by using the experimental value of n and letting $w = {}^1/_3$. In changing to this form the expressions for A, D, T_B and $0.5 + Cy + Dz = 0$ do not change but the other relations become

$$K - \alpha = C + 3 - n - 0.30103q$$

$$\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_{\mathrm{Cr}} = \frac{n + \alpha x - \frac{q'}{2}}{1 - K + (w + 1)\alpha - \frac{q'}{2}}$$

$$0 = \frac{C + 3}{C + 2}\left\{\frac{C}{D}(C + D)y^2 + \frac{C}{D}y + 0.25C + 1\right\} - \left\{\frac{q'}{4} + w\,(w + 1)\alpha\right\}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_{\mathrm{Cr}}^2 - \left\{\frac{q'}{2} - 2x\,(w + 1)\alpha\right\}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_{\mathrm{Cr}} - x\,(x + 1)\alpha + \frac{3}{4}\,q'$$

The constants, as determined for nitrogen, are $n = 3.427$, $C = 1.007$, $D = 0.24956$, $A = 6.78549$, $q = 0.72330$, $K = 0.38022$, $\alpha = 0.01796$, $x = 0.16798$, $y = 0.37965$, $z = -3.53541$, $w = {}^1/_3$, $T_B = 2.48$.

By converting values found by this equation to $n = 3.424$, the value for argon, by means of the stretch formula the changes in volume correspond closely with the experimentally determined volume changes for argon[4] from 2000–15,000 kg./sq. cm. at 55° and the volume at 3000 kg./sq. cm. and 55° is found to be 0.765 cc./g.

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[4] P. W. Bridgman, "The Physics of High Pressure," The Macmillan, Co., New York, N. Y., 1931.

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RECEIVED SEPTEMBER 20, 1937

COMMUNICATIONS TO THE EDITOR

THE EFFECT OF HYDROXYL GROUPS ON THE APPARENT DIENE VALUES OF VEGETABLE OILS AND FATS

Sir:

In a letter to the editor of *Chemistry and Industry*, **56**, 937 (1937), entitled, "Maleic Anhydride Value or Diene Value," R. J. Bruce and P. G. Denley called attention to certain anomalous results which they obtained on determining the M. A. V. of oxidized linseed, perilla, and soybean oils. They state "It occurred to us that the M. A. V. might not be solely indicative of conjugated double bonds, but that it might include any maleic anhydride that entered into combination with hydroxyl groups already in the oil or formed during oxidation."

In order to test the validity of this assumption they determined the M. A. V. of dihydroxystearic acid, blown oleic acid, commercial castor oil, and blown linseed, perilla, and soybean oils by the Ellis and Jones method using a one-hour period of reflux. Maleic anhydride values, ranging from 5.2 in the case of blown oleic acid to 31.4 for dihydroxystearic acid, were observed.

This Laboratory has been engaged for some months on a study of the applicability of the Ellis and Jones, and the Kaufmann, Baltes, and Büter, diene methods, as a means of following changes in the polyethenoid linkages of soybean oil under various conditions of heat bodying. As in the case of Bruce and Denley, it was noted that the presence of hydroxyl groups led to anomalous diene values. Consequently, the M. A. V. and diene value of a number of purified hydroxylated compounds were determined before and after blocking the hydroxyl group by acetylation. The compounds examined included methyl 12-hydroxystearate, glyceryl monoricinoleate, methyl ricinoleate, α-monopalmitin, α,α'-distearin, ethylene glycol, acetone-glycerol, and glycerol. It was observed that in all but one case (α,α'-distearin) significant M. A. V. and diene values were observed with the hydroxylated compounds; whereas, following acetylation, the magnitude of these values dropped in all cases to practically zero.

In a similar manner were examined a variety of oils, including, besides variously treated soybean oils, also linseed, castor, perilla, oiticica, and tung. Castor oil exhibited the characteristic behavior of hydroxylated compounds, giving an appreciable M. A. V. and diene value which fell to nearly zero after acetylation. Tung oil also exhibited a small decrease in M. A. V. and diene value after acetylation. However, the M. A. V. and diene values of linseed and soybean oils, which were initially low, rose appreciably after acetylation. In the case of these two oils the increase in the diene value (800–1000 per cent.) was accompanied by an increase in the refractive index, a decrease in the iodine value, and a shortening of the drying time; all of which indicated a shift of the polyethenoid bonds toward a conjugated system.

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RECEIVED NOVEMBER 23, 1937

THE SYNTHESIS OF ALDOBIONIDES

Sir:

Aldobionic acids are disaccharides containing a uronic acid as one of the sugar constituents. These sugar acids were found among the products of hydrolysis of the immunologically specific carbohydrates of certain encapsulated pathogenic microörganisms [M. Heidelberger and W. F. Goebel, *J. Biol. Chem.*, **70**, 613 (1926); W. F. Goebel, *ibid.*, **74**, 619 (1927)]; they have since been obtained from various plant gums as well. The synthesis of two aldobionic acids, gentiobiuronic acid and the aldobionic acid of gum acacia, has been described recently [R. D. Hotchkiss and W. F. Goebel, *J. Biol. Chem.*, **115**, 285 (1936)]. The chemical constitution of a third aldobionic acid, cellobiuronic acid obtained from the specific polysaccharide of pneumococcus, Types III and VIII, have also been established [R. D. Hotchkiss and W. F. Goebel, *ibid.*, **121**, 195 (1937)].

Since it is our desire to prepare for chemoimmunological study, artificial carbohydrate-protein antigens containing these three aldobionic acids, a method for the synthesis of aldobionides has now been developed. The preparation of the acetobromo derivatives of the methyl esters of the acacia aldobionic acid (6-β-glucuronosido-galactose) and of cellobiuronic acid (4-β-glucuronoside-glucose) was achieved in the following manner.

When the heptaacetyl methyl ester of cellobiuronic acid or of the acacia aldobionic acid, is allowed to stand in the presence of acetic acid saturated with hydrogen bromide, the α-bromohexaacetyl methyl ester of the corresponding aldobionic acid is in each instance formed. The derivatives may be isolated from the reaction mixtures in excellent yields. The α-bromohexaacetyl methyl ester of 4-β-glucuronosido-glucose is obtained as glistening needles melting at 200° (uncorrected) $[\alpha]^{24}\text{D}$ +99.4° in $CHCl_3$ (C, 1%) (found, Br, 11.66). The α-bromohexaacetyl methyl ester of 6-β-glucuronosido-galactose crystallizes as rosets of needles. The melting point of the pure substance is 201–202° (uncorrected) $[\alpha]^{23}\text{D}$ +194.7° (C, 1%) (found, Br, 11.52). When the latter derivative is condensed with methyl alcohol in the presence of silver oxide the methyl ester of hexaacetyl-6-β-glucuronosido-methylgalactoside is formed in yields of 60%. The derivative crystallizes as prismatic needles melting at 134° (uncorrected) $[\alpha]^{25}\text{D}$ +86.4° (C, 1%) (found, OCH_3 9.96). We have certain evidence which indicates that the synthetic methyl glycoside of the aldobionic acid derivative is the α instead of the anticipated β-glycoside.

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RECEIVED NOVEMBER 20, 1937

FREE ROTATION ABOUT CARBON-CARBON BONDS

Sir:

Montgomery, McAteer and Franke [THIS JOURNAL, **59**, 1768 (1937)] find for the reaction

$$n\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10}$$

an equilibrium constant of about 4.0 in the liquid phase at 27°; the corresponding value for the vapor phase is calculated to be 5.5. This result when combined with Rossini's accurate value $\Delta H_{298} = -1630$ cal. gives $\Delta S_{298} = -2.08 \pm 0.55$ e. u. The third law measurements of Parks, Shomate, Kennedy and Crawford [*J. Chem. Phys.*, **5**, 359 (1937)] gave -5.8 ± 1.2 e. u. Statistical calculations of Pitzer [*ibid.*, **5**, 473 (1937)] assuming potential barriers of 3400–3800 cal. opposing free rotation gave -4.3 e. u., as compared with -4.1 e. u. calculated by Kassel [*ibid.*, **4**, 276 (1936)] on the basis of free rotation. Direct experiment thus shows isobutane to be significantly more stable than is indicated by any calculation; unpublished work done in this Laboratory supports this conclusion.

A major argument against the assumption of free rotation has been the consistency with which statistical entropies based on it exceeded third law determinations. It now appears, however, that the difference of the third law values for the two butanes is in error by 3.7 e. u. Modern determinations of this sort can only be wrong by failure to attain equilibrium in the crystal, and hence can only be low. The third law value for isobutane must therefore be at least 3.7 e. u. low, and the correct value of S_{298} is at least 73.7 e. u.