

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

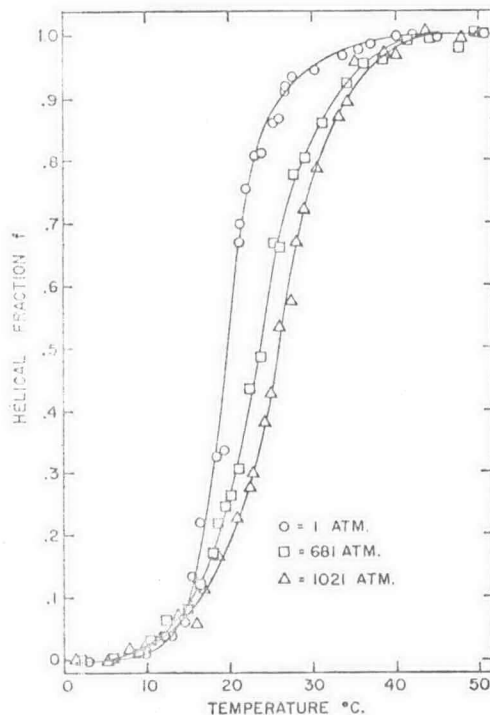


Figure 5. Effect of temperature on helical fraction ( $f$ ) of PBG at various pressures.

adequately determined without resorting to special methods.

The effect of pressure on fraction  $f$  noted in Figure 5 yields an average value of  $-4.6 \times 10^{-4}/\text{atm.}$  for  $(\partial f/\partial P)_{T, f=1/2}$  with  $T$  approximately 296°K. Using Zimm and Bragg's value for  $\sigma$  ( $2 \times 10^{-4}$ ), the  $\Delta V_m^\circ$  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  $\Delta V_m^\circ$  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  $\sigma$  is used with the experimental evaluation of  $(\partial f/\partial T)_{P, f=1/2}$  at the center of the transition, then  $\Delta H_m^\circ$  may be calculated for the three pressure determinations using eq. 4. Table I summarizes the results. Values of  $\Delta H_m^\circ$  are seen to increase with increasing pressure and transition temperature. Since  $\Delta V_m^\circ$  is very small, we shall assume the variation of  $\Delta H_m^\circ$  is governed by the change in temperature and  $\Delta C_p$ . 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 tempera-

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	1	-1400
24.1	680	5	-800
25.9	1020	6	-600

ture was found to increase by the effect of increasing pressure and yields a value of  $5.6 \times 10^{-3}$  deg./atm. for  $(\partial T/\partial P)_{f=1/2}$ . By eq. 5 the positive sign of this result shows that both  $\Delta H_m^\circ$  and  $\Delta V_m^\circ$  must have the same sign. Since  $\Delta V_m^\circ$  has been shown to be negative,  $\Delta H_m^\circ$  must also be negative. This is in agreement with the known negative value of  $\Delta H_m^\circ$ .<sup>15,16</sup>

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  $\Delta V_m^\circ$ , the smallness of the calculated  $\Delta V_m^\circ$  makes a direct determination highly unfavorable. It therefore appears that a direct evaluation of the  $\sigma$ -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.<sup>15,16</sup>