of magnitude of the number of plates required, but consideration of the holdup and the 30 to 1 reflux ratio actually used in these distillations would certainly increase the estimates considerably.[9]

Consideration of Holdup and Reflux Ratio.—All the above computations are on the assumption that reflux was nearly total and that holdup was zero so that the conclusions are for maximum sharpness of separation and minimum plates required. No statement of the holdup in the Podbielniak–Simons–Taylor[8] column is given but it must be appreciable compared with the amount of any one component and quite large compared with the amounts of the components present in small amount so that the separations involving these would be expected to be much less sharp than the above discussion indicates.

Summary

Calculations have been made to show that a minimum of 400 or more theoretical plates are required for sharp separation of certain close boiling hexenes, and that the use of a fractionating column with a small number of theoretical plates can produce no appreciable separation in such cases even with low holdup and high reflux ratio.

STATE COLLEGE, PA. RECEIVED NOVEMBER 20, 1939

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[9] Arthur Rose, L. M. Welshans and H. H. Long, *Ind. Eng. Chem.*, **32**, May (1940).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Attempted Separation of Isomeric Hexenes by Fractional Distillation

BY FRANK C. WHITMORE, M. R. FENSKE, D. QUIGGLE, H. BERNSTEIN, T. P. CARNEY, S. LAWROSKI, A. H. POPKIN, R. B. WAGNER,[1a] W. R. WHEELER AND J. S. WHITAKER

These laboratories have long been interested in the separation of difficult mixtures, especially of olefins, by fractional distillation. Consequently, it was hoped that the recent work by Goldwasser and Taylor[1] would point the way to separations hitherto not possible. We are indeed sorry to have to report that this hope has not been realized.

The Podbielniak–Simons–Taylor column[1] seems to be an excellent one of its type but has an efficiency of only about fifteen theoretical plates. Whereas the published results[1] seem to indicate a successful separation of six hexenes with a total boiling point spread of 2.5°, we have found it impossible to obtain separations even with two binary mixtures of pure hexenes having boiling point spreads of 1.5 and 2.7°, or with a ternary mixture having an over-all spread of 2.7°.

It is interesting to note that a calculation of the column efficiency needed to effect the indicated separation of the six hexenes[1] gives a value of at least 450 theoretical plates.[2]

Goldwasser and Taylor[1] use the boiling point and density to identify an olefin. This is at least difficult because of the conflicting values recorded for these constants.

Inconsistencies appear in the paper.[1] Thus, on pp. 1753–1754 there is a confusion of the *cis* and *trans* forms of 3-methyl-2-pentene. Agreement with the work of van Risseghem[3] is cited "to emphasize the confidence that may be placed in the fractionations obtained." As a matter of fact such agreement is lacking. The authority cited[3] obtained three fractions in the careful distillation of the hexenes from 3-methyl-3-pentanol, *viz.*: I, b. p. 65.1–65.7°; II, 67.2–67.8°; III, 69.9–70.2°. She states that I and III are stereoisomers of 3-methyl-2-pentene and that II is a mixture containing some of the methylene isomer. The boiling points given by Goldwasser and Taylor (Table 1a[1]) for the two 3-methyl-2-pentenes are 65.7–66.2° and 67.6–68.2°. These differ from those actually reported by van Risseghem,[3] which are 65.1–65.7° and 69.9–70.2°.

In certain cases where geometrical isomerism is possible, one constant used for identification[1] belongs to the *trans* form, while the other belongs to the *cis*. The literature values given for the isomers of 3-hexene are: *cis*, b. p. 70–71.2°, d^{20}_{4} 0.7190; *trans*, 67.3–67.5°, 0.7170. However, in the dehydration of 1-hexanol, 3-hexene was identified by the observed values, 67.5° and 0.720.

For 4-methyl-2-hexene the accepted values[4] are:

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[1] Goldwasser and Taylor, THIS JOURNAL, **61**, 1751, 1762, 1766 (1939).

[1a] Submitted in partial fulfillment for the Ph.D. degree.

[2] Rose, THIS JOURNAL, **62**, 793 (1940).

[3] Van Risseghem, *Bull. soc. chim. Belg.*, **47**, 47 (1938).

[4] Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Company, New York, 1939. Doss, "Physical Constants of Principal Hydrocarbons," The Texas Company, New York, 1939.

1 isomer, b. p. 87.1–87.6°, d^{20}_{4} 0.7007; 2 isomer, 85.1–85.6°, 0.6981. In reporting the presence of 4-methyl-2-hexene the literature values given by Goldwasser and Taylor[1] are 85.1–85.6° and 0.7007 and the observed values[1] are 85.1–85.2° and 0.701.

The significance of the cyclopropane mechanism suggested[1] for the formation of the suspected isomeric olefins need not be discussed.[5]

Experimental

Distillation Equipment.—Column I was of the total condensation partial take-off type.[6] It was packed with $^{1}/_{8}$-inch inside diameter single turn glass helices.[7] The packed section was 65 × 1.5 cm., and its efficiency was about 13 theoretical plates. A calibrated thermometer gave the head temperature.

Column II was also of the total condensation partial take-off type. It was packed with $^{3}/_{32}$-inch single turn stainless steel helices made from no. 30 wire.[8] The packed section was 100 × 1.0 cm., and its efficiency equal to at least 35–40 theoretical plates. The still was heated by an air-bath that was controlled automatically by utilizing the pressure drop through the column. A calibrated thermometer gave the head temperature.

Column III was identical with Column I, but with a packed section 45 × 0.9 cm. It had an efficiency of about 12 theoretical plates.

Column IV was built exactly as described by Goldwasser and Taylor[1] in their reported separation of the isomeric hexenes. It was a Podbielniak type column, the section within the jacket being 150 × 0.45 cm. The jacket was evacuated to below 10^{-6} mm. The head was of the total condensation partial take-off type designed by Simons.[9] Column V was made exactly like Column IV, except that the jacket was air-filled instead of being evacuated. The efficiencies of columns IV and V are given in the next section.

Determination of Theoretical Plate Values.—The theoretical plate values were determined for columns IV and V using carbon tetrachloride–benzene mixtures.[10] This method was also used to determine the efficiencies of Columns I, II, and III.

The operating conditions varied with respect to rate of refluxing at the condenser and the control of the jacket temperature. Three rates of refluxing were used, namely, a very slow rate of one drop per minute, an intermediate rate of 150 drops per minute, and a very fast rate of approximately 360 drops per minute. The last was just below flooding. The jacket temperature for the two columns was varied 1° above and 1° below the head temperature, and in the case of Column V also 5° above and 5° below the head temperature. A typical run will be described in detail.

About 100 cc. of a carbon tetrachloride–benzene mixture in a 200-cc. flask was used in making the tests. The refractive indices, $n^{20}\mathrm{D}$, of the carbon tetrachloride and benzene were 1.4595 and 1.4999, respectively. The column was brought to equilibrium with total refluxing at a rate just below flood stage. The jacket thermometers read 1° below the head thermometer. Samples of 1 cc. were taken from the flask and from the head at the end of each specified time. The following data will illustrate the operating conditions: reflux time fifteen minutes, bath 118°, jacket 74°, head 75°, flask $n^{20}\mathrm{D}$ 1.4960, head $n^{20}\mathrm{D}$ 1.4820, theoretical plates 12.6. Identical theoretical plate values were obtained at 60, 90, 120, and 180 minutes. Other runs duplicated this procedure and the results are summarized in Table I.

TABLE I

Condition	Theoretical plates with air jacket (Column V)	Theoretical plates with vacuum jacket (Column IV)
Rapid rate		
Jackets 1° below head	14.0	13.4
1° above	14.0	12.6
5° above	14.6	..
5° below	14.6	..
Intermediate rate		
Jackets 1° below head	11.7	12.1
1° above	..	12.7
5° above	10.8	..
5° below	13.7	..
Very slow rate		
Jackets 1° below head	11.4	11.5
1° above	11.4	12.7
5° above	..	..
5° below	12.5	..

Thus columns IV and V are equivalent under these test conditions to approximately 13 theoretical plates regardless of the rate of operation or the use of a vacuum jacket. This is to be compared with the value of 450 theoretical plates calculated by Rose and Welshans[2] as necessary for the separations reported by Goldwasser and Taylor.[1]

The above studies on distillation Columns IV and V were made according to the analytical technique used by Goldwasser and Taylor.[1] However, they did not report any test data. In addition, a separate investigation on the efficiency of Column IV, as well as on analytical distillation columns in general, gave the results summarized in Table II. These results show that the single-turn wire helices combine at one time the four important qualities so necessary in packing for analytical fractionating columns; namely, they are efficient as shown by the low H. E. T. P. values given in Column 4, they allow a high operating throughput as shown by Column 2, they have a low holdup as shown by Column 5, and they make possible operation at low pressure drops as shown by Column 6. The data presented are representative of hundreds of tests and it is believed that the manner of presentation of the data will facilitate the work of the designer of packed fractionating columns.

Preparation of 2-Ethyl-1-butene.—2-Ethyl-1-chlorobutane, b. p. 83° at 202 mm. and $n^{20}\mathrm{D}$ 1.4222, was prepared

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(5) *Cf.* Wallis in Gilman's "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, pp. 733–736.

(6) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(7) Wilson, Parker and Laughlin, *ibid.*, **55**, 2795 (1933).

(8) Tongberg, Lawroski and Fenske, *Ind. Eng. Chem.*, **29**, 957 (1937).

(9) Simons, *Ind. Eng. Chem., Anal. Ed.*, **10**, 29 (1938).

(10) Fenske, Tongberg and Quiggle, *Ind. Eng. Chem.*, **26**, 1169 (1934).

TABLE II

SUMMARY OF DATA ON VARIOUS PACKINGS AT NORMAL PRESSURES

Packing	(1)[c] Column dia., mm.	(2)[d] Throughput l./hr./cm.^{2}	(3)[e] No. theo. plates	(4)[f] H. E. T. P., cm.	(5)[g] Holdup cc./theo. plate	(6)[h] Press. drop mm. Hg/theo. plate
A.[a] Open tube with no. 20 gage wire spiral (Column IV)	4.5	0.3	14	10.7	0.17	0.02
		.6	15	10.0	.19	.05
		1.0	16	9.4	.29	.10
B.[a] $^1/_8$-in. i. d. single turn glass helices	10	0.2	11	3.9	.70	..
	10	.6	11	3.9	.77	..
	12	.2	21	3.8	..	..
	12	.6	18	4.3	..	..
C.[a] $^1/_{16}$-in. i. d. single turn helices of no. 34 stainless wire	8	.3	55	1.3	.16	..
	25.4	.1	65	1.6	1.2	.02
	25.4	.2	62	1.7	1.6	.07
	25.4	.6	43	2.5	3.3	.65
D.[a] $^3/_{32}$-in. i. d. single turn helices of no. 30 stainless wire	8	.4	27	2.6	0.29	..
	12	.4	37	2.2	.54	..
	25.4	.1	140	1.9	1.2	.013
	25.4	.2	126	2.1	1.6	.05
	25.4	.6	88	3.0	3.4	.57
	50.8	.1	58	3.9	13.5	.009
	50.8	.2	54	4.2	16.3	.048
	50.8	.6	44	5.2	31.0	.72
E.[b] Empty tube	9.5	.2	7.2	8.5	..	..
	9.5	.3	4.0	15.3	..	..
	19	.1	3.6	17.0	..	..
	19	.2	1.2	50.9	..	..
	19	.3	1.0	61.0	..	..
	25	.1	1.7	35.9	..	..
	25	.2	1.6	38.1	..	.
F.[b] Stedman packing No. 105	9.5	.21	56.4	1.08	0.14	.07
(Max. efficiency)	9.5	.30	41	1.49	.22	.23
(Max. rate)	9.5	.32	39	1.56	.24	.30
G.[b] Stedman Packing No. 104	19	.05	50.3	1.21	.21	.01
(Max. efficiency)	19	.10	44	1.4	.28	.05
	19	.20	31.5	1.93	.76	.42
(Max. rate)	19	.23	27.8	2.19	.92	.60
H.[b] Stedman Packing No. 112	25	.03	48.4	1.25	.19	.004
(Max. efficiency)	25	.10	31.1	1.96	.77	.10
	25	.20	25	2.42	1.36	.60
(Max. rate)	25	.22	24	2.54	1.50	.74

[a] Packings A, B, C, and D were tested in this Laboratory. [b] Packings E, F, G, and H were tested by Bragg, *Ind Eng. Chem., Anal. Ed.*, **11**, 283 (1939). [c] Column (1) is the inside diameter of the test fractionating column in mm. [d] Column (2) is the liquid boilup or throughput under total reflux as liters of liquid per hour per square cm. of column cross section. [e] Column (3) is the number of theoretical plates in the packed section of the fractionating column. With packings A, B, C, and D a series of careful tests were made under total reflux using pure binary hydrocarbon mixtures such as heptane–toluene, heptane–methylcyclohexane, and methylcyclohexane–toluene. Packings E, F, G, and H were tested with benzene–ethylene dichloride mixtures. [f] Column (4) is the height of packing in cm. equivalent to one theoretical plate. [g] Column (5) is the dynamic holdup in cc. per theoretical plate (cc. of liquid per theoretical plate retained in the packed section while operating). With packings A, B, C, and D the principle described in *Ind. Eng. Chem.*, **26**, 1215 (1934), was used to obtain such dynamic holdup data. With packings E, F, G, and H the holdup was obtained by diverting the vapors and measuring the liquid draining from the packing, allowing for the static holdup. However, such holdup values are believed to be definitely low, for static holdup values for this type of packing appear to be 0.05–0.1 cc. of liquid per cc. of packing, while the values reported for packings F, G, and H are about one-fifth to one-tenth of this value. [h] Column (6) is the pressure drop as mm. of mercury per theoretical plate for the corresponding throughputs tabulated in Column (2).

from 2-ethyl-1-butanol (Carbide and Carbon), 439 g. thionyl chloride, and pyridine in 74% yield.

A 2-liter three-neck flask was attached by one neck to Column I, set for total reflux, and a mercury-seal stirrer and dropping funnel were placed in the other two necks. In the flask were placed 647 g. (14.5 moles) of absolute ethyl alcohol and 336 g. (6 moles) of potassium hydroxide. This mixture was heated to refluxing and stirred. When solution of the potassium hydroxide was complete, 439 g. (3.6 mole) of 2-ethyl-1-chlorobutane was added at the rate of one drop per second. After the addition of the halide had begun, the reflux temperature dropped from 76 to 54°. Product was then taken off at a reflux ratio of 20:1. The distillation was continued until the distillate did not form two layers upon the addition of water. The combined upper layers were washed several times with water, dried, filtered, and distilled through Column I. There resulted 64 g., or a 21% yield, of 2-ethyl-1-butene, b. p. 63° at 728 mm. and n^{20}_{D} 1.3967.

This olefin, combined with that obtained from a later run, was redistilled through Column II at 734 mm. to give fractions: 1, 2.0 g., b. p. 59–63.3°, n^{20}_{D} 1.3948; 2, 2.2 g., 63.6°, 1.3967; 3–11, 52.9 g., 63.6°, 1.3968; residue 5.5 g.

Fractions 4–10 were distilled at 733 mm. through Column IV following exactly the technique of Goldwasser and Taylor[1] to give fractions: 12, 3.0 g., b. p. 63.7°, n^{20}_{D} 1.3967; 13–16, 26.8 g., 63.8°, 1.3968; 17, 5.0 g., 63.8°, 1.3969; residue 2.0 g.

Only fractions 13–16 were used to make the isomeric hexene mixtures for the attempted separations using Column IV. Physical constants for the 2-ethyl-1-butene used were Cottrell b. p. (50%) 63.75 ± 0.05° at 731 mm., n^{20}_{D} 1.3968 ± 0.0001, d^{20}_{4} 0.6992 ± 0.0002.

It should be noted that this material is the best from successive distillations through Columns I, II, and IV.

Preparation of 2-Methyl-1-pentene.—Into a one-liter flask with a one-liter dropping funnel, a mercury-seal stirrer, a thermometer, and a reflux condenser was placed 77.4 g. (0.86 mole) of redistilled 2-methyl-3-chloro-1-propene (Shell Technical), b. p. 70.2–73.0° at 732 mm. and n^{20}_{D} 1.4270. Ethylmagnesium bromide prepared from 105 g. (0.96 mole) of redistilled ethyl bromide, b. p. 37.8° at 727 mm., and 23 g. (0.96 mole) of magnesium turnings was filtered through glass wool under nitrogen pressure into the dropping funnel. The Grignard reagent was added dropwise to the halide with vigorous stirring, keeping the reaction mixture below 0° with a salt–ice-bath. The addition was completed in twelve hours, and stirring was continued for an additional ten hours. To the reaction mixture surrounded by a salt–ice-bath was added with vigorous stirring 300 cc. of ice water, which was sufficient to dissolve the magnesium chloride. The layers were then separated and the ether layer washed once with water. The combined water layers were then extracted several times with ether, and the combined ether extracts dried over anhydrous potassium carbonate. The ethereal solution was then filtered and distilled through Column III, the ether being removed with a reflux ratio of 10:1. The distillation, carried out at 731 mm., yielded fractions: 1–5, 22.8 g., b. p. 34.5–60.0°, n^{20}_{D} 1.3616–1.3903; 6–11, 28.2 g., 61.0°, 1.3923–1.3925; 12–13, 6.7 g., 61.0°, 1.3933–1.3935.

Fractions 6–11, combined with 2-methyl-1-pentene from a similar run making a total of 54.4 g., were distilled through Column II at 737 mm. to give fractions: 14–16, 6.3 g., b. p. 41–61.3°, n^{20}_{D} 1.3794–1.3919; 17–18, 8.3 g., 61.3°, 1.3925; 19, 3.9 g., 60.5–61.3°, 1.3924; 20–21, 9.6 g., 61.3°, 1.3925; 22–23, 7.1 g., 61.3°, 1.3927.

Fractions 17, 18, 20, and 21 were distilled through Column IV at 737 mm. using the technique of Goldwasser and Taylor[1] with the resulting fractions: 24, 2.0 g., b. p. 61.3°, n^{20}_{D} 1.3923; 25–26, 7.2 g., 61.3°, 1.3925; 27–28, 5.3 g., 61.3°, 1.3926–1.3927.

Only fractions 25 and 26 were used with isomeric hexenes for attempted separation through Column IV. The physical constants for the 2-methyl-1-pentene used were Cottrell b. p. (50%) 61.35 ± 0.05° at 738 mm., n^{20}_{D} 1.3925 ± 0.0001, d^{20}_{4} 0.6817 ± 0.0002.

Preparation of 1-Hexene.—The method of preparation was similar to that used for 2-methyl-1-pentene. *n*-Propylmagnesium bromide was prepared from 615 g. (5 moles) of *n*-propyl bromide, b. p. 70–71° at 738 mm. and n^{20}_{D} 1.4340, and 121 g. (5 moles) of magnesium. This was added to 500 g. (4.1 mole) of allyl bromide, b. p. 70–71° at 735 mm. and n^{20}_{D} 1.4653. Ether was first removed through Column I at 739 mm. using a 10:1 reflux ratio. Continued distillation yielded fractions: 1–6, 62.8 g., b. p. 53–61.2°, n^{20}_{D} 1.3720–1.3886; 7–15, 82.7 g., 61.2–63.0°, 1.3886–1.3889; 16–21, 53.5 g., 63.0°, 1.3889–1.3885; 22–30, 74.6 g., 63.0°, 1.3883–1.3880.

Fractions 7–21 were distilled through Column II at 737 mm., and there resulted fractions: 31–36, 30.4 g., b. p. 60.3–60.7°, n^{20}_{D} 1.3901–1.3889; 37–39, 15.3 g., 60.7–62.5°, 1.3890–1.3897; 40, 4.6 g., 62.5°, 1.3893; 41–48, 32.8 g., 62.5°, 1.3890; 49–52, 9.3 g., 62.5°, 1.3889–1.3883.

Fractions 41–48 were distilled through Column IV at 733 mm. using the technique of Goldwasser and Taylor[1] to give fractions: 53–54, 7.0 g., b. p. 62.5°, n^{20}_{D} 1.3892; 55–57, 16.3 g., 62.5°, 1.3891; 58, 5.6 g., 62.5°, 1.3890; 59–60, 5.8 g., 62.5°, 1.3889.

Only fractions 55–58 were used with isomeric hexenes for attempted separation with Column IV. The physical constants for the 1-hexene used were Cottrell b. p. (50%) 62.52 ± 0.05° at 737 mm., n^{20}_{D} 1.3891 ± 0.0001, d^{20}_{4} 0.6873 ± 0.0002.

Table III shows a comparison of our physical constants with those of Boord and his co-workers.[11,12,13]

Attempted Separation of Isomeric Hexenes.—Three mixtures for distillation were made up as follows: 1, 15 cc. of 1-hexene (fractions 55–58) and 15 cc. of 2-ethyl-1-butene (fractions 13–16); 2, 11.6 cc. of 2-ethyl-1-butene (fractions 13–16) and 9.0 cc. of 2-methyl-1-pentene (fractions 25–26); 3, the distillates from the above two distillations were combined to give a mixture containing 50% 2-ethyl-1-butene, 26% 2-methyl-1-pentene, and 24% 1-hexene. The latter figures are weight %, and were calculated from refractive index–composition curves.

The procedure followed was exactly that used by Goldwasser and Taylor,[1] even to the extent of requiring one-half hour after the heat was applied for the material to boil. The rate of reflux was just below the flood stage, or approximately 360 drops per minute. The rate of

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[11] Hull and Boord, Ohio State Univ., Abstr. Doctor's Dissertation, No. 18, 191, 1936.

[12] Schmitt and Boord, THIS JOURNAL, **53**, 2427 (1931); **54**, 754 (1932).

[13] Rudel, Thesis, Ohio State Univ., Sept., 1938.

TABLE III

Hexene	B. p., °C. Expt.	B. p., °C. Lit.	n^{20}_D Expt.	n^{20}_D Lit.	d^{20}_4 Expt.	d^{20}_4 Lit.
1-Hexene	63.4	63.4–63.7	1.3891[a]	1.3870	0.6873[a]	0.6732
2-Ethyl-1-butene	64.9	64.9–65.1	1.3968	1.3970	.6892	.6899
2-Methyl-1-pentene	62.2	61.5–62.0	1.3925	1.3921	.6827	.6817 .6831

[a] The higher values obtained were probably due to impurities of hexadiene not removable by distillation. Since our 1-hexene was a constant boiling constant index material during three distillations through efficient columns, it was suitable for checking Column IV.

take-off was 1 drop every five seconds. Jackets were kept within 0.1° of the reflux temperature. The reflux temperature was noted for every 0.2 cc. of product obtained and a curve plotted while the distillation was in progress. At the end of each horizontal part of the resulting curve the column was put at total reflux for five minutes. In case the reflux temperature dropped to the preceding value and the horizontal continued for another 1 cc., total reflux was again used for five minutes. The care with which this technique was followed is illustrated by the exaggerated distillation curve in Fig. 1. One-cc. fractions were collected in a 1-cc. receiver calibrated to 0.01 cc.

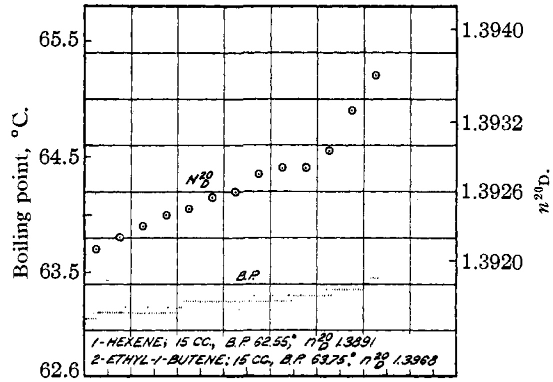

Fig. 1.—Fractionation of 2-ethyl-1-butene and 1-hexene through column IV.

Figures 2, 3, and 4 illustrate three attempts to separate isomeric hexene mixtures. Each distillation was followed by both the boiling point and index of refraction. The continuous lines in the accompanying figures are the theoretical distillation curves assuming perfect separation, while the experimental points are shown by dots.

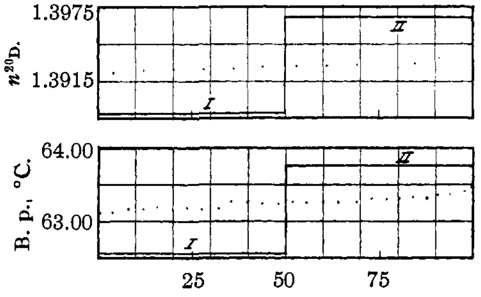

Fig. 2.—I, 50%, 1-hexene; II, 50%, 2-ethyl-1-butene.

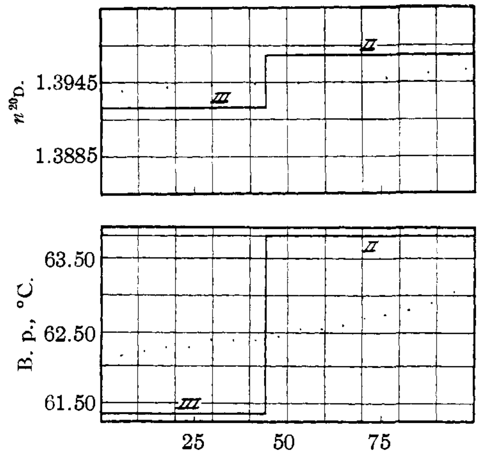

Fig. 3.—II, 56%, 2-ethyl-1-butene; III, 44%, 2-methyl-1-pentene.

It will be seen that the over-all temperature spreads produced in the course of these fractionations are much less than the temperature differences stated to exist between the boiling points of the pairs of substances in question. This obviously means that little separation occurred in the course of the fractionations. The same is true for indices of refraction. Density values further substantiate the data on temperature and refractive index, namely, that little if any separation resulted.

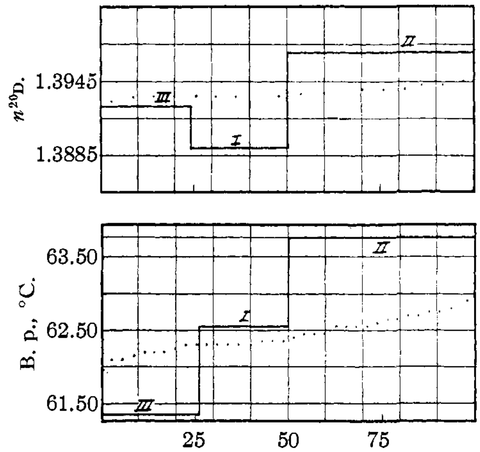

Fig. 4.—I, 24%, 1-hexene; II, 50%, 2-ethyl-1-butene; III, 26%, 2-methyl-1-pentene.

Acknowledgment is made to the following members of the Petroleum Refining Laboratory for help in connection with the data compiled in Table IV: J. P. Haimovicz, G. Herbolsheimer, J. H. Jones, R. H. McCormick, A. E. Schubert, and K. A. Steel.

Summary

1. The identification of olefins as reported by Goldwasser and Taylor in their dehydration of certain alcohols is questioned.

2. The Podbielniak–Simons–Taylor column has an efficiency of about fifteen theoretical plates.

3. Fruitless efforts were made to separate by distillation through the Podbielniak–Simons–Taylor column two binary mixtures having boiling point spreads of 2.7 and 1.5°, and a ternary mixture having an over-all boiling point spread of 2.7°. Our failure is in sharp contrast to the reported separation and identification of six hexenes with an over-all boiling point spread of 2.5°.

4. The Podbielniak–Simons–Taylor column is compared in Table IV with other types of fractional distillation columns.

STATE COLLEGE, PENNSYLVANIA

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Ionic Character and Dipole Moments

BY FREDERICK T. WALL

In discussing the nature of the chemical bond in hydrogen halides, Pauling[1] has found it convenient to regard the normal states of those molecules as superpositions of ionic and covalent states. As a measure of the fraction of ionic character in the molecules he took the values of μ/er where μ is the dipole moment and r the internuclear separation. In this paper the notion is extended somewhat, and a theory of dipole moments for the normal and first excited states is developed.

In a previous paper[2] the author considered the problem by supposing that the wave function (unnormalized) for the molecule can be taken as

$$\psi = \psi_c + a\psi_i$$

where ψ_c is a purely covalent function and ψ_i a purely ionic function, and a is a parameter. To get the best energy value from that function, the energy expression was minimized with respect to a. If W represents that minimized value and W_c and W_i the covalent and ionic energies, then it was shown that

$$a^2 = \frac{W - W_c}{W - W_i} \qquad (1)$$

By use of equation (1) estimates of values for a^2 were obtained for the different hydrogen halides at their equilibrium internuclear separations and the results roughly correlated with dipole moment values.

A more precise relationship between dipole moment and ionic character will now be developed and some conclusions drawn from it. Using the function $\psi = \psi_c + a\psi_i$ in which ψ_c and ψ_i are each normalized to unity, then the general expression for the dipole moment becomes

$$\mu = \frac{\mu_{cc} + 2a\mu_{ci} + a^2\mu_{ii}}{1 + 2a\Delta + a^2} \qquad (2)$$

where μ_{cc} is the moment of the covalent structure, μ_{ii} that of the ionic structure and μ_{ci} the corresponding integral of the moment expression over the states ψ_i and ψ_c. That is

$$\mu_{ci} = \int \psi_c^* \mu \psi_i d\tau = \int \psi_i^* \mu \psi_c d\tau$$

Also

$$\Delta = \int \psi_c^* \psi_i d\tau = \int \psi_i^* \psi_c d\tau$$

Now the moment of the covalent structure can be taken as zero and that of the ionic structure as er. It remains then to find the value of μ_{ci}.

In order to get an idea as to the nature of μ_{ic}, consider the hypothetical case of resonance between HH and H^+H^-. (For the actual hydrogen molecule, the structure H^-H^+ is equally as important as H^+H^-,[3] but it will not be considered here in order that the results can be used for the hydrogen halides for which only the structures HX and H^+X^- are important.) Setting up a purely covalent function of the Heitler–London[4] type for HH and a simple ionic function such as was used by Weinbaum[3] for H^+H^-, the integral μ_{ic} readily can be evaluated. In this case it turns out that

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[1] Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, II-8.

[2] F. T. Wall, THIS JOURNAL, 61, 1051 (1939).

[3] S. Weinbaum, *J. Chem. Phys.*, **1**, 593 (1933).

[4] W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).