

THERMODYNAMIC PROPERTIES OF POLYOLEFINS

by

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I. INTRODUCTION

The plastics industry is one of the largest and fastest growing industries in the world today. There are thousands of polymers and copolymers in commercial usage manufactured by many different processes and fabricated by many techniques. Although several billion pounds of polymeric materials are sold every year, there are surprisingly little thermodynamic or engineering data available.

The fabrication of plastic articles is more of an art than a science. If a molder of plastic articles wants to design a mold to compensate for shrinkage of the molded item while cooling in the mold, he must rely on past experience or expensive trial and error to determine the proper mold dimensions. To determine the proper temperature for a given molding pressure or vice versa also requires a costly and time consuming trial and error procedure.

The object of this work was to prepare thermodynamic charts of the Mollier type which would enable an engineer to determine heat requirements for extrusion or molding, compensate for mold shrinkage, or solve with a good degree of confidence any other problems that might arise during the fabrication or manufacture of the polymers investigated in this work.

II. LITERATURE REVIEW

This investigation utilized the polymers polyethylene and propylene and the copolymer of ethylene and propylene. A polymer is described as a very large molecule of repeated structural units⁽³²⁾. The repeated structural units are termed mers⁽²⁴⁾. A mer unit comes from the reacting chemical which is called a monomer⁽³²⁾.

The materials investigated all belong to a special class of polymeric materials called polyolefins or ethenic polymers⁽³⁴⁾. Ethenic polymers tend to be linear in structure⁽³³⁾. Since the hydrocarbon based ethenic polymers are derived from olefins, they are called polyolefins. The three materials investigated are derived from ethylene and propylene.

Nature of the Polymer Molecules

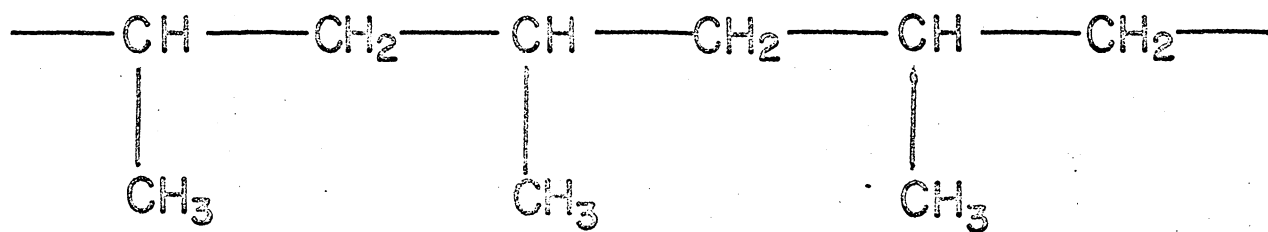
Polyethylene. Polyethylene is polymerized ethylene gas. There are two commercial processes for the manufacture of polyethylene. The original process is called the high pressure process and produces low density polyethylene while the newer process, called the Ziegler, Phillips, or low pressure process, produces linear, or high density, polyethylene⁽³⁵⁾. The linear or high density polymer is the type used in this investigation. The low density polymer possess less crystallinity and more branching than the high density polymer. The linear

polyethylene molecule consists of repeated ($-\text{CH}_2\text{CH}_2-$)_n groups.

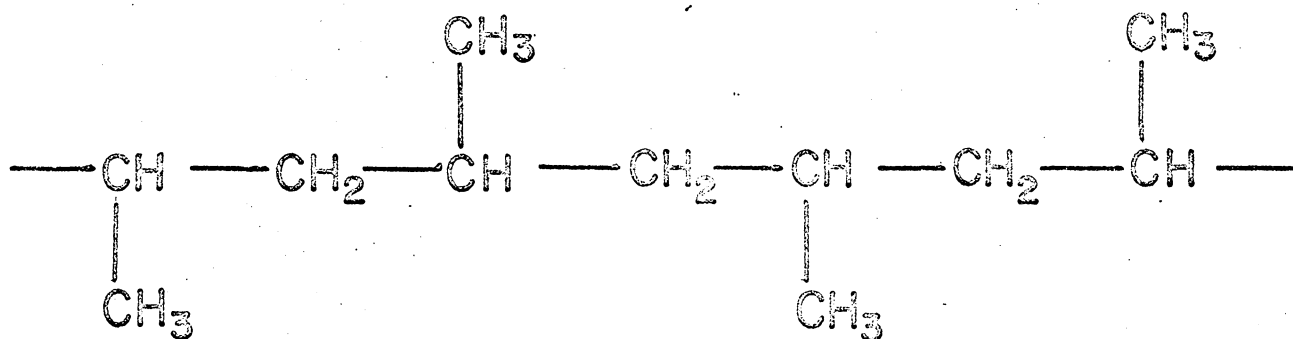
Polypropylene. Polymerization of polypropylene can be carried out by a low pressure process similar to that for high density polyethylene⁽⁴⁾. Polypropylene may assume several structural configurations. (Diagram 1). The repeated structural unit for polypropylene is ($-\underset{\text{CH}_3}{\text{CH}}\text{CH}_2-$)_n. When all the pendant methyl groups lie in a plane on the same side of the main chain, the polymer is said to be isotactic⁽¹⁾. If the pendant methyl groups are arranged in an alternately ordered manner above and below the main chain of the polymer, the polymer is termed syndiotactic⁽¹⁾. If the pendant methyl groups are arranged in a random sequence of positions, the configuration is said to be atactic⁽¹⁾. The structural configuration of the polypropylene produced depends on the catalyst system used and the polymerization conditions⁽⁴⁾. The ability of isotactic polypropylene to crystallize makes it the only configuration of commercial interest.

Ethylene-Propylene Copolymer. The ethylene-propylene copolymer is made by the addition of propylene gas to the ethylene monomer in the low pressure polyethylene process⁽²³⁾. The copolymer is characterized by the number of pendant methyl groups.

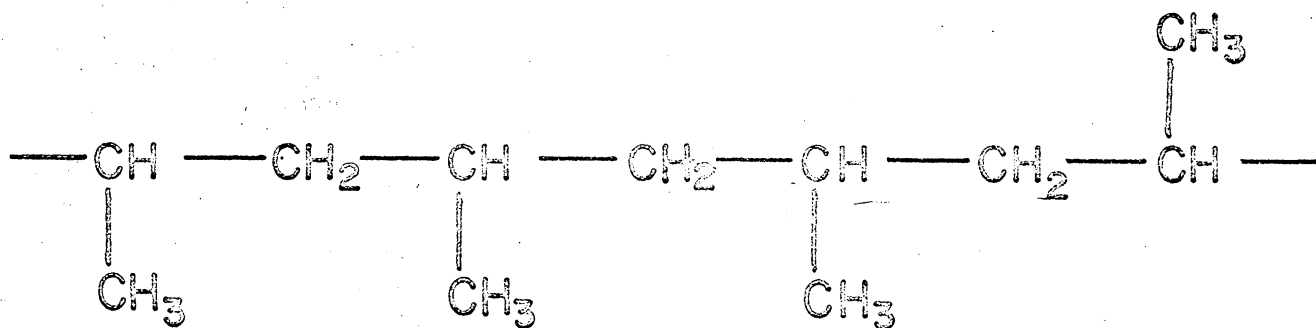
The linear and ordered nature of the materials investigated leads to crystallinity in the polymers. The polymers actually consist of an



ISOTACTIC



SYNDIOTACTIC



ATACTIC

DIAGRAM. STRUCTURAL CONFIGURATIONS OF POLYPROPYLENE

amorphous and crystalline phase at room temperature. The disappearance of the crystalline phase at the melting point leads to discontinuous changes in density and specific heat⁽²⁾. The temperature interval for fusion decreases with increasing molecular weight and increases with increasing breadth of molecular weight distribution⁽³⁾.

Equations of State

In the field of p-v-t measurements, equations of state have been applied to reduce the need for extensive p-v-t data. Use of the equation of state enables extrapolation of data to uninvestigated fields, interpolation of data, and simplifies calculation of the thermodynamic properties of a material. Early workers in the field were van der Waals, Beattie and Bridgeman, and Benedict, Webb, and Rubin who developed equations for liquids and gases. Their work did not include polymeric materials⁽¹³⁾.

Canjar refitted the Benedict, Webb, Rubin equation to extensive p-v-t data for ethane and methane to enable calculation of the thermodynamic properties of the materials⁽⁵⁾. Canjar's work includes a detailed description of the construction of Mollier type diagrams from p-v-t data for ethane and methane.

Spencer and Gilmore modified van der Waal's equation of state and applied it to polystyrene⁽²⁶⁾. In a later publication they extended

their work to cover other polymers including polyethylene. Spencer and Gilmore's work is the only literature reference to application of an equation of state of polymeric materials.

P-V-T Data

P-V-T data for the polymers investigated was not extensive. Data for polypropylene and ethylene-propylene copolymer is practically non-existent. A number of investigators, Bridgeman(1948), Parks and Richards (1949), Spencer and Gilmore (1949, 1950), Weir (1950, 1953, 1954), Matsuoka and Maxwell (1958), and Heydemann and Guicking (1963), have measured polymer compressibilities. Weir presents compression data for polyethylene between 1,000 and 10,000 atmospheres⁽³¹⁾. Weir presents a third order virial equation for the compression process and gives the value of the virial coefficients for polyethylene at 20 °C.

Matsuoka presented a complete set of p-v-t data for linear polyethylene for pressures up to 1,000 atmospheres and a temperature of 200 °C⁽¹⁸⁾. An earlier article by Matsuoka presents p-v-t data for polyethylene at lower temperature and pressures⁽¹⁷⁾. Many other articles and books use Matsuoka's work for reference.

Calorimetric Data

Data concerning the physical properties of polymers is extremely limited. Dole has collected specific heat and heat of fusion data for many polymers. Dole indicates that the melt specific heat is nearly independent of the degree to which the polymer is branched whether high or low density⁽³⁶⁾. Calorimetric data required for this investigation and not in the literature was taken from Foster⁽¹⁴⁾.

Thermodynamic Data

The literature only contained two references concerning the thermodynamic properties of polymeric materials. Lupton shows diagrams showing the effect of pressure, volume, and temperature on the entropy and enthalpy of polyethylene resins⁽¹⁶⁾. Lupton states that the pressure effect on enthalpy is independent of chain branching. Lupton's data points out a discontinuity between the melt and solid region in volume and, therefore, the related thermodynamic properties. Lupton's data covers a pressure range from zero to 1,000 atmospheres and a temperature range from zero to 200 °C.

Parks and Richards present similar data to that of Lupton. The results are compared to long chain hydrocarbons and waxes. The article shows plots of entropy and enthalpy versus temperature at

constant pressure. The article only investigated pressures of one, 500, 1000, and 2000 atmospheres and only went as high as 160 °C. Parks and Richards state that the melting point of the polymer increases 0.02 °C per atmosphere increase in pressure. The work of Parks and Richards was on low density polyethylene.

III. EXPERIMENTAL

Plan of Experimentation

The plan of experimentation was to take raw p-v-t data by Foster⁽¹⁴⁾ on polyethylene, polypropylene, and an ethylene-propylene copolymer and construct charts of the thermodynamic properties of the polymers. Literature values of needed calorimetric data were used when available. Required calorimetric data not available in the literature was taken from the data of Foster⁽¹⁴⁾.

The raw data was first smoothed by fitting it to a modified version of van der Waal's equation of state as determined by Spencer and Gilmore. The technique of smoothing is generally the first step in the preparation of thermodynamic charts. Smoothing by this method requires determination of residual volumes and/or pressures and construction of curves of the residuals from which the actual smoothing is done⁽²⁷⁾.

A datum was selected for zero enthalpy and entropy for the polymers and specific values of these functions were calculated at atmospheric pressure from calorimetric data. The entropy and enthalpy were plotted against pressure giving a series of isotherms. To construct each isotherm, the values of entropy and enthalpy had

to be corrected for pressure. The results were presented as enthalpy, entropy, and volume plotted against pressure at constant temperature.

Materials

The three polymer types used in this investigation were polyethylene, polypropylene, and an ethylene-propylene copolymer.

Ethylene-Propylene Copolymer. Sample number 43,373.

Obtained from Phillips Petroleum Company.

Polyethylene. Type P.E. 84. The polyethylene used in this investigation was of the linear or high density type. Obtained from the E. I. du Pont de Nemours and Company.

Polypropylene. Type B-8761. Obtained from the E. I. du Pont de Nemours and Company.

Computation Device. Friden desk calculator model ST.

San Leandro, California

Drop Calorimeter. Dilatometric Dead weight gauge. Obtained from the Virginia Polytechnic Institute Chemical Engineering Department.

Method of Procedure

This thesis is a mathematical analysis of experimentally derived data and required no special equipment or manual technique.

For purposes of clarity and continuity the sample calculations for each step are included in this section

Smoothing of Raw Data. The raw data⁽¹⁴⁾ for the materials investigated are shown in Tables I, II, and III. The body of these tables contain values of specific volume as a function of temperature and pressure.

Spencer and Gilmore modified van der Waal's equation of state to the following form⁽²⁶⁾.

$$(P + \pi) (V - W) = RT$$

where:

P = external pressure

π = internal pressure or cohesive energy density

V = specific volume

W = close packed volume or the volume at absolute zero

R = gas constant

T = absolute temperature

The value of π was shown as 3,240 atmospheres. The close packed volume, W, was taken to be 0.875 cc/gm and the gas constant was 2.92 atm-cc/gm-°K. The values of π and W are arbitrary for smoothing and were selected to make calculation and plotting of the

data during the smoothing process simpler. The formulae for smoothing are:

$$1. \quad P_{\text{calc}} = \frac{2.92T}{V_{\text{obs}} - 0.875} - 3240$$

$$2. \quad V_{\text{calc}} = \frac{2.92T}{P_{\text{obs}} + 3240} + 0.875$$

TABLE I

Specific Volume* as a Function of Pressure and
Temperature of Linear Polyethylene P. E. 84

Tempera- ture	Pressure, atm.						
	1	79.3	158.5	232	316	474	618
23 °C	1.0429	1.0428	1.0425	1.0425	1.0423	1.0422	1.0419
50 °C	1.0549	1.0547	1.0545	1.0543	1.0538	1.0537	1.0528
75 °C	1.0680	1.0676	1.0669	-----	1.0650	-----	1.0621
100 °C	1.0861	1.0855	1.0852	-----	1.0844	-----	1.0827
125 °C	1.1162	1.1157	1.1152	-----	1.1143	-----	1.1095
130 °C	1.1549	1.1540	1.1530	-----	1.1490	-----	1.1284
140 °C	1.2852	1.2793	1.2725	-----	1.2628	-----	-----
175 °C	1.3211	1.3124	1.3062	1.3007	1.2951	1.2759	1.2679
210 °C	1.3539	1.3452	1.3355	1.3268	1.3179	1.2987	1.2899
250 °C	1.3932	1.3804	1.3694	1.3567	1.3432	1.3285	1.3187

* CC/GM

TABLE II

Specific Volume* as a Function of Pressure and Temperature
of Polypropylene B-8761

Tempera- ture	Pressure, atm.						
	1	79.3	158.5	232	316	474	618
23 °C	1.1007	1.0986	1.0943	1.0908	1.0870	1.0856	1.0838
50 °C	1.1138	1.1106	1.1082	1.1069	1.1058	1.1028	1.1008
75 °C	1.1270	1.1259	1.1244	1.1232	1.1217	1.1217	1.1150
100 °C	1.1429	1.1419	1.1401	1.1387	1.1355	1.1311	1.1266
125 °C	1.1620	1.1615	1.1605	1.1592	1.1571	1.1516	1.1470
150 °C	1.1920	1.1909	1.1888	1.1854	1.1813	1.1727	1.1656
160 °C	1.2130	1.2122	1.2084	1.2038	1.1925	1.1863	1.1761
168 °C	1.2433	1.2341	1.2258	1.2181	1.2181	1.2020	1.1932
180 °C	1.3210	1.3157	1.3029	1.2941	1.2528	1.2306	1.2144
200 °C	1.3401	1.3256	1.3218	1.3108	1.2995	1.2861	1.2728
210 °C	1.3509	1.3408	1.3304	1.3186	1.3092	1.2930	1.2885
250 °C	1.3850	1.3714	1.3547	1.3408	1.3268	1.3122	1.3007

* CC/GM

TABLE III

Specific Volume* as a Function of Pressure and Temperature
of Ethylene-Propylene Copolymer

Tempera- ture	Pressure, atm.						
	1	79.3	158.5	232	316	474	618
23 °C	1.0779	1.0777	1.0761	1.0752	1.0729	1.0695	1.0654
50 °C	1.1000	1.0970	1.0925	1.0886	1.0850	1.0780	1.0708
75 °C	1.1231	1.1210	1.1163	1.1116	1.1069	1.0982	1.0891
100 °C	1.1532	1.1509	1.1455	1.1390	1.1335	1.1246	1.1170
110 °C	1.1929	1.1912	1.1856	1.1785	1.1715	1.1631	1.5101
125 °C	1.2563	1.2514	1.2423	1.2349	1.2130	1.1989	1.1899
150 °C	1.2768	1.2705	1.2652	1.2602	1.2513	1.2394	1.2217
175 °C	1.3002	1.2947	1.2865	1.2785	1.2693	1.2543	1.2463
210 °C	1.3291	1.3206	1.3102	1.3024	1.2913	1.2748	1.2641
250 °C	1.3644	1.3517	1.3424	1.3299	1.3164	1.2995	1.2953

* CC/GM

Using Equation 1, the observed volume at a given temperature was inserted in the equation and the pressure calculated. The same procedure was followed for Equation 2 with the difference being that volume is calculated. The following formulae show how the residuals were found:

$$3. \quad r_v = V_{\text{obs}} - V_{\text{calc}}$$

$$4. \quad r_p = P_{\text{obs}} - P_{\text{calc}}$$

where:

r_v = residual volume

r_p = residual pressure

V_{obs} = observed volume

V_{calc} = calculated volume

P_{obs} = observed pressure

P_{calc} = calculated pressure

The residuals were then plotted against pressure at constant temperature. A series of isotherms was thus developed. It was found that use of residual volumes in the solid region and residual pressures in the liquid region resulted in the smoothest curves. Polyethylene in the solid region is used as an example of residual volume calculations. Equations 2 and 3 will be used for the solid region.

$$V_{\text{calc}} = \frac{2.92 T}{P + 3240} + 0.875$$

where:

$$P = 158.5 \text{ atmospheres (from Table I)}$$

$$T = 403 \text{ }^\circ\text{K (130 }^\circ\text{C from Table II)}$$

$$V_{\text{calc}} = \frac{2.92 \times 403}{158.5 + 3240} + 0.875$$

$$V_{\text{calc}} = 1.220 \text{ cc/gm}$$

$$r_v = V_{\text{obs}} - V_{\text{calc}}$$

$$V_{\text{obs}} = \text{from table IV}$$

$$r_v = 1.1530 - 1.220$$

$$r_v = -0.066 \text{ cc/gm}$$

Figure 1 is a plot of the residual volumes against pressure for the solid region of polyethylene. Similarly shaped curves were obtained for pressure residuals in the melt region. The solid lines on the figure represent the residuals as calculated. The dashed portion of the 130 °C isotherm is the smoothed portion of the data. The dashed line was drawn to parallel the other isotherms. For a given pressure on the dashed portion of the isotherm, the corresponding residual was read from the figure and a volume calculated for the conditions using Equation 2 on page 12. The calculated volume is added to the residual volume to get the new smoothed observed volume.

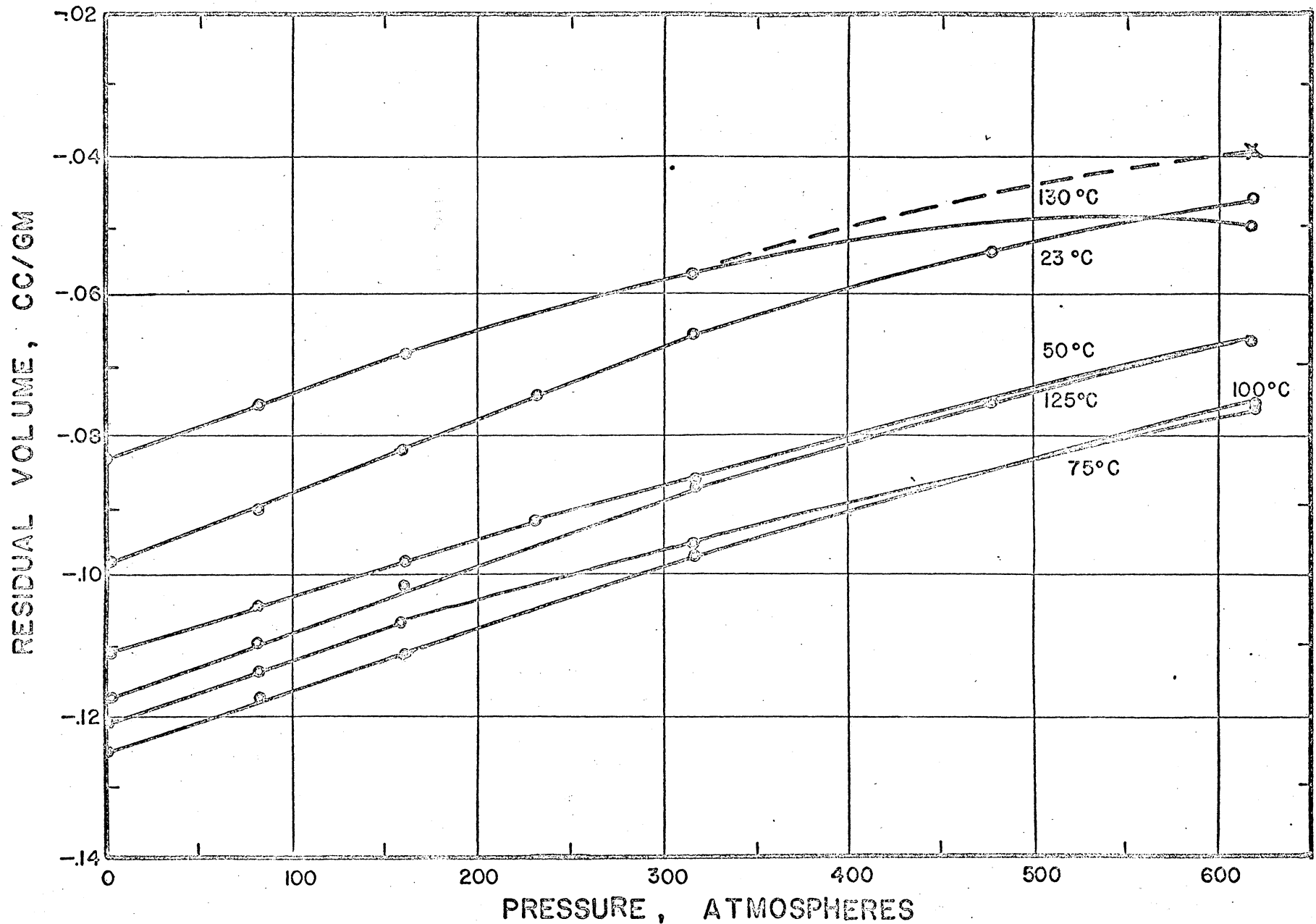


FIGURE I. RESIDUAL VOLUME FOR SOLID PHASE POLYETHYLENE

At a pressure of 618 atmospheres on the dashed portion of the 130 °C isotherm of Figure 1, the corresponding residual volume is -0.0395.

$$\begin{aligned}r_v &= V_{\text{obs}} - V_{\text{calc}} \\-0.0395 &= V_{\text{obs}} - 1.1800\end{aligned}$$

where:

V_{calc} is calculated in the same manner as shown on page 17 using a pressure of 618 atmospheres and a temperature of 130 °C.

$$V_{\text{obs}} = 1.1405 \text{ cc/gm}$$

This smoothed observed volume is shown in Table IV. Tables IV, V, and VI are the smoothed p-v-t data for the polymers studied. Figures 2, 3, and 4 are plots of the smoothed data. The dashed lines on Figures 3 and 4 represent isotherms through the liquid-solid region. The lines are dashed because the liquid-solid region could not be accurately defined from the data available. The dashed lines are an estimation.

Since the results of this investigation were intended for engineering purposes, the smoothed data was converted to english engineering units as shown in Tables VII, VIII, and IX.

TABLE IV

Smoothed P-V-T Data for Polyethylene

Temperature	Pressure, atm.						
	1	79.3	158.5	232	316	474	618
23 °C	1.0429*	1.0427	1.0425	1.0425	1.0923	1.0422	1.0419
50 °C	1.0549	1.0547	1.0543	1.0542	1.0540	1.0537	1.0528
75 °C	1.0680	1.0676	1.0669	1.0660	1.0650	1.0640	1.0621
100 °C	1.0861	1.0857	1.0853	1.0852	1.0843	1.0840	1.0827
125 °C	1.1162	1.1157	1.1152	1.1140	1.1137	1.1119	1.1101
130 °C	1.1549	1.1540	1.1530	1.1513	1.1490	1.1446	1.1405
140 °C	1.2852	1.2193	1.2725	1.2675	1.2607	1.2493	1.2393
175 °C	1.3211	1.3132	1.3047	1.2979	1.2899	1.2759	1.2679
210 °C	1.3526	1.3430	1.3336	1.3254	1.3147	1.2983	1.2887
250 °C	1.3925	1.3784	1.3653	1.3549	1.3431	1.3282	1.3187

*CC/GM

TABLE V

Smoothed P-V-T Data for Polypropylene

Tempera- ture	Pressure, atm.						
	1	79.3	158.5	232	316	474	618
23 °C	1.1007*	1.0984	1.0963	1.0942	1.0924	1.0876	1.0838
50 °C	1.1138	1.1105	1.1087	1.1073	1.1057	1.1026	1.1006
75 °C	1.1270	1.1256	1.1241	1.1229	1.1217	1.1184	1.1150
100 °C	1.1429	1.1419	1.1395	1.1370	1.1370	1.1333	1.1290
125 °C	1.1620	1.1619	1.1607	1.1592	1.1567	1.1512	1.1467
150 °C	1.1920	1.1906	1.1885	1.1851	1.1808	1.1727	1.1655
160 °C	1.2130	1.2118	1.2083	1.2083	1.2030	1.1972	1.1786
168 °C	1.2433	1.2342	1.2245	1.2165	1.2170	1.2006	1.1925
180 °C	1.3250	1.3149	1.3044	1.2930	1.2537	1.2322	1.2167
200 °C	1.3365	1.3280	1.3188	1.3104	1.3001	1.2860	1.2753
210 °C	1.3509	1.3401	1.3293	1.3194	1.3088	1.2941	1.2867
250 °C	1.3840	1.3702	1.3553	1.3414	1.3270	1.3080	1.3005

* CC/GM

TABLE VI

Smoothed P-V-T Data for Ethylene-Propylene Copolymer

Tempera- ture	Pressure, atm.						
	1	79.3	158.5	232	316	474	618
50 °C	1.1000*	1.0971	1.0934	1.0893	1.0855	1.0778	1.0701
75 °C	1.1231	1.1209	1.1163	1.1116	1.1071	1.0993	1.0972
100 °C	1.1532	1.1509	1.1455	1.1406	1.1348	1.1257	1.1170
110 °C	1.1929	1.1911	1.8561	1.1804	1.1745	1.1631	1.1530
125 °C	1.2564	1.2514	1.2423	1.2349	1.2155	1.1989	1.1885
150 °C	1.2768	1.2733	1.2666	1.2605	1.2517	1.2363	1.2268
175 °C	1.3002	1.2947	1.2865	1.2785	1.2688	1.2541	1.2443
210 °C	1.3644	1.3523	1.3400	1.3290	1.3164	1.2964	1.2858

*CC/GM

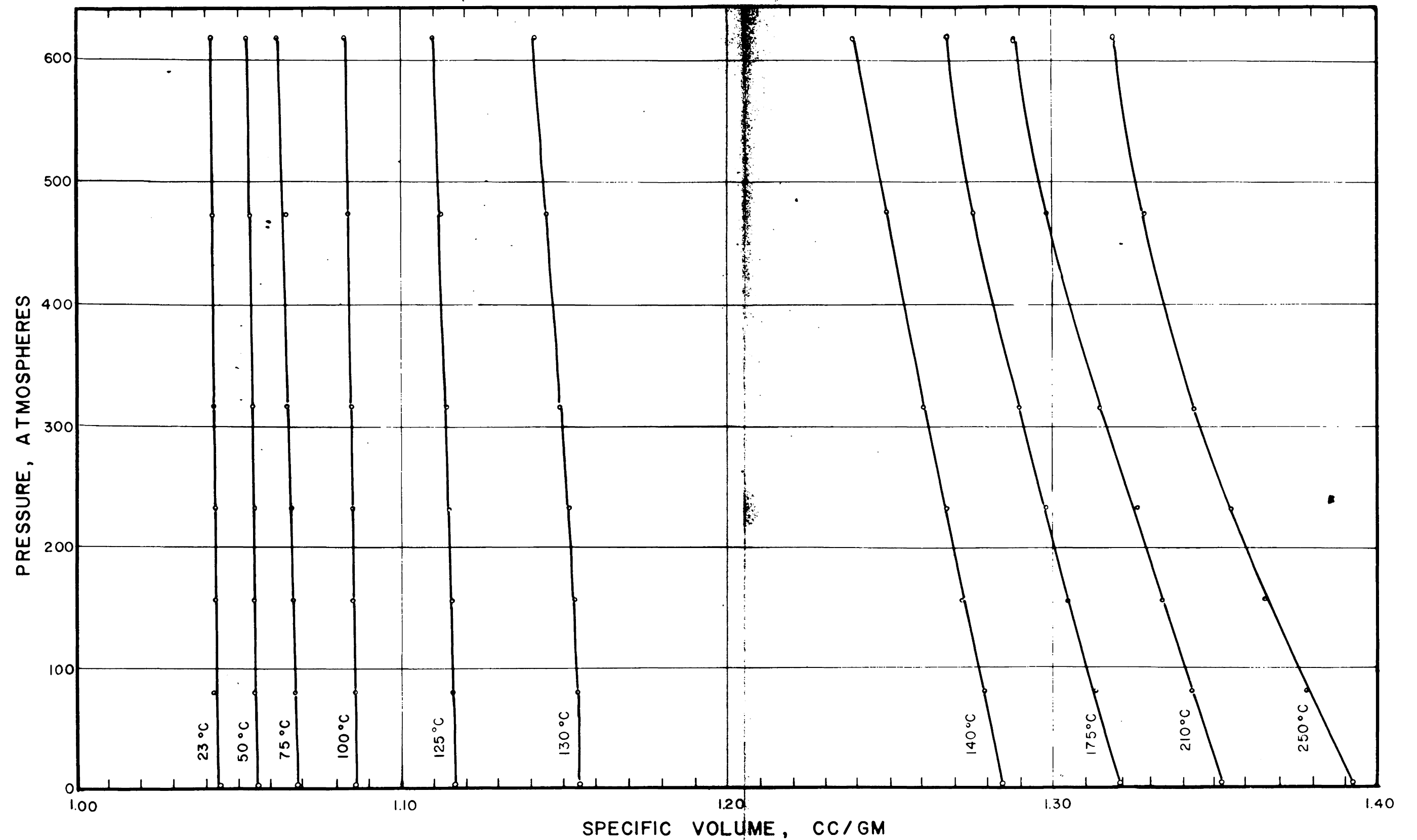


FIGURE 2.

SMOOTHED PRESSURE-VOLUME DATA FOR POLYETHYLENE

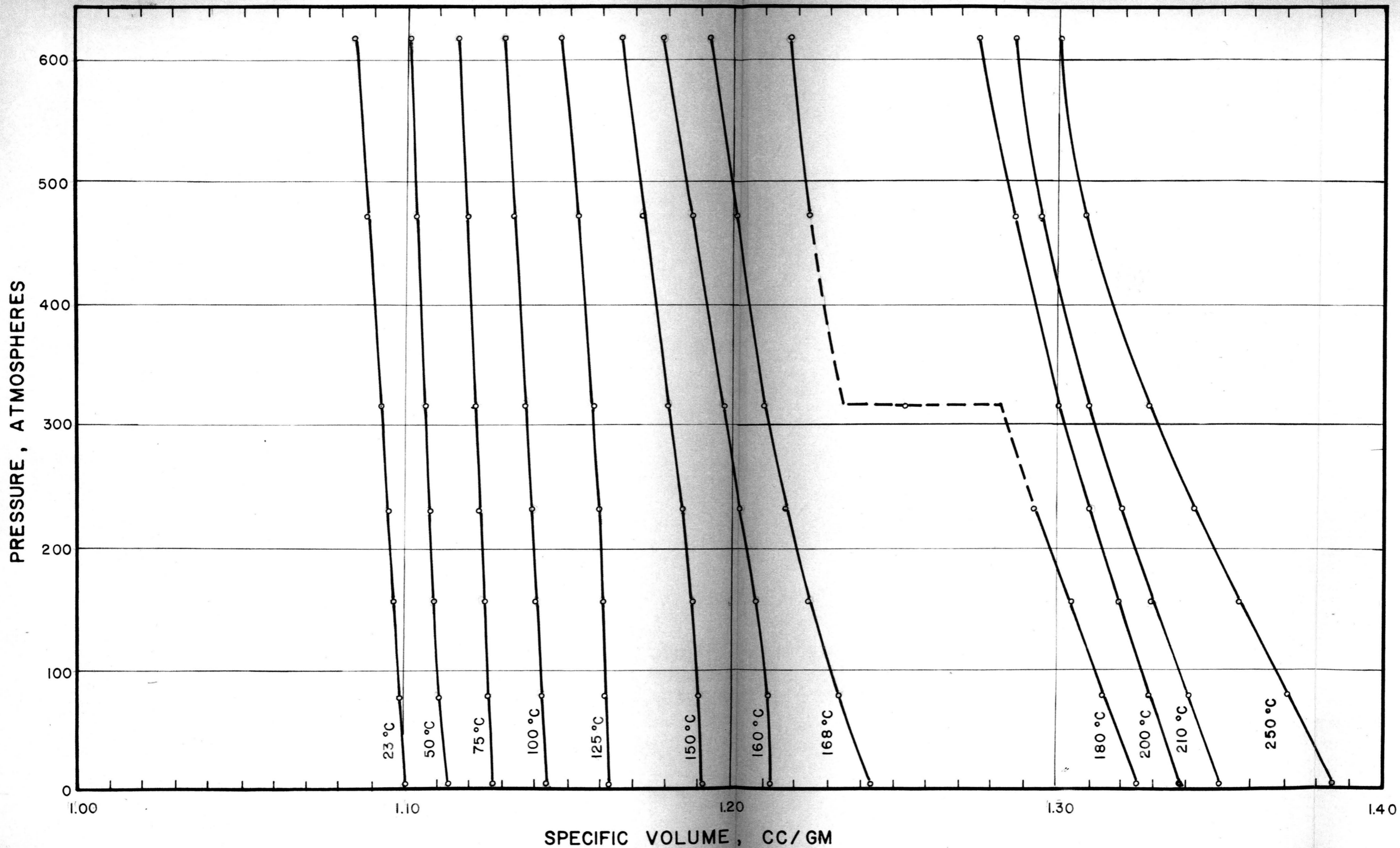


FIGURE 3. SMOOTHED PRESSURE-VOLUME DATA FOR POLYPROPYLENE

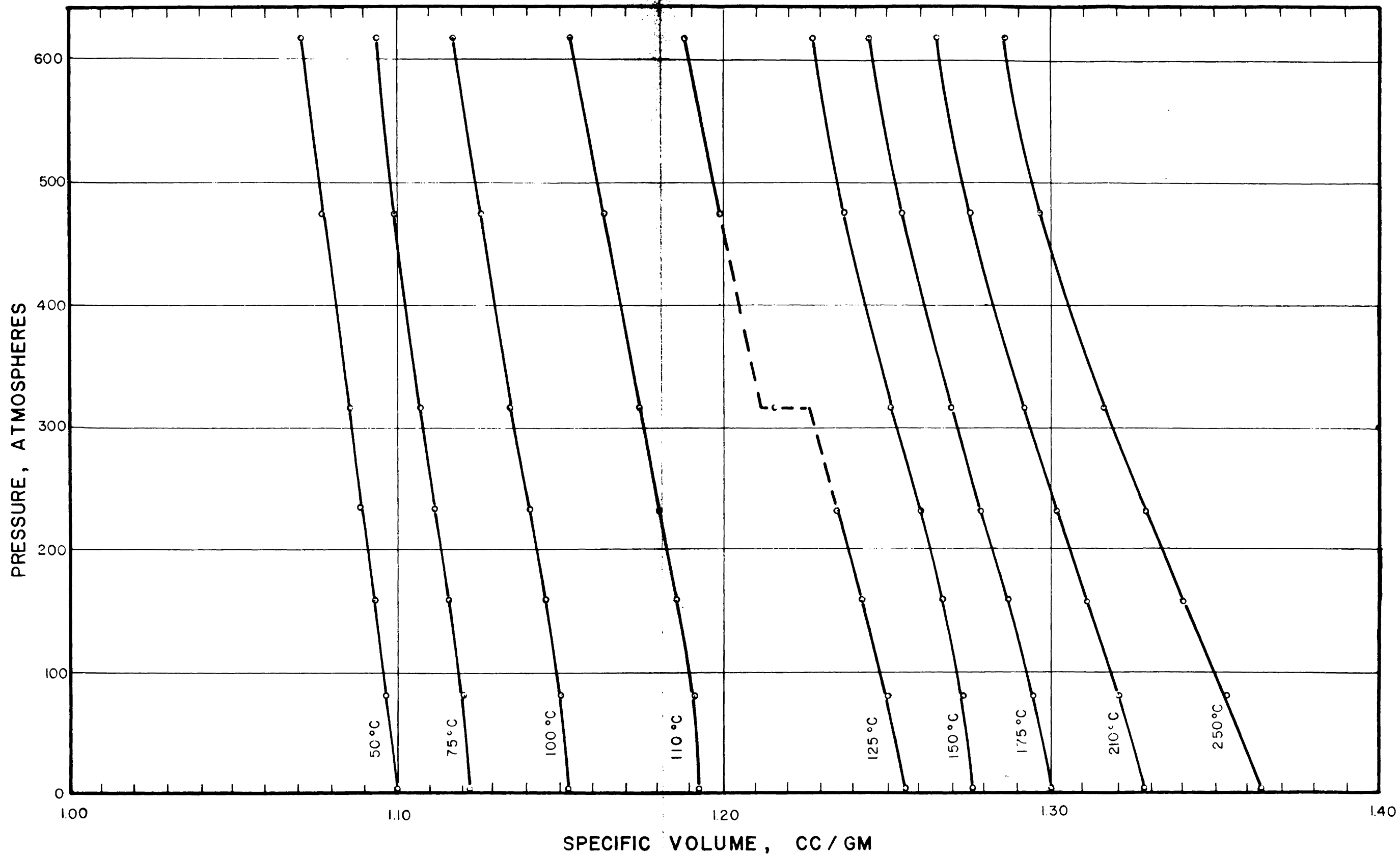


FIGURE 4. SMOOTHED PRESSURE-VOLUME DATA FOR ETHYLENE-PROPYLENE COPOLYMER

TABLE VII

P. E. Smoothed P-V-T Data

°F Temp.	Pressure, PSIA						
	14.7	1166	2330	3410	4645	6968	9085
73.4	1.6700*	1.6697	1.6693	1.6693	1.6690	1.6689	1.6684
122	1.6892	1.6889	1.6882	1.6881	1.6878	1.6873	1.6858
167	1.7102	1.7095	1.7084	1.7070	1.7054	1.7038	1.7007
212	1.7392	1.7385	1.7379	1.7377	1.7363	1.7358	1.7337
257	1.7874	1.7866	1.7858	1.7838	1.7834	1.7805	1.7776
266	1.8493	1.8479	1.8463	1.8436	1.8399	1.9328	1.8263
284	2.0580	2.0485	2.0376	2.0296	2.0187	2.0005	1.9845
347	2.1155	2.1028	2.0892	2.0783	2.0655	2.0431	2.0303
410	2.1659	2.1505	2.1355	2.1224	2.1052	2.0790	2.0636
482	2.2298	2.2072	2.1862	2.1696	2.1507	2.1268	2.1116

* $\frac{\text{ft}^3}{\# \text{ mass}} \times 10^2$

TABLE VIII

Smoothed P-V-T Data for Polypropylene

°F Temp.	Pressure, PSIA						
	14.7	1166	2330	3410	4645	6968	9058
80	1.7657*	1.7614	1.7579	1.7547	1.7518	1.7454	1.7396
120	1.7830	1.7774	1.7744	1.7726	1.7689	1.7646	1.7613
160	1.8013	1.7979	1.7955	1.7936	1.7914	1.7869	1.7821
200	1.8227	1.8208	1.8191	1.8168	1.8136	1.8088	1.8023
240	1.8481	1.8471	1.8455	1.8445	1.8400	1.8330	1.8256
280	1.8836	1.8820	1.8798	1.8751	1.8711	1.8604	1.8503
320	1.9424	1.9404	1.9348	1.9264	1.9171	1.9011	1.8873
400	2.1477	2.1344	2.1188	2.1047	2.0882	2.0657	2.0516
440	2.1967	2.1734	2.1542	2.1307	2.1131	2.0854	2.0748
460	2.2080	2.1850	2.1635	2.1401	2.1201	2.0905	2.0799

* $\frac{\text{ft}^3}{\# \text{ mass}} \times 10^2$

TABLE IX

Smoothed P-V-T Data for Ethylene-Propylene Copolymer

°F Temp.	Pressure, PSIA						
	14.7	1166	2330	3410	4645	6968	9058
122	1.7614*	1.7568	1.7509	1.7443	1.7382	1.7259	1.7135
167	1.7984	1.7949	1.7875	1.7800	1.7728	1.7603	1.7487
212	1.8466	1.8429	1.8343	1.8264	1.8171	1.8026	1.7886
257	1.9102	1.9073	1.8985	1.8902	1.8807	1.8625	1.8463
266	2.0117	2.0039	1.9893	1.9774	1.9464	1.9198	1.9031
284	2.0445	2.0389	2.0282	2.0184	2.0043	1.9797	1.9645
347	2.0820	2.0732	2.0601	2.0473	2.0317	2.0082	1.9925
410	2.1283	2.1150	2.0993	2.0847	2.0677	2.0413	2.0244
482	2.1848	2.1654	2.1457	2.1281	2.1079	2.0759	2.0589

* $\frac{\text{ft}^3}{\# \text{ mass}} \times 10^2$

Base Point Determination. The absolute value of entropy or enthalpy was not calculated. A reference point or datum was selected, one atmosphere total pressure and 32 °F, and the changes in entropy and enthalpy with pressure at constant temperature were calculated assuming that the entropy and enthalpy at the datum was zero. Curves of enthalpy versus temperature at one atmosphere total pressure for the polymers investigated were taken from Foster⁽¹⁴⁾. The base points at one atmosphere for the pressure-enthalpy curves were thus established.

The enthalpy data was then used to calculate specific heats from which the base entropies could be calculated. The following is an example of the calculation for polyethylene at 120 °F and one atmosphere total pressure:

$$H - H_{\text{ref}} = C_p(T - T_{\text{ref}})$$

where:

H = enthalpy at one atmosphere and temperature T
H_{ref} = enthalpy at one atmosphere and reference temperature
T_{ref} (equals zero)

$$41.4 = C_p (120 - 32) \text{ } ^\circ\text{F}$$

$$C_p = 0.471 \text{ BTU/lb- } ^\circ\text{F}$$

The changes in entropy were then calculated using the following formula:

$$\Delta S = C_p \ln (T_2/T_1)$$

where:

$$\Delta S = S_{120} - S_{32}$$

$$C_p = 0.471 \text{ BTU/lb- } ^\circ\text{F}$$

$$T_2 = 120 ^\circ\text{F} + 460 = 580 ^\circ\text{R}$$

$$T_1 = 32 ^\circ\text{F} + 460 = 492 ^\circ\text{R}$$

$$\Delta S = 0.471 \ln \frac{580}{492} = 0.078 \text{ BTU/lb/ } ^\circ\text{R}$$

The base points were thus established for entropy and enthalpy. To construct pressure-enthalpy and pressure-entropy diagrams, the changes in entropy and enthalpy with pressure at constant temperature were calculated and added to the base values.

Calculation of Entropy and Enthalpy Change Due to Pressure.

The following formulae were used to calculate the change in entropy and enthalpy with pressure at constant temperature.

$$\begin{aligned} 5. \quad S - S_{\text{ref}} &= - \int_{P_{\text{ref}}}^P \left(\frac{\partial V}{\partial T} \right)_p dp \\ 6. \quad H - H_{\text{ref}} &= \int_{P_{\text{ref}}}^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right] dp \end{aligned}$$

where:

- S = entropy at some pressure
- S_{ref} = entropy at reference = 0
- H = enthalpy at some pressure
- H_{ref} = enthalpy at reference = 0
- P = pressure
- P_{ref} = reference pressure, one atmosphere
- T = absolute temperature
- V = specific volume
- $\left(\frac{\partial V}{\partial T} \right)_p$ = change in specific volume with temperature at constant pressure

The partial derivative is the slope of a curve of volume versus temperature at constant pressure⁽²⁵⁾. Numerical values of the partial derivative were obtained by plotting the volume-temperature curves with pressure as a parameter and calculating the slopes at a

series of temperatures for each pressure.

The slope of the volume-temperature curve was determined by numerical differentiation. A Taylor series expansion for tabular values of non-equidistant points was used to calculate the slopes⁽²¹⁾.

The formula is of the following form:

$$\left(\frac{dy}{dx}\right)_i = \frac{1}{\alpha(\alpha+1)h} \left[Y_r - (1-\alpha^2)Y_i - \alpha^2 Y_l \right]$$

where:

$$\left(\frac{dy}{dx}\right)_i = \left(\frac{\partial V}{\partial T}\right)_p \text{ at some temperature } i$$

Y_i = specific volume at temperature i

Y_r = specific volume of data point adjacent to and greater than Y_i and at the same pressure

Y_l = specific volume of data point adjacent to and less than Y_i and at the same pressure

h = $(T_r - T_i)$ or $(T_i - T_l)$, whichever is smaller

α = $\frac{(T_r - T_i)}{h}$ or $\frac{(T_i - T_l)}{h}$, whichever is larger

On page 26, Table VII presents the information required to evaluate the partial derivative. Evaluation of the partial derivative at 266 °F and 2330 pounds per square inch absolute pressure, the following information was required from Table VII.

$Y_i = 0.018463$	$T_i = 266 \text{ }^\circ\text{F}$
$Y_r = 0.020376$	$T_r = 284 \text{ }^\circ\text{F}$
$Y_l = 0.017858$	$T_l = 257 \text{ }^\circ\text{F}$

The partial was then evaluated using the formula on page 32, above.

$$h = (T_i - T_1) = 266^\circ\text{F} - 257^\circ\text{F} = 9^\circ\text{F}$$

$$\alpha = \frac{(T_r - T_i)}{h} = \frac{284^\circ\text{F} - 266^\circ\text{F}}{9^\circ\text{F}} = 2$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{2(2-1) \times 9} \left[0.02038 - (1-2^2) 0.01846 - 2^2 \times 0.01786 \right]$$

$$\left(\frac{\partial V}{\partial T}\right)_p = 80.1 \times 10^{-6} \text{ ft}^3/\text{lb-}^\circ\text{F at 2330 psia and 266}^\circ\text{F}$$

Values of the partial derivative were calculated for each data point.

The values of the partial derivative were then plotted against pressure at constant temperature to yield a series of isotherms. Figure 5, page 34 is an example of the plot for the 120^oF isotherm of polyethylene.

Figure 5 was used to determine the change in entropy with pressure for polyethylene at 120^oF. A curve similar to Figure 5 was constructed to determine the change in enthalpy with pressure. Instead of plotting $\left(\frac{\partial V}{\partial T}\right)_p$ against pressure, $(V - T\left(\frac{\partial V}{\partial T}\right)_p)$ was plotted against pressure. The value of V is taken at the same conditions of temperature and pressure for which the partial was evaluated.

The change in entropy or enthalpy was determined by graphical integration of curves similar to Figure 5 between the pressures in question. Graphical integration was used to solve Equation 6 on page 31 also. Graphical integration was accomplished with the trapezoidal rule⁽²²⁾. The effect of pressure on entropy and enthalpy was investigated for 1,000 pound per square inch changes in pressure. The calculation for entropy change in polyethylene at 120^oF was done as follows:

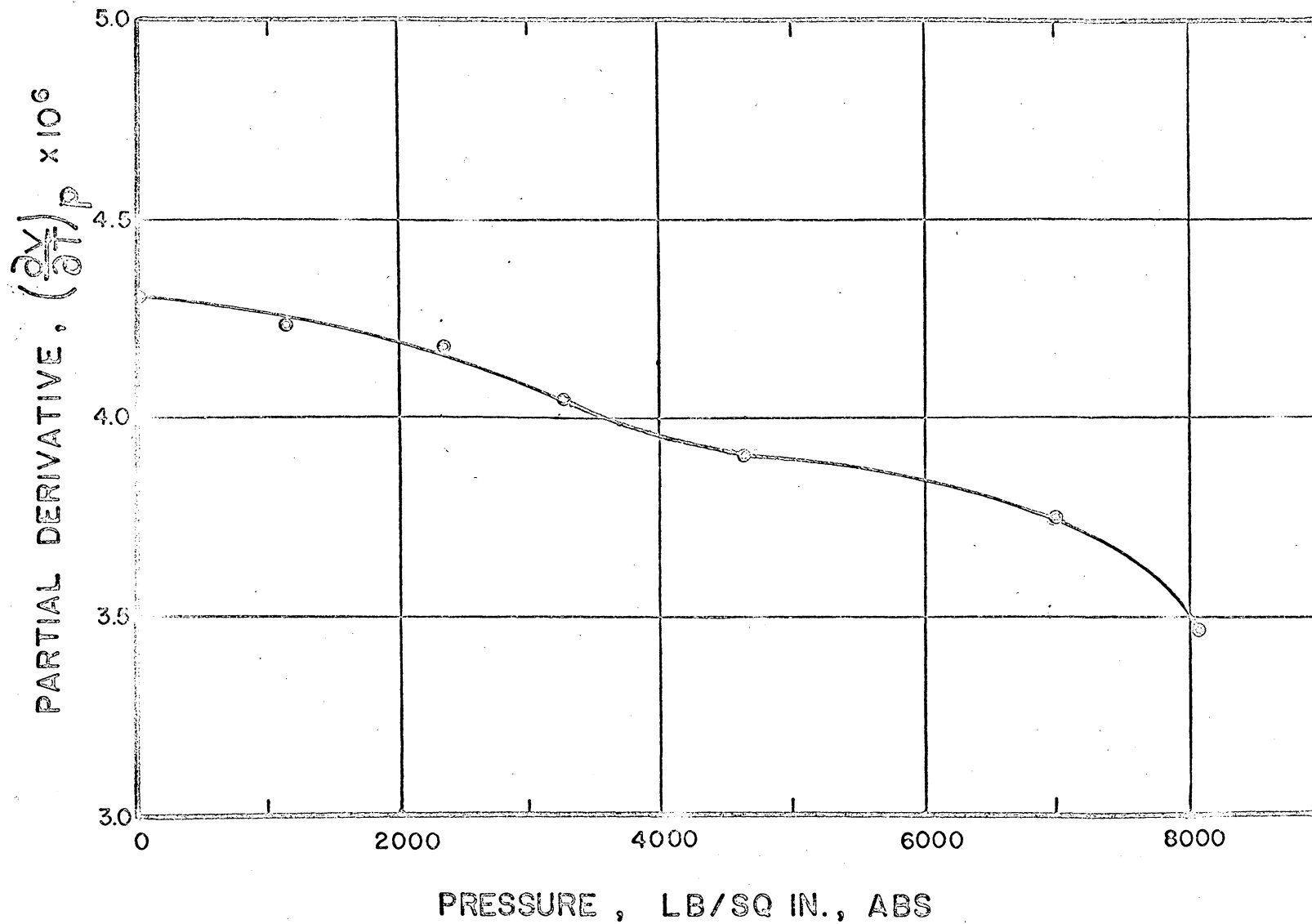


FIGURE 5. $(\frac{\partial v}{\partial T})_p$ VS. PRESSURE FOR POLYETHYLENE AT 120 °F

$$S = h \frac{Y_0}{2} + Y_1 + Y_2 + Y_3 + \frac{Y_4}{2}$$

where:

$$h = 250 \text{ psia (interval between } Y_n \text{ and } Y_{n+1})$$

$$Y_n = \left(\frac{\partial V}{\partial T} \right)_p \text{ from Figure 5 between zero and 1,000 psia}$$

$$S = -250 \frac{4.3}{2} + 4.3 + 4.3 + 4.29 + \frac{4.27}{2} \times 10^{-6}$$

$$S = 4293.75 \times 10^{-6} \frac{\text{ft}^3 \text{ lb}}{\text{lb}^\circ \text{R in}^2}$$

$$S = \frac{-4293.75 \times 144}{778} \times 10^{-6} \frac{\text{BTU}}{\text{lb}^\circ \text{R}}$$

$$S = -794.7 \times 10^{-6} \frac{\text{BTU}}{\text{lb}^\circ \text{R}}$$

This change in entropy was then added to the base value of entropy previously determined for polyethylene at 120 °F. The entropy change between 1,000 and 2,000 pounds per square inch pressure was then determined and the procedure was repeated until the isotherm of enthalpy versus pressure was complete. The procedure was repeated for every isotherm. The results are the pressure-entropy diagrams, Figures 6, 7, and 8.

The change in enthalpy with pressure is found in the same manner as that described above for entropy. The value of Y_n in the trapezoidal rule is changed from $\left(\frac{\partial V}{\partial T} \right)_p$ to $V-T \left(\frac{\partial V}{\partial T} \right)_p$. The trapezoidal rule was then added to the previously determined base values as was done for entropy and the pressure-enthalpy diagrams, Figures 9, 10, and 11 were constructed.

Tables X, XI, and XII present enthalpy and entropy data as a function of temperature and pressure over the ranges investigated for each material.

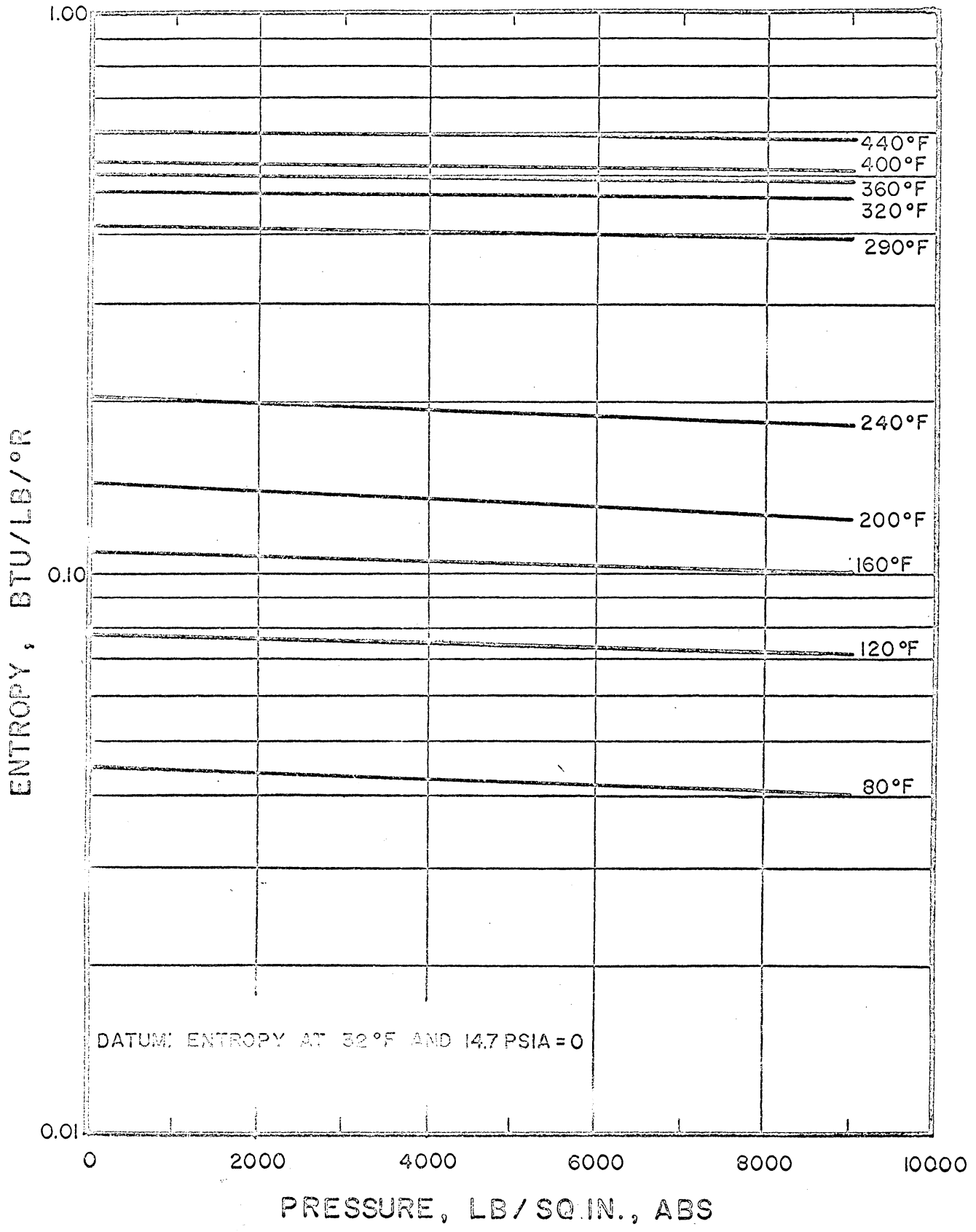


FIGURE 6. PRESSURE-ENTROPY DIAGRAM FOR POLYETHYLENE

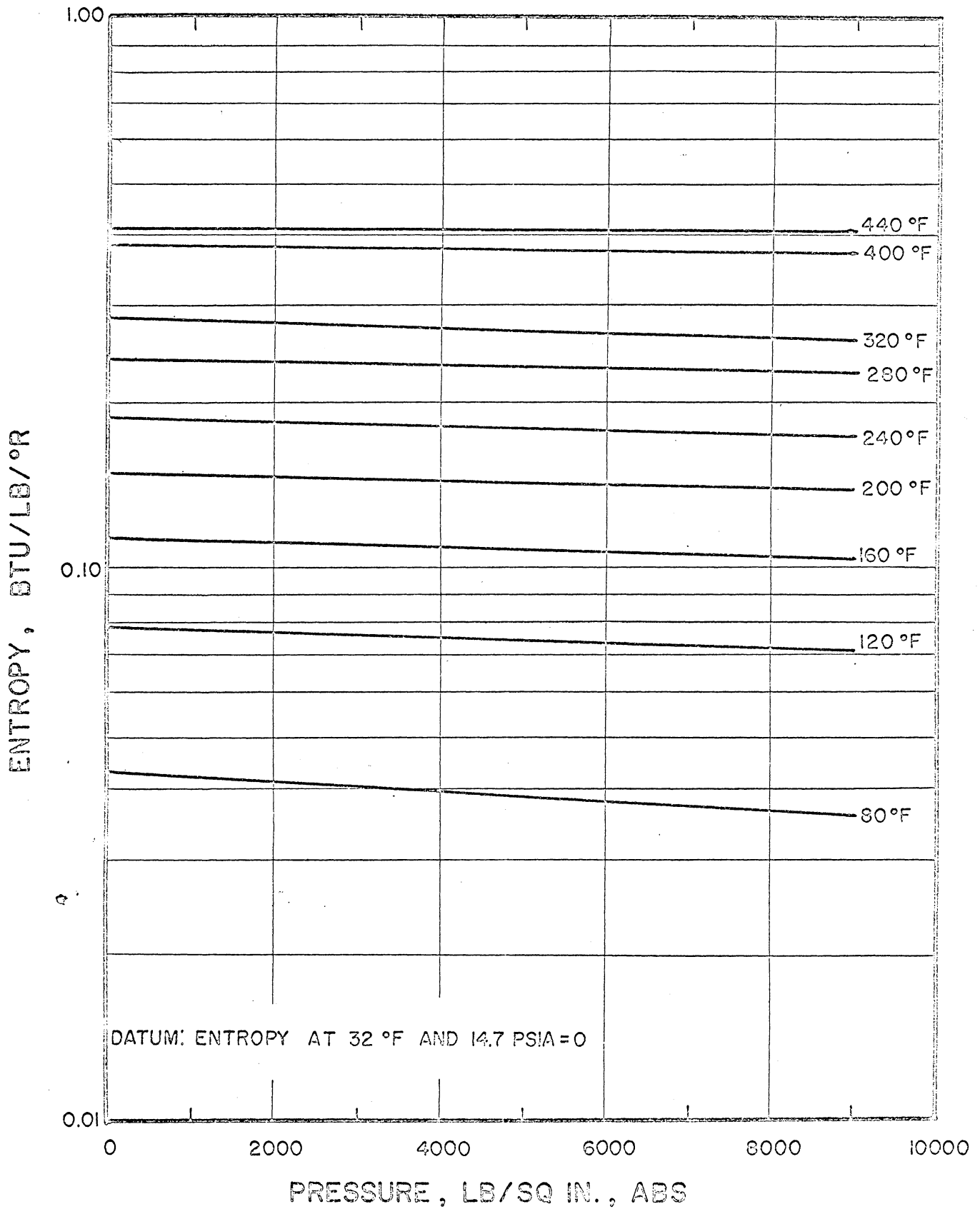


FIGURE 7. PRESSURE-ENTROPY DIAGRAM FOR POLYPROPYLENE

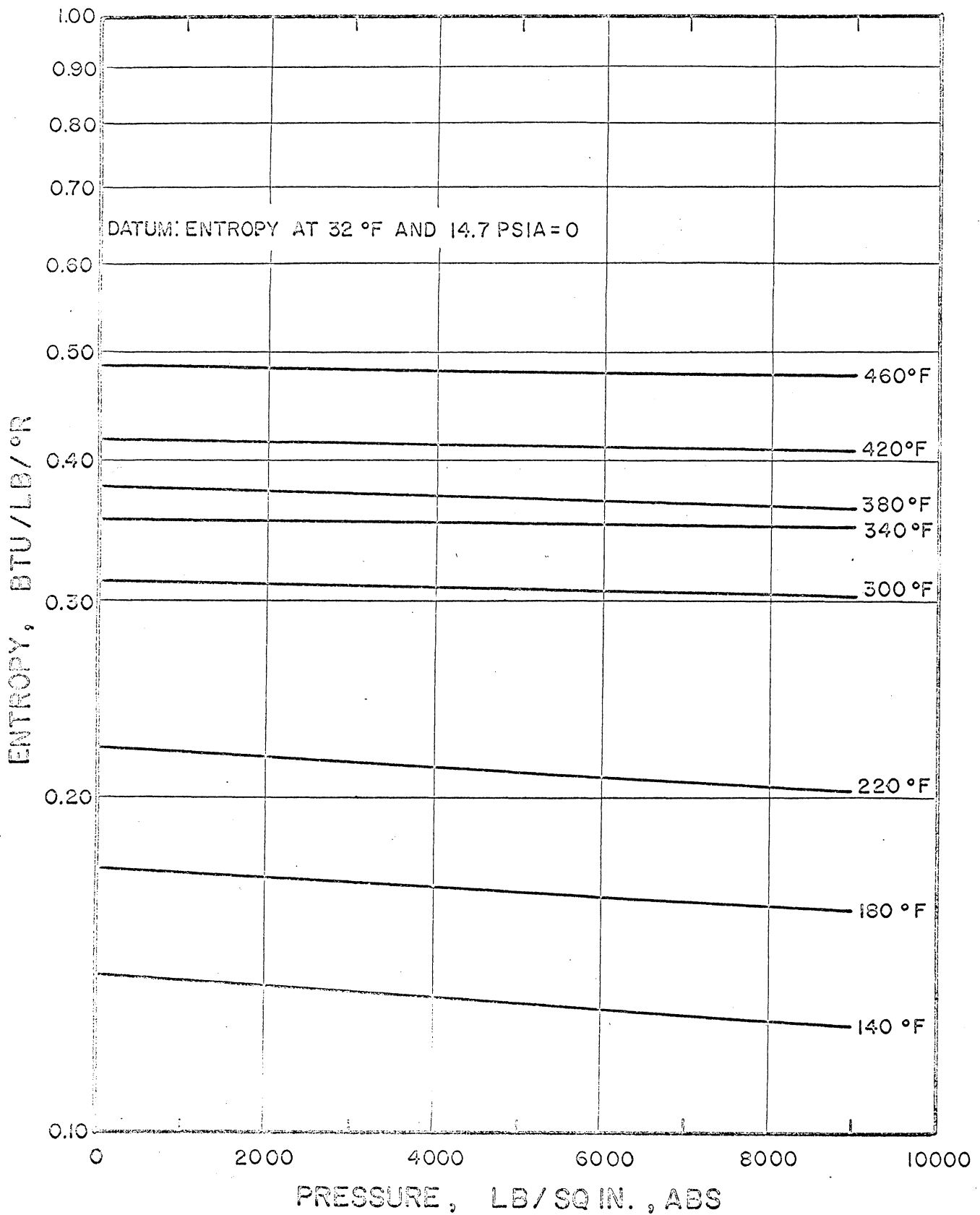


FIGURE 8. PRESSURE-ENTROPY DIAGRAM FOR ETHYLENE-PROPYLENE COPOLYMER

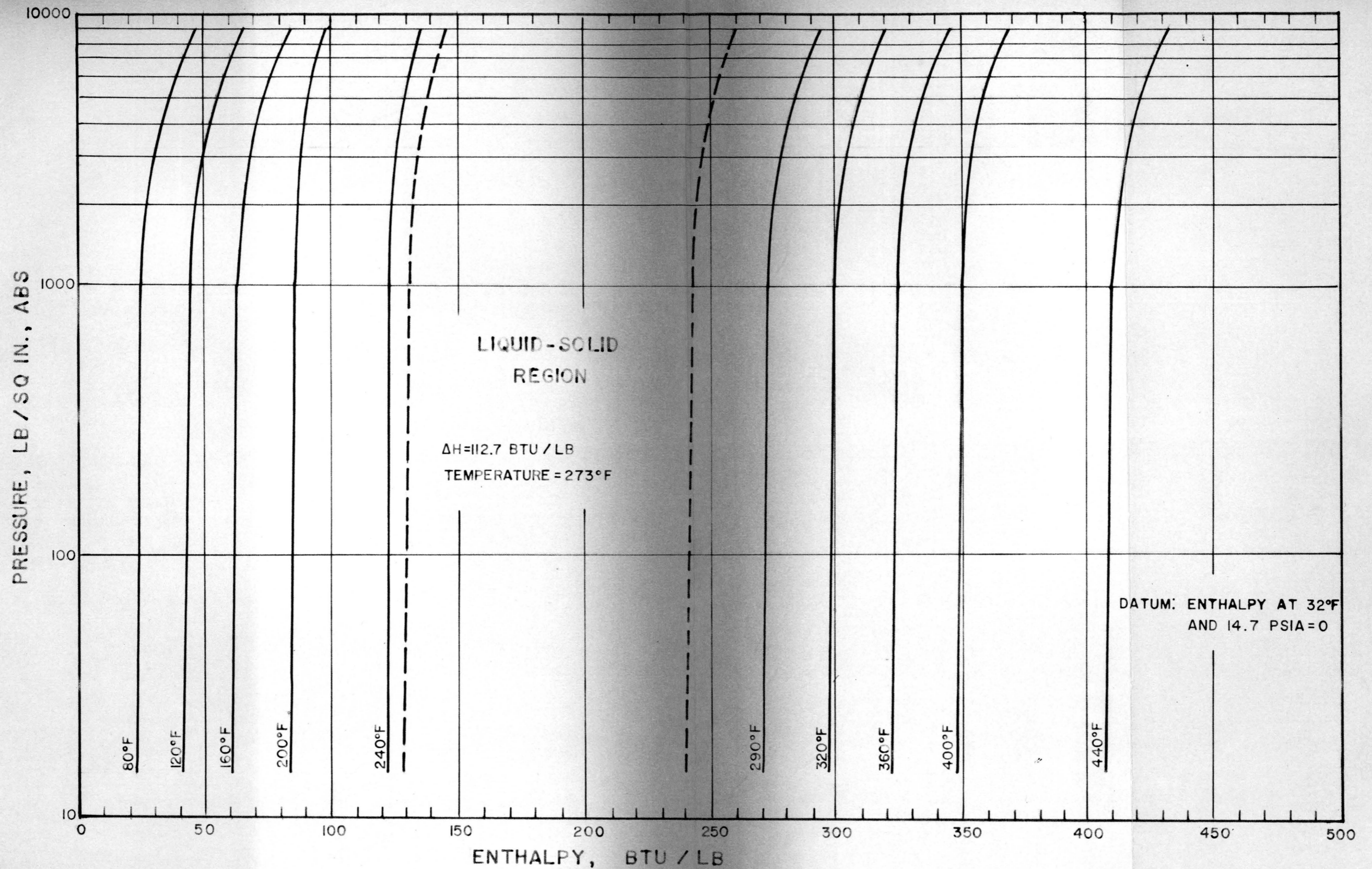


FIGURE 9 . PRESSURE - ENTHALPY DIAGRAM FOR LINEAR POLYETHYLENE

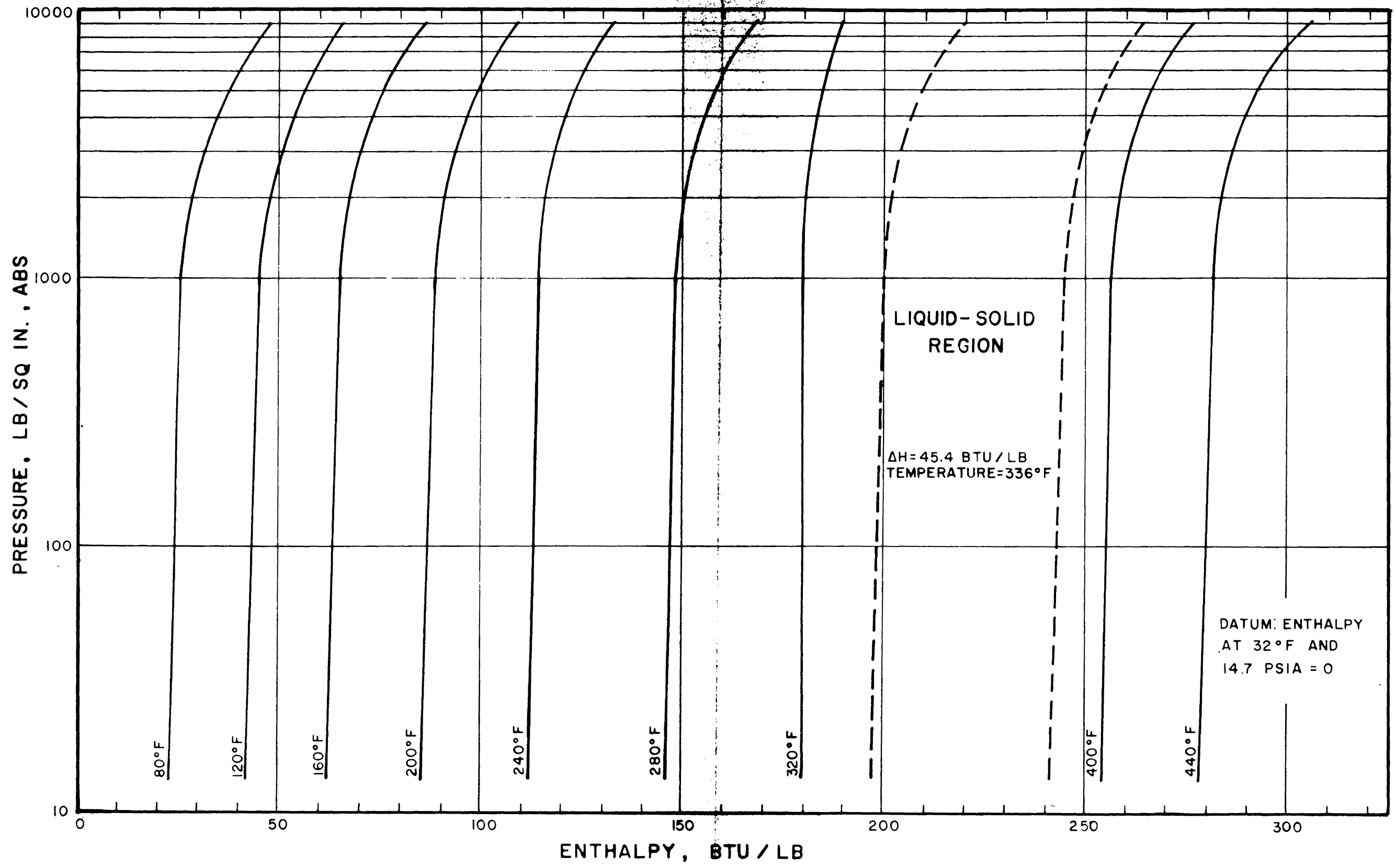


FIGURE 10.

PRESSURE-ENTHALPY DIAGRAM FOR POLYPROPYLENE

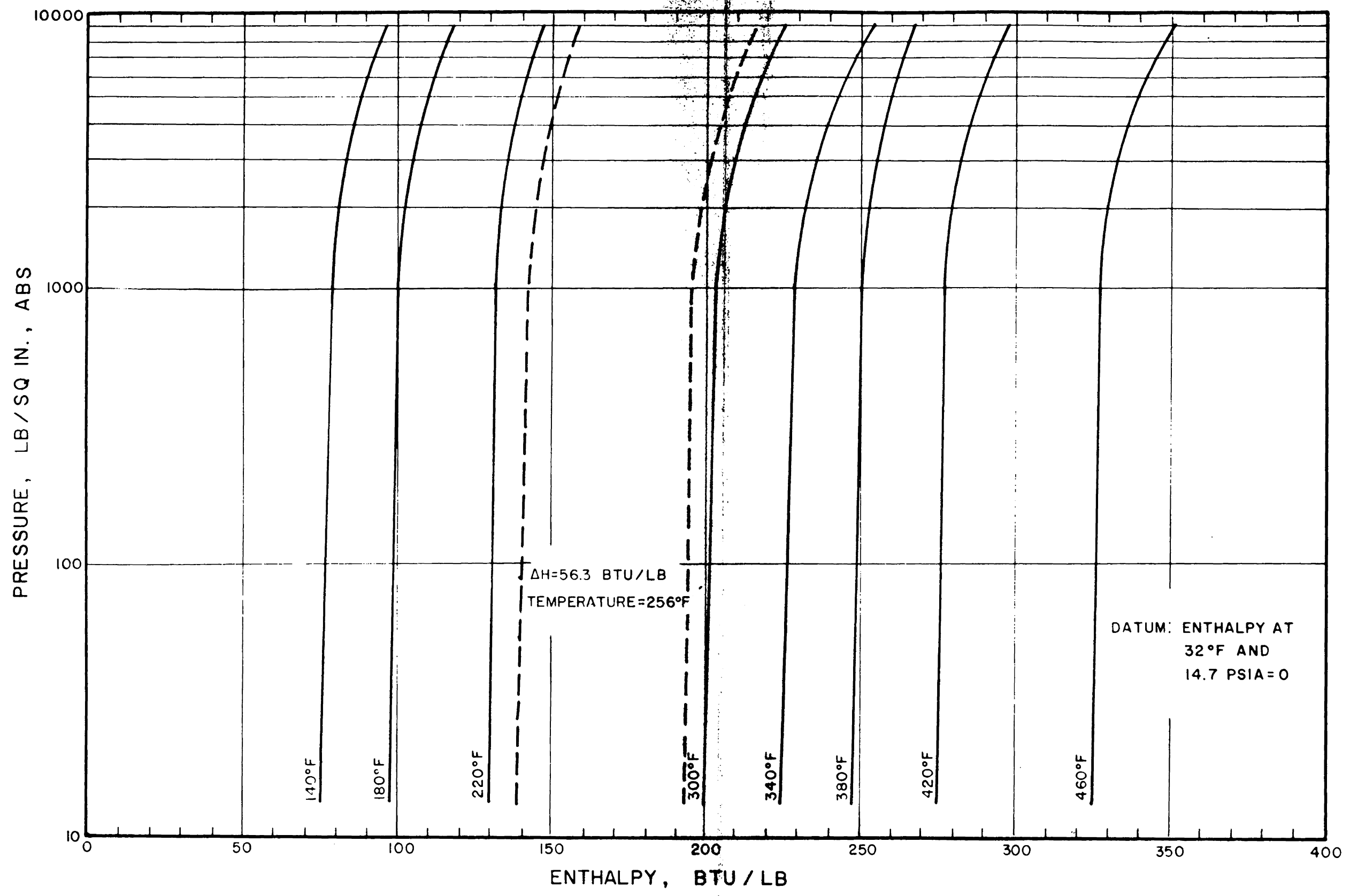


FIGURE II. PRESSURE-ENTHALPY DIAGRAM FOR ETHYLENE-PROPYLENE COPOLYMER

TABLE XI

Enthalpy-Entropy Table for Polypropylene

T		80 °F	120 °F	160 °F	200 °F	240 °F	280 °F	320 °F	400 °F	440 °F
P										
14.7	H	22.40 ^a	42.00	62.30	85.60	112.20	146.10	179.70	254.10	278.40
	S	0.0436 ^b	0.0789	0.1136	0.1499	0.1890	0.2405	0.2875	0.3855	0.4120
1000	H	25.23	44.80	65.01	88.24	114.52	148.41	179.91	256.26	281.11
	S	0.0428	0.0780	0.1126	0.1488	0.1874	0.2389	0.2831	0.3834	0.4105
2000	H	28.10	47.58	67.71	90.86	116.82	150.76	180.56	258.62	283.93
	S	0.0421	0.0772	0.1116	0.1471	0.1858	0.2374	0.2793	0.3815	0.4092
3000	H	30.97	50.34	70.38	93.47	119.12	153.13	181.45	261.11	286.83
	S	0.0414	0.0763	0.1106	0.1465	0.1842	0.2359	0.2759	0.3799	0.4080
4000	H	33.82	53.09	73.05	96.08	121.38	155.58	182.70	263.74	289.90
	S	0.0407	0.0754	0.1095	0.1459	0.1926	0.2345	0.2729	0.3784	0.4080
5000	H	36.66	55.83	75.73	98.72	123.65	158.05	184.01	266.37	293.05
	S	0.0399	0.0745	0.1085	0.1443	0.1810	0.2332	0.2701	0.3770	0.4062
6000	H	39.53	58.55	78.40	101.36	125.96	160.56	185.36	269.01	296.25
	S	0.0391	0.0735	0.1075	0.1432	0.1794	0.2319	0.2672	0.3756	0.4054
7000	H	42.23	61.25	81.07	104.01	128.28	163.11	186.73	271.66	299.50
	S	0.0381	0.0726	0.1064	0.1422	0.1779	0.2306	0.2645	0.3742	0.4047
8000	H	44.88	63.94	83.75	106.67	130.62	165.70	188.16	274.32	302.76
	S	0.0371	0.0716	0.1054	0.1411	0.1764	0.2295	0.2618	0.3728	0.4041
9000	H	47.49	66.63	86.45	109.34	132.97	168.32	189.65	276.99	306.01
	S	0.0359	0.0706	0.1045	0.1401	0.1750	0.2284	0.2592	0.3711	0.4035

^a BTU/#^b BTU/# - °R

TABLE XII

Enthalpy-Entropy Table for Ethylene Propylene Copolymer

T		140 °F	180 °F	220 °F	300 °F	340 °F	380 °F	420 °F	460 °F
P									
14.7	H	75.00 ^a	98.00	130.00	200.00	226.00	248.00	273.30	324.00
	S	0.1379 ^b	0.1738	0.2223	0.3125	0.3565	0.3795	0.4190	0.4880
1000	H	77.36	100.11	131.88	202.87	228.90	249.97	276.05	326.71
	S	0.1364	0.1719	0.2200	0.3113	0.3553	0.3772	0.4176	0.4866
2000	H	79.71	102.24	133.81	205.75	231.90	252.07	278.87	329.51
	S	0.1348	0.1700	0.2178	0.3101	0.3543	0.3751	0.4164	0.4853
3000	H	82.09	104.41	135.75	208.60	235.05	254.23	281.71	332.34
	S	0.1334	0.1682	0.2157	0.3089	0.5535	0.3731	0.4152	0.4841
4000	H	84.47	106.58	137.63	211.46	238.33	256.45	284.98	335.27
	S	0.1319	0.1664	0.2134	0.3077	0.3529	0.3712	0.4140	0.4831
5000	H	86.85	108.72	139.52	214.31	241.58	258.70	287.29	338.25
	S	0.1305	0.1646	0.2113	0.3065	0.3522	0.3694	0.4128	0.4821
6000	H	89.24	110.86	141.44	217.08	244.83	260.96	290.12	341.29
	S	0.1291	0.1628	0.2091	0.3053	0.3516	0.3676	0.4117	0.4812
7000	H	91.63	113.11	143.37	219.74	248.16	263.27	292.90	344.42
	S	0.1277	0.1612	0.2071	0.3040	0.3511	0.3659	0.4106	0.4804
8000	H	94.01	115.42	145.32	222.37	251.52	265.62	295.64	347.58
	S	0.1263	0.1597	0.2050	0.3026	0.3506	0.3642	0.4094	0.4797
9000	H	96.37	117.70	147.30	225.02	254.84	267.98	298.38	350.81
	S	0.1249	0.1581	0.2030	0.3012	0.3502	0.3626	0.4082	0.4790

^a BTU/#
^b BTU/# - °R

TABLE X

Enthalpy-Entropy Table for Polyethylene

T		80 °F	120 °F	160 °F	200 °F	240 °F	290 °F	320 °F	360 °F	400 °F	440 °F
14.7	H	23.40 ^a	41.40	61.20	84.60	120.50	271.0	297.0	322.00	348.0	407.0
	S	0.0464 ^b	0.0780	0.1101	0.1476	0.2026	0.4120	0.4740	0.5040	0.5290	0.6030
1000	H	26.19	44.06	63.75	86.21	122.18	273.46	299.45	324.73	350.14	409.67
	S	0.0457	0.0772	0.1091	0.1452	0.2003	0.4102	0.4722	0.5025	0.5269	0.6015
2000	H	28.99	46.73	66.30	87.82	123.88	276.02	301.93	327.97	352.34	412.44
	S	0.0450	0.0764	0.1081	0.1428	0.1981	0.4085	0.4705	0.5012	0.5298	0.6001
3000	H	31.68	49.40	68.86	89.39	125.59	278.70	304.47	329.20	354.59	415.29
	S	0.0443	0.0756	0.1072	0.1403	0.1959	0.4071	0.4688	0.4998	0.5229	0.5989
4000	H	34.38	52.10	71.43	90.92	127.32	281.36	307.05	331.90	356.92	418.18
	S	0.0435	0.0749	0.1062	0.1378	0.1937	0.4056	0.4673	0.4983	0.5210	0.5977
5000	H	37.09	54.80	74.01	92.45	129.03	283.97	309.65	334.59	359.39	421.08
	S	0.0428	0.0742	0.1053	0.1353	0.1915	0.4041	0.4657	0.4969	0.5194	0.5965
6000	H	39.83	57.51	76.59	93.98	130.73	286.61	312.27	337.37	361.88	423.95
	S	0.0422	0.0735	0.1044	0.1327	0.1893	0.4026	0.4643	0.4956	0.5178	0.5954
7000	H	42.58	60.22	79.17	95.44	132.49	289.31	314.93	340.29	364.34	426.78
	S	0.0415	0.0728	0.1035	0.1301	0.1871	0.4012	0.4628	0.4945	0.5162	0.5942
8000	H	45.31	62.94	81.76	96.85	134.28	292.04	317.60	343.28	366.83	429.57
	S	0.0408	0.0721	0.1026	0.1274	0.1850	0.3999	0.4615	0.4935	0.5147	0.5930
9000	H	48.01	65.65	84.37	98.22	136.08	294.74	320.21	346.24	369.39	432.35
	S	0.0401	0.0714	0.1020	0.1246	0.1829	0.3986	0.4600	0.4926	0.5132	0.5918

^a BTU/#
^b BTU/# - °R

Enthalpy of Two Phase Region. Figures 9, 10, and 11 are pressure-enthalpy curves for the polymers studied. The curves represent the change in enthalpy with pressure for several isotherms. The enthalpy at one atmosphere total pressure was taken from the data of Foster⁽¹⁴⁾.

Figures 9, 10, and 11 show liquid-solid regions delineated by a dashed line. These regions are approximations. The extreme difficulty inherent in obtaining reproducible dilatometric data in the liquid-solid region for polymeric materials necessitated these approximations.

The melting points and heats of fusion shown on the figures were taken from Foster's work⁽¹⁴⁾ which employed the technique of differential thermal analysis to arrive at the values shown. Knowing the enthalpy, heat of fusion, and melting point at one atmosphere total pressure, the liquid-solid region envelope was constructed by correcting for pressure with the aid of the Clasius-Clapeyron equation⁽¹⁵⁾. The calculation was performed as follows:

$$\frac{dp'}{dT} = \frac{\Delta H}{T \Delta V} \quad \text{Clasius-Clapeyron Equation}$$

where:

The values of $\frac{dp'}{dT}$ and ΔV were taken from an article by Shiro Matsuoka⁽¹⁸⁾.

$$\left. \begin{aligned} \frac{dp'}{dT} &= 11.4285 \text{ at 1 atmosphere} \\ \frac{dp'}{dT} &= 12.5427 \text{ at 618 atmospheres} \end{aligned} \right\} \frac{\text{cal/gm-mole-}^\circ\text{C}}{\text{cc/gm}}$$

$$V_{\text{fusion at one atmosphere}} = 0.1957 \text{ cc/gm}$$

$$V_{\text{fusion at 618 atmospheres}} = 0.1771 \text{ cc/gm}$$

at one atmosphere,

$$\frac{dp'}{dT} = 11.4285 = \frac{H}{407^\circ\text{K} \times 0.1957}$$

$$\Delta H = 117.04 \text{ Btu/lb}$$

At 618 atmospheres,

$$\frac{dp'}{dT} = 12.5427 = \frac{H}{427^\circ\text{K} \times 0.1771}$$

$$\Delta H = 121.95 \text{ Btu/lb}$$

The above calculation for polyethylene indicates that the heat of fusion is nearly constant over the pressure range investigated. Assuming this to be true for polypropylene and ethylene-propylene copolymers, the boundaries for the liquid solid region were drawn parallel to the neighboring isotherms.

IV. DISCUSSION

Discussion of Literature

The quantity of literature on the thermodynamic properties of polymers is scarce. Nothing could be found for polypropylene or ethylene-propylene copolymers. An attempt was made to find literature concerning the thermodynamics of solids or Mollier type diagrams for solids. This search was fruitless.

There is extensive literature available for the thermodynamic properties of hydrocarbons and common liquids and gases. There are excellent Mollier type diagrams available for ammonia⁽²⁹⁾, freon-12⁽²⁹⁾, carbon dioxide⁽²⁹⁾, and other common refrigerants. Canjar and co-workers have completed a series of Mollier diagrams for several of the lower hydrocarbons⁽⁶⁾.

An article by Lupton shows thermodynamic diagrams for polyethylene resins of different densities⁽¹⁶⁾. Lupton did not calculate entropy data but his enthalpy data is in very close agreement with the results of this investigation. Lupton does not indicate the source or accuracy of the p-v-t required to construct his temperature enthalpy diagrams.

Parks and Richards presented pressure-enthalpy and pressure-entropy diagrams for polyethylene⁽¹⁹⁾. Their data is for low density

polyethylene and as a consequence their pressure-volume data differs from that in this investigation. The entropy and enthalpy curves were constructed in the same manner as was done in this investigation, but the source or accuracy of the calorimetric data is not indicated. The pressure-entropy and pressure-enthalpy curves approximate those in this investigation. The difference is due to the difference in densities of the polyethylenes used.

Discussion of Procedure

The accuracy of the results of this investigation was dependent upon the accuracy of the raw data and the error inherent in the methods used for numerical analysis. An accuracy of from 99.8 per cent to 99.9 per cent was present in the volume data of Foster. The pressure data was correct to greater than 99 per cent accuracy and temperatures were held to within plus or minus 0.1 C° .

The work of Canjar has shown that raw data is not good enough to use untreated for thermodynamic calculations⁽⁵⁾. Therefore, the data was smoothed using a modified version of van der Waal's equation of state.

A Taylor series expansion was used to calculate slopes as shown on page 32. The error in this numerical method approaches zero as fast as the square of h . The value of h was, therefore, always taken

to be as small as possible. Also, an error of 10 per cent would have no effect since the order of magnitude of the number is so much smaller than the base value of enthalpy or entropy to which the modified result of the Taylor expansion is added. The result was modified by the graphical integration as shown on page 35.

Again, the very small order of magnitude of the value compared to the base value does not require great accuracy of the numerical methods.

Discussion of Results

The results of this investigation were intended to be of benefit to fabricators and manufacturers of the polymers studied. Injection molding pressures for the polymers studied range from 10,000 to 20,000 pounds per square inch, but the raw data only covered a range from one atmosphere pressure to 9,000 pounds per square inch pressure. The pressure-entropy and pressure-enthalpy curves are plotted semi-logarithmically. The isotherms present a predictable pattern. The entropy and enthalpy values can be extrapolated to 15,000 pounds per square inch pressure with very good confidence and to 20,000 pounds per square inch with fair confidence.

The isotherms with the dashed lines on Figures 3 and 4 run through the liquid-solid region. The dashed portion of the line is an approximation. Dilatometric data is extremely difficult to obtain in the liquid-solid region.

The pressure-enthalpy results of this investigation agree very well with the results of Lupton for polyethylene⁽²⁵⁾. Lupton did not present entropy data. The pressure-volume curves of Lupton also agree well with those of this investigation.

The data of Parks and Richards is for low density polyethylene⁽¹⁹⁾. The p-v-t data, therefore, differed from that of Foster⁽¹⁴⁾ and the entropy and enthalpy necessarily differed.

Recommendations

The fabrication temperatures of the polymers studied is as high as 600 °F. It is recommended that the data be extended to this temperature range.

Fabrication pressures for the polymers studied run as high as 25,000 pounds per square inch. It is recommended that the pressure range of the investigation be extended sufficiently to allow at least extrapolation with good confidence to this pressure range.

Dilatometric data in the liquid-solid region is lacking for polymeric materials. It is recommended that an investigation be made exclusively of the dilatometric properties of polymers in the liquid-solid region.

It is recommended that a study be made to determine the effect of varying copolymer composition on the thermodynamic properties of the copolymer.

Limitations

The only limitations in an investigation of this type are the range and accuracy of the raw data.

V. CONCLUSIONS

The preparation of thermodynamic diagrams of polyethylene, polypropylene, and ethylene-propylene copolymer led to the following conclusions:

1. The effect of the copolymer is to yield a melting point lower than either the polyethylene or the polypropylene.
2. The addition of methyl groups to the polypropylene results in an increase in the heat of fusion.
3. The pressure-enthalpy curves for polyethylene and polypropylene are nearly identical below 240 °F.
4. The entropy values for the materials studied are all nearly constant.
5. The pressure-entropy curves for polyethylene and polypropylene are nearly identical below 240 °F.
6. Polyethylene is more crystalline than either polypropylene or ethylene-propylene copolymer. This is verified by the sharper melting point of Figure 2 as compared to Figures 3 and 4.

VI. SUMMARY

The purpose of this investigation was to determine thermodynamic properties for linear polyethylene, polypropylene and an ethylene-propylene copolymer, from previously determined p-v-t and calorimetric data.

The entropy and enthalpy were calculated from calorimetric and p-v-t data using a datum of entropy and enthalpy equal to zero at 14.7 pounds per square inch pressure absolute and 32 °F. Entropy and enthalpy were plotted against pressure for a series of isotherms. The values of entropy and enthalpy were then corrected for pressure to arrive at the resultant diagrams.

The results are shown in Figures 2, 3, 4, 5, 7, 8, 9, 10, and 11. In Figures 6, 7, 9, and 10 it can be seen that the thermodynamic properties of polyethylene and polypropylene are very similar up to 240 °F.

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the scanned document**

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ABSTRACT

The purpose of this investigation was to determine thermodynamic properties for linear polyethylene, polypropylene and an ethylene-propylene copolymer, from previously determined p-v-t and calorimetric data.

The entropy and enthalpy were calculated from calorimetric and p-v-t data using a datum of entropy and enthalpy equal to zero at 14.7 pounds per square inch pressure absolute and 32 °F. Entropy and enthalpy were plotted against pressure for a series of isotherms. The values of entropy and enthalpy were then corrected for pressure to arrive at the resultant diagrams.

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