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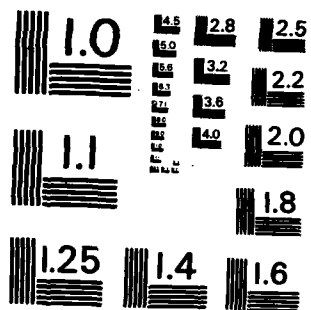UNCLASSIFIED   TR-2 N00014-82-K-0608   F/G 11/9   NL

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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temperature scaling parameters, respectively. P^*, V^*, and T^* are found to obey
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fitting the data to the hole theory, it is found that the hole fraction, $1-y$,
can be used as an ordering parameter to describe the pressure dependence of T_g.

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PRESSURE-VOLUME-TEMPERATURE STUDIES OF A POLYURETHANE

ELASTOMER

by

D. L. Quested

K. D. Pae, J. I. Scheinbeim, and B. A. Newman

PRESSURE-VOLUME-TEMPERATURE STUDIES OF A POLYURETHANE ELASTOMER

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Experimental pressure-volume-temperature data for a polyurethane elastomer above T_g are fitted to equation of state theories. The cell and hole theories, as applied to polymer liquids, both represent the data fairly well for appropriate choices of P^*, V^*, and T^*; the characteristic pressure, volume, and temperature scaling parameters, respectively. P^*, V^*, and T^* are found to obey a semi-empirical equation which holds for a large number of polymers, and, by fitting the data to the hole theory it is found that the hole fraction, $1 - y$, can be used as an ordering parameter to describe the pressure dependence of T_g.

I.   Introduction

Equation of state theories based on the cell theory of liquids have proven successful at predicting pressure-volume-temperature (PVT) data of polymer liquids. The essence of the theories involves the evaluation of the partition function, Z, for a set of s-mer molecules. These molecules are placed on a quasicrystalline lattice and the equation of state is obtained from the condition, $P = kT(\partial logZ/\partial V)_T$. The cell theory for polymer liquids results in the following equation of state[1]:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = 6 + (1 - 2^{1/6}\tilde{V}^{-1/3})^{-1}$$

$$+ 7.227(1.001\ \tilde{V}^{-2} - 2.409)^{-1}$$

$$+ (\tilde{V}^{-2}/\tilde{T})(1.011\tilde{V}^{-2} - 1.2045) \tag{1}$$

in which $\tilde{P} = P/P*$, $\tilde{V} = V/V*$, $\tilde{T} = T/T*$,

where P*, V*, and T* are the characteristic pressure, volume, and temperature scaling parameters. These quantities are characteristic of the structure of the polymer segments and so are constant for a particular polymer.[2]

The hole theory is derived from the cell theory by introducing holes into the quasilattice on which the cell theory is based. The hole theory, therefore, contains an additional variable, the fraction of occupied sites, y, or, alternatively, the hole fraction, 1 - y. The value of y for each state is obtained by minimizing the free energy of the state with respect to y. The resulting equation of state for the hole theory is[3]:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = [1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1}$$

$$+ (2y/\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045] \tag{2}$$

and the minimization of the free energy with respect to y results in

$$(s/3c)[(s - 1)/s - y^{-1}\ln(1 - y)]$$

$$= [2^{-1/6}y(y\tilde{V})^{-1/3} - 1/3][1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1}$$

$$+ (y/6\tilde{T})(y\tilde{V})^{-2}[2.409 - 3.003(y\tilde{V})^{-2}], \tag{3}$$

where 3 c is the number of volume dependent degrees of freedom of the s-mer molecule. It is usually assumed that s/3c is unity and that s is very much greater than 1 thereby eliminating these quantities from Eq. 3.[4]

To fit Eq. 1 to experimental data, the quantities P*, T*, and V* must be evaluated. T* and V* are obtained from the atmospheric pressure (P=0) isobar data, then P* is obtained from high pressure data. The same quantities can be evaluated in a similar manner for the hole theory, but in each case Eqs. 2 and 3 must be solved iteratively.

II. Experimental and Materials

Since the experimental procedure used for making PVT measurements on Solithane has been given previously,[5] only a brief outline will be given here.

Changes in volume were measured in a high pressure dilatometer using a linear variable differential transformer (LVDT). Measurements were made over a 0-6 kilobar pressure range from -40° to 120° C. During each measurement, pressure was held constant, and temperature was varied at 1°C/min. This was the only temperature rate studied in these experiments. Measurements were performed by both heating and cooling the specimens.

The materials used in these studies was a polyurethane elastomer (Solithane 113, Thiokol Chemical Corp.) which has an atmospheric pressure glass transition temperature of -20°C. Wide angle x-ray studies on the elastomer at pressures up to 10 kbar indicated that no crystallinity exists at atmospheric pressure nor is any induced at higher pressures.

III. Results and Discussion

The PVT data for Solithane 113 are shown in Fig. 1 plotted as specific volume versus temperature at pressures from atmospheric to 6 kilobars. The predictions of the cell and hole theories are also shown in the rubbery state (above T_g). For the cell theory, the calculated values of V*, T*, and P* are as follows:

$$V* = 0.844 \text{ cm}^3/\text{g}, \quad T* = 7870^\circ\text{K}, \quad P* = 20.7 \text{ kbar}.$$

For the hole theory the same quantities have the following values:

$$V* = 0.889 \text{ cm}^3/\text{g}, \quad T* = 8300^\circ\text{K}, \quad P* = 10.6 \text{ kbar}.$$

As mentioned earlier, T* and V* were obtained from the atmospheric pressure isobar. P* was obtained only from data at 1 kbar. A better fit could have been obtained by using data at higher pressures; still the fits of both theories are quite good as far as the volumetric data itself is concerned. The hole theory does a somewhat better job of predicting the thermal expansivities.

A semiempirical correlation has been put forward relating the quantities P*, V*, and T* obtained from the hole theory. This equation is

$$\ln(P*V*/T*) = 1.319 - (3/2.01)(T* \times 10^{-4}). \tag{4}$$

Equation 4 has been demonstrated to hold approximately for a large number of polymer and oligomer systems.[2,6] For the values obtained for Solithane P*V*/T* = 1.135. The right side of Eq. 4 predicts a value for P*V*/T* of 1.083.

The value of Eq. 4 is that it allows the prediction of PVT properties on the basis of atmospheric pressure data only. Using P*V*/T* = 1.083 and the measured values of V* and T* a value of P* = 10.1 kbars is obtained. This differs by less than 5% from the measured value of P*. Although Eq. 4 proves quite satisfactory for Solithane, it has been demonstrated that it does not hold for a number of polymer systems[7,8] and that the applicability of Eq. 4 is likely only within certain ranges of values of V*, P*, and T*.[9]

Figure 2 shows the thermal expansivities from the Solithane data along with predictions from the cell and hole theories. At low pressures the two theories provide upper and lower bounds to the data. At high pressures, however, the data agrees well with the hole theory.

Figure 3 shows values of the hole fraction, 1 - y, versus temperature at various pressures. These values were obtained from Eqs. 2 and 3. The x's and dots indicate glass transition temperatures for two types of glass formation processes.[5] The x's represent the usual glass transition temperatures, meaning the T_g obtained by cooling from the rubbery state at constant pressure. The physical states of glasses formed at different pressures will be different[4,10] which will be reflected in differences in density at atmospheric pressure.

The dots in Fig. 3 mark the glass transition temperatures of glasses formed only at atmospheric pressure. The glass transition temperature is determined by pressurizing the glass then heating through the glass transition region. The glass transition temperature for the atmospheric pressure glass will be referred to as T_g^*. We have followed the convention of McKinney and Goldstein[10] where our atmospheric pressure glass is the same as their constant formation glass at 1 bar. Because the atmospheric pressure glass has only one formation pressure, it corresponds to only one thermodynamic state (e.g., it corresponds to only one surface in PVT space). This is the reason for the observation that $dT_g^*/dP = \Delta\beta/\Delta\alpha$ whereas $dT_g/dP < \Delta\beta/\Delta\alpha$. The quantities $\Delta\beta$ and $\Delta\alpha$ are the changes in compressibility and thermal expansivity, respectively, upon crossing the transition region. For a single glassy state making a transition into a single liquid state, the equality must hold.

T_g^* is always greater than T_g because a glass formed at atmospheric pressure will have a higher specific volume than a glass formed at higher pressures. Since the glass transition is defined by the point of intersection of the specific volume curves above and below the transition, the glass with the higher specific volume will have the higher apparent glass transition temperature. The equilibrium state (above T_g) is, of course, constant.

Figure 4 shows the hole fraction, $1 - y$, at the respective glass transition temperatures plotted against pressure. The hole fraction was obtained from Eqs. 2 and 3. Both Figs. 3 and 4 show that the hole fraction is constant at T_g^* for the glass with a constant formation pressure. The hole fraction at T_g, however, decreases with increasing pressure. Similar results have been obtained for other polymers.[4,7] So $(1 - y)$ reflects the change in the glassy state due to variations in formation pressure. For this reason it has been suggested that the hole fraction can be identified with a single ordering parameter necessary to describe the glass transition. If this is the case, then the following will result[4]:

TABLE I. Comparisons of the pressure dependence of the glass transition

P (kbar)	dT_g/dP	dT_g^*/dP	$\Delta\beta/\Delta\alpha$	RHS of Eq. 5	RHS Eq. 6
0	19.0	33.0	37.5	23.5	19.5
1	15.0	29.0	28.0	16.0	17.0
2	12.0	23.5	21.0	10.5	12.5
3	10.5	--	18.0	7.5	--

$$\frac{dT_g}{dP} = \frac{\Delta\beta}{\Delta\alpha} + \left(\frac{dT_g}{dy}\right) \left(\frac{dy}{dP}\right) . \tag{5}$$

The quantities dT_g/dP and dy/dP can be evaluated from Figs. 3 and 4 respectively. All of these quantities are compared in Table I. Also shown in Table I is a comparison between dT_g/dP and dT_g^*/dP similar to Eq. 5:

$$\frac{dT_g}{dP} = \frac{dT_g}{dP} + \left(\frac{dT_g^*}{dy}\right) \left(\frac{dy}{dP}\right) . \tag{6}$$

This comparison is made since dT_g^*/dP should equal $\Delta\beta/\Delta\alpha$. dT_g^*/dP can be measured with greater accuracy than $\Delta\beta/\Delta\alpha$, and as can be seen from Table I Eqs. 5 and 6 hold within experimental errors.

IV. Conclusions

The cell and hole theories of polymer liquids have been applied to PVT data for a polyurethane elastomer. Both theories fit the PVT data quite well with the hole theory providing a somewhat better correlation with the thermal expansivity, α, as a function of pressure.

The characteristic pressure, temperature, and volume: P*, T*, and V*, respectively, were evaluated, and for the hole theory it was found that the characteristic scaling parameters followed a useful, semiempirical correlation. This correlation permits an estimation of the pressure-volume-temperature response of Solithane from volume-temperature data alone. The value of such a correlation is particularly useful for Solithane which has been studied as a model elastomer to be used as a viscoelastic material standard.[11]

Lastly, it has been shown that the hole fraction, $1 - y$, can serve as an ordering parameter to describe the pressure dependence of the glass transition. This is in agreement with studies on other polymer systems.[4]

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Acknowledgment

Legends for Figures

Figure 1 - Specific volume versus temperature at various pressures.

Figure 2 - Thermal expansivities as a function of pressure.

Figure 3 - Hole fraction, 1-y, versus temperature at various pressures.

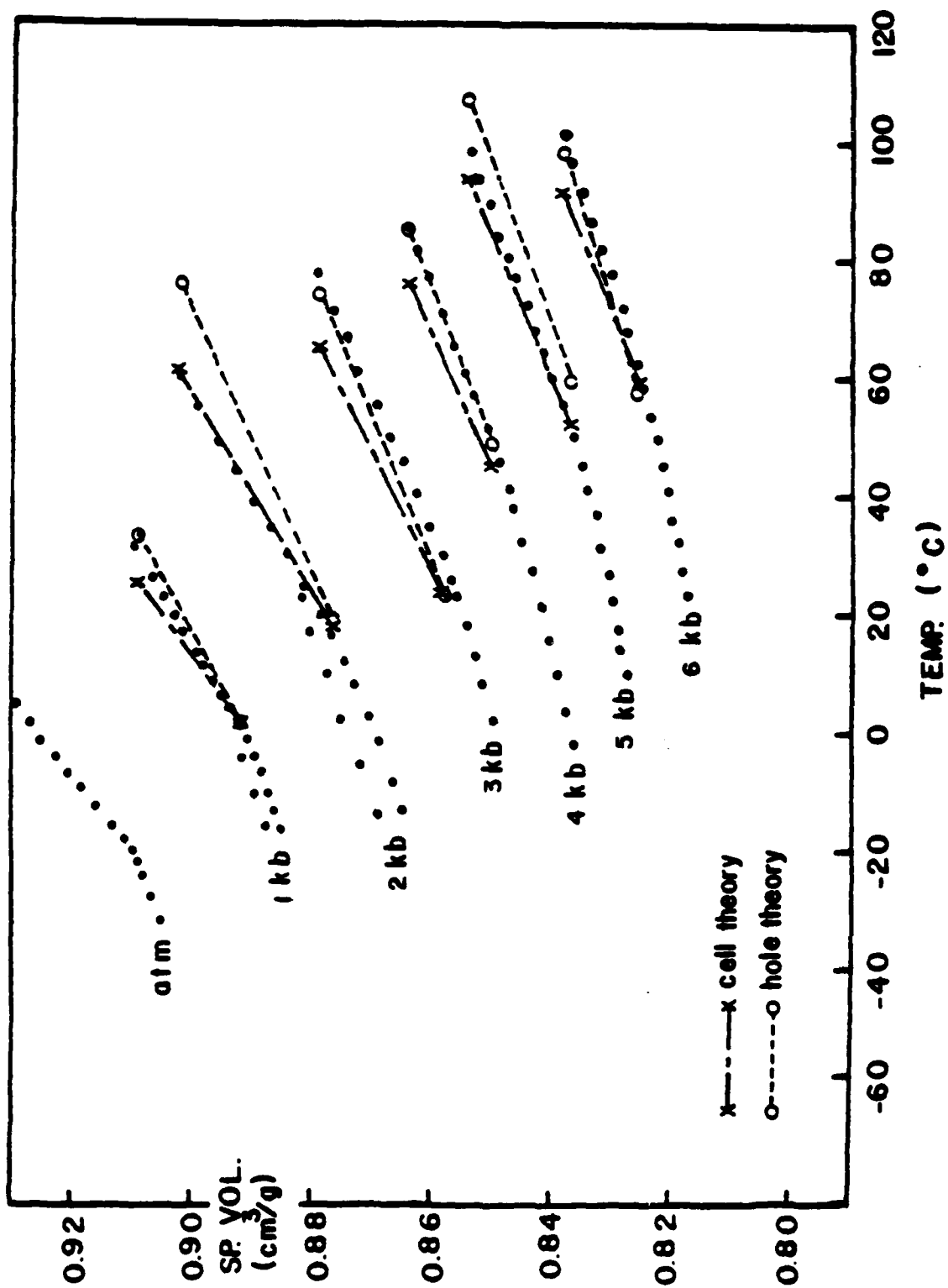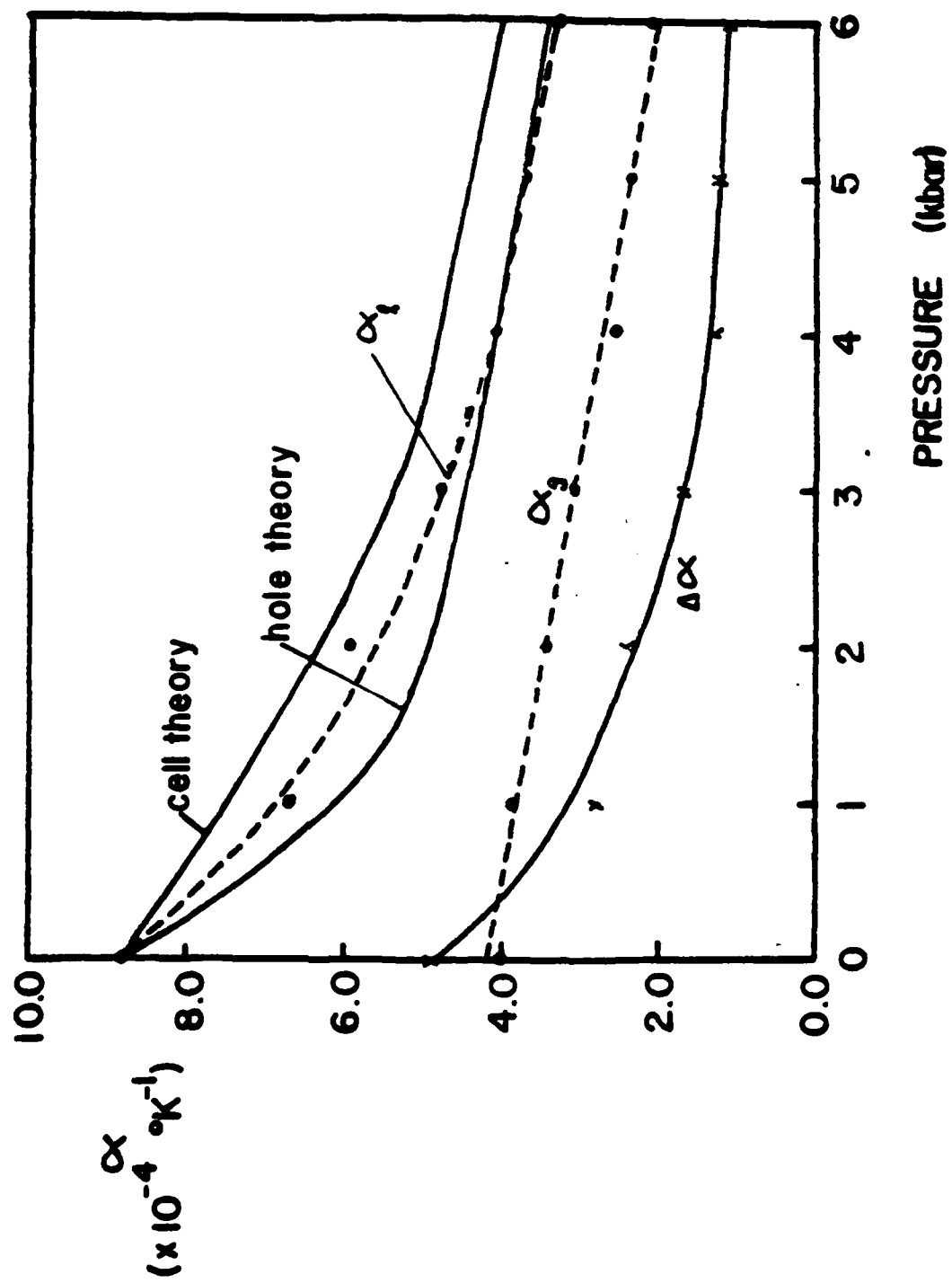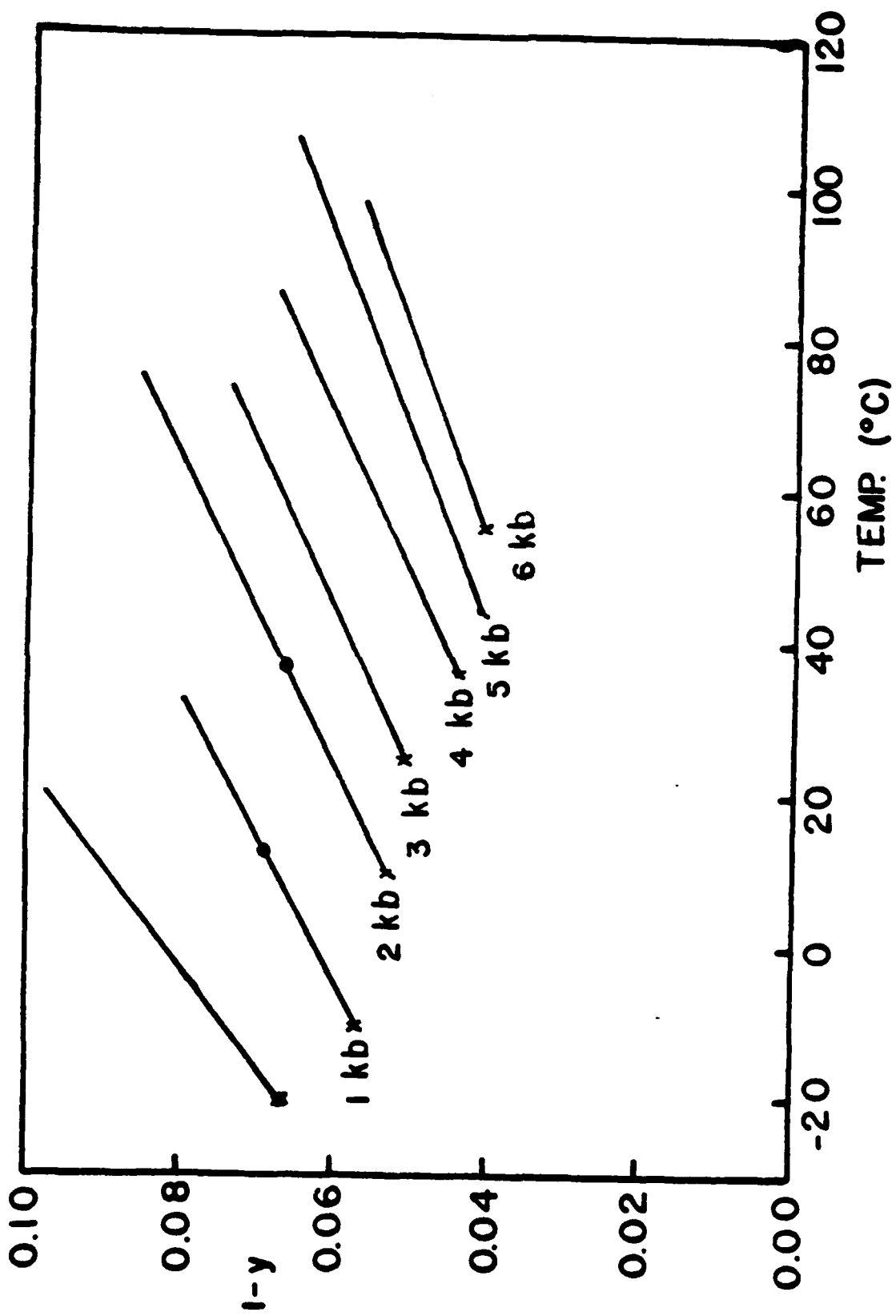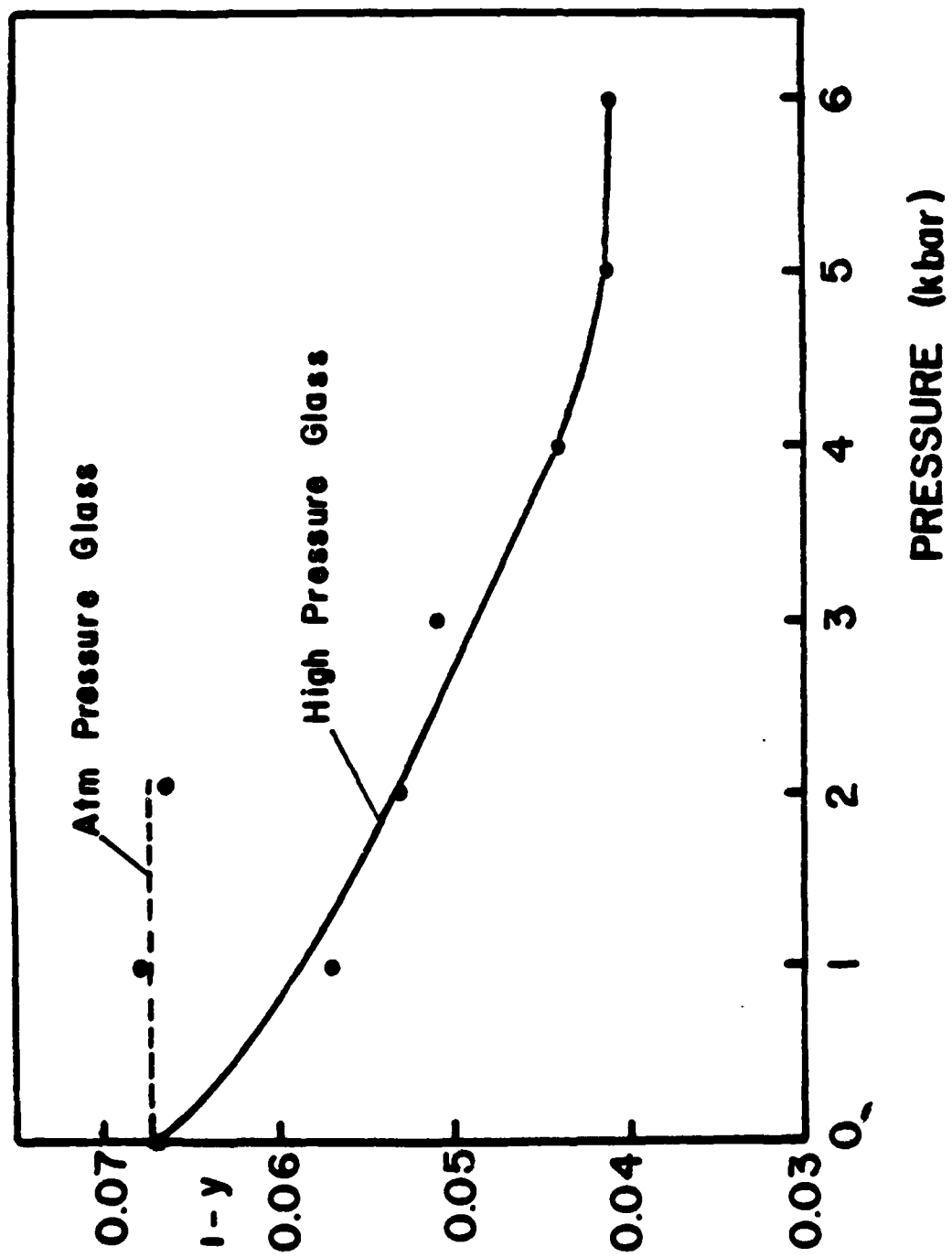Figure 4 - Hole fraction, 1-y, at T_g and T_g^* versus pressure.

FIG. 1

α
(×10⁻⁴ °K⁻¹)

cell theory

hole theory

α_ℓ

α_3

$\Delta\alpha$

PRESSURE (kbar)

FIG. 2

FIG. 3

Atm Pressure Glass

High Pressure Glass

1-y

0.07
0.06
0.05
0.04
0.03

0   1   2   3   4   5   6

PRESSURE (kbar)

FIG. 4

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