which show that $\gamma_{HClO_4} = \gamma_{HCl}$ up to 0.4 molal. The difference between the activity coefficients in dilute solution calculated from vapor pressure data directly and calculated from the more extensive hydrochloric acid data indirectly are probably due in the main to experimental error in the former measurements, for the assumption of errors of 0.001–0.006 mm. in the vapor pressure of water above the perchloric acid solutions in the points discarded would bring the calculations into agreement. We choose, therefore, the Landolt–Börnstein values as the most probable ones until more experimental work is done.

The Pearce and Nelson activity coefficient values were used to calculate the potentials of the hydrogen half-cells in perchloric acid and also of the perchloric–nitric acid liquid junctions in a series of researches by Professor A. A. Noyes and collaborators[5–9] on the oxidation potentials of strong oxidizing agents. The corrected activity coefficients lead to values of the argentous-argentic potential in 4 *m* perchloric acid[8] of **1.970** v. at 0.2° and **1.987** v. at 25.0°, changes of −12 and −13 mv., respectively. The corrections to the values in mixed nitric–perchloric acid solutions[8] have the small effect of changing the slope of the line in Fig. 2 (representing an average number of nitrates per silver atom in the argentic nitrate complex) from 1.6 to 1.5.

The hydrogen half-cell and the liquid junction potential corrections are of opposite sign and nearly cancel each other in the measurements of the argentous–argentic potential in nitric acid,[5,8] the cerous–ceric,[6] the thallous–thallic,[7] and the cobaltous–cobaltic[9] potentials in nitric acid. Dr. C. S. Garner[10] has corrected these potentials taking into account the newer Landolt–Börnstein values for the activity coefficient of nitric acid also. The over-all corrections range from −1.3 to +0.6 mv. and are probably negligible in view of the uncertainties in the liquid junction potentials. No other arguments or conclusions in these papers are affected by these changes.

I wish to acknowledge with gratitude the help and advice of Professor Bray, Dr. C. D. Coryell and Dr. C. S. Garner in preparing this note.

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RECEIVED AUGUST 1, 1938

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(5) Noyes and Kossiakoff, THIS JOURNAL, **57**, 1238 (1935).

(6) Noyes and Garner, *ibid.*, **58**, 1265 (1936).

(7) Noyes and Garner, *ibid.*, **58**, 1268 (1936).

(8) Noyes, DeVault, Coryell and Deahl, *ibid.*, **59**, 1326 (1937).

(9) Noyes and Deahl, *ibid.*, **59**, 1337 (1937).

(10) Garner, Thesis, Calif. Inst. of Tech., 1938.

The Physical Constants of *cis*-Pentene-2

BY MARY L. SHERRILL AND ELIZABETH H. LAUNSPACH

In a recent article[1] the synthesis of *cis*-pentene-2 by the semi-reduction of pentyne-2 was reported. The designation of this pentene-2 as the *cis* form was based on the method of preparation and the assignment of structure was confirmed by its ultraviolet absorption in the Schumann region.[2] Because the quantity of the pentene-2 was insufficient for column fractionation, it was thought that there might be traces of pentyne present which would have the most marked effect on the boiling point and the density. The work has been repeated and the pentene-2 fractionated twice through a Fenske column (Column A). This column was 35 × 1.5 cm., with 1-turn 4-mm. glass helices. The reflux ratio for the two fractionations of the pentyne-2 was 1:20. The index of refraction was identical with that of the earlier preparation but the boiling point and the density were appreciably lower. The physical constants remained unchanged by the second fractionation and it is believed that the values so obtained constitute the most reliable data for the pure *cis*-pentene-2. Absorption spectrum measurements on this product gave no evidence of the presence of any of the *trans* isomer. These results therefore confirm the assignment of the *cis* structure to the higher boiling pentene-2, as is the case for the higher boiling isomer of butene-2.

The pentyne-2 was prepared in satisfactory yield from 2,3-dibromopentane by the action of alcoholic potassium hydroxide. This reaction takes place in two stages: the first being the formation of the pentyne-2 together with a mixture of 2-bromopentene-2 and 3-bromopentene-2. In the second stage of the reaction with more concentrated potassium hydroxide and prolonged heating at a higher temperature, these bromopentenes are converted into pentyne-2. In some cases appreciable amounts of pentyne-1 were also obtained; by further treatment with alcoholic potash this was transformed into pentyne-2. It is of interest to note that the 2,3-dibromopentane was prepared from pentene-2 which was a mixture of 25% of the *cis* and 75% of the *trans* isomer. In the course of fourteen different preparations of pentyne-2 there was always a 25% yield of pentyne-2 in the first stage of the reaction.

Half mole portions of a constant boiling frac-

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(1) Sherrill and Matlack, THIS JOURNAL, **59**, 2134 (1937).

(2) Carr and Stücklen, *ibid.*, **59**, 2138 (1937).

tion of pentyne-2 (b. p. 55.9 ± 0.05° at 760 mm., n^{20}_D 1.4040, d^{20}_4 0.7115) were hydrogenated in an alcohol–water solution in the presence of colloidal palladium. Slightly less than the theoretical quantity of hydrogen was used. The pentene with alcohol distilled from the mixture through a Vigreux column at 34–36°. The hydrocarbon (78.5% yield) freed from alcohol had a refractive index n^{20}_D 1.3824. One fractionation through Fenske column A gave (1) 5% boiling at 36.8–37.0° and (2) 90% boiling at 37.0 ± 0.05°; the refractive indices of these fractions were, respectively, n^{20}_D 1.3824 and 1.3822, that of the residue was n^{20}_D 1.3840. In a second fractionation of (2) the entire distillate (98%) boiled constantly at 37.0 ± 0.05°, had a refractive index n^{20}_D 1.3822 and a density d^{20}_4 0.6562. The refractive index of the residue was n^{20}_D 1.3826.

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RECEIVED AUGUST 1, 1938

The Specific Heat of "Lucite" (Methyl Methacrylate Polymer)

BY FRANK T. GUCKER, JR., AND WILLIAM L. FORD

We have found the polymerized methyl methacrylate plastic now made by the du Pont Company under the trade name of "Lucite" a useful insulating material in our calorimetric work. Many of its physical properties have been tabulated.[1] For our purposes, the specific heat was important and, since we could not find it listed, we determined it as follows.

Fifteen disks each 3 mm. thick were cut from a Lucite rod, $^3/_8$ inch (9 mm.) in diameter. A small hole was drilled in the center of each. The disks were then threaded on pieces of fine copper wire and suspended from the thermel tubes in one calorimeter of the apparatus developed in this Laboratory[2] for measuring heat capacities of aqueous solutions. The disks were spaced apart to allow free circulation of water, with which the calorimeter was filled to the standard height. The resistance ratio required to balance this calorimeter against the tare was then measured in the usual way, with an accuracy of about 0.01%. The heat capacity of the Lucite was calculated from this ratio and the known heat capacities of the water, the calorimeter and the copper wire. Since the heat capacity of the 3 g. of Lucite was only about 0.3% of that of the whole system, the uncertainty in its value is about 3%. The results of two independent experiments actually agreed somewhat better than that, yielding 0.342 and 0.344, and we may take as the probable value of the specific heat 0.343 (±0.005) cal. deg.$^{-1}$ g.$^{-1}$.

Although its specific heat is larger than that of Pyrex glass, its density is only half as great, and the heat capacity *per unit volume* is only 82% of that of glass. This factor, in combination with a thermal conductance less than half that of glass, equal transparency, great mechanical strength and easy machining, makes Lucite a useful substitute for glass as an insulating material in calorimetric work.

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RECEIVED JULY 5, 1938

The Methylation of Sugars

BY B. CLIFFORD HENDRICKS AND ROBERT E. RUNDLE

The importance of fully methylated sugars as reference compounds in carbohydrate chemistry has led to many attempts to find more satisfactory methods for their synthesis. Irvine and Purdie[1,2] used methyl iodide and silver oxide in their preparation. A more generally used method[3] is that of Haworth in which dimethyl sulfate and sodium hydroxide are the reagents used. More recently West and Holden[4] have modified the method of Haworth by using carbon tetrachloride as a solvent, a more concentrated alkali and a different method of hexoside hydrolysis to obtain the free methylated sugar.

The authors found that the concentrated alkali, used by West and Holden for the last step in the methylation, produced sugar decomposition. Their first steps, however, were satisfactory for partial methylation.

Muskat[5] has shown that methylation may be accomplished by using free alkali metal and methyl iodide on a hexoside in liquid ammonia. He used potassium which is expensive and prepared only small amounts of the sugars. If sodium metal is substituted for the potassium the cost is reduced but for larger quantities of reactants the insolubility of the tetrasodium salts

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[1] "Methacrylate Resins," *Ind. Eng. Chem.*, **28**, 1160 (1936).

[2] Gucker, Ayres and Rubin, THIS JOURNAL, **58**, 2118 (1936).

[1] Irvine and Purdie, *J. Chem. Soc.*, **83**, 1021 (1903).

[2] Irvine and Purdie, *ibid.*, **85**, 1052 (1904).

[3] Haworth, *ibid.*, **107**, 11 (1915).

[4] West and Holden, THIS JOURNAL, **56**, 930 (1934).

[5] Muskat, *ibid.*, **56**, 695 (1934).