

Calorimetric Properties of Polytetrafluoroethylene (Teflon) from 0° to 365° K¹

George T. Furukawa, Robert E. McCoskey, and Gerard J. King

The thermal properties of polytetrafluoroethylene (Teflon) samples were investigated, using an adiabatic-vacuum calorimeter. The effect of the annealing and quenching processes on the heat capacity of a molded Teflon sample was studied. The heat-capacity data were used to compute the heat capacity, enthalpy, and entropy of the polymer samples at 5-deg intervals from 0° to 365° K. The heat-capacity results with the molded, annealed, and quenched samples of Teflon show the possibility of a glass transformation at about 160° K. The lack of a more definite glass-transformation effect is attributed to inter- and intramolecular hindrances to configurational changes in the Teflon polymer. The existence of first-order transitions at 293° and 303° K, previously reported by Quinn, Roberts, and Work, was confirmed.

1. Introduction

The examination of current scientific and industrial literatures indicates that the investigation and application of fluorine and fluorine compounds are becoming increasingly broader. Products containing fluorine are being used in such applications as heat-transfer agents, pest control, fire control, lubricants, pharmaceuticals, plastics, intermediates in synthesis, and many others. Although the fluorocarbons have molecular structure somewhat similar to their hydrocarbon analogs, their chemical and physical properties are greatly different. Similarly, fluorine-containing compounds have been found in many instances to behave very differently from the other halogen analogs. From these considerations it seems a systematic experimental investigation of "key" fluorine compounds would aid in the present far-reaching studies involving fluorine and its compounds.

The Bureau has undertaken a program for the study of thermodynamic properties of both simple and more complicated fluorocarbons. In the recent years the fluorocarbon plastic, polytetrafluoroethylene, has come into wide use, on account of its remarkable thermal and chemical stability, as gasket, packing, electrical insulation, and protective coating for vessels handling corrosive materials. Obviously, thermodynamic study of this material and its monomer, tetrafluoroethylene, would be highly desirable in the further understanding of polymerization processes and fundamental structure of polymers in general. This report deals with the heat-capacity investigations of two polytetrafluoroethylene samples. One sample was in the form of powder and the other in molded sheets. The enthalpy and entropy values were calculated from the heat-capacity data. The investigation confirmed the existence of two first-order transitions [1]², one at 293° K and a much less pronounced one at 303° K. The heat-capacity results show the possibility of a glass transformation at about 160° K.

2. Experimental Procedure and Sample

The calorimetric apparatus and experimental procedures were essentially the same as used in the investigation of the thermal properties of diphenyl ether [2]. The details of the design and operation of a similar calorimeter are given in the paper on 1,3-butadiene by R. B. Scott, et al. [3]. Briefly, the experimental method was as follows: Each of the samples was placed in a copper container provided with vanes to promote the rapid attainment of thermal equilibrium and with a central well for a platinum resistance thermometer and heater assembly. The sample was pumped (vacuum about 10⁻⁴ mm Hg) for 2 days at room temperature and for 1 day at about 50° C to eliminate volatile impurities. There was no indication of continuous evolution of gases or loss of material during the pumping process. After the container was sealed with a small quantity of helium gas, it was suspended within the adiabatic shield system. At all times during the calorimetric experiments the shield was maintained at the same temperature as the container by means of differential thermocouples and shield heaters. The outer surface of the container and the adjacent shield surface were polished to minimize heat transfer by radiation. The vacuum surrounding the container was 10⁻⁵ mm Hg or better. The electric-power input to the calorimeter heater (about 100 ohms) was measured by means of a Wenner potentiometer in conjunction with a standard resistor and a volt box. The resistance of the platinum resistance thermometer was measured by using a Mueller-type bridge. The length of a heating period was determined with an interval timer run on standard 60 cycles furnished by the Radio Section of the Bureau. The timer was periodically compared with the time signals from the Time Section and was found to vary not more than 0.02 sec for a heating period, which was never less than 2 min. All electric instruments were recently calibrated at the Bureau.

The experimental measurements were usually made by first cooling the material to the lowest temperature attainable with the particular refrigerant. During this process the space surrounding the sus-

¹ This paper is based on the work sponsored by the Ordnance Corps, U. S. Department of the Army.

² Figures in brackets indicate the literature references at the end of this paper.

pendent sample container was filled with a few centimeters of helium gas to permit rapid cooling. For slow cooling, however, the space was maintained at a high vacuum. Upon attaining the desired temperature, the helium gas was pumped out, and the experiments were made continuously up the temperature scale, the final temperature of the first heating period being the initial temperature of the second and so on. At the lower temperatures, where the slope of the heat-capacity curve changes rapidly, the temperature rise for a heating period was made as small as 2 to 3 deg to make negligible the curvature correction in the heat-capacity value obtained. At the higher temperatures, where the curvature is small, temperature intervals of about 5 to 10 deg were taken.

The heat-capacity measurements were made in the temperature range 15° to 370° K;³ first, with the empty container, and then with the container plus the samples. The net heat capacities were obtained by subtracting the smoothed heat capacities of the empty container from the observed gross heat capacities. The net heat capacities so obtained are given in section 3.

Four series of experimental measurements were made with two samples of polytetrafluoroethylene, or Teflon.⁴ One sample was a powder, and the other was in the form of $\frac{1}{8}$ -in. sheet. The latter sample was prepared by molding the powder material. These materials are considered to be typical of the products currently made by the E. I. du Pont de Nemours Co. The Teflon powder was transferred directly into the copper container without further treatment, but the Teflon sheet was cut into small cubes of about $\frac{1}{8}$ in. on the edge before placing it in the container. This latter material without any further treatment will be designated as molded Teflon in order to distinguish it from the Teflon samples that were subjected to heat treatments prior to the heat-capacity experiments. In order to determine the extent to which an annealing process would increase the crystallinity in the Teflon sheet, the latter material was heated at 350° C under vacuum for 4 hr and cooled slowly to room temperature. This material will be designated as annealed Teflon. The fourth series of experiments was made with the Teflon sheet that had been heated to about 350° C until clear and quenched in liquid nitrogen. Renfrew and Lewis [4] obtained clear Teflon film by heating the film until clear and subsequently quenching it in water. The quenched $\frac{1}{8}$ -in. Teflon sheet used in this investigation, however, was not clear. The heat-capacity experiments with the quenched Teflon were made only over a limited temperature range, about 120° to 330° K.

3. Results and Discussion

The experimental results, net heat capacities, from the four series of heat-capacity measurements with the powder, molded, annealed, and quenched Teflon

samples are plotted in figures 1, 2, 3 and 4, respectively. The heat-capacity measurements with the Teflon powder were made after rapidly cooling the polymer (run 2) from room temperature to liquid-nitrogen temperature. This was followed by experiments with the sample slowly cooled (run 4). Similar series of experiments were carried out with the molded Teflon (runs 1 and 2 were after cooling rapidly; run 5 was after cooling slowly). The heat-capacity results were not affected significantly by the rate of cooling. The experiments with the annealed and quenched Teflon samples were therefore made without varying the rate of cooling. The experimental values with the powder, molded, and annealed samples were smoothed graphically, and the smoothed values are given in tables 1, 2, and 3, respectively, at 5-deg intervals from 0° to 365° K. The values below 15° K were obtained by extrapolating a Debye function [2], which was fitted to the experimental values in the temperature range 15° to 30° K. The heat-capacity values between 280° and 310° K, where Teflon undergoes two first-order transitions, have been omitted in the tables. The smoothed heat capacities from the four series of experiments are compared in figure 5. No table of smoothed heat capacity of the quenched sample is given.

During the heat-capacity measurements persistent upward thermal drifts of about 1 mdeg min⁻¹ were observed in the range 160° to 170° K with the Teflon powder. Similar upward drifts were found with the molded, annealed, and quenched Teflon samples in the range 145° to 175° K. The thermal drift is probably related to the much larger drifts observed with the rubber polymers [5] in the temperature range of glass transformation. The heat-capacity curves with the Teflon samples, however, do not exhibit the steep rise found with rubber polymers and other polymers, supercooled liquids, and noncrystalline solids at the glass-transformation temperature [6]. However, the results with the molded Teflon do show a slightly more rapid rise in the curve at about 160° K. The Teflon powder does not exhibit any unusual behavior in this temperature range. The quenched sample, in which greater amorphous character was expected to be frozen-in, does not exhibit any more pronounced rise in the curve at this temperature. Actually, the molded and quenched samples give almost identical heat-capacity values (fig. 5). This would indicate that the polymeric chain segments in Teflon are not sufficiently flexible or capable of rotation [6] to make a significant contribution to glass transformation. Also it is likely that the heating and the subsequent quenching processes did not freeze in sufficient amorphous character [4] or open structure in the polymer on account of its high melt viscosity [8]. Renfrew and Lewis [4] found, according to X-ray diffraction photographs, almost as much crystallinity in a Teflon sample heated above its high-temperature transition point and quenched in water as in a sample cooled slowly. According to the theory of viscous flow [7] the polymer segments cooperate in the flow by a simultaneous configurational change involving rotation of the polymer

³ The temperatures expressed in degrees Kelvin were obtained from the relation °K = °C + 273.16°.

⁴ The authors are indebted to W. D. Bowersox of the E. I. du Pont de Nemours Co. for the samples.

segments. As pointed out by Hanford and Joyce [8], the rigidity of the Teflon polymer to rotation is manifested in the high melt viscosity and in the ability of the polymer to be form-stable under its own weight above its melting temperature (about 327°C). These considerations seem to corroborate the non-existence of a pronounced glass-transformation effect in Teflon. The annealing process, on the other hand, seems to have lowered the rise in the heat-capacity curve found for the molded and quenched Teflon samples at 160° K. This would indicate that the annealing process has increased the order in the Teflon polymer and that what little glass-transformation effect that was present was decreased. Teflon is considered to exist in a high degree of crystallinity [4, 8, 11], and thus the polymer has a closed, well-packed structure that would further inhibit glass transformation. The lowering of the heat capacity with the annealed Teflon supports this effect of crystallization on the glass transformation.

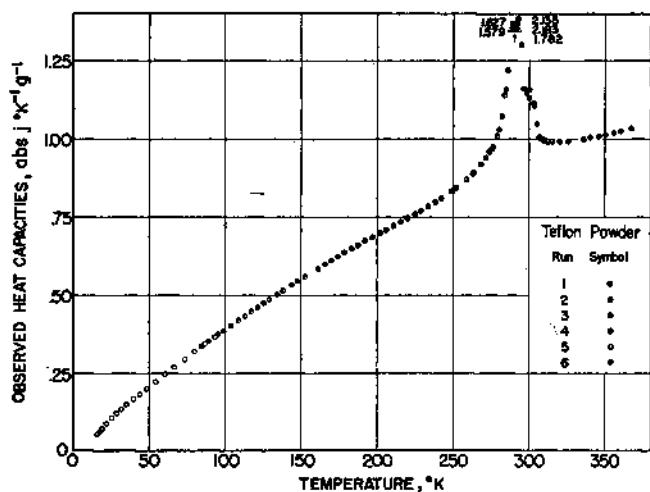


FIGURE 1. Observed heat capacities of Teflon powder.

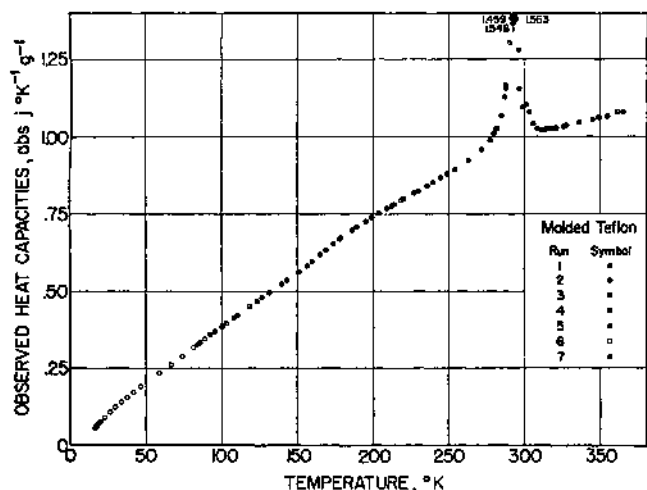


FIGURE 2. Observed heat capacities of molded Teflon.

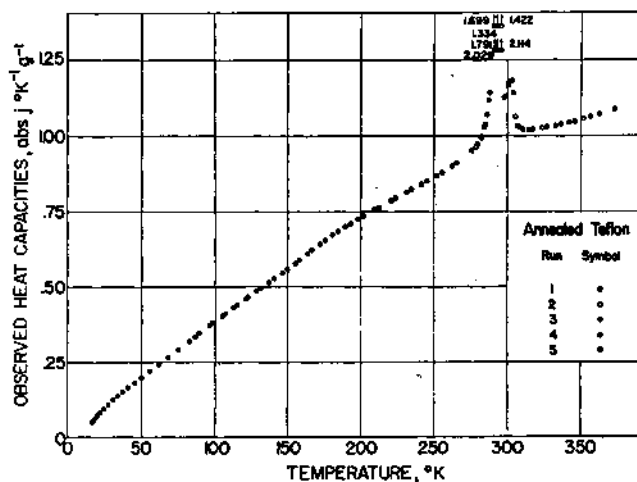


FIGURE 3. Observed heat capacities of annealed Teflon.

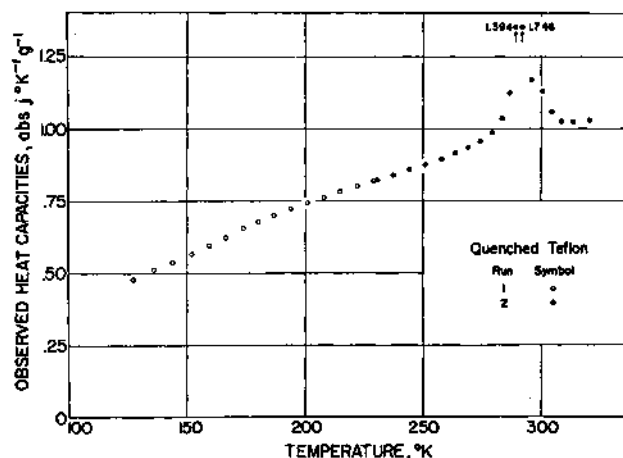


FIGURE 4. Observed heat capacities of quenched Teflon.

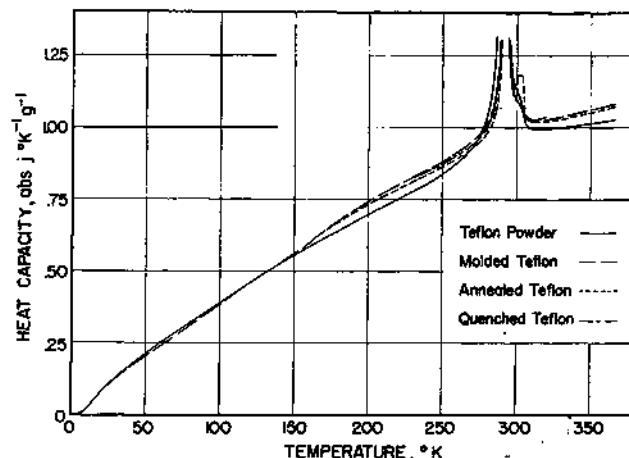


FIGURE 5. Comparison of the heat capacities of powder, molded, annealed, and quenched Teflon samples.

TABLE 1.—Heat capacity, enthalpy, and entropy of Teflon powder at intergal temperatures

T	C	$H_T - H_0^s$	$S_T - S_0^s$
$^{\circ}K$	abs $j^{\circ}K^{-1}g^{-1}$	abs jg^{-1}	abs $j^{\circ}K^{-1}g^{-1}$
0	0	0	0
5	0.0024	0.003	0.0008
10	.0179	.046	.0062
15	.0472	.206	.0188
20	.0767	.519	.0365
25	.1033	.966	.0665
30	.1271	1.544	.0775
35	.1486	2.233	.0987
40	.1696	3.030	.1200
45	.1871	3.922	.1410
50	.2064	4.903	.1616
55	.2258	5.980	.1821
60	.2458	7.159	.2026
65	.2651	8.437	.2231
70	.2836	9.809	.2434
75	.3017	11.27	.2636
80	.3205	12.83	.2837
85	.3385	14.48	.3036
90	.3561	16.21	.3235
95	.3731	18.04	.3432
100	.3897	19.94	.3628
105	.4069	21.93	.3822
110	.4240	24.01	.4015
115	.4410	26.17	.4207
120	.4578	28.42	.4399
125	.4743	30.75	.4589
130	.4905	33.16	.4778
135	.5066	35.66	.4966
140	.5224	38.23	.5153
145	.5378	40.88	.5339
150	.5529	43.61	.5524
155	.5677	46.41	.5708
160	.5825	49.26	.5890
165	.5975	52.23	.6072
170	.6123	55.26	.6253
175	.6270	58.36	.6432
180	.6410	61.53	.6610
185	.6556	64.77	.6788
190	.6698	68.08	.6965
195	.6819	71.46	.7140
200	.6950	74.90	.7315
205	.7083	78.41	.7488
210	.7217	81.98	.7660
215	.7354	85.63	.7832
220	.7492	89.34	.8002
225	.7629	93.12	.8172
230	.7770	96.97	.8341
235	.7914	100.9	.8510
240	.8063	104.9	.8678
245	.8221	109.0	.8846
250	.8393	113.1	.9014
255	.8579	117.3	.9182
260	.8794	121.7	.9351
265	.9041	126.1	.9520
270	.9359	130.7	.9692
275	.9771	135.5	.9867
280	1.036	140.5	1.005
310	.9959	178.6	1.134
315	.9925	183.5	1.150
320	.9932	188.5	1.166
325	.9940	193.5	1.181
330	.9979	198.5	1.196
335	1.002	203.5	1.211
340	1.006	208.5	1.226
345	1.010	213.5	1.241
350	1.014	218.6	1.256
355	1.018	223.7	1.270
360	1.022	228.8	1.284
365	1.026	233.9	1.298

In the range 280° to 310° K, the Teflon samples exhibit a transformation involving a large enthalpy change. The heat-capacity curve rises sharply and falls with a small "shoulder." The experiments with the annealed sample resolved the "shoulder" into a small peak. These effects are shown and compared in different samples in figures 1 to 5. The authors believe that, from the nature of the two peaks, two first-order transitions are present. During the heat-capacity experiments persistent downward thermal drifts were observed in this temperature range. These thermal drifts are quite similar to

TABLE 2. Heat capacity, enthalpy, and entropy of molded Teflon at integral temperatures

T	C	$H_T - H_0^s$	$S_T - S_0^s$
$^{\circ}K$	abs $j^{\circ}K^{-1}g^{-1}$	abs jg^{-1}	abs $j^{\circ}K^{-1}g^{-1}$
0	0	0	0
5	0.0024	0.003	0.0008
10	.0182	.047	.0063
15	.0477	.209	.0190
20	.0764	.524	.0369
25	.1016	.975	.0670
30	.1247	1.542	.0776
35	.1455	2.218	.0984
40	.1647	2.994	.1191
45	.1833	3.864	.1395
50	.2017	4.827	.1598
55	.2198	5.881	.1799
60	.2380	7.025	.1998
65	.2562	8.261	.2196
70	.2745	9.588	.2392
75	.2929	11.01	.2588
80	.3120	12.52	.2783
85	.3312	14.13	.2978
90	.3500	15.83	.3173
95	.3680	17.62	.3367
100	.3857	19.51	.3560
105	.4035	21.48	.3752
110	.4212	23.54	.3944
115	.4390	25.69	.4135
120	.4568	27.93	.4326
125	.4740	30.26	.4516
130	.4910	32.67	.4706
135	.5080	35.17	.4894
140	.5250	37.75	.5081
145	.5423	40.42	.5269
150	.5598	43.18	.5455
155	.5775	46.02	.5642
160	.5955	48.96	.5828
165	.6130	51.99	.6015
170	.6305	55.14	.6203
175	.6487	58.38	.6391
180	.6772	61.72	.6579
185	.6940	65.15	.6766
190	.7102	68.66	.6954
195	.7257	72.25	.7141
200	.7498	75.91	.7326
205	.7556	79.66	.7511
210	.7701	83.47	.7695
215	.7842	87.36	.7878
220	.7982	91.31	.8060
225	.8120	95.34	.8241
230	.8257	99.43	.8421
235	.8394	103.6	.8600
240	.8533	107.8	.8778
245	.8673	112.1	.8955
250	.8818	116.5	.9132
255	.8971	120.9	.9308
260	.9133	125.5	.9484
265	.9315	130.1	.9659
270	.9520	134.8	.9833
275	.9765	139.6	1.001
280	1.012	144.6	1.019
310	1.021	179.3	1.137
315	1.023	184.4	1.153
320	1.027	189.5	1.169
325	1.032	194.7	1.185
330	1.038	199.8	1.201
335	1.044	205.1	1.217
340	1.049	210.3	1.232
345	1.055	215.5	1.248
350	1.061	220.8	1.263
355	1.068	226.2	1.278
360	1.074	231.5	1.293
365	1.081	236.9	1.308

those observed in the investigation of crystallization in rubber polymers [5]. The thermal drifts are believed to arise as the bulky macromolecules slowly alter their configuration. The heat-capacity results would be thus dependent somewhat on the time allowed for thermal equilibrium. As experience with rubber polymers [5] show that these thermal drifts can continue for an undesirably long period, the thermal drifts were not followed for longer than 30 min. The existence and the long duration of the thermal drifts in this temperature range are substantiated by the long periods required for volume

TABLE 3. Heat capacity, enthalpy, and entropy of annealed Teflon at integral temperatures

T	C	H _T -H ₀ ⁰	S _T -S ₀ ⁰
°K	abs j °K ⁻¹ g ⁻¹	abs j g ⁻¹	abs j °K ⁻¹ g ⁻¹
0	0	0	0
5	0.0024	0.0030	0.0006
10	.0182	.0470	.0063
15	.0433	.2089	.0190
20	.0759	.5204	.0367
25	.1012	.9641	.0564
30	.1244	1.529	.0770
35	.1453	2.204	.0977
40	.1642	2.978	.1184
45	.1833	3.847	.1388
50	.2020	4.811	.1591
55	.2200	5.866	.1792
60	.2378	7.010	.1991
65	.2560	8.245	.2189
70	.2744	9.571	.2385
75	.2929	10.99	.2581
80	.3119	12.50	.2776
85	.3313	14.11	.2971
90	.3500	15.81	.3166
95	.3682	17.61	.3360
100	.3858	19.49	.3553
105	.4037	21.47	.3746
110	.4215	23.53	.3938
115	.4391	25.68	.4129
120	.4565	27.92	.4320
125	.4738	30.25	.4509
130	.4910	32.66	.4699
135	.5080	35.16	.4887
140	.5250	37.74	.5075
145	.5418	40.41	.5262
150	.5587	43.1C	.5449
155	.5756	45.99	.5634
160	.5921	48.92	.5821
165	.6164	51.96	.6007
170	.6350	55.09	.6194
175	.6531	58.31	.6381
180	.6704	61.62	.6567
185	.6866	65.01	.6753
190	.7019	68.48	.6938
195	.7164	72.03	.7122
200	.7306	75.64	.7306
205	.7445	79.33	.7488
210	.7583	83.09	.7669
215	.7720	86.91	.7849
220	.7854	90.81	.8028
225	.7986	94.77	.8206
230	.8115	98.79	.8383
235	.8244	102.9	.8559
240	.8373	107.0	.8734
245	.8504	111.3	.8908
250	.8639	115.5	.9081
255	.8776	119.9	.9253
260	.8918	124.3	.9425
265	.9090	128.8	.9596
270	.9256	133.4	.9768
275	.9422	138.1	.9940
280	.9761	142.9	1.011
310	1.023	179.4	1.135
315	1.021	184.5	1.151
320	1.023	189.6	1.168
325	1.027	194.7	1.183
330	1.031	199.9	1.199
335	1.036	205.0	1.215
340	1.042	210.2	1.230
345	1.048	215.4	1.245
350	1.052	220.7	1.260
355	1.061	228.0	1.275
360	1.068	231.3	1.290
365	1.075	238.7	1.305

equilibrium found in dilatometer experiments [11, 12]. The first peak, or the transition involving the greater enthalpy change, is estimated to be at about 293° K, and the second peak to be at 303° K. Rigby and Bunn [11], using a dilatometer method, observed a single first-order transition in Teflon at 20° C. These authors also obtained X-ray diffraction photographs of the polymer at various temperatures, and reported a change from a more ordered to a less ordered crystal structure as the temperature was increased. These authors mentioned further that the two states are not sharp and distinct. More

TABLE 4. Comparison of the enthalpy and entropy change in the interval 280° to 310° K

Sample and run	ΔH	ΔS
	abs j g ⁻¹	abs j °K ⁻¹ g ⁻¹
Teflon powder:		
Run 4.....	38.02	0.1293
Run 6.....	38.04	.1294
Molded Teflon:		
Run 3.....	34.88	.1177
Run 4.....	34.75	.1180
Annealed Teflon:		
Run 2.....	36.42	.1236
Run 4.....	36.53	.1240
Quenched Teflon:		
Run 2.....	35.49	.1205

recently, Quinn, et al. [1], using a volume dilatometer method, observed two first-order transitions in their volume-temperature curve at 20° and 30° C. Their results give evidences of large hysteresis in the volume-temperature curve. Similarly, Pierce, et al. [12] obtained X-ray diffraction photographs with Teflon and attributed the first change in crystal order, occurring from 17° to 20° C, to first-order transition. However, the second change occurring in the range of temperature above 20° C was reported as being from second-order transition (glass transformation). The three investigations [10, 11, 12] mentioned above show that the transitions involve a change in the volume of about 1 to 1.2 percent. Renfrew and Lewis [4], using both time-temperature cooling and heating curves, found two first-order transitions in the range of temperature from 318° to 327° C. These authors suggested the possibility of the existence of two crystalline forms with their melting points closely spaced. The existence of two crystalline forms would seem possible on the basis that both left- and right-handed helical polymers exist due to the high rotational hindrance. Probably the two forms exist independently even within the same polymer molecule. Furthermore, each helical form probably can exist in two crystalline states as found by Bunn and Garner [13] with polyamides, either of the two states being obtained by relative translation along the chain axes [11]. The two room-temperature transitions in Teflon probably can be attributed to the crystal-crystal transformation in each of the helical forms.

The enthalpy change between 280° and 310° K is compared in table 4 for the four Teflon samples. The results show that Teflon powder has the largest enthalpy change. Both annealing and quenching processes seem to have increased the enthalpy change in this temperature interval, the annealing more so than the quenching process. Assuming the average heat capacity over the range 280° to 310° K to be 1 abs j °K⁻¹ g⁻¹, the heat of transition associated with the two first-order transitions would be about 4 to 8 abs j g⁻¹, depending upon the physical state of the polymer.

The enthalpy and entropy values, given in tables 1, 2, and 3, were obtained by tabular integration of the heat capacities using the four-point Lagrangian integration coefficients [14]. The values at 15° K and below were obtained by evaluating the Debye function [2] fitted to the heat-capacity results in the

temperature range 15° to 30° K. Between 280° and 310° K, the experimental net heat capacities were used to evaluate the enthalpy and entropy change. The enthalpy change was obtained by summing the products of the net heat capacity and the temperature change for the intervals. The entropy change was obtained similarly by summing the $C\Delta T/T^2$ s, where C is the net heat capacity, ΔT the temperature change, and T the corresponding midtemperature of the interval. As in the case of rubber polymers [4], the Teflon polymer may be expected to have a residual entropy at the absolute zero of temperature due to its being a mixture of polymers of varying molecular weights, and to the random orientation of the polymer chains.

It is interesting to note (tables 1, 2, and 3), in comparing the enthalpies and entropies at 310° K of the powder, molded, and annealed Teflon samples, that these thermal quantities are almost equal. The large differences in these quantities at 280° K are offset by the adjusting effect of the two first-order transitions occurring between 280° and 310° K. The molded and annealed Teflon samples exhibit heat-capacity values quite similar above 310° K, and thus the enthalpy and entropy values continue to be close. On the other hand, the Teflon powder has considerably lower heat-capacity values above 310° K, and thus the thermal quantities above 310° K differ more.

The experimental results with the four Teflon samples show that the heat capacity of a Teflon specimen would be dependent upon its mechanical and thermal history. The heat treatment with respect to the high-temperature transition points (about 318° to 327° C) affects the heat capacity significantly. On the other hand, as pointed out previously, rapid or slow cooling of the polymer from room temperature does not show a significant effect upon the heat-capacity values. The deviation plot of the net heat capacities, except in the range 280° to 310° K, showed that above 50° K the results have a maximum spread of 0.1 percent, regardless of the rate at which the sample was cooled. In most

cases the spread is much less than this value. From various considerations, the authors believe that the results for the same Teflon sample have an error⁵ of 0.2 percent.

The authors are indebted to W. Bruenner and M. L. Reilly for some of the measurements and calculations.

4. References

- [1] F. A. Quinn, Jr., D. E. Roberts and R. N. Work, *J. Applied Phys.* **22**, 1085 (1951).
- [2] G. T. Furukawa, D. C. Ginnings, R. E. McCoskey, and R. A. Nelson, *J. Research NBS* **46**, 195 (1951) RP2191.
- [3] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, *J. Research NBS* **35**, 39 (1945) RP1661.
- [4] M. M. Renfrew and E. E. Lewis, *Ind. Eng. Chem.* **36**, 870 (1946).
- [5] G. T. Furukawa, R. E. McCoskey and Gerard J. King, *NBS Reports* 1016 (CR No. 2704), 1118 (CR No. 2804) and 1520 (CR No. 2961) to the Reconstruction Finance Corporation, Synthetic Rubber Division.
- [6] W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).
- [7] W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.* **62**, 3113 (1940).
- [8] W. E. Hanford and R. M. Joyce, *J. Am. Chem. Soc.* **68**, 2082 (1946).
- [9] H. C. Raine, R. B. Richards, and H. Ryder, *Trans. Faraday Soc.* **41**, 56 (1945).
- [10] E. Hunter and W. G. Oakes, *Trans. Faraday Soc.* **41**, 49 (1945).
- [11] H. A. Rigby and C. W. Bunn, *Nature* **164**, 583 (1949).
- [12] R. H. H. Pierce, Jr., W. M. D. Bryant and J. F. Whitney, *American Chemical Society Meeting* (Buffalo, New York, March 23 to 27, 1952).
- [13] C. W. Bunn and E. V. Garner, *Proc. Roy. Soc. (London)* [A] **189**, 39 (1947).
- [14] *Tables of Lagrangian Interpolation Coefficients* (Columbia University Press, New York, N. Y., 1944).

WASHINGTON, D. C., June 13, 1952.

⁵ For these experiments a true probable error cannot be statistically computed. The value given is an estimate arrived at by examining contributions to the inaccuracy from all known sources, and it is to be considered as the authors' best estimate of the error, which is just as likely to be exceeded as not.