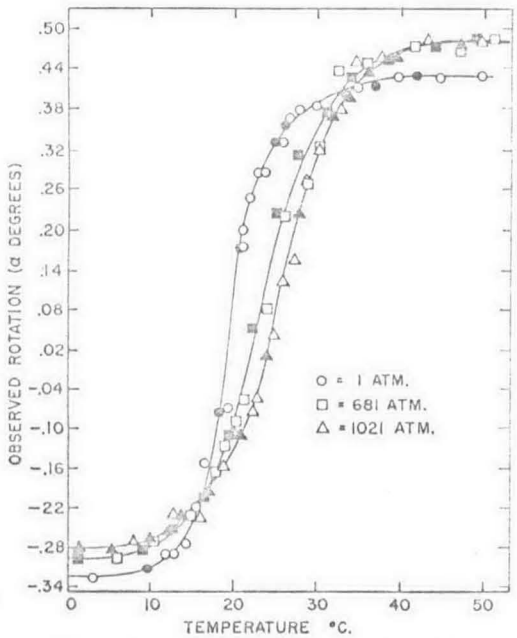

Figure 4. Effect of temperature on observed rotation at 589 mμ and various pressures for a 4.330 wt. % solution of PBG in a 76:24 vol. % solvent of DCA and EDC, respectively.

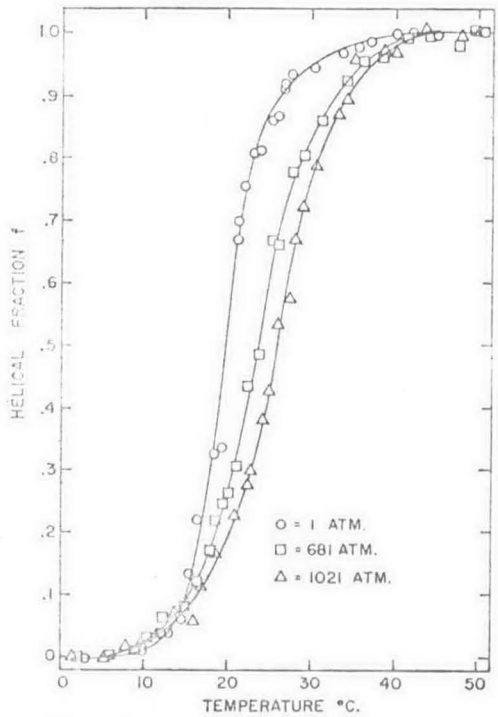

Figure 5. Effect of temperature on helical fraction (f) of PBG at various pressures.

adequately determined without resorting to special methods.

The effect of pressure on fraction f noted in Figure 5 yields an average value of -4.6×10^{-4}/atm. for $(\partial f/\partial P)_{T,f=1/2}$ with T approximately 296°K. Using Zimm and Bragg's value for σ (2×10^{-4}), the ΔV_m° is found to be -0.6 ml./mole of monomer or -0.003 ml./g., which substantiates the difficulty encountered in the attempt of the direct determination. It should be noted that ΔV_m° is negative which means that the folded configuration has a slightly larger partial molar volume than does the unfolded form.

If Zimm's value of σ is used with the experimental evaluation of $(\partial f/\partial T)_{P,f=1/2}$ at the center of the transition, then ΔH_m° may be calculated for the three pressure determinations using eq. 4. Table I summarizes the results. Values of ΔH_m° are seen to increase with increasing pressure and transition temperature. Since ΔV_m° is very small, we shall assume the variation of ΔH_m° is governed by the change in temperature and ΔC_p. This yields a value of approximately 140 cal./mole-deg. This finding might be explained by noting that the helical configuration has less degrees of freedom than the coiled form.

As may be noted in Table I, the transition temperature was found to increase by the effect of increasing pressure and yields a value of 5.6×10^{-3} deg./atm. for $(\partial T/\partial P)_{f=1/2}$. By eq. 5 the positive sign of this result shows that both ΔH_m° and ΔV_m° must have the same sign. Since ΔV_m° has been shown to be negative, ΔH_m° must also be negative. This is in agreement with the known negative value of ΔH_m°.[15,16]

Table I

Transition temp., °C.	Press., atm.	$(\partial f/\partial T)_{f=1/2} \times 10^2$	$\Delta H_m^\circ \pm 20\%$, cal./mole
20.2	1	3	−1400
24.1	680	5	−800
25.9	1020	6	−600

Although it has been possible to determine the effect of pressure on the helix–coil transition of PBG and thereby calculate an expected change of ΔV_m°, the smallness of the calculated ΔV_m° makes a direct determination highly unfavorable. It therefore appears that a direct evaluation of the σ-parameter for this transition will have to depend upon the direct measurement of the enthalpy change in conjunction with the effect of temperature on the transition.[15,16]