[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Density, Thermal Expansion, Vapor Pressure, and Refractive Index of Styrene, and the Density and Thermal Expansion of Polystyrene

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The density of styrene has been reported by a number of investigators,[1] but the values are not in good agreement. We have measured the density of styrene over the range 30–120° with the aid of a dilatometer, and the results of these measurements are plotted in Fig. 1. The points in circles and triangles are our measurements on two samples, and the lettered points indicate the previously published values.[1] The styrene used was obtained from the Dow Chemical Co. and from the Standard Telephones and Cables, Ltd., in England. Each sample was purified by fractional distillation at 80 mm., the middle fractions of constant boiling point and refractive index being taken for measurement of density.

In Fig. 2 is plotted log vapor pressure *versus* $1/(t + 230)$ of data taken from the literature[2] (lettered points), and of our samples which boiled at 76.2–76.7° at 80 mm. A good straight line can be drawn through these points, and it indicates a boiling point of 145.1° at 760 mm. This is in good agreement with an experimentally determined boiling point on very pure styrene of 145.0–145.4°.[1x]

In Fig. 3 is a plot of refractive index *versus* temperature, the lettered points again

(1) (a) Auwers and Eisenlohr, *J. prakt. Chem.*, [2] **82**, 85 (1910); (b) Biltz, *Ann.*, **A296**, 275 (1897); (c) Brühl, *ibid.*, **235**, 13 (1886); (d) Gladstone, *J. Chem. Soc.*, **45**, 224 (1884); (e) Gladstone, *ibid.*, **59**, 292 (1891); (f) Klages and Keil, *Ber.*, **36**, 1632 (1903); (g) Krakau, *ibid.*, **11**, 1260 (1878); (h) Lemoine, *Compt. rend.*, **125**, 530 (1897); (i) Nasini and Bernheimer, *Gazz. chim. ital.*, **15**, 84 (1885); (j) Perkin, *J. Chem. Soc.*, **69**, 1224 (1896); (k) Sabetay, *Bull. soc. chim.*, **45**, 69–75 (1929); (l) Schiff, *Ann.*, **220**, 93 (1883); (m) Waterman and de Kok, *Rec. trav. chim.*, **53**, 1133 (1934); (n) Weger, *Ann.*, **221**, 69 (1883); (o) Otto and Wenzke, THIS JOURNAL, **57**, 294 (1935); (p) Müller, *Physik. Z.*, **38**, 283 (1937); (x) private communication, Dow Chemical Co.

(2) (q) Fittig and Binder, *Ann.*, **195**, 135 (1879); (r) Auwers, Roth and Eisenlohr, *ibid.*, **282**, (1910); (s) Linder, *J. Phys. Chem.*, **35**, 531 (1931); (t) von Richenberg, "Einfache und fractionierte Distillation," p. 201 (1923); (u) Dolliver, Gresham, Kistiakowsky and Vaughan, THIS JOURNAL, **59**, 831 (1937); (v) Zartman and Adkins, *ibid.*, **54**, 1668 (1932); (w) Gorman, Davis and Gross, *Physik. Z.*, **39**, 181–185 (1938); and Ref. 1b, f, i, k, m, n, o, x.

Fig. 1.—Density of styrene.

would have the opposite effect, but our samples were found to contain less than 0.25% (limit of sensitivity of our test) of this impurity, if any at all.

referring to the literature.[3] Our measurements, made with the aid of an Abbé refractometer, appear to be somewhat higher than many of the others, which, however, is to be expected if the earlier samples contained saturated impurities such as ethylbenzene. Phenylacetylene, however,
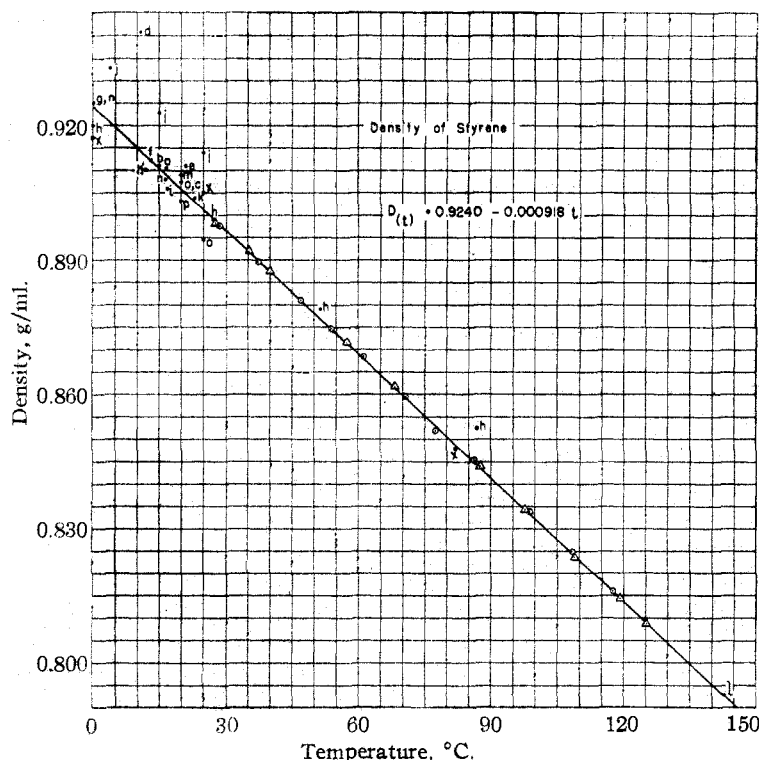
The density of resinous polystyrene was measured with the aid of a dilatometer for solids, the immersion liquid being mercury. Figure 4 is a plot of density *versus* temperature for two samples. Note that the curves consist of two straight lines that intersect at a point. At the temperature corresponding to this point there is apparently a fundamental change in the structure of the polymer. Sample I was prepared by heating pure, degassed styrene in a sealed tube under pressure

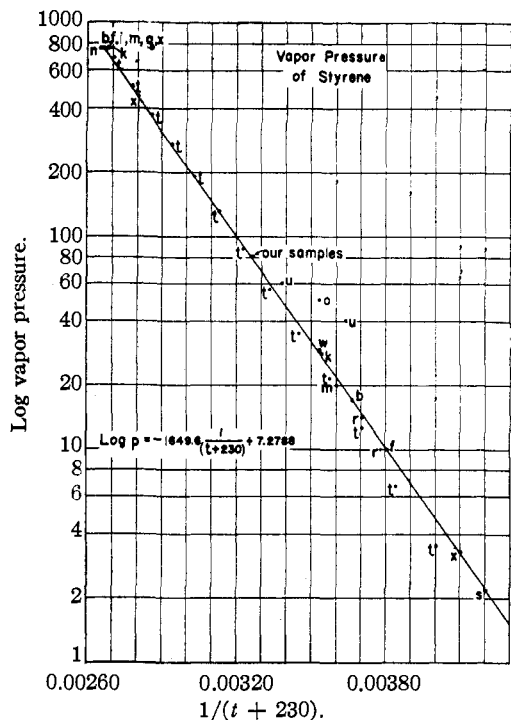(3) Ref. 1a, b, e, f, i, k, m, o, x; Ref. 2u, w.

Fig. 2.—Vapor pressure of styrene.

of mercury for several weeks at 100° and then for three additional weeks at 125°. Sample II was prepared by heating for four weeks in a sealed tube at 150°, a piece of polystyrene that had spontaneously polymerized in a bottle at room temperature over a period of about six months. Although the purity of this sample was unknown, it is believed to have been over 98% styrene. As a measure of the relative average molecular weights of the samples measured, their specific viscosities, $\eta_{sp.} = \eta_r - 1$, of 1 g. of polymer in 40 g. of benzene were measured at 26°, and found to be 2.04 for Sample I and 1.42 for Sample II. These values are in contradiction to the general rule that the lower the temperature of polymerization, the higher the molecular weight of the polymer, and
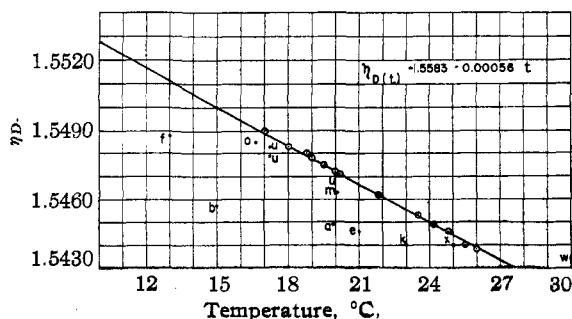

Fig. 3.—Refractive index of styrene.

may be attributed to the fact that Sample II was subsequently heated at 150°, which brings up the interesting question of change in average molecular weight with temperature, and the possibility of equilibria. An attempt to measure the density of the piece of polystyrene that had been formed at room temperature, and had never been heated, was successful at low temperatures only; at 70° and above the volume decreased continuously with time, probably owing to continued polymerization.
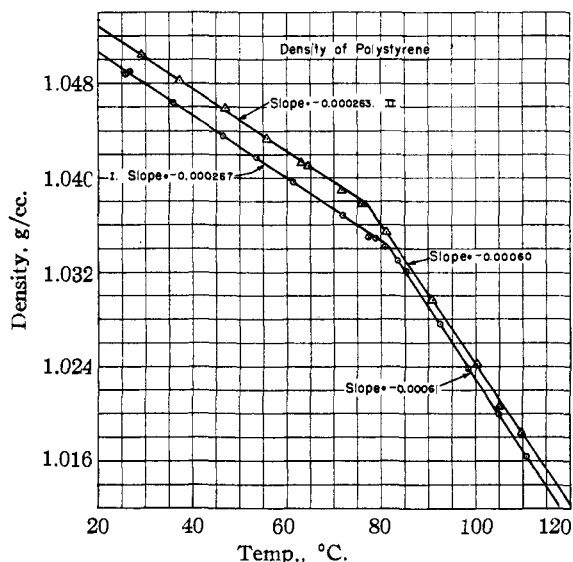

Fig. 4.—Density of polystyrene.

The data plotted in Fig. 4 were readily reproducible, even though the samples were repeatedly heated and cooled. It was necessary, however, to wait for considerable time, sometimes hours, for the volume to become constant at constant temperature, apparently long after temperature equilibrium had been established. This slow, persistent change in volume is a common property of glasses. The relative densities of the two samples are real, although the absolute density of each was found to be about 0.1% higher when measured by weighing in air and in water. The transition temperatures of the two samples are 81.5 and 77.5°. Measurement of the "high elasticity temperatures" of the same two samples by J. J. Russell in this Laboratory gave the values of 86 and 81°. Although these values are not identical with those for the transition temperature, they are in the same relative order. This lends further evidence to the assumption that polystyrene undergoes a fundamental change in struc-

ture at a definite temperature, depending upon the sample, which in some respects resembles the melting of crystals. It is also interesting to observe that although the densities and transition temperatures of these two samples are different, the slopes of the curves are identical.

Recently Jenckel and Ueberreiter[4] published a long paper describing the change in specific volume of polystyrene with temperature which confirms the general phenomena described above, and in addition they conclude that the transition temperature is depressed not only by a low average molecular weight of the polymer, but also by the presence of impurities in the resin such as monomeric styrene, paraffin, or polystyrene of very low molecular weight. Their data indicate an upper limit for transition temperature of slightly above 100° regardless of molecular weight, although their data for transition temperature and molecular weight do not fall upon a smooth curve. Neither do their values for density bear any regular relationship to average molecular weight or to transition temperature, although some such relationship might be expected. And, finally, their values for coefficient of expansion, as indi-

cated by the slopes of the specific volume–temperature curves, show no regular relationship to molecular weight. This lack of regularity may indicate either that their measurements are in error by quantities greater than the differences found, or that the measured properties are influenced greatly by factors which have but little influence upon the viscosities of solutions of the polymers.

This bi-linear thermal expansion of polystyrene, the sharp transition temperature, and the closely accompanying sharp "high elasticity temperature" all point to the conclusion that polystyrene is a body of fairly definite composition and structure. It would be interesting to examine other linear polymers in the light of these observations, and to investigate the effect of cross-linking on the transition temperature.

Summary

This paper includes the density, thermal expansion, vapor pressure, and refractive index of styrene, and the density and thermal expansion of polystyrene. A discussion of these latter properties is given in relation to other properties of the polymer.

(4) Jenckel and Ueberreiter, Z. physik. Chem., **182A**, 361 (1938).

The Radioactive Determination of Protactinium in Siliceous Terrestrial and Meteoritic Material

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In order to test more completely the validity of the general rule that the abundance ratio of the isotopes of any element is a constant, independent of the source or of the mode of combination of the element, it is of interest and importance to determine such abundance ratios in meteorites, which represent the only available specimens of extraterrestrial matter. Atomic weight or isotopic abundance ratios have been determined for carbon, oxygen, silicon, chlorine, iron, cobalt and nickel, by various workers[1]; and in the case of all

the elements studied the isotopic abundance ratios are not measurably different in meteoritic and in terrestrial matter.

In the case of radioactive elements, such as uranium, these abundance ratios assume additional interest, in that by means of them a knowledge may be obtained of the difference in age between these atoms in the meteorite specimen and in terrestrial substances containing the same element. This subject was discussed in some detail by Evans,[2] who on the working assumption that the "isotopic ratio of any element is a constant of nature, and is independent of its place of origin in the galactic system," derived the following expression for the differential age in years of

(1) Baxter and Thorvaldson, THIS JOURNAL, **33**, 337 (1911); Baxter and Hoover, ibid., **34**, 1657 (1912); Baxter and Parsons, ibid., **43**, 507 (1921); Baxter and Hilton, ibid., **45**, 694,(1923); Baxter and Dorcas, ibid., **46**, 357 (1924); Jaeger and Dykstra, Koninkl Akad. Wetenschappen. Amsterdam, **27**, 393 (1924); Harkins and Stone, THIS JOURNAL, **48**, 938, 3233 (1926); Baxter and Ishimaru, ibid., **51**, 1729 (1929); Manian, Urey and Bleakney, ibid., **56**, 2601 (1934); Jenkins and King, Publ. Astr. Soc. Pac., **48**, 323 (1936); Nier and Gulbransen, THIS JOURNAL, **61**, 697 (1939).

(2) Evans, Pop. Astronomy, **46**, 159–170 (1938).