydrostatic pressure on the temperature dependence of relaxation time [30]. The effect of hydrostatic pressure on relaxation of polymer glasses is analyzed statistically [31,32]. Based on molecular dynamics, predictions are made for volume recovery in polymer glasses [33]. High-pressure-jump experiments on volume relaxation of polystyrene have been reported and compared with temperature-jump results [34]. The dependence of $\log \tau$ on pressure is linear within the limited pressure range studied (about 0.6 KBar). The WLF equation has been modified to describe the time-temperature-pressure superposition of stress relaxation data under combined state of pressure and temperature [35-37]. The modified expression, originally developed from tensile stress relaxation data, has been applied to shear stress relaxation data [38]. In this work, the relaxation behavior Solithane 113, a polyurethane elastomer, will be analyzed under combined pressure and temperature.

2. Material

Solithane 113 is a commercially available urethane elastomer (Thiokol Chemical Co.). It is formed from the reaction of a resin and a catalyst. The resin is a prepolymer formed by extending castor oil with tolylene-diisocyanate. The catalyst also consists essentially of castor oil [39,40]. By varying the amounts of catalyst and resin, the properties of the resulting elastomer can be greatly varied. In the present study only the equivoluminal (50/50) composition

was examined. For this composition the specific volume at atmospheric and room temperature was $0.97 \text{ cm}^3/\text{g}$ and at atmospheric pressure it has a glass transition temperature of -20°C . On the basis of swelling measurements the average molecular weight between cross-links was determined to be about 2000 g/mole [40].

3. Experimental

Time-independent mechanical behavior of Solithane 113 has been determined earlier in the liquid and the glassy states at high pressures up to 5.0 KBar and room temperature (20°C) by Questad et al. [41,42]. The three order of magnitude of increase of Young's modulus within this pressure range at room temperature was observed. In this study, the Young's modulus of solithane glass is obtained as a function of pressure and temperature state, path by which the states were arrived, and aging time. We have used compression tests to determine the stress-strain curves from which the modulus was determined. The experimental apparatus and pressure medium have been reported elsewhere [41].

An elastomeric glass at a given specific state (P, T) would show a characteristic mechanical behavior of that state and would undergo relaxation as a function of aging time. Initially our experiments were based on the scheme as shown in Fig. 1, where the phase diagram of solithane was obtained from the experimental conditions described in earlier work [42]. Since the T_g is the manifestation of kinetic conditions, the phase diagram given in Fig. 1 is a nonequilibrium one. An equilibrium phase diagram of solithane should be shifted toward right, or high pressures.

As shown in Fig. 1, the glassy state of 3.0 KBar and -5.5°C is reached through two paths. By high pressure path, a liquid (rubbery) sample is, first, pressurized from atmospheric pressure to 3.0 KBar and then temperature lowered

from 20°C to -5.5°C. By low pressure path, the temperature of the rubbery sample is first lowered from room temperature to -5.5°C and then the pressure raised to 3.0 KBar. In all cases of experiments reported in this work, the pressurization rate of 0.25 KBar/min. and the cooling rate of 0.5°C/min. are used to reach the (P,T) state. The glass sample formed by high pressure path is aged for 0.5 hour at the (P,T) state and compressive load is applied to get the stress-strain curve. In another test, a new liquid sample, similarly brought to the same (P,T) state is aged for 2.0 hours and then tested in compression. A series of samples were subsequently tested with longer aging time. The mechanical response of the glass formed by low pressure path is obtained for various aging times in a similar way as that obtained for high pressure path. It is emphasized here that, in any set of aging experiments, we always start with a new rubbery sample. Thus the chronology of glass-history in aging experiments is preserved without ambiguity [43].

The compressive stress-strain curves of the glasses obtained at various aging time for high and low pressure paths are shown in Fig. 2 and Figs. 3, respectively. The stress-strain curves clearly show the path dependence as 0.5 hour curve for high pressure path is much lower in the elastic modulus (E), yield strength (σ) and stored elastic energy (e) than those of the low pressure path curve. The stress-strain curves are shifted upward as functions of aging time, exhibiting increased E , σ and e . Figure 4 shows the aging time dependence of E [44]. The E of the high pressure path samples crosses over the low pressure path curve indicating the relaxation processes of the glassy state by two paths are entirely different, that is, the high pressure path glass relaxes faster than the low pressure path glass.

4. Results

Figure 5 shows the values of Young's modulus (E) of the glasses formed by isobaric paths (isobaric glasses) at various states of pressure and temperature (P_i, T_i) for an aging time of 30 min. Figure 6 shows the same for the glasses by isothermal paths (isothermic glasses). The test procedure followed for an isobaric glass at 3.0 KBar and 4.5°C, for example, was that a rubbery sample at room temperature was pressurized first to 3.0 KBar and then the temperature was lowered to 4.5°C. Once the state of 3.0 KBar and 4.5°C was reached, it was aged for 30 min and loaded immediately at a strain rate of 0.02 inch/min for the elastic response. Annealing, if any, during the travel time to reach various states has been ignored.

For isobaric glasses, as shown in Fig. 5, the modulus at 30 min, as well as at 600 min, aging increases but with a decreasing rate with decreasing temperature. For example, the modulus of the atmospheric glass, the glass being formed under atmospheric pressure and at -20°C, rises very rapidly with decreasing temperature of aging, in the neighborhood of the transition temperature but the rapid rise diminishes below about -25°C. By increasing the glass formation pressure from 1 bar to 1, 2, 3 and 4 Kbar, it can be observed that the rate of the increase of the modulus with decreasing temperature of aging slows with pressure. A similar observation can be made on isothermic glasses; that is, the rate of increase of the modulus decreases with decreasing temperature of aging (Fig. 6).

The Young's modulus is, therefore, dependent on aging time, temperature, pressure and path (i) by which the state is reached:

$$E^i = E^i(P, T, t) \quad (1)$$

Figs. 5 and 6 are replotted in the form of $\log E$ vs $1/T$, as shown in Fig. 7 for isobaric glasses and $\log E$ vs. $1/P$, as shown in Fig. 8 for isothermic glasses.

The experimental data are fit in a form of equation

$$y = A + Bx + Cx^2 + Dx^3 + \dots \quad (2)$$

for both glasses and the coefficients are calculated. Using the coefficients it was determined that the modulus converges at -144.8°C for isobaric glasses and at 9.67 KBar for isothermic glasses. As also shown in Fig. 5, 600 min aged samples behaved in similar manner as that of 30 min aged samples. We now assume that the magnitude of the extrapolated modulus will be the *thermodynamic equilibrium modulus* for isothermal [it] and isobaric [ib] glasses, i.e.

$$\begin{aligned} E_{\infty}^{ib} &= 2.818 \times 10^{10} \text{ Dynes cm}^{-2} \text{ at } -144.8^\circ\text{C} \\ E_{\infty}^{it} &= 2.239 \times 10^{10} \text{ Dynes cm}^{-2} \text{ at } 9.67 \text{ KBar} \end{aligned} \quad (3)$$

Analogous to δ , the relative departure of volume from equilibrium [45], we introduce

$$\delta^E = \frac{E_{\infty} - E(P, T, t)}{E_{\infty}} \quad (4)$$

to study the relaxation behavior of the glass under combined pressure and temperature conditions in which E_{∞} obtained in Eq. (3) may be used.

Figures 9 and 10 show, respectively, the replotting of the experimental data in the form of δ^E versus T of Fig. 5 and P of Fig. 6. It is now possible to pick off from Figs. 9 and 10 the value of temperature or pressure at which $\delta^E \approx 1$.

If we consider that $\delta^E \approx 1$ at the glass transition points, we can draw two distinct pressure dependent glass transition lines for the two paths because of the temperature rate (q) and pressure rate (p) used, as shown in Fig. 11. The transition line due to isothermic glass lies above that of isobaric glass. At high pressure and temperature, the transition lines of glasses formed by both

paths seem to diverge. This new P-T phase diagram was used in determining the locations of various (P,T) states at which the relaxation studies were to be carried out.

Now we present the results of the longer time relaxation experiments on Solithane glasses. The aging effect of Solithane 113 is studied at different (P,T) states for the various glasses being formed by isobaric or isothermic paths according to the scheme given in Figs. 12 and 13. The transition lines from Fig. 11 is used in Figs. 12 and 13. To form a specific glass by isobaric path, the liquid sample is heated to 35.0°C from room temperature, subjected to different pressure levels, and cooled immediately with pressure 1.0 KBar, 2.0 KBar, 3.0 KBar, and 4.0 KBar, respectively. The specific isobaric glass formed this way is cooled to a specific (P,T) state, aged for a specific time and then loaded for the elastic response. The test is repeated for various (P,T) states at various aging times with a new sample for each test and a typical aging behavior of 4 KBar glass is shown in Fig. 14. The relaxation experiments on the isothermic glasses are carried out at various states (P,T) as marked in Fig. 13 for which the new transition curve from Fig. 12 was also used.

Figures 14 and 15 show typical relaxation behavior of isobaric and isothermic glasses, respectively, at different (P,T) states. As shown in Fig. 14, the Young's modulus of 4 KBar-glass increased at different rates, depending upon its temperature state. Samples were tested at -10°C, 0°C, 4.5°C, and 15°C, but all at the same pressure, 4 KBar. The % increase of E at 10 hours aging was indicated in the figure. E increased at a very slow rate when T is either very close to or very far away from T_g (=24°C) at 4 KB. Thus, the maximum increase of E occurred at an intermediate T, namely at 15°C. The Young's modulus of 4.5°C-isothermic glass (glass formed at 1.4 KBar) increased at various rates, depending upon the aging pressure (Fig. 15). The maximum percent increase of E in 10 hours of aging

occurs at an intermediate pressure of 3 KBar. The increase at 2 KBar, which is near the P_g , is less and at 4 KBar which is farther away from the P_g , is also less than that at 3 KBar.

5. Discussion

The experimental results show that the Young's modulus (E) increased with aging time and the increase depended upon (P,T) state at which the aging occurred and the path (isobaric or isothermal) by which the (P,T) state was arrived at. It can be shown that the change in the Young's modulus (E) is directly proportional to the change in volume or the δ due to physical aging, provided that the short-time compressive response is linear elastic, as

$$\frac{1}{E} = A(P,T,\text{path}) \left[\frac{1}{\delta} - \frac{1}{\delta_{\infty}} \right] \quad (5)$$

where the proportionality function A is a function of P,T , and the path. It should be obvious that the physical aging depends on the (P,T) state at which aging is carried out. If a (P,T) state is in the neighborhood of the glass transition (T_g) for that given P , or far away from T_g , the aging would be slow. At an intermediate (P,T) state, the aging is rather fast. The path dependency is, of course, due to different glass (ξ -glass), which were formed at different pressure (P) with different pressure rates (p) and temperature rates (q) used.

The plot of $\log E$ vs. $\frac{1}{p}$ for isothermic glasses (Fig. 8) shows that all the curves appear, when extrapolated, to emerge to a point. The extrapolation was accomplished by the best least source fit technique. The value of pressure at this point is approximately 10 KBar and the value of E is 2.24×10^{10} dyne cm^{-2} which was used as the value of the equilibrium modulus in evaluating δ^E . The equilibrium modulus for isobaric glasses similarly obtained from the plot of $\log E$ vs. $\frac{1}{T}$ is about 2.82×10^{10} dynes cm^{-2} which occurred at $T = -145^\circ\text{C}$.

At these conditions, namely $P = 10$ KBar or $T = -145^\circ\text{C}$ any molecular motion would be unlikely for Solithane elastomer.

The concept of equilibrium modulus is also necessary to establish the kinetics of relaxation. Analogous to KAHR model [49], the recovery of glasses at a given state of pressure and temperature can be analyzed in terms of a very sensitive rate parameter, called $\tau_{\text{effective}}$ and defined by

$$\tau_{\text{eff},P,T}^{-1} = - \frac{1}{\delta^E} \left. \frac{d\delta^E}{dt} \right|_{P,T} > 0 \quad (6)$$

We may calculate the effective relaxation time based on this equation for all relaxation data of different states for both glasses in order to obtain the $\log \tau_{\text{eff}}$ vs. δ^E plots. Figures 16-18 shows some of the plots for both isobaric and isothermic glasses.

Figure 16 shows the $\log \tau_{\text{eff}}$ plot for 1.0 KBar isobaric glass. The solid lines are drawn based on the experimental data. Using this time window we look at the complete relaxation process up to equilibrium through the dashed lines which are extrapolated from the solid lines. The intersection of a dashed line with the ordinate ($\delta^E = 0$) gives the time which will be required to reach equilibrium for a particular (P,T) state. By decreasing the temperature from -20.0°C to -30.0°C , the slope of these curves becomes higher leading to longer relaxation time to reach equilibrium.

Figure 17 shows the same trend that, by decreasing the temperature from -6.5°C to -30.0°C , longer relaxation time is needed to reach equilibrium for 2.0 KBar isobaric glass. But the magnitudes of the equilibrium relaxation times for 2.0 KBar isobaric glass at different temperature studied are relatively shorter than those of 1.0 KBar isobaric glass at different temperature. For example, at -20.0°C , it takes $10^{2.45}$ hours to reach equilibrium for 2.0 KBar isobaric glass.

whereas it takes $10^{33.4}$ hours for 1.0 KBar isobaric glass. In short, by decreasing the temperature, an isobaric glass takes a longer time to reach equilibrium. This is expected because the mobility of the polymer chains is restricted more and more by lowering the temperature. By increasing the glass formation pressure, the relaxation of isobaric glass is faster in reaching equilibrium. This is reasonable because, by increasing the glass formation pressure at relatively high temperatures, more and more high energy conformations are frozen in [11,8] and they relax faster than the frozen conformations of the glass formed at low pressure and temperature.

Figure 18 shows the relaxation behavior of isothermic glass formed at -15°C at different pressures. From the slopes of all these curves, it appears that the effective relaxation time of the atmospheric pressure glass at -15°C increases with pressure. This is true for cases of low glass formation pressures and is in accordance with the observation by others [34]. Summarizing, at glass formation pressure of low magnitude, the effective relaxation time increases with increase of pressure [34]. However, it was observed that, at elevated glass formation pressure and consequently high temperature, the effective relaxation time decreases with increase of pressure. This reverse phenomenon appears to occur at between -6.5°C ($P_g = 0.7$ KBar) and $+4.5^{\circ}\text{C}$ ($P_g = 1.4$ KBar).

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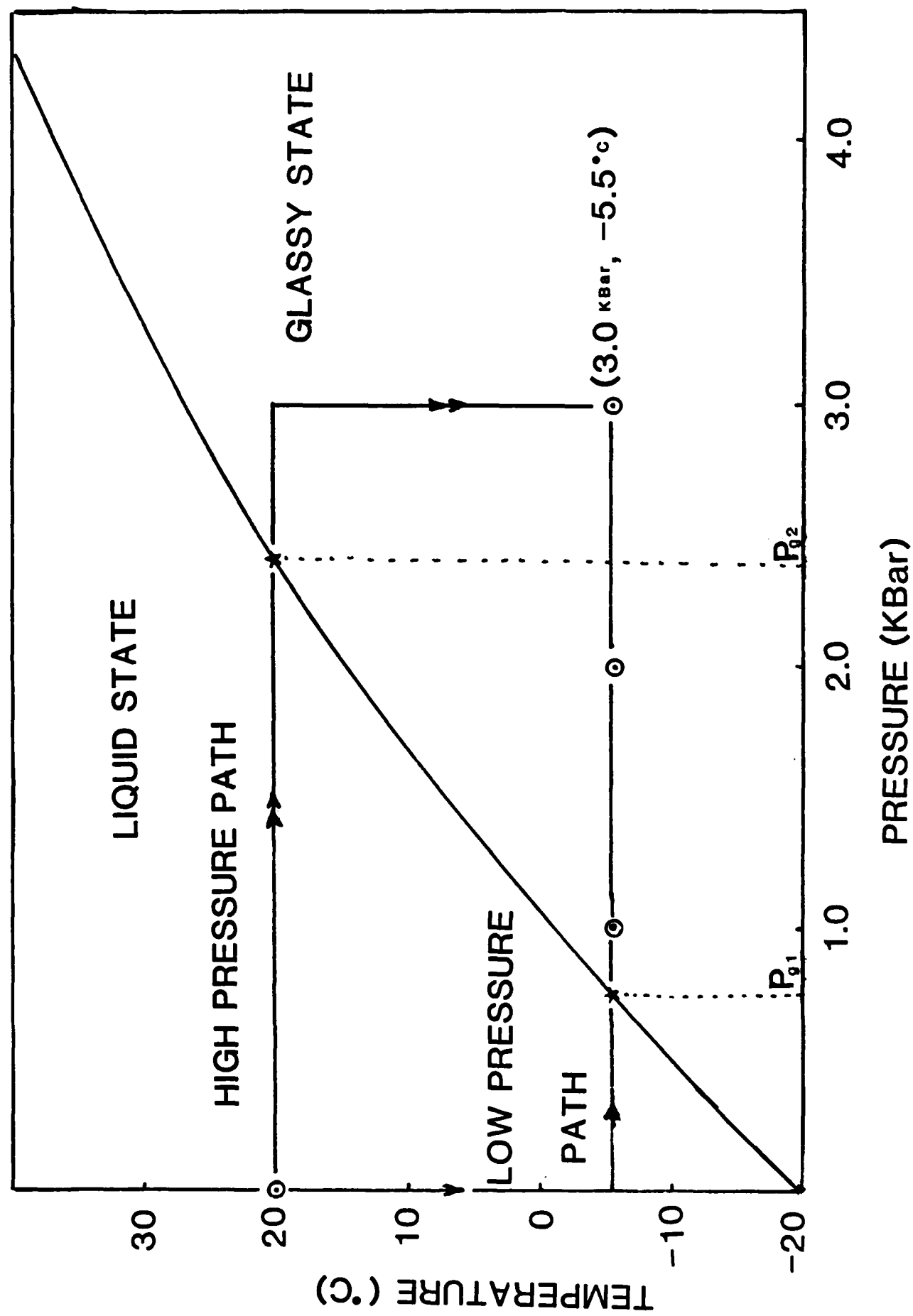
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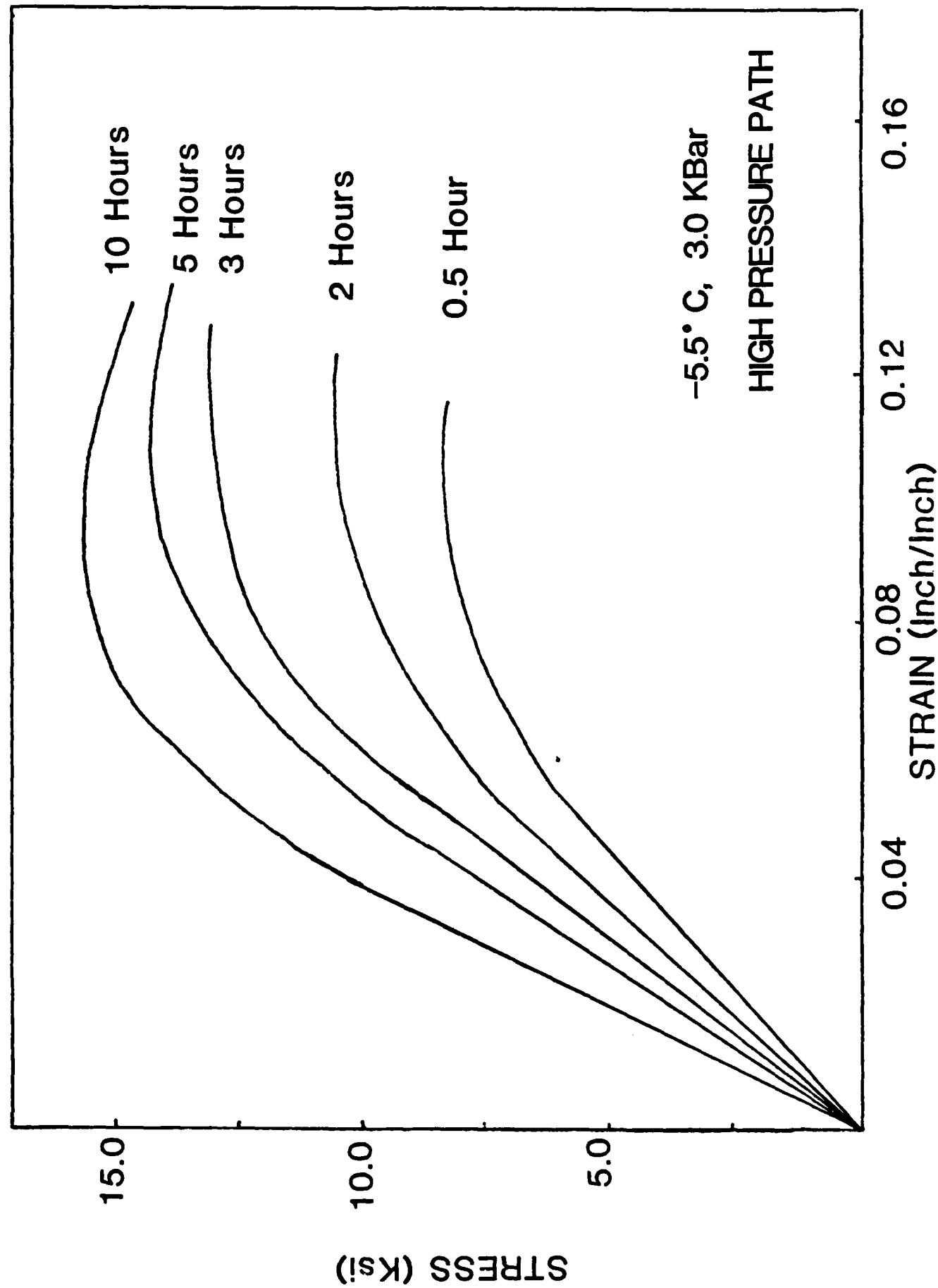
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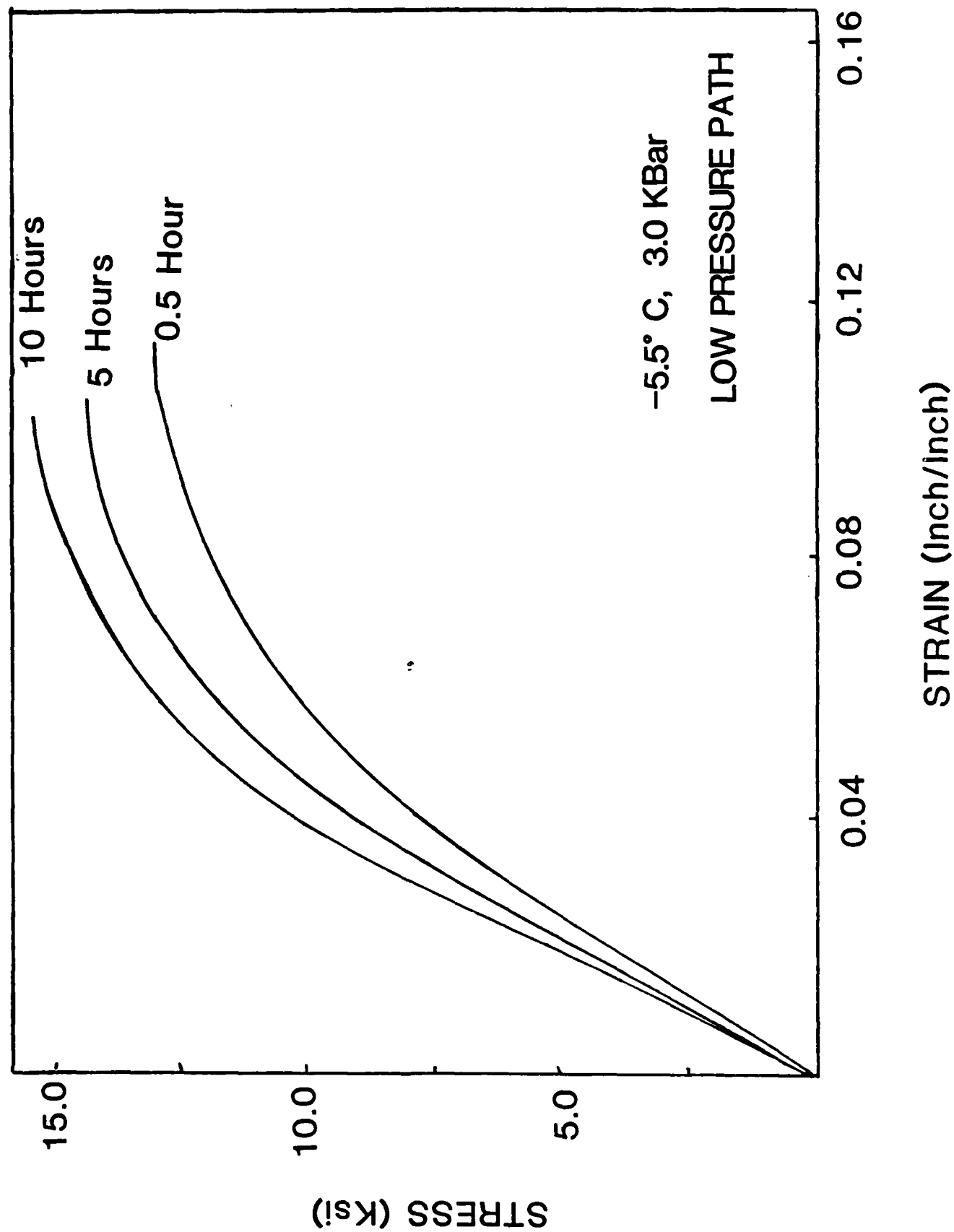
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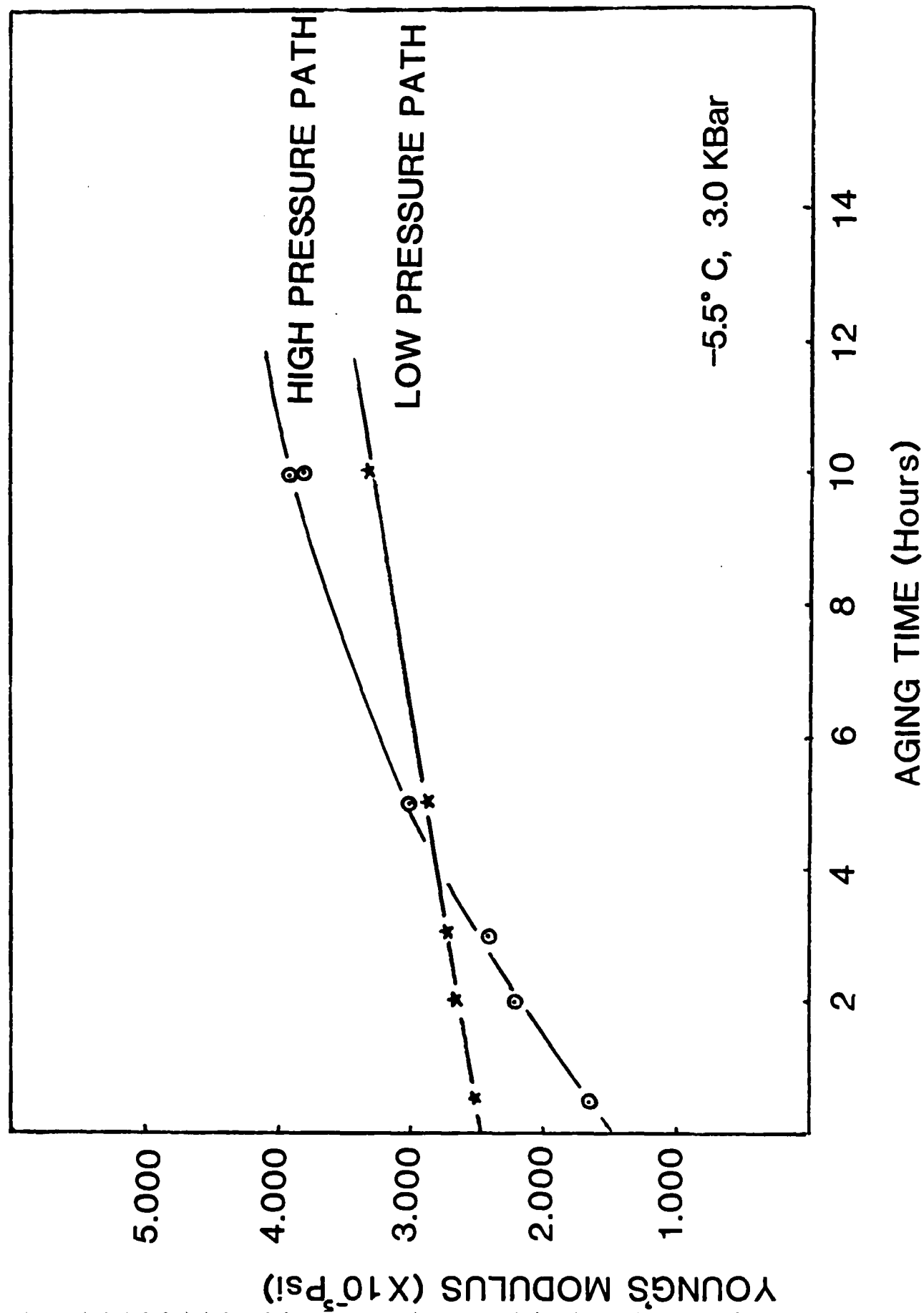
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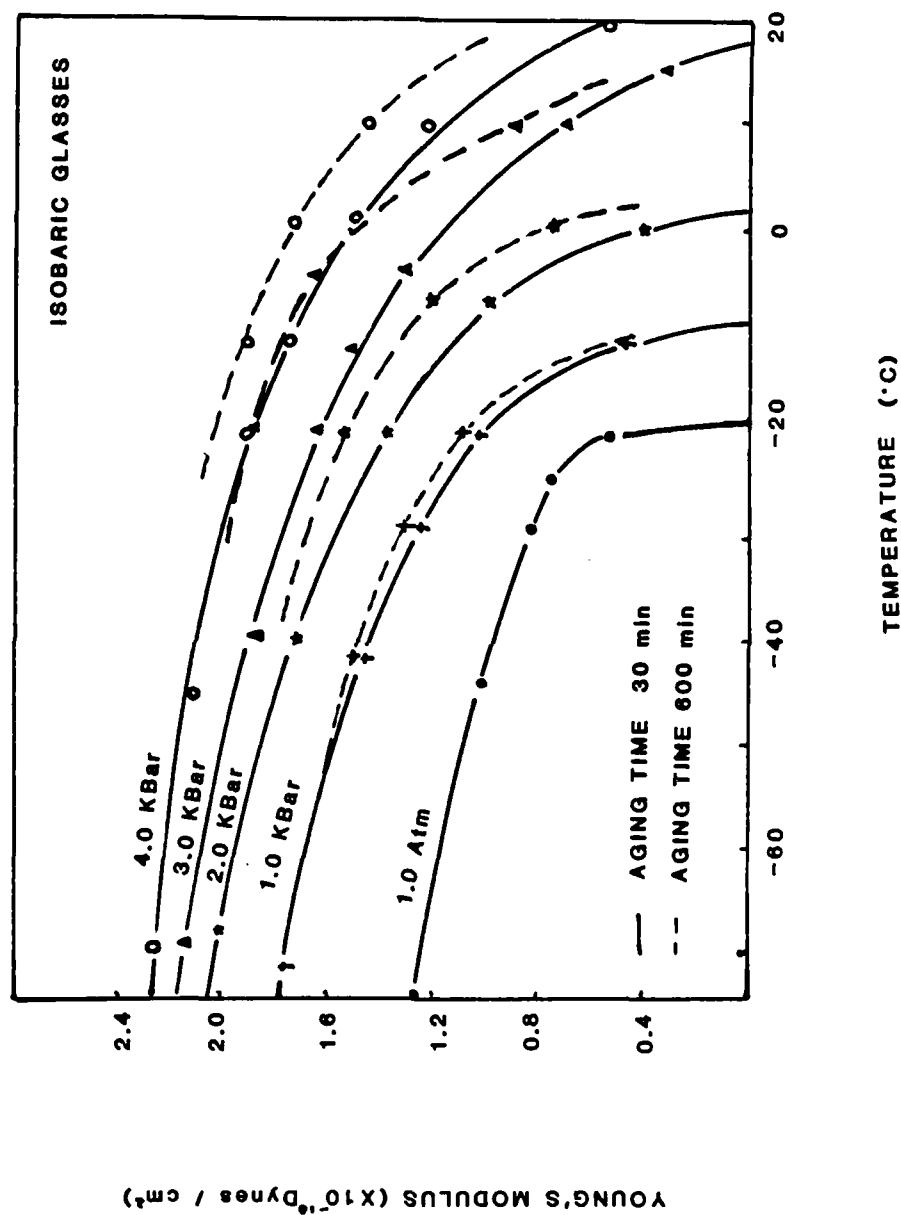
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- Fig. 2. Aging time dependence of compressive stress-strain curves at (3.0 KBar and -5.5°C), the state being reached by high pressure path.
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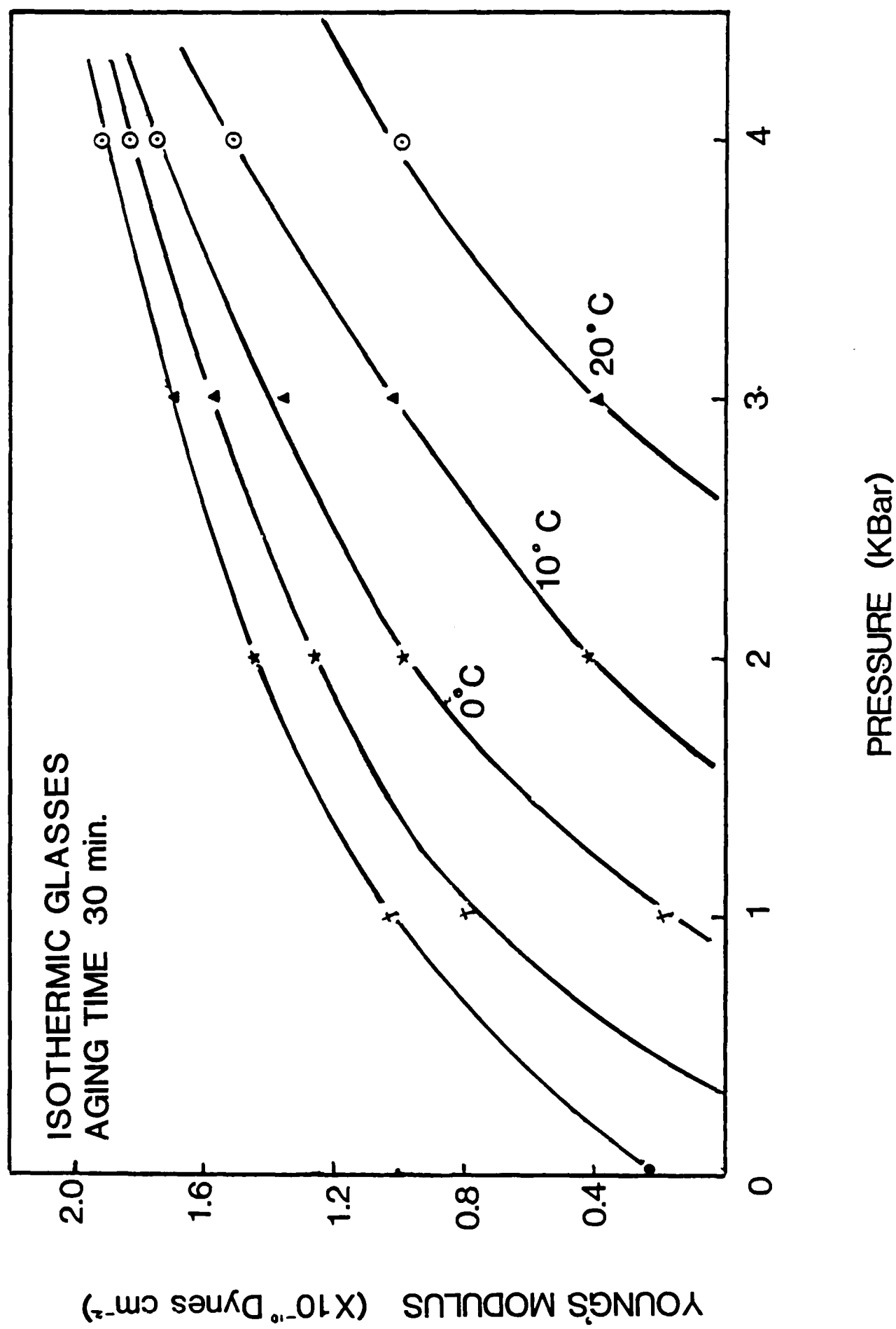


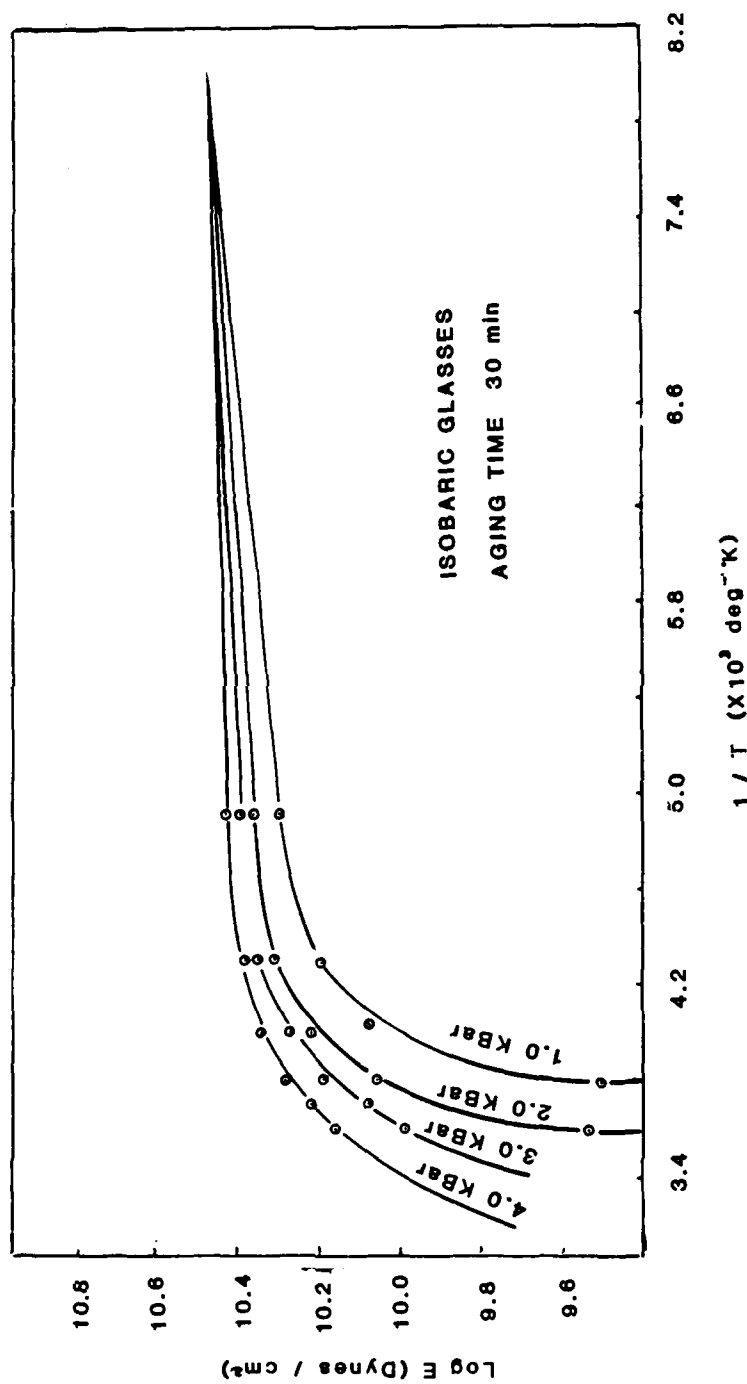


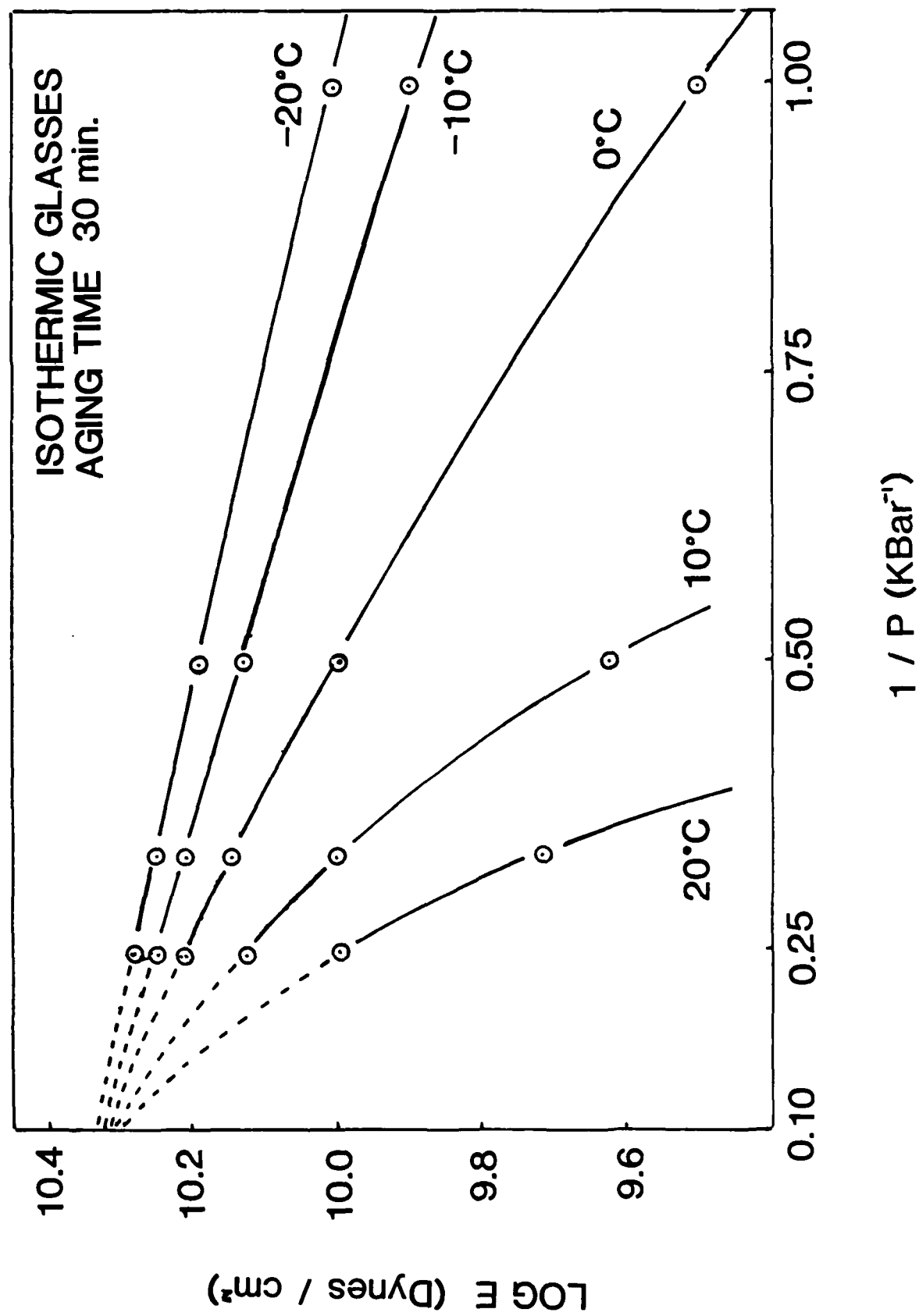


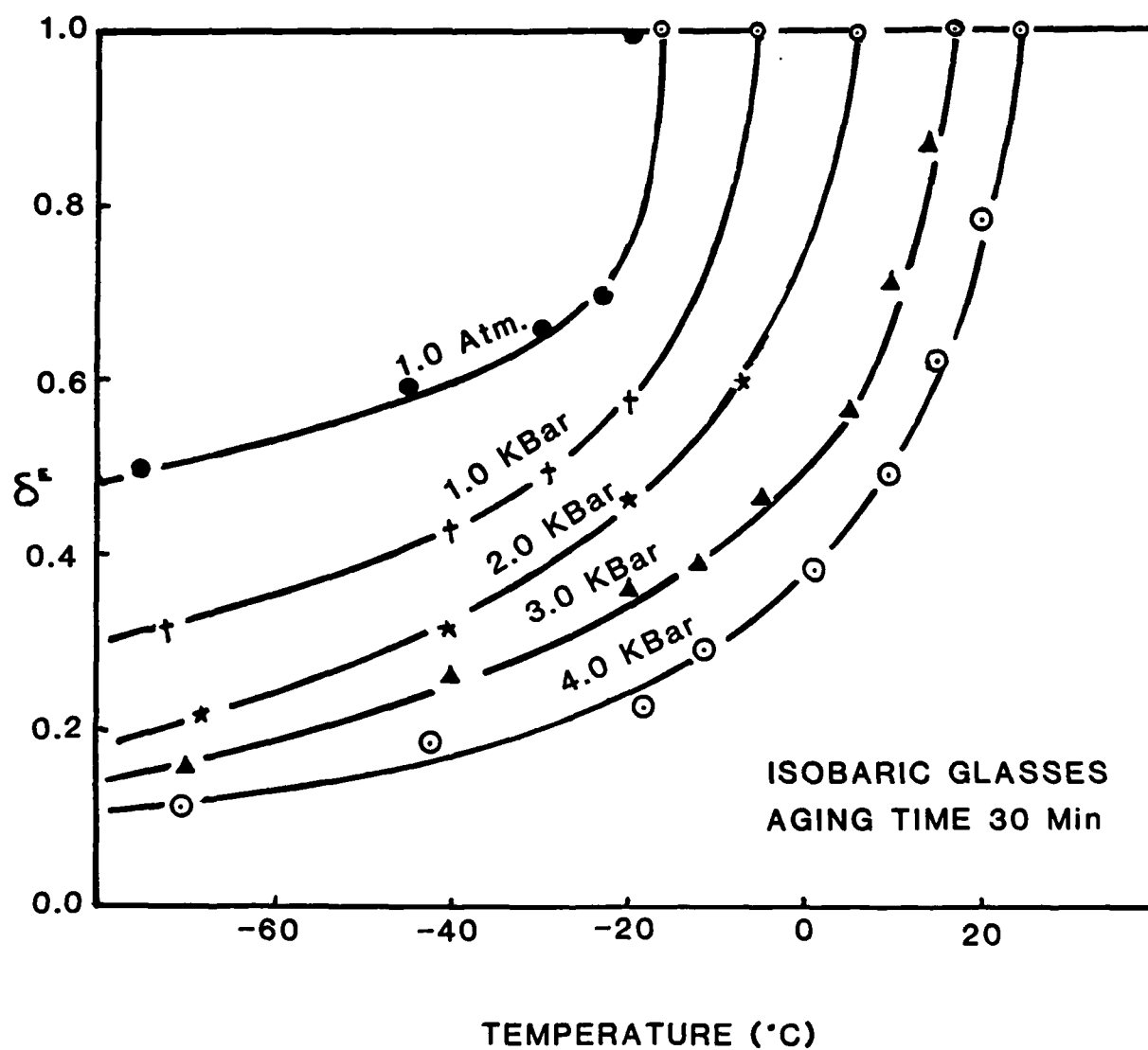


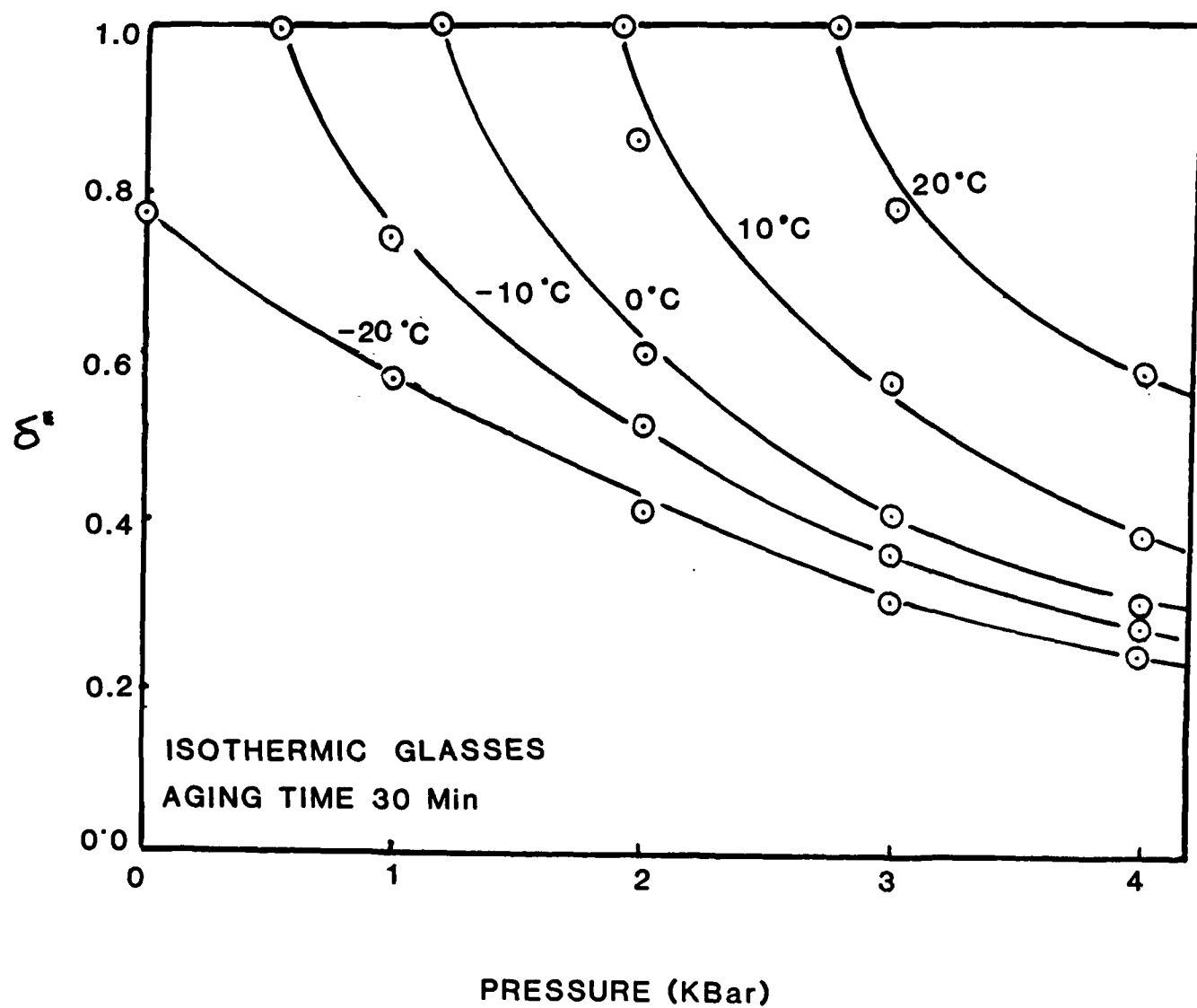


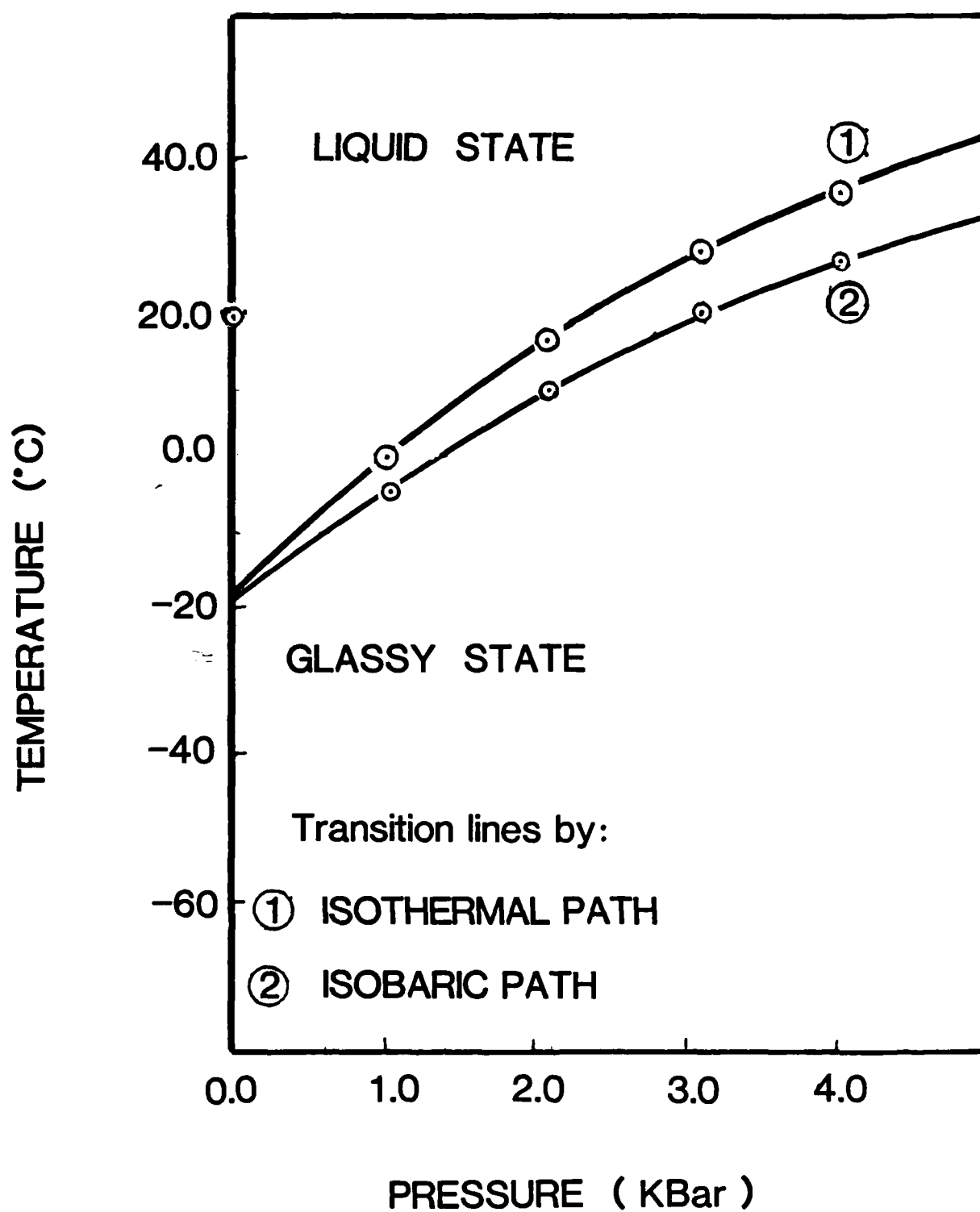




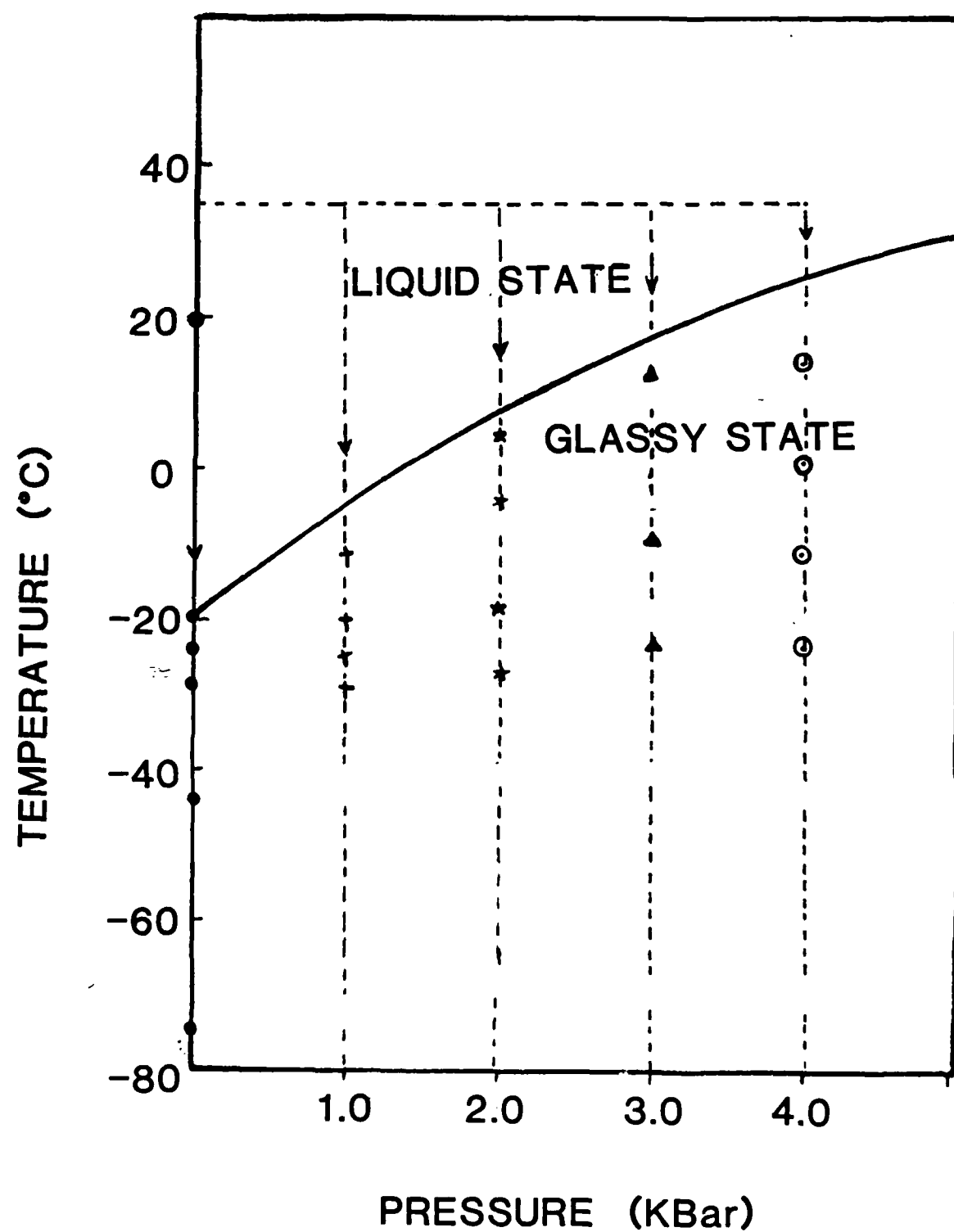




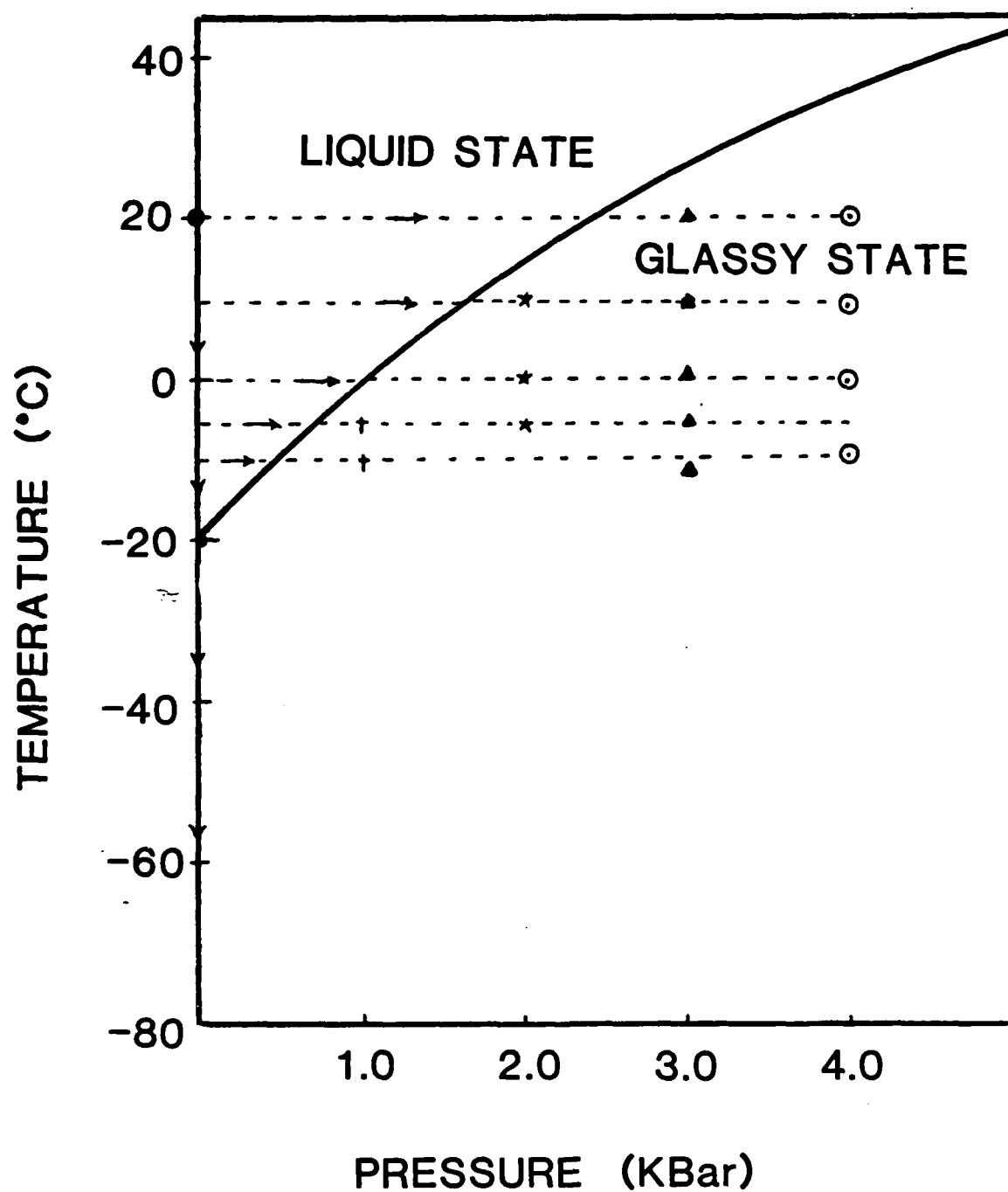


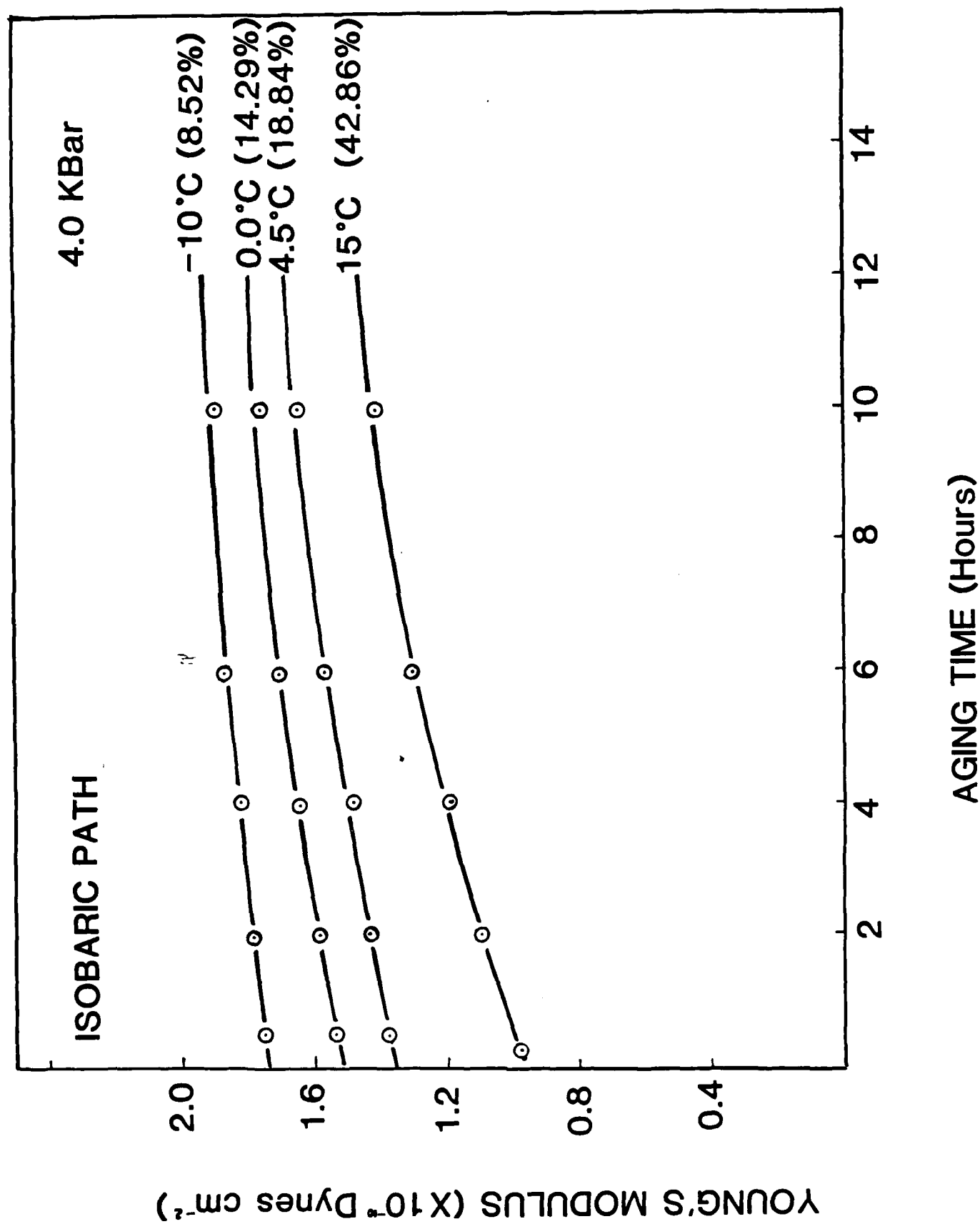


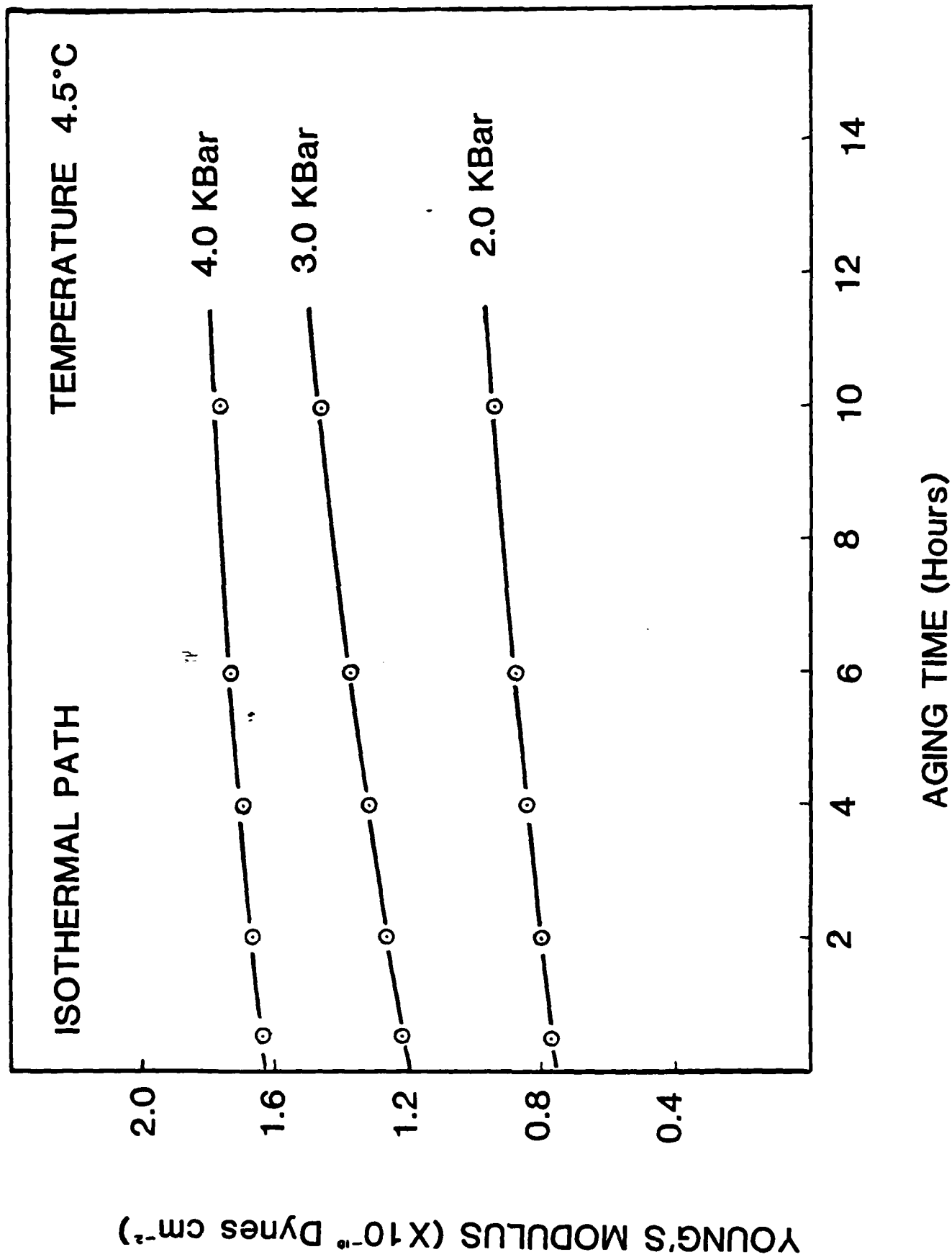
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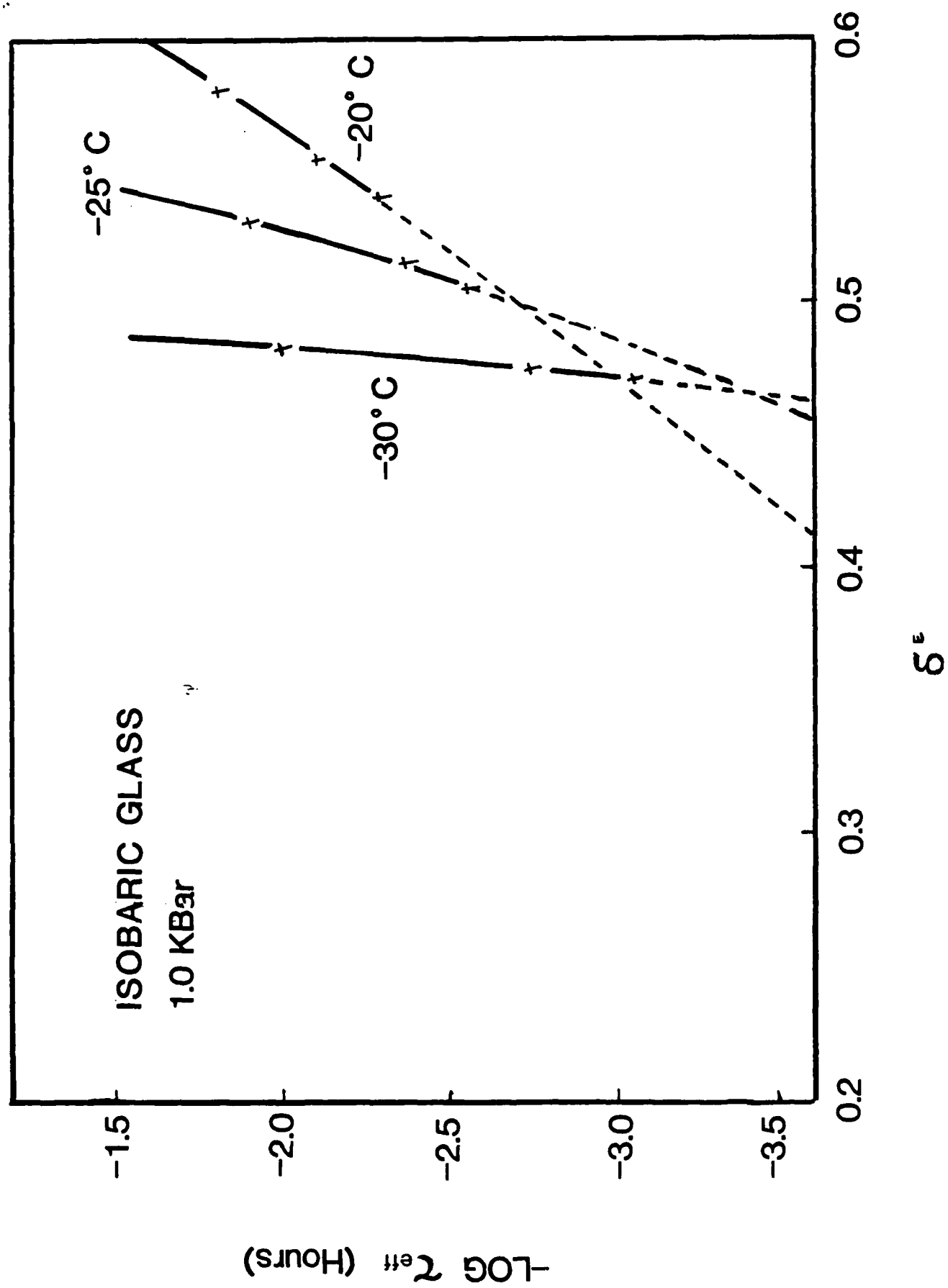


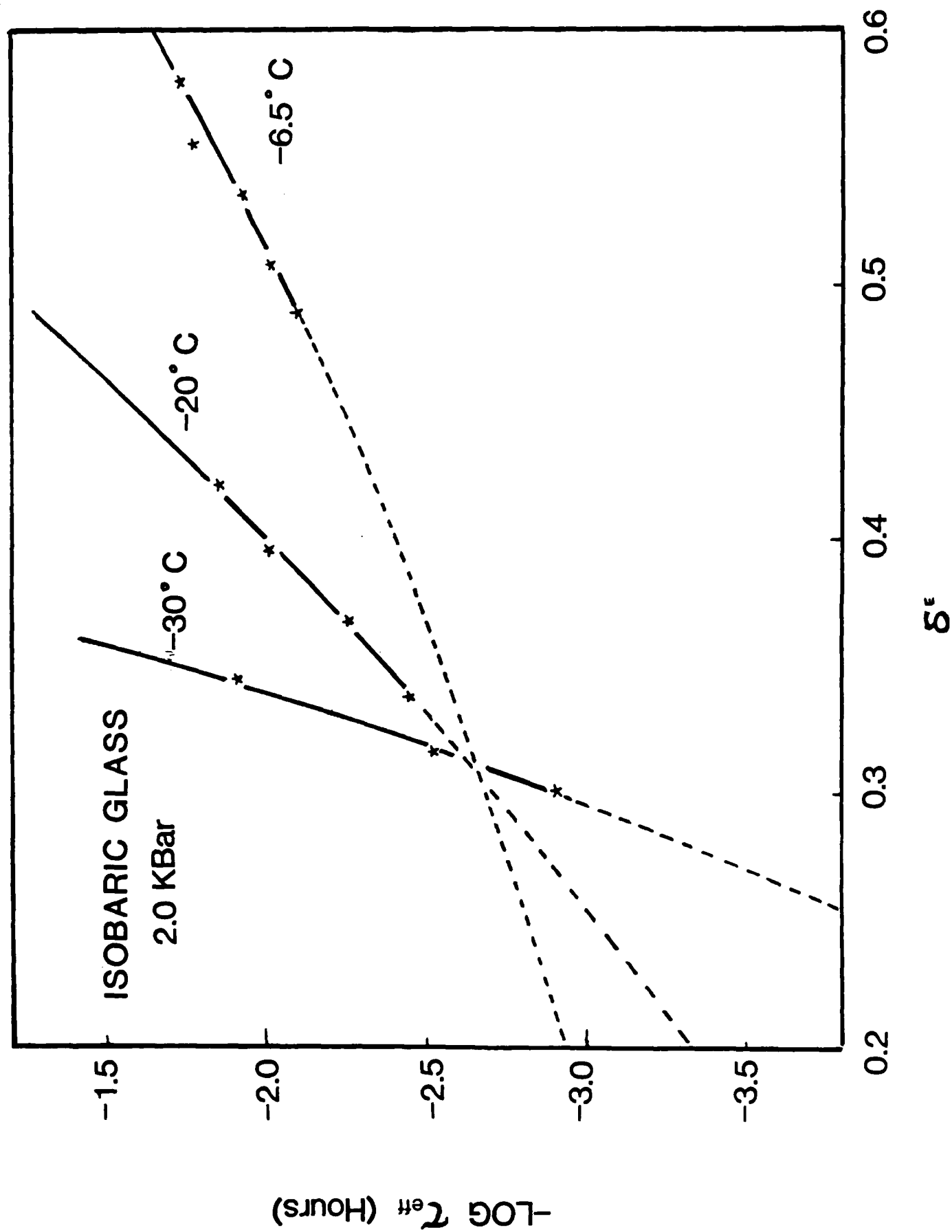
ISOTHERMAL PATH

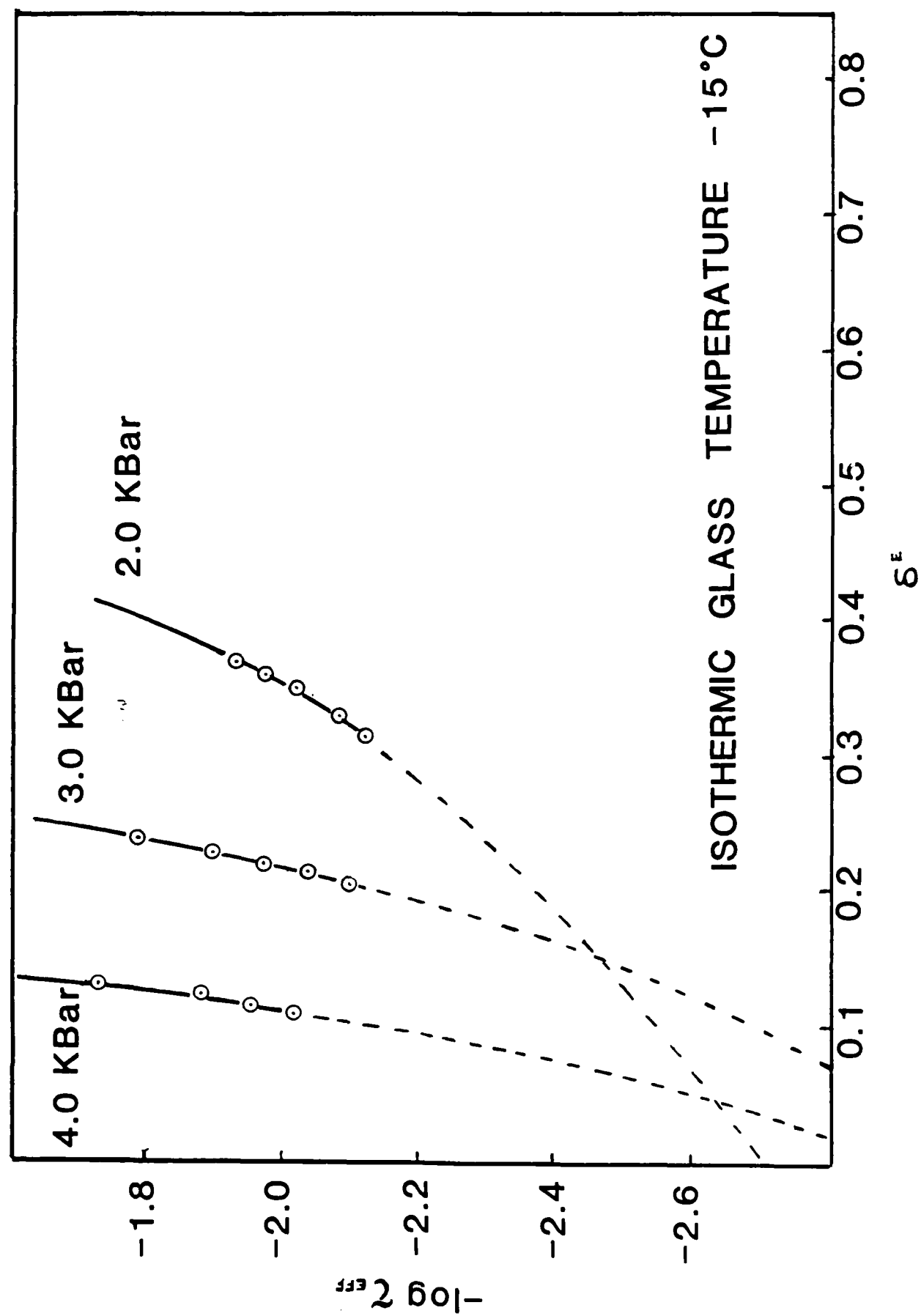












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