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THE DEPENDENCE OF DIELECTRIC RESPONSE OF AN ELASTOMER
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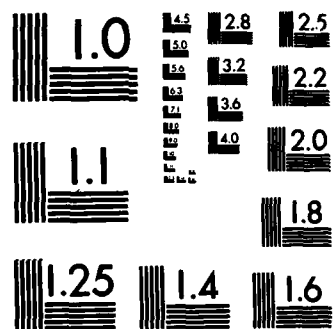
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20. Abstract (continued)

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THE DEPENDENCE OF DIELECTRIC RESPONSE OF AN ELASTOMER ON
HYDROSTATIC PRESSURE

by

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Synopsis

Dielectric methods have been employed to study the high pressure behavior of a polyurethane elastomer (Solithane 113) in the vicinity of its α -transition. The α -loss peak is shifted to higher temperatures and broadened somewhat with the application of hydrostatic pressure up to 6.4 kilobars. The slope of the T_{α} versus P, or dT_{α}/dP , obtained at low frequencies was found to be equal to dT_g/dP obtained by volumetric method. Moreover, it attained a non-zero limiting value at high pressures for each frequency tested (3-30,000 Hz) and the limiting value itself increased with increasing frequency from 10.5 oc/kbar at 3Hz to 18°C/Kb at 30,000 Hz. The activation enthalpy was found to be nearly constant over the pressure range tested, but the activation volume decreased with increasing pressure. The relation $(dT_{\alpha}/dP) = T(\Delta V^*/\Delta H^*)$ was shown to hold for the elastomer.

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Introduction

Dielectric methods have been used extensively to study the relaxation behavior of many types of polymeric materials [1]. To a lesser extent dielectric techniques have been used to study the effect of pressure on the relaxations of phase materials [2-9]. By varying pressure, temperature and frequency, one can separate the activation energy and activation volume contributions to the activation enthalpy [4]. Also, in light of theories concerning the effect of pressure on the glass transition, it is of interest to study the limiting effects which pressure has on transition temperature [10].

In amorphous polymers the α -transition is related to the glass transition in that both indicate changes in the long range mobility of the polymers. The effect of pressure has been shown to increase the T_g and the T_α . For some polymers the T_g increase linearly with increasing pressure [11,12]. For some others the rate of increase of the T_g with pressure decrease at higher pressures [12,14] suggesting that the T_g might reach a limiting value at high enough pressures. The glass transition temperature versus pressure curve for Solithane 113 shows curvature in the low pressure region; at higher pressures, however, a linear relation between T_g and pressure develops, so no high pressure limiting value of T_g is attained [15].

The contribution of the activation volume term, $P\Delta V^*$, to the activation enthalpy is generally small compared to the activation energy contribution, ΔE^* [2,5]. This results in activation enthalpy curves at various pressures which are nearly parallel to each other. The activation volume usually decreases more rapidly than the activation enthalpy as the pressure is raised [2].

It is the purpose of this paper to examine the pressure dependence of the α -transition in Solithane 113 elastomer. Activation enthalpies and volumes will be evaluated, and high pressure limiting values of (dT_α/dP) will be examined.

Experimental

Materials

Solithane 113 is a polyurethane elastomer made from the reaction of castor oil with tolylene diisocyanate. It is supplied in the form of resin and catalyst which can be mixed in varying ratios to achieve different amounts of cross linking. The material examined in this study was composed of equal volumes of resin and catalyst. The samples had a molecular weight between cross linking of 2000 g/mole [16] and a specific volume at atmospheric pressure of $0.97 \text{ cm}^3/\text{g}$. The glass transition temperature, T_g , and atmospheric pressure was -20°C .

Dielectric Measurements

Dielectric measurements were made at 3 Hz with a Piezotron Model U (Toyo Seiki Co., Japan) and from 3 Hz to 30,000 Hz with a lock-in amplifier (E.G. & G. Princeton Applied Research - Model 5204) using a current sensitive preamplifier. A sample ($\sim .05 \text{ cm}$ thick) was electroded on both sides and placed between brass electrodes and ceramic heating elements. The entire assembly was placed inside a high pressure vessel and surrounded by 5 cs. silicone oil as a pressure medium.

Sample temperature was measured and controlled using a chromel-alumel sheathed thermocouple which was imbedded in the brass anelectrode and was connected to a temperature controller and programmer (Eurotherm Corp.). Temperature was varied at a rate of one degree K per minute. At a pressure of 4 kilobars and a frequency of 30,000 Hz the dielectric loss (ϵ'') was shifted to a temperature which could not be reached by the ceramic heater, thus this point is missing from the data.

Dynamic Mechanical and Ultrasonic Measurements

At 3 Hz and at atmospheric pressure, a dynamic mechanical loss peak (E'') was obtained with the Piezotron. At 5 MHz and at various pressures, longitudinal

ultrasonic attenuation maxima were obtained using a Matec Pulse Modulator and Receiver (Model 6600). Both of these types of loss peaks were compared with the dielectric loss maxima for the α -relaxation.

Results and Discussion

Figure 1 shows the dielectric loss factor, ϵ'' , at a frequency of 3 Hz versus temperature at various pressures. The peak maximum shifts to higher temperatures as increasingly higher pressure is applied. At the same time, the height of the peak diminishes and the breadth of the peak increases both only slightly, as the pressure is raised. This broadening of the peaks indicates a widening of the distribution of relaxation times with pressure, although the area under the peak stays nearly constant.

In Fig. 2, the temperature of the α -peak maximum (measured at 3 Hz) is plotted against pressure. Also shown in the figure is the glass transition temperature (T_g), measured by means of volume changes as a function of pressure. This figure shows that the slopes of the two curves are the same over the entire pressure range; in other words, $dT_g/dP = [dT_\alpha(3\text{Hz})/dP]$. The temperature of the α -peak maximum is plotted against pressure at different frequencies in Fig. 3a. The shapes of the curves follow the same general trends as those in Fig. 2. The T_α initially increases parabolically until a pressure of two kilobar is reached. Above this pressure the slope, dT_α/dP , attains a constant value or limiting value over the rest of the pressure range. Furthermore, Fig. 3a shows that the limiting value of dT_α/dP increases with increasing frequency. Data on polymethyl acrylate shows a similar frequency (or relaxation time) dependence of dT_α/dP [7]. However, dT_α/dP for polyvinyl acetate is not dependent on frequency [6]. It has been demonstrated that the effect of frequency on dT_α/dP depends on the way in which dT_α/dP is measured [7].

Figure 3b shows limiting value of dT_α/dP versus log frequency taken from

Fig. 3a. At low frequencies it approaches a constant value and becomes equal to dT_g/dP as shown in Fig. 2. At high frequencies it appears to increase with $\log f$ at an increasing rate. If an upper limit of $\frac{dT_g}{dP}$ exists, it must occur at a frequency greater than 30,000 Hz.

Also shown in Fig. 3a are results from ultrasonic and dynamic mechanical (E'') measurements. The dynamic mechanical data was measured at 3 Hz and atmospheric pressure only. The ultrasonic attenuation maxima were measured at 5 MHz over the pressure range from atmospheric to 6 Kbars. Both of these tests reflect the response of the elastomer to a mechanical stimulus, whereas the dielectric measurements primarily indicate the response to an electric field of the polar parts of the elastomer segments. The 3 Hz E'' peak temperature at atmospheric pressure is about twenty degrees below the 3 Hz ϵ'' peak at that pressure. The E'' peak, however, coincides essentially with the T_g in Fig. 2, even though the "rate effect" influences the actual values of T_g determined by steady dynamic measurement and the slow cooling method in a complex manner in general.

In order for a segment to undergo a reorientation it must increase its free energy by the amount, ΔF^* [4]. The probability of undergoing a reorientation will be proportional to $\exp(-\Delta F^*/kT)$, and the frequency of maximum reorientation will be

$$f_{\max} = f_0 \exp[-\Delta F/kT] = f_0 \exp[-(\Delta E^* - T\Delta S^* + P\Delta V^*)/kT] \quad (1)$$

where ΔE^* , ΔS^* and ΔV^* are the activation energy, entropy and volume, respectively, in order for a reorientation to occur. These quantities can be evaluated for the α -relaxation from data on the α -loss peak maximum. The slope of a $\log f$ versus $1/T$ plot gives the activation enthalpy, $\Delta H^* = \Delta E^* + P\Delta V^*$; and the slope of a $\log f$ versus P plot gives the activation volume.

Replotting of the experimental data in Fig. 3a in the form of $\log f$ versus $1/T$ at various pressures and $\log f$ versus P at various temperatures for Solithane 113 are shown in Figs. 4 and 5, respectively. The slope of each curve in Fig. 4 increases as the temperature decreases. This is normal for WLF behavior [1], and, in fact, the curves through the data points are plots of the WLF equation. The curves at various pressures are nearly parallel with regard to shifts along the $1/T$ axis. This indicates the relatively small contribution of $P\Delta V^*$ to the activation enthalpy, ΔH^* . Values of ΔH^* at 3 Hz and various pressures are listed in Table 1. Values of the activation volume, ΔV^* are obtained from the slope of the curves in Fig. 5, according to:

$$\Delta V^* = -RT \left[\frac{\partial (\log f_{\max})}{\partial P} \right]_T \quad (2)$$

Along an isotherm ΔV^* decreases with increasing frequency, and at constant frequency ΔV^* decreases with increasing pressure.

Values of ΔV^* are given in Table 1 at 3 Hz and various pressures. It is seen that ΔV^* decreases with increasing pressure, though the rate at which it decreases becomes less as the pressure increases. The quantity $P\Delta V^*$ is also given in Table 1. This quantity increases at a decreasing rate with increasing pressure. Again it is noted that $P\Delta V^*$ is much smaller than ΔH^* , and for this reason the activation enthalpy curves (Fig. 4) are essentially parallel. Table 3 compares ΔV^* of Solithane 113 with that of other polymers for the α -relaxation.

For poly(vinyl chloride) it has been suggested that the following relationship holds [18]

$$T \frac{\Delta V^*}{\Delta H^*} = \left(\frac{\Delta \beta}{\Delta \alpha} \right) \quad (3)$$

where $\Delta\beta$ is the change in compressibility which occurs upon passing through the glass transition, and $\Delta\alpha$ is the corresponding change in thermal expansivity. The $\Delta\beta$ and $\Delta\alpha$ are themselves functions of pressure and temperature [15]. The left and right hand sides of Eq. 3 are compared in Table 2 for Solithane 113. The values of $\Delta\beta/\Delta\alpha$ were obtained from previous PVT measurement [15]. Values of $\Delta\alpha$ were obtained by subtracting the thermal expansivity below T_g , α_g , from that above T_g , α_l , for a sample cooled continuously through T_g . $\Delta\beta$ was obtained by measuring the compressibility caused by small increments of pressure as the polymer was cooled through T_g along an approximate isobar. Table 2 lists the measured values of $\Delta\alpha$ and $\Delta\beta$. As can be seen from the data, $\Delta\beta/\Delta\alpha$ is about twice $T(\Delta V^*/\Delta H^*)$. It has been observed for many polymers that $\Delta\beta/\Delta\alpha$ is about twice dT_g/dP [11,12,14]. This has also been observed for Solithane [15] and suggests that the following holds instead of Eq. 3:

$$T \frac{\Delta V^*}{\Delta H^*} = \left[\frac{dT_g}{dP} \right] \quad (4)$$

where $dT_g/dP = dT_g/dP$ for low frequency measurements. The values from the right hand side of Eq. 4 are also shown in Table 2. The agreement is much better than for Eq. 3.

The agreement between (dT_g/dP) and $T(\Delta V^*/\Delta H^*)$ is not surprising. Equation 4 can be obtained in a similar way to the first Ehrenfest relation obtained from volume considerations. At a constant frequency:

$$df = 0 = \left[\frac{\partial \log f}{\partial P} \right]_T dP + \left[\frac{\partial \log f}{\partial (1/T)} \right]_P d(1/T) \quad (5)$$

from which

$$\left(\frac{dT\alpha}{dP}\right) = \frac{\frac{\partial \log f}{\partial P} T}{\frac{1}{T^2} \left(\frac{\partial \log f}{\partial \left(\frac{1}{T}\right)}\right)_P} = T \frac{\Delta V^*}{\Delta H^*} \quad (6)$$

since $(\partial \log f / \partial P)_T = -\Delta V^* / RT$ and $[\partial \log f / \partial (1/T)]_P = -\Delta H^* / P$.

The first Ehrenfest relation [6],

$$\frac{dTg}{dP} = \frac{\Delta \beta}{\Delta \alpha} \quad (7)$$

results from considering the volume change which occurs across a thermodynamic second order transition. Since the experimentally observed glass transition is influenced by kinetic factors (meaning the rate at which volumetric tests are performed) Eq. 7 does not hold for T_g except under conditions where the kinetic factors are intentionally avoided [9]. For the frequencies tested, the dielectric loss maxima do not change their location with the heating or cooling rate used ($1^\circ\text{K}/\text{min}$). This is due to the fact that the α -peak represents a response in the equilibrium rubbery state above T_g . It should be noted that for very low frequency tests (D.C. conductivity measurements) the location of the loss maximum does depend on annealing time, indicating that at low enough frequencies glassy state relaxations will come into play [17].

The qualitative observation from Fig. 3 that $(dT\alpha/dP)$ increases with increasing frequency is also predicted by Eq. 4. Figures 4 and 5 show that both ΔH^* and ΔV^* decrease with increasing frequency. ΔH^* decreases more rapidly than ΔV^* , so the left hand side of Eq. 4 will increase with increasing frequency. Therefore, Eq. 4 predicts an increase in $(dT\alpha/dP)$ with increasing frequency.

Conclusions

Hydrostatic pressure induced the dielectric α -loss peak to shift to higher temperatures and the amount of the shift depends upon the test frequency used. At 3 Hz it shifted from 2°C at atmospheric pressure to 53°C at 4 Kbar while at 3 KHz it changed from 27°C to 90°C for the same pressures. The rate of the shift with pressure, or $\frac{dT_\alpha}{dP}$ at 3 Hz was equal to the $\frac{dT_g}{dP}$ obtained from volumetric measurements [15]. The $\frac{dT_\alpha}{dP}$ attained a nonzero limiting value at a certain pressure level and the limiting value increased with the test frequency, viz. from 10.5°C/Kbar at 3 Hz to 18°C/Kbar at 30 Hz. The pressure at which the limiting value is attained decreased with increasing frequency as expected.

The activation enthalpy (ΔH^*) determined from Fig. 4 is not a constant value along each isobar but is a decreasing function of $\log f$. For instance, at atmospheric pressure, it varied from 77.9 Kcal/mol at atmospheric pressure to 70.0 Kcal/mol at 4 Kbar. The same relative changes appear to occur (see Fig. 4) along each isobar studied. The activation volume (ΔV^*) determined from Fig. 5 is also a constant along an isotherm but is a decreasing function of $\log f$. It varied for 3 Hz from 143.7 cm³/mol at 1 Kbar to 87.4 cm³/mol at 4 Kbar. However, the quantity $P\Delta V^*$ increased from 0 Kcal/mol at atmospheric pressure to 4.8 Kcal/mol at 4 Kbar (see Table 1). The relationship $\frac{dT_\alpha}{dP} = T \frac{\Delta V^*}{\Delta H^*}$ (Eq. 4), agrees well with the experimental data for Solithane 113 for the temperature, pressure, and frequency ranges studied.

Acknowledgment

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TABLE 1

All Values for $f = 3 \text{ Hz}$

<u>P</u> <u>(kb)</u>	<u>ΔH^*</u> <u>(k cal/mole)</u>	<u>ΔV^*</u> <u>(cm³/mole)</u>	<u>$P\Delta V^*$</u> <u>(k cal/mole)</u>
0	77.9	---	0
1	73.9	143.7	2.0
2	73.0	120.3	3.3
3	74.8	101.1	4.1
4	70.0	87.4	4.8

TABLE 2

All Values for $f = 3 \text{ Hz}$

<u>P</u> <u>(kb)</u>	<u>T_α</u> <u>(°K)</u>	<u>$T_\alpha \left(\frac{\Delta V^*}{\Delta H^*} \right)$</u> <u>(°K/Kb)</u>	<u>$\Delta\alpha$</u> <u>(°K⁻¹ × 10⁴)</u>	<u>$\Delta\beta$</u> <u>(Kb⁻¹ × 10²)</u>	<u>$\Delta\beta/\Delta\alpha$</u> <u>(°K/Kb)</u>	<u>(dT_α/dP)</u> <u>(°K/Kb)</u>
0	275	---	4.9	1.80	37	18
1	292	13.6	2.8	0.78	28	15
2	305	12.0	2.4	0.53	22	12
3	316	10.2	1.7	0.29	17	11
4	326	9.7	1.3	---	---	10.5

TABLE 3

<u>Polymer</u>	<u>ΔV^* (cm³/mole)</u>	<u>Ref.</u>
Solithane 113	~175	Extrapolated from data in Table 1
PVC	321	12
PVA _C	139	6
Amorphous PET	518	9

Legends for Figures

- Figure 1 - Dielectric loss constant (α -peak) versus temperature at various pressures indicated (Test frequency 3 Hz).
- Figure 2 - Transition temperature T_g , volumetric) and α -peak (T_α , dielectric, 3 Hz (versus pressure.
- Figure 3 - (a) Temperature of dielectric α -peak versus pressure at various frequencies. Also shown temperature of ultrasonic (5 MHz) absorption peak versus pressure and temperature of loss modulus (E'' at 3 Hz) at atmospheric pressure.
(b) Limiting dT_α/dP versus log frequency
- Figure 4 - Log f - dielectric α -peak versus $1/T$ at various pressures. (---) WLF equation.
- Figure 5 - Log f - dielectric α -peak versus P at various temperatures.

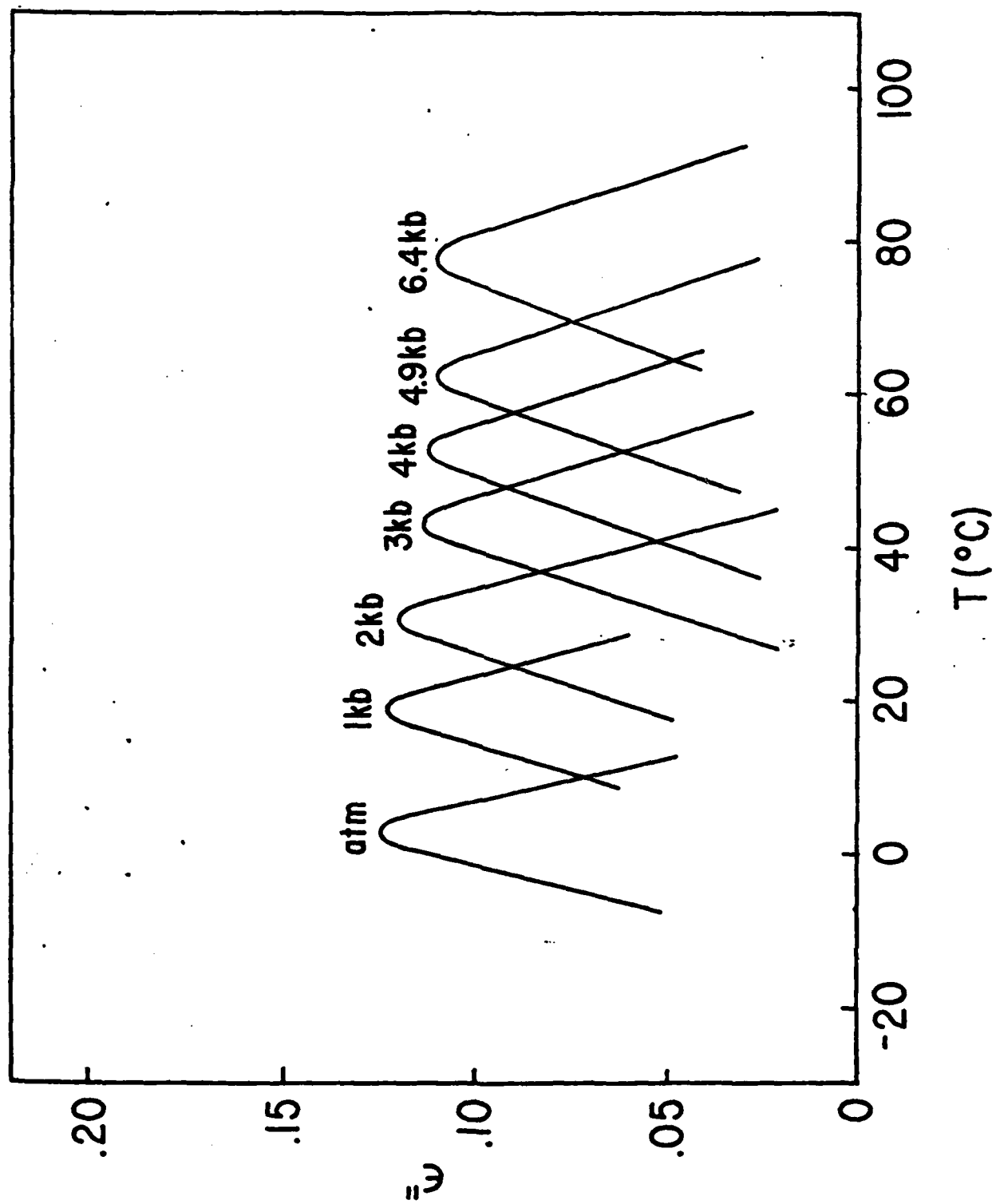


Fig. 1

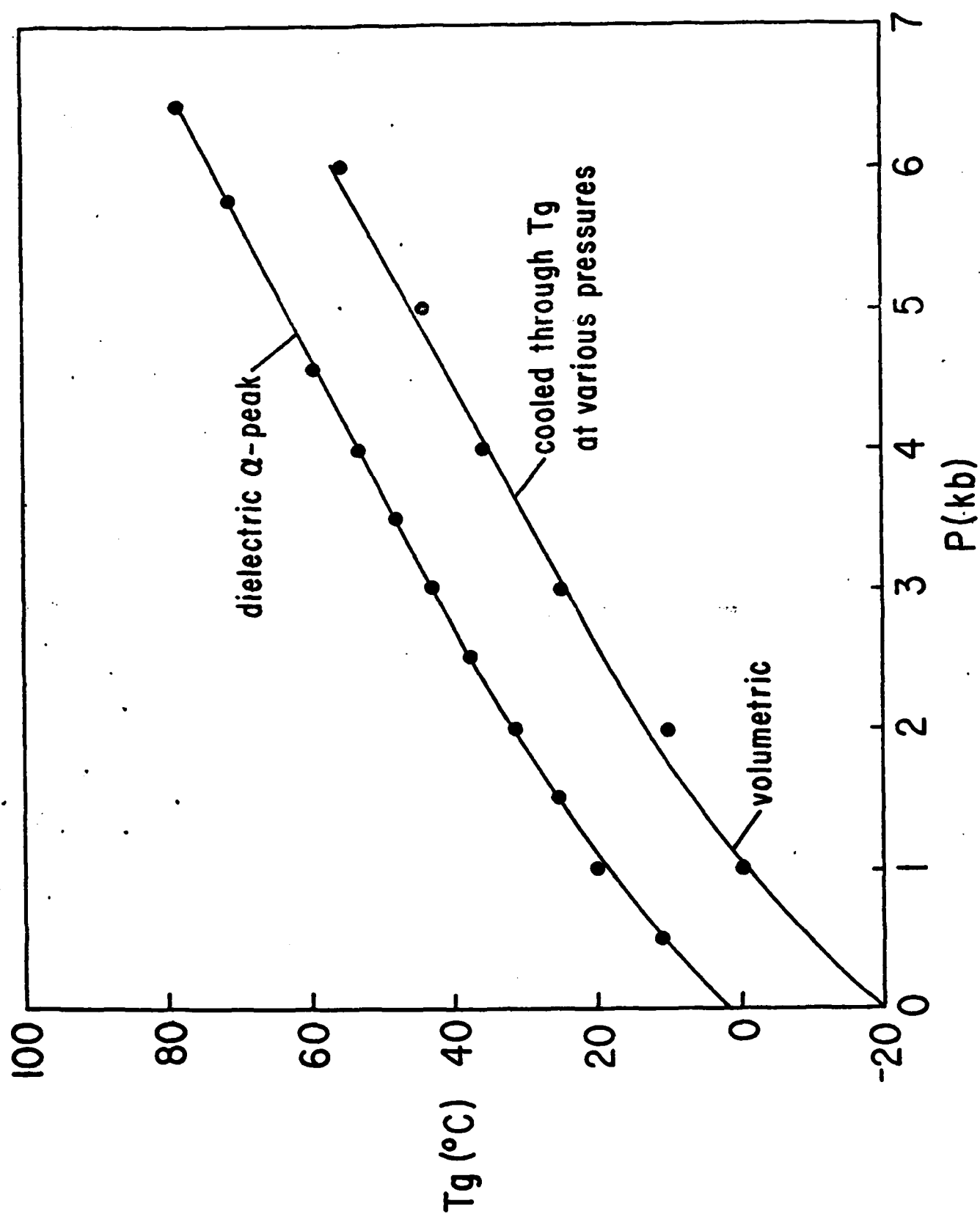


Fig. 2

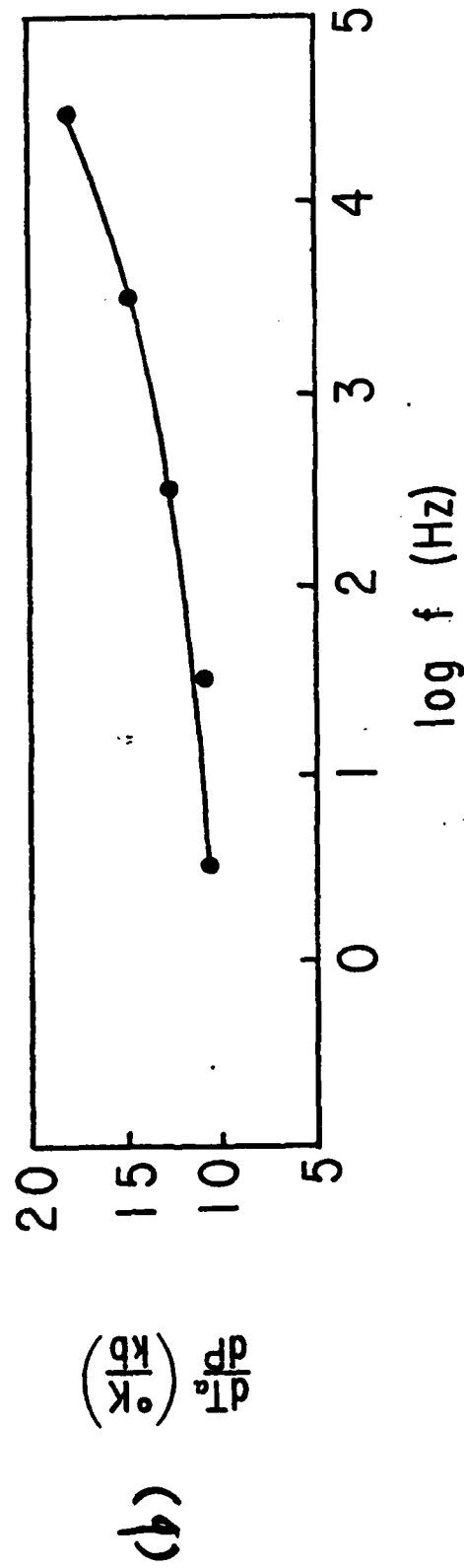
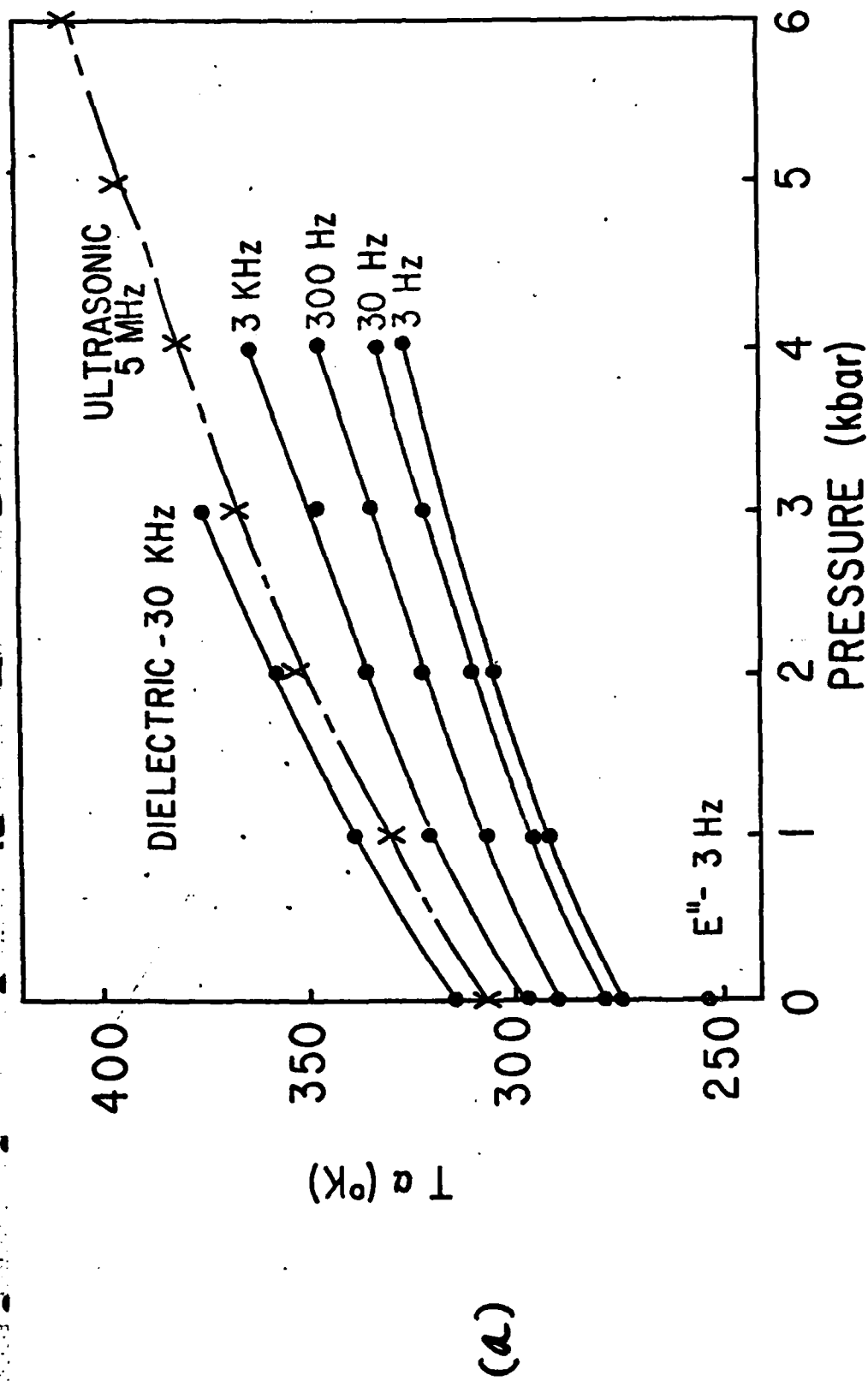


Fig. 3

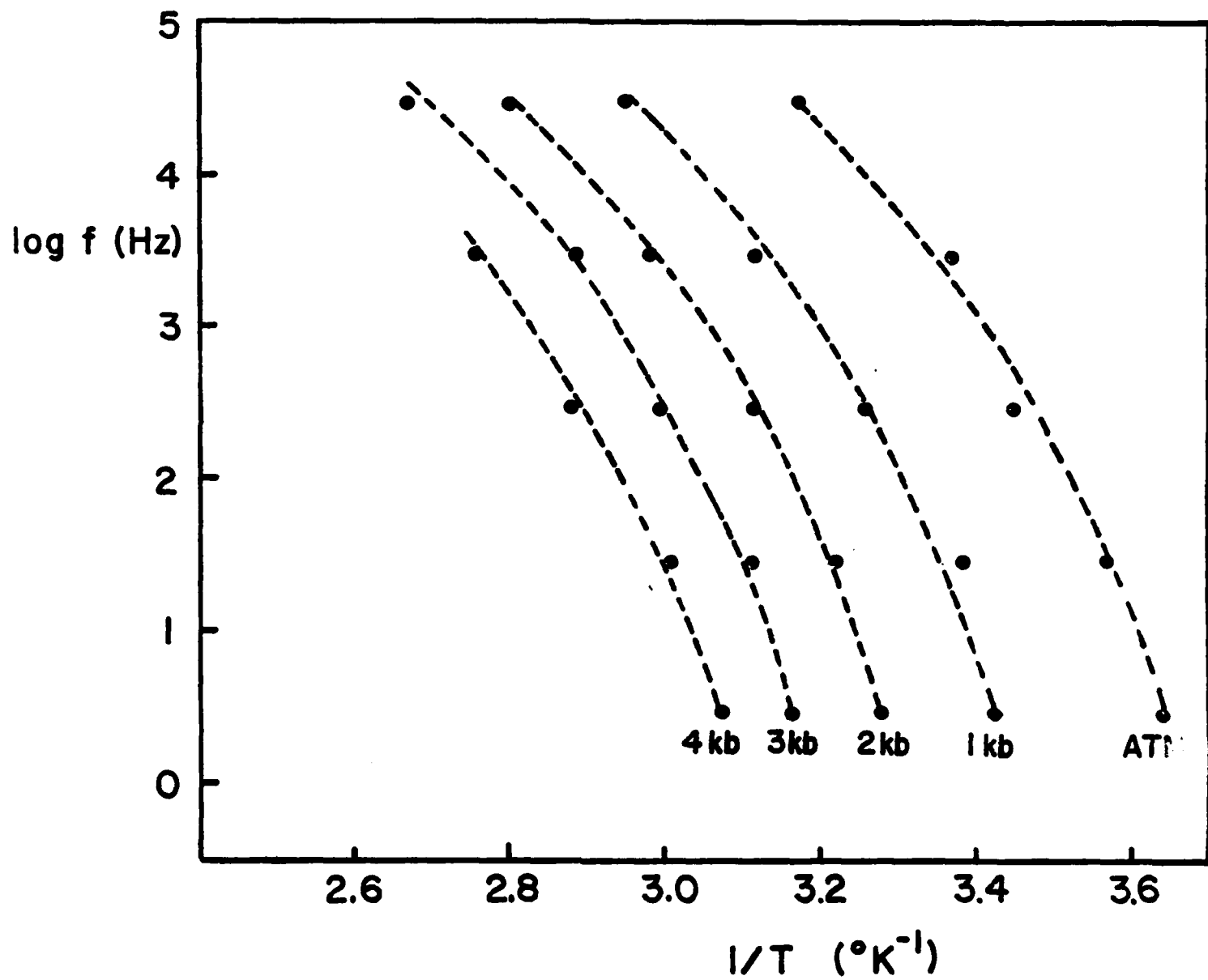


FIG. 4

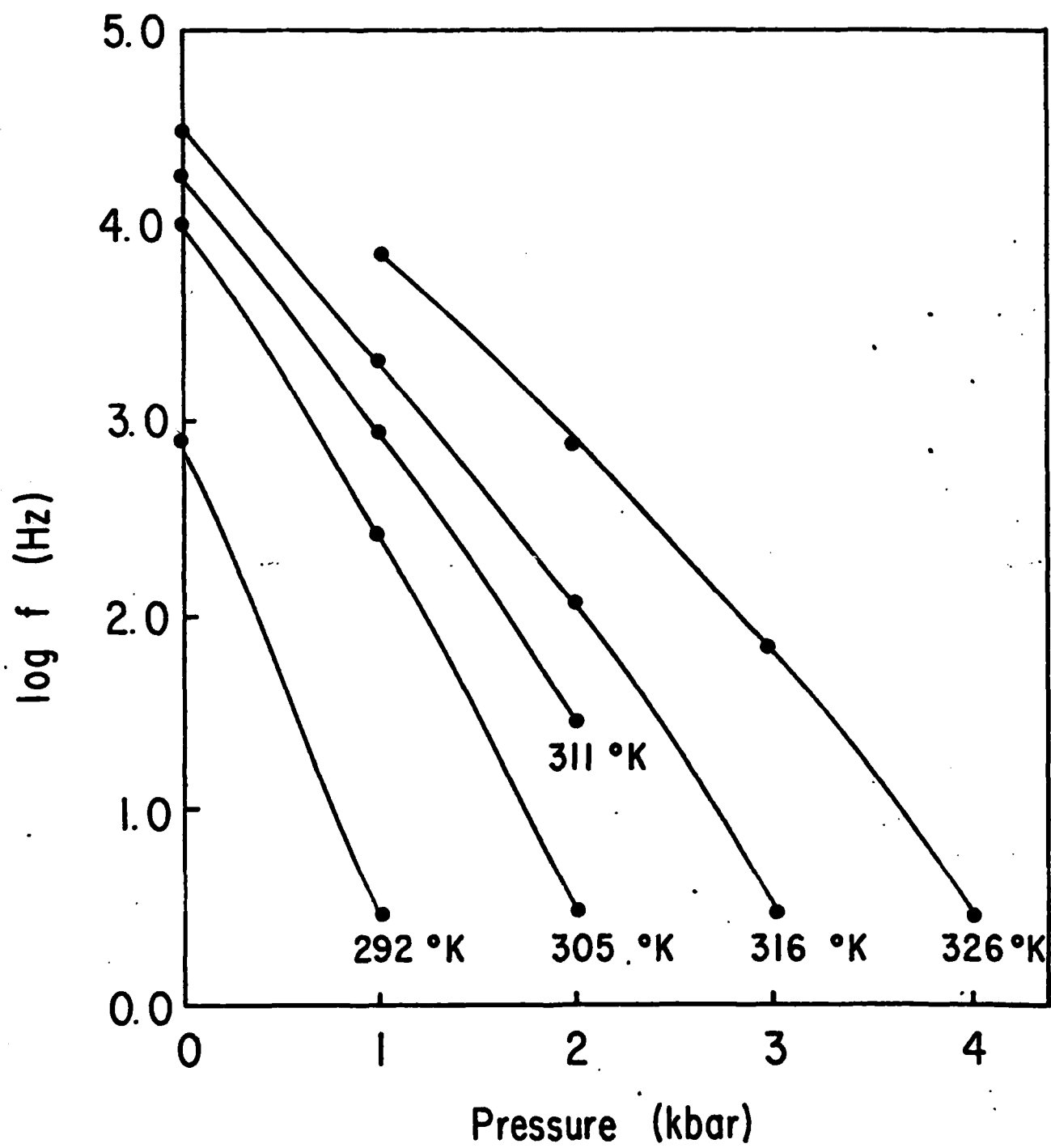


FIG. 5

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