

the cooling which is preliminary to carbonation. By so doing, the yield is improved because otherwise oxygen from the atmosphere would be pulled in and react with the Grignard reagent. In a 0.2 mole run the yield of cyclohexanecarboxylic acid based on an 80% yield of cyclohexylmagnesium bromide was 83%; and the yield of acid based on a 92% yield of cyclohexylmagnesium chloride was 93%. It is recommended that the solution be diluted with ether (300-500 cc. in a 0.2 mole run) prior to carbonation, because of the sparingly soluble salt (RCOOMgBr) which is formed.

Summary

Cyclohexylmagnesium chloride and bromide can be prepared in excellent yields. In its reaction with magnesium, bromocyclohexane differs significantly from other secondary bromides. General recommendations are given for the use of RCl in preference to RBr and RI compounds for the preparation of Grignard reagents.

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PHYSICAL PROPERTIES OF THE NORMAL PARAFFIN HYDROCARBONS, PENTANE TO DODECANE

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This paper presents some physical constants of the normal paraffin hydrocarbons, from pentane to dodecane, inclusive. These compounds have been prepared from a common source, and have all been purified by the same method and to the same extent. Consequently, physical measurements obtained with such samples are more comparable among themselves than are the isolated results obtained by various workers who have used different methods of synthesis, purification and measurement.

Preparation of the Samples.—The starting material was a special gasoline with a normal paraffin hydrocarbon content of about 70%. It was obtained from The Standard Oil Company of Indiana through the courtesy of R. E. Wilson. It was roughly separated into its constituents by distillation. Each cut was then treated with chlorosulfonic acid until a one-week treatment no longer altered the density. The details of this treatment have been reported previously.¹ Further purification was accomplished by careful fractionation through a flat spiral fractionating column, equipped with an efficient dephlegmator. The progress of the purification was measured by the density variations of the distillates. The purification was regarded as having reached its practical limit when the over-all density differences of several successive distillate fractions did

¹ Shepard and Henne, *Ind. Eng. Chem.*, **22**, 356 (1930).

not exceed a few units of the fifth decimal. Table I summarizes the experimental results.

TABLE I
PREPARATIVE DATA

<i>n</i> -Paraffin	Properties after preliminary fractionation			ClSO ₃ H treatment		Pure product		
	d_4^{25}	Engler distillation range, °C.		Amount treated, cc.	Days required	Volume recovered, cc.	Recovered, %	Over-all density range of product
		0-100%	10-90%					
Pentane ^a						550		0.00003
Hexane	0.672	1.1	0.6	2000	20	490	24	.00001
Heptane	.695	1.0	0.6	2880	49	650	23	.00001
Octane	.710	2.2	1.1	2545	45	730	29	.00001
Nonane	.724	2.2	0.7	2500	55	665	27	.00002
Decane	.739	3.0		1700	37	640	38	.00001
Undecane	.746	2.4	1.0	1550	54	745	48	.00002
Dodecane	.759	2.6	1.1	585	37	192	33	.00007

^a Chlorosulfonic acid treatment of pentane is unnecessary; cf. S. Young, *J. Chem. Soc.*, 71, 440 (1897); 75, 172 (1899).

Repeated fractional crystallizations of these compounds gave no further separation; the freezing ranges were smaller than 0.1°.

Purity Tests.—Two criteria have been relied upon to indicate the degree of purity obtained, namely, the total boiling range (distillation curve) and the total freezing range (freezing curve). Details of the measurements are as follows.

Boiling ranges were determined on large samples of the hydrocarbons, usually 250 cc. The specimens were slowly distilled from a tube of the dimensions specified for the determination of the boiling point of sulfur.² The tube was provided with a side arm 17 mm. in diameter and was heated directly only on a small area at the bottom.

Temperature readings were made as in an Engler distillation and the barometer was read at the same time. Superheating occurred when the last 5-10% of the sample was being taken off. To minimize this, the

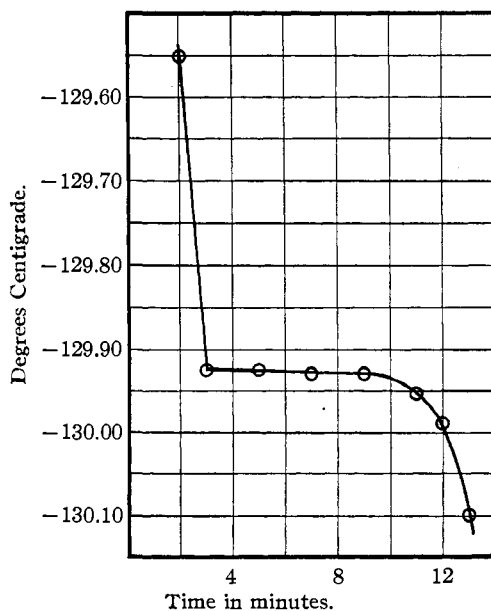


Fig. 1.—*n*-Pentane.

² Mueller and Burgess, *THIS JOURNAL*, 41, 745 (1919).

thermometer was covered with 0.5 g. of cotton,³ which prevented superheating fairly effectively without changing the other distillation points or holding back much material. Where the substances boiled above 100°, a radiation shield of the type recommended by Mueller and Burgess² was used.⁴ The boiling points were duplicated within $\pm 0.01^\circ$.

Since the accuracy of the absolute temperature measurements may have been less certain, the method of measuring is described. A platinum resistance thermometer (Leeds and Northrup No. 8162) was used. The Wheatstone bridge employed in the resistance measurements was of the

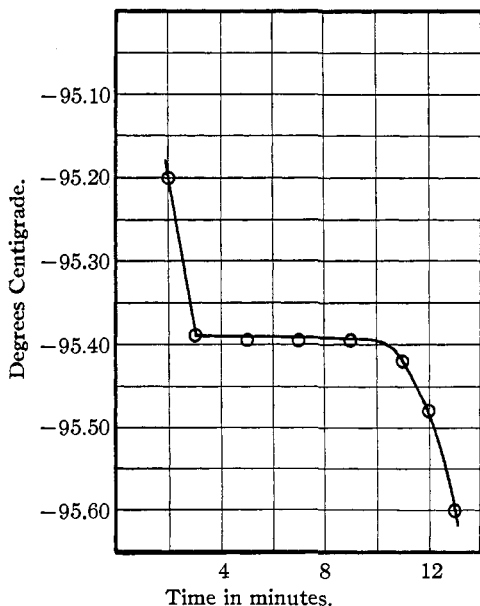


Fig. 2.—*n*-Hexane.

Mueller type; the coils were checked among themselves and against primary standards, and corrections were made for temperature changes. A D'Arsonval galvanometer was used to determine the bridge balance; it was sufficiently sensitive to permit the measurements of less than 0.00001 ohm with the measuring current of 0.01 ampere which was used.

Calibration of the thermometer was made in the standard way at the ice, steam and sulfur points, taking the boiling point of sulfur as 444.60° .⁵ The constants of the thermometer were as follows: R_0 , 2.5079 ohms; R_{100} , 3.4882 ohms; $R_{443.22^\circ}$, 6.62855 ohms.

The fundamental coefficient calculated from these data is 0.003909 and Δ is 1.504, which constants indicate the platinum to be of the requisite purity. Checks on the calibration were obtained at the transition point of sodium sulfate decahydrate, and at several other temperatures between 0 and 100° against an instrument newly calibrated by the Bureau of Standards. All the instruments were frequently rechecked and agreement to $\pm 0.01^\circ$ was obtained in all cases.

A Fortin barometer was used in all the work; it was checked against the

³ An equivalent volume of glass wool was used when undecane and dodecane were distilled.

⁴ The use of this shield made no change in the observed boiling points of water and of octane.

⁵ Glazebrook "Dictionary of Applied Physics," Macmillan Co., London, 1922, Vol. I, p. 706.

local Weather Bureau instruments and the necessary corrections were made for temperature, elevation, latitude and capillarity. Boiling points were determined at several pressures near 760 mm. and were corrected to standard conditions with the aid of the dt/dp noted in Table II. The values thus obtained agreed in general to $\pm 0.01^\circ$.

TABLE II
BOILING RANGES OF HYDROCARBONS

n-Paraffin dt/dp % Distd.	C ₅ H ₁₂ 0.039	C ₆ H ₁₄ 0.042	C ₇ H ₁₆ 0.045	C ₈ H ₁₈ 0.048	C ₉ H ₂₀ 0.050	C ₁₀ H ₂₂ 0.052	C ₁₁ H ₂₄ 0.054	H ₁₇ C ₁₈ 0.056
0	35.99	68.70	98.37	125.57	150.69	174.04	195.80	216.16
10	36.00	68.70	98.38	125.58	150.70	174.05	195.81	216.19
20	36.00	68.71	98.38	125.58	150.70	174.06	195.81	216.20
30	36.00	68.71	98.38	125.59	150.71	174.06	195.82	216.21
40	36.00	68.71	98.38	125.59	150.71	174.06	195.83	216.22
50	36.00	68.71	98.38	125.59	150.71	174.06	195.84	216.23
60	36.01	68.71	98.38	125.59	150.72	174.06	195.84	216.24
70	36.01	68.71	98.38	125.60	150.73	174.07	195.85	216.25
80	36.02	68.72	98.39	125.60	150.73	174.07	195.86	216.27
90	36.03	68.72	98.39	125.60	150.74	174.08	195.87	216.30
95	36.03	68.72	98.39	115.61	150.74	174.09	195.89	216.35
Dry	36.05	68.73	98.40	125.61	150.74	174.10	195.92	216.42

NOTE.—Undecane and dodecane did not appear to be absolutely stable to distillation at atmospheric pressure. The distilled specimens gave a slight brown color to concd. sulfuric acid on shaking with it, and the acid on dilution had the odor of a higher alcohol. The pure materials gave no color on shaking with this acid, and no odor on dilution.

Freezing points were determined on 120-cc. samples. The resistance thermometer used had been calibrated for low temperature work by the Bureau of Standards. The constants of the thermometer were as follows: R_0 , 25.575 ohm; R_{100} , 35.532; and Δ and β in the modified Callendar equation for use at low temperatures were 1.48 and 0.115, respectively. The freezing curves are given in Figs. 1-8.

Physical Properties.—The following properties have been measured.

Boiling Points and Freezing Points.—The experimental details are reported in the preceding paragraphs. For typographical reasons, only every fourth experimental point is reproduced on the freezing curves.

TABLE III
BOILING POINTS, MELTING POINTS AND DENSITIES

n-Paraffin	B. p., °C.	M. p., °C.	d_4^{20}	d_4^{25}
Pentane	36.00	-129.93	0.62632
Hexane	68.71	- 95.39	.65945	0.65502
Heptane	98.38	- 90.65	.68378	.67963
Octane	125.59	- 56.90	.70279	.69882
Nonane	150.71	- 53.68	.71780	.71398
Decane	174.06	- 29.76	.73014	.72643
Undecane	195.84	- 25.65	.74025	.73667
Dodecane	216.23	- 9.73		.74542

Densities.—Densities have been taken at 20 and 25°. They were measured in 40-cc. pycnometers of the Sprengel type. The necessary temperature control was obtained with a thermostat held constant to $\pm 0.01^\circ$, and the absolute accuracy of the temperature was checked against three Bureau of Standards thermometers. Weighings were made with standardized weights. All densities were reduced to vacuum and are accurate to ± 0.00003 .

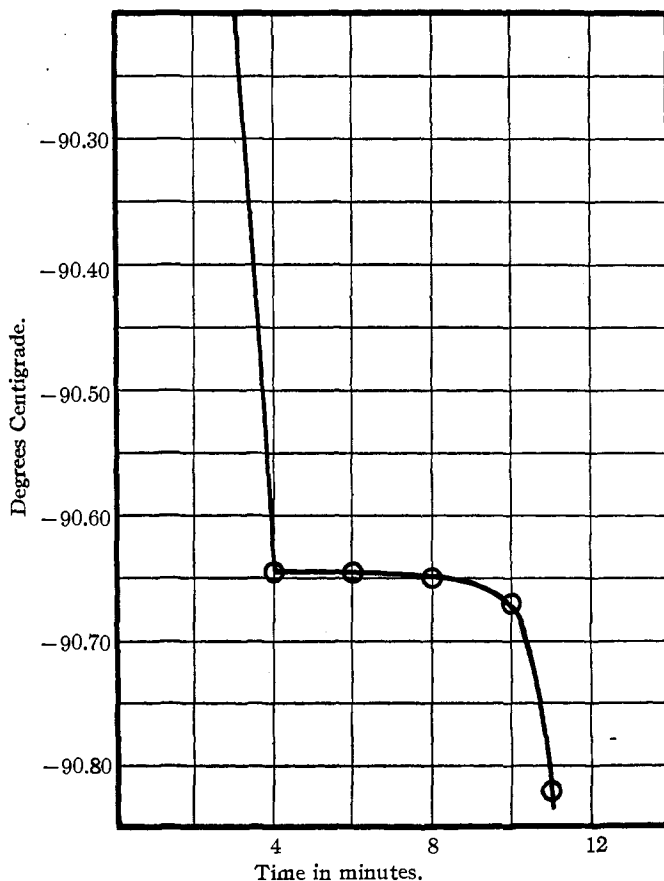


Fig. 3.—*n*-Heptane.

Refractive Indices and Molecular Refractions.—Refractive indices relative to air were measured with a Pulfrich refractometer for the α , β and D lines. The refractometer was calibrated with pure water and the temperature desired was maintained by a current of water from a thermostat regulated to $\pm 0.01^\circ$, the temperature of which had been checked with two Bureau of Standards thermometers. The refractometer prism was at the

temperature indicated. Determinations were made at 20, 25 and 45.3° and are given in Table IV. Table V gives the molecular refractions and dispersions at 25°, calculated by the Lorentz-Lorenz formula, and by the more exact empirical formula of Eykman.⁶

TABLE IV
REFRACTIVE INDICES OF HYDROCARBONS

	Temp., °C.....	20°			25°			45.3°		
		n_α	n_D	n_β	n_α	n_D	n_β	n_α	n_D	n_β
Pentane		n_α	1.35581		1.35309					
		n_D	1.35769		1.35495					
		n_β	1.36208		1.35930					
Hexane		n_α	1.37310		1.37043		1.35924			
		n_D	1.37506		1.37230		1.36132			
		n_β	1.37979		1.37695		1.36567			
Heptane		n_α	1.38580		1.38345		1.37303			
		n_D	1.38775		1.38553		1.37519			
		n_β	1.39261		1.39035		1.37970			
Octane		n_α	1.39557		1.39328		1.38334			
		n_D	1.39760		1.39534		1.38561			
		n_β	1.40255		1.40030		1.39037			
Nonane		n_α	1.40356		1.40125		1.39181			
		n_D	1.40563		1.40340		1.39389			
		n_β	1.41077		1.40846		1.39883			
Decane		n_α	1.40994		1.40771		1.39831			
		n_D	1.41203		1.40986		1.40047			
		n_β	1.41728		1.41492		1.40549			
Undecane		n_α	1.41514		1.41300		1.40384			
		n_D	1.41727		1.41516		1.40611			
		n_β	1.42252		1.42036		1.41111			
Dodecane		n_α	1.41965		1.41752		1.40852			
		n_D	1.42188		1.41967		1.41081			
		n_β	1.42720		1.42501		1.41588			

TABLE V
MOLECULAR REFRACTIONS AND DISPERSIONS (FROM DATA AT 25°)

<i>n</i> -paraffin	Lorentz-Lorenz formula													
	MR_α		MR_D		MR_β		Dispersion		$H_\beta - H_\alpha$					
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
$C_5H_{12}^a$	25.14	25.17	25.26	25.29	25.54	25.57	0.40	0.40						
C_6H_{14}	29.77	29.77	29.90	29.91	30.23	30.24	.46	.47						
C_7H_{16}	34.41	34.36	34.57	34.53	34.95	34.91	.54	.54						
C_8H_{18}	39.01	38.96	39.19	39.14	39.62	39.57	.61	.61						
C_9H_{20}	43.63	43.56	43.84	43.76	44.32	44.24	.69	.69						
$C_{10}H_{22}$	48.25	48.15	48.48	48.38	49.01	48.91	.75	.76						
$C_{11}H_{24}$	52.87	52.75	53.11	53.00	53.70	53.58	.83	.83						
$C_{12}H_{26}$	57.49	57.35	57.75	57.62	58.39	58.25	.90	.90						

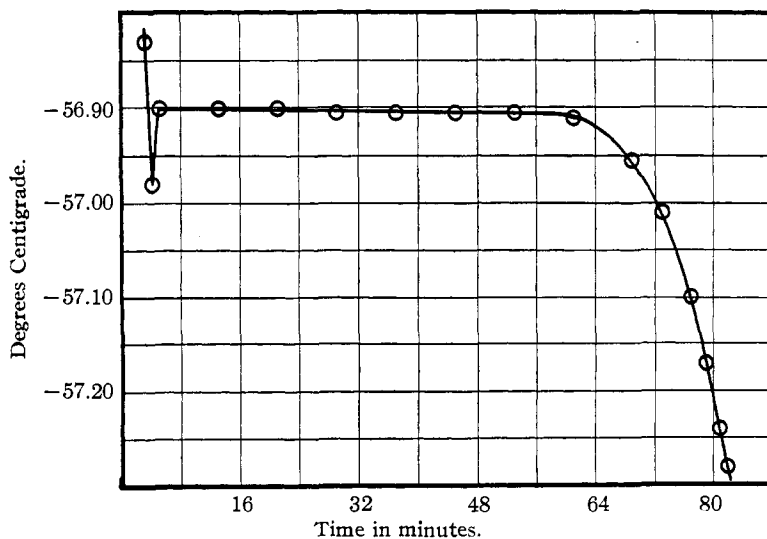
⁶ J. P. Eykman, *Rec. trav. chim.*, **15**, 52 (1896).

TABLE V (Concluded)

n-Paraffin	Eykmán formula					
	Obs.	MR_{α}	Calcd.	Obs.	MR_{β}	Calcd.
$C_6H_{12}^a$	54.95		54.99	55.88		55.86
C_6H_{14}	65.20		65.26	66.29		66.29
C_7H_{16}	75.50		75.51	76.78		76.73
C_8H_{18}	85.73		85.77	87.19		87.16
C_9H_{20}	96.02		96.03	97.64		97.59
$C_{10}H_{22}$	106.28		106.29	108.05		108.02
$C_{11}H_{24}$	116.54		116.55	118.50		118.45
$C_{12}H_{26}$	126.81		126.81	128.94		128.88

^a From data at 20°.

Critical Temperature of Solution.—The critical temperature of solution of each hydrocarbon was measured in freshly distilled dry aniline having a boiling range $<0.1^\circ$. Known amounts of aniline and the hydrocarbons were sealed in tubes and placed in a holder which was immersed in a large insulated water-bath. The bath was provided with an efficient

Fig. 4.—*n*-Octane.

stirrer and the tubes were continuously shaken while observations were being made. The Critical Temperature of Solution was observed on raising and lowering the temperature of the bath, and the rate of heating and cooling was such that the values obtained on heating and cooling checked to 0.1° . Temperatures were measured with a Beckmann thermometer which was frequently checked against two standard instruments. The results are believed to be reproducible to only $\pm 0.1^\circ$ because of the

personal factor involved in judging the exact temperature of complete solution. Fig. 9 shows the results obtained.

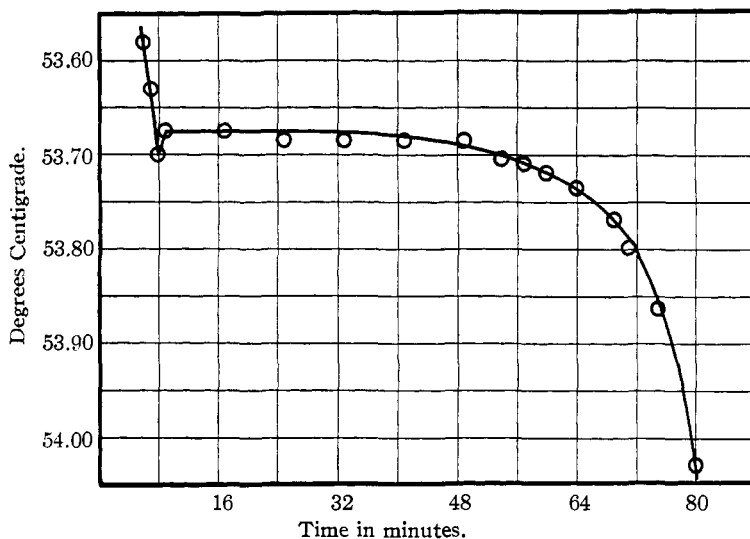


Fig. 5.—*n*-Nonane.

Viscosities.—Viscosities were measured in a pyrex viscometer of the type recommended by Washburn and Williams.⁷ In view of the element of uncertainty attendant to the use of a kinetic energy correction,⁸ the dimensions of the instrument were so adjusted that the kinetic energy correction amounted to less than 0.5% of the viscosity value in the case of *n*-pentane. The correction was neglected in computing the viscosities. The temperature was controlled to $\pm 0.02^\circ$ during the measurements; the values obtained are accurate to 0.5%.

Other Properties.—Several other properties have been

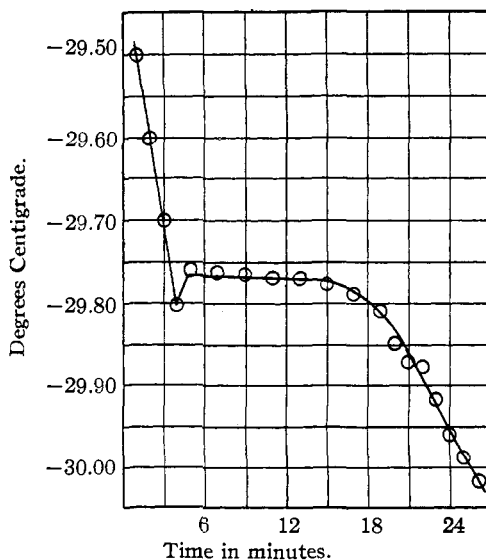
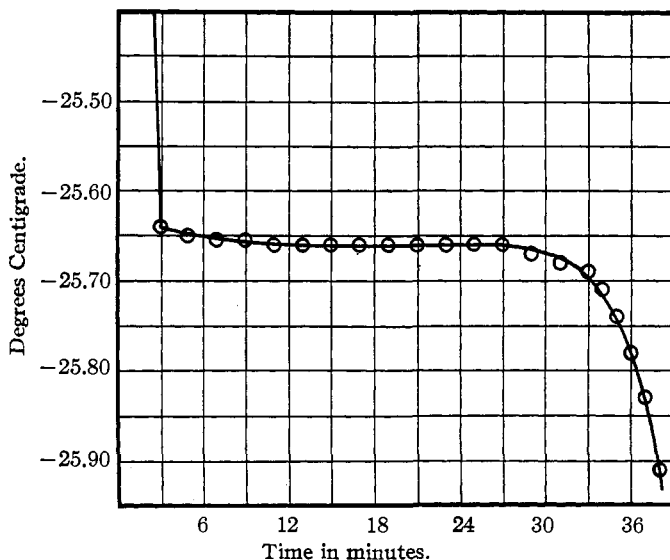


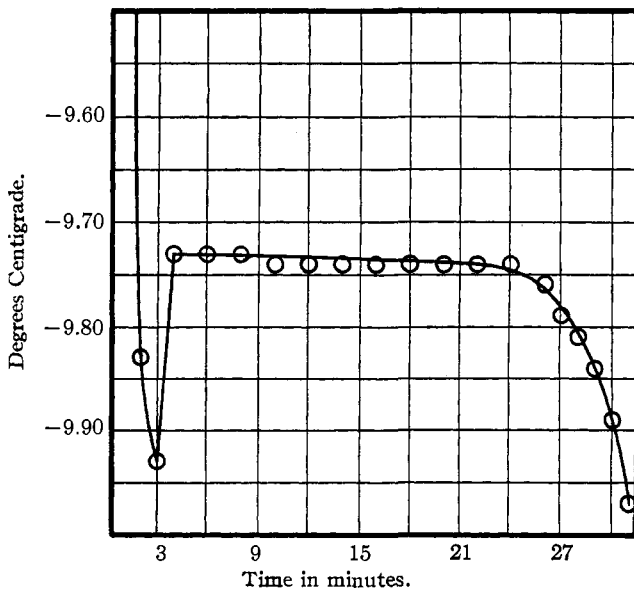
Fig. 6.—*n*-Decane.

⁷ Washburn and Williams, *THIS JOURNAL*, **35**, 737 (1913).

⁸ F. Martin, *Bull. soc. chim. Belg.*, **34**, 81 (1925).

Fig. 7.—*n*-Undecane.

measured by other experimenters, to whom we here express our gratitude for measuring these properties and also for checking those already obtained in this Laboratory. The specific heats and heats of fusion have been measured by G. S. Parks of Stanford University, the dielectric constants and

Fig. 8.—*n*-Dodecane.

densities by R. W. Dornte and C. P. Smyth,⁹ the fluidity by E. C. Bingham and H. J. Fornwalt,¹⁰ while at the present time the Bureau of Standards is measuring the heats of combustion and vapor pressure curves and the General Motors Research Laboratory is determining the Raman spectra.

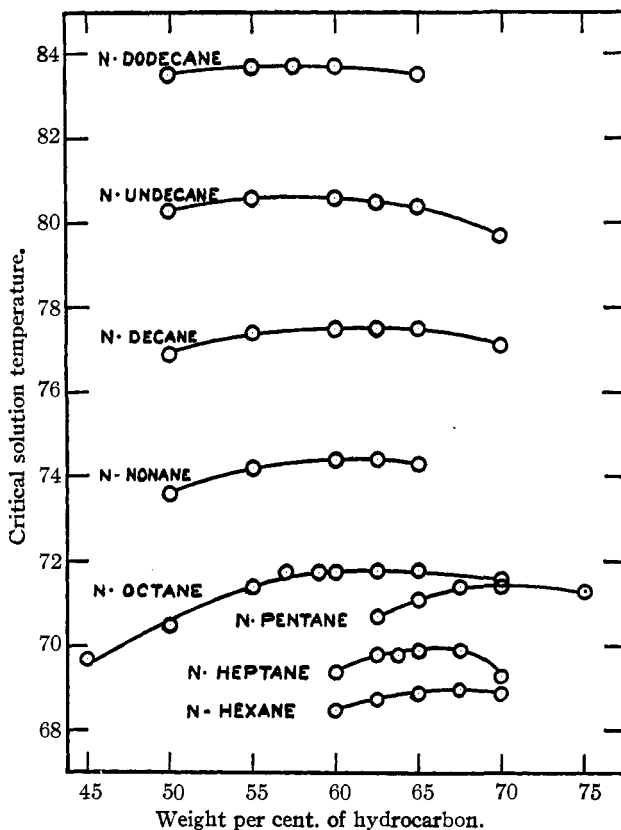


Fig. 9.

Empirical Relation Involving the Boiling Points, Molecular Weight, Refractive Indices and Densities.—Nekrasov¹¹ has proposed the relation

$T \frac{\sqrt{MR}}{M - MR} = \text{constant}$, where T is the boiling point in °K., M is the molecular weight, and MR is the molecular refraction calculated by means of the Lorentz-Lorenz formula. He computed the constants of the normal paraffins by using data from the Landolt-Börnstein tables. They are reported in the second column of Table VII. They seem to exhibit a

⁹ R. W. Dornte and C. P. Smyth, *THIS JOURNAL*, **52**, 3546 (1930).

¹⁰ E. C. Bingham and J. H. Fornwalt, *J. Rheology*, **1**, 372 (1930).

¹¹ B. Nekrasov, *Z. physik. Chem.*, [A] **140**, 342 (1929).

TABLE VI
 VISCOSITIES AND CRITICAL TEMPERATURES OF SOLUTION

<i>n</i> -Paraffin	Viscosity at 25° C. G. S. units × 10 ⁵	Fluidity at 25° ÷ 10 ⁵	C. T. S. in aniline
Pentane	216.6	461.6	71.4°
Hexane	293.7	340.4	69.0°
Heptane	385.9	259.1	69.9°
Octane	508.3	196.7	71.8°
Nonane	662.1	151.0	74.4°
Decane	852.7	117.3	77.5°
Undecane	1081	92.5	80.6°
Dodecane	1353	73.9	83.7°

functional variation, but when they are recomputed, to include the second decimal, this functional variation disappears. However, when the experimental data reported in this article were substituted for the Landolt values, a functional variation reappeared. The Nekrasov constants computed from densities and refractive indices measured at 25° are reported in the three last columns of Table VII; they were computed for the α , D and β lines, respectively.

TABLE VII
 NEKRASOV'S CONSTANTS

	Nekrasov's computed values	Experimental values		
		K_{α}^{25}	K_D^{25}	K_{β}^{25}
Pentane	33.2	33.048	33.208	33.591
Hexane	33.3	33.105	33.259	33.640
Heptane	33.3	33.161	33.323	33.702
Octane	33.3	33.148	33.307	33.685
Nonane	33.1	33.127	33.286	33.662
Decane	33.1	33.076	33.233	33.604
Undecane	32.9	33.006	33.161	33.532
Dodecane	32.8	32.919	33.069	33.442

Summary

The normal paraffin hydrocarbons, from pentane to dodecane inclusive, have been prepared from a common source, by a single method, and in a comparable state of purity. Their boiling points, freezing points, densities, refractive indices, viscosities and critical temperature of solution in aniline have been determined. Evidence is presented to support the degree of accuracy claimed for the measurements. The boiling points and molecular refractions have been correlated by means of the Nekrasov equation.

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